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Summaries of FY 1996 Research in the Chemical Sciences

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U.S. Department of Energy
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Division of Chemical Sciences

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PREFACE

This summary book is published annually to provide information on research supported by the Department of Energy's Division of Chemical Sciences, which is one of four divisions of the Office of Basic Energy Sciences in the Office of Energy Research.

These summaries provide the scientific and technical public, as well as the legislative and executive branches of the Government, information, either generally or in some depth, about the Chemical Sciences program. Areas of research supported are indicated in the section, "Selected Topics of General Interest," and the summaries themselves. Energy technologies that may be advanced by use of the basic knowledge generated in this program are included in the "Selected Topics of General Interest" list and are often referenced in the summaries.

Scientists interested in proposing research for support will find the publication useful for gauging the scope of the present basic research program and it's relationship to their interests. Proposals that expand this scope may also be considered or directed to more appropriate offices. The primary goal of the research summarized here is to add significantly to the knowledge base in which existing and future efficient and safe energy technologies can evolve. As a result, scientific excellence is a major criterion applied in the selection of research supported by the Division of Chemical Sciences, but another important consideration is emphasis on science that is advancing in ways that will produce new information related to energy.

The program takes place in several different kinds of performing organizations. About one-third of the projects are at DOE laboratories and the rest mostly at universities, with a small number of projects at industrial laboratories. In DOE laboratories, much of the research utilizes special unique facilities which, in some instances, are national user facilities. These are described in a special section of this publication.

Questions about the detail of an individual project may be directed to the investigators involved or the persons in charge at DOE laboratories (who are identified at appropriate places in this publication). Other questions about the program may directed to the undersigned.

Robert S. Marianelli, Director
Division of Chemical Sciences
Office of Basic Energy Sciences

Division of Chemical Sciences Organizational Chart

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Special Projects - Vacant

Environment Safety and Health

Secretary - Ms. Diane Matthews
Telephone: 301-903-5804

Staff

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Mr. Ted Tomczak	903-6919

Fundamental Interactions
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Secretary - Ms. Terry Jones
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Photochemical & Radiation Sciences	
Dr. Mary E. Gress	903-5827
Chemical Physics	
Dr. Andrew E. DePristo*	903-6891
Dr. William H. Kirchhoff	903-5809
Atomic, Molecular, & Optical Physics	
Dr. J. V. Martinez	903-5825
Facilities Operations	
Dr. Robert S. Marianelli	903-5808

Molecular Processes
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Secretary - Ms. Lori Jernigan
Telephone: 301-903-5802

Chemical Energy	
Dr. Robert A. Beyerlein**	903-3285
Dr. Howard P. Stephens†	903-2367
Separations and Analysis	
Dr. William S. Millman	903-5805
Dr. Paul H. Smith‡	903-5806
Heavy Element Chemistry	
Dr. Paul H. Smith‡	903-5806
Chemical Engineering Sciences	
Dr. William S. Millman	903-5805
Advanced Battery Research	
Dr. Paul H. Maupin	903-4355

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* On leave from Iowa State University
**On leave from Texas A&M University
† On leave from Sandia National Laboratories, New Mexico
‡ On leave from Los Alamos National Laboratory

PROGRAM SUMMARIES

Each team of the Division of Chemical Sciences is divided into programs that cover various disciplines. The following summaries describe these programs. The staff members responsible for each program are indicated in the organizational chart. The Division has the responsibility for seeing that the research programs and facilities it supports are operated in a safe manner with due regard for the health of participants and the protection of the environment. The staff who do this for the Division and the Office of Basic Energy Sciences are in the Division of Chemical Sciences and the Material Sciences Division. The Chemical Sciences Environment Safety and Health (ES&H) staff are also indicated on the organization chart.

Fundamental Interactions Team (KC-03-01)

Photochemical and Radiation Sciences (KC-03-01-01)

The Photochemical and Radiation Sciences program consists of research on the interactions of radiation with matter. Emphasis is placed on exploration of fundamental photochemical processes aimed at the capture and conversion of solar energy. The solar photochemistry research encompasses organic and inorganic photochemistry, electron and energy transfer in homogeneous and heterogeneous media, photocatalysis, and photoelectrochemistry. The photosynthetic reaction center is studied as a model for design of efficient photoinduced charge separation in biomimetic/photocatalytic assemblies. The radiation chemistry research is concerned with the chemical effects produced by absorption of energy from ionizing radiation. Electron pulse radiolysis techniques provide information on the nature of transient intermediates, kinetics, and mechanisms of chemical reactions in the condensed phase.

Chemical Physics (KC-03-01-02)

The Chemical Physics program supports research on fundamental molecular processes related to the mission of the Department in the areas of combustion, catalysis, and environmental restoration. Specific areas of emphasis include gas phase chemical reaction theory, experimental dynamics and spectroscopy, thermodynamics of reaction intermediates, chemical kinetics and reaction mechanisms at high temperatures in the gas phase and at surfaces, combustion diagnostics, and chemical dynamics and kinetics at surfaces and with metal and semiconductor clusters.

A major user-oriented facility, the Combustion Research Facility at Sandia National Laboratories, California, is supported by this program. This facility offers the use of advanced instrumentation and computation to interested combustion scientists from industry, universities, and national laboratories.

Atomic, Molecular, and Optical Physics (KC-03-01-03)

The Atomic, Molecular, and Optical Physics Program supports experimental and theoretical studies relevant to energy technologies. These include studies of atom and atomic ion structures, energy levels and lifetimes of quantum states, and of transport and exchange processes associated with energy and momentum transfer. These studies seek to obtain the most accurate and complete fundamental knowledge of the properties and interactions of photons, electrons, atoms, and ions. Relatively high energy atomic physics research involving atoms stripped of all or almost all electrons and of atoms and ions in which electrons are promoted to upper energy levels provide basic information to assist thermonuclear energy development. The study of processes that lead to the production of coherent radiation and its statistical manifestations in atomic physics are included in this program to assist development of other less well characterized energy technologies. Research on the manipulation of atoms with coherent photon fields, on the behavior of plasmas generated by intense laser beams, and on the physics of low-temperature plasmas relevant to materials processing is also supported.

Facilities Operations (KC-03-01-04)

DOE operates large scientific facilities for the benefit of the scientific community. Major user facilities permit forefront research to be conducted in areas important to DOE by scientists from industry and universities in addition to DOE contractors/grantees. Operating support for these expensive, unique facilities that are open to all qualified researchers is provided by DOE. Many of the facilities are user oriented. The four operated by the Chemical Sciences Division are the following: the Combustion Research Facility (CRF) at Sandia, Livermore, the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford, and, shared with the Material Sciences Division, the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. They represent research resources for the general scientific community, and qualified scientists not associated with the host laboratory are encouraged to make use of them. However, any activity that can be carried out at commercially available laboratories is not appropriate for these DOE-supported facilities. The process by which an off-site scientist can use a facility is discussed in each summary.

In addition, another facility at Oak Ridge is operated as a service to the scientific community: the Radiochemical Engineering Development Center (REDC).

Other facilities described in the "Special Facilities" section are also available for use through collaboration with staff scientists. The names of individuals to contact for further information and technical data on available instrumentation at each facility are described.

Molecular Processes Team (KC-03-02)

Chemical Energy (KC-03-02-01)

The Chemical Energy program includes basic chemistry research related to chemical transformations or conversions which are fundamental to new or existing concepts of energy production and storage. Of particular interest are those research activities with the objectives of understanding the chemical aspects of (1) catalysis, both heterogeneous and homogeneous; (2) the chemistry of fossil resources, particularly coal, including characterization and transformation; (3) the conversion of biomass and related cellulosic wastes; and (4) the chemistry of precursors to advanced materials. The disciplines of organic, organometallic, inorganic, physical, thermo- and electrochemistry are central to these programs. The emphasis is on understanding the fundamental chemical principles underlying the new and developing technologies and on innovative chemical research with potential for new energy concepts.

Separations and Analysis (KC-03-02-02)

The separations part of the program supports basic research directed toward improving our understanding of methods for separating mixtures of gases, liquids, solids, and their component molecules, cations, and anions. The program covers a broad spectrum of separations concepts, including membrane processes, extraction under both standard and supercritical conditions, adsorption, chromatography, photodissociation, complexation, etc. The research involves elucidating fundamental chemical phenomena for improved or new separations rather than developing specific processes.

The analysis part of the program supports research on phenomena basic to analytical methods, the goal being to improve sensitivity, reliability, and/or productivity of analytical determinations. Chemical and physical principles which can lead to entirely new methods of analysis are investigated, although this program does not support instrument development. Research progress is reported quickly in the open literature so that those interested in instrumental development can build on work supported herein. The program is aimed at obtaining a thorough understanding of the basic chemistry of analytical techniques so that their utility can be improved, rather than solving specific problems in analysis.

Heavy Element Chemistry (KC-03-02-03)

The Heavy Element Chemistry program focuses on a study of the chemical and certain physical properties of the actinide elements, principally the transuranium elements, because of the importance of these elements to DOE's nuclear technology programs and to an understanding of the basic science in general. A variety of investigations are pursued, including (1) organometallic chemistry, (2) chemistry of excited spectroscopic states, (3) thermochemistry of actinide elements and compounds, (4) chemistry of actinides in near-neutral aqueous solutions and the reactions of aqueous actinide ions with various complexing agents, (5) development of preparative methods for actinide metals and compounds, and (6) characterization of actinides in the solid state under pressure.

This research is performed principally at the national laboratories because of facilities required for handling radioactivity.

Chemical Engineering Sciences (KC-03-02-04)

This program addresses energy aspects of chemically related engineering topics, including thermodynamics, turbulence related to combustion, and physical and chemical rate processes. Particular attention is given to experimental and theoretical aspects of phase equilibria, especially of mixtures, including supercritical phenomena, and to the physics of gas phase turbulence. Also included are fundamental studies of thermophysical and thermochemical properties. Emphasis is given to improving and/or developing the scientific base for engineering generalizations and their unifying theories.

Advanced Battery Research (KC-03-02-04)

The Advanced Battery Research program supports fundamental research in areas critical to understanding the underlying limitations in the performance of non-automotive electrochemical energy storage systems. Areas of research include anode, cathode, and electrolyte systems and their interactions with emphasis on improvements in battery size, weight, life, and recharge cycles. Although both primary and secondary battery systems are considered, the greatest emphasis is placed on rechargeable (i.e., secondary) battery systems. The program covers a broad spectrum of research including fundamental studies of composite electrode structures, failure and degradation of active electrode materials, and thin film electrodes, electrolytes, and interfaces. Problems of electrode morphology, corrosion, electrolyte stability, and the transport properties of electrode and electrolyte materials and surface films are also addressed. Investigations in computational modeling and simulation of the underlying chemistry; including reactions, structure-function properties, interactions at critical interfaces, film formation, phase change effects on electrodes, and electrochemical characterization of crystalline and amorphous materials are also of interest.

LABORATORY ADMINISTRATION

Listed below, by laboratory and department or division, are persons who are or will be in charge of the Division of Chemical Sciences projects at DOE laboratories. These individuals are laboratory, department, or division administrators who can provide information about specific programs or refer inquiries to appropriate individuals.

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NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
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Fundamental Interactions Program

1. ***Raman Spectroscopy of Model Photosynthetic Systems***
   Cotton, T.M.; Chumanov, G.D. **$106,000**
   515-294-9887
   tmcotton@ameslab.gov

The objective of this project is to study heterogeneous electron transfer between different molecular assemblies at metal surfaces with the ultimate goal to prepare model photosynthetic systems. Monolayers and multilayers composed of donor acceptor species are fabricated by self-assembly and Langmuir-Blodgett techniques. This approach allows the control of structure and composition of these molecular assemblies. The distinguishing feature of this project is the use of metal substrates as a means of enhancing different optical phenomena as well as photoinduced electron transfer. Such enhancement occurs due to excitation of the plasmon resonances on specially prepared metal surfaces. Recently, a completely new concept was developed based on the coupling of the plasmon resonances of individual metal particles in highly organized two-dimensional arrays. The coupling produces nonradiative energy transfer between particles resulting in highly efficient light collection. Such substrates (termed Colloidal Metal Films) were successfully prepared using surface chemistry to immobilize small silver and gold particles on glass surfaces. Currently, their properties are under investigation with the goal of developing an artificial light antenna system. In the future, this artificial antenna will be coupled to different model photosynthetic systems in order to increase significantly their efficiency.

2. ***Laser Spectroscopy and Electronic Energy Transfer of Light Conversion Systems***
   Small, G.J.; Hayes, J.M.; **$226,000**
   Reddy, N.R.S.; Jankowiak, R.
   515-294-3859
   gsmall@ameslab.gov

The primary events of electronic excitation and electron transport in photosynthesis are studied in order to determine and characterize the key aspects of nature's highly evolved and efficient solar energy conversion processes. The problem is important because the understanding of natural photosynthesis will provide design criteria for artificial solar energy conversion systems. To identify the critically important features (structure-function relationships) of photosynthesis, the light harvesting and reaction center protein-chlorophyll complexes of green plants, bacteria and algae are studied. An adequate understanding of natural photosynthesis requires understanding the excited electronic states of interacting chlorophylls bound to protein, how chlorophyll and protein vibrations mediate the transport processes and how the inherent glass-like structural disorder affects the rates of excitation and electron transfer. The high resolution spectroscopic technique of spectral hole burning is employed to obtain relevant data which are used to test theoretical models and, if necessary, develop new ones. Hole burning is combined with high pressure to investigate the pressure and temperature dependence of the kinetics of primary events. This unique facility has led to valuable new insights, e.g. the mechanism of the 1 picosecond B800→B850 energy transfer process in the LH2 antenna complex of purple bacteria.

3. ***Ultrafast Spectroscopy and Energy Transfer***
   Struve, W.S.; Savikhin, S. **$308,000**
   515-294-4276
   wstruve@ameslab.gov

Ultrafast laser spectroscopy is applied to studies of electronic energy transfer, vibrational cooling, and charge separation on the femtosecond time scale in natural and artificial photosynthetic systems. Recent areas of emphasis have been energy transfer studies of light-harvesting antennae from purple photosynthetic bacteria, bacteriochlorophyll-protein complexes from the green bacterium *Chlorobium tepidum*, and oligomeric bacteriochlorophyll antennae in chlorosomes from green bacteria. This program has recently achieved the first-characterization of level-to-level energy transfers in a strongly coupled antenna, a major milestone in the study of structure-function relationships in natural antennae. A biomimetic project is being pursued in a collaboration with other investigators in the Ames Laboratory. This project has focussed on phthalocyanine-based artificial antennae using two approaches. The first deals with synthetic pigment-protein and pigment-polymer arrays, engineered for efficient excitation delivery to reaction centers. The second approach, based on Coulomb tetraazaphthalocyanine-phospholipid bilayers in Langmuir-Blodgett transfer films, has been successfully used to prepare two-dimensional antennae with high optical density, efficient energy transfer, and minimal pigment aggregation.

Argonne National Laboratory
Argonne, IL 60439-4831

Chemistry Division

4. ***Time-Resolved Molecular Structure Determination in Photoinduced Electron Transfer Processes***
   Chen, L.X.; Thurnauer, M.C.; **$70,000 Operating**
   Wasielewski, M.R. **$250,000 Equipment**
   630-252-3533
   lchen@anlchm.chm.anl.gov

The objective of the research is to determine transient molecular structures in photochemical reactions, in particular, those related to photoinduced electron transfer and solar energy conversion and storage, with time-domain X-ray absorption spectroscopy (TRXAS) using synchrotron radiation. Many photoinduced charge separation processes are achieved via excited states or a series of intermediate states having electronic structures distinctively different from those of the ground state molecules. The determination of the structures of these transient species is the key to understanding the fundamental chemistry of photoinduced charge separation. The TRXAS experiments will implement "pump-probe" X-ray absorption spectroscopy (XAS) at the Advanced Photon Source at Argonne, where a short laser pulse is used as a "pump" for creation of photoinduced intermediates, and an X-ray pulse, as a "probe" for monitoring the structural changes. The XAS spectra of a particular intermediate state of electron donor-acceptor molecules will be collected at a certain delay time from the laser "pump" pulse based on the kinetic information obtained with optical and magnetic resonance measurements. The information on structural changes of the electron donor-acceptor molecules following photoinduced electron transfer will reveal new insights into the correlation of nuclear motion with electron transfer, that, in turn, will provide new grounding for theoretical modeling of electron transfer and guidance in designing new molecular systems for solar energy conversion and storage.

5. *Electron Transfer and Energy Conversion*

Miller, J.R.; Meisel, D.; **$1,066,000**
Curtiss, L.A.
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This project involves fundamental research on intramolecular electron transfer and charge transfer at interfaces in microheterogeneous environments. Recent efforts concern: (a) exploration of how electron transfer between molecules is controlled by distance, energy, and molecular structure; (b) electron transfer at surfaces of semiconductor nanoparticles and between such particles; (c) the nature and dynamical characteristics of excited states of radical ions and free radicals. Experimental methods to couple high-speed lasers to an electron linear accelerator are under development for the study of radical species and for the possible extension to light-driven electron transfer reactions of these species. The pulsed electron radiolysis technique is uniquely suited to investigate the role of important variables such as distance, energy, ion pairing, and solvent polarity on electron transfer, because it enables experiments which clearly delineate the role of each variable. These capabilities are augmented in this program by coupling to theory at the ab initio level.

6. *Hierarchical Photosynthetic Systems for Photochemical Energy Conversion*

Thurnauer, M.C.; Tiede, D.M.; **$778,000**
Tang, J.
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This program investigates mechanisms for linking ultrafast photoinduced charge separation to the production of chemical and electrochemical products. Natural photosynthesis is being studied as an example of a photochemical system in which ultrafast photophysical processes are nearly optimally linked to chemical energy conversion. The natural systems have a hierarchical design, consisting of discrete chemical subsystems that break photosynthesis up into a sequence of individual photochemical and chemical reaction steps. This program examines how linkages between different photosynthetic subsystems are achieved, and delivers strategies for the design of novel, hierarchical artificial systems for enhanced photochemical energy conversion. The biological systems under investigation include the bacterial photosynthetic reaction center, and the photosystems I and II from algae and plants. Surface-modified, semiconductor colloid photocatalysts are being synthesized and investigated as models of synthetic hierarchical photochemical systems. Novel pulsed EPR, time-resolved EPR, CW EPR, neutron and X-ray diffraction experimental techniques and theoretical modeling are being developed to investigate structure and photochemical activity in hierarchical photochemical systems. Notable contributions from this program have been the resolution of structures and sequences of electron transfer events in natural photosynthesis, and following from this, the design and synthesis of surface-modified semiconductor colloids that exhibit photoinduced sequential electron transfer steps leading to charge separation.

7. *Stable Isotope Labeling of Photosynthetic Materials and Structural Analysis*

Tiede, D.M. **$65,000**
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This project produces photosynthetic materials enriched with non-natural, stable isotopes that offer unique opportunities for structural and photochemical analyses of complex natural and synthetic photochemical systems using magnetic resonance and neutron scattering techniques. A central problem for unraveling mechanisms for solar energy conversion lies in detecting photochemistry and structure of individual components buried within larger molecular arrays. The isotopically labeled materials produced by this program provide an elegant, nonperturbative solution to this problem. Primary emphasis is on the production of 99.7% deuterium enriched algae and photosynthetic bacteria. Deuteration greatly simplifies the electron paramagnetic properties of free-radical intermediates produced by light-induced chemistry. Neutron scattering experiments also benefit from deuteration by amplifying the coherent neutron scattering signal from the labeled molecules and suppressing incoherent scattering. These features are being exploited for the determination of photochemistry and structure in natural photosynthesis using new, high-resolution, state-of-the-art pulsed and CW magnetic resonance spectroscopies and neutron scattering techniques. In addition, the photosynthetic materials are being used as sources for the isolation of fully deuterated chlorophylls, bacteriochlorophylls, chlorins, quinones, carotenoids and lipids. These molecules are used for the reconstitution of selectively labeled natural photosynthetic assemblies, and for the synthesis of artificial assemblies with selected isotopic composition. This program is providing new materials for probing the components, structure, and mechanisms of charge separation as performed by natural and artificial photosynthetic systems.

8. *Reactive Intermediates in the Condensed Phase: Radiation and Photochemistry*

Trifunac, A.D.; Bartels, D.M.; **$1,773,000**
Jonah, C.D.; Shkrob, I. A.; Werst, D.W.
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Fundamental studies of chemical effects of ionizing radiation focus on the early time events in radiolysis and photoionization. The purpose is to provide molecular details of the energy and charge transport phenomena in liquids and in solids subjected to ionizing radiation. The knowledge developed in the course of this research will benefit diverse areas of technology such as radioactive waste management, polymer processing, treatment of hazardous wastes, and the broad use of silicon-containing materials. The study of charge transport, ion reactions, and newly discovered transient species encompasses polar and nonpolar liquids and crystalline and amorphous solids. The role of solvation in controlling reactivity of charged species is analyzed experimentally and theoretically. Solid-state studies of ions provide insights into control of chemistry via matrix-ion interaction and have led to development of new analytical methods for probing catalytic effects of silicon-based solids like zeolites. The role of excited states of neutrals and of ions is explored in photoionization studies of water and of hydrocarbon solutions. Ultrafast studies of water photoionization yield new details on the role of excited states of water. Studies of aromatic solutes in hydrocarbon solutions via two-color laser photoionization reveal the occurrence of hole transfer into the solvent manifold when highly excited aromatic radical ions are produced. These studies are carried out using state-of-the-art time domain tools which include a picosecond linear accelerator, a Van de Graaff accelerator, subpicosecond and nanosecond UV lasers coupled to specialized detection equipment.

9. *Molecular Systems for Photochemical Energy Conversion and Storage*

Wasielewski, M.R.; Chen, L.X.; Gosztola, D.; Wiederrecht, G.P. **$843,000**
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The principal goal of this project is to design, prepare, and study the fundamental properties of molecular systems that will efficiently convert light energy into useful chemical energy. The picosecond, high quantum yield photochemical charge separation that occurs in natural photosynthesis serves as a conceptual model for the systems studied in this project. Artificial photosynthetic charge separation systems are designed to yield photocatalysts that will perform well in practical chemical environments. New supramolecular systems that consist of covalently linked arrays of electron donors and acceptors have been synthesized. These systems utilize visible light to separate charge with 80% efficiency and separation lifetimes that exceed 1 millisecond. The organic electron donors and acceptors within these supermolecules maintain well-defined structural, solvation, and electronic relationships among themselves. Current research focuses on issues that are fundamental to optimizing charge separation and storage efficiencies in the solid state. This includes the interplay between the properties of the organized donor-acceptor array and the molecular organization of the surrounding medium. Ultrafast laser spectroscopy is used to probe the molecular interactions that occur in these ordered systems.

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Department of Applied Science

10. *Porphyrin Chemistry*

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This program focuses on bioenergetic reactions mediated by porphyrins with particular emphasis on the mechanisms by which light is harvested and converted into chemical energy in photosynthesis. The expanding body of structural, theoretical, and experimental data evolving from the photoconversion modeling is readily extended to the multielectron catalyses of nitrogen assimilation, regiospecific reactions, and carbon dioxide conversion mediated by the broad generic classes of porphyrins. To model these energy and electron transfer reactions, the project uses photochemistry, spectroelectrochemistry, magnetic resonance, X-ray, and synchrotron radiation techniques which are further supported by theoretical methods. Recent results with conformationally designed models have provided particularly simple synthetic avenues to controlling optical, redox, and excited state properties as well as sites of reactions in vitro. In combination with theoretical calculations, the synthetic models offer useful insights into photochemical and catalytic reactions that often occur on picosecond time scales in vivo. The cumulative thrust of the combined theoretical, structural, and experimental approaches is to characterize transients and mechanisms in bioenergetic conversion, and to provide specific guidelines for the development of synthetic photocatalytic systems.

11. *Electrochemistry and Photoelectrochemistry*

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The objective of this program is to provide new insights into the mechanisms of electrochemical and photoelectrochemical phenomena. The experimental objective is to understand the role of interfacial structure and organization in a variety of interfacial processes e.g., double-layer relaxations, charge (ion or electron) transfer between the solution and the electrode, electron transfer between electrode and immobilized or adsorbed redox moieties. The current focus is on heterogeneous electron transfer between a metal-electrode and redox species attached to the electrode, generally in the form of a self-assembled monolayer. The determination of the distance dependence of heterogeneous electron transfer is of particular interest. The experimental approach utilizes an indirect laser-induced interfacial temperature-jump (ILIT) technique. At its present level of development, ILIT can access interfacial rate processes occurring in the nanosecond time domain, arguably a leading-edge experimental approach exceeding the capabilities of other state-of-the-art electrochemical approaches. Theoretical analyses and computer simulations attack a broad range of electrochemical and photoelectrochemical problems that may be generally described as heterogeneous electron (or hole) transfer coupled with homogeneous chemical reactions.

Chemistry Department

12. ***Thermal, Photo- and Radiation-Induced Reactions in Solution***
Sutin, N.; Brunschwig, B.S.; **$2,770,000**
Cabelli, D.; Castner, E.W.;
Creutz, C.; Fujita, E.; Holroyd, R.A.;
Newton, M.D.; Schwarz, H.A.;
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This program addresses issues fundamental to the efficient capture and storage of light energy: excited-state formation, chemistry, and photophysics; energy transduction by electron-transfer reactions; and energy storage through chemical transformations. Theoretical and experimental efforts are elucidating the factors controlling excited-state lifetimes and electron-transfer rates; the roles of electronic configuration, donor/acceptor separation, bridging groups, nuclear-configuration and free-energy changes, as well as the role of solvent dynamics are being investigated through studies of transition-metal complexes and other donor/acceptor systems. Electron pulse radiolysis and flash photolysis techniques are being used to generate and characterize transient species important in solar energy conversion, including the preparation and properties of transition-metal complexes in unusual oxidation states and their ability to bind and activate small molecules, and to determine bimolecular and intramolecular electron-transfer rates. The properties and reactions of electrons and other ions in dielectric fluids are being studied utilizing both X-ray and high energy electron sources. The long-term storage of solar energy as fuels or valuable chemicals requires efficient coupling of light absorption and chemical transformation processes. Mechanistic studies of systems which couple photoinduced electron-transfer processes to the bond-forming reactions required in the photogeneration of hydrogen and the photoreduction of carbon dioxide to useful chemicals are a major focus.

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Structural Biology Division

13. ***Chemistry with Near Infrared Photons***
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The objective of this project is to establish useful chemistry that can be accomplished with the sun's most abundant, long-wavelength photons. Current focus is on reactions that suggest new concepts in red and near-infrared light-assisted synthesis of organic building blocks, high-value compounds, and fuels from abundant chemicals. Photochemistry of cage reactant pairs is being explored for controlled synthesis in zeolite matrices. Highly selective partial oxidation of small alkenes, alkanes, and substituted aromatics by molecular oxygen has been achieved with visible light at room temperature. Examples include conversion of toluene to benzaldehyde, propylene to acrolein, and cyclohexane to cyclohexanone. This is the first selective method for hydrocarbon oxidation by oxygen at high conversion. A central aspect of the new method is the exploitation of the very high electrostatic field inside the zeolite cage. It stabilizes the excited hydrocarbon-oxygen charge-transfer state by 1.5–3.0 electron volt, thus allowing initiation of the reaction with low-energy visible photons. Time-resolved FT-infrared absorption spectroscopy (step-scan technique) at ten nanosecond resolution has been developed as a new tool for mechanistic studies. The first transient infrared spectrum of a molecule in a zeolite matrix has been obtained. Elucidation of elementary steps of photochemical reactions in zeolites on the nano-to-millisecond time scale is in progress.

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Basic Sciences Division

14. ***Surface-Modified Semiconductor Electrodes and Novel Electrolyte-Semiconductor Interfaces***
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This research addresses basic issues in the photochemical conversion of light energy to electrical or chemical energy relating to understanding charge transfer processes at the semiconductor/redox electrolyte interface as a basis for tailoring the semiconductor surface or redox electrolyte to control photocorrosion, charge recombination, and electron transfer catalysis. The work includes the synthesis, characterization, and use of advanced surface modifying reagents for semiconductor photoelectrodes. The current research concerns the development of a simple quantitative model for understanding interfacial charge transfer, charge recombination studies of dye-modified nanocrystalline TiO_2 photoelectrochemical (PEC) solar cells, studies of multiple bandgap photoelectrodes for water splitting, transient and steady-state studies of the light-induced charge generation/recombination mechanism of sexithiophene films for photoelectrodes, and the development of a new solid-state PEC cell based on a plasticized polymer-redox electrolyte.

15. ***Photoconversion Processes in Liquid Crystal Porphyrin Films and Other Molecular Semiconductors***
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This research examines fundamental aspects of photoconversion processes in molecular semiconductors. Current emphasis is on understanding the dynamics of exciton motion and dissociation, since these processes control the production and initial separation of charge carriers. Steady state and time-resolved luminescence measurements have shown that exciton motion is extremely rapid in films of perylene diimides, with intermolecular hopping times on the order of 100 fs. Exciton dissociation by interfacial electron transfer must be able to compete with this hopping process in order to generate charge carriers. Various contacting films are being employed to elucidate the factors that control exciton dissociation or reflection at the interface. Some conducting polymer films have been found to promote rapid exciton dissociation at interfaces with perylene diimide films; the dynamics of the electron transfer process at such interfaces are being investigated. The conducting polymer/perylene diimide interface is one of the few known systems in which exciton dynamics occur on the same time scale as in the natural photosynthetic system. A detailed exploration of exciton dynamics in molecular semiconductor films will contribute to understanding natural photosynthesis and to the ultimate development of organic-based solar energy conversion systems.

16. Synthesis and Characterization of Novel III-IV and II-VI Semiconductor Quantum Dot Structures for Solar Photochemical Conversion

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The photochemical and photophysical properties of quantum dot structures are being investigated for solar photochemical conversion. Quantum dots of InP, GaP and $GaInP_2$ with the diameters ranging from 20 to 65 Å were synthesized as well-crystallized nanoparticles with bulk zinc blende structure. X-ray powder diffraction patterns of $GaInP_2$ quantum dots exhibit the zinc blende structure with lattice spacings which are approximately the average of the diffraction peaks of InP and GaP bulk materials. Colloidal solutions of InP, GaP and $GaInP_2$ quantum dots show optical absorption and emission spectra blue-shifted compared to bulk material. The high sample quality of the InP and GaP quantum dots results in excitonic features in the absorption spectra. For 20 Å- and 30 Å-GaP quantum dot preparations, the absorption spectra indicate that GaP has not undergone a transition from indirect to direct semiconductor. It seems that the GaP quantum dots remain an indirect semiconductor, but the selection rules are relaxed to allow indirect transitions because of symmetry-breaking effects produced by small quantum dot size. The GaP and $GaInP_2$ quantum dot colloids exhibited very intense (quantum yields of 15%) visible photoluminescence at room temperature. The photoluminescence for InP preparations showed highly efficient band-edge photoluminescence (lowest energy HOMO-LUMO transition) after the particles were etched. The quantum yield is 30% at room temperature and 60% at 10 K which is tunable with particle size.

17. Carrier Dynamics and Quantization Effects in Photoelectrochemistry

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The dynamics of photoinduced charge transfer at semiconductor-liquid interfaces, for both macroscopic and size-quantized structures, is being investigated both theoretically and experimentally. New, rigorous ab initio calculations of electron transfer kinetics at model semiconductor-liquid redox systems have been performed which treat, for the first time, the full electronic structure of the coupled semiconductor-solvent-redox couple system. Experimental studies of electron transfer dynamics at semiconductor-liquid junctions are being conducted in the ns to fs time scales using transient photoluminescence spectroscopy based on upconversion and time-correlated single photon counting; the theoretical predictions are being tested against experiment. A model to extract the heterogeneous rate constants from the photoluminescence decay data has been developed. Results for p-GaAs electrodes capped with a thin $GaInP_2$ surface barrier show nearly ideal kinetic behavior and an electron transfer rate that is apparently electric field-dependent; this electrode also shows an ideal concentration dependence of the current-voltage characteristic. Studies are being made of the electron cooling and electron transfer dynamics in excellent quality InP quantum dots. These quantum dots exhibit highly efficient band-edge emission and an apparent "dark" excitonic ground state; they show much faster electron transfer to methyl viologen cations compared to cobaltocenium ions.

18. Fundamental Studies of Electron Injection Dynamics at Dye-Sensitized Nanostructured Semiconductors in Photochemical Solar Cells

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The kinetics of electron injection from dye molecules adsorbed on nanostructured TiO_2 films into the TiO_2 conduction band is being investigated in the fs to ns time regime using fs to ns transient absorption spectroscopy and ns to ps transient photoluminescence spectroscopy. These spectroscopic systems have been constructed and are operational. An experimental procedure to reproducibly synthesize excellent quality TiO_2 colloidal particles that can be subsequently formed into nanostructured electrodes has been developed. This capability is critical since the electron injection dynamics in nanostructured films will be very sensitive to the morphology, size, and surface properties of the TiO_2 particles. We will attempt to help resolve a major controversy in this field related to the magnitude of the electron injection rate, which has been reported to vary from fs to ns. This project is part of an integrated effort of basic and applied research to develop and evaluate the potential of photochemical (i.e., dye-sensitized semiconductor) solar cells as a viable technology. The basic research contained in this project will underpin the applied/development effort.

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Radiation Laboratory

19. Sulfur-Centered and Other Heteroatom-Based Organic Radicals

Asmus, K.D.; Hug, G.L.; **$697,000**
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This project is concerned with the properties of radicals derived from heteroatom-containing organic compounds, particularly those with the radical site located at the heteroatom itself. The emphasis on sulfur-organic molecules reflects the significance of this group of compounds in radiation-induced biological damage. Of primary interest are odd-electron bonded species in which antibonding electrons exert a bond-weakening effect on existing or newly formed bonds. Other systems which can participate in this type of bond and are important for comparison to the sulfur systems are radicals containing the elements N, P, O, Se, and the halides. These studies have fundamental implications for understanding the formation and breakage of chemical bonds. Current studies deal with S∴N, Se∴Se, S∴S and S∴P $2\sigma/1\sigma^*$ three-electron-bonded radical cations and anions, resulting from an intramolecular interaction of an unpaired electron on the oxidized heteroatom with a free electron pair of another heteroatom. Conformational preferences have been theoretically determined for cyclic S∴N radical cations, and optical and vibrational frequencies have been calculated in excellent agreement with experimental measurements obtained by electron pulse radiolysis and Raman spectroscopy. The optical absorption spectra of these systems respond very sensitively to small changes in electronic and structural parameters.

20. Reactive Intermediates and Elementary Chemical Processes in Solution

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The primary aim of this project is the study of chemical reaction mechanisms which are initiated by or involve free radicals. These basic studies are a prerequisite for the optimization and control of radical reaction systems. The investigations rely on time-resolved radiation chemical techniques using optical and electron spin resonance (ESR) spectroscopic detection, complemented by photochemistry, steady-state radiolysis, electrochemistry, mass spectrometry and chromatographic analysis. Free radical and redox-initiated degradation of halogenated organic compounds often proceeds through halogenated peroxyl radicals. It has now been established that these species undergo an overall two-electron transfer process with various organic sulfur and selenium compounds and inorganic iodide, involving radical adduct intermediates and solvent participation. Substantial progress has been made in understanding the decarboxylation mechanism of sulfur-containing amino acids and the role of this process in their overall redox chemistry. The unusual ESR behavior of e_{aq}^- with oxidizing radicals has been explained by correlating the energetics of the reaction with the excited state energies of the products. Electron transfer quenching of the triplet excited state of 2,2'-biphenol by fumarate has been established. The kinetic behavior has been determined with high accuracy for the reaction of methyl radicals with iodine species in aqueous solution, a system of potential significance in nuclear reactor accidents. Detailed investigation of the $^{\cdot}OH$ induced oxidation of thiocyanate has established the existence of very short-lived $SCN(OH)^{\cdot}$ and $^{\cdot}SCN$ radicals as precursors of $(SCN)_2^{\cdot -}$.

21. Structure and Chemical Properties of Radiation-Produced Intermediates

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Highly reactive free radical and molecular excited state intermediates produced by radiolysis or photolysis are studied to determine their often unusual structures and bonding characteristics and to relate these to the chemical properties, kinetics, and mechanisms of the reactions they undergo. This will enhance our ability to design new chemical systems that store, convert, or liberate energy in desired ways. Time-resolved experimental approaches include resonance Raman spectroscopy, electron spin resonance, and microwave absorption, which are complemented with theoretical calculations of electronic structure based on modern methods of quantum chemistry. Recent work on aminobenzoic acid radicals has established the role of excited states in intramolecular electron transfer leading to bond dissociation and accounted for the marked pH dependence of the nature and yields of the reaction products. A structural explanation has been found for the greatly enhanced proton reactivities of carboxylic and amide groups when bonded to semireduced pyridine, and unambiguous evidence has been obtained for protonation of the amide group at oxygen, rather than at nitrogen. New quantum mechanical operators have been developed that improve efficiency of theoretical hyperfine coupling calculations. Accurate hyperfine coupling constants have been determined for HNCN radical to aid interpretation of the observed laboratory spectra. Dipole moments of the lowest singlet excited states of coumarin and aminophthalimide donor-acceptor molecules have been measured to facilitate their use as probes of solvent polarity and dielectric relaxation behavior.

22. Mechanisms of Redox Processes in Coordination Compounds

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This project involves determination of the contributions from the electronic and molecular structures of metal complexes to the rates of redox reactions in which they participate. Such reactions are essential components of the overall processes of carbon dioxide fixation, the splitting of water, and the destruction of chemical contaminants. Magnetokinetic effects, which probe electronic interactions in reactions of a transition metal complex with a radical or another metal complex, have been investigated by experimental and theoretical means. The Zeeman mechanism, spin-orbit coupling and hyperfine coupling, among other perturbations to the Hamiltonian, are being unravelled by comparing several series of compounds of the transition metal ions Ni(III), Co(II) and Mn(II). Recent studies have explained the roles of the orbital angular momenta and the nuclear and electronic spins, whether interacting with each other or with a magnetic field. Ongoing work involves the determination of the role of the dynamic probability factor, and its convolution with the spin evolution, on magnetokinetic effects in radical-ion reactions. Mechanistic studies are aimed toward promoting the activation of small molecules such as carbon dioxide, nitrate or sulfur dioxide by transition metal complexes in unusual oxidation states. Such studies have demonstrated structural contributions to the charge localization, either in a ligand or at the metal center, in porphynoid, phthalocyanine, and simple macrocyclic complexes.

23. ***Photochemical and Photoelectrochemical Processes for Energy Conversion***
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Mechanistic and kinetic aspects of excited state and redox behavior of organic dyes, functionalized fullerene derivatives and semiconductor nanoclusters are being studied. Electron pulse radiolysis and laser flash photolysis are used to investigate the primary chemical events in these systems. Surface modification of large-bandgap semiconductors such as TiO_2, ZnO and SnO_2 with either squaraine and oxazine dyes or small-bandgap semiconductors such as CdS and CdSe provides a convenient method to extend the semiconductor photoresponse into the infrared and to improve the efficiency of charge separation. Photoelectrochemical, microwave conductivity and spectroelectrochemical measurements of dye-modified semiconductor films indicate that electron injection between an excited sensitizer and the semiconductor nanocrystallite can be controlled by suitable choice of experimental conditions. The back electron transfer between an injected electron and the sensitizer cation radical as well as the role of redox couple in sensitizer regeneration will be a major focus of future work. Charge-separated products have been confirmed in mechanistic studies on intramolecular electron- and energy transfer reactions of fullerenes bearing covalently attached photo- or electroactive substituents. Variation of the active centers and modification of the spacing between donor and acceptor sites have differentiated electron transfer from excimer formation involving singlet excited fullerene states.

24. ***Heavy Ion Radiolysis and Track Structure***
LaVerne, J.A.; Pimblott, S.M.; **$455,000**
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The effects of particle track structure on radiation chemical processes are examined using experimental and theoretical techniques in order to provide basic knowledge on the variation of radiation damage with different types of ionizing particles. Single photon counting studies with heavy ions from the Notre Dame Nuclear Structure Laboratory show, for the first time, that the yields and lifetimes of the excited states in neat liquid benzene are dependent on particle type. Examination of the Fricke dosimeter with ^{58}Ni and ^{238}U ions suggests that even for very high linear energy transfer particles there is a significant escape of radicals from the track which has important radiation chemical and biological implications. Detailed theoretical studies using complete Monte Carlo track simulation methods demonstrate that the spatial distribution of energy deposition by electrons in water changes from a centered sphere through an ellipsoid to a teardrop shape as the energy increases. Kinetic simulations reveal the effects of electron energy and track structure on the yield of the Fricke solution and aid in the reconciliation of the time-dependent kinetics and scavenger yield studies of the hydrated electron in electron radiolysis of water. Energy partition between the core and penumbra of heavy-ion tracks in liquid argon slightly favors the core.

25. ***Radiation Chemistry Data Center***
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Chemical property data for reactive intermediates in solution are being compiled, evaluated and collected into databases, focusing on free radicals and excited states produced in radiation chemical studies. Electronic publication of these databases on-line facilitates easy retrieval of timely kinetic data. Scientists and engineers modeling chemical systems involving free-radical intermediates use these values as input to their calculations. Complementary data from the photochemical literature are also included in this information retrieval effort. A compilation of rate constants for reactions of aliphatic carbon-centered radicals in aqueous solution has been completed and published. The center provides on-line resources for searching the Radiation Chemistry Data Center (RCDC) bibliographic database, and numeric databases containing condensed-phase triplet-triplet absorption spectral data, and rate constants for inorganic radicals in aqueous solution. A world wide web site (http://allen.rad.nd.edu) has been developed for the RCDC, containing an updated critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH / O-) in aqueous solution, and a compilation of kinetic data on the decay and reactivity of singlet molecular oxygen in fluid solution.

Chemical Physics

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Fundamental Interactions Program

26. ***Chemical Theory***
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One focus of this research is the theoretical description of the structure and dynamics of metal clusters. The goal is to determine the structure and energy of various clusters and to investigate the relationship between these properties and the reactivity of clusters with different gas-phase molecules. Close connection is made to the program of Riley and coworkers (at Argonne National Lab) which addresses many of the same questions via experimental measurements. First principle and semiempirical electronic structure techniques are utilized along with classical dynamics. Theoretical developments are directed toward discovery and testing of new one-electron density functional methods which would allow self-consistent electronic structure calculations on large systems. A second focus involves analysis of the kinetics and nonequilibrium structure associated with irreversible or far-from-equilibrium adsorption and catalytic reaction processes on solid surfaces. A smaller effort involves development of rigorous quantitative methods for ab-initio electronic structure calculation of PES, in particular based on multiconfiguration self-consistent field approaches. Applications are made to important catalysis-related reactions involving metal clusters and to combustion-related gas phase reactions.

27. ***Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals***
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The goals of this program are (1) to obtain accurate thermochemical data, such as ionization energies and bond dissociation energies, for neutral polyatomic molecules, radicals, and their ions; (2) to study the photoionization and photodissociation dynamics of molecules and radicals induced by the absorption of UV and VUV photons; and (3) to investigate the reaction dynamics and mechanisms of fast radical-molecule and radical-radical reactions. One current focus is on the studies of organosulfur radicals and transition metal carbonyl compounds and their fragments. Oxidation of organosulfur compounds, which are emitted to the atmosphere due to the incomplete combustion of coal and oil, ultimately lead to the formation of SO_2 and acid rain. Previous studies indicate that the oxidation rate for organosulfur pollutants increases substantially in the presence of UV radiation. The study of the UV and VUV photochemistry of organosulfur species is relevant to the modeling of atmospheric sulfur chemistry cycles. Motivated to obtain a detailed understanding of the catalytic ability of transition metal ions, experiments have been initiated to examine systematically the energetics and reactivities of transition metal carbonyl compounds and their fragments. Recent focuses have also been expanded to include oxygen-containing hydrocarbon radicals.

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Chemistry Division

28. ***Metal Cluster Chemistry Research***
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The goal of this program is to understand how cluster structure depends on cluster size and how cluster properties depend on structure, thereby contributing to a better understanding of surface chemistry and heterogeneous catalysis. Experimental and theoretical studies of the chemical and physical properties of clusters of catalytically active transition metals are pursued. Experimentally, the reactivity of clusters with small molecules is investigated. These investigations include measurements of absolute reaction rate constants and adsorbate binding energies, and determinations of product compositions, the nature of adsorbate binding sites, and cluster geometrical structure. A complimentary experimental effort which uses various laser techniques to obtain the optical, infrared, and photoionization spectra of metal clusters and cluster-adsorbate complexes provides size-specific electronic structure and ionization potential information as well as detailed insights into cluster-adsorbate interactions. The theoretical effort involves studies of stable and metastable structural forms of clusters and interconversion between these, cluster phases and phase changes, thermal stability and fragmentation, reactive and nonreactive cluster-molecule interactions, etc. Both single-component and two-component (alloy) clusters are investigated using existing and newly-developed semiempirical potentials and ab initio approaches. The goal is to understand cluster properties and the mechanisms defining them in terms of the nature of the interatomic forces.

29. ***Photoionization-Photoelectron Research***
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This program focuses on the investigation of gas-phase species using the photoionization mass-spectrometric method and its derivatives (TPES, PEPICO, ZEKE, MATI). The technical capabilities of this program are being currently complemented by the addition of pulsed laser-based experiments. The scientific emphasis is on reactive intermediates in combustion and other energy-producing processes, and on key species involved in subsequent atmospheric chemistry. These ephemeral species are produced in situ using selected techniques (abstraction reactions, discharges, on-line synthesis, pyrolysis, laser photodissociation, etc.) The primary motivation of our research is to provide accurate and reliable thermochemical data and spectroscopic and structural details that are crucial in comprehending pertinent chemical reactions. In addition to detailed data, we seek to extract useful generalities, which yield new insights into the nature of chemical bonds or dynamical processes accompanying photoionization. The desired level of details is unraveled by combining suitable experimental techniques with subsequent data analysis using novel fitting methods. Our current measurements on CF_3OH, CF_2O, and CF_3-containing species address important open questions regarding the environmental soundness of the latest generation of refrigerants. Other recent measurements, such as those on C_2H_5O and CH_3O isomers, CH_nS (n=1-3), and HNCX and NCX, (X=O, S) have provided valuable new data related to combustion of hydrocarbons, alcohols, and sulfur-containing fuels, and to the industrially important $RAPRENO_x$ process. Our experimental results also play a very important role in testing the most sophisticated ab initio calculations, which have demonstrated near-chemical accuracy for small molecules, but have not yet established a clear track record for larger (>3 nonhydrogen atoms) systems.

30. ***Chemical Dynamics in the Gas Phase***
Wagner, A.; Davis, M.; Harding, L.; Shepard, R.; MacDonald, R.; Michael, J.; Hessler, J.; Gray, S. **$2,417,000**
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The program mission is to characterize the gas-phase chemical reactivity of small molecules and radicals, especially those involved in combustion, by a combination of both theory and experiment. The experimental effort involves high-temperature reaction rate studies by UV absorption in two shock tubes and low-temperature product distribution studies by IR absorption in a flow tube. A companion data analysis effort has expanded the use of sensitivity coefficients and error propagation in accounting for secondary chemistry. Recent measurements have included the dissociation rate constants of chlorofluorocarbons (CFCs) and their alternates, the HCN product distributions from CN attack on alkanes, and the reactions of methyl radicals with themselves and with oxygen. The theoretical effort involves large-scale studies to compliment the above measurements and others done outside the group. Associated methods development emphasizes the efficient exploitation of advanced computers, especially massively parallel ones. Recent theoretical activity has included electronic structure studies of potential energy surfaces, classical and quantum dynamics studies of reactivity on those surfaces, hierarchical studies for the assignment of highly excited spectra, and low dimensional manifold studies for the simplification of coupled kinetic equations. The close coupling between theory and experiment brings a unique combination of expertise to bear on problems of chemical reactivity.

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Department of Applied Science

31. ***Combustion Kinetics and Reaction Pathways***
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The mission objectives of this basic research project are to improve the understanding of combustion kinetics and thermodynamics. Specific interest is focused on: (1) determining absolute rate coefficients for gas phase reactions and identifying pathways for multichannel reactions; and (2) characterizing the photoionization properties and thermochemistry of relevant molecules and free radicals. For kinetics studies, the project features a shock tube to obtain reliable kinetic measurements over a wide range in temperature (800K to 2500K). Also, theoretical calculations are performed in conjunction with experiments on the unimolecular dissociation of combustion-related molecules. For thermodynamics and reaction pathways studies, a discharge flow-photoionization mass spectrometer apparatus is employed in determining primary products from multichannel reactions and in performing photoionization studies on reactants, free radicals and stable reaction products. In addition to its intrinsic scientific interest, this work provides fundamental information to other researchers such as theorists (who need reliable experimental data with which to test their calculations) and modellers (who require rate constants and thermodynamic values in order to study practical problems like fuel efficiency, pollutant formation and destruction, flame suppression and waste chemical incineration).

32. ***Gas-Phase Molecular Dynamics***
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Research in this program explores the energetics, dynamics and chemical reactions resulting from molecular collisions in the gas phase. We are interested in the microscopic factors affecting the structure, dynamics and reactivity of short-lived intermediates in gas-phase chemical reactions important in combustion chemistry. Molecular species are studied using both experimental and theoretical tools including high-resolution spectroscopic probes, quantal wavepacket propagation, and time-independent quantal calculations. A new initiative in radical-radical chemical reaction kinetics is being started to augment these studies. The goal of the work is a fundamental understanding of the transient species involved in chemical processes related to combustion chemistry.

33. ***Photoinduced Molecular Dynamics***
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The general aims of this program are the detailed study of molecular photofragmentation dynamics and the characterization of the structure, spectroscopy and intramolecular dynamics of chemical intermediates important in combustion chemistry. Coherent VUV and ultra-fast laser sources are used to induce photo-processes such as ionization, dissociation, intramolecular motion and desorption, the dynamics of which are probed by a variety of state- and energy-resolved ionization-based techniques and nonlinear pump-probe spectroscopy. State-resolved dissociation and photoionization measurements focus on the partitioning of energy and angular momentum in elementary photofragmentation processes at low and very high laser intensities. The latter investigate the response of molecules to intense fields well beyond the perturbative regime which introduces new selectivity and "field induced" fragmentation pathways. Further studies of the effects of well characterized fields on simple, isolated systems are also under investigation with the ultimate goal of optimal control of physical and chemical processes. State-resolved, VUV detection methods are also being implemented in new studies of photoinduced desorption and reactions of molecules on surfaces. These studies are focused on elucidating the mechanism of photoinduced processes via measurements of the quantum state and energy distributions of the desorbed molecules and/or molecular fragments. Other studies utilize in-situ, time-resolved, sum frequency generation spectroscopy for probing the structure and dynamics of surfaces.

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Chemical Sciences Division

34. ***Energy Transfer and Structural Studies of Molecules on Surfaces***
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The goal of this research is to study the dynamics of excited electronic states on surfaces, at interfaces, and in condensed phases and to develop new laser techniques for studying these dynamics. The research program is both theoretical and experimental in character, and includes nonlinear optical and ultrafast laser techniques in addition to a variety of standard surface science tools for characterizing surfaces and adsorbate-surface interactions. Recent work has centered on developing and applying femtosecond two-photon photoemission to study the dynamics of electrons at metal-polymer and magnetic interfaces. The ultrathin layers under study range from 4 Å to 4 nm in thickness. The results of this program have a direct bearing on high-speed technological devices and materials, the fundamental physics of two-dimensional systems, and on other problems of general interest such as surface photochemistry and optical processes at interfaces.

35. ***Chemical Dynamics***
Lee, Y.T.; Chen, Y.; Head-Gordon, M.; Lester, W.A.; Miller, W.H.; Moore, C.B.; Neumark, D.; Johnston, H.S.; Suits, A.G. **$2,187,000**
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The objectives of this program are to develop the basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions that have a major impact on combustion and advanced energy production technologies. Recent emphasis has been to determine the structure and chemical behavior of reactive free radicals and highly-excited polyatomic molecules, and to provide microscopic details of primary dissociation and bimolecular processes. These objectives are achieved with a strongly coupled experimental and theoretical-computational approach, using emerging technologies. Dynamical studies use advanced molecular beam and laser methods including photofragmentation translational spectroscopy, ion imaging and fast-beam photodissociation techniques. Kinetics studies employ IR laser flash kinetic spectroscopy, IR-UV double resonance and high-resolution UV-VUV laser spectroscopy. New theoretical methods and models are developed both to provide insight into chemical reactivity and the dynamics of reactive processes, and to provide more accurate and efficient means of calculating reaction rates and molecular structures. Current studies include crossed-beam reaction dynamics and photochemistry with emphasis on processes involving reactive hydrocarbon radicals and carbon atoms. Studies continue to probe the structure and dynamics of the chemical transition state and the microscopic mechanisms of primary chemical processes. New studies take advantage of the Chemical Dynamics Beamline recently commissioned at the Advanced Light Source, providing greatly enhanced experimental capability for studies of primary photochemical and photoionization processes and reaction dynamics.

36. ***Physical Chemistry with Emphasis on Thermodynamic Properties***
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The object of this project is the measurement and the theoretical calculation of the thermodynamic and related properties of novel or prototype systems. Recently, the emphasis has been on ionic fluids under near-critical or supercritical conditions. Binary fluids have been selected and measured that model a pure ionic fluid but have critical points at experimentally accessible temperatures. Critical exponents have been determined by phase equilibria and light scattering methods. Recent results show a clear crossover from Ising to classical (mean field) exponents as the temperature moves away from the critical point. Other recent research has included comprehensive equations of state for the important systems such as $NaOH\text{-}H_2O$ and $CaCl_2\text{-}H_2O$. For the latter, new theoretical basis was developed based on mixtures of dipole (H_2O) and quadrupole ($CaCl_2$) molecules for which Monte Carlo calculations were made. This represented a good first approximation that was refined by small semi-empirical adjustment terms. Investigations often involve collaboration with Lawrence Livermore National Laboratory (LLNL), Oak Ridge National Laboratory (ORNL), or the United States Geological Survey (USGS).

Energy and Environment Division

37. ***Combustion Chemistry***
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Combustion processes are governed by chemical kinetics, energy transfer, transport, fluid mechanics, and the complex interactions among these. The pathways for energy movement and the competition among the pathways determines reaction rates, product yields, and product state energy distributions. Understanding the fundamental chemical processes offers the possibility of optimizing combustion processes. The objective of our research is to address fundamental issues of chemical reactivity in combustion systems. We emphasize studying chemistry at both the microscopic and macroscopic levels. Our current activities are concerned with 1) developing models of combustion process with complex (realistic) flow fields that include detailed chemical mechanisms; 2) developing tools to establish limits of model validity; 3) using functional sensitivity analysis to explore relationships between dynamic observables and the potential energy surface structure that are important in rate coefficient calculations; and 4) calculating rate coefficients. A theme of our research is to bring new advances in computing, and, in particular, parallel computing to the study of important, and computationally intensive combustion problems.

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Division of Applied Physics

38. ***Chemical Kinetics Modeling***
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This project emphasizes numerical modeling of chemical kinetics of combustion. Combustion modeling applications in both practical combustion systems and in controlled laboratory experiments are included. Elementary reaction rate parameters are combined into mechanisms, which then describe reaction of the fuels being studied. Detailed sensitivity analyses are used to identify those reaction rates and product species distributions to which the results are most sensitive and therefore warrant the greatest attention from other experimental and theoretical research programs. Experimental data from a variety of environments validate the reaction mechanisms, including results from laminar flames, shock tubes, flow systems, detonations, and even internal combustion engines. Particular attention will be given to chemical factors including fuel molecular size and structure, emphasizing differences in combustion of isomers of selected hydrocarbons.

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Environmental Molecular Sciences Laboratory

39. ***Chemical Structure and Dynamics***
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The Chemical Structure and Dynamics program responds to the need for a fundamental molecular-level understanding of chemistry at environmental interfaces, by providing insight into condensed-phase chemistry and developing and validating ab-initio theories. There are three primary program elements: (1) Interfacial Chemistry, with a special focus on water-oxide interfaces; (2) High-Energy Processes at Environmental Interfaces; and (3) Understanding the Condensed Phase Through Cluster Models, recognizing atomic and molecular clusters as a form of matter whose properties lie outside the realm of general chemical experimental science, and that not only provide a quantitative basis for comparison with theory, but are also the source of a microscopic understanding of the condensed phase. The approach includes (1) synthesis of unique and well-characterized surfaces and interfaces by controlled deposition of atoms, molecules, and clusters using molecular-beam epitaxy; (2) characterization of surfaces and interfaces by atomic-resolution surface mapping (e.g., scanning tunneling microscopy) and near-field optical microscopy, in addition to various state-of-the-art surface science and optical spectroscopic methods combined with molecular scattering and diffusion studies; (3) synthesis of atomic and molecular clusters that mimic the structures of surface sites and of solvated species in solutions and at interfaces; (4) laser methods for studying atoms and molecules with time resolution sufficient to measure chemical dynamics in real time; and (5) direct photon and/or electron excitation of surfaces, interfaces, and molecules to model chemical processes important in mixed waste storage (radiolysis) and in the energetic destruction of wastes.

40. Molecular Theory and Modeling
Dunning, T.H.; Garrett, B.C.; **$2,425,000**
Corrales, L.R.; Dang, L.X.;
Feller, D.F.; McCarthy, M.I.;
Palmer, B.J.; Peterson, K.A.
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The molecular theory and modeling project is designed to increase understanding of molecular processes important in environmental chemistry. The project integrates ab initio studies of fundamental molecular processes in model systems (e.g., clusters) with modeling of the complex molecular systems found in the environment. Four research areas are emphasized: (1) properties (e.g., structure and energetics) of aqueous clusters and aqueous solutions containing inorganic species (e.g., metal and radionuclide ions) and organic species (e.g., chlorinated hydrocarbons, CHCs), including the studies of molecular processes at aqueous-vapor and liquid-liquid interfaces (e.g., water-CHC interfaces); (2) structure and energetics of ion-ligand complexes (such as metal ions with crown ethers) and the dynamics of complex formation in aqueous solutions, including studies of factors influencing selectivity and efficiency (e.g., ligand design, solvation, etc.); (3) properties of aqueous-mineral interfaces that control the binding of ions and molecules to soil minerals and the dynamics of molecular processes at these interfaces, including adsorbate kinetics and solvent and adsorbate structure at the interface; (4) properties of amorphous materials that control their dissolution (e.g., by water) and degradation (e.g., by radiolysis), including the structure and thermodynamics of bulk materials, surfaces, and interfaces with other phases. This knowledge will further the development of new processes for the separation of metals from liquid wastes, the construction of reliable models of contaminant transport and transformation in soils and groundwater, and the assessment of amorphous materials proposed for long term isolation of radionuclides.

Sandia National Laboratories, California Livermore, CA 94551

Combustion Research Facility

41. Turbulent Reacting Flow Research
Barlow, R.S.; Schefer, R.W.; **$1,300,000**
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This experimental and computational research project is directed toward an increased understanding of the coupling between chemical kinetics and turbulent mixing in reacting flows. Current research efforts address fundamental issues, such as the effects of differential diffusion; unsteady strain and flame curvature; the influence of heat release on the scalar dissipation field in nonpremixed flames; the geometric properties of turbulent premixed flames; and the role of turbulence-chemistry interactions in the formation of pollutants. Quantitative techniques for simultaneous imaging of multiple scalars are used to determine the spatial structure of turbulent reaction zones. The temporal evolution of flame structures is investigated by obtaining two co-planar images of CH with a variable time delay. The influence of turbulent mixing on thermochemical states is determined by simultaneous point measurements of NO, OH, the major species, temperature, and mixture fraction. These detailed multiscalar data reveal instantaneous relationships among scalars and constitute a unique basis for evaluation and refinement of turbulent combustion models. Fundamental aspects of reacting flow are studied computationally by direct numerical simulation, where all scales of fluid motion are computed. Two-dimensional flow simulations with detailed chemical kinetic mechanisms are used to investigate hydrocarbon flame response to unsteady flow-induced strain rate and curvature. Recent focus has included migration to massively parallel architectures, adaptive mesh refinement, and stiff time-integration techniques to enhance computational efficiency.

42. Enhanced Research Capabilities in Chemical Dynamics Research
Chandler, D.W. **$255,000 Equipment**
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A new user facility in the Combustion Research Facility at Sandia National Laboratories is being built for the study of individual reactions and processes that are important to combustion. This facility includes a crossed molecular-beam apparatus, a molecular-beam / ion-imaging apparatus and a set of tunable, high-intensity lasers. Unimolecular dissociation of small molecules will be studied to determine bond strengths, branching ratios and dissociation mechanisms. The measurement of vector correlations between fragments will be of particular interest. Collisional energy transfer processes will be studied in order to determine the amount of energy transferred between a hot polyatomic molecule and cold "bath" molecules. These bath molecules will typically be atoms or diatomic molecules. Bimolecular reactions such as the H + O_2 and H + CO_2 reaction will also be studied using the unique crossed molecular-beam apparatus incorporating ion-imaging techniques for the detection of the reaction products. This technique utilizes narrow band lasers and spatially resolved ion detection to determine the velocity and quantum state of the ions formed. This information provides a stringent test of potential energy surfaces that dictate the reaction kinetics.

43. *Chemical Dynamics and Kinetics*

Chandler, D.W.; Miller, J.A.; **$1,750,000**
Rohlfing, E.A.; Hayden, C.C.;
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The goal of this research is to understand the details of fundamental chemical processes that occur in combustion. Experiments in chemical kinetics use approaches such as laser-photolysis/laser-induced fluorescence, long-path IR absorption, mass spectrometric and laser diagnosed flow-reactor studies, and high-temperature shock-tube measurements. Recent systems of interest have included the reactive systems CH + CO, O_2 and Cl + hydrocarbons and the collisional quenching of electronically excited OH. These experimental studies are aided by quantum chemical and statistical theoretical calculations. Experiments in chemical dynamics emphasize collecting data for elementary processes and individual molecules resolved to a quantum-state level. Techniques utilized include ion imaging of unimolecular and bimolecular reactions, femtosecond time-resolved approaches (transient absorption, photoelectron spectroscopy, and stimulated Raman scattering), and linear and nonlinear laser spectroscopies. Recent applications have included ion-imaging studies of the product angular distributions of the H atom fragments and H_2 fragments from the multiphoton excitation of methane. Femtosecond time-resolved studies using photoelectron spectroscopy have focused on the investigation of internal conversion dynamics in conjugated polyenes. Recent spectroscopic studies have emphasized the application and development of two-color resonant four-wave mixing and laser-induced grating techniques for molecular spectroscopy and photodissociation dynamics, with application to the important HCO and CH_2CHO radicals.

44. *Novel Laser Facility for Basic Research in Optical Diagnostics*

Farrow, R.L.; Paul, P.H. **$50,000 Operating**
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It has become clear that continued progress in developing quantitative optical diagnostics requires an increasingly rigorous and detailed understanding of collisional phenomena. We propose to construct an innovative system of high-repetition rate, short-pulse lasers optimized for excite/probe studies of collisional processes. The lasers will be highly configurable with respect to pulse widths and output wavelengths, and will offer near-transform-limited pulse widths in the range 10-100 ps and at ~2 ns. This system will allow us to 1) significantly extend our previous RET experiments over a wider range of temperatures, to more subject species, and to foreign-gas colliders; 2) measure mass transport properties, energy transfer, and reorienting collisions in transient species using novel laser-induced grating techniques; 3) measure electronic quenching rates of species with short upper-state lifetimes; and 4) develop new picosecond-pulse diagnostic techniques that are less sensitive to collisional effects than conventional methods. These capabilities will have a significant impact on the advancement of optical diagnostic techniques such as CARS, LIF, degenerate four-wave mixing (DFWM) and absorption spectroscopy, through enhanced understanding of collisional processes, leading to more quantitative diagnostics modeling. The availability of sub-nanosecond pulses will allow basic studies to be conducted under combustion-like conditions. In addition, the lasers will provide powerful new capabilities when applied directly as diagnostics tools. The system will be located in a dedicated laboratory available for collaborative experiments by external users and CRF staff. External researchers will benefit from the facility in two ways: through improved diagnostics codes and scientific publications available from the CRF, and through use of the equipment during visits. Interested researchers should consult the section on CRF user facilities elsewhere in this document.

45. *Combustion Research Facility (CRF) Diagnostics Research: Nonlinear Spectroscopic Processes*

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This project involves the development, support, and application of nonlinear spectroscopic diagnostics for Combustion Research Facility programs. Emphasis is on coherent anti-Stokes Raman spectroscopy (CARS), resonant four-wave mixing techniques, and cavity ringdown spectroscopy for measurements in reacting gases. CARS is a relatively mature technique that provides spatially and temporally precise measurements of temperature and major species concentrations. Degenerate four-wave mixing (DFWM) has recently emerged as a coherent diagnostic roughly similar to CARS but offering greatly increased sensitivity. Cavity ringdown spectroscopy is a laser absorption technique that provides greatly enhanced sensitivity compared to conventional methods. The work is focused on investigations of fundamental issues involved in quantitative applications of DFWM. Topics include experimental studies of isolated DFWM line shapes and intensities as influenced by collisional and Doppler broadening, electronic quenching, predissociation, thermal-grating generation, and laser saturation effects. High-resolution pulsed laser systems, in both the ultraviolet (UV) and infrared (IR) wavelength regions, are used for detailed spectral studies. The experimental results are compared to theoretical calculations, leading to quantitative but simpler models for spectral analysis software. Computer codes for analyzing CARS and DFWM spectra are being developed and made available to diagnostics and combustion researchers. Polyatomic molecules in flames and discharges have been detected by exciting IR transitions using DFWM and cavity ringdown techniques. The use of IR excitation here is new, and will dramatically increase the number of species detectable by these methods. A technique for measuring the methyl radical, a transient polyatomic species important in combustion and diamond film growth, has been developed based on DFWM with UV excitation. Current work is aimed at further quantifying a method of detecting carbon monoxide by multiphoton-excited laser-induced fluorescence (LIF). Ionization and two-photon cross sections are being investigated to provide a more accurate model for analyzing LIF data for carbon monoxide concentration measurements.

46. ***Flame Chemistry: Modeling and Experiments***
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This research program represents an integrated effort to understand the chemistry of combustion both qualitatively and quantitatively through the development of predictive mathematical models. There are three aspects of the program: (1) the mathematical modeling of flame experiments and other macroscopic experiments where chemistry is a critical factor, (2) the theoretical prediction of rate coefficients and product distributions of critical elementary reactions using a combination of statistical and dynamical methods in conjunction with ab initio potential energy surfaces, and (3) low-pressure flame experiments in which laser-induced florescence and mass spectrometry are the principal diagnostic tools. The focus of the research is on combustion-generated pollutants (nitrogen oxides, soot and its precursors, and other air toxics) and on limit phenomena in combustion (flammability limits, extinction limits, etc.).

47. ***Diagnostics Research: Novel Techniques and Strategies***
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The research goals of this project include the conception and development of novel laser-based diagnostic techniques for Combustion Research Facility programs. New techniques involving ultrafast phenomena, wave-mixing, and thermo-acoustic scattering as well as new strategies in planar laser-induced fluorescence (PLIF) and resonant multiphoton excitation are being actively pursued. Frequency-resolved optical gating techniques provide full characterization of single ultrashort laser pulses. These new capabilities and recently developed ultrashort-pulse lasers are being exploited further to develop transient absorption and time-domain resonant wave-mixing combustion diagnostics for measurements of temperature, pressure, and relative concentrations. Investigations of thermo-acoustic scattering processes, exposed in degenerate four-wave-mixing research, are being pursued for potential application as diagnostics of velocity, viscosity, temperature, and concentration. Time-resolved PLIF for quantitative two-dimensional measurements are limited by low signal strengths and a strong sensitivity to quenching processes. Studies of collisional energy transfer and quenching processes are leading to predictive models of quenching cross sections for molecules such as NO and OH. Results from these and other fundamental studies, combined with new laser or camera technologies, are providing new capabilities to combustion researchers.

Atomic, Molecular, and Optical Physics

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Physics Division

48. ***Accelerator Based Atomic Physics***
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This program is focused primarily on atomic structure measurements with an emphasis on precision measurements useful in testing many-body relativistic atomic structure calculations. The experimental work is principally conducted at three accelerator facilities, ATLAS and BLASE (both located in the ANL Physics Division), and UNILAC/SIS at GSI, Darmstadt. Together these facilities provide access to essentially all charge states of all elements, ideal for the study of the atomic physics of highly-ionized atoms. In FY1996, the ATLAS-based heavy ion program completed a measurement of the spectral distribution of the two-photon decay in helium-like Kr. This work provides a test of the calculations of the transition probability for this decay and had never previously been measured although non-relativistic theoretical predictions exist. These measurements test our understanding of the entire structure of an ion since a sum over the complete set of intermediate states is required and both energy levels and wavefunctions must be understood. Also at ATLAS, a two-foil technique to measure ultrashort lifetimes in the 100 fs to 10 ps regime for highly-charged ions was investigated. In this technique, the first foil is used to excite the ion and the second foil is used to probe the excited state population. Measurements of the final charge state distribution as a function of foil separation provides an independent confirmation of power-law dependence of Rydberg-fed atomic transitions observed in beam-foil studies. The VUV spectroscopy program at ATLAS shifted emphasis from 2-electron systems to multielectron systems and studies of 3-, 4-, and 5-electron krypton are underway. The program to investigate collisions of fast highly-charged ions with C_{60} found that the weak photon emission branch of the collisionally-excited system was masked by prominent photon emission from atomic C ions. Future efforts will include continued analysis of the uranium Lamb-shift data from GSI (complementary to work done on Ni and Kr at ATLAS) and development of a polarized beam of metastable (2s) ions of H-like argon at ATLAS.

49. ***Synchrotron Radiation-Based Atomic Physics***
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Our research program in atomic, molecular and optical (AMO) physics using X-rays from synchrotron radiation sources has concentrated during FY1996 on preparations for AMO physics at the Argonne Advanced Photon Source (APS). The primary goal of the program is to increase the understanding of photon-atom interactions at high photon energies. Initial experiments will concentrate on two unique aspects of high-energy photon-atom interactions: the increasing importance of x-ray scattering processes relative to photoabsorption, which dominates at lower photon energies; and the coherent nature of excitation and decay processes involving resonance and threshold states of deep inner-shells. Characterization of x-ray scattering from a free atom will be useful in testing advanced scattering theories (second-order S-matrix) as well as the commonly used form-factor approximation in crystallography. A careful decomposition of the elastic and inelastic x-ray scattering channels will permit study of the effects of electron binding on electron momentum distributions deduced from Compton scattering, a widely-used tool in solid-state physics. Study of resonance and threshold phenomena using atomic x-ray fluorescence will yield a deeper understanding of this region where excitation and decay processes are strongly coupled. Preparations include design of a bent-crystal x-ray spectrometer, scattering cell, recoil-ion spectrometer and laser-excited targets. As part of on-going research activities, the group has published the first detailed study of non-dipole effects on the angular distribution of Ar 1s, and Kr 2s, 2p photoelectrons, covering electron energies up to 3000 eV; this demonstrated the current central-field calculations to be adequate for the estimation of non-dipole effects in regions away from resonance. The investigation of double ionization in photoabsorption and Compton scattering, studies done in collaboration with the University of Frankfurt and Kansas State University at ALS in Berkeley and ESRF in Grenoble, are of prime importance in understanding the role of electron correlations. In these studies a novel technique has been used, recoil ion momentum spectroscopy, which due to its large solid angle and unique capabilities, is expected to play a prominent role in the AMO program at the APS, and thus participation in these experiments lays the foundation for future studies.

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Chemical Sciences Division

50. *Search for the Electric Dipole Moment of the Electron*

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An elementary particle can possess an electric dipole moment (EDM) only by virtue of an interaction that violates parity (P) and time reversal (T) invariance. The possible existence of an electron EDM (hereafter called d_e) is an issue of great current interest in connection with the unsolved problem of CP violation. Although the unmodified standard model of elementary particle interactions predicts a value of d_e far too small to be observed experimentally, a number of other plausible theoretical models of CP violation predict values of d_e within experimental range. In particular, there is great interest lately in grand unified supersymmetric models, which predict that d_e should be in the range 10^{-27} to 10^{-28} e cm. For the last few years we have been engaged in an experimental search for d_e. Our present published experimental upper limit on d_e is $4 \mathrm{x} 10^{-27}$ e cm. This result was obtained using ^{205}Tl atoms in an atomic beam magnetic resonance experiment employing separated oscillating fields, laser optical pumping for state selection and analysis, and a very intense electric field. Since arriving at this result we have been preparing a new and improved version of our experiment, which still makes use of the same general method, but has important new features as follows: 1) In addition to ^{205}Tl atomic beams, we now have sodium atomic beams, generated in the same ovens and collimated by the same slits. The essential point here is that sodium atoms are susceptible to the same major systematic effects as are thallium atoms and are in fact more sensitive to them. However, sodium atoms would not exhibit a measurable EDM effect because the atomic number of sodium is $Z=11$ and the EDM effect increases in proportion to the cube of the atomic number Z. Thus sodium is of great value for comparison and calibration purposes. 2) A new electric field assembly has been constructed which permits simultaneous comparison of two beams of thallium (and at the same time two beams of sodium) in equal and opposite electric fields. This feature will sharply reduce a major contribution to noise that limited the precision of our latest published limit. In addition to these major features, a number of other significant improvements have been made to increase signal and reduce noise. We have now completed construction of the new apparatus, and have been testing it extensively during the last half-year or so. These tests yield very encouraging results: all our design goals have been met or surpassed. We hope to achieve an experimental sensitivity of $2 \mathrm{x} 10^{-28}$ e cm for d_e in the coming year.

51. *High-Energy Atomic Physics*

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The goals of the High Energy Atomic Physics program are to: (1) Achieve an experimental and theoretical understanding of charge changing collisions at relativistic energies including electron capture from pair production and heavy particle capture from pair production; (2) Determine if there exists a small charge-parity violating permanent electric dipole moment (EDM) of the electron. Recent results include the: (1) Measurement of charge changing cross sections, including electron capture from pair production at 10.8 GeV/nucleon (2) Integrated calculation of capture from pair production, ionization, and excitation in relativistic ion-atom collisions using massively parallel computing; (3) Invention of the orthotropic source - a source that produces a highly collimated beam of neutral atoms with 100% efficiency. Present activities include: (1) Extending capture from pairs to particles heavier than electrons, by using bremsstrahlung photons produced at the LBNL Advanced Light Source; (2) Theoretical support for this activity; (3) Building a new cold atom fountain experiment with a sensitivity to an electron EDM of 10^{-30} e-cm.

52. *Atomic Physics*

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This program conducts detailed studies of the structure and interactions of atomic systems to provide accurate and detailed descriptions of their behavior and to stimulate and challenge theoretical understanding. The program exploits the ability of two state-of-the-art electron cyclotron resonance (ECR) ion sources at LBNL to produce intense, highly charged, continuous ion beams for the conduct of low energy ion-atom and ion-molecule collision studies. Current emphasis is upon determination of the complex amplitudes, and their scattering angle dependences, for excited substates produced in multiple electron transfer collisions, the production and properties of large, highly charged molecules, and momentum spectroscopic studies of the products of ion collisions with He atoms. The program benefits from collaborative efforts with colleagues from outside LBNL.

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Physics Department

53. ***Spectroscopy and Collision Studies with Highly Charged Ions Produced by Electron Beam Ion Traps***
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The project focuses on the spectroscopy and interactions of highly charged ions produced in the LLNL Electron Beam Ion Traps (EBITs), which produce stationary ions up to fully stripped uranium. High-resolution, highly accurate measurements of transition energies of few-electron high-Z ions are performed to provide benchmarks for evaluating QED, nuclear, and relativistic correlation effects in high-Z systems. These include studies of the fine structure of few-electron uranium ions and of the hyperfine structure of hydrogenic ions such as Ho66+, which test the Bohr-Weisskopf effect and have resulted in revised values of the nuclear magnetic moment. Studies of electron interactions are performed to provide benchmarks for distorted-wave and close-coupling calculations. Current efforts investigate the magnetic sublevel populations generated by electron-impact excitation and dielectronic recombination processes that results in anisotropic line emission. The EBIT facilities also allow measurements of radiative lifetimes of highly charged ions in regimes inaccessible to traditional sources. We have developed techniques to measure very long-lived lifetimes in the regime 1 microsecond - 1 second, such as the 3.92-ms lifetime of the triplet level in heliumlike N5+, as well as ultrashort lifetimes <10 fs, including a 1.65-fs lifetime of a level in neonlike Cs45+.

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Physics Division

54. ***Accelerator Atomic Physics***
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The project objective is to achieve a detailed understanding of the interactions of high-energy, multiply-charged ions with gas and solid targets, and with electrons. The ORNL facilities used for this research are the EN Tandem Accelerator and the Holifield Radioactive Ion Beam Facility (HRIBF). A unique feature of the EN Tandem Facility is the Elbek high resolution magnetic spectrograph. This is coupled with a new recoil momentum spectrometer to allow complete energy disposition studies. Using heavy ions of different Z but the same charge state, the Z dependence of the energy shift of the Binary Encounter peak energy has been studied. To determine the relative importance of electron-electron vs. electron-nucleus interactions in excitation and ionization, neutral and charged ions in collision with He gas are measured, as are the collision partners in coincidence. Electrons contained in a crystal channel can be quantitatively treated as a dense electron gas target. A swift ion passing through the channel can be excited by collisional excitation, by dielectronic processes, or by resonant coherent excitation in which the periodicity of the crystal lattice provides an oscillator, which can separately excite specific m states of the moving ions. The strong phase coherent electric fields that the projectile experiences inside the crystal can also be used to selectively cause constructive and destructive interferences. At CERN in Geneva, lead beams at energies of 33 TeV are used to study electron capture from the negative continuum and lepton pair production cross sections as a function of angle, lepton energy, and target Z. In collaboration with Swedish scientists, experiments have been performed at the Stockholm Heavy Ion Storage Ring to measure dissociative recombination between electrons and molecular ions, e.g., HeH^+, H_3^+.

55. ***Collisions of Low-Energy Multiply Charged Ions***
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In this activity, multicharged ion interactions with atoms, molecules, and surfaces are studied at the lowest attainable energies. At such energies, the stored electronic potential energy of the multicharged ions becomes an appreciable fraction of the total interaction energy, and inelastic collisions depend strongly on the detailed quasi-molecular potentials of the interacting systems. Emphasis is currently on merged-beam measurements of absolute electron-capture and ionization cross sections in the energy range from 0.01 to 1000 eV/amu, to provide benchmark data for the evaluation of theoretical approaches under development for this still poorly characterized energy regime, as well as to investigate low-collision-energy phenomena such as orbiting resonances and other cross section enhancements arising from trajectory effects. Experimental studies of the neutralization of multicharged ions during grazing interactions with metal, semiconductor, and insulator surfaces are also in progress. The current focus is on measurements of the angular and charge state distributions of scattered ions, as well as the characterization of the energy and angular distributions of ejected electrons, in order to better understand the detailed mechanisms by which the multicharged ions" potential energy is dissipated as the ions are neutralized at the surface.

56. ***Theoretical Atomic Physics***
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The atomic theory program studies the dynamics of strongly perturbed atomic systems which requires the development of new physical models and new mathematical and computational techniques. The program is intimately related to state-of-the-art experimental programs at ORNL and other laboratories. Particular attention is focused on both fundamental and complex systems which play a role in many branches of energy research such as collisions of ions with atoms, solids, and surfaces, as well as atoms subject to high-intensity electromagnetic radiation. Because of the nonperturbative nature characterizing these interactions, and the nonseparability and high dimensionality of the equations describing them, this project is quite computationally intensive and requires the development of efficient numerical algorithms and their implementation on high-performance computers. These studies are interdisciplinary as the methods developed provide a link between atomic, solid state, plasma sciences, and chemical sciences. Specifically, the time-dependent dynamics of atomic systems is investigated using quantum mechanical, semiclassical, and classical approaches. Efforts to develop and apply fully quantum treatments involve direct numerical solution of the Schrodinger equation on a lattice, methods related to the time-dependent Hartree-Fock approach, and coupled channels techniques. Partial support is also provided through this program for a joint appointment of a Distinguished Scientist/Professor at ORNL and the University of Tennessee, Knoxville.

57. *EN Tandem Operations*

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The EN Tandem Van de Graaff is operated for atomic physics research. A wide variety of light ions and multiply-charged heavy ions are furnished by the EN Tandem at MeV energies for the accelerator atomic physics group and for outside users from other divisions of Oak Ridge National Laboratory (ORNL), universities, and industry. Neutral beams of 0.1 to 0.5 MeV/nucleon carbon and oxygen have recently been added. Terminal voltages up to 7 MV are routinely available and ion sources are sufficiently versatile to provide beams of all ions from protons through fluorine and silicon through chlorine, as well as beams of many heavier ions including nickel, iodine, gold, and uranium. A VAX-11/750 and Macintosh PC/CAMAC-based data acquisition systems, an Elbek magnetic spectrograph with position sensitive ion detectors, high-resolution electron spectrometers, Si(Li) X-ray detectors, and a curved crystal X-ray spectrometer are available to users. Recent major beam usage has included the channeling of carbon and nitrogen ions through thin crystals to examine resonant coherent excitation of one-electron ions, coincidence measurements of emitted electrons with recoiling target ions and various projectile charge states, and measurements of Auger electrons in coincidence with recoiling helium, neon, and argon atoms.

Chemical Energy

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Molecular Processes Program

58. *Organometallic Complexes in Homogeneous Catalysis*

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The aim of this research is to provide an understanding of the details of processes involving homogeneous and heterogeneous catalysis. One such process is the hydrodesulfurization (HDS) of petroleum feedstocks. From studies of model organometallic complexes of thiophene and related organosulfur compounds, it has been established that π-bonded thiophenes are activated to undergo reactions that lead to cleavage of the carbon-sulfur bonds in the thiophene. Such reactions on HDS catalyst surfaces would be expected to lead to desulfurization of the thiophene. To test this hypothesis, reactor studies of thiophene with deuterium over molybdenum-based catalysts were performed. The deuterium location in the butadiene product is consistent with activation of thiophene by π-bonding to metal sites on the catalyst surface. Future studies include exploring new approaches to the HDS of dibenzothiophenes, a family of compounds in petroleum that are highly resistant to desulfurization. Other studies involve measurements of the strength of adsorption of isocyanide ligands on metal surfaces and investigations of reactions of isocyanides that are catalyzed by the metal surfaces.

59. *Chemical Kinetics and Reactivity of Transition Metal Complexes*

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New catalytic reactions are being developed to learn what otherwise-sluggish but important reactions can be made to occur, and to understand how they take place, with a goal of developing new processes. These reactions relate to environmentally-benign chemical processing and to selective oxidations. The effects of catalyst composition, reagent concentrations, structural variations, solvents, salts, etc. are being used to determine their mechanisms. A major target is selective oxidation, presently with hydrogen peroxide but with oxygen activation as a secondary goal. Methylrhenium trioxide (MTO), a soluble organometallic oxide, activates hydrogen peroxide for catalytic attack by a significant number of substrates. Sulfides, phosphines, styrenes, alkenes, alkynes, anilines, β-diketones and halide ions are among the molecules that can be efficiently oxygenated by the rhenium catalyst. The mechanism involves a peroxorhenium intermediate that contains an electrophilically activated peroxide chelated to rhenium. From these findings we postulated that a "carbene equivalent" might be able to engage in the catalytic transfer of a carbene unit, just as the peroxo complex transfers an "oxene" (i.e., an O atom). For example, it should be able to convert an alkene to a cyclopropane, analogous to the conversion of an alkene to an epoxide.

60. *Fundamental Studies of Supported Metal Catalysts*

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The fundamental processes occurring at the surface of heterogeneous catalysts are investigated by a combination of NMR with traditional techniques (kinetic studies, selective chemisorption, infrared spectroscopy). We are focused on catalysts that find numerous applications in the petroleum and chemical industries and in pollution control technology. Most of our effort in this area is concentrated on characterizing the surfaces of working catalysts, probing the chemisorption behavior and surface reaction of various molecules and studying the synergistic effects of adding a second element; the second element can be another metal to form a bimetallic or it can be a promoter, poison or a support modifier. The other area of effort in our program is the application of new nuclear spin dynamics and new solid state NMR techniques to studies of glasses, thin diamond films and zeolites. This program develops and applies solid-state NMR techniques to significant problems in catalysis and surface science as well as other areas in material science. Recent catalytic work has demonstrated the ability of solid state NMR to probe the kinetics of hydrogen chemisorption on supported metal catalysts. For example, it was found that small ruthenium particles (25% dispersion) had a sticking coefficient for hydrogen adsorption significantly higher than ruthenium single crystals. However, the introduction of Ag reduced the apparent sticking coefficient to the values seen on Ru(001). It was postulated that Ag blocked edge and corner sites which are significantly more active than basal planes for hydrogen adsorption. Microcalorimetry studies of these same catalysts gave complementary information. Other recently completed work investigated CO and hydrogen adsorption on Rh_6/NaY catalysts via ^1H and ^{13}C NMR and microcalorimetry. Also, crotonaldehyde selective hydrogenation over Pt bimetallic catalysts was studied.

61. *New Synthetic Routes to Inorganic Catalytic Materials Using Organometallic Precursors and Molecular "Stepping Stones"*

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My group's research objective in this program is to explore and develop new strategies toward the synthesis and characterization of novel inorganic solids for potential applications in catalysis and energy storage. We combine aspects of both organometallic and solid state chemistry in order to synthesize transition metal compounds with metal-metal bonds that adopt either layered or microporous morphologies. Our initial efforts are directed toward layered materials containing reduced Nb_3 and Ta_3 triangles. Compounds we have synthesized and characterized can be reduced by up to two electrons per formula without decompositions or significant structural change. Intercalation and hydrogen activation studies are currently underway.

62. *Solid State NMR Studies: Catalytic Chemistry and Materials*

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Transient techniques in nuclear magnetic resonance (NMR) are used to probe the physics and chemistry of materials involved in heterogeneous catalysis and material science. Examples of recent studies include: (1) in situ ^1H NMR investigations of the dynamic behavior (adsorption, desorption, motions, exchange phenomena) and reaction of hydrogen and small hydrocarbon molecules on silica and alumina supported metallic catalysts (e.g., Rh/Al_2O_3, $Rh\text{-}Pt/Al_2O_3$, Ru/SiO_2) in temperature and pressure range used in important industrial applications; (2) high resolution ^1H and ^{13}C studies of hydrogen, CO and small hydrocarbon molecules on small rhodium clusters in Rh exchanged NaY zeolite; (3) measurement of high-resolution NMR spectra of half-integer quadrupolar nuclei using the recently developed two dimensional multiple quantum MAS NMR experiment. Other projects include development of new research capabilities in solid state NMR (e.g., a combination of in situ NMR with mass spectrometry), and application of new nuclear spin dynamics to the studies of surfaces and surface phenomena.

63. *Spectroscopic and Kinetic Characterization of Metal Oxide Catalysts*

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This research is providing new fundamental information about catalysis by metal oxides, including the mechanisms of catalytic reactions, the structure and composition of catalysts, and the properties of surfaces. The metal oxides being investigated are used extensively by industry for selective oxidation, particularly for the activation of paraffins for fuels and chemicals production. A complement of experimental approaches is being used to perform kinetic measurements and comprehensive catalyst characterization. Recent kinetic approaches have been focused on transient techniques to examine the nature of reduction-oxidation mechanisms in reducible molybdate and vanadate selective oxidation catalysts. In situ spectroscopic techniques, such as laser Raman and Fourier transform infrared spectroscopies (FTIR) are emphasized since they can be used to examine functioning catalysts. The goal of this research program is to provide fundamental relationships between structure, composition, oxidation state, and surface properties and catalytic activity and selectivity.

64. *High-Temperature Gas-Phase Pyrolysis of Organic Compounds*

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The goal of this research is to understand in detail fundamental thermal reactions of organic compounds, especially those related to the pyrolysis of coal and coal-derived liquids. Primary products of thermal reactions are often highly reactive neutral species such as radicals, carbenes, diradicals, and reactive molecules (i.e., species with no overall electronic charge, but with an exceptionally reactive bond or group of bonds). Much of the work of this project focuses on reactive molecules that are important in thermal reactions and includes development of novel methods to prepare them and study of their spectroscopic and chemical properties. Studies have concentrated on quinodimethanes, a large class of reactive molecules. The work with reactive molecules has resulted in novel and effective ways of producing diradicals, and the reactions of these intermediates are under study. Recently, several new thermal rearrangements of hydrocarbons and related hetero-atom derivatives were discovered that fit a proposed two-step mechanism that involves formation of a transient diradical by an intramolecular thermal hydrogen-atom transfer. The results suggest that this two-step process is very general and may be a major new way to account for rearrangements which occur when organic compounds are heated to high temperatures.

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Chemical Technology Division

65. ***Fluid Catalysis***
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This program uses an array of in situ high-pressure spectroscopic and kinetic techniques to explore the catalytic reaction chemistry of small molecules that serve as precursors in many industrial processes. Precursors of interest include those of the C_1 chemical industry, e.g., CO, CO_2, and CH_4; the ammonia synthesis precursors, H_2 and N_2; and the ceramic precursors, e.g. $(CH_3)_4Si$ and $(CH_3)_3B$. The efficient utilization of these molecules is potentially of great economic significance; however, in many cases the required conversion chemistry is difficult to achieve by present strategies. Recent research of the Fluid Catalysis Program encompasses (1) in situ high-pressure NMR exploration of phosphine-modified catalysts for the hydroformylation of olefins in supercritical fluids, (2) the development of the toroid cavity imager, an R&D 100 Award winning MRI device, for the investigation of ceramic precursor processes at elevated temperatures and pressures, and (3) the study of extremely robust polyfluorophthalocyanine catalysts for hydrocarbon activation processes.

Chemistry Division

66. ***Premium Coal Sample Program***
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This program provides uniform, well-preserved coals for fundamental coal science research. Eight coals are available ranging in rank from a lignite to a low-volatile bituminous coal. These samples have been sealed under nitrogen in glass ampoules. Over 23,000 samples have been distributed worldwide. More than 900 shipments totaling over 23,500 ampoules have been shipped thus far. A Users Handbook, including bibliographic information for published data generated from APCS samples is updated periodically and is available on request (see contact below). This information is also now available on-line via World Wide Web (http://www.anl.gov:80/PCS/pcshome.html). Information is continuously added to these databases.

67. ***Characterization and Reactivity of Coals and Coal Macerals***
Winans, R.E.; Anderson, K.B.; **$1,954,000**
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The goal of this program is to provide a detailed view of coal structure ranging in scale from microscopic to molecular. An objective is to be able to predict the reactivity of the Argonne Premium Coals under a variety of conditions from models based on the fundamental information derived from this program and other studies. The chemistry of large molecules is a major focus, which has led to research on the synthesis and the characterization of large-pore, layered clay catalysts for upgrading large complex organic molecules. The heterogeneous nature of coal adversely influences its reactivity, and complicates processing technologies for the production of usable, high-quality fuels and chemical feedstocks. To reduce heterogeneity, we have been systematically studying physical methods for the separation of coal into its fundamental organic constituents (macerals). Further, chemical modification methods are coupled with structural and spectroscopic measurements, such as synchrotron X-ray spectroscopy and scattering, solid- state NMR spectroscopy and imaging, laser desorption time-of-flight mass spectrometry, high-resolution tandem mass spectrometry, and small angle neutron scattering, to probe coal structure, in particular, the large molecular building blocks. For the first time, the synthesis of clays has been followed by anomalous small angle X-ray scattering (ASAXS). To further advance this and other elements of the program, we are building the next generation ASAXS instrument at the ANL Advanced Photon Source. The different types of carbons in macerals have been imaged using X-ray synchrotron microscopy. Pyrolysis high-resolution mass spectrometry results on Argonne Premium Coals suggest that strong bonds may be responsible for holding the aromatic clusters together. Finally, nitrogen-containing aromatic clusters appear to be larger than other types of aromatic clusters found in coals of all ranks.

68. ***A Facility at APS for Time Resolved/Anomalous Small Angle X-ray Scattering: Applications in Condensed Matter Research***
Winans, R.E., Thiyagarajan, P.; **$85,000 Operating**
Crawford, R.K.; **$315,000 Equipment**
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The objective of this project is to construct an X-ray scattering instrument on the undulator beamline of the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) at the Advanced Photon Source (APS) that will offer unprecedented opportunities for studying static and dynamic atomic order in condensed phases and nanoscale materials. The high flux at the APS will enable time-resolved structural studies on dynamic systems using techniques that require high energy resolution of the probing X-rays and high counting statistics. Anomalous small angle X-ray scattering, ASAXS, became possible only after the advent of synchrotron sources. The power of ASAXS for structural resolution of materials in non-crystalline states has been demonstrated in such diverse areas as biophysics and metallic alloys. The high brilliance of the X-rays from the undulators at APS will, for the first time, enable the full potential of both the time-resolved and anomalous scattering techniques to be realized in such areas as heterogeneous catalysis, ceramics, metallic glasses, organometallics, and photochemical energy conversion. The proposed ASAXS facility will offer new capabilities for measuring atomic order within macromolecular assemblies in disordered media on a length scale of 6-6000 Å. This capability will offer opportunities to resolve the structural basis for catalytic function. We will use this facility to conduct groundbreaking experiments on the structure and fundamental chemistry of novel metal oxide catalysts, macromolecular photochemical energy conversion assemblies, coal and carbons, and phase separation in metallic alloys.

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Department of Applied Science

69. ***Metal Hydrides***
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Knowledge of the behavior and properties of hydrogen/metal systems is essential for the successful implementation of many energy-related processes and applications. The prime concern of this program is to increase that store of knowledge through the determination of their thermodynamic, kinetic, and structural parameters. A particular goal is to relate all pertinent data and hypotheses in order to develop a predictive capability regarding the behavior of a given system. This capability permits the synthesis of compounds having optimum properties for particular applications. Current areas of research are electrochemical characterization of metal-hydrogen systems, preparation of corrosion-resistant and high-capacity metal hydride electrodes, kinetics of the formation and decomposition of hydride phases and the characterization of a new class of hydrogen bronzes prepared from complex oxides. This involves the use of various tools and techniques including thermodynamic and electrochemical measurements, X-ray diffraction, in situ X-ray absorption spectroscopy methods and electrochemical corrosion measurements.

Chemistry Department

70. ***Catalysis: Reactivity and Structure***
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The goal of this program is to provide an improved understanding of chemical catalysis by elucidating details of the fundamental properties of molecules, surfaces, and their reactions that are critical to catalysis. Reactivity-structure correlations are a key aspect of these studies. Complexities stemming from the inherent multi-component aspects of heterogeneous catalysis are explored using both ultra-high-vacuum surface science investigations of well-defined model systems, and powder diffraction and x-ray absorption studies of more "real-world" systems. In the former, emphasis is placed on understanding the effects of catalyst modifiers at a molecular level and on rationalizing the distinctive behaviors of bimetallic surfaces that simulate important industrial bimetallic catalysts. X-ray and ultraviolet photoelectron spectroscopies at the National Synchrotron Light Source (NSLS) are essential to this work. In the latter systems, some of the first in situ, time-resolved studies of the formation and transformations of zeolitic materials, supported metals, and metal oxides under catalytic reaction conditions are now possible using our improved x-ray diffraction/absorption facility at the X7B beamline at the NSLS. Homogeneous catalysis efforts in the group are centered around transition metal hydride complexes and sustainable feedstocks. Reactivity studies of metal hydrides are designed to elucidate the factors that determine the rates and mechanisms of M–H bond cleavage and associated atom transfer reactions that are central to the participation of metal hydrides and molecular hydrogen complexes in catalysis. Our understanding of hydride chemical reactivity and bonding is further enhanced by the uniquely accurate structural data for these complexes obtainable from neutron diffraction studies at the High Flux Beam Reactor (HFBR). The knowledge gained from these studies is utilized to assist in the development of new types of catalytic reactions, especially those designed to yield non-oxidative approaches to oxygenated organics from sustainable resources, such as biomass and carbon dioxide. In this regard, novel aspects of metal-carbohydrate chemistry are being explored, with a focus on selective complexation, reactivity studies, and catalytic conversions.

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Materials Science Division

71. ***Selective Conversion of Light Hydrocarbons to Chemicals and Fuels***
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The U.S. chemical and fuel industries are major sources of industrial waste and significant consumers of energy. Considerable savings in energy, carbon dioxide emissions, and feedstock costs could be achieved by developing catalytic processes for the selective oxidative dehydrogenation of alkanes to alkenes and the selective oxidation of alkanes directly to products such as alcohols, ketones, epoxides, and carboxylic acids. Achieving these goals requires an understanding of the of the relationships between the structure and composition of the catalyst and its function. This project addresses two major areas. The first is understanding how to control the oxidative dehydrogenation of methane and C2+ alkanes over both heterogeneous and homogeneous catalysts. Selective oxidation of C2+ alkanes and alkenes is the theme of the second area of activity. The synthesis of novel oxide nanocl12usters within microporous and mesoporous solids and of monomeric reducible cations at zeolitic exchange sites will be investigated, since these exhibit unique reduction-oxidation and acidic properties that can be exploited to control the availability and reactivity of oxygen. It is also planned to investigate the photo-oxidation of alkanes and alkenes with NO_2 under mild conditions (a process that uses NO as a catalyst and O_2 as terminal oxidant), in order to achieve high selectivity to oxygenated products. Visible light-driven alkane oxidation by O_2 in cation-exchanged zeolites will be explored for the direct conversion to alcohols.

Chemical Sciences Division

72. *High-Energy Oxidizers and Delocalized-Electron Solids*

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The aim of this work is the synthesis and characterization of new two-and-three dimensional solids that may be useful in electrical energy storage. Fluorides are emphasized because fluorine is highly electronegative, small, and lightweight; thus, high oxidation-state fluorides such as those of cobalt, nickel, copper, or silver have high oxidizing potential and low formula weights. Emphasis is placed on the thermodynamically unstable fluorides, which have sufficient kinetic stability to be easily stored. Such fluorides are not only powerful oxidizers, but the metal center in each is comparable in electronegativity to fluorine. It is probable, therefore, that some of the thermodynamically unstable fluorides will be metallic or even superconducting (like some copper oxide systems). Access to such fluorides is provided by salts of anions that are thermodynamically stable (e.g., NiF_6^{2-}). Kinetically stable, thermodynamically unstable fluorides, as reagents, can probably substitute for anodic oxidation processes (Simons process) for the preparation of fluorochemicals. Lithium cations in open-channel fluorides could provide ionic conductors stable to oxidation. New synthetic routes also provide access to ordered mixed rutile materials (e.g., $MnNiF_4$). These should be ferrimagnets. Other "rutile" systems such as MNF (isoelectronic with MO_2) like CrO_2, could be metallic.

73. *Catalytic Conversion of C_1 Compounds*

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The purpose of this program is to develop an understanding of the fundamental processes involved in the catalytic conversion of C_1 compounds such as carbon monoxide, carbon dioxide, methane, formaldehyde, and methanol to gaseous and liquid fuels. Attention is focused on defining factors that limit catalyst activity, selectivity, and resistance to deactivation, and the relationship between catalyst composition/structure and performance. In recent studies, the hydrogenation of CO and CO_2 has been investigated over both Rh and Cu. In the case of Rh, in situ infrared observations show that CO_2 adsorbs dissociatively, and that the adsorbed CO undergoes hydrogenation via a pathway that is identical to that followed during the hydrogenation of gas phase CO. In the case of Cu, only a small portion of the CO_2 adsorbs dissociatively. Infrared observations show that CO_2 undergoes hydrogenation to form formate species which are then converted to methylenebisoxy, formaldehyde, and methoxy species. Hydrogenation of the last of these species produces methanol. Promotion of Cu with zirconia enhances the rate of methanol formation due to an increase in the concentration of formate species. The activation of methane has also been investigated over supported metals and metal oxides. Thermal decomposition of methane on Ru produces CH_x species which polymerize to form alkyl species. ^{13}C NMR spectroscopy has revealed the structure of the adsorbed species. Hydrogenation of the adsorbed species produces a hologous series of alkanes. The interactions of methane with supported BaO_2 and PdO have been investigated as well as part of an effort to understand the elementary processes involved in methane coupling to form ethylene and methane combustion, respectively. Raman spectroscopy has proven useful in revealing the dynamics of oxide consumption and the formation of new catalyst phases.

74. *Transition Metal Catalyzed Conversion of CO, NO, H_2, and Organic Molecules to Fuels and Petrochemicals*

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The goals of this project are: (1) to develop new chemical reactions in which transition metals interact and chemically transform organic materials, (2) to understand how these reactions work, and (3) to apply this information to the development of new potentially useful chemical transformations. Several years ago a major discovery on this project was the first alkane-transition-metal C–H oxidative addition reaction (C–H activation). This involved the direct reaction of C–H bonds with an iridium center in the +1 oxidation state (Ir(I)). More recently, a series of Ir(III) C–H activating complexes has been discovered. Subsequent research has been directed at examining the scope and mechanism of these C–H activation reactions and working toward utilizing them in the conversion of alkanes to functionalized organic molecules. Recent activities on this project include (1) use of liquefied xenon and krypton as inert solvents for C–H activation; (2) design of experiments aimed at determining whether weak metal-noble gas and metal-alkane complexes intervene as intermediates in these processes; (3) exploratory studies on the extension of C–H activation methods to C–F activation; (4) improvement in the techniques utilized for flash kinetic studies aimed at directly measuring the rates of reaction of coordinatively unsaturated C–H activating intermediates with alkanes, and (5) utilizing the Ir(III) C–H activating systems in the synthesis of new novel organometallic materials, such as carbene complexes.

75. *Chemical Routes to Tailored Oxide Networks Based on Molecular and Polymeric Precursors*

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Advanced solid-state materials with useful properties increasingly involve intricate three-dimensional networks, characterized by complex stoichiometries (e.g., in ceramic superconductors such as $HgBa_2Ca_2Cu_3O_{8+d}$) and/or metastable architectures (e.g., in zeolites). New generations of materials will undoubtedly result from chemically directed, low-temperature synthetic routes. Our approach involves use of synthesis, coordination chemistry, and condensation reactions to build novel three-dimensional networks. Primary targets have been oxide-based materials, which are built from tailored, oxygen-rich precursor molecules. This project involves synthesis and characterization of candidate precursor molecules, and then examination of chemical processes by which a metal oxide building block can be transferred to a growing network. Initial directions are based on the finding that metal complexes of the siloxide ligand $OSi(O^tBu)_3$ eliminate isobutylene and water cleanly at remarkably low temperatures (100–200°C) to form $M_xSi_yO_z$ materials. For example, $M[OSi(O^tBu)_3]_4$ (M=Zr, Hf) complexes undergo very clean conversions at about 100°C to homogeneous $MO_2{\cdot}4SiO_2$ materials. The chemistry of this network formation allows control over the growth of ZrO_2 nanoparticles at higher temperatures. Other precursors being examined include the Al/P oxide cluster $Al_4(O^iPr)_8[O_2P(O^tBu)_2]_4$ and the $[ZnO_2Si(O^tBu)_2]_\infty$ polymer. The low temperatures at which such conversions take place allow for the formation of networks in refluxing hydrocarbons, thereby offering an alternative to the sol-gel approach to thin films, porous ceramics, fibers, etc. (which usually employs alcohol solvents). Initial experiments also indicate that thermolyses of precursor molecules in the crystalline solid state can generate surprisingly ordered microstructures for the resulting oxide materials. Such observations are followed with attempts to add directionality to the network formation, via added templates or "ancillary" ligands in the precursor that might orient the condensation reactions. The ultimate goal of this research is to provide tailored materials with new and specific structural, electronic, optical, and/or catalytic properties.

76. Potentially Catalytic and Conducting Polyorganometallics
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This project utilizes the principal investigator's expertise in synthetic organic methodology and organometallic reaction mechanisms in an interdisciplinary approach to the designed construction of polymetallic arrays, anchored rigidly on novel π ligands that enforce hitherto unprecedented metallic topologies. It has provided access to a range of new soluble organotransition-metal clusters with great potential as catalysts for known and new organic transformations and as building blocks for novel electronic materials. Recent advances include: (1) the discovery of a rapid synthetic entry into "star" oligocyclopentadienylmetals, containing novel ligands in which a cyclic π system is completely substituted along its periphery by cyclopentadienyl units; (2) the development of improved regioselective coupling strategies on route to permetallated linear ter- and quatercyclopentadienyls; and (3) the use of electron-reservoir sandwiches [FeCp(arene)] as efficient and selective electrocatalysts for the synthesis of fulvalene homo- and heterodimetallic zwitterions.

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Physics and Space Technology Department

77. Plasma-Assisted Catalytic Decomposition of NO_x
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Plasma-assisted heterogeneous catalysis is an innovative technique for improving the reduction of nitrogen oxides (NO_x) under conditions that normally make it difficult for known catalysts to function with high activity and durability. The goals of this project are to (1) explore the effects of a plasma on the NO_x reduction activity and temperature operating window of various catalytic materials, and (2) develop a fundamental mechanistic understanding of the interaction between the gaseous-phase plasma chemistry and the heterogeneous chemistry on catalyst surfaces. Chemical kinetics models based on elementary reaction rate parameters are being developed to describe the mechanisms in the plasma, on the surface, and at the plasma-surface interface where excited molecules, radicals, ions and electrons interact with adsorbates on the catalyst surface. Experimental validation of the chemical kinetics is performed using an existing state-of-the-art test facility. This facility includes a plasma/catalyst reactor that can easily be modified to accommodate a wide variety of electrode and catalyst support configurations, a set of chemical diagnostics for quantifying the concentrations of species in the gas and on the surface, an electrical power conditioning unit, and a set of electrical diagnostics for quantifying the energy consumption of the $deNO_x$ reactor. The temperature in the reactor can be maintained at up to 600°C, and may be upgraded to accommodate higher temperatures if necessary. Studies are being performed using nonzeolitic and zeolitic catalysts, as well as novel metal oxide aerogel catalysts. Plasma-assisted catalytic schemes based on direct NO_x decomposition and selective catalytic reduction are being explored.

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Chemical Science and Technology Division

78. Transition Metal Mediated Reactions of SO_2, H_2, and Other Small Molecules
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The binding and activation of environmentally and energy-related small molecules, particularly H_2, SO_2 and halocarbons, by transition metal complexes is the main thrust. Synthesis, structural characterization, and delineation of the reactivity patterns of a wide variety of such molecules on 16-electron Group 6, 7, and 10 complexes such as $Mo(CO)(diphosphine)_2$ are being carried out. Goals include characterizing metal-dihydrogen and related sigma-bond complexes (e.g. metal-silane), and mapping out and comparing the reaction coordinates for cleavage of H–H and Si–H bonds on metal complexes. This oxidative addition process is critical to catalysis and many types of chemical/biochemical conversions. A new unsaturated cationic complex, $[Mn(CO)(dppe)_2]^+$, was found to contain two agostic phenyl C-H interactions and reversibly bind H_2 and N_2. We will vary the ligand sets and large noncoordinating anion to better define H_2 activation on this highly electrophilic fragment and also synthesize new types of Mn agostic complexes such as $[Mn(CO)_3(PR_3)_2]^+$. A cationic Pt(II) system $[PtH(P\text{-}i\text{-}Pr_3)_2L]^+$ was prepared by protonation of $Pt(P\text{-}i\text{-}Pr_3)_2(SO_2)$ and found to bind weak ligands, L, including H_2 and halocarbons (dichloromethane, bromobenzene). These will be further investigated. Early transition metal sulfides such as $[CpTiS(\mu\text{-}S)]_2^{2-}$ will be examined for SO_2 activation, and reduction of SO_2 by hydride complexes will be studied.

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Basic Sciences Division

79. ***Basic Research in Synthesis and Catalysis***
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The major objectives of research carried out by the Synthesis and Catalysis Group are the development of catalysts for electrochemical reduction of carbon dioxide, and the synthesis and characterization of organometallic precursors for preparing semiconductor particles and thin films. Electrochemical reduction of CO_2 to methanol would provide an attractive route for converting electricity to a liquid fuel with high energy density. The successful development of efficient and stable catalysts for these reactions could have a major impact on the development and use of renewable energy. Current efforts to increase catalytic rates involve the design of catalysts capable of binding carbon dioxide at multiple sites. Studies of catalyst decomposition products are being used to develop catalysts with longer lifetimes. The preparation of more efficient and lower cost semiconductor materials would have a significant impact on the cost and performance of solar cells and other devices. Current research efforts in this area are focusing on the development of new precursors to thin films and semiconductor nanocrystals. This research involves the synthesis and characterization of new organometallic complexes and nanoparticle precursors and the study of their transformation to thin films.

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Chemical Technology Division

80. ***Kinetics of Enzyme-Catalyzed Processes***
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The objective of this program is the study of fundamental kinetics and enzyme catalysis of chloroplast reducing power related to fuels and chemicals production from renewable inorganic resources. Fundamental studies that probe the function of the cellulase enzyme components in relation to their structure are also being performed. Kinetic and mechanistic aspects of photosynthesis will be studied using a unique experimental approach. Areas of investigation include: (1) simultaneous light-driven production of hydrogen and oxygen; (2) separation of the two light reactions of photosynthesis; (3) construction of photosynthetic photoelectrochemical cells; (4) precipitation of metallic catalysts on photosynthetic membranes. Sustained photoassimilation of atmospheric CO_2 and simultaneous photoevolution of molecular hydrogen and oxygen as well as photoautotrophic growth has been observed in Photosystem I deficient mutants B4 and F8, of *Chlamydomonas reinhardtii.* Absence of Photosystem I was demonstrated by P700 differential absorption spectroscopy. The sensitivity of the technique permits a threshold detection limit of 3–5%. Even if Photosystem I were present at that level, it would still be insufficient to account for the observed rates of photosynthesis. It is concluded that Photosystem II is capable of performing complete photosynthesis. These results may account for the origin and development of photosynthesis in the Earth's primordial atmosphere. The interaction between catalytically active and inactive Trichoderma reesei cellulase components and cotton fibers has been examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Cellobiohydrolase I (CBH I), the major component, was rendered catalytically inactive by its treatment with ammonium hexachloropalladate; however, the inactive enzyme still had the ability to bind to cotton fibers.

Chemical and Analytical Sciences Division

81. ***Organic Chemistry and the Chemistry of Fossil Fuels***
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The objective of this program is to conduct basic research that provides new knowledge on the chemical structure and reactivity of fossil and renewable resources such as coal, lignin, and biomass. The knowledge gained from this research will contribute to the scientific foundations required for the future development of novel commercial processes for the conversion of these complex, organic materials into chemicals or fuels in an environmentally responsible manner. Solid-state NMR methods are being developed for the structural analysis of chemically modified coals and lignins, which also can be applied to the analysis of other complex organic solids such as derivatized charcoals, graphites, and polymers. Current research is focusing on high resolution, solid state ^{19}F–NMR and triple resonance techniques that utilize the ^{13}C–^{19}F dipolar interaction to provide local structure information in fluorinated organics.

Reaction chemistry for the selective fluorination of organic functional groups is also under development. Reaction kinetics and mechanisms that underpin thermal and catalyzed reactions of coal and lignin are being investigated through the use of fluid-phase, silica-immobilized, and polymeric organic model compounds. Key issues currently being addressed include the influence of heteroatoms on pyrolysis mechanisms, impact of restricted mass transport on reactions involving free-radical and carbocation intermediates, and elucidation of reaction pathways associated with retrogressive reactions in coal processing and with the clay-catalyzed maturation of lignin. Thermolysis of oxygen-containing functional groups prevalent in low rank coals and lignin such as carboxylic acids, ethers, and phenols are a current focus, and research on flash pyrolysis mechanisms for biomass model compounds has been initiated.

82. *Basic Aqueous Chemistry at High Temperatures and Pressures*

Mesmer, R.E.; Palmer, D.A.; Ho, P.C.; Simonson, J.M.; Gruszkiewicz, M.S. **$695,000**
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The purpose of this program is the experimental study of aqueous chemistry of broad classes of solutes at high temperatures and pressures to establish basic principles governing chemical equilibria and the thermodynamic properties of electrolytes. The advancement of both experimental methods and new models for representation and prediction of behavior over wide extremes of temperature and pressure are important parts of the program. A number of complimentary techniques are used up to and beyond the critical temperature of water and its solutions. Current research uses: flow calorimetry, densimetry, isopiestic apparatus, electrochemical cells, electrical conductance apparatus, vapor-liquid partitioning cells, and Raman spectroscopy. Chemical equilibria under study are ionization-ion association, metal complexation, metal ion hydrolysis, solubilities, volatilities, and adsorption reactions. Reaction thermodynamic quantities and excess properties of electrolytes are of interest. New results are bridging the troublesome transition from strong to weak electrolyte behavior, and reaction behavior of new classes of ions and species. Models are being developed for describing variations of both standard state and excess thermodynamics quantities over wide ranges to temperature and pressure. Computer simulations to relate macroscopic observations to microscopic structure have been initiated. Initial work addresses ion pairing in the near critical region. Results impact strongly the communities in basic solution chemistry and hydrothermal geochemistry, steam generator technology, geothermal technology, environmental chemistry, and nuclear and hazardous waste disposal.

83. *Heterogeneous Catalysis Related to Energy Systems*

Overbury, S.H.; Huntley, D.R.; Mullins, D.R.; Grimm, F.A. **$610,000**
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The objective of this program is to develop a fundamental understanding of catalytic reactions at surfaces. Two areas of catalysis have been emphasized, hydrodesulfurization catalysis and emission control catalysis. Previously, reactions and mechanisms for desulfurization of organosulfur molecules and the relationship of these reactions to surface structure were studied. Increasingly the emphasis is shifting to studies of interactions between reactive metals and reducible metal oxides in catalytic reduction of NO and oxidation of CO and small hydrocarbons. A major theme is to analyze synergisms between the metal and the support as related to the adsorption state, reactions rates and mechanisms. The approach is experimental and is based upon the use of surface analytical techniques to identify and monitor surface adsorbate species and their effects upon the substrate vs reaction conditions. Techniques include alkali ion scattering and electron diffraction for surface structure determination, temperature programmed desorption for analysis of gaseous reaction products, soft x-ray photoemission using synchrotron radiation, and high resolution electron energy loss spectroscopy for analysis of adsorbates. Equipment in development will interface a catalytic reactor with vacuum surface characterization. Substrates have included clean and modified single crystal metallic and bi-metallic surfaces, and in the future will include metals (Rh, Pt, Cu) supported on oxide surfaces.

84. *Photolytic Transformations of Hazardous Organics in Multiphase Media*

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The objective of this program is to conduct fundamental investigations into the influence of local chemical-environment on the mechanisms of photochemical transformation and destruction of hazardous organics. Studies of photochemical events at interfaces (solid/liquid and solid/gas) and in aqueous media are the primary focus of this research. Product analysis and in situ spectroscopic techniques are the principal methods used in the investigations. Results from the studies conducted in this laboratory are enhancing our basic understanding of photochemical processes occurring at industrially and environmentally important interfaces and in aqueous solutions. Surface morphology, strength of substrate/surface interactions, and surface acidity are among the factors that control the interfacial photochemistry. The photochemistry of polycyclic aromatic hydrocarbons (PAHs) has been the focal point of these studies because of the connection between these materials and fossil fuel production and consumption and the status of many PAHs as EPA priority pollutants. Highly polar surfaces, such as those of silicas and aluminas, have been shown to have dramatic effects on the photochemistry of weakly interacting organics, as typified by unsubstituted PAHs. Contributions from electron transfer and singlet molecular oxygen mediated PAH oxidation pathways have been elucidated. The extent to which each of these two oxidation mechanisms is operative is a function of PAH structure. Likewise, water has been shown to be a medium that exerts significant influence on the rates and product distributions observed for PAH photochemistry. Among other benefits to be derived from this research is a better understanding of those factors that control the environmental fate and residence times of PAHs and related anthropogenic materials.

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Chemical Sciences Department

85. ***Free-Radical Chemistry of Coal***
Franz, J.A.; Alnajjar, M.S.; Autrey, T.; Linehan, J.C.; Camaioni, D.M. **$664,000**
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This project develops kinetic, thermochemical, and theoretical information describing the potential energy surfaces of reactions of organic and organometallic free radicals, particularly those involving sulfur, nitrogen, and oxygen important to coal, hydrocarbon and lignin chemistry. Hydrogen transfer and bond scission pathways are examined in studies using kinetic EPR, laser photoacoustic spectroscopy, CIDNP, and kinetic optical spectroscopic and product study competition kinetics. Select bond strengths of heteroatom-containing organic hydrocarbons are determined using redox thermochemical cycles and thermal decomposition studies. Advanced ab initio calculations are employed to study novel hydrogen transfer and radical rearrangement reactions. Mechanisms of reactions of nanometer FeS particles with organic substrates leading to bond scission are investigated. High pressure liquid NMR is applied to study ligand and hydrogen transfer reactions of organometallic hydrides and complexes. Triple-Resonance Solid NMR techniques are developed for characterization of heteroatom structures in carbonaceous materials.

86. ***Theoretical Investigations of Heterogeneous Catalysis***
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The purpose of this research program is to develop and apply atomic level molecular and solid state theoretical methods to the study of catalytic processes occurring at the internal and external surfaces of metal oxides and zeolites. These studies provide information on the geometric and electronic structure of surface and surface adsorbate complexes including the energetics of physisorption, chemisorption and dissociative chemisorption events. Particular emphasis is placed on understanding the effect of topological and electronic defects, metal adatoms and explicit size effects on the reactivity and selectivity of these materials. The complex geometric and electronic structure of transition metal oxides and substituted zeolites combined with the need to accurately predict the small energy changes associated with fundamental processes such as adsorption and desorption is a challenging task for the current generation of theoretical methods. Our approach to increasing the capabilities of solid state quantum mechanical methods that can efficiently describe the ground state properties of these compounds is based on the mathematical development of low order scaling methods that are designed to be implemented on large scale parallel computing systems. To this end we have developed a new all electron periodic Gaussian basis density functional approach that provides fully self-consistent solutions to the Kohn-Sham equations for systems periodic in 3-(crystals), 2-(surfaces) and 1-(polymers) dimension. This new method is implemented in the program GAPSS and is currently being used on large scale parallel computers to study several metal oxide and transition metal oxide systems. These studies strive to provide reliable information on quantities of importance which are difficult to obtain by experimental means. The specific systems being investigated are generally chosen jointly with our experimental collaborators to maximize the interplay between theory and experiment.

87. ***Environmental Molecular Sciences Laboratory Fundamental Studies of Oxygen Storage Materials: Transient Effects on NO_x Reduction Kinetics and the Role of Aging on These Material Properties***
Peden, C.H.F.; Chambers, S.A.; Kay, B.D. **$150,000**
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The goal of this research is to fill a gap in the fundamental understanding of catalyst activity and durability with respect to the transient NO_x reduction performance in automotive catalytic converters. Our overall objective is to obtain detailed chemical kinetics data on idealized but well-characterized catalyst systems useful for understanding the important elementary converter reactions. A particular focus of the work will be on how the catalytic chemistry is effected by the oxygen uptake, storage, and release processes carried out by the oxygen storage material. The fundamental understanding of critical rate-determining processes in this complex system will provide insight into the material properties required for improved, more durable catalysts. For example, we will elucidate and quantify the mechanisms responsible for the improved performance with the use of ceria/zirconia mixtures relative to ceria alone formulations. The kinetic data to be obtained in this program will also be used for the further development of a full process model to describe the performance of an actual vehicle running the Federal Test Procedure (FTP). Ultimately, this detailed understanding will lead to the ability to model both the performance and durability of catalysts on actual vehicles. While this is a considerable challenge and clearly a long-term (>10 year) goal, there are a number of recent developments that have enabled considerable progress to be made in this area. This work is providing an excellent opportunity to couple the powerful fundamental research capabilities of Pacific Northwest National Laboratory with a currently ongoing applied research program at General Motors Research Laboratories.

Separations and Analysis

Ames Laboratory
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Molecular Processes Program

88. ***Analytical Separations and Chemical Analysis***
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The project objective is to devise practical, innovative methods for analytical separations and chemical analysis. Capillary electrophoresis (CE), and ion chromatography are used to separate and determine anions and metal cations in complex samples. A novel CE method enables neutral organic compounds of very similar chemical structure to be separated effectively without resorting to the use of micelles. New resins and techniques are developed for solid-phase extractions and for chromatographic separations. Resins of small particle size are incorporated into membranes to obtain rapid mass transfer. Chelating reagents and chemicals are prepared for isolation of selected metal ions prior to their measurement by atomic or mass spectroscopy. Low-cost resins are being developed for effective cleanup of toxic metal ions in wastes.

89. Analytical Spectroscopy
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The basic principles and practical aspects of several important methodologies for ultratrace analysis are studied in this project. Plasma sources for atomic spectroscopy and mass spectrometry are emphasized, particularly mechanistic and analytical investigations of the inductively coupled plasma (ICP). New directions in ICP mass spectrometry include basic studies of the sample introduction and ion extraction processes, development of instrumental methods for removing interferences, and the use of ICP–MS in conjunction with chromatographic separations for measurement of elemental speciation. These ICP studies have resulted in state-of-the-art analytical methodologies that are utilized extensively elsewhere in DOE and in the outside analytical community. New studies in ion trapping and ion formation in electrospray mass spectrometry are also being initiated.

90. Chemical Analysis at Liquid-Solid Interfaces
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This project explores novel approaches to the design, synthetic fabrication, and molecular level characterization of monomolecular and thin polymeric films at liquid-solid and gas-solid interfaces. Projects this year have entailed (1) fabricating chemically-gatable interfaces with size selective molecular recognition properties, (2) examining the nucleation and growth of spontaneously adsorbed monomolecular films formed from alkanethiols at gold and silver surfaces, and (3) probing solvent-monolayer interactions at such interfaces with in situ infrared reflection and Raman spectroscopies. The molecular recognition effort examines the incorporation of ionizable size-selective channels in long alkyl chain monolayers. The nucleation and growth studies are aimed at unraveling the origins of structural defects (e.g., grain boundaries) within such structures. The in situ investigations employ infrared reflection and Raman spectroscopies, optical ellipsometry, electrochemistry, and contact angle measurements. The overall objective is to develop relationships that form a basis for broader correlations between the composition and molecular arrangement (spatial orientation and packing density) of organic interfaces with macroscopic physical and chemical properties (e.g., lubrication, catalysis, adhesion, and chemical analysis).

91. Electrochemically Transformable Extraction Phases for the Separation of Critical Metal Ion Constituents and High Level Wastes
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Remediation of the large volumes of high level wastes (HLWs) in the DOE complex requires separating radioactive materials into high and low level waste streams. Remediation also dictates the minimization of HLW stream volumes to reduce long term storage costs. This program explores the reversible electrochemical transformation of selective chelates tethered to carbon packings as a novel method for concentrating highly radioactive constituents in HLWs. The aim is to exploit the unique capabilities of a new series of metal-ion selective crown ethers (CEs) that incorporate redox transformable moieties like catechol and hydroquinone within the CE cavity. Since the stability constants for metal ion binding are expected to decrease markedly by the oxidation of these types of transformable moieties, a new separation process can be envisioned in which a column can be switched between concentration and stripping modes by the respective reduction and oxidation of the immobilized chelate. This program is aimed at assessing the range and scope of this new separation concept.

92. Lasers in Analytical Chemistry
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With the development of new energy technologies, materials problems, environmental pollution, and health effects present challenges to the analytical chemist. We are developing several laser-based analytical techniques to gain unique insight into elemental, organic, and gaseous pollutants associated with energy utilization, to study chemical changes of ultrasmall samples, and to probe variations in the surface composition of materials. We emphasize (1) studies of the fundamental processes in atom sources such as laser-generated plumes; (2) liquid chromatographic and capillary electrophoretic determination of organic, inorganic, and biochemical species using more sensitive or more selective detectors; (3) laser-based detection of large molecules deposited or adsorbed on surfaces of materials; and (4) real-time spectroscopic probes of chemical reactions down to the single-molecule limit.

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Chemistry Division

93. Separations Science Related to Nuclear and Hydrometallurgical Technology
Horwitz, E.P.; Barrans, R.E.; **$1,039,000**
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The objectives of this program are (A) to develop new and improved reagents that may be applied to help solve major problems in environmental remediation and waste management and (B) to elucidate the basic chemistry involved in utilizing these new reagents. The major subdivisions of the program are (1) the study of basic interactions between the extractant and diluent with the goal of achieving major alterations in extractant behavior, particularly with regard to both enhancing extraction efficiency and improving the physical properties of the system; (2) the study of isomer effects on molecular recognition by macrocyclic polyethers with the goal of understanding how conformational changes in the macrocyclic ring affect metal complex stability and macrocycle selectivity; (3) the design, synthesis, and characterization of new classes of multifunctional extractants that show extraordinary selectivities for selected metal ions; and (4) the design, synthesis, and characterization of a new class of aqueous-soluble molecules that will serve as selective guests for chelated metal ions and subsequently form a precipitate. All four objectives are directed towards application in nuclear technology, such as actinide separations, waste processing, by-product recovery from nuclear wastes, and hydrometallurgical processing.

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Department of Applied Science

94. ***Structure and Function in Electrochemistry***
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The objective of this program is to enhance the understanding of the relationship between the structure of an electrode surface and its function in an electrochemical process. A unique feature of this work is the emphasis on in situ determination of the structure of an electrode surface with atomic resolution during the course of an electrochemical reaction, i.e., the identification of atomic geometry of the reaction sites, as well as the identification of adsorbates, intermediates and products, with molecular specificity. Besides insights into fundamental surface electrochemistry and electrocatalysis, the results will have potential applicability in electrochemical energy conversion, electroorganic synthesis and sensors. X-ray scattering (utilizing the National Synchrotron Light Source) scanning tunnelling microscopy, (nonenhanced) Raman scattering and Fourier transform infrared spectroscopy will be the primary in situ probes. Specific studies will focus on determination of structures of metal atom, anion and molecular adsorbates in the absence and in the presence of several important electrocatalytic reactions and exploring of laws of ordering of the adsorbates on surfaces. These results will help to establish the correlations between the surface structure and its electrocatalytic activity and provide a basis for prediction of surface electrocatalytic properties.

95. ***Microparticle Analysis by Laser Spectroscopy***
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Aerosol particles are present abundantly and ubiquitously in nature and in environments associated with many energy-conversion systems, industrial processes, and health-related areas as well. These microparticles need to be characterized by their physical state and chemical composition, thus requiring the exploration of physical and chemical principles which can lead to entirely new methods of analysis specific to microparticles. This program focuses specifically on a basic understanding and novel applications of laser based spectroscopic methods for in situ characterization of suspended microparticles. Because of the nondestructive and species specific nature of Raman scattering, a unique single particle- Raman spectroscopy technique is currently being developed for physical and chemical characterization of microparticles. Progress has been made in establishing the detection limits for various Raman processes on microparticles. Sensitivity enhancement by resonance Raman scattering is being investigated. In addition, the single-particle levitation technique, in conjunction with spectroscopic tools to probe the physical and chemical state of molecular and ionic species in microparticles, is ideally suited for obtaining insight into the nature of ion association and solute phase transformation at high concentrations otherwise unattainable in bulk solutions. Thus, new amorphous metastable states that exist only in hygroscopic microparticles, but not in the bulk phase, have been identified. This research will not only continue to discover and elucidate heretofore unknown properties unique to microparticles, but also will provide the science and technology basis for advanced analytical techniques.

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96. ***Negative Ionization Mass Spectrometry***
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The elucidation of mechanisms for the formation of gas phase ions from high temperature inorganic condensed state matrices is the main thrust of this program. There are two main approaches for producing these ion emitters; embedding the desired pre-synthesized species in a suitable matrix, and production of the desired species via a chemical reaction as the ions are emitted. Several instruments have been devised to assist in these studies. Tube ion sources have been developed in which large samples of these ion emitting matrices can be pressed into refractory metal tubes and heated to ion emission temperature. These sources can be exchanged between an ion/neutral mass spectrometer, a conventional magnetic sector mass spectrometer and an ion source imaging instrument. The ion/neutral mass spectrometer was completed this past year, and allows the ions and neutrals subliming from the emitters to be measured in sequence. Preliminary data from this instrument demonstrates that important insights into ion emission mechanisms can be gained from this approach. Gases can also be diffused through the material in the tube so that high temperature gas/solid reactions can be studied in the mass spectrometers. Imaging of emitters have demonstrated that ion emission is exclusively from the surface of the bulk of the emitter, and that cracks in the emitter allow greatly enhanced emission. Understanding the role of cracks in the transport of ions has allowed new design concepts to be developed to increase ion intensity from these emitters. This work indicates that these emitters are micro chemical factories which either produce the species needed for ion emission, or preserve the pre-synthesized species. This understanding has led to new techniques for the custom design of emitters. A new line of study will test the theory that ions can be stored on surfaces and then pulsed out, using a repulsive electric field to hold the ions on the surface, and then an attractive field to cause them to desorb. A time-of-flight mass spectrometer has been modified to conduct these studies. In order to model the interactions of ions in electrostatic and magnetic fields, ion optic models have been developed. SIMION 6.0 was developed on this program and released this past year.

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Energy and Environment Division

97. ***Repetitively Pulsed Laser/Material Interaction***
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The interaction of a high-powered pulsed laser beam with solid materials offers widespread importance to many areas within the DOE and U.S. industries, including environmental analysis, nonproliferation, materials, electronics, and medical. Importantly, the laser material interaction (LMI) is a powerful technology for chemical separations and analysis. A pulsed, high-powered laser beam ablates constituent elements from any sample material into the vapor phase, which can be analyzed by classical spectroscopic techniques. However, the explosive laser material interaction is not fundamentally defined for general application. Critical issues to resolve are the fundamental mechanisms underlying the interaction, mass ablation rate behavior, and stoichiometric ablation. This Basic Energy Sciences supported research endeavors to elucidate fundamental mechanisms of the laser-material interaction and to develop laser sampling capabilities for DOE needs in chemical separations and analysis. The research emphasizes the study of repetitive-pulsed laser material interactions at atmospheric pressure. Atomic emission spectroscopic (AES) data from an inductively coupled plasma (ICP) demonstrate changes in the laser material interaction as a function of laser and material properties. ICP-AES is one of the only technologies for studying LMI at atmospheric pressure. Piezoelectric sensors are used to study the propagation of acoustic waves induced in the material by the pulsed irradiation. Probe-beam deflection is employed to determine the onset of material removal and the formation of a laser initiated surface plasma. Fundamental mechanisms describing the laser material interaction are developed by drawing correlations between these acoustic, deflection, and atomic emission data. Improved capabilities for direct solid sample chemical analysis are reported to the DOE and scientific community through technical publications and conference meetings.

Oak Ridge National Laboratory
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Chemical Technology Division

98. ***Chemical and Physical Principles in Multiphase Separations***
Byers, C.H.; DePaoli, D.W.; **$339,000**
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This program is comprised of several fundamental studies that explore the use of electromagnetic fields to enhance the efficiency of multiphase separations processes. Experimental, theoretical, and computational methods are employed to investigate the effect of electromagnetic fields on transport processes in liquid-liquid, gas-liquid, and solid-liquid systems. This work will provide information necessary to devise novel means to dramatically improve transport rates in these systems, and thus will have widespread benefit for separations processes such as solvent extraction and distillation as well as applications in environmental and biotechnology areas. There are three areas of current focus: (1) interface deformation and breakup, including analyses of electrostatic spraying of droplets and bubbles, drop formation, pendant drop oscillations, stretching liquid bridges, and drop impact; (2) electrocoalescence, including electrostatic and hydrodynamic interactions between charged, deformable drops; and (3) magnetic separations, including a fundamental analysis of high-gradient magnetic flocculation and filtration.

99. ***Interactions of Solutes, Solvents, and Surfaces: Adsorption and Supercritical Extraction***
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The striking properties of solutions in supercritical solvents can be understood in terms of the underlying fluid microstructure and molecular interactions. Fundamental understanding of these properties is the aim of theoretical and experimental studies. Such solutions are important in novel separations technologies such as supercritical extraction and supercritical chromatography and in other technologies as well. Understanding of supercritical solutions of simple fluids has been gained through our past theoretical studies, molecular simulations, and neutron scattering experiments of solutions of noble gas mixtures. This understanding is being extended to more complex fluids of practical importance to industry—for example, solutions in supercritical water and solutions of polymers with supercritical solvents—using molecular simulation techniques. We have also performed neutron scattering and x-ray scattering studies of polymers and of reverse micelles containing polymers in supercritical CO_2. With our new molecular simulation codes for calculations on massively parallel supercomputers we have begun studies of ion speciation in supercritical water; other codes have been developed for studying polymer systems. Complementary applied research is performed to support U.S. industry in areas such as supercritical water oxidation of hazardous wastes, polymerization in supercritical CO_2, and extraction of fatty acids in bioprocessing.

100. *Chemistry of Actinides and Fission Products*

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This project is one of only a few remaining fundamental research efforts that are concerned with the physical-chemical characteristics of the actinides and fission products as related to separations schemes. Although the efforts are generally focused on spectroscopic and photochemical approaches, other techniques such as neutron/X-ray small angle scattering have been employed as a means of identifying more macroscopic properties of these systems (e.g., the sizes and geometries of colloidal species). The fundamental concerns are aimed at defining the chemistry of (1) molten salt systems containing actinides or fission products (which have some potential for separations or waste isolation development); (2) these elements trapped and photolyzed in the controlled environment of a solid matrix (which could encourage novel separations under these conditions); and (3) hydrolytic polymers (namely, the factors controlling their formation, reactivity, and ultimate size, which ultimately influences separations involving these species). The common thread in this effort is speciation, seeking to relate the macroscopically observed chemical properties, eg., changes in thermodynamic properties, to variations in the molecular species found in the systems. Recent impact of these fundamental studies is found in several EM programs including the Molten Salt Reactor Experiment Remediation project.

Chemical and Analytical Sciences Division

101. *Single Photon Laser Photoionization of Oxygenated Compounds*

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The objective of this work is to conduct research and development on laser photoionization (PI) in combination with tandem mass spectrometry for real-time detection and measurement of oxygenated compounds in automotive exhaust. Current analytical protocols for analysis of some classes of vehicle emissions, including oxygenated compounds, require collection of exhaust samples and off-line analysis in an analytical laboratory. We propose to use single-photon ionization with coherent vacuum ultraviolet (118 nm, 10.5 eV) light in combination with ion trap tandem mass spectrometry to obtain the improvements in speed, sensitivity, and specificity needed for real-time analysis of complex automobile emissions. Because ionization potentials (IP's) for many oxygenated and other organics are below 10.5 eV, PI should, with a few exceptions, be universal for these exhaust components. Furthermore, several potential interferences (H_2O, CO_2, SO_2, and N_2O) have IP's well above 10.5 eV, and thus will not be ionized. Because some exhaust components have identical molecular weights, isomer discrimination through tandem mass spectrometry (MS/MS) will also be explored. The increased specificity of compound identification via MS/MS relies both on the mass of the parent ion formed by PI and the mass(es) of the product ion(s) formed from unimolecular decomposition under MS/MS conditions. The quadrupole ion trap mass spectrometer, which is intrinsically suited for use with pulsed ionization methods such as laser PI, is capable of executing ion manipulation operations for MS/MS and MS^n experiments on the time scale (tens-hundreds of msec) necessary for real-time emissions monitoring.

102. *Advanced Spectroscopic Methods for Chemical Analysis*

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In recent years the availability of monoenergetic beams of positrons has given rise to a spectacular increase in the utility of positron spectroscopy and has demanded a better understanding of the fundamental interactions of positrons with atoms and molecules. It is believed that the formation of positronium compounds occurs in a large number of cases, and thus an effort to explicitly identify these intermediates has begun. Evidence for the formation of positronium hydroxide (PsOH) has been seen. Positrons displace protons, which are detected by time-of-flight mass spectrometry. The heat of formation of the PsOH lowers the threshold energy required by the positrons by about 0.6 eV. There is even stronger evidence of the formation of positronium chloride (PsCl), for which the heat of formation has been calculated to be about –2 eV. In the ionization of CH_3Cl a break was seen in the ion current-vs-positron energy plot, which was about this magnitude. The resolution and peak-to-background ratio of the time-of-flight mass spectrometer have been improved sufficiently to allow measurements of the sub-positronium ionization cross sections for helium and the other inert gases. Secondary electron emission from organic compounds undergoing sub-positronium interactions will be studied. Collaborators in the above work include Fisk University, Maquette University, the University of Texas, Arlington, Arhus University, Denmark, University College London, and two Japanese scientists, from the Electrotechnical Institute and the National Institute for Chemistry and Materials.

103. *Chemical and Structural Principles in Solvent Extraction*

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Research in this program concerns the synthesis, structure, and thermodynamics of crown compounds and related selective extractants for the solvent extraction and ion exchange of metal ions from aqueous solution. The major fundamental issue currently being investigated is the relationship between extractant structure and both the efficiency and selectivity of extraction for alkali metal cations and their counteranions. This issue is being addressed in the context of the often-extraordinary influence of the solvent environment. Principles of chemical recognition form the basis for probing the influence of complementarity, exclusivity, preorganization, strain, inductive effects, and steric factors on host-guest interactions. With input from molecular-mechanics calculations, synthetic efforts target large- and small-ring crown compounds having systematically varying structural features. NMR methods and X-ray crystallography provide detailed structural information on extractants and their complexes. Extraction efficiency and selectivity are evaluated by distribution studies, using ion chromatography, ICP spectrometry, and radiotracer methods. Potentiometry, calorimetry, and FTIR and UV/vis spectroscopies provide additional information. Interpretation of the extraction results is aided by advanced equilibrium analysis using our unique program SXLSQI to develop accurate speciation models. Overall, results potentially benefit applied USDOE programs (e.g., Office of Environmental Management) and industries concerned with separations.

104. Advanced Chemical Measurement Research

Ramsey, J.M.; Barnes, M.D.; **$514,000**
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The objective of this program is to utilize fundamental developments in optics, lasers, chemistry, and physics to enable the development of new laser-based techniques to improve the sensitivity and/or specificity of chemical measurements. These techniques are applicable to a broad range of chemical measurement problems in fields encompassing environmental monitoring, process control, materials analysis, and biotechnology. Areas of research include ultrasensitive fluorescence detection, nonlinear optical processes, and resonance ionization mass spectrometry. We are addressing fundamental principles that must be understood to advance the area of single molecule detection. Microdroplet sampling is utilized to achieve picoliter to femtoliter probe volumes for the detection of single fluorescent molecules. These small probe volumes and the absence of diffusional losses has allowed detection of single chromophore molecules at high sensitivity (S/N 8950). Further understanding of cavity quantum electrodynamic effects and increased spontaneous emission rates for chromophores in microdroplets promises to enhance the sensitivity of these experiments. Surface nonlinear optical probes will be used to study surface chemistry within the top monolayer of thin films during growth in chemical vapor deposition reactors. These probes are expected to assist understanding of materials growth mechanisms. Multiphoton ionization experiments coupled with mass spectrometry are being investigated for isotopic analysis of elements and to further understand molecular energetics of trapped ions. A custom laser system is being constructed to advance the objectives of this program.

105. Mass Spectrometric Research for Inorganic Analyses

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The goal of this research is to advance the state-of-the-art in inorganic mass spectrometry. Areas of interest include glow discharge, isotope ratio, secondary ion, and inductively coupled plasma mass spectrometries. Areas of concentration in glow discharge mass spectrometry include development of a rf glow discharge cell for analysis of non-conducting materials and interfacing of a glow discharge to an ion trap. The ion trap holds great promise for both applied and fundamental studies. Metal ion chemistry and collision-induced dissociation are being explored, and the trap's properties provide several ways to address molecular interferences, thus enhancing capabilities for quantification. Fundamental studies using our sector mass spectrometer have been undertaken to elucidate the formation of rare species such as metal argides in a glow discharge; both rare and reactive gases are being used. The goal is to gain a better understanding of plasma chemistry through, for example, the closing of various thermodynamic cycles. An ICP sector mass spectrometer equipped with seven collectors is being evaluated for measurement of isotope ratios. In secondary ion mass spectrometry, our primary effort is directed toward understanding the relationship between the chemical composition of the sample and variations in instrumental bias in the measurement of isotope ratios. A linear relationship with respect to chemical composition between two end members (e.g., FeO and MgO) was established; this work is currently being extended to more complex systems. The relative merits of high resolution and extreme energy filtering when applied to the S isotope ratios were evaluated, with extreme energy filtering being the more accurate. Speciation of toxic metals in soils using gas chromatography-mass spectrometry has recently been undertaken; the goal is to quantify both inorganic and organic forms of the element in a single sample.

106. Research in Secondary Ion Mass Spectrometry

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This research concerns advancing the applicability of secondary ion mass spectrometry (SIMS) by identifying the fundamental causes of barriers to applicability, characterizing these barriers, and then finding a suitable method to overcome the barrier. For example, primary ion damage limits the utility of SIMS for mapping the distributions of organic compounds. We found that the effects of chemical damage could be mitigated by using a beam of cluster ions in conjunction with a primary Cs^+ beam to ablate the surface. Currently, we are modifying this approach by using a focused beam of cluster ions to perform ionization and ablation simultaneously; this will permit direct imaging by cluster ion impact, and should permit analysis of higher molecular weight molecules. As another example, we are developing methods for imaging and isotope ratio measurement of targeted elements from geologic samples. Here, the historic barriers have included limited precision and reproducibility. These barriers arise from the peculiarities of the mass spectrometer. To overcome them, we are using a mass spectrometer that permits simultaneous detection of isotopic ions and alternate measurement of an isotopic standard with measurements from the sample.

107. Mass Spectrometry Research for Organic Analysis

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The goal of this research program is to enhance organic mass spectrometry as an analytical tool via improved understanding of the underlying chemical and physical processes involved. A broad range of chemical reactions and physical processes can occur within the context of an organic mass spectrometry experiment due to the extremely wide range of reaction conditions that can be established. Unimolecular, bimolecular, and termolecular reactions (gas-phase processes) can occur as well as the wide variety of processes associated with ionization (gas-phase and solution processes). Ionization by glow discharge, laser irradiation, and electrospray are of primary interest in this program. The current research effort is focused on three main areas of investigation: electrostatic spray ionization, gas-phase reactions of polyatomic multiply-charged ions, and quadrupole ion trap mass spectrometry. The work with electrostatic spray systems, such as the electrospray (ES) and electrohydrodynamic (EH) ion sources, focuses on understanding the fundamental operation of these condensed-phase ion sources so as to widen their applicability and overall analytical utility. In particular, chemical, electrochemical, and optical techniques are used to correlate the solution chemistry of analytes with the gas-phase ions produced by these ion sources. These same techniques are also used to create ionic species for gas-phase study. Elucidating the effects of the coulombic field of multiply-charged ions on their gas-phase structure, stability, and reactivity is the focus of the ion chemistry studies. The use of ion-molecule and, more recently, ion-ion reactions is central to this work. Understanding the fundamental physical and chemical effects of operational parameters on gas-phase ions is a major theme in the quadrupole ion trap work. One major effort in this regard is the ongoing refinement of a detailed theoretical model for the collision-induced dissociation process (CID) as it occurs within the ion trap. Enhanced analytical utility of ion trap CID (i.e., tandem mass spectrometry) for structural determinations is one expected outcome from this advanced theory. This theory also shows that the ion trap might be used as a fundamental research mass spectrometer to garner such basic physical and chemical information as critical dissociation energies.

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Chemical Sciences Department

108. Fundamentals of Phase Partitioning in Supercritical Fluids

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The objective of this program is to describe the molecular interactions underlying separations in supercritical fluids. The scope of these studies spans the range from simple bi-molecular solute/solvent interactions to more complex multi-molecular clustering, ion-pair formation, chelation, and micellization phenomena. Molecular level studies in supercritical fluids will provide an improved understanding of both fluids and condensed-phase interactions by bridging the gap between the gaseous and liquid states. This program focuses on the fundamental chemistry that controls solute/solvent intermolecular interactions and the behavior of complex molecular assemblies in supercritical fluids through experimental and theoretical investigations. The experimental effort entails the use and expansion of various spectroscopic techniques such as FTIR, Raman, NMR, XAFS, and small angle X-ray scattering for supercritical fluids. The parallel theoretical effort involves molecular dynamics simulations describing the fundamental behavior of fluid solvents. Continued studies seek to characterize angstrom- to micron-sized molecular assemblies in supercritical fluids, e.g., alcohol aggregates, chelates, hydrated ions, and reverse micelles. Newly initiated investigations involve the study of the photophysics of organometallic ligand substitution reactions using high-pressure NMR in addition to investigations of ion solvation in supercritical water and the solvation structure of metal chelates in supercritical carbon dioxide using XAFS spectroscopy. It is anticipated that this program will provide the basis for new and improved analytical separations and for larger scale separations and reactions needed in environmental remediation.

Materials and Chemical Sciences Department

109. Laser-Based Analytical Techniques

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Prior studies of trace constituent analysis with simple and double-pulse laser ablation, followed by optical emission detection, have observed highly variable analysis results, with compositions varying by 40% or more from given bulk compositions. The highly non-linear dependence of the ablation process on laser pulse energy and matrix composition and morphology, as well as self-absorption by emitting species, electronic densities, and uncertainties in absolute transition strengths have been identified as major contributors to these deviations. Current studies are using high-resolution, time-resolved absorption measurements to determine the concentrations and physical environment of atomic species within laser ablation plumes. Under vacuum conditions, two distinct components of the atomic absorption are observed. The first component is short lived with a duration of approximately 1 μs. The absoption line is red shifted by up to 10 GHz consistent with both pressure induced shifts and Stark shifting at high electron densities. Also, the absorption linewidth is broad and highly time dependent. Analysis of linewidth as a function of time indicate the presence of a significant density of neutral atoms with effective temperatures in excess of 10,000K. This short-lived component is attributed to the expansion of the initially formed laser ablation plasma. A second, longer-lived (up to several hundred μs) component is observed at unshifted wavelength and with time dependent Doppler widths corresponding to temperatures of 500-1500K. This component is attributed to thermal evaporation from the ablation site after the initial ablation-plasma etching process is completed. This thermal evolution is expected to produce high fractionation of the bulk constituents. Similar studies have also been performed in the presence of a low pressure (<1 torr) cover gas and three distinct time components are observed. The new component, at intermediate times of 3–10 μs, is tentatively assigned to shock-wave formation at the boundary of the plasma expansion, however, a bimodal Doppler distribution, as would be expected for two shock fronts at opposite sides of the expansion, has not yet been observed. Continuing studies will examine the dependence of the slow and fast components as a function of ablation laser wavelength, pulse duration and energy, and substrate material in order to quantify the conditions which yield plume compositions that are most representative of the bulk composition.

Heavy Element Chemistry

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Chemistry Division

110. ***Heavy Element Chemistry Research***
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The central emphasis of this program is to develop an understanding of the fundamental chemical and physical properties of f-elements which characterize their interactions with the surrounding environment. One goal is to understand the mechanisms by which f electrons influence the properties of materials containing them. The unique thrust of this effort is to utilize the specific properties of different f elements to alter the electronic behavior of a substance. Basic knowledge obtained from these experiments will be used to design materials with predetermined electronic and cooperative properties for use in such widely diverse physical applications as optical switches, electrical conductors, and catalysts. In parallel research, the electronic and magnetic properties of the heavy elements are probed, using laser-based methods that include optically detected nuclear magnetic resonance and photochemical studies, and modeled in order to attain predictive insight. The understanding achieved is applied to important fundamental and technological issues throughout the nuclear fuel cycle, for example, as a basis for new methods for the decontamination of uranium enrichment plants. A third thrust involves investigation of actinide behavior in solution phases using a variety of spectroscopic, electrochemical, and thermochemical techniques. Combined results from thermodynamic, kinetic, X-ray diffraction, spectroscopic, and molecular modeling experiments are used to characterize the solution/coordination chemistry of actinides in all oxidation states, and the interaction of the metal ions and their complexes with aqueous and organic solvents.

111. ***An Actinide Facility for Synchrotron Research in Molecular and Environmental Sciences***
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The state-of-the-art beamlines currently under construction at the Advanced Photon Source (APS) will be able to perform an enormous variety of experiments. The goal of this Actinide Facility is to make the largest number of beamlines accessible to experiments involving radioactive samples, and to do so with the least amount of effort on the part of either the experimenter or the targeted-beamline personnel. Funded by a DOE-Facilities Initiative, the Chemistry division at Argonne National Laboratory will make available presently existing, dedicated hot-laboratory facilities to researchers wishing to conduct experiments on actinide-containing samples at the APS. The hot-laboratory space will be provided for simple chemical and physical manipulations of samples before and after experiments. In addition, specialty equipment will be available, both in the form of safety monitoring devices to be used at the hutches, as well as equipment necessary for performing experiments. One example is a purpose-built portable glovebox that can be loaded in the hot-laboratory, and used at the beamline to permit sample manipulations. In addition to equipment, there will also be personnel available for consultation on both the experimental and safety aspects of the experiments. This Facility is driven by members of both the synchrotron community and the actinide community who wish to take advantage of the APS to conduct state-of-the-art research.

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112. ***Actinide Chemistry***
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Development of new technologies for the use, safe handling, storage, and disposal of actinide materials relies on further understanding of basic actinide chemistry and the availability of trained personnel. This research program is a comprehensive, multifaceted approach to actinide chemistry and to the training of students to address future issues. Research efforts include synthetic chemistry to develop new chemical reagents and actinide materials, their chemical and physical elucidation through characterization techniques, and thermodynamic/kinetic studies for evaluation of complex formation. One aspect is the development of complexing agents that specifically sequester actinide ions for the decorporation of actinides in humans and for the separation of actinides in the environment. Extensive studies are underway to prepare organometallic and coordination compounds of the f-block elements that show the differences and similarities among the f-elements and between the f- and d-transition series elements. Interpretation of optical and magnetic studies on actinide ions in ionic and molecular solids gives information about electronic properties as a function of atomic number. X-ray absorption spectroscopy techniques at the Stanford Synchrotron Radiation Laboratory are employed to investigate both the fundamental and environmental chemistry of transuranic and fission product materials. Soft x-ray synchrotron radiation at the Advanced Light Source is being utilized to characterize actinide solid-state materials.

113. ***Actinide/Environmental Beamline User Facility at the Advanced Light Source***
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The Actinide/Environmental Endstation project addresses the utilization of the Advanced Light Source (ALS) for synchrotron investigations of actinide and environmental science in the vacuum ultra-violet/soft x-ray spectral region. The tunability of the photon source permits the use of absorption techniques, optimization of cross-sectional effects for photoemission measurements, and the ability to change electron escape lengths. In order to make measurements on extremely small single crystals, thin film materials, particulates, and on a wide range of radioactive samples from waste sites, it is necessary to work with samples which are substantially more radioactive than can be handled in a general user beamline endstation at the ALS. The characteristics of the photon beam from ALS beamlines (tunability, brightness, flux, and stability) are paramount in transuranium/environmental research because they allow the use of exceptionally small samples, which greatly reduce safety concerns. A dedicated experimental user endstation is being constructed for the investigation of radioactive/hazardous materials to exploit the available beamtime on existing beamlines and to permit the safe handling of larger quantities of more highly radioactive materials than are currently permitted in endstations currently located on the experimental floor. The endstation is of a multiple ultra-high vacuum chamber system mounted on a low vibration (for microscopy efforts) moveable frame that can be easily transported and positioned onto several different ALS beamlines. The endstation will consist of an angle integrating electron spectrometer, "hot" preparation chamber, and a "cold" preparation-introduction chamber.

Nuclear Science Division

114. Chemistry of the Heaviest Elements

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The chemical properties of the heaviest elements are being investigated to explore the architecture of the periodic table of the elements at its furthest reaches and to compare their properties with those of their lighter homologs. Investigations of the dramatic changes in properties which occur in going from the actinides, which end with lawrencium (element 103), to the transactinides are especially important. Methods for studying the chemical properties of elements 102 through 106 are developed even though some of the half-lives are only seconds and only small numbers of atoms can be produced. Chemical separations of elements 102–105 have been used to determine their most stable oxidation states in aqueous solution, thus confirming their positions in the periodic table. Both liquid-liquid extractions and isothermal gas chromatography are used to study and compare the halide complexes of elements 104 and 105 with those of their lighter homologs. The detailed studies of chemical properties of the heaviest elements have shown anomalous trends which cannot be predicted on the basis of simple extrapolations of known periodic table trends. It is important to extend studies to even heavier elements and to compare the results with predictions of fully relativistic calculations. During FY-96, our group hosted a collaboration of Norwegian, Swedish, and German scientists which successfully used the fast liquid-liquid extraction system, SISAK, in conjunction with a flowing liquid scintillation system to study the chemical properties of hahnium (105) using 1.8-second ^{261}Ha produced at the LBNL 88-Inch Cyclotron. Participation in an international collaboration to use the full range of automated liquid and gas-phase chemical separation systems to perform the first ever chemical studies of seaborgium (Sg, element 106) using the recently reported longer-lived isotopes of Sg is in progress.

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Chemical Science and Technology Division

115. Actinide Organometallic Chemistry

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These investigations seek to extend our understanding of the chemical behavior and electronic structure of complexes of the actinide elements. Synthetic studies of the nonaqueous coordination and organometallic chemistry of the actinides play a key role in improving our knowledge of redox chemistry and metal-ligand bond strengths. This type of information is critical to the development of advanced chemical processes, analytical tools, and predictive models applicable in actinide recovery, waste treatment, and environmental restoration activities. Efforts over the past year have focused on understanding factors which stabilize chemical complexes of actinides in higher oxidation states (e.g. hexavalent uranium). During the past year, we have developed much more general synthetic pathways for the introduction of imido functional groups at actinide centers, permitting the isolation of saturated alkylimido complexes. The enhanced nucleophilicity of the alkylimido derivatives can be exploited in the generation of products derived from H–H, Si–H, and C–H bond activation (including the isolation of an unusual example of an uranium metallocene which has undergone activation of a ring substituent). We have also been able to develop multi-electron transfer reactions which can either break bonds in substrates (such as the cleavage of azobenzene to generate the bisimido complex $(C_5Me_5)_2U(NPh)_2$) or make bonds to generate coupled products (e.g. alkyne coupling). While the chemistry of uranium is similar in some respects to that of the Group 4 transition metals, this multi-electron transfer capability only finds precedent in the chemistry of the Group 6 metals. Current studies are aimed at identifying whether this result suggests an enhanced degree of covalency in chemical bonding in the higher valent actinide complexes.

116. Actinide Chemistry in Near-Neutral Solutions

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The project objective is to provide fundamental physicochemical knowledge pertinent to the behavior of transuranic elements under environmental near-neutral pH conditions. Advances continue in the application of C–13 and O–17 NMR, Raman, NIR, and XAS spectroscopy towards determining the stability fields and molecular structures of actinyl (U, Np, Pu) carbonato complexes. Bulky cations (TMA, TBA) afford a relatively high solubility for Np(V) mono, bis, and tris carbonato complexes, $NpO_2(CO_3)^-$ (I), $NpO_2(CO_3)_2^{3-}$ (II), and, $NpO_2(CO_3)_3^{4-}$ (III). Thermodynamic data establish the stoichiometry of I–III, NIR spectra verifies that individual EXAFS solutions of I–III contain a single species, and spectra provide structural details. II and III show hexagonal bipyramidal coordination geometries with bidentate carbonate ligands, while I shows pentagonal bipyramidal coordination. All complexes show bidentate carbonate ligation, with the remainder of equatorial sites occupied by water molecules. Axial Np=O distances span

1.86–1.84Å, while equatorial Np–O distances are 1.85±0.02Å. Bidentate carbonate ligation is indicated by the Np–C distances of 2.93–2.99Å and the number of carbons is half the number of equatorial carbonate oxygens. These carbonato complexes of Np(V) have been known for over a decade, but this work is the first elucidation of the molecular structures of these environmentally important compounds. The solid-liquid equilibrium of Np(V) was studied in NaCl at 25°C and 0.01 atm CO_2. The equilibrium solids were characterized using powder X-ray diffraction, and the Np(V) solution species were characterized using NIR absorption spectroscopy. The solid phases $NaNpO_2CO_3 \cdot nH_2O$ at $[CO_3^{2-}] < 0.001$ M and $Na_3NpO_2(CO_3)_2 \cdot nH_2O$ at $[CO_3^{2-}] > 0.001$ M were found as solubility limiting solid equilibrium phases. The comparison of Np(V) solubility data in NaCl and $NaClO_4$ solutions indicated a stabilization of Np(V) in solution due to the interaction with chloride ions. The Pitzer approach was applied to parameterize experimental data and to predict Np(V) solubility in brine solutions.

117. *Actinide Chemistry in Alkaline Radioactive Waste*

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The project objective is to systematically prepare and study high valent actinide complexes formed under highly alkaline conditions similar to that of aging radioactive waste tanks at Hanford, Savannah River, INEL, West Valley, and Oak Ridge. Under strongly alkaline conditions ($[OH^-] = 2–14$ M), actinide elements can be significantly more soluble and have unusual sorption characteristics, causing difficulty in separations and the ultimate partitioning into high level and low level waste components. Under alkaline conditions, actinide ions can form a relatively stable heptavalent state. Solids of formula $MNpO_4 \cdot nH_2O$ (M = Cs, K, Na, Li) have been prepared and are reported to be very stable in the solid state. A few single crystal X-ray structures have been determined for salts which display the highly unusual tetragonal bipyramidal $NpO_4(OH)_2^{3-}$ central core (but there are no data to support which structural motif exists in alkaline solution. This year we performed an EXAFS study of Np(VII) in alkaline solution to resolve this important issue. Alkaline Np(VII) solutions were prepared by bubbling O_3 through 2.5M NaOH containing $NpO_2(OH)_2$, and the resulting dark green solution characterized using Vis-NIR spectroscopy which revealed two absorption features with maxima at 410 and 625 nm consistent with those reported previously for dark green Np(VII) solutions. The EXAFS data show unequivocally that the Np(VII) species in alkaline solution must contain a trans dioxo ion (Np=O = 1.85Å), formally based on the NpO_2^{3+} central unit, which must be coordinated to five OH^- and one OH_2 ligands with Np–O distances of 2.18 and 2.42Å, respectively. This structural type has not been previously observed for Np(VII).

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Chemistry Division

118. *Chemistry of Transuranium Elements and Compounds*

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The program's objectives are to promote a fundamental and technological understanding of the chemistry, physics and materials science of actinide elements, compounds and alloys. The primary goal is to define and understand chemical and physical behaviors in terms of fundamental electronic interactions, thermodynamics and scientific principles. The science of these materials is advanced through systematic investigations, which establish trends and differences in behavior with changing electronic configurations. Both experimental and theoretical approaches are employed in pursuing this goal. Experimental research focuses on the vapor- and solid-state science of the actinides. Primary experimental disciplines and capabilities include: high-pressure studies; high-temperature mass spectrometry and X-ray diffraction; laser ablation mass spectrometry; thermal analyses; optical spectroscopy; and novel/microscale synthetic techniques. Selected areas of investigation are phase behaviors of metal systems; oxidation state behavior in solids and vapors; high-temperature vaporization processes and thermodynamics; vapor state cluster chemistry; and spectroscopic investigations of electronic levels and transfer processes. Theoretical and computational studies (quantum chemistry and statistical mechanics) are employed for interpretation of experimental findings, modeling and deriving scientific information via first-principle considerations.

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119. *Controlled Clean Lab Enclosure for XAFS Studies of Radioactive and Toxic Samples on Beam Line 11 at the Stanford Synchrotron Radiation Laboratory*

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During the past few years, there has been increasing demand at the Stanford Synchrotron Radiation Laboratory by national laboratory and university scientists for beam time on high-flux, insertion-device beam lines to characterize the chemical forms (speciation) of radionuclides and toxic heavy metals in environmental samples. To help meet the needs in this new research area, DOE-BES-Chemical Sciences is funding a new wiggler beam line at SSRL (BL-11) devoted to molecular environmental science research. This new beam line is currently under construction and should be commissioned in early 1998. An essential component of this new environmental sciences beam line is a controlled clean laboratory that will be built around the experimental hutch. This facility is required to permit safe sample handling, temporary storage, and XAFS spectroscopy studies on environmental samples containing radionuclides, particularly transuranics, and highly toxic or carcinogenic species. This project will provide the funding to construct this controlled experimental area on BL-11. Because this will be a permanent installation, with all the necessary equipment for radiation monitoring and safe sample handling and containment, it will also permit increased numbers of radioactive and toxic samples to be studied without the time-consuming and inefficient set-up and dismantling times now required on SSRL Beam Line 4-2, where XAFS studies of samples containing these elements are typically carried out. We are currently exploring various design features for this clean lab with members of the BL-11 Advisory Committee and plan to have a detailed plan developed within the next four months. Construction of the clean lab and experimental hutch is planned in 1997. When BL-11 and the controlled clean laboratory are completed, a major new synchrotron radiation facility for XAFS studies of radioactive and toxic elements in natural samples, man-made waste forms, and simplified synthetic analog systems will be available to the growing number of environmental science users at SSRL. The results of these studies (speciation of contaminants, spatial distribution of different contaminant species, chemical and biochemical factors affecting transformations among species, and the kinetics of such transformations) will have a major impact on improving the technologies needed to address and solve contamination and waste management problems within the U.S. weapons complex and at numerous sites contaminated as a result of past and present agricultural and industrial activities, mining, and manufacturing.

Chemical Engineering Sciences

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Chemical Sciences Division

120. *Molecular Thermodynamics for Phase Equilibria in Mixtures*
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Phase equilibria are required for design of efficient separation processes (e.g., polymer devolatilization or selective precipitation of a target protein from an aqueous protein mixture) in the chemical and related industries and for development of new chemical products and materials. In this context, "efficient" refers to optimum use of raw materials and to conservation of energy. Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all equilibria from experiment. Therefore, the objective of this research is the development of molecular thermodynamics for interpretation and correlation of reliable experimental data toward confident prediction of phase equilibria for chemical process and product design. The correlations are expressed through semi-theoretical, physicochemical models based on statistical and classical thermodynamics and on our own as well as published experimental data. Particular attention is given to those materials that may be useful for innovative low-energy-consuming separation processes such as polymers, gels, and polyelectrolyte systems with applications in biotechnology. However, attention is also devoted to conventional materials for applications in fuel technology, for recovery of salts from large-scale gas-scrubbing processes, and for proteins used in nutrition or pharmaceutics. Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it requires simultaneous awareness of progress in molecular science and of realistic requirements for engineering application.

Energy and Environment Division

121. *Turbulent Combustion*
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The objective of this program is to investigate, primarily experimentally, the interaction and coupling between turbulence and combustion. These turbulent combustion processes are characterized by scalar and velocity fluctuations with time and length scales spanning several orders of magnitude. Our approach is to gain a fundamental understanding through detailed investigation of idealized laboratory flames with flow and flame geometries amenable to theoretical analysis. These laboratory flames are accessible to detailed interrogation by laser diagnostics. The programmatic emphasis is on gaining a physical understanding of the coupled effects of turbulence and flame geometry on heat release, turbulent burning rate, stability limits and flame extinction. Such knowledge is essential for the development of turbulent combustion theories. A primary and continuing effort is the investigation of flames with moderate turbulence under which the chemical reaction rates are high compared to those of turbulence. The burning rate can be inferred from the flame wrinkles scales for direct comparison to turbulence scales. Our current focus is on investigating the relative effects of shear and non-shear turbulence. The research on moderate turbulent flames forms the foundation for the investigation of flames with intense turbulence. Intense turbulent flames are closer simulations of the combustion processes in practical systems where turbulence may alter the reaction rates, cause flame quenching and affect the formation of pollutants. The use of planar laser induced fluorescence techniques to study intense turbulent flames is our current emphasis.

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Theoretical Division

122. *Thermophysical Properties of Mixtures*
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The thermophysical properties of mixtures of particles interacting through simple interaction potentials are evaluated, using both equilibrium Monte Carlo and molecular dynamics, as well as nonequilibrium molecular dynamics. The properties under investigation include the equation of state and transport properties, including mutual and self diffusion, shear and bulk viscosity, thermal conductivity, and thermal diffusion. Fundamental questions arising in the theory of fluids and fluid mixtures are addressed where numerical "experiments" are appropriate. Current research is concentrated on the phase diagram of hard-sphere mixtures having diameter ratios no greater than 0.2 and compositions in which the molecular volume of the two species are similar. Theoretical predictions of fluid phase demixing have been made for such mixtures in recent years, contradicting the conventional understanding arising from the Lebowitz solution to the Percus-Yevick integral equation. The Gibbs ensemble Monte Carlo method permits the study of the coexistence of disordered phases, but current implementations are inadequate to overcome the ergodic difficulties attendant upon the disparate hard-sphere interactions. Advanced methods have been development to permit the study of this mixture as well as others having large disparities in the interactions. For the binary mixture of hard spheres having a diameter ratio of 0.2 and a mole fraction of 0.008 for the large spheres, calculations in the constant pressure ensemble at a reduced pressure, $\phi=pv_0/kT$, (where p is the pressure, T is the temperature, k is Boltzmann's constant, $v_0=(x_1\sigma_1^2+x_2\sigma_2^2)$, x_i and σ_i are the mole fraction and diameter of species i) of 6 exhibit demixing for systems of 5832 and 8000 particles but preliminary results for 10648 particles shows no evidence thereof. Additional calculations have been initiated for $\phi=8$. While all these calculations approach equilibrium very slowly, the number of large particles in each subsystem rapidly becomes essentially fixed. Nonetheless, the new algorithm still enables small fluctuations in these numbers, leading one to believe the Monte Carlo procedure to be ergodic, i.e. to explore all important regions of configuration and composition space.

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Department of Fuels Research

123. Thermodynamic Properties for Polycyclic Systems by Noncalorimetric Methods
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This project develops thermodynamic properties for petroleum processing polycyclic molecules via assigned spectra and statistical mechanics. Polycyclics studied fall into two categories, a rigid class built of ring systems that contain some degree of aromaticity, such as furan and indole, and a second class that differs by hydrogenation of a single ring bond, e.g., 2,5-dihydrofuran and indoline, which increases ring flexibility. The experimental work entails measurement of vibrational frequencies by the recording of infrared and Raman spectra, while theoretical models are sought to assist and verify the assignment of fundamentals and evaluation of thermodynamic data. The primary thrust during the next two years is to simplify the vibrational frequency calculations by incorporating the empirical results from the past three years and also to examine improved modeling methods. This will be accomplished firstly by vertically integrating the many steps in the presently used semi-empirical scaled quantum mechanical methodology and secondly, by launching full ab initio techniques to generate the initial vibrational force constant matrix, given the anticipated acessibility of higher speed computers. Highlights of the past year's research include: (1) A series of papers published on the vibrational spectra and thermodynamics of indene and derivatives: In part I, *Spectrochimica Acta* **1995**, *51A*, 1255, compelling justification of the vibrational assignment for indole, benzofuran, benzothiophene, benzoxazole, and benzothiazole was provided using the scaled AM1 force field technique; in part II, *Spectrochimica Acta* **1995**, *51A*, 1273, the spectra, assignment, and vapor-liquid wavenumber shifts for benzothiophene and benzothiazole were discussed; in part III, *Spectrochimica Acta* **1995**, *51A*, 1291, the spectra and assignment for indole, benzofuran and benzoxazole were described, and dramatically improved ideal-gas entropies were demonstrated for benzoxazole. (2) The paper "Vibrational Assignment and Analysis for 2,3-Dihydrofuran and 2,5-Dihydrofuran" appeared in print, *Spectrochimica Acta* **1994**, *50A*, 1725.

Sandia National Laboratories, California
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Combustion Research Facility

124. Analysis of Turbulent Reacting Flows
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The goal of this project is to develop numerical simulation techniques for the understanding of reacting turbulent flows. The objective is to show the mechanisms of turbulent mixing and reaction. A model of premixed flame propagation along the core of a vortex indicates that the generation of new vorticity may cause significant enhancement of the flame speed. This generation occurs when the pressure gradient created by the vortex swirling motion is normal to the density gradient across the flame, known as the baroclinic effect. Previous experiments with a burning vortex ring showed a factor of twenty enhancement in the flame speed. This behavior may also occur within the intense vortex structures observed in turbulent flows. The linear-eddy mixing model, unique in its representation of the distinct influences of convective stirring and molecular diffusion, is being used to investigate the spatial correlations of chemical species in turbulent reacting flows.

Advanced Battery Research

Ames Laboratory
Iowa State University
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Department of Materials Science and Engineering

125. Design and Processing of High Purity and Ultrafine Electrodes for High Performance Nickel/Metal Hydride Batteries
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All major battery manufacturers are aware that their rechargeable Ni/Cd products are currently poised on the edge of an outright ban or a heavy tax due to the extreme toxicity of Cd. As a consequence, an acceptable substitute must be found. The Ni/metal hydride (Ni/MH) rechargeable battery has emerged as one of the most promising environmentally acceptable substitutions for current Ni/Cd rechargeable batteries in nonautomotive applications for the consumer and industrial market. A key to realization of this potential lies in coupling of the development of both high performance positive and negative electrode materials with the development of efficient, well-controlled electrode processing approaches for each new electrode material. Another key is the close collaboration of a high level research team with a capable and aggressive manufacturer of Ni/MH batteries. This coupled development and industrial collaboration can produce not only improved battery performance and effective manufacturability but also will promote a rapid transfer of materials and process research results from the laboratory to the manufacturing floor and marketplace. This program's focus includes the fundamental, systematic development of a significantly improved alloy composition (especially with respect to chemical and phase purity levels) and electrode fabrication technique for the negative electrode centered on the AB_5 (based on $LaNi_5$) intermetallic compounds. The objective of this work is to greatly reduce self-discharge and to double cycling life characteristics of this electrode material over the competing AB_2 compounds. Also, focus is on development of a unique processing approach for the NiOOH positive electrode that will permit fabrication of new ultrafine pitch electrodes. Such an ultrafine pitch electrode with homogeneously dispersed particulate has the potential to increase the energy storage density by about 50%, thereby reducing size and weight of this new generation of Ni/MH batteries. This program is being carried with intimate contact between the Ames Laboratory and Harding Energy Systems Inc., an emerging domestic battery manufacturer.

Argonne National Laboratory
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Chemical Technology Division

126. A Fundamental Study of Lithium Polymer Electrolytes: Neutron and X-ray Scattering Experiments and Electronic Structure Calculations
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This project is a complementary experimental and theoretical study of the structure, dynamics, and transport properties of lithium polymer electrolytes. The goal is to obtain a fundamental understanding of the ionic transport properties in these electrolytes in order to help optimize their performance in lithium secondary batteries. The experimental part of the study involves neutron scattering measurements at the Intense Pulsed Neutron Source (IPNS) at Argonne and X-ray scattering measurements at the Advanced Photon Source (APS) at Argonne. Application of scattering techniques to lithium polymer electrolytes will provide information on ion solvation and the attendant effects of ion pairing, which affect the ionic transport in these systems. The theoretical part of the project involves electronic structure calculations based on ab initio molecular orbital theory. These calculations are being used to investigate energetic, structural, and dynamical properties of ion-ion and ion-polymer interactions at the molecular level. The computational studies are providing accurate potentials for molecular dynamics studies being carried out at the University of Minnesota. The calculations will also be used to help interpret the experimental data. At a later stage these methods will be used to study processes ocurring at electrode/electrolyte interfaces in batteries.

127. Ion Transport Properties Determined by In-Situ NMR Spectroscopic Imaging
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This program uses in situ magnetic resonance imaging (MRI) to better define electrode-electrolyte interfaces and solid-state ion transport mechanisms. Recent results have demonstrated that toroid cavity NMR imaging has sufficient sensitivity and distance resolution to accurately map out the ionic concentration profiles that result during the electrochemical cycling of lithium polymer-electrolyte battery materials. In addition, a new spin labeling method for the determination of diffusion coefficients has been developed. Nuclear spin labeling has been achieved at a distance resolution of 2 μm in low-viscosity organic solvents. A method has been proposed for distinguishing between short-and long-range ion motion using diffusion coefficient measurements and is being tested on polymer electrolyte materials. The in situ NMR imaging techniques that are being developed should be generally useful for the analysis of the chemical composition at electrode-electrolyte interfaces, growth factors responsible for passive film formation, ion concentration gradients within solid-state batteries, conformational dynamics of polymeric electrolytes, ion penetration depths within graphite insertion electrodes, and dendrite formation on lithium anodes.

128. New Electrode Materials: Synthesis, Characterization and Modeling

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This is a new project which will address the development and characterization of novel or modified metal oxide electrodes for non-aqueous rechargeable lithium batteries. The advent of lithium-ion batteries in products such as cellular phones and laptop computers has led to an increasing awareness of their possible application in heavy duty devices such as electric vehicles. However, state-of-the-art metal oxide electrodes are limited by performance factors such as structural instability to lithium insertion/extraction reactions, particularly at the end of discharge/charge, and an instability to temperature rise effects.. Furthermore, the capacity of the metal oxide electrodes and cycle life of lithium batteries need to be improved. These limitations are slowing the progress of lithium battery technology. There is therefore an urgent need to explore the possibility of finding alternative materials for these batteries. This project, which is exploratory in nature, has two complementary tasks. The first task will be to search for novel or improved electrode materials (notably metal oxides), to optimize materials processing techniques and to characterize the materials in terms of their structural and electrochemical properties. The second task will focus on the modeling of both "known" and "hypothetical" materials using ab initio methods: theoretical calculations and modeling can provide invaluable insight and guidance for understanding and tailoring the structure and behavior of materials. The project will make use of the extensive battery expertise that exists at Argonne National Laboratory, and its unique facilities, for example, the Intense Pulsed Neutron Source (IPNS) for undertaking detailed structure analyses of materials. Materials characterization will also include convergent-beam electron diffraction (CBED) and high-resolution transmission electron microscopy (HRTEM) to provide "real-life" pictures of the structures of materials which cannot be obtained from "time-averaged" structural representations provided by X-ray or neutron diffraction techniques alone.

Chemistry Division

129. Template Mediated Synthesis of New Carbon Negative Electrode

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This program seeks to understand the chemistry and physics of carbon anodes in lithium secondary batteries. The approach is to design and prepare carbons with specific molecular properties. Inorganic templates such as pillared clays are being used to prepare molecularly porous, disordered carbons. The carbons have been characterized by a number of methods, including small angle neutron scattering (SANS) and synchrotron X-ray spectroscopy. SANS data have shown that after removal of the pillared clays, the carbon sheets contain holes the size of the original pillars. In electrochemical studies, these carbons exhibit high reversible capacities (up to 850 mAh/g) and coulombic efficiencies higher than 80%.

Material Science Division

130. The Study of Electrochemical Interfaces Important to Energy Storage and Conversion Processes at the Advanced Photon Source

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The primary objective of this interdisciplinary research is the fundamental understanding of the solid/solution interfacial structure of materials important to energy storage and to energy conversion. The problem areas include electrocatalysis, surface morphology of metal deposition/dissolution, intercalation/deintercalation mechanism, and structure of the electric double layer. The final aim is to contribute seminal guidance to the development of improved energy storage/conversion materials with increased energy and power density and charge/discharge rate for a variety of battery and fuel cell systems. While we expect that the results of our investigation will provide impetus for technological developments, they will also be of fundamental scientific importance in the field of interfacial electrochemistry. The research program that we carry out couples in situ synchrotron-based x-ray measurements with electrochemical transient techniques and theoretical modeling. An example of our investigations is the study in real time of the actual and complete phenomena occurring in ultracapacitor storage devices. The ultracapacitor stores energy using several different phenomena of interfacial changes restricted within a 1–100Å layer such as the electrochemical double layer and the adsorption pseudocapacitance involving redox. All these phenomena can be observed at a third-generation-synchrotron facility such as the Advanced Photon Source.

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Department of Applied Science

131. Synthesis and Characterization of Metal Hydride Electrodes

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The purpose of this work is to elucidate the structural, thermodynamic, and metallurgical parameters that affect the stability, kinetics, and energy density of metal hydride electrodes. It is focused on alloy development and the application of in situ methods such as X-ray absorption (XAS), X-ray diffraction (XRD), X-ray tomography, magnetic susceptibility, and scanning tunneling microscopy (STM) to determine the roles that various hydride phases and alloying elements play in hydrogen storage and corrosion inhibition. In situ methods are complemented by ex situ studies such as neutron diffraction, electrochemical, thermodynamic, and metallurgical characterization of candidate alloys. The information thus gained will be used to develop metal hydride electrodes with improved cycle life and energy density.

132. Chemistry and Electrochemistry of Hydrogen Insertion Electrodes
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The purpose of this effort is to elucidate the structural, thermodynamic, and metallurgical parameters that affect the stability, kinetics and energy density of hydrogen insertion electrodes. It is focused on multicomponent alloy hydrides and develops and applies in situ methods such as x-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), x-ray tomography, magnetic susceptibility and scanning tunneling microscopy (STM) to determine the roles of various hydride phases and alloying elements in hydrogen storage and corrosion inhibition. In situ methods are complemented with ex-situ studies employing x-ray and neutron diffraction as well as electrochemical, thermodynamic and metallurgical characterization of candidate alloys. The information thus gained will be used to develop metal hydride electrodes with improved cycle life, energy density and lower costs.

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Chemical Sciences Division

133. Characterization of the Li–Electrolyte Interface
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A detailed understanding of the reactions that occur between metallic Li and the individual molecular constituents of electrolytes used in Li batteries will be developed. Ultrahigh vacuum (UHV) deposition methods are used to prepare ultraclean Li surfaces of preferred orientation. Molecular films of solvent and/or solute molecules are deposited onto the clean surfaces in UHV at a very low temperature. The reaction between Li and the molecular films is followed using a combination of UHV surface analytical techniques, including Auger electron spectroscopy (AES), secondary ionization mass spectroscopy (SIMS), vacuum UV and X-ray photoelectron spectroscopy (UPES and XPS), and the recently developed variant of XPS termed photoelectron diffraction. The connection between films formed on Li in UHV and films formed at ambient temperature and pressure on Li in liquid electrolyte is made by the use of a common spectroscopy, ellipsometry. Using the fingerprint method, the ellipsometric signatures obtained in UHV for different surface layers having various known structures and compositions are used to identify the structure and composition of the film formed on the Li electrode in liquid electrolyte.

Energy and Environment Division

134. Fundamental Studies of Materials and Processes in Rechargeable Lithium Batteries
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Rechargeable lithium batteries are attractive for vehicular energy storage applications because of the low equivalent weight and low electronegativity of lithium. However, large-size (capacities greater than a few Ah) rechargeable lithium batteries have not been developed because of problems with rechargeability, safety and cost. Fundamental problems associated with interfacial processes, sensitivity to overcharge and overdischarge, material stability, and electrolyte chemistry have prevented successful battery scale-up and commercialization. We propose to address these problems by carrying out fundamental studies of key interfacial processes, cell overcharge chemistry, and cell materials. The theme of our research closely follows the approach recommended on p. 8 of the document "Basic Research Needs for Vehicles of the Future" (P. Eisenberger, ed., published by the Princeton Materials Institute, 1995)

135. Application of Pulsed Laser Deposition to the Study of Rechargeable Battery Materials
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The aim of this project is to study the performance-limiting phenomena of complex transition metal oxides of significance to high-performance rechargeable batteries and to suggest practical means for improving their performance and lifetime. This is done by preparing thin dense oxide films on electronically conductive and/or transparent substrates with the pulsed laser deposition (PLD) technique. The films are characterized using such techniques as XRD, SEM, EDS, RBS, and XPS. Transmission FTIR spectra can also be recorded for films deposited on transparent substrates. Electrochemical and other properties of the thin-film oxides on stainless steel substrates, such as active species diffusivity, electrocatalyst kinetics and film corrosion behavior, are measured for geometries with well-defined electrode-electrolyte interfaces. Thin dense films of many complex oxides have been prepared, including La0.6Ca0.4CoO3, Bi2Ru2O7 and LixNi0.15Mn1.85O4. Films of LixMn2O4 have been cycled electrochemically over various voltage ranges to study the mechanisms for the capacity fade which is often reported for LixMn2O4 electrodes. The FTIR spectra of LixMn2O4 powders at various states-of-charge and after cycling have been recorded for reference purposes. Preliminary FTIR characterization of thin-film LixMn2O4 electrodes suggest that significantly higher resolution spectra are obtained by using thin-film materials.

136. EXAFS and NMR Studies of Electrode Materials for Lithium Batteries
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This project seeks to correlate the electrochemical performance of lithium insertion materials with the atomic and electronic structural changes that occur as a result of the insertion process. X-ray

Absorption Spectroscopy (XAS) is used to characterize the atomic and electronic structure of the insertion electrode, whereas electrochemical performance is determined through cell cycling and cyclic voltammetry. Performance yardsticks include reversible capacity, cycle life, and rate capability. The XAS and electrochemical information are used to determine the solid-state reaction mechanism of the lithium insertion process, identify performance hampering characteristics of the electrode material, and point the way towards improved electrode compositions. The $Li_xMn_2O_4$ spinel system is the baseline system for this study. This electrode material possesses a 4 volt potential (versus Li/Li^+) for $x < 1.0$ and a 3 volt potential (versus Li/Li^+) for $x \geq 1.0$. It is known from the literature that $Li_xMn_2O_4$ remains a single-phase, cubic spinel in the 4 volt region ($x < 1.0$) and transforms to a tetragonal spinel in the 3 volt region ($x \geq 1.0$). During the past year a set of lithium inserted $Li_xMn_2O_4$ electrodes were studied with XAS at the Mn K-edge and Mn $L_{2,3}$-edge. The lithium content varied from $x = 0.1$ to $x = 2.0$ which comprises the useful range for this material. The Mn K-edge XAS techniques utilized were X-ray Absorption Near Edge Structure (XANES), Extended X-ray Absorption Fine Structure (EXAFS), Site-Selective X-ray Absorption Near Edge Structure (SSXANES), and K_β Emission Spectroscopy. These measurements took place at the Stanford Synchrotron Radiation Laboratory and the National Synchrotron Light Source. The XANES data showed the features of cubic Mn–O octahedral symmetry throughout the 4 volt region ($x < 1.0$). For samples in the 3 volt region ($x \geq 1.0$), the XANES possessed a feature similar to square-planar transition-metal compounds where a tetragonal-type of spectra was expected. The reason for the difference between the expected and experimental spectra is attributed to the presence of the inserted Li altering the Mn electronic structure. K_β Emission Spectroscopy showed that the Mn in $Li_xMn_2O_4$ for all x is present in the high-spin state which supports the hypothesized Jahn-Teller basis of the cubic to tetragonal phase transformation occurring in the 3 volt region ($x \geq 1.0$). The EXAFS and SSXANES data are presently undergoing analysis. Mn $L_{2,3}$-edge absorption measurements took place at the Advanced Light Source. L-edge techniques are extremely sensitive to first row transition-metal oxidation state since transitions to the metal 3d levels are involved. The $L_{2,3}$-edge absorption spectra of the $Li_xMn_2O_4$ samples revealed the presence of Mn(II) for $x = 2.0$. The ability to detect Mn(II) makes this technique useful for studies of capacity fading via electrode dissolution since Mn(II) is soluble in the organic electrolytes employed in these systems. The $L_{2,3}$-edge absorption spectra also showed that the $Li_xMn_2O_4$ system is a Mn(III)/Mn(IV) mixed valent system which is consistent with literature reports that $LiMn_2O_4$ is a small-polaron semiconductor. These results illustrate the value of XAS in characterizing the insertion behavior of lithium battery electrodes because of the sensitivity to both the atomic and electronic structure of the absorbing element. In the coming year, these XAS techniques will be applied to spinels with Mn substituted by other transition-metal cations. Evaluating the resulting spectra against those from $Li_xMn_2O_4$ and comparing the electrochemical data will lead to greater insight into how atomic and electronic structure correlates with electrochemical performance. The NMR portion of this project will be initiated within the next few weeks. It is intended that the same family of materials will be studied using both XAS and NMR, allowing the study of both the Mn atoms (by XAS), and the Li atoms by NMR. This set of techniques, combined with the electrochemical studies will provide excellent power in fully understanding a range of important materials for rechargeable Li cells.

137. *Fundamental Characterization of Carbon-Based Materials for Electrochemical Systems*

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The objective of this research is to develop an understanding of the relationship between the physicochemical properties of carbon-based materials and their electrochemical properties. The role of surface modification on the electrochemical behavior of carbonaceous materials and techniques to develop carbon electrodes with well-defined structures and with the appropriate edge orientation to enhance the rate of electrode kinetics are being investigated. Experiments were conducted to modify carbon electrodes by electrochemical and chemical techniques, to utilize various analytical techniques to identify the surface functional groups, and to determine their influence on double-layer charge storage. Dramatic changes in the electrochemical double-layer capacitance were evident when a technique involving catalytic etching was used to modify the surfaces of low-surface-area carbon fibers (rayon-based, PAN-based, and mesophase carbon fibers). The capacitances of the untreated rayon and the PAN fibers were much higher than that of the untreated mesophase carbon fiber. After oxidation in air, the capacitance of the rayon and PAN fibers increased about 60% and the mesophase carbon fibers showed a capacitance increase of about 100%. After the catalytic treatment the capacitance of the fibers increased dramatically. The mesophase carbon fibers showed an increase of capacitance of about twenty times while those for the other two fibers doubled.

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Center for Materials Science

138. *Development of Materials for Advanced Ni/Metal Hydride Cells*

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We investigate materials for rechargeable nickel–metal hydride (Ni–MHx) cells with emphasis on (1) a high-energy storage density; (2) high cyclic life; (3) low H_2 overpressure operation; (4) low cost; and (5) minimal impact of manufacturing, disposal, or recycling on the ecology. This investigation concentrates on alloys of the type AB_5 (e.g., $LaNi_5$) and AB_2 (e.g., TiV_2). Alloy powders are prepared by mechanical alloying, a high-energy ball milling technique. This technique enables the preparation of homogeneous alloy powders and two-phase powders with layered morphologies. The program investigates the relation of composition and microstructure to the kinetics of hydrogen absorption–desorption, the hydrogen storage capacities, and the degradation of the hydride material after a number of charging–discharging cycles in concentrated KOH containing various additives. Under–deposition of zinc from the electrolyte is being investigated as a dynamic means to decrease the corrosion of the hydride electrode.

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Basic Sciences Division

139. *Microstructure and Ion Transport in Vanadium Oxide Electrodes for Rechargeable Batteries*

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Vanadium oxide is one of the most promising electrode materials used in secondary lithium batteries and its development is actively pursued by U.S. industry. This task investigates the fundamentals of ion transport, charging/discharging and the failure mechanisms in these vanadium oxide electrodes, to gain a better understanding of the factors which affect the performance, lifetime and safety of lithium rechargeable batteries. Pulsed Laser Deposition (PLD) has been used in this work to prepare vanadium oxide films with improved charging capacity and long term stability. Crystalline vanadium oxide films can be prepared at 200°C. These films exhibit a capacity of ~1.5 lithium per vanadium when cycled at a current density of 0.02 mA/cm^2. The capacity dropped to 1.2 lithium per vanadium when cycled at a current density of 0.1 mA/cm^2. The capacity loss in these films is less than 2% after 100 cycles. Although thermally evaporated films exhibited similar initial capacity under the same charging conditions, they lose more than 17% of their charging capacity after 100 cycles. The improved cycle stability can be partially attributed to the improved morphology of the PLD films. The deterioration mechanisms of these electrodes in the cycling process will be the subject of further examination. Based on both the kinetic data and a new theoretical model/calculation algorithm developed recently in our laboratory, we will simulate the ion transport processes in a solid state battery to maximize performance and minimize material requirements under typical charge/discharge conditions. The potential failure mechanisms and inherent safety problems in the batteries involving vanadium oxide electrodes will be investigated. Application of our expertise in the charging/discharging processes of electrochromic materials is expected to provide valuable cross-fertilization and new insights into the ion insertion kinetics of vanadium oxide and related components for lithium rechargeable batteries.

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Solid State Division

140. *Rechargeable Thin-Film Lithium Batteries*

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The purpose of this program is to conduct the research needed for further advancement and commercialization of thin film rechargeable lithium batteries developed at the Oak Ridge National Laboratory. These batteries, based on V_2O_5, $LiMn_2O_4$, $LiMn_x M_{2-x}O_4$, M = Ni, Ti, Al, and $LiCoO_2$ cathodes, have potentially many applications as small power supplies that can be integrated into electronic circuits at the board, chip carrier, or the chip level. Several important issues addressed in this research are crucial to the commercialization of this technology. These include exploring the structure and transport properties of the cathode-electrolyte interface which is the major source of cell impedance, conducting long-term cycle testing and investigating the origin of capacity fading in crystalline and amorphous cathodes, determining cell performance as a function of temperature and discharge current density, and devising methods for fabricating multicell batteries. The program also includes investigating the possible use of the lithium phosphorus oxynitride (Lipon) electrolyte discovered at ORNL as a protective coating that could improve the performance of existing rechargeable lithium-solid polymer electrolyte and lithium-liquid electrolyte batteries. Part of this research is carried out under a Cooperative Research and Development Agreement with a commercial firm. Joint research is also conducted with groups at the Argonne National Laboratory as well as groups at several universities.

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Exploratory Batteries Department

141. *Doping of Lithium Manganese Oxide for Improved Battery Performance*

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Lithium manganese spinel compounds demonstrate considerable promise as cathodes in the next generation of rechargeable batteries due to their high specific capacity, long cycle life, and benign effect upon the environment. In order to evaluate potentially new cathode materials based on the $LiMn_2O_4$ spinel structure, we have used an atomistic theoretical approach. The atomic simulations employ an energy optimization of the crystal structure based on the summation of Coulombic, short-range repulsive, and van der Waals interactions. A minimum energy structure is obtained under the constraint of P1 symmetry and constant pressure conditions, thereby allowing all 56 atoms of the spinel unit cell and the cell parameters to relax while maintaining an isometric crystal. A shell model that accounts for electronic polarization is used to refine the model. Pure $LiMn_2 O_4$ and various doped spinels were examined in this study in order to determine the lattice energy, unit cell volume, and the relative stability of the doped structures. We are studying the effect selected dopants on the theoretical lattice parameter of spinels as a function of the ionic radii of the substituted metal ion and dopant amount. Having validated the model, we are developing structure/property relationships that impact cathode performance in rechargeable lithium battery systems. The doped lithium manganese dioxide materials were prepared at Sandia using a proprietary non-aqueous precipitation technique. Ti^{4+} and Nb^{5+} doped spinels exhibit significant unit cell expansion (and energy destabilization), while Al^{3+} and Co^{2+} doped compounds exhibit only slight unit cell contraction. Cathode performance will be intimately linked to lattice expansion and contraction upon lithiation and delithiation of the spinel. Molecular dynamics simulations are being used to compare the relative diffusion rates of lithium ions in these various structures. We are also measuring kinetic parameters in these materials by electrochemical impedance spectroscopy (EIS). A single EIS experiment can provide information on both electron transfer and diffusion limited reactions. Smaller diffusion constants are observed for doped materials with contracted unit cells.

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

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Department of Chemistry

142. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion
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The primary objective of the research is to gain a fundamental understanding of the factors governing the efficiency of charge and energy transfer processes in molecular systems of interest, or pertinence, to photochemical energy conversion. The major focus of the current study is on the excited-state intermolecular interactions between two moieties that are brought together in close proximity, either by a short covalent linkage or by ground-state intermolecular association. Excited-state interactions ranging from strong charge transfer to weak van der Waals forces are being investigated in solution and in supersonic free jets, using laser-based techniques. Where appropriate, and feasible, quantum chemical methods are also used to gain theoretical understanding of the charge and energy transfer processes.

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Department of Chemistry

143. Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids
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The current goal is to evaluate the role of polar media in the mechanism of carotenoid cation radical formation and decay and to determine the special properties of carotenoids bound to pigment-protein complexes in photosynthetic membranes that enable them to serve both as antennae and as photoprotective agents and as a possible component of electron transfer processes. Simultaneous electrochemical and electron spin resonance measurements, simultaneous electrochemical and optical measurements, and simultaneous electrochemical and resonant Raman measurements have been carried out. From these studies, the reason has been deduced for the observation of carotenoid radicals in some photosystems and not others. In the solid state, the energy of the cis isomers falls close enough to that of the all trans isomers that the solid host can stabilize higher energy cis isomers. All trans or cisoidal carotenoid cation radicals can exist on solid supports and possibly in solution. The reason for the preference of the higher energetic twisted solid state configurations of the carotenoids in reaction centers has been determined. Semiempirical molecular orbital (RHF-INDO/SP) calculations of the canthaxanthin cation radical in solution are in excellent agreement with the electron nuclear double resonance measurements. The host matrix is being manipulated in such a manner as to understand the carotenoid function and to ultimately develop predictive mechanisms for directing the outcome of photochemical events.

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Department of Chemistry

144. Supramolecular Structures for Photochemical Energy Conversion
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Photosynthetic solar energy conversion is the ultimate energy source for essentially all life and is one of the most durable and efficient solar conversion "technologies." The goal of this project is to synthesize artificial photosynthetic reaction centers that employ the basic chemistry and physics of photosynthesis to help meet energy needs. Specifically, the research involves the preparation and study of photochemically active multicomponent molecules that functionally mimic photosynthetic light harvesting, photoprotection from light-initiated singlet oxygen damage, and, most importantly, photoinduced multistep electron transfer to generate long-lived charge-separated states with a quantum yield close to unity. One current project involves the preparation of molecular triads and tetrads featuring new linkages between the donor and acceptor moieties that lead to ultrafast electron transfer both in fluid solution and in glassy solids at low temperature. Another investigation deals with new methods for the stabilization of charge separation through intramolecular proton transfer. Recently, we have expanded our mimicry of photosynthetic processes to include the conversion of intramolecular redox potential to chemical energy manifest as a proton potential gradient across a bilayer lipid membrane. This has been accomplished by the assembly of molecular triad-based artificial reaction centers and collateral quinones into a liposome-based model system that uses light energy to translocate protons across the bilayer. Upon excitation, electron transfer processes in the triad generate reduction potential near the outer surface of the bilayer and oxidation potential near the inner surface. In response to this vectorial redox potential gradient, a freely-diffusing quinone alternates between its oxidized and semiquinone forms to transport protons across the bilayer. These experiments demonstrate the conversion of light energy to transmembrane proton motive force in a purely synthetic, biomimetic system.

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Department of Chemistry

145. Photoinduced Electron Transfer in Ordered Polymers
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Investigations involve the design and characterization of systems capable of photochemical electron transfer between electron donor and acceptor groups that are bound to polymer or biopolymer chains. Objectives of the research include the observation of the effects of polymer, peptide, or protein microenvironments on the efficiency and rate of electron transfer between groups that are separated by distances that can be controlled within the macromolecular domain. For these systems the (bio)polymer acts as a template or scaffolding for assembly of chromophores and photoactive species. Of special interest is charge migration among groups located at the ends of short peptide chains or within the domain of a peptide [alpha] helix. For use in these polymer-based arrays, a family of new chromophores based on the acridinium ion has been synthesized. On photoexcitation these structures engage in intramolecular charge separation within picoseconds of an excitation pulse. Decay of the electron transfer intermediates (the time scale for molecular "switching") is variable over at least four orders of magnitude, reaching the 10-nanosecond time domain. Domain-forming vinyl polymers and glasses are especially effective in extending the lifetime of charge separation. Current work also includes the synthesis of amphipathic helices that will potentially provide protein "bundles" z for assembly of synthetic reaction centers. Methods that are employed in these investigations include peptide synthesis, laser flash photolysis and fast kinetics, fluorescence probes, circular dichroism, and molecular modeling. In these studies, emphasis is placed on the opportunities for construction of highly functionalized synthetic polymer materials in which reactive groups are held in relatively rigid arrays that provide controls at the molecular level of charge separation and photochemical energy storage. The work is important to the understanding of charge transport in both natural and biomimetic systems and the development of energy conversion devices based on reversible electron transfer.

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Department of Chemistry

146. Mechanistic Studies of Excited State Chemical Reactions
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This program aims to elucidate fundamental mechanisms of endergonic redox reactions in solution, so that general factors governing the efficiency of such processes can be understood and optimized. Kinetics and primary radical yields are studied by flash photolysis and other techniques to provide data and basic parameters for testing theories of electron transfer.For example, reductive quenching of triplet C_{60} by halides is a reaction involving spherical centers and therefore uniquely appropriate for treatment by Marcus-Hush theory. Recent new directions in our work concern the characterization of the important class of reactions in which electron transfer is concerted with proton movement. These processes are studied in self-assembled model systems in which rates and radical yields are greatly enhanced by hydrogen-bonding of reductive or oxidative quenching agents to a third molecule. Thus, quenching by phenols is enhanced by addition of pyridines and quenching by quinones is enhanced by alcohols. Such structurally imposed proton coupling provides means for controlling both the free energies and reorganization energies of endergonic processes, as well as the rates of dissipative back reactions that involve heavy-particle movement. Kinetic behavior of such systems is correlated with key parameters, including hydrogen bonding equilibria, redox potentials and acid-base properties of incipient radical products. Deuterium isotope effects are also studied to help characterize the form of the proton-binding potential. Collaborative sub-picosecond flash experiments are being done to establish the relative phasing of electron and proton movement.

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Department of Chemistry

147. Picosecond Dynamic Studies of Electron Transfer Rates at III–V Semiconductor/Liquid Interfaces
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Photoelectrochemical cells based on semiconductors as working electrodes have been shown in numerous cases to yield stable, efficient current-voltage properties at a lower cost than solid-state devices. However, several fundamental questions about the semiconductor surface remain unanswered at present. For example, the rate constants for charge transfer across a semiconductor/liquid interface are largely unknown. Also, little is known about the surface reactivity of semiconductors typically used in solar energy applications. The answers to these questions are needed to gain insight into how to improve the efficiency of desirable electrode/electrolyte combinations and the stability of photoelectrodes, especially in aqueous systems. Indium phosphide is an ideal candidate for study because of its importance in optoelectronic applications, its optimal bandgap for solar energy conversion, and its well-behaved current-voltage characteristics in non-aqueous solvents. Charge transfer rate constants were measured for four n-InP/electrolyte systems which exhibited exchange currents dominated by the rate of electron transfer across the semiconductor/liquid interface. To determine the expected rate constants, the Marcus theory expression for liquid-liquid interfaces was modified for the semiconductor/liquid interface In all four experimental cases, the measured rate constants ranged from 10^{-17}–10^{-16} cm^4 s^{-1}, very close to the calculated maximum possible rate constant, supporting the theory. Next, the photoluminescence (PL) decay of n-type InP in contact with ferrocenes in nonaqueous electrolytes was monitored as a function of the applied voltage for a series of low and intermediate excitation intensities using the time-correlated single photon counting technique. The PL-response reflects the total decay kinetics of both the delocalized minority carriers in the bulk semiconductor and those at the surface.

It was observed that the voltage dependence of the PL-decay varies significantly with the excitation intensity. Computer simulations using the Two-Dimensional Semiconductor Analysis package ToSCA demonstrate how the voltage dependence of the PL-decay reflects the influence of the charge transfer rate constant. Recently, long-chain alkanes have been covalently attached to InP surfaces. Work is currently being done to attach redox active molecules to the surfaces by the same means, so that the effect of distance on the electron transfer rate constant can be determined.

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Department of Chemistry

148. ***Theoretical Studies of Electron Transfer in the Photosynthetic Reaction Center***
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The structure, dynamics, and free energies pertaining to electron-transfer in complex systems are analyzed through large-scale numerical simulations and through analytical methods. The research on electron transfer is concerned with (1) the mechanism of charge transfer in photosynthetic systems; (2) derivation of analytical theories of electrostatics and solvation, tested by numerical simulation and used to explain measured free energetics for electron-transfer reactions; and (3) derivation of simplified quantum dynamical theories for electron transfer processes. These dynamical theories will be used to interpret and guide current simulation studies and to suggest new experimental work.

149. ***Femtosecond Photoinduced Dynamics in Transition Metal Complexes: Probing the Elementary Processes of Excited-State Relaxation***
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The proposed research involves the application of femtosecond excited-state spectroscopy for studying the photoinduced dynamics of transition metal complexes. The overall goals are to understand at a fundamental level the nature of excited-state relaxation immediately following photon absorption but prior to excited-state thermalization. Tailored chemical synthesis is being coupled to these ultrafast studies in order to systematically examine the roles of electronic energy, and solvent in influencing wave packet dynamics as well as ultrafast electron and energy transfer processes. Preliminary results have revealed dynamics which are inconsistent with widely accepted models of excited-state behavior, suggesting that significant conceptual advances for understanding the photoinduced properties of molecular systems are possible.

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Department of Chemistry and Biochemistry

150. ***Energy and Charge Transfer Processes at Nanocrystalline Silicon Interfaces***
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The objective of the proposed work is to understand fundamental energy and charge-transfer processes at nanocrystalline silicon interfaces. Energy- and charge-transfer rates between luminescent porous Si and solutions of organic dye molecules, molecular donors or molecular acceptors will be measured. The processes will be studied with steady-state and time-resolved photoluminescence quenching, photoaction spectroscopy, and infrared and Raman experiments. The experiments should provide a detailed picture of the energetics of Si quantum crystallites. In particular, the studies should provide insight into the fundamental relationship between the bulk band structure, the size-quantized states, and surface states in this material.

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Department of Chemistry

151. ***Exploring Energetics of Photoinduced Electron Transfer in Integral Membrane Proteins***
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The goal of this work is to understand better the primary events of natural photosynthesis for practical implementation. The proposed work is divided into two experimental areas: 1) the exploration of the energetics of backward primary charge recombination for comparison with forward primary charge separation using a series of reaction centers modified by site directed mutagenesis and 2) the investigation of reorganization energy and electron transfer rates in previously unexplored integral membrane proteins. The work has three specific goals: 1) the measurement of the intermediate energy gap and the reorganization energy for both forward charge separation and backward charge annihilation in the bacterial reaction center with the aim of clarifying the mechanism of forward primary electron transfer in photosynthetic bacteria, 2) the determination of reorganization energy of new integral membrane proteins to see if the bacterial reaction center is unique in having low reorganization energy for charge separation, and 3) the development of a new electron transfer model system based on the light harvesting antenna of bacterial photosynthesis.

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Department of Chemistry

152. ***Electron Transfer Dynamics at Semiconductor Nanocluster Interfaces***

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This research program deals with the synthesis, characterization and electron/hole dynamics in semiconductor nanoclusters. Specifically the research focuses on electron transfer across the nanocluster/solution and nanocluster/solid interfaces. These electron transfer reactions are of great importance in the development of photocatalysts. Most of our studies involve layered metal chalcogenide semiconductors, such as MoS_2, WSe_2, PtS_2, etc. The interest in these systems is due to their great photostability. Dyes, electron donors and electron acceptors have been adsorbed on the nanocluster surfaces and the interfacial electron transfer rates measured by time-resolved optical spectroscopy. The dependence of these rates on the energetics, solvent polarity, and nature of the nanocluster trap states may be determined and understood in terms of modern theories of electron transfer. Most of the research thus far has been on MoS_2 nanoclusters with adsorbed electron acceptors. These MoS_2 nanoclusters consist of a single S–Mo–S trilayer with diameters of 2.5–4.5 nm. Variation of the nanocluster size changes the extent of quantum confinement of the electron/hole pair, and thus the electron transfer energetics. The electron acceptors are substituted 2,2'-bipyridines, and the nature of substituents affects their reduction potentials. By varying the size of the nanocluster and the substituents on the electron acceptor, a wide range of electron transfer driving forces may be obtained. Marcus "normal" and "inverted" behavior of the electron transfer rates have been obtained. Further studies will include examining solvent effects and other electron transfer reactions.

153. ***Studies of High Quantum Yield Sensitization Processes at Semiconductor Electrodes***

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Dye sensitization has the potential to increase the light utilization of large band gap semiconductors. The excited state of a dye molecule adsorbed onto the surface of the semiconductor electrode can inject electrons into the conduction band of an n-type semiconductor. These electrons can then be detected as a energies less than the band gap of the semiconductor. The quantum yield for electrons collected per photon absorbed by the dye at single crystal oxide electrodes was always less than a few percent. The quantum yield per absorbed photon can approach 100% when two dimensional chalcogenides are used as photoelectrodes. Recently methods for increasing the surface area of SnS_2 photoelectrodes have been developed. By photoelectrochemically etching the surface in either acid or basic solutions, increases in the quantum yield for electron flow per incident photon have been obtained. The adsorption isotherm for methylene blue on etched and unetched surfaces has the same shape but shows an increase of 20 times more in the quantum yield. An in situ scanning tunneling microscopy (STM) method is being developed for detecting the position and energy levels of dye molecules adsorbed on these surfaces with molecular resolution. This is accomplished by modulating a light source at the wavelength of the dye absorption maximum and extracting the photoinduced contribution to the tunneling current via a lock-in amplifier. A simultaneous picture of photocurrent response and topography can then be obtained. Questions such as the state of dye aggregation on the surface and whether dye molecules are adsorbed on special sites could then be answered. The photo-STM technique has already been applied to semiconductor surfaces with bandgap light. Methods are also being developed to produce organized layers of dye molecules on these surfaces. Two dimensional layers of perylene dyes have been formed and imaged with the STM and squarilium dyes have been doped into two dimensional liquid crystal matrices on layered compound surfaces.

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Department of Chemistry and Biochemistry

154. ***Mechanistic Aspects of Photoconversion at Semiconductor-Liquid Junctions and in Facilitated Transport Membranes***

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The goal of this research is understanding how solar energy can be utilized in photoelectrochemical cells (PEC's) and facilitated transport membranes. Reactions of "hot" electrons that are created by light absorption in a semiconductor electrode have the potential to increase the energy conversion efficiency or to alter the product distribution in PEC's. Current investigations involve studying the photoreduction of organobromide compounds in the presence of oxidized metallocenes. Rotating ring disk electrochemical methods are used to determine the products of the photoreduction reactions. These data can be used to infer relative rate constants for thermalized and "hot" electron reactions. The materials being investigated include p-InP and p-GaAs capped with $GaInP_2$. Photochemistry in membranes can allow chemical species to be transported against their concentration gradients. In principle, this process can be used in a variety of contexts ranging from environmental restoration to energy storage. Membranes that contain photochemically active carriers are prepared and characterized. Illumination of these membranes allows ions or molecules to be selectively separated and concentrated. A mathematical model based on molecular parameters (reaction rates, excited state lifetimes, interfacial kinetics, etc.) that describes this type of membrane process is being developed. This model will be used to guide subsequent experiments aimed at improving the selectivity, productivity and photoefficiency of photochemically controlled membrane transport.

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Department of Chemistry

155. Charge Generation and Separation at Liquid Interfaces
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Polarity is an important parameter affecting chemical and physical processes in bulk solution as well as at liquid interfaces. While this quantity is well studied in bulk liquids, interface polarity is less well understood. We have developed a novel means of investigating interface polarity based on surface-specific second harmonic (SH) spectroscopy of polarity indicator molecules. We have used this approach to determine the polarity of the air/water and organic/water interfaces, using two polarity indicator molecules; n,n-diethyl-p-nitroaniline (DEPNA) and Reichardt's Dye ($E_T(30)$). Our experiments on these two different molecules, characterized by distinct solvatochromic behavior, yield the same polarity value for the air/water interface which supports the generality of an approach using SH spectroscopy of solvatochromic molecules as an interfacial polarity probe. We have recently demonstrated that second harmonic generation (SHG) can be obtained from the surfaces of spherical particles in bulk isotropic solution. Although SHG is generally described as being electric-dipole forbidden in centrosymmetric media such as liquids, this implicitly assumes that there is centrosymmetry on a length scale orders of magnitude less that the wavelength of light. Our observation of SHG from the surfaces of centrosymmetric particles in bulk solution results from the separation of adsorbed molecules of opposite orientation. We have observed not only SHG due to molecules on the particle surfaces but also SHG due to the polarization of solvent species by charged surface groups. This promising discovery provides a powerful spectroscopic method for the investigation of physical and chemical processes on the surfaces of small particles in centrosymmetric environments.

156. Theoretical Studies of Electron Transfer and Optical Spectroscopy
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This project involves development of new theoretical methods for studying electron transfer and optical spectroscopy with particular applications to small semiconductor particles and long range electron transfer through intervening media. For semiconductor particles, an empirical pseudopotential model has been developed that predicts bandgaps to ~0.1eV as a function of particle size for a significant number of semiconductors, e.g. CdS, CdSe, Si, and GaP. For electron transfer, a Redfield relaxation model capable of treating multilevel electronic systems with intervening bridges has been developed, with an initial application to long distance electron transfer through a molecular bridge. A novel mechanism, virtually independent of distance, was obtained and possible relevant to electron transfer through a DNA bridge was discussed. Finally, ab initio electronic structure methods have been applied to the computation of electron transfer matrix elements. Using novel numerical methods, large systems are tractable, for example two bacteriochlorophyll molecules, in modest CPU times on a single workstation, at the Hartree-Fock level. This approach will be applied to a variety of systems, such as molecule/solid electron transfer and transfer through various complex molecules. Future work will also include using ab initio methods to determine structures and electronic states at the surface of semiconductor particles.

157. Photo-CIDNP of Photosynthetic Reaction Centers
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The Chemically Induced Dynamic Nuclear Polarization (CIDNP) process is used to observe the nuclear magnetic resonance (NMR) spectra of ^{15}N-labeled photosynthetic reaction centers. In simple echo-detected Bloch decay spectra collected under magic-angle spinning with or without proton decoupling, nuclear polarization has been detected for the nitrogens in the tetrapyrroles of the bacteriochlorophyll special pair ("P"), associated imidazoles, and the primary acceptor pheophytin ("I") that are far from Bolzmann equilibrium. The resulting NMR lines are emissive and 300 times the intensity of the thermally relaxed nuclei. The polarization is not observed if the quinones are present and preoxidized. The signals presumably result from a transient nonequilibrium mixing of the singlet and triplet states of the initially formed charge transfer pair, P^+I^-. Selectively labelled samples are used to assign the signals. Ongoing efforts aimed at extensions to the plant reaction centers have identified polarized signals from photosystem I of cyanobacteria.

Department of Electrical Engineering

158. Translational-Energy-Resolved Studies of Photogenerated Carrier-Induced Reactions on UHV Semiconductor Surfaces
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Studies of the photodissociation of methyl halides (CH_3X, X=Br,Cl,I) on GaAs (110) using time-of-flight (TOF), temperature programmed desorption (TPD), and photoluminescence (PL) in ultrahigh vacuum (UHV) has revealed the operation of several photochemical processes on semiconductor surfaces. For example, photogenerated substrate electron-hole pairs promote adsorbate dissociation *via* an electron attachment mechanism to form a negative ion resonance with subsequent cleavage of the C–X bond. The angular variation of the photoyield suggests that the adsorbate adopts a strongly tilted geometry with respect to the surface normal; a hypothesis confirmed by a "direct" measurement of the adsorbate geometry via the NEXAFS technique and by modeling of the magnitude of the adsorbate-adsorbate repulsive interaction manifested in TPD spectra. Also, recent theoretical modeling by our group using ab initio calculations have also confirmed this geometry for the case of CH_3Br interacting with a GaAs cluster. Extension of these studies to the similar case of CH_3CH_2X [(X=Br, Cl, I)] also reveals strikingly anisotropic photofragment angular distributions which reflect the orientation of the bond undergoing fission. Other recent experiments have applied a similar experimental approach to an investigation of the more complex dissociation dynamics of methylated metal-organic chemical molecules [$(CH_3)_2X$, X=Zn, Cd] on model III-V and II-VI semiconductor surfaces. While complex dissociative thermal chemistry is found to dominate the adsorption process on GaAs surfaces, molecular adsorption/desorption phenomena are the dominant thermal processes for the case of adsorption on the CdTe(110) surface. In this system, photodissociation of the molecular adsorbate with TOF analysis of the resulting photofragments reveals that the photodissociation process is in this case dominated by direct photon absorption by the adsorbate. The observed photofragment dynamics are indicative of a complex curve crossing between excited states. A photon stimulated desorption process is also observed which results from the deposition of large amounts of vibrational energy in the overlayer following the surface mediated quenching of electronically photoexcited molecules.

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Department of Chemistry

159. ***Photoinduced Dipoles and Charge Pairs in Condensed Media***
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The objective is to understand photoionization in liquids and solids comprising organic molecules. One goal is to understand the formation and recombination or separation of hole-electron pairs formed by absorption of visible photons in electron donor-acceptor materials. Fast current measurements are used to follow the separation of the resulting holes and electrons (or ions). The fast photocurrent measurements led to measurement of the dipole moments of excited molecules in solution with the same techniques. The dipole moment technique has proved useful in the study of both intramolecular and intermolecular charge transfer. A dipole moment of 89 D (corresponding to a charge separation of 1.8 nm) has been measured for a donor-acceptor triad molecule, synthesized at Argonne National Laboratory. Charge separation of 0.7 nm is seen in the triplet exciplex formed by C_{60} and a substituted benzene donor. While in the C_{60} exciplex the charge transfer is complete; in many other exciplexes it is not. Smaller dipoles and partial charge transfers are being studied in weaker donor-acceptor pairs. Current investigations include the solvent polarity dependence of intramolecular dipoles, exciplexes, contact ion pairs, and solvent-separated ion pairs.

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School of Chemistry and Biochemistry

160. ***Time-Resolved Laser Studies of the Proton Pump Mechanism of Bacteriorhodopsin***
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There are two basic systems in nature that convert solar energy into chemical energy, i.e., undergo photosynthesis. The first is the chlorophyll-based system present in green plants and the other is bacteriorhodopsin (bR) present in *Halobacterium Salinarium.* In both systems, solar energy is first converted into electric energy and then into chemical energy stored in the chemical bonds of adenosine triphosphate (ATP). The final step in the solar to electric energy conversion involves the formation of proton gradients. In both systems, the mechanism of the conversion of the proton gradients into ATP is the same while the molecular mechanism of the conversion of the solar energy into proton gradient is very different. In chlorophyll, it involves electron pumps while in bR the absorption of light leads to very rapid (450 femtosecond) retinal isomerization, separation of positive and negative charges, and protein conformation changes that finally lead to pumping protons from inside the cell to the membrane surface, thus creating the proton gradients; thus bR is a solar proton pump. This pump requires metal cations for its function. Our present research is focused on trying to answer two fundamental questions regarding the proton pump: (1) What are the molecular mechanisms by which the protein catalyzes the retinal photoisomerization in bR and (2) What role do metal cations play in the proton pump? We are presently determining the femtosecond time and quantum yield of retinal photoisomerization in bR and in its modified derivatives, e.g. mutants in which charged and hydrogen bonding residues in the retinal cavity are individually replaced by neutral nonhydrogen bonding ones. Studies at different pH and temperature are also being carried out. The observed results are examined in terms of the electronic and steric effects on the retinal excited state potential energy surface in bR. In order to understand the role of metal cations in the bR function, their location must first be determined. In this effort, their binding constants have been determined in bR and in a number of its mutants. The two high affinity cations, one of which is vital to the function, are electrostatically coupled to the charged residues within the retinal cavity. Now attempts are being made to locate the position of these two metal cations by use of anomalous X-ray and extended X-ray absorption fine structure techniques using the Synchrotron Radiation Source at Brookhaven National Laboratory.

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161. ***Charge Separation in Photoredox Reactions***
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This research is directed toward a better molecular understanding of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies especially vesicles and microporous silicas. Control of the location of an electron donor will be achieved by attachment of variable length alkyl chains to porphyrins. Control of the electron acceptor location is also being initiated. Photoyields will be monitored by electron spin resonance and the photoproduced cation location will be assessed by deuterium electron spin echo modulation. Molecular electron acceptors will also be studied. The results will help determine the structural requirements for optimizing photoinduced charged separation for the storage of light energy.

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162. *Electron Transfer Dynamics in Efficient Molecular Solar Cells*
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Regenerative solar cells based on dye sensitization of wide band gap semiconductors have recently experienced an order of magnitude increase in light-to-electrical energy conversion. Results in this laboratory and others have shown high efficiency and excellent stability, indicating an economically competitive approach to solar energy conversion. This remarkable breakthrough marks the first time that devices which operate on a molecular level are competitive with traditional solid state photovoltaics. With further optimization, significant improvements in efficiency and stability are expected. In this program the use of novel sensitizers will be explored for dye-mediated light-to-electricity conversion in photoelectrochemical cells based on nanostructured wide band gap materials. Specifically, Ru(II) and Os(II) polypyridyl sensitizers will be attached to nanostructured TiO_2 photoanodes fabricated using sol-gel processing techniques and explore their photoelectrochemical and electron transfer characteristics. The materials processing and synthesis will be carried out in conjunction with characterization of cell performance, detailed investigation of operating mechanisms, and modeling of charge transfer and transport in these systems.

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Department of Chemistry

163. *Organized Photochemical Assemblies Based on Y-Zeolite Supports*
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The essential goal of this project is the preparation and characterization of molecular assemblies entrapped within the supercage network of Y-zeolite. Current efforts are focused on the synthesis of assemblies based on polypyridine complexes of divalent ruthenium. Extensive photophysical characterization of zeolite-entrapped trisbipyridine ruthenium ($Ru(bpy)_3^{2+}$) preparations, at various loading levels, document strong interactions between excited states of complexes occupying adjacent supercages. Synthetic methods have been developed to generate isolated adjacent-cage dyads of related complexes, wherein the two complexes are strongly coupled with respect to energy and electron transfer interactions. Photoredox studies of such particles, which have been loaded with an excess of common acceptors, such as methylviologen or related species, document a significant increase in photoinduced net charge separation relative to zeolite based systems which contain randomized loadings of the sensitizer complexes. Such increases in charge separation efficiency are most reasonably attributed to minimization of the (reduced) acceptor-to-(oxidized) sensitizer back electron transfer reaction via rapid reduction of the oxidized sensitizer by the adjacent cage (donor) complex.

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164. *Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions*
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Research focuses on the application of time-resolved Electron Paramagnetic Resonance (TR-EPR) techniques in the study of photoinduced electron transfer reactions. The application of TR-EPR in this area of research is of interest for several reasons. First, high spectral resolution makes it possible to identify paramagnetic molecules and to obtain information on their interaction with the environment. Second, the time development of the spectra generally is affected by chemically induced dynamic electron polarization (CIDEP). These CIDEP effects provides unique mechanistic insights. Third, relaxation data can be used to study the effect of temperature and medium on molecular motion. Fourier transform EPR has been used to investigate oxidative and reductive electron transfer quenching of C_{60} triplets ($^{33}C_{60}$)in homogeneous and heterogeneous media as well as photochemical reactions in which C_{60} acts as a light harvester and photosensitizer. The method is also applied in studies of the mechanism and kinetics of photoinduced redox chemistry at the surface of semiconductor particles.

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Department of Chemistry

165. *Femtosecond Time-Resolved Experiments on the Solvated Electron and Intermolecular Charge Transfer in Solution*
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The photophysical properties of the solvated electron have been studied using a unique 20 fs transient absorption spectrometer. The technique involves three separate laser pulses. The first pulse generates solvated electrons, the second pulse excites the electron from the ground state to the first excited state, and the third pulse probes the dynamics of the ground state repopulation and the ground and excited state relaxation. The first results using this spectrometer have resolved the inertial dynamics of the excited state of relaxation of the electron. This observation is critical in evaluating theoretical models for the solvated electron relaxation dynamics. In addition, the excited state proton transfer kinetics of the solvated electron in alcohols has been resolved for the first time. Future studies will concentrate on the comparison of theory and experiment for the early time dynamics of the solvated electron in various solvents.

Photoinduced charge separation and reverse electron transfer will be examined in charge transfer complexes.

166. The Photophysical Properties of Organic Liquids at High Excitation Energies

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The absorption and excitation spectra of concentrated solutions of simple aromatics (benzene, toluene, etc) have been examined from 220 to 150 nm. The intense $S_0 \rightarrow S_3$ absorption, which is the dominant excitation in this region, is observed to dramatically redistribute its oscillator strength with increase in the aromatic concentration. Dispersion theory with Lorentz-Lorenz corrections to the local field predict this spectral behavior and also predict well the spectral positions of the extrema in the refractive index of the neat liquid and the spectral position of the maximum of the energy loss function. Calculations suggest that the terminal states of the $S_0 \rightarrow S_3$ absorption in these concentrated solutions may have a significant collective component. Parallel studies on the effect of concentration to alter the fluorescence excitation spectrum in the region from 220 to 150 nm, appear to support this assignment. The recovery of the aromatic fluorescence that develops at ca. 195–185 nm, and only in concentrated solutions, correlates well with the predicted development of collective excitations in this region of very high spatial and spectral oscillator strength density. The effect is attributed to a very efficient non-radiative coupling of the fluorescent state to the higher-lying collective states due to the effect of spatial diffusion of the excitation density to reduce nuclear distortions. Further manifestations of collective effects are being examined. In a separate study, the general theory of hyperfine-driven spin evolution of a geminate pair of ions diffusively recombining has been found to predict the shapes and positions of observed resonances in the effect of a magnetic field on the quantum yield of geminate recombination fluorescence of isooctane cations with hexafluorobenzene anions generated by photoionization of the isooctane at 124nm. Determination of the magnetic fields at which the resonances occur provide a simple technique for determination of hyperfine constants of short-lived anions. Additionally, the magnetic field dependence provides a new technique for examining the range distribution of ionized electrons.

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Chemical Kinetics and Thermodynamics Division

167. Electron Transfer Reactions of Metalloporphyrins

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The pulse radiolysis technique is applied to the study of electron transfer processes involving metalloporphyrins. Reactive intermediates are produced in solution by electron pulse irradiation and the kinetics of their reactions are followed by time resolved absorption spectrophotometry. Complementary experiments are carried out with laser flash photolysis and supportive product analyses are done with various techniques following photolysis or gamma radiolysis. The studies focus on the unique ability of pulse radiolysis to provide absolute rate constants for many fast reactions of metalloporphyrins, which permits evaluation of these strongly light absorbing molecules as sensitizers and intermediates in solar energy conversion. Metalloporphyrins react with free radicals via electron transfer, involving the ligand or the metal center, or via bonding to the metal, leading to a variety of chemical species whose behavior is also investigated. One of the important potential applications of metalloporphyrins under investigation is as catalysts for reduction and binding of carbon dioxide.

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Department of Chemistry

168. Electronic and Nuclear Factors in Intramolecular Charge and Excitation Transfer

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The research focuses on the molecular level control of the rate and efficiency of the photoinduced electron and excitation transfer processes. Carefully selected model systems relevant to energy conversion and design of molecular electronic devices are being synthesized and investigated. The current projects include the study of: 1) the interplay between the MO symmetry and the density of states in "symmetry forbidden" vibronically coupled excitation transfer; 2) the liquid medium contribution to the electronic coupling between rigidly linked donors and acceptors; 3) the role of the low frequency medium modes in intramolecular charge transfer; 4) preferential solvation and ionic aggregation in the vicinity of charge separated species in mixed media. The work involves time resolved spectroscopic measurements in liquids, glasses and jets. New transient Raman and subpicosecond transient emission/absorption capabilities are being implemented.

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Department of Chemistry

169. Biomimetic Porphyrin Light Harvesting Arrays

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A molecular building block approach is being used to synthesize biomimetic multiporphyrin light-harvesting (LH) arrays containing from 2 to 20 pigments. The major objective of this work is to elucidate molecular design issues for efficient light-harvesting in synthetic systems. The versatility of these synthetic systems will complement studies of the more complex natural systems. The model systems are being characterized spectroscopically in collaboration with Prof. David Bocian (UC-Riverside), Prof. Graham Fleming (U-Chicago), and Prof. Dewey Holten (Washington U). Energy migration rates are determined by measurement of fluorescence lifetimes including polarization studies, and time-resolved donor-acceptor experiments. Temperature and medium effects will be examined. Exciton annihilation experiments will be attempted in order to characterize exciton mobilities in various arrays. Resonance Raman experiments of neutral complexes, and EPR studies of various oxidized arrays will be performed to assess electronic communication in the arrays. Other experiments such as time-resolved Raman spectroscopy may be attempted as required to identify mechanisms of energy migration. The data from these spectroscopic studies will be used to guide the molecular design of more efficient light-harvesting model systems.

University of North Carolina at Chapel Hill
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Department of Chemistry

170. ***Excited State Processes in Transition Metal Complexes. Redox Splitting in Soluble Polymers***
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Polypyridyl complexes of Ru(II), Os(II), and Re(I) are being investigated for applications in photochemical energy conversion. These molecules have well understood light absorption and excited state properties. They undergo facile electron and energy transfer, and in molecular assemblies they show promise in molecular conversion. This chemistry is being extended through new synthetic procedures for a family of black absorbers that absorb light efficiently throughout the near-UV visible region. These molecules emit in the near infrared, are photochemically stable, and have excited states whose lifetimes are sufficiently long to be accessible to energy conversion processes. Emission and resonance Raman spectroscopies are being used to explore electronic structure, coupled vibrations, and the role of medium on properties and lifetimes. Synthetic methods have been developed based on ether or amide links for preparing assemblies based on soluble polymers. These assemblies contain both light absorbers and electron or energy transfer relays. Photophysical studies on the resulting materials have demonstrated photoinduced electron or energy transfer on single polymeric strands. This has led to the design of efficient "antenna" polymers for collecting and storing visible light.

Northwestern University
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Department of Chemistry

171. ***Dynamic Structural Studies of Light-Induced Charge Transfer and Electronic Localization/Delocalization Phenomena in Metal-Based Molecular Systems***
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This project involves (1) time-dependent scattering studies of vibrational structural changes accompanying chemically important photoredox processes; (2) collaborative studies of femtosecond charge-transfer kinetics in fully vibrationally characterized systems; (3) electronic Stark effect studies of one-electron transfer distances; and (4) resonant vibrational characterization of delocalized intervalence transitions. Recent work in area (3) has now yielded unprecedented orbital-specific charge transfer distances, solvent reorganization energies and nonadiabatic electronic coupling energies. Work in area (4) has yielded a quantitative experimental description of the vibrational and electronic factors that drive electronic localization events in strongly interacting systems.

172. ***Light-Driven Charge Separation in Face-to-Face Donor-Spacer-Acceptor Supramolecular Systems***
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The objective of this project is to investigate the kinetics of charge separation and recombination in donor-spacer-acceptor systems of well-defined geometry in which the spacer is an aromatic molecule or an array of aromatic molecules. The unique molecular architecture of tertiary aromatic amides and ureas will be used to construct supramolecular systems in which the donor and acceptor are held either in an edge-to-face or face-to-face geometry with respect to the aromatic spacer. The urea structure can be elaborated to place two or more spacers between the donor and acceptor. The analogous secondary amide and ureas have extended structures, providing a basis for comparison of extended and folded structures. Base pairing in duplex DNA provides a well-defined geometry in which the aromatic bases are held in a parallel stack. Charge separation will also be investigated in synthetic DNA hairpins and dumbbells which possess acceptor and donor molecules at one or both ends of a region of duplex DNA. The unique feature of these systems is the location of the donor and acceptor on opposite faces of the aromatic spacer(s). The shortest distance for electron transfer in these molecules is through the aromatic spacer rather than the sigma-bonded framework connecting the donor and acceptor.

173. ***Vibrational Dynamics in Photoinduced Electron Transfer***
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Theory and experiment suggest that molecular vibrations and distortions are important controlling elements for electron transfer. The objectives of the project are to develop a new molecular understanding of electron transfer processes. The unique method of picosecond infrared absorption spectroscopy is being used to monitor electron transfer kinetics. The first case of vibrational state dependent electron transfer has been experimentally determined. The electron transfer is between two cobalt metal atoms interacting in a solvent-caged, contact ion pair. The compound has a cobaltacinium cation and a cobalt tetracarbonyl anion with a visible absorbing charge-transfer band. The neutral pair created by a pulse of visible light has a rate of return electron transfer that is dependent on vibrational quantum number. The vibrational excitation in the ion pair formed after the electron transfer also was measured. Recently a similar ion pair complex with a vandium hexacarbonyl anion was found that also shows vibrationally resolved electron transfer rates with over a two-fold change in rate for each quantum of vibration in a CO stretching vibration. This molecular structure is amenable to detailed modeling so that quantum calculations of molecular structure and vibrations as well as electron transfer models are being developed to understand these results. Additional spectroscopic and kinetic measurements are being done on these and other molecules.

Ohio State University
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Department of Chemistry

174. ***Energy and Electron Transfer Properties of Photochemical Assemblies in Zeolites***
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In designing artificial photosynthetic assemblies, the choice of molecules, their spatial arrangement and their environment is fundamental to the success of the process as evidenced in nature. Zeolitic microporous frameworks are being investigated as a means to spatially arrange molecules for efficient energy and electron transfer processes. Azobenzene molecules are being aligned in zeolite channels, and spectroscopic properties of these aggregates, including absorption, fluorescence, Raman and second harmonic generation are being investigated to explore the possibility of energy migration along these dipole chains. Zeolites are also being investigated as supports for photochemical redox assemblies. Efficient photoelectron transfer from intrazeolitic $Ru(bpy)_3^{2+}$ to a neutral viologen in solution is possible by mediation of an intrazeolitic viologen in the absence of a sacrificial electron donor. Choice of the intermediary viologen is critical in promoting rapid forward electron transfer but slowing down the back electron transfer reaction. This depends on several factors, including the reduction potential of the viologen. The dynamics of the electron transfer process is being examined for a series of viologens whose reduction potential vary over a range of 500 mV. The reaction of water with the photochemically generated intrazeolitic $Ru(bpy)_3^{3+}$ to make dioxygen is being studied. This species is unstable in aqueous solution at neutral to basic pH because of intermolecular reactions leading to degradation. Because of the lack of translational mobility in the zeolites, the reaction of $Ru(bpy)_3^{3+}$ with water leads to dioxygen formation. The route this reaction follows involves hydroxide ion attack on the bipyridyl ligand followed by release of hydroxyl radicals. These radicals attack the viologen molecules. Thus, Mn and Ru based oxides as well as their bipyridyl complexes are being investigated as multielectron catalysts which, in a four-electron concerted step, can convert water to oxygen.

University of Oregon
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Department of Chemistry

175. ***Photochemical Water-Splitting Using Organometallic Oxides as Sensitizers***
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The project objective is to split water photochemically into hydrogen and oxygen using homogeneous molybdenum oxide catalysts. NMR experiments and manometric measurements showed that molybdocene reacts quantitatively with water to form molybdocene oxide and hydrogen. (The molybdocene was generated by irradiation of molybdocene dihydride.) However, the water-splitting cycle could not be completed because earlier experiments could not be reproduced in which visible light irradiation of molybdocene oxide formed oxygen and molybdocene. One possible explanation is that the oxygen that is formed is reacting with the molybdocene oxide. Control experiments showed that the Mo-containing products of the photoreactions were indeed the same as those that form when oxygen reacts with molybdocene oxide. Attempts to sweep out the oxygen gas product before it could react with the starting material were unsuccessful, however. Efforts in the forthcoming year will focus on finding ways to remove the oxygen gas from the system before it can react with the starting material. Other, less oxygen-sensitive, sensitizers will also be studied. Mechanistic studies of the hydrogen and oxygen producing reactions are underway. This system represents one of the first homogeneous systems in which both hydrogen and oxygen are formed from the same catalyst in solution.

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Department of Chemistry

176. ***Electron Transfer Reactions in Microporous Solids***
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This project uses microporous solids and surface assemblies as organizing media for light-induced intermolecular electron and energy transfer reactions. The role of the solid is to control the juxtaposition of redox-active and photoactive molecules in space, and also, in some cases, to participate as an active component of the electron or energy transfer cascade. One aspect of the project involves the sensitization of layered oxide semiconductors, such as alkali niobates and titanoniobates, with ruthenium polypyridyl photosensitizers. When loaded with interlamellar metal catalysts, these materials are catalysts for photogeneration of hydrogen from water and non-sacrificial electron donors, such as iodide. Surface modification of these materials with polyelectrolytes increases the efficiency of charge separation and hydrogen evolution, and this strategy is now being applied to improving the efficiency of dye-sensitized photoelectrochemical cells. A new technique has been devised for exfoliating lamellar semiconductors and restacking them on high surface area substrates, with control over the stacking sequence at the monolayer level. This method is now being used to prepare multicomponent electron and energy transfer chains, in which individual electroactive and photon harvesting polymer monolayers are separated by single sheets of oxide semiconductors or insulating metal phosphates. The kinetics of light-induced electron transfer reactions are being studied by flash photolysis techniques, and heterostructures designed for the visible light photolysis of water are being synthesized.

177. *Polar Solvation, Dielectric Friction, and Electron Transfer*

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The focus of this project is on understanding how polar solvents influence electron and other charge transfer reactions in solution. Of special interest are dynamical aspects of the solvation process and the role that such dynamics play in determining charge transfer rates. A number of recent theories have predicted a proportionality between the rate of electron transfer and solvent reorganization rates. Time-resolved fluorescence studies on simple intramolecular charge transfer reactions are used to explore this connection. An important part of the work currently in progress also involves obtaining a prerequisite understanding of the dynamics of solvation in nonreactive systems. Results obtained to date indicate that the time scales of solvation in polar liquids are poorly predicted by simple continuum models of solvation, but it is just such models that have been used to theoretically study the connection between solvation, and electron transfer. In order to build a more adequate understanding of charge transfer in solution it is first necessary to better understand and model the dynamics of solvation in simple, nonreactive situations. Time-resolved experiments and molecular dynamics computer simulations are being used to probe the dynamics of solvation in a variety of solvents and solvent mixtures. The goal of this work is to develop and test simple models of the static and dynamic aspects of polar solvation of relevance to the solvent-reaction coupling.

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Department of Chemistry

178. *Evaluation of Electronic Coupling In Photoinduced Electron Transfer Reactions*

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The primary objective of this project is to delineate the relative and absolute importance of the factors that determine the dimension of the electronic coupling matrix element (H_{ab}) for photoinduced and thermal charge recombination electron transfer processes. These studies are being carried out with several families of donor-spacer-acceptor (D–Sp–A) complexes that utilize electronically excited porphyrin donors and quinone acceptors. A key feature of this effort lies in the detailed focus on the role played by the tunneling medium in such reactions and the parameters that should affect the dimension of H_{ab} such as absolute D–A energetics, medium topology, and medium electronic structure. Experimental work in the progress focuses on probing the nature of charge tunneling interference phenomena as well as how medium band energetics, σ-π electronic coupling, π-manifold orientation, and medium excited electronic states establish the magnitude of H_{ab}. The fundamental information obtained in these studies will be useful in directing and controlling the electron and energy transfer processes essential to effective photoconversion.

University of Pittsburgh
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Department of Chemistry

179. *Experimental Studies of Photoinduced Charge Carrier Processes at Semiconductor/Electrolyte Interfaces*

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This project aims to develop a quantitative understanding of the kinetics of photogenerated carriers in semiconductor electrodes and at the semiconductor/electrolyte interface. This goal is being pursued on three fronts. First, an understanding of bandgap emission and its utility for monitoring the transport and relaxation of charge carriers will be established. An analytical model and computer algorithm are being developed to model the fluorescence decay of semiconductor band gap emission. Experimental studies are proceeding on the fluorescence decay of InP. These studies are probing its voltage and dopant level dependence. Second, self-assembled monolayers of octadecylthiols on InP electrodes have been prepared, and these insulating barriers are being used to probe the nature of the electron tunneling through the layer. The third area is investigating how functionalized monolayer films can be used to modify the interfacial recombination rate and electron transfer rate processes at these interfaces.

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Department of Chemistry

180. *Asymmetric Polymeric Porphyrin Films for Solar Energy Conversion*

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This project involves the synthesis and characterization of thin films of polymeric porphyrins, where such films are potentially useful as components of solar energy conversion methods. Two different approaches have been used to create polymeric films of substituted tetraphenylporphyrins on transparent electrodes: (a) interfacial polymerization of a pair of reactive monomers into a thin film, later deposited onto an electrode, or (b) oxidative electropolymerization of electron-rich porphyrins directly onto an electrode. For interfacial polymerization, an aqueous solution of either tetra (4-hydroxyphenyl) porphyrin (THPP) at pH 11 or tetra

(4-aminophenyl) porphyrin (TAPP) at pH 3 is layered atop a dichloromethane solution of tetra (4-chlorocarbonylphenyl) porphyrin (TCCPP), creating a thin polyester or polyamide film at the interface. Such films are highly crosslinked, with a distinctive asymmetry of functional groups that creates a gradient of porphyrin redox potentials across the film. Observed photopotentials are directional, with the charge separation following the predicted direction of the redox potential gradient. Continued work in this area is aimed at characterizing the unique structural asymmetry and developing a model of the directional charge transport processes within the film. Electropolymerized films of TAPP are also being studied as possible conductive mediators for dye-sensitized semiconductor solar cells.

University of Rochester
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Department of Chemistry

181. Photochemistry of Platinum Group Element Complexes: Applications to Energy Conversion and Bond Activation
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Diimine dithiolate complexes of platinum(II) and other d^8 metal ions are being investigated for their potential use as chromophores in the conversion of light-to-chemical energy. Studies in previous years on Pt diimine dithiolate complexes have shown that these solution emissive compounds have a directional charge transfer excited state involving a mixed Pt(d)/S(p) orbital as the filled donor function and a π^* orbital of the diimine as the acceptor function. A detailed study of the Pt diimine dithiolate chromophore published during the year reveals that excited state properties such as emission energy, lifetime, redox potentials, electron transfer quenching rates and relaxation dynamics can be systematically tuned by ligand variation. Current efforts are focussing on the development of a supramolecular photochemical system for light-driven hydrogen generation. Such a system would consist of a platinum diimine dithiolate chromophore, a dark reaction catalyst and a redox center. The components are connected by ligand bridges. The simplest of these bridges is dipyridocatecholate (dpcat) which has been made in high yield and has been used to link two metal centers together. Characterization of new dpcat complexes is in progress. The use of Pt(diimine)(dithiolate) chromophores in new multi-component systems builds on the understanding that has been achieved regarding their luminescence and excited state properties. The dark catalyst in systems will be either a noble metal colloid or a macrocyclic complex and will have two or more chromophores attached to it. Finally, new Schiff base complexes of rhodium have been synthesized and characterized regarding their electronic structures and reaction chemistry. Square pyrimidal Rh(III) complexes exhibit weak solution luminescence and undergo photolysis to generate metalloradical species that are important in substrate activation reactions. Particular emphasis in ongoing studies is being given to synthesizing Schiff base complexes of rhodium and iridium having N_2S_2 donor sets that are capable of binding to d^7 metalloradicals more strongly.

182. Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Solutions
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This project is comprised of a study of light-induced electron transfer reactions in solution, the solid state, and thin films. It focuses on potentially useful net chemical conversions that can occur following single electron transfer quenching of excited states. Typically, these reactions are initiated by photoexcitation of visible or near ultraviolet light absorbing electron donors (or acceptors) and subsequent quenching by single electron transfer. In the cases examined in these studies either the acceptor or donor or both contain a potentially fragmentable bond. The compounds are stable as the even electron precursors and hence the fragmentation is only accessible in one or both of the photogenerated radical ions due to a drastic and selective reduction of bond dissociation energies in these species. Such a change in bond dissociation energies has been found to be quite general for a number of different species upon one electron oxidation or reduction. Donors that can fragment from their cation radicals include amines, diamines, aminoketones, aminoalcohols and pinacols. Acceptors that can undergo corresponding fragmentations include organic halides, ethers and esters. Polymeric systems containing photoexcitable acceptors and fragmentable donors that can be reacted in solid state, solution, and thin films have been designed, synthesized, and studied. Amphiphilic donors and acceptors that can be incorporated into various organized media are also under investigation. Co-fragmentation reactions involving excited pinacols reacting with various organic halides are also under investigation. In some cases, especially with oxygen present, the co-fragmentation reactions can include a chain process resulting in highly efficient generation of acid and potentially useful radicals.

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Department of Chemistry

183. Electron Transfer in Constrained Helical, Constrained Peptides and Hydrogen Bonding Networks
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This project is an investigation of the electron mediating properties of peptide bonds, amino acid side chains, and hydrogen bonds in the control of long-range electron transfer in proteins. In this research, well-defined, rigid peptide systems where photoactive metal donors and metal acceptors are covalently attached at the peptide terminals and amino acid side chains, resulting in the formation of linear, cyclic and poly-cyclic peptide networks possessing specific secondary structures. Peptide and/or hydrogen bonding networks are designed to emphasize special features such as the number of peptide bonds, H-bonding networks, connectivity of redox centers to main chain and side chain of the peptide, as well as the overall distance dependence in rigid molecules. Results from metal derivatized peptide networks show that electron transfer rate through a solvent stabilized helix $(Pro)_n$ bridge (n>4) shows unusually small distance dependence in comparison to saturated hydrocarbons. This implies that specific secondary structures may be promoting these efficient electron transfer pathways. Also the effect of hydrogen-bonding networks in cross-linked α-helical peptides and guest-host assemblies may also be implicated. Overall, results of this research have shown that the number and the nature of connectivity between the donor and the acceptor, the secondary structure of the bridge and solvent structure around the complex all play an important role in increasing the distance across which rapid long-range electron transfer can be observed.

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Department of Chemistry

184. ***Photoinduced Electron Transfer and Electronic Excitation Transport in Complex Systems***
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The problems of photoinduced electron transfer and geminate recombination in liquids and in restricted geometry systems, e. g., micelles, are being addressed both experimentally and theoretically. A major advance in the theory is the inclusion of realistic finite-volume solvent effects. The finite volume of solvent molecules gives rise to a non-uniform distribution of particles around an electron donor. The non-uniform particle distribution significantly affects the electron transfer rates and the distribution of ion pairs formed by forward electron transfer. In addition, finite solvent size affects the rate of relative diffusion between donor-acceptor pairs. These "hydrodynamic effects" slow down the interparticle diffusion rates when near contact, resulting in a major change in the long time behavior of photoexcited electron transfer systems. Experiments were perform and analyzed with the full theory to determine the dynamics of photoinduced electron transfer. Fluorescence measurements were made with picosecond time correlated single photon counting. These experiments, combined with the theoretical analysis, yield the first realistic description of through-solvent photoinduced electron transfer. In addition, pump-probe experiments measuring geminate recombination were performed on the same donor, acceptor, solvent systems. The new theory was used to analyze the geminate recombination data. The first rigorous calculation of photoinduced electron transfer and geminate recombination in finite volume, complex geometry systems were performed. The method was applied to the problem of donors and acceptors diffusing on the surface of micelles. Ion spatial distributions as a function of time were calculated and used to understand the possibility of achieving long-term ion separation. The validity of the theory was confirmed by comparison to Monte Carlo. The first studies of photoinduced electron transfer for donors and acceptors on micelle surfaces have been conducted on three micelle systems. Very efficient electron transfer occurs because the acceptors are concentrated near the donor. The data analysis uses the new restricted geometry electron transfer theory. New theoretical descriptions of excitation transport in complex geometry systems have been developed. The work has focused on systems of clustered chromophores, in particular diblock copolymers which can form polymer micelles. The sensitivity of the rate of excitation transfer to the structure of the polymer micelles was investigated.

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Department of Chemistry

185. ***Studies of Radiation-Produced Radicals and Radical Ions***
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The objective of this project is to characterize both the structure and reactivity of selected organic free radical and radical ion intermediates generated by irradiation of molecular systems. Of particular interest is the study of the radical ions that are generated in the primary chemical processes resulting from the absorption of high-energy radiation, since these charged species play an important role in the mechanisms of both radiation and photochemical effects. Specific projects include structural and reactivity aspects of novel species including (a) 1,3- and 1,4-cycloalkanediyl radical cations where one electron is delocalized over two nonadjacent carbon centers, (b) twisted structures in olefin (1,2-diyl) radical cations, (c) bisallylic (5π electrons) radical cations involving through-space interactions, (d) distonic radical cations where spin and charge are separated in the same molecule, and (e) studies of thermal and photoinduced rearrangements of radical cations in rigid matrices proceeding by hydrogen transfer, ring opening, ring closure, and sigmatropic shifts. Many of these thermal radical cation rearrangements can be interpreted in terms of the role of vibronic coupling between the ground state and the first excited state of the radical cation. There is also a special focus on the photochemistry of radical cations in the visible region of the solar spectrum, with emphasis on the role of orbital, configuration, and state symmetry in going from the photoexcited state of the reactant to the ground state of the product.

University of Texas at Arlington
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Department of Chemistry and Biochemistry

186. ***Interfacial Chemistry at the Chalcogenide Semiconductor/Electrolyte Junction***
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This research involves two projects: (1) new electrosynthetic routes to the fabrication of chalcogenide semiconductors at support electrode surfaces; and (2) real-time in situ correlations of the interfacial chemistry and the electrical performance of a semiconductor electrode/electrolyte junction. Proof-of-concept experiments have been completed and have opened a new route to the electrosynthesis of chalcogenide semiconductors that is based on a chemically-modified support electrode. Specifically, a sulfur-modified gold electrode is electroreduced in a medium containing a targeted metal ion (or ions) to yield immobilized metal sulfide particles at the gold surface.

The utility of this approach for molecular-level ordering of the immobilized semiconductor particles and the role of the sulfur layer as a "template" is being investigated. A second topic is the development and use of new families of real-time/in situ probes for the characterization of semiconductor/electrolyte interfaces. These include the complementary probes, laser Raman spectroscopy and electrochemical quartz crystal microgravimetry. A photoelectrochemical version of the latter technique has been developed to facilitate microgravimetry measurements on metal/semiconductor interfaces under illumination. Experiments have been completed on the growth and characterization of copper sulfide layers. Composite photoelectrodes containing semiconductor particles in a nickel or polymer matrix have also been prepared and characterized. Finally, reversible photochromism at a titanium dioxide/methylene blue dye interface has been observed.

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Department of Chemistry and Biochemistry

187. ***Vectorial Electron Transfer in Spatially Ordered Arrays***
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Chemically modified semiconductor surfaces are being studied mechanistically as sites for controlled photomediated oxidation and reduction reactions. New methods for synthetic manipulation of the surfaces are being explored, along with new methods for preparation and characterization of coordination polymers and solar light harvesting polymeric layers. These polymeric coatings are then associated with optically transparent electrodes, producing a multicomponent system that can be used to probe quantitative aspects of electrocatalysis, electrosorption, and chemisorption. The use of new polymerization methods for preparing rectifying mono- and bilayer electrode coatings are being explored, with the attainment of vectorial migration of excitons and electrons being an ultimate project goal.

188. ***Photophysics and Photoredox Processes at Polymer-Water Interfaces***
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This research has focused on the use of chromophores covalently attached to amphiphilic polymers in order to enhance the yield of ion-pairs produced in photoredox reactions. Using anionic polymerization methods triblock polymers of polystyrene, vinyldiphenylanthracene (vDPA) and methacrylic acid have been prepared. The block length of the vDPA segment is relative short, 3-4 units, while the other blocks are on the order of 200 units. These triblock polymers self-assemble into micelles. Excited state electron transfer has been studied using a zwitterionic viologen (SPV) as a quencher. The fraction of singlet state quenching events that lead to ion-pair separation is excellent (ca. 0.5–1.0) and the lifetime of the SPV anion radical is exceptional, with almost no decay over a 10 ms. In fact it is possible to build up a steady state populations of SPV anion radical that persists for hours in the absence of oxygen. However the corresponding anthracene cation radical is not observed on any time scale, from ps to minutes. Evidently some component of the polymer micelle system is acting as a sacrificial reagent to reduce the cation radical. Alternatively the unusual environment of the cation radical may be broadening or distorting the absorption spectrum such that it is not detected.It was found that C60 or C70 and styrene would copolymerize with standard free-radical methods. The photophysical properties of the fullerene are strongly modified after copolymerization The resulting polymers have the normal solution properties of polystyrene and one can easily prepare deeply colored solutions or films. C60 can be polymerized with water soluble monomers (e.g. polymethacrylic acid) or reacted with amine-terminated polyethylene glycol, thereby producing a water soluble fullerene derivative. The latter material appears to have unusual surfactant properties with respect to unreacted C60, such that a water emulsion of C60 can be prepared. Studies of the photophysics of these fullerene derivatives in water are under way.

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Department of Chemistry

189. ***Photochemical Studies of Two Component Organic Systems within the Restricted Spaces of Zeolites***
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Because of lack of knowledge on the location and mobility of organic guest molecules within zeolites, photochemical studies in this medium have largely been restricted to one component materials. As a result, our ability to control photoprocesses through a second molecule within zeolites has been restricted. The present project addresses this problem. Within zeolites, more than one type of organic molecule within contact distances will be assembled and the 'supramolecular assembly' will be used to bring about changes on photochemical processes of guests that may be otherwise difficult to achieve. In this context, energy and electron transfer will be examined. With respect to energy transfer, the aim is to establish that two components can be assembled within zeolites in such a way that energy transfer and a chemical reaction resulting from energy transfer will take place. As an illustration of the concept of energy transfer, singlet oxygen will be generated, characterized, and reacted within zeolites. A part of the program focuses on exploring the use of zeolite matrices to carry out electron transfer-mediated photoreactions. The rate of back electron transfer in the case of a few donor-acceptor pairs has been shown to be at least five orders of magnitude slower on zeolite surfaces than in solution. This feature will be utilized to generate radical ions within zeolites. Interest in radical ions within zeolites is centered around performing quantum chain reactions. In the proposed investigation, the medium plays the central role. Mechanistically well-studied reactions and experimentally well-examined donor-acceptor pairs will be used as probes to explore in what way zeolites are different from isotropic solvents as media for photochemical processes which involve more than one molecule.

190. Photoinduced Energy and Electron Transfer Reactions in Light Harvesting Arrays of Transition Metal Complex Chromophores

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Recent results have shown that multimetallic transition metal complexes can serve as effective sensitizers for photoelectrochemical cells based on wide band gap semiconductors. Photon to current efficiencies approaching unity have been achieved using a trimetallic Ru (II) diimine complex adsorbed on nanocrystalline TiO_2 deposited on optically transparent tin oxide electrodes. This research has focused on (1) understanding excitation energy migration in multimetallic transition metal complexes and (2) devising new light harvesting arrays capable of absorbing a higher fraction of incident photons per particle. Through systematic investigations of intramolecular energy transfer in bimetallic complexes, bridging diimine ligands (linked bis-2,2'-bipyridyl ligands) have been found that are capable of mediating energy migration between adjacent metal centers with 100% efficiency. In addition, simple synthetic strategies have been developed for preparing the most effective of these ligands. Using these ligands, arrays of chromophores can be prepared at interfaces via sequential reaction of complimentary components. For example, films having alternating Ru (II) and Fe (II) centers can be prepared by alternate reaction of aqueous Fe (II) and the complex $[Ru(tpht)_2]^{2+}$ with a surface initially treated to have an attached terpyridine ligand. Dendrimeric surfaces can be prepared by alternate reaction of a 2,2'-bipyridine modified surface with $[Ru(II)(DMSO)_4Cl_2]$ and bphb. These surfaces have light harvesting arrays of eight or more chromophores linked by a bridge capable of efficiently mediating energy migration to the reactive surface bound complex. New ways to make multimetallic arrays are currently being explored which do not involve ligand chelation at a chromophoric center.

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Department of Chemistry

191. Investigations of Charge-Separation Processes in Metal Complexes

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This research is directed toward the elucidation of the excited states of metal complexes. Species containing Rh(III), Pt(II), Re(I), bimetal species [M_1,M_2 = Au(I), Pt(II), Rh(I), Ir(I)] and trimetal species containing Rh(I) and Ir(I) are under investigation. The intent is to synthesize stable complexes capable of utilizing incident radiation for chemical reactions, energy transfer, and storage. Analyses of luminescence decay times as a function of temperature, the measurement of relative polarizations of absorption and emission bands, and the determinations of the optical effects of intense magnetic fields (0–5 Tesla) are the principal tools of investigation. Recent data are providing values for the energy gaps separating states of disparate orbital parentages, the Arrhenius activation energies for photochemical reactions, and the paths of energy migration in excited systems. The ultimate goal of the research is to provide fundamental information on charge-separation processes in well-defined metal complexes.

192. Membrane-Organized Chemical Photoredox Systems

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This research is designed to improve our conceptual understanding of reaction mechanisms in two general areas related to solar photoconversion: (1) catalysis of water oxidation to O_2 and (2) transmembrane separation of photoredox products across artificial bilayer membranes. Both areas are critical to developing membrane-based integrated chemical systems for photogeneration of fuels. The immediate objective in the catalysis studies is to identify the oxygen-evolving species formed by oxo-bridged ruthenium dimers in the presence of strong oxidants. These studies entail structural analyses by resonance Raman and electron paramagnetic resonance methods, made in conjunction with steady-state kinetic measurements of O_2 evolution rates. The focus of the transmembrane product separation studies will be upon developing multifunctional molecules that can act both as oxidative quenchers of photoexcited dyes and as transmembrane cotransporters of electrons and protons. The conceptual basis for these studies is our recent demonstration that a prototypic compound, N–methyl–4–cyanopyridinium, can function as a highly efficient oxidative quencher/transmembrane charge carrier in vesicle-containing systems.

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193. Femtosecond Spectroscopy of Energy Transfer Dynamics in Photosynthetic Bacterial Antennas

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Photosynthetic antennas are pigment/protein complexes that collect sun light and pass the excitation energy on to a "reaction center" where, consequently, a chemical potential develops. This, in a nutshell, is how sunlight is stored. There are different kinds of antenna complexes in a given system and, in the purple photosynthetic bacteria, there are two major types of complexes and these have distinct absorption spectra in the near-infrared. The mode and mechanism of the transfer of the electronic excitation is being studied within and between the antenna complexes of the purple bacterium *Rhodobacter sphaeroides*. Excitation transfer is very fast, ocurring in a trillionth of a second or less. In the experiment, a laser pulse lasting 50 femtoseconds or less (1 femtosecond = one thousandth of a trillionth of a second) excites one of the complexes selectively and the changes in the absorption spectrum are monitored as a function of time. The evolution of the absorption spectrum reveals details about the transfer of excitation from one type of complex to another. The knowledge gained from these experiments allows for the postulation of the spatial and energetic arrangement of the antenna complexes in the photosynthetic membrane, which information is essential for fabricating efficient synthetic antenna systems.

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194. ***Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates***
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The major goals of this research project involve the systematic investigation of models that describe various aspects of the photoinduced transfer of charge, or the migration of energy between donor and acceptor transition metal-complexes. Research involves the design and synthesis of molecular systems to be used as mechanistic probes and the characterization of photochemical transients using very sensitive detection techniques. Work in progress varies from studies of the general problem of electronic coupling in donor-acceptor systems to specific problems relating to the pathways for intramolecular energy transfer from the lowest energy excited state of chromium (III). Considerable electronic coupling of donor and acceptor seems to be an important characteristic of polynuclear transition-metal complexes with CN^- bridging groups, and the effects of this coupling are manifested in excited-state electron-transfer rates, ground-state spectroscopic behavior, and electrochemical behavior. In complexes for which the donor is (^{3}CT) Ru (bpy) $_3^{2+}$ and the acceptor is a covalently linked metal complex, the donor and acceptor centers usually behave reasonably independently. The systematic comparison of the properties of some homologous series of complexes has indicated that: (1) the donor-acceptor coupling inferred from electrochemical measurements is consistently much larger than that inferred from a Hush/Mulliken interpretation of the spectroscopic measurements; and (2) there is an unusual shift to lower energies of the bridging cyanide stretching frequency. This shift of the CN-stretch is proportional to the D/A coupling, and it is symmetry dependent. These and some other observations on this class of complexes are accommodated by a simple vibronic model in which the electronic and nuclear motions are coupled. Studies in progress are designed to examine implications of this model.

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195. ***Mixed-Metal, Multielectron Photocatalysts for Solar Energy Conversion***
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The design, synthesis, and examination of the photophysical properties of potential solar energy photocatalysts is the focus of this research. The photophysical properties of complexes of ruthenium, rhenium and platinum have been investigated. The platinum systems have examined the dependence of emission lifetimes on the type of bidentate ligand and the type of bis(diphenyl phospine) ligand coordinated to the platinum center. Attention in ruthenium chemistry has centered on the chemical behavior of the diazafluorenone ligand which undergoes an unusual ring opening reaction. The rhenium systems investigated have involved pyridyl-pyrimidine complexes which emit with lifetimes in the low nanosecond time regime.

Chemical Physics

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196. ***Generalizations Concerning Vibrational and Rotational Energy Redistribution within Polyatomic Molecules***
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This project employs high-resolution infrared single- and double-resonance spectroscopy to explore the possibility of establishing broadly based generalizations about the rate and mechanism of intramolecular vibrational energy redistribution (IVR). The presence of rapid IVR determines the collisional and reactive properties of vibrationally excited molecules in combustion systems or wherever they occur. The role of molecular flexibility in accelerating IVR, the dependence on the nature of the initially prepared vibration, and a possible correlation between rate and mechanism are explored in this work. Specific molecular systems include propyne, methanol, and methylamine, which will be studied in the 3000 to 7000 cm^{-1} energy range. The experiments resolve clumps of discrete molecular features, called molecular eigenstates, for which the good quantum numbers are completely assigned. The needed information about the rate and mechanism of IVR is contained in the frequencies and intensities of these discrete features. The experimental work is supported by random matrix calculations, which are capable of quantifying the contributions of anharmonic and Coriolis (3 types) coupling mechanisms.

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197. ***Electronic Structure and Reactivities of Transition Metal Clusters***
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The objective of this research is to seek answers to fundamental and intriguing questions pertinent to the electronic structure and reactivities of transition metal clusters. The geometries, binding energies, energy separations of excited states, ionization potentials, and other properties of clusters, including their reactivities, are theoretically computed as functions of cluster size. Theoretical studies on the dimers and trimers are focused on the energy separations (T_e) of several excited states and their spectroscopic constants (r_e, Ω_e, μ_e). Computations on the potential energy surfaces are undertaken to shed light on the reactivity of these species. Spectroscopic constants of several low-lying states of WN, and other transition metal nitrides, as well as carbides such as RhC, TaC, etc., are computed including spin-orbit effects. The observed spectra are too complex to explain without theoretical studies. Comparisons with observed spectra are made.Transition metal carbides such as YC_n, TaC_n, LaC_n, LaC_n^+, TaC_n^+, HfC_n, RhC_n, Y_2C_n for the values of n between 3 and 13 are studied. The geometries, binding energies, energy separations of low-lying electronic states, etc., are being computed. The geometries of these carbide clusters are being fully optimized. Geometries and energy separations of transition metal clusters such as Rh_4, Rh_5, W_3, W_4, Zr_5, Hf_4, etc.,are being computed using high-level relativistic ab initio methods. The potential energy surfaces of transition metal dimers with carbon monoxide (CO) will be computed to gain insight into the nature of surface+CO interactions. Specific reactions being studied are Ir_3+CO and Rh_3+CO, which are being investigated through the computation of the potential energy surfaces. These studies use complete active space MCSCF (CASSCF) followed by multireference configuration interaction (MRCI) computations that include several million configurations. Spin-orbit effects are included using the relativistic configuration interaction (RCI) method.

198. Generation Detection and Characterization of Gas-Phase Transition-Metal Aggregates and Compounds

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Characterization of the gas-phase products generated in the reaction of early transition metals (Sc, Ti and Y) and late transition metals (Ir and Pt) with alkanes, H_2S, NH_3 and N_2O has been the main focus of recent investigations. The early transition metal containing systems are expected to be more readily modeled because of their limited number of valence electrons and serve as excellent tests for the reliability of semi-empirical and ab initio bonding predictions. The late transition metals are exceedingly important in metal-mediated transformations of alkenes and alkanes, but because of the near degeneracy of the $6s^2 5d^n$, $6s^1 5d^{n+1}$, and the $6s^0 5d^{n+2}$ configurations and the similar radial extent of the 6s and 5d orbitals the description of bonding is very complex. A laser ablation supersonic molecular beam spectrometer, using LIF detection, has been constructed. The optical Stark effect in PtX (X=O, N, S and C) and IrX (X=C and N) molecules were measured and the permanent electric dipole moments determined. A simple, single configuration, molecular orbital correlation diagram was developed to explain the observed trends. New polyatomic molecules, YCC and ScNH have been detected. This is the first spectroscopic detection of a gas-phase metal dicarbide.

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199. Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding

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The continued purpose of this research program is to obtain detailed experimental information on the different fundamental ways metals bond and activate organic molecules. Our approach is to directly probe the electronic interactions between metals and molecules through a wide variety of ionization spectroscopies and other techniques, and to investigate the relationships with bonding modes, structures, and chemical behavior. The following specific research accomplishments have taken place during this year of the project. (a) We have published our study of the ligand-mediated metal-metal interactions in bimetallic fulvalene complexes. The metal-metal interactions, which are entirely through the pi orbitals of the ligand, are different for cobalt and rhodium because of different orbital delocalizations, and this controls the electrochemical behavior of the complexes. (b) We have acquired high resolution photoelectron spectra of CpNiNO. The quality of these spectra provide a definitive answer to a dispute concerning the electronic interactions in this system, which has attracted widespread attention. (c) We have studied the influence of acetylide substituents and metal electron richness upon the interactions of acetylides with metals. In addition to the common occurrence of metal-acetylides in catalytic systems, these complexes are also of interest for nonlinear optical properties. Others have stressed the ability of acetylides to withdraw pi electron density from the metal center, but these experiments show that the acetylide ligand behaves more as a pi electron donor. (d) We have investigated the electronic communication between two metals through a bridging acetylide ligand. Again, the interaction is primarily through the pi bonding framework. (e) We have studied the electronic perturbations caused by cyclopentadienyl perhalogenation in metal complexes. Electronic and steric perturbations caused by chemical substitutions on cyclopentadienyl ligands are an important means of tuning chemical and catalytic reactivity. We find that the electron withdrawal that accompanies highly electronegative halogen substitutions is tempered by the pi donor nature of the halogens toward the cyclopentadienyl pi electrons. During this period, there have also been numerous developments of the equipment for these investigations, and a number of projects are underway which give a promising outlook for the coming period of the program.

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200. *High-Resolution Raman Spectroscopy of Complexes and Clusters in Molecular Beams*

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The project objectives are twofold. The first is to develop methods of nonlinear Raman spectroscopy for application in studies of sparse samples. The second is to apply such methods to structural and dynamical studies of species (molecules, complexes, and clusters) in ultracold supersonic molecular-beam samples. In the past year we have made significant progress in extending the application of mass-selective ionization-detected stimulated Raman spectroscopies (IDSRS) to the study of intermolecular vibrational transitions in molecular clusters. This progress has resulted from several developments. First, we have increased the spectral resolution of our apparatus by an order of magnitude to about 0.02 wavenumbers. Second, with this higher resolution we have succeeded in observing the manifestations of the pendular states that arise via the interaction of high-intensity optical fields with species having permanent polarizability anisotropies. Such observations have been a considerable aid in the assignment of observed intermolecular Raman bands to intermolecular vibrations in the clusters. Third, higher resolution has enabled us to observe the weak, narrow intermolecular Raman bands that gain their intensity from the intermolecular-interaction-induced modulation of a cluster's polarizability. Previously, we had been effectively blind to these important vibrational modes. Finally, the increased sensitivity available from the higher-resolution apparatus has enabled the observation of intermolecular combination bands and overtones. Characterization of such transitions is critical to the elucidation of intermolecular potential-energy surfaces. In the year ahead we plan to extend our Raman methods to the study of species that are relevant to combustion processes (i.e., radicals and ions).

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Department of Chemistry

201. *Interactions of Highly Vibrationally Excited Molecules with Clean Metal Surfaces*

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In the last 12 months we have commissioned a new ultrahigh vacuum surface science machine for use in the title experiments. The surface science machine is fully operational and all components are functioning properly. In order to obtain important information on one of the most heavily studied prototypical surface reactions, we have undertaken the study of the associative desorption of atomic Hydrogen from Cu(111). We have determined that the reaction of two Hydrogen atoms adsorbed on a Cu(111) surface produces molecular Hydrogen which leaves the surface with a "helicoptering" motion; that is, a motion where the rotation of the desorbing molecules is preferentially aligned in a plane parallel to the surface. Furthermore, we find that this alignment increases strongly with increasing rotational angular momentum. These results imply a clear steric effect in the time-reversed dissociative adsorption process for high j-states which disappears at low j. Specifically, adsorption of high j-states of molecular Hydrogen occurs preferentially for collisions with the internuclear axis parallel to the surface. Adsorption of low j-states exhibits little or no steric effect, perhaps due to molecular realignment by the adsorption potential energy surface. These conclusions result from observations of single rovibrational states of H_2, D_2 and HD desorbing from a Cu(111) permeation source under ultrahigh vacuum conditions. To achieve this, the output of a doubled dye laser is tripled in Xenon to generate tunable radiation in the range 104.5–110 nm. This radiation is used to excite specific one-photon transitions in the three isotopic variants of the Hydrogen (B–X) system, while the fundamental (313.5– 330 nm) subsequently ionizes the B-state. This 1+1' REMPI scheme is sensitive to the rotational alignment of the desorbing Hydrogen molecules relative to the polarization of the radiation. A photo-elastic modulator is used to control the polarization of the radiation so that it is either parallel or perpendicular to the surface normal. Our results are in qualitative agreement with recent calculations. They will provide an important experimental benchmark for further theoretical comparison.

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Department of Chemistry

202. *Studies of Combustion Kinetics and Mechanisms*

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The goal of this research is to obtain new quantitative knowledge of the kinetics and mechanisms of the elementary reactions of polyatomic free radicals, which are important in hydrocarbon combustion processes. Polyatomic free radicals are generated in a heatable (up to 1100 K) flow reactor by the photodecomposition of suitable molecules using a pulsed uv-laser. The ensuing reactions are monitored in time-resolved experiments using photoionization mass spectrometry. In order to obtain basic information regarding the reactivity of these free radicals, reaction rate constants are measured as a function of temperature and pressure (0.5 to 25 torr) and, when possible, the primary reaction products are determined and their branching fractions measured. These experimental studies are coupled with theoretical ones to obtain an improved understanding of the factors governing reactivity and to provide a rational basis for extrapolating the observed kinetic behavior of free-radical processes from laboratory conditions to the harsher environment of actual combustion processes. Recent studies have focused particularly on the reactions of the vinyl radical, the simplest unsaturated hydrocarbon free radical and one that has been implicated as a soot precursor. Reactions studied include the unimolecular decomposition of C_2H_3 and its reactions with O_2, H_2 and acetylene.

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203. Chemical Reaction Dynamics of Combustion Intermediates and Products

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The studies develop our predictive ability for bimolecular and unimolecular reactions of combustion intermediates and products. The first experiments investigate the photolytic generation and reactivity of bimolecular reaction intermediates important in combustion such as the HOCO intermediate of the OH + CO ->H + CO_2 reaction and the HONO intermediate of the OH + NO ->H + NO_2 reaction. The second set of experiments investigates how state-specific parent vibrational excitation of molecules such as CH_3SH and CH_3NH_2 can, upon photodissociation, alter the branching ratio between competing product channels. The change in branching between the product channels is determined with photofragment velocity and angular distribution analysis in a crossed laser molecular beam apparatus. The final experiments probe how the relative orientation of the reactants in bimolecular reactions like H + O_2 ->OH + O, a key rate limiting, chain branching step in combustion processes, can influence the reaction cross section. Orienting the diatomic reagent in analogous systems, H + XY ->X + YH, with respect to the velocity vector of the H atom reagent allows us to investigate how the effective barrier changes with relative orientation and how nonadiabatic recrossing influences the reaction cross section.

204. Quantum Dynamics of Fast Chemical Reactions

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In this research we want to determine accurate values of thermal rate constants and state-to-state cross sections for elementary bimolecular reactions in the gas phase including photodissociation. In these studies we develop and use accurate and efficient quantum methods. The thermal rate constants have been calculated both from the quantum thermal averaged flux-flux correlation function (evaluated by diagonalizing the Hamiltonian in a three-body DVR) and from the cumulative reaction probability, N(E). Recently we have developed methods that use only real square integrable representations on a finite (small) range in order to represent the continuum scattering processes. We have applied these to the photodissociation of van der Waals molecules and the UV photodissociation of a model for methyl mercaptan. Applications to other 3-D reactions are in progress. We have also treated the dynamics of electronically nonadiabatic collisions using the two diabatic surfaces, together with an appropriate interaction term. Nonadiabatic effects are common in photodissociation and in some chemical exchange reactions. An additional focus has been on the development of a "quantum transition state theory" based on operator expressions for N(E). Time evolution of the "transition state wavepackets" once yields their contributions to the cumulative reaction probability at all energies. Applications to the H_2 + OH reaction in full 6-D yields excellent results. Finally we have developed a new efficient method for correcting or interpolating potential energy surfaces using spectral data or the ab initio values at relatively few points.

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205. Laser Photoelectron Spectroscopy of Ions

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The combustion of aromatic compounds is an important process. The manner in which an aromatic ring is cracked by dioxygen is an intriguing one for chemists. There is a recent proposal that a dioxiranyl might be the key intermediate in the ring opening of benzene. We have begun to study the chemistry and spectroscopy of two possible intermediates in benzene oxidation, the C_6H_5 radical, and the phenyl peroxy radical, C_6H_5OO. We have measured the IR absorption spectrum of the C_6H_5radical in an Ar matrix and we have photodetached the HO_2^- and $(CH_3)_3CO_2^-$ ions. In order to understand the spectroscopy and thermochemistry of the phenyl peroxy radical, we plan to measure the gas phase acidity of C_6H_5OOH and to photodetach the $C_6H_5OO^-$ ion. Phenylhydroperoxide (C_6H_5OOH) is a very dangerous molecule to prepare consequently we have begun our initial studies with tert-butylhydroperoxide, $(CH_3)_3COOH$. The $(CH_3)_3CO_2^-$ ion, m/z 89, was prepared by a discharge with tert-butylhydroperoxide. We observe photodetachment $\tilde{X}\,^2A''$ $(CH_3)_3CO_2 \leftarrow \tilde{X}\,^2A'$ $(CH_3)_3CO_2^-$ and find EA $[(CH_3)_3CO_2] = 1.1 \pm 0.2$ eV which compare with EA$[HO_2] = 1.078 \pm 0.010$ eV. The $\Delta E(^2A',^2A'')$ splitting is 1.2 ± 0.2 eV in the organic peroxide which contrasts with 0.867 ± 0.001 eV for HO_2. In the future, a measurement of $\Delta_{acid}G_{298}[(CH_3)_3COO\text{-}H]$ will afford us $\Delta_{acid}H_{298}[(CH_3)_3COO\text{-}H]$ which can be combined with EA$[(CH_3)_3CO_2]$ to yield $\Delta H_{298}[(CH_3)_3COO\text{-}H]$. Since $\Delta_f H_{298}[(CH_3)_3COOH]$ is known, our value of $\Delta H_{298}[(CH_3)_3COO\text{-}H]$ will provide us with the absolute heat of formation of the tert-butyl peroxyl radical, $\Delta_f H_{298}[(CH_3)_3COO]$. This value will immediately yield $D_0[(CH_3)_3CO\text{-}O]$ and $D_0[(CH_3)_3C\text{-}OO]$. The phenyl radical (C_6H_5) is an important species in organic chemistry and combustion processes. The energy of this radical has recently been reported $[\Delta_f H_0(C_6H_5) = 84.3 \pm 0.6 \text{ kcal mol}^{-1}]$ and is derived from the bond energy of benzene $[D_0(C_6H_5\text{-}H) = 112.0 \pm 0.6 \text{ kcal mol}^{-1}]$; the high reactivity of C_6H_5 has made its spectroscopic characterization very difficult. We have measured the infrared absorption spectrum of the phenyl radical in an argon matrix at 12 K and propose assignments for both the frequencies and intensities for all of the 24 IR active modes. We observe the IR absorption spectra of the phenyl radical in an Ar matrix at 12 K when we photolyze either the acyl peroxide, $C_6H_5CO_2\text{-}OCOC_6H_5$ or the anhydride, $C_6H_5CO\text{-}O\text{-}COC_6H_5$. Benzoyl peroxide is by far the most effective precursor of phenyl. Our irradiated matrix has an EPR spectrum that is identical with the known EPR spectrum of the phenyl radical; C_6H_5. The EPR spectrum of phenyl is consistent with a C_{2v} "σ radical" whose ground electronic state is $\tilde{X}\,^2A_1$. To find the IR fundamentals of C_6H_5, we monitored the time course of an extensive number of infrared spectra as we photolyzed $C_6H_5CO_2\text{-}OCOC_6H_5$. We identify 24 prominent bands that are formed at the same rate as the benzoyl peroxide bands disappear. Then we check our 24 bands by monitoring the rate of destruction of the C_6H_5 features as we warm the matrix up to 30 K and observe the appearance of the IR spectrum of biphenyl, (2). Only those bands that a) are produced at the same rate as benzoyl peroxide is destroyed and b) disappear at the same rate as

C_6H_5-C_6H_5 is produced are identified with C_6H_5. A comparison of the integrated intensity of the CO_2 bands and those of phenyl permits us to estimate the absolute infrared intensities of C_6H_5. Our matrix frequencies are expected to be within ± 1% of the gas phase values (ν/cm^{-1}) while our intensities (A/km mol^{-1}) are within ± 10% those of the isolated C_6H_5.

206. *Time-Resolved FTIR Emission Studies of Laser Photofragmentation and Chain Reactions*

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Spectrally resolved infrared emission is used to study combustion processes of radical-radical reactions and radical-molecule collision events. A time-resolved Fourier transform infrared emission apparatus has been developed for these measurements. New studies involve the detailed investigation of a novel five-membered ring transition state in the reactions of O atoms with molecules such as ethyl iodide and propyl iodide, which forms HOI. The reaction proceeds by attack of the O atom at the iodine followed by a potential surface crossing that allows the O atom to abstract an H atom from an adjacent carbon. Detailed spectroscopic information has been obtained to determine the structure of the HOI product molecule for the first time. A jet-cooled source of molecules has been developed to study infrared emission from photofragments and reactions. In preliminary work, the dynamics of NH_2 from the photodissociation of NH_3 has been explored under the highly compressed spectral condition of jet-cooling.

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207. *Energy Partitioning in Elementary Gas-Phase Reactions*

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The reactions of O(^{3}P) with a series of alkynes has been studied by laser induced fluorescence detection of the nascent H atoms and CO. The most startling discovery is that the CO products are invariably vibrationally and rotationally cold in spite of the fact that the reactions are very exothermic. The general explanation is as follows. The O atom attaches itself to an unsaturated carbon atom forming a vibrationally excited C-O bond. However, a hydrogen atom or alkyl radical is bound to that same carbon atom; the CO molecule cannot be liberated until the H atom or alkyl radical migrates to an adjacent carbon atom. The energy within the CO bond is used to overcome the potential barrier to the 1,2 migration. The substituted ketene which is then formed decomposes too rapidly for vibrational energy to flow back to the CO. On the other hand, the linearity of the ketene CCO group produces a rotationally cold CO molecule. The larger alkynes yield a variety of radicals whose identity and ionization potentials are being determined by vacuum ultraviolet photoionization. Experiments similar to the above are planned for the reactions of O(^{3}P) with alkenes.

208. *Laser-Enhanced Chemical Reaction Studies*

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This project employs extremely high resolution infrared diode lasers to study fundamental combustion and collision dynamics and photochemical reaction processes. High energy atoms, molecules, and chemically reactive radicals, produced by excimer laser photolysis or dye laser excitation, are used as reagents to investigate collisional excitation, collisional quenching, and chemical production of individual rotational and vibrational states of molecules. Translational energy recoil of the target molecules is determined by measuring the time dependent Doppler profile of the molecular infrared transitions. This experimental method has been used to probe the quenching step in the famous Lindemann unimolecular reaction model in which vibrationally hot molecules with chemically significant amounts of energy are cooled by collisions with a cold bath molecule. Loss of energy by these highly excited molecules has been found to proceed via two distinct mechanisms. The first vibrational energy transfer mechanism is characterized by very large bath rotational and translational energy uptake with no vibrational excitation, the clear signature of an impulsive short range force collision. In the second mechanism, vibrationally excited states of the bath molecule are excited in a collision with a highly excited donor. Quite amazingly, when the vibrations of the bath molecule produced in the collision are high frequency (energy spacing large compared to kT) almost no energy is imparted to the rotational or translational degrees of freedom of the molecule. This is the clear signature of a "long range" force mechanism in which soft collisions dominate the energy transfer. Indeed, temperature dependent studies confirm this conclusion, since the excitation probabilities increase as the temperature decreases. Perhaps even more surprising is the fact that vibrationally excited states of the bath that are infrared inactive, having no dipole transition matrix element to the ground state, are also excited by a long range mechanism. This suggests excitation of the bath can be mediated by quadrupole interactions as well as dipole interactions. The detailed chemical and collision dynamics of a number of processes are being studied using optical parametric oscillators to prepare single initial quantum states of the reactants. A general super radiant laser process has been discovered using this apparatus. The data obtained in all of these experiments is of fundamental as well as practical interest in testing theoretical computations based on approximate potential energy surfaces and in providing an improved understanding of combustion and atmospheric chemical processes.

209. *Single-Collision Studies of Energy Transfer and Chemical Reaction*

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This research project addresses the dynamics of chemical reactions that are important in combustion processes, or that serve as prototypes of important combustion reactions. Our current interest is in reactions of free radicals, such as H atoms, with vibrationally excited hydrocarbons, such as CH_4. We are trying to learn how reactions of vibrationally excited molecules differ, both qualitatively and quantitatively, from reactions of ground vibrational state molecules. This is an important issue in understanding combustion processes, since vibrationally excited species are relatively abundant at combustion temperatures, and reactions with them can make a large contribution to the overall rate of reaction. Our primary interest is in radical + polyatom combustion reactions. However, in carrying out benchmark studies of atom + diatom reactions we have found that current understanding of even these simple reactions is not very good when the reactant diatom is vibrationally excited, so we are putting effort into studies of atom + diatom reactions as well. We do both experimental and computational studies. The experiments–state-to-state dynamics experiments under single-collision conditions–use a sequence of precisely timed nanosecond laser pulses to create the free radical reactant, to vibrationally excite the reactant molecule, and to detect the products and determines their energy distributions. The computational simulations are quasi-classical trajectory calculations. The state-to-state reactive cross sections that come from our experiments are used to provide a rigorous test of the accuracy of the computational simulations of the reactions. When validated by comparison with experimental results, the computational simulations provide insight about the dynamics of combustion reactions, and are used to develop models of these reactions that have predictive power.

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210. *Spectroscopy of Combustion Radicals*

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A knowledge of reaction pathways leading to the formation of chlorinated aromatic compounds in the combustion of halogenated organic compounds and the development of monitoring methods for hazardous emissions will assist the DOE in the management and disposal of hazardous chemical wastes. Selective laser ionization techniques are used in this project for the measurement of concentration profiles of radical intermediates in the combustion of chlorinated hydrocarbon flames. A novel flame-sampling tunable VUV photoionization mass spectrometer is in use for these studies. Both CH_4/O_2 and H_2/O_2 flames seeded with chlorocarbons including C_2HCl_3, C_2H_3Cl, CH_3Cl, $CHCl_3$, CH_2Cl_2, and CH_3Cl are under study. A number of radicals, previously unmonitored in a flame environment, are detected in the work to date. These include Cl, CCl, CHCl, CH_2Cl, C_2Cl, C_2HCl, C_2HCl_2, C_2H_2Cl, and C_2Cl_2. Profiles of the relative concentrations of flame species are compared with the predictions of kinetic models for chlorocarbon combustion to confirm and extend postulated reaction mechanisms. Near-threshold photoionization spectroscopy with the tunable VUV laser system is used for the measurement of ionization potentials for chlorocarbon radicals.

Department of Chemistry

211. *Studies of Combustion Reactions at the State-Resolved Differential Cross Section Level*

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The technique of product imaging is being used to investigate several processes important to a fundamental understanding of combustion. The imaging technique produces a "snapshot" of the three-dimensional velocity distribution of a state-selected reaction product. Research in three main areas is planned. First, differential cross sections are being measured for several reactions, perhaps the most important of which is the H + O_2 reaction. Second, the imaging technique is being used to detect only zero kinetic energy fragments from a photodissociation near threshold. Since these fragments are produced primarily when the photolysis light is resonant with an internal level of the activated complex, it should then be possible by scanning the photolysis light to obtain a "spectrum" of the transition state. Third, the imaging technique is being used to learn the distribution of translational energy when a highly vibrationally excited molecule collides under well-defined single-collision conditions with a partner. This distribution of translational energy is directly related to the distribution of vibrational energy removed by collisional deactivation, a quantity of importance to a theoretical understanding of two important combustion processes, unimolecular dissociation and radical recombination.

Laboratory of Atomic and Solid State Physics

212. *Photochemical Dynamics of Surface-Oriented Molecules*

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This project focuses on the elucidating of the detailed mechanisms of nanosecond and femtosecond laser induced surface reactions and the determination of the time scales involved in the breaking and formation of chemical bonds on the surface. The depth of our understanding of the experimental results was obtained via modeling and simulations of nanosecond and femtosecond laser induced dynamical quantum processes involving molecules adsorbed on solid surfaces, which provide detailed information on energy related processes such as catalysis, combustion, and materials synthesis and processing. Our approach is to investigate: 1. unimolecular reaction (photodesorption) and 2. bimolecular reaction (photoreaction). For the study of photodesorption, the adsorption systems were O_2 adsorbed on Pt(111), O_2/Pt(111), and NO/Pt(111), while O_2 coadsorbed with CO on Pt(111), O_2/CO/Pt(111), leads to a bimolecular reaction to produce CO_2. The translational distributions were obtained as a function of the laser fluence, wavelength, and the time delay between pairs of femtosecond laser pulses in two-pulse correlation measurements. A number of remarkable hallmarks of femtosecond laser induced surface chemistry were revealed when compared to that induced by nanosecond laser pulses. In addition, the desorption rate reaches a maximum value about 500 fs after the laser pulse.

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Department of Chemistry

213. *Theoretical Studies of Combustion Dynamics*

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The objectives of this research project are the development and application of rigorous theoretical methods to describe dynamical processes of importance in gas-phase combustion. The focus of the research is on bimolecular and unimolecular reactions of importance in combustion. The dissociation of HCO and DCO via Feshbach resonances has been studied using a high quality ab initio potential. The recombination rate of H+CO to form stable HCO (in the presence of an Ar buffer gas) has also been calculated using a new theory of Professor W. H. Miller (still within the strong collision approximation). Scattering calculations of state-to-state energy transfer in Ar+HCO collisions have also been done, using a model Ar-HCO interaction potential. These calculations have been extended to energies above the dissociation threshold, and have revealed the importance of resonances in the dissociation mechanism. Reduced dimensionality quantum calculations have been done on the reaction $OH+CO \leftarrow H+CO_2$. This reaction is dominated by HOCO resonances, and thus represents an important prototype radical-radical reaction system. Satisfactory agreement with the experimental thermal rate constant was obtained by lowering the exit channel barrier slightly.

214. *Kinetics of Elementary Processes Relevant to Incipient Soot Formation*

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Kinetics and mechanisms of elementary processes important to incipient soot formation have been investigated experimentally and theoretically. In the experimental studies, the cavity ring-down method, which has been developed in this project for kinetic measurements of NH_2 and C_6H_5 radical reactions, was extended for C_6H_5O detection and the C_6H_5O + NO reaction. In addition, we have employed a laser-photolysis/mass spectrometric method to measure for the first time the absolute rate constant for the recombination of C_6H_5 radicals, k = 2.0E13.exp(−190/T) cm^3/mole.s. Theoretically, we have carried out ab initio molecular orbital calculations using a modified Gaussian-2 and other advanced levels of theory to study the kinetics and mechanisms of $C_6H_5O + NO = C_6H_5ONO$, $O + C_6H_5O = O_2 + C_6H_5$, $CH_3 + C_5H_5$ = fulvene + 2H and the fulvene-to-benzene isomerization reaction. The results of these studies are relevant to the formation of the first aromatic ring in combustion and also cast doubt on the existing data for $D(C_5H_5-H)$ and the activation energy for the fulvene isomerization reaction.

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Supercomputer Computations Research Institute

215. *Ab Initio Electronic Structure Studies of Pyrolytic Reactions of Polycyclic Aromatic Hydrocarbons and their Derivatives*

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Substituted phenyl radicals produced from (poly)chlorobenzenes by abstraction of hydrogen or chlorine are the subject of our continuing theoretical research on the pyrolysis of simple polycyclic aromatic hydrocarbons (PAHs) and their derivatives. These radicals recombine to form polychlorinated biphenyls (PCBs) that, because of their carcinogenecity and persistence in soil, are one of the most dangerous industrial pollutants known. Electronic structures, energies and geometries of all the possible isomers of the (poly)chlorophenyl radicals are being calculated at the BLYP/6-311G** level of theory. Systematization of the computed data, which involves the development of simple additive rules for the prediction of the energetically preferable sites of the C-H and C-Cl bond dissociations in chloroderivatives of benzene, is currently under way. In a separate but related research effort, studies of the thermal rearrangements of PAHs are about to be initiated. Such rearrangements, which occur in the course of combustion processes at higher (ca. 1500°C) temperatures, are believed to provide an important pathway to the formation of carcinogenic PAHs from biologically less active precursors. Thermal rearrangements of several model compounds will be studied in detail and their mechanisms will be carefully examined.

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Center for Computational Quantum Chemistry

216. *Spectroscopy at Metal Cluster Surfaces*

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Microscopic metal clusters composed of a variety of pure component systems and metal mixtures are produced and studied in a molecular beam environment. These same methods are used to produce metal complexes, which have small molecules "physisorbed" on the surface of the metal cluster particles. Electronic spectroscopy is applied to these clusters to investigate the fundamentals of metal-metal and metal-adsorbate bonding. These studies produce vibrational frequencies, bond distances, and bond energies for metal clusters and their complexes. Recently studied systems include Cu-Li, Ag-Li, Ag-Ar, Ag-Kr, Ag-Xe, Cu-Ar, Cu-Kr, Cu-Xe and $In-N_2$. Studies of larger clusters focus on the metal-carbon systems known as "met-cars" clusters. In these systems, the M_8C_{12} stoichiometry is formed preferentially, and a cage-like structure has been proposed to explain this preference. We are measuring dissociation products and ionization potentials for different M_8C_{12} metal analogues (Ti, Fe, V, Nb). Additional studies have identified preferential formation of $M_{14}C_{13}$ clusters believed to have face-centered cubic crystallite structures. Recent progress in this area includes the first measurements of ionization potentials for M/C clusters (e.g., Ti_8C_{12}, IP=4.9 eV) and the preparation of new metal carbide clusters (silver, antimony, bismuth). The measurements of the fundamental interactions exhibited by clusters are used to evaluate their potential as models for bulk surface chemistry and catalysis.

Department of Chemistry

217. Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions
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High level quantum mechanical methods are now a significant source of specific predictions concerning molecular systems that may be very important, but inaccessible to experiment. An important example is the study of molecular species and chemical reactions of fundamental importance in combustion processes. This research involves both the development of theoretical methods and their application to hydrocarbon chemistry. Quantum mechanical electronic structure methods intermediate between extensive configuration interaction and high level perturbation theory are being developed. Chemical reactions being studied in molecular detail include the dissociation of HNCO and ketene and the different aspects of the $C_2H_5 + O_2$ reaction. Other work in progress includes studies of the elementary reaction of quartet methylidyne (CH) with methane, the highly strained tetra-tert-butylethylene molecule, the ring opening of cyclopropylidene, a comparison of the cyclic and chain forms of the HO_2 dimer, and the secondary deuterium kinetic isotope effects on the isomerization of the trimethylene diradical to cyclopropane.

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Division of Applied Sciences

218. Fundamental Spectroscopic Studies of Carbenes and Hydrocarbon Radicals
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This research provides definitive identification of reactive hydrocarbon radicals and carbenes and fundamental spectroscopic data needed for diagnostic probing in combustion systems. The reactive hydrocarbons are produced in a pulsed supersonic molecular beam and observed with a newly constructed Fourier transform microwave (FTM) spectrometer. Radical chain reactions are the dominant mechanism for the decomposition of acetylene and polyacetylenes at high temperatures, but little is known about the thermodynamic and kinetic properties of C_nH radicals other than C_2H. Our recent detection of the C_7H, C_8H, C_9H, and $C_{11}H$ radicals establishes that highly unsaturated reactive chains containing up to 11 carbon atoms are stable and allows refinements in the estimates of thermodynamic properties assumed in chemical models. The cumulene carbenes H_2C_5 and H_2C_6 (isomer of triacetylene, HC_6H) in their singlet electronic ground states, which we also detected by the same technique, probably play a prominent role in the synthesis of unsaturated hydrocarbons. The number densities of the C_nH radicals, cumulene carbenes, and cyanopolyynes $HC_{11}N$ and $HC_{13}N$ in our molecular jet are sufficiently high to detect the electronic spectra by standard laser spectroscopic techniques. This combined program of microwave and laser spectroscopy of reactive hydrocarbons in supersonic jets, should help guide four-wave mixing and other laser diagnostic techniques now being developed in other laboratories to understand the detailed processes that occur in combustion.

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Department of Chemical Engineering

219. Kinetics of Combustion-Related Processes at High Temperature
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The purpose of this project is to determine rates and mechanisms for fuel hydrocarbon pyrolysis and other reactions at high temperatures. The measurements are made in a shock tube (providing arbitrary, precise, and externally set temperatures) with two very high resolution laser diagnostic techniques: laser schlieren measurement of density gradients (net endothermic rate) and the new method of excimer laser flash absorption, which provides absorption profiles in the UV with 0.05 microsecond resolution. Previous work included a study of the dissociation of vinylacetylene, which led to the proposal of a new mechanism for acetylene polymerization. Also, studies of large-molecule dissociation at extreme temperatures, such as the retro-Diels Alder dissociation of cyclohexene, tetrahydropyridine, and norbornene, have provided the first observations of unimolecular falloff in such dissociations. The norbornene study also offered the first measurements of incubation times in a large-molecule dissociation. Additional work involves measurements of vibrational relaxation in large molecules; dissociation, isomerization, and aromatic formation in allene/propyne; and dissociation rates in several halocarbons. A theoretical analysis of large anharmonic effects (restricted internal rotations) on the rate of dissociation of unsaturated hydrides has been developed and applied to HCN, C_2H_2, and now to C_3H_4. Recent work includes a study of the pyrolysis of pyrazine and pyrimidine, as well as an investigation of decomposition, isomerization, and incubation in the oxirane/acetaldehyde system.

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Department of Mechanical and Industrial Engineering

220. ***Investigation of Saturated Degenerate Four-Wave Mixing Spectroscopy for Quantitative Concentration Measurements***
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A combined experimental and theoretical approach is used for the development and evaluation of strategies for quantitative degenerate four-wave mixing (DFWM) concentration measurements in flames. The DFWM process is investigated theoretically by solving the time-dependent density matrix questions by direct numerical integration. During the past year our studies on the effect of Doppler broadening on concentration measurements was concluded. A corrected Abrams-Lind reflectivity expression was developed that will be tested experimentally in our laboratory in the coming year. The use of short-pulse lasers for quantitative DFWM concentration measurements was investigated theoretically; the use of picosecond lasers for DFWM in atmospheric pressure flames has been suggested as a means of overcoming complications due to collisions. Our studies indicate that even when the laser pulse length is much shorter than the characteristic collision time, the DFWM signal becomes independent of collisions only for resonance lines that are predominantly Doppler-broadened. We have begun a theoretical investigation of the effects of level degeneracies (Zeeman states) on DFWM signal generation in the saturation regime. Collisional effects and different laser polarization schemes will be investigated using our degenerate-level DFWM code. We have also ported our DFWM code to a massively parallel computer and will investigate the effects of multi-frequency-mode laser radiation in the coming year. Experimentally, we have constructed a low-pressure flame facility and have begun to perform OH DFWM measurements. The results of OH DFWM measurements over a wide range of flame pressures and stoichiometries will be compared with our theoretical calculations of DFWM signal levels, saturation intensities, and detection limits.

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Department of Chemistry

221. ***Investigations of Reactions and Spectroscopy of Radical Species Relevant to Combustion Reactions and Diagnostics***
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Chemical reactions that do not conserve total electron spin, spin-forbidden reactions, play an essential role in combustion chemistry. Several spin-forbidden reactions are currently under investigation. The mechanism of the electronic quenching reaction $CH(a^4\sigma^-) + CO \rightarrow CH(X^2\Pi) + CO$ has been analyzed. This reaction proceeds through an intermediate complex model. The mechanism of the reaction $N(^4S) + CH_3(^2A') \rightarrow H_2 + HCN$ is currently under consideration. Ultimately the electronic structure data necessary for the theoretical prediction of the rate constants of these reactions will be determined. Recently it has been shown that the Berry phase effect, induced by conical intersections, can have important implications for molecular reaction dynamics. The reaction $OH + H_2 \rightarrow H_2 + H_2O$ is a key combustion reaction. The potential impact of the Berry phase effect on this adiabatic ground state reaction is being considered.

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Department of Chemical Engineering

222. ***Aromatics Oxidation and Soot Formation in Flames***
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The oxidation of aromatics and the formation of soot in flames are being studied with emphasis on experimental identification of important molecular species, including fullerenes, characterization of soot structure, and measurement of concentration profiles of molecular species and soot through the reaction and post flame zones of low-pressure one-dimensional flames. The species identifications, soot structures characteristics, and net reaction rates calculated from the concentration profiles are used to test and to refine hypothesized reaction mechanisms. Proposed mechanisms of benzene oxidation are being tested, and refined as appropriate, using measured concentration profiles of radical and stable species present during benzene oxidation in flames. The research on soot formation is concerned with the particle inception or nucleation stage and the study of soot structure at all stages of growth in order to obtain mechanistic information from evidence of growth steps recorded in the structure of particles. The ultimate objective is to understand how nascent soot particles are formed from high molecular weight compounds, including the roles of planar and curved PAH and the relationship between soot and fullerenes. The objective of the research on fullerenes is to identify the range of fullerenes formed in flames, the nature of the precursor species, and the mechanisms and kinetics of the formation reactions.

Department of Chemistry

223. ***Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules***
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Studies of intramolecular vibrational redistribution (IVR) and unimolecular isomerization have focused on the acetylene molecule (C_2H_2) and have utilized the spectroscopic techniques of dispersed fluorescence (DF), stimulated emission pumping (SEP), and infrared-ultraviolet (IR-UV) double resonance DF and SEP. Sensitive and selective absorption-based spectroscopic techniques, suited for both detection and characterization, have also been under development. These techniques are based on the combination of magnetic rotation spectroscopy (MRS), which provides selectivity to the lowest rotational levels of free radicals, and frequency modulation (FM) spectroscopy. In a collaboration with T. Sears and G. Hall at Brookhaven National Laboratory, the velocity and internal state distributions of photolytically generated free radicals (CN) were sensitively monitored by transient FM spectroscopy. In a collaboration with E. Eyler at the University of Delaware, the sideband phase and amplitude stability, on which the sensitivity of FM spectroscopy depends, was shown to be preserved when an FM'ed cw dye laser was pulse amplified and frequency tripled. The study of IVR in acetylene is based on a superpolyad model in which the initial stages of IVR are described by a few spectroscopically determined resonance parameters. The superpolyad model describes the frequency and intensity patterns in the spectrum and the rates and pathways for energy flow in a computationally simple form, which is explicitly scalable in $E_{vibration}$. The model also guides selection of initial states, accessible via IR-UV-SEP, that are optimally coupled to dynamical features such as the acetylene-vinylidene isomerization coordinate. Despite severe overlap of polyad features in the DF spectrum of acetylene, it has proven possible to "unzip" the spectrum into separate polyads. This provides a quick survey of the unimolecular dynamics at energies where breakdown of the predicted polyad patterns would signal the onset of isomerization.

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Department of Chemical Engineering

224. *Probing Flame Chemistry with MBMS, Theory, and Modeling*
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Elementary reactions in combustion are studied using molecular-beam mass spectrometry (MBMS) of free-radical and stable species in flames, ab initio calculations of thermochemistry and transition states, new kinetics from reaction theories, and tests of mechanisms using whole-flame modeling. The present focus is on oxidation and molecular-weight growth chemistry in forming aromatics. Complete MBMS data sets have been mapped for the first time in high-temperature ethene flat flames, $\phi=0.75$ and $\phi=1.90$. We obtain new measurements of the kinetics for H and OH + C_2H_4, C_2H_3 decomposition, and $C_2H_3+O_2$. With the BAC-MP4 method, we have calculated thermochemistry and rate constants for these reactions and those of CH_3CHO, CH_3CO, CH_2CHO, C_3H_5 isomers, and C_3H_xO formation and destruction.

Department of Chemistry

225. *Theory of the Dissociation Dynamics of Small Molecules on Metal Surfaces: Finite Temperature Studies*
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Realistic theoretical models are used to examine the dynamics of some molecule-surface reactions important in catalysis. Time-dependent techniques are used to treat the necessary degrees of freedom quantum mechanically. The dissociative adsorption of molecular hydrogen and its isotopes on metals has been studied in detail. The dissociation of methane is currently under study. New methods are being devised to evolve the wave function and to include the effects of lattice vibrations, in an attempt to resolve some long-standing disputes. Dissociation probabilities are being computed as a function of beam energy, molecular state, and surface temperature. Studies have been made of Eley-Rideal processes in which a gas phase H or D atom reacts with an adsorbed H, D, or Cl atom. Experimentally observed activation energies have been explained in terms of enhanced reactivity due to adsorbate vibrational excitation. Fully quantum three-dimensional calculations have been implemented, allowing for the determination of reaction cross sections and product translational and ro-vibrational state distributions. Detailed studies of the reaction dynamics have been made for several potential energy surfaces and isotopic combinations, and excellent agreement has been found with experiment. The dynamics have been elucidated in terms of a competition between reaction and trapping. More detailed studies are examining the effects of impact angle and surface corrugation.

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Department of Atmospheric, Oceanic, and Space Sciences

226. *Energy-Transfer Properties and Mechanisms*
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This project studies the mechanisms and properties of energy transfer involving moderate-sized molecules. A fuller understanding of highly excited molecules is obtained by a combination of experiments and modeling. The aim is to develop a theoretical model for prediction of energy transfer properties. In the experiments, the excited molecules are monitored with various techniques, including time- and wavelength-resolved IR emission and resonance-enhanced multiphoton ionization. The disposal of energy in translational, rotational, and vibrational degrees of freedom is monitored as highly excited molecules are deactivated. In the modeling effort, collisional/reaction master equation formulations are developed and used to investigate how molecular energy transfer affects chemical reaction systems in combustion and in other systems that experience temperature and pressure extremes.

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Department of Chemistry

227. *Variational Transition State Theory*
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This project involves the development and application of variational transition state theory (VTST) and semiclassical transmission coefficients for gas-phase reactions. The work involves new theoretical formulations and the development of practical techniques for applying the theory to various classes of transition states and for interfacing reaction-path dynamics calculations with electronic structure theory and applications to specific reactions. We have developed new general strategies for obtaining potential energy surface information for reaction-path dynamics calculations, and we are developing practical methods that eliminate the need for fitting electronic structure data to analytic forms. The new methods are called direct dynamics. We have developed one approach to direct dynamics that we call interpolated variational transition state theory (IVTST). In this approach, we base the dynamics calculations on electronic structure data, including energies, gradients, and hessians, at the reactants, products, saddle point, and zero, one, or two additional points near the saddle point. Our newest direct dynamics scheme is called VTST with interpolated corrections (VTST-IC) or dual-level direct dynamics or triple-slash (///) dynamics. This approach involves using straight direct dynamics with NDDO-SRP parameterization or a low-level ab inito calculation as a first step; in the second step this is augmented by high-level data at selected geometries along the reaction path. Applications are being made to combustion processes, including the reaction of OH with propane. In addition the new techniques are being incorporated in our portable POLYRATE program.

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Chemical Science and Technology Laboratory

228. ***Optically Driven Surface Reactions: State-Resolved Probes of Surface Dynamics***
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Lasers and state-resolved diagnostics are used to initiate and follow chemical processes on solid surfaces. Optical excitations allow the study both of thermal and non-equilibrium chemistries that might arise naturally during catalytic reaction and materials processing. Laser wavelengths ranging from the IR through the UV are available to initiate chemical transformations by creating thermal, adsorbate-localized, or substrate-mediated excitations. Quantum state resolved diagnostics of the reaction products allow for a better understanding of the detailed reaction mechanism(s) that follow and the dependence of reaction pathway(s) on the excitation mechanism. Previous work in this laboratory clearly demonstrated the first evidence for the importance of hot-carrier-driven chemistry on a metal surface [NO/Pt(III)], surface state-driven chemistry on a semiconductor [NO/Si(III) 7x7], and substrate and adsorbate quenching effects in adsorbate photolysis [$Mo(CO)_6$/Si(III)]. Current work is directed at understanding the dynamics of photostimulated oxidation of carbon surfaces and testing theoretical models of molecular desorption induced by femtosecond laser pulses.

229. ***Kinetics Database for Combustion Modeling***
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The computer simulation of combustion processes provides a means of making optimum use of increasing capabilities in computational power and fundamental understanding to supplement physical testing. It can therefore have important influences on design and optimization of combustion devices for energy efficiency and pollution minimization. The key ingredient for taking advantage of this technology is the availability of a reliable database of chemical kinetic and thermodynamic information bearing on all the species, stable and unstable, that are formed in the course of the reaction. This project seeks to fulfill this need through the development of a database of evaluated and estimated chemical kinetic and thermodynamic information. The procedure has been to start with the simplest of hydrocarbons, methane, and then add increasingly complex and more realistic fuel molecules containing the functional groups that are the key to their reactivity and the basis for estimation. Thus smaller saturated alkenes, alkynes, and aromatics have now been examined. An important aspect of this work is the examination of techniques for estimation. Much progress has now been made in developing an understanding of the limitations of the general procedures for extrapolation of data to the high temperatures required for combustion applications.

Physics Laboratory

230. ***Spectroscopic Investigation of the Vibrational Quasi-Continuum Arising from Internal Rotation of a Methyl Group***
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This project studies the vibrational quasi-continuum in acetaldehyde, methanol, and related molecules because internal rotation is important in promoting intramolecular vibrational redistribution (IVR). It aims to understand: (1) torsional motion below and above the barrier, (2) traditional vibrational states, and (3) interactions involving levels with excitation of both kinds of motion. Although a few unresolved problems remain, work on the purely torsional problem is gradually winding down, while work on IVR-enhancing interactions is being intensified. A vibration-torsion-rotation formalism for treating these interactions quantum-mechanically has been developed, in which internal rotation is assumed to be slow compared to the other vibrations, so that Born-Oppenheimer considerations now lead to a separation of rotation and internal rotation from the other vibrations, rather than a separation of rotation from internal rotation and the other vibrations. A verdict on the usefulness of this new formalism, which gives rise to some unusual group theoretical features apparently related to Berry's phase, should emerge during applications this coming year. A new computer program is being applied to torsionally mediated vibrational interactions in acetaldehyde (skeletal bending region) and methanol (C–H stretching region) to determine if a two-state Fermi-resonance model can explain (qualitatively or quantitatively) the "large and inverted" torsional splittings which are observed.

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Department of Chemistry

231. ***Identification and Temporal Behavior of Radical Intermediates Formed during the Combustion and Pyrolysis of Gaseous Fuel***
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The pyrolyses of nitrogen containing aromatic ring compounds are of interest in combustion science particularly with regard to coal and its products. A complementary shock tube study of the decomposition of the simplest of these ring compounds, pyrazine, using laser schlieren densitometry (John Kiefer, UIC) and our time-of-flight mass spectrometric analysis has revealed nonlinear growth of a key product, cyanoacetylene. The temperature dependent maxima and subsequent decay rates of cyanoacetylene and its sensitivity to the initial concentration of H_2 played an important role in formulating a new chain mechanism for pyrazine decomposition. The laser schlieren experiments provided excellent rate data for the initiation reaction, C–H fission, as well as the early rate of chain acceleration over the temperature range 1460–2300K. A value of 96.6 kcal/mol was established for the initiation step. The major products are HCN and C_2H_2; the minor products are C_4H_2 and cyanoacetylene. The existence of a chain reaction with CN radical as the major chain carrier was confirmed. A value of 96 kcal/mol for the heat of formation for cyanoacetylene was selected to match the late time, high temperature profiles as observed by time-of-flight mass spectrometry.

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Department of Chemistry

232. ***Accurate Polyatomic Quantum Dynamics Studies of Combustion Reactions***
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New computational methods are being developed for the time-dependent approach to polyatomic combustion reactions. The new development is aimed at tackling more complex reaction systems that require a large number of basis functions in quantum dynamical approach. The proposed method (normalized angular quadrature scheme) enables one to obtain stable and accurate results without the need for large-matrix storage and large-matrix multiplications. As a result, the benchmark H_2 + OH and its isotopic reaction HD + OH can now be calculated efficiently on a medium-sized workstation. Application of this new method to other combustion reactions is in progress.

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Department of Chemistry

233. ***Unimolecular Reaction Dynamics of Well Characterized Ionic Reactions***
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The dissociation dynamics of energy selected ions are investigated by photoelectron photoion coincidence (PEPICO). Molecules are prepared in a molecular beam so that their internal as well as translational temperature is near 0 K. The primary experimental information includes ionization and fragment appearance energies, and ion time-of-flight (TOF) distributions. The latter permit the measurement of dissociation rates and product energy distributions. One of the broad goals of this research project is the development of simple methods for modeling unimolecular reactions with ab initio molecular orbital calculations and the RRKM statistical theory. Progress in recent years has shown that the dissociation rate constants of simple reactions with well established dissociation energies can be successfully calculated. However, many unimolecular reactions involved in combustion processes are complex in that the molecules isomerize to lower energy isomers prior to dissociation. We have investigated a number of similarly complex ionic reactions and have developed the experimental and mathematical tools to extract valuable information about such processes. In the case of the pentene ion and tri-methyl-borate ion dissociation, we have succeeded in modeling these reactions with three wells and have managed to extract all six rate constants (4 isomerization and 2 dissociation) from the data. The results have been analyzed by a combination of ab initio molecular orbital, and RRKM statistical theory calculations. These experiments point the way toward analyzing complex reactions in combustion systems, where in general much less information is available. New experiments are planned at the Chemical Dynamics Beam Line of the Advance Light Source. The greater photon flux should make possible PEPICO experiments on dimer ions which dissociate to interesting free radicals. These studies should provide heats of formation of free radicals important in combustion processes. Alternatively, they yield ground state energies of neutral and ionic dimers.

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Department of Chemistry

234. ***Infrared Laser Studies of the Combustion Chemistry of Nitrogen***
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The project under investigation is part of a broad effort to understand at a molecular level the detailed kinetics of combustion processes. The studies in our laboratory concentrate on radical-radical and radical-molecule chemical reactions which either form or destroy NO_x. Many of these reactions are important in NO_x control strategies such as thermal de-NO_x and NO-reburning. The emphasis is primarily on the quantitative determination of product branching ratios for reactions that have several possible channels. We used UV laser photolysis to initiate these reactions, and infrared diode laser spectroscopy to probe reaction products. Some of the reactions recently studied and/or currently under study include $NH + NO$, $NH + NO_2$, $NH_2 + NO_2$, and $CH_2 + NO$.

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Department of Chemistry

235. Dynamical Analysis of Highly Excited Molecular Spectra

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A framework for analysis of highly excited vibrational states of polyatomic molecules is investigated using techniques of nonlinear dynamics, especially bifurcation theory. The goal is classification of the motions of molecules excited to the regime of chaotic dynamics, and determination of patterns resulting from these motions in experimental spectra. Several research areas are being investigated with application to species and methods of interest in combustion processes. The first is a method based on diabatic correlation diagrams applied to polyatomic spectra with chaotic dynamics, specifically, triatomics such as H_2O, and larger molecules such as acetylene. For the triatomics, the critical points of an effective Hamiltonian used for fitting spectra are analyzed, giving the large-scale bifurcation structure of the molecular phase space. An assignment procedure using the bifurcation analysis, in tandem with the correlation diagram procedure, is being investigated. A more phenomenological extension to acetylene is being investigated, where the bifurcation structure is harder to obtain, and at present, unknown. The final research area, with application to experimental spectra of CS_2, is bifurcation and semiclassical quantum analysis of two degree-of-freedom systems with such strong coupling that earlier methods of analysis of chaotic systems are inapplicable.

Pennsylvania State University, University Park
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Department of Chemistry

236. Metal Cluster Alloys and Oxides Elucidating Structural and Electronic Effects in Governing the Reactivity and Catalytic Role of Matter in Finite Dimensions

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Catalytic processes pervade our society, being involved in the efficient utilization of the energy supply of the nation, providing new ways of producing fuels, effecting the control of pollutant emissions, and improving the efficiency of many industrial processes. The enormous benefits which would arise from having the ability to design catalysts with a high degree of selectivity, and ones that could yield the facile formation of a desired reaction product, have been long realized. The present program is addressed to investigations that are intended to provide new insights into the physical basis for catalysis. There is growing awareness that systems comprised of oxides–both in terms of their own innate catalytic activity, as well as their use as supports for other metal catalysts – and in carbides which often display considerable selectivity as catalysts, represent promising materials for further development. An understanding of their general role as catalysts is still in a stage of infancy, but it is recognized that their oxidation state, stoichiometry and charge are intimately associated with their effectiveness as catalysts. Cluster research provides one valuable approach and is the basis for the research being conducted herein. The research program encompasses four general lines of inquiry: (i) investigation of the reactivity of metal-carbon and metal-oxide clusters to determine the influence of oxidation- and charge-state on their reactivity, (ii) determination of the kinetics of absorption and the reaction kinetics of selected molecules that are catalyzed by these metal compound clusters, (iii) thermochemical studies of adsorption onto metal-carbide and metal-oxide cluster systems, and (iv) studies of catalytic reactions which have counterparts to ion-molecule reactions. Investigations are directed to certain well-defined classes of oxides and metal-carbon compounds in terms of the reactions of species formed in combustion processes whose abatement will contribute to the enhanced quality of the environment, and to a study of the build-up of potential higher hydrocarbon fuels through oxidative conversion reactions of small organic molecules. During the last year we gained a great deal of new insight into certain reactive processes involving carbides and oxides of various stoichiometries. Considerable attention has been focused on the reactivity of Met-Cars (M_8C_{12}, where M = early transition metals) which are unique cluster materials discovered several years ago in our laboratory. Particularly noteworthy is work reported dealing with gas-phase reactions of Met-Cars with acetone and methyl iodide and also related studies of these complexes which provide new insight into the structure of Met-Cars and into adsorption reactions. It is found that the formed complexes bear analogies to the nature of bonding involved in the attachment of π-bonded molecules to metal surfaces. In another interesting development in the Met-Car field, we discovered that selected Met-Car cations can be produced through the oxidation of neutral metal-carbon clusters. In other studies of the catalytic properties of niobium oxide clusters, we completed some recent investigations of the oxidation of alkanes and reactions of ketones (acetone) with these species which are common catalysts in related surface reactions. The findings have shown specific cluster size dependencies for various oxygen atom transfer reactions, providing new insights into these important classes of reactions.

University of Pennsylvania Philadelphia, PA 19104

Department of Chemistry

237. *Collisional Energy Transfer of Highly Vibrationally Excited Molecules*
Dai, H.L. **$110,000**
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Using a recently developed Time-Resolved Fourier Transform Emission Spectroscopy technique in the IR region we have studied collisional deactivation of highly vibrationally excited molecules. Collisional energy transfer is crucial for activating and/or deactivating thermal and photoinduced unimolecular and bimolecular reactions of molecules that are important to energy production and environment concerns. Collisional energy transfer of NO_2 (excited to as high as 22,000 cm^{-1}), SO_2 (32,000 cm^{-1}), CS_2 (32,000 cm^{-1}), and pyrazine (40,000 cm^{-1}) to a variety of collisional partners has been characterized. Among the many interesting observations are the ones that point to a surprising revelation that the mechanism responsible for energy transfer of highly excited molecules, in contrast to those excited at lower energies, is dominated by long range, Coulombic interactions. These observations are: 1) The transition-dipole coupling model quantitatively describes the V-V transfer probability. 2) Even though the V-T transfer probabilities for molecules excited at lower energies appear to be dominated by kinematic effects associated with hard sphere collisions, for molecules excited at much higher energies it seems that collisional partners with higher polarizability are more effective. 3) For excited molecules such as NO_2 and CS_2 with strong vibronic coupling at higher energies, the amount of energy transferred appears to increase dramatically with molecular excitation passing a threshold. The threshold energy for a specific excited molecule is always at the same value for all collision partners and correlates well with the beginning of vibronic coupling within the excited molecule, indicating again the effect of transition dipole coupling. These observations have pointed to a most effective mechanism for energy transfer out of highly excited molecules: the large amount of energy transferred, wither through V-V or V-T/R channels, to an ambient collider is through long range, Coulombic interactions!

238. *Intermolecular Interactions of Hydroxyl Radicals on Reactive Potential Energy Surfaces*
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This program is focused on the characterization of the interaction potentials between the hydroxyl radical in its ground X $^2\Pi$ and excited A $^2\Sigma^+$ electronic states with collision partners of relevance to combustion. Recently, binary complexes of OH and H_2/D_2 have been stabilized in the attractive well region of the entrance channel to the $OH + H_2 \rightarrow H_2O + H$ reaction and probed via electronic spectroscopy. These studies are providing a detailed picture of the OH (A $^2\Sigma^+$, X $^2\Pi$) + H_2/D_2 potential energy surfaces and the reaction dynamics taking place on these surfaces. Current work is aimed at understanding the OH (A $^2\Sigma^+$) + H_2/D_2 and OH (A $^2\Sigma^+$) + N_2 systems and the curve crossings and/or reactive channels that lead to collision-induced quenching of OH (A $^2\Sigma^+$).

University of Pittsburgh Pittsburgh, PA 15260

Department of Chemistry

239. *Optical Imaging in Microstructures*
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Our research is focused on developing morphology-dependent stimulated Raman scattering (MDSRS) into an analytic optical imaging tool that can be used to monitor spatial variations of chemical composition and molecular structure in axisymmetric microstructures. MDSRS relies on using the cavity modes associated with microstructures to enhance optical signal generation. Since different cavity modes occupy different regions in space, location-specific spectra can be generated, i.e. the effect is analogous to that seen in magnetic resonance imaging. In the past year we have demonstrated that MDSRS imaging is feasible. We did this by imaging water structure in the diffuse part of a charged water droplet's electric double layer.

Princeton University Princeton, NJ 08544

Department of Chemistry

240. *Analysis of Forward and Inverse Problems in Chemical Dynamics and Spectroscopy*
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This research is concerned with fundamental issues in molecular science and practical solutions in chemical kinetics engineering problems. The first part of the research aims to develop and apply new algorithms to optimally draw on ab initio quantum chemistry calculations and available laboratory data in order to gain a quantitative understanding of the effect of molecular interactions on spectroscopic, dynamical, and kinetic events. Specifically, mathematical and numerical tools based on functional sensitivity analysis, inverse problem theory, and reproducing kernel theory have been developed for identifying the relationship between potential energy surfaces and observables (forward analysis), and for constructing physically acceptable potential energy surfaces from either laboratory data or ab initio calculations. The second part of the research aims to develop effective dimension reduction methods for constructing simplified, yet accurate, combustion models. Here a recently formulated algebraic-based method, along with nonlinear perturbation theory, has been employed to develop rigorous and efficient nonlinear lumping schemes for combustion model simplification.

Department of Mechanical and Aerospace Engineering

241. *Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis*

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This program addresses improving understanding of combustion chemistry through experimental flow reactor studies in the temperature range 550-1200 K, the pressure range 0.3-20 atmospheres, and with characteristic reaction times from 0.02-3.0 seconds. Through the use of techniques based on elemental gradient-feature sensitivity and path analyses, computations are performed to obtain elementary rate information and to develop and study comprehensive chemical kinetic mechanisms. Elementary kinetic data are obtained from perturbation studies of the $CO/H_2/$ oxidant reaction system by small amounts of hydrocarbons and/or hydrocarbon oxygenates. Of special interest here are the reactions of HO_2 with CH_3 and other species. Reaction systems of interest include those for pyrolysis and oxidation of simple oxygenates (especially formaldehyde, acetaldehyde, and dimethyl ether), simple olefins (especially ethene and propene), and ethane. The research emphasizes the extension of the present knowledge, based on reaction mechanisms of these small molecules, to pressures and temperatures where the reaction of radicals with oxygen and the reactions involving RO_2 and HO_2 are important.

242. *Aromatic-Radical Oxidation Kinetics*

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Elucidation of the details of the oxidation of the aromatic ring of monocyclic aromatic species, key elements in automotive and industrial fuels, has been the main focus of this research effort. Special attention has been focused on the oxidation of C_5 species, in particular cyclopentadiene (CPD), that early work in this laboratory has shown to play an important role in the sequence of steps that bridge the opening of the aromatic ring and the eventual production of carbon dioxide and water. Other species, phenol and anisole, shed light on the chemical mechanism of aromatics oxidation and have also been examined. A brief summary of recent results is now given. After extensive characterization of the Princeton Flow Reactor in order to determine the dependence of previously reported anomalous CO_2 on temperature, equivalence ratio and concentration of reactants, a set of operating conditions was determined that maximizes homogeneous gas phase chemistry and minimizes catalytic surface effects that have plagued previous experiments. At these operating conditions data were obtained at lean, stoichiometric and rich conditions that allow comparison with detailed chemical kinetic model predictions. Preliminary results of the modeling show good agreement with respect to the product profiles, through not the rates which are somewhat slow. Work on improving the model is in progress. A complementary study of anisole is being conducted as a means of more thoroughly examining the oxidation chemistry of the cyclopentapentadienyl radical in the context of a different radical environment. The decomposition of anisole to the cyclopentadienyl radical is accompanied by the production of the methyl radical which is accomplished via cleavage of the methylphenoxy bond followed by a ring contraction to yield CO and cyclopentadienyl.This chemistry has been examined in the Princeton Flow Reactor at a variety of temperatures and stoichiometries that provide reliable data for comparison with models of the pyrolysis and oxidation of anisole. The development of these detailed chemical kinetic models is in progress. Cyclopentadienyl reactions are also being probed though oxidation studies of phenol. Loss of hydrogen from phenol to produce phenoxy is followed by expulsion of CO and ring contraction to form cyclopentadienyl radical. The chemistry of the cyclopentadienyl radical is being inferred from the stable species profiles obtained at a variety of stoichiometries during the oxidation of phenol in the flow reactor.

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Department of Chemistry

243. *Multiresonant Spectroscopy and the High-Resolution Threshold Photoionization of Combustion Free Radicals*

Grant, E.R. **$216,371**
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This project is aimed at characterizing the thermochemistry, spectroscopy and intramolecular relaxation dynamics of an important set of combustion intermediates, which includes radical alkoxides and hydrides of the first-row non-metals. We will prepare these radical systems by the photolysis of established precursors in the expansion region of pulsed free-jets in our differentially pumped laser-ionization source quadrupole mass spectrometer and similarly configured zero electron-kinetic-energy (ZEKE) threshold photoionization spectrometer. Using multiresonant methods which have been well established in our laboratory, we will select individual rotational states and overcome Franck-Condon barriers associated with neutral-to-cation geometry changes to promote transitions to individual autoionizing series and state-resolved ionization thresholds. Systematic characterization of rotational structure and associated lineshapes will provide experimental data on autoionization dynamics as input for theoretical modeling. Extrapolation of series combined with direct threshold photoelectron detection will yield precise ionization potentials that will constitute an important contribution to the thermochemical base of information of these critical combustion intermediates.

244. *Probing Activated Chemical Reactions in Diacetylene and Vinylacetylene*

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The spectroscopy and chemistry of the metastable state(s) of diacetylene (C_4H_2) and vinylacetylene (C_4H_4) are the focus of this research project. Cavity ring-down spectroscopy is being used to study the very weak absorption spectrum of the spin-forbidden $^3\Delta_u \leftarrow {}^1\Sigma_g^+$ transition in C_4H_2. The upper state of this transition is thought to be responsible for much of the photochemistry of C_4H_2 in the ultraviolet. To study the chemistry of these metastable states, a two laser pump-probe scheme is employed in which metastable diacetylene (C_4H_2*) is formed following ultraviolet excitation by intersystem crossing from the singlet manifold. Primary reactive encounters with various small hydrocarbons are probed by exciting C_4H_2 while the gas mixture is in a short reaction tube attached to a pulsed valve. Reaction occurs during the traversal of the reaction mixture down the tube and is quenched as the mixture expands into vacuum. Products are identified using either single-photon vacuum ultraviolet ionization or resonant multiphoton ionization time-of-flight mass spectroscopy. Recent results indicate that the reaction of C_4H_2* with 1,3-butadiene produces two aromatic products: benzene and an as yet unidentified product of mass C_8H_6. These reactions may be important as alternative routes to the first aromatics in soot formation.

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Department of Chemistry

245. ***Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals***
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This research is directed at the detection, monitoring, and study of the chemical kinetic behavior by infrared absorption spectroscopy of small free radical species thought to be important intermediates in combustion. Recently, investigation of the chemical kinetics of the nitrogen containing radical, HCCN, has been initiated. This species has a triplet ground state and a very interesting balance in electronic structure between a diradical structure with one unpaired electron on the terminal C and the other on the N and the triplet carbene structure with both unpaired electrons on the terminal carbon. Thus it is likely to exhibit chemistry with attack at both the terminal C atom and at the N atom. HCCN has been found to react rapidly with NO and O_2 and the rate constants at room temperature for both reactions have been measured as $3.8(3)\times10^{-11}$ cm^3s^{-1} and $2.3(2)\times10^{-12}$ cm^3s^{-1} respectively. Reactivity with ethylene, acetylene, methane, carbon dioxide, and hydrogen at room temperature was found to be slower than the smallest rate we can measure which is approximately 10^{-13} cm^3s^{-1}. A search for reaction products is being carried out. Work previously described on the rate of reaction between singlet methylene and acetylene has been completed and recently published.

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Department of Chemistry

246. ***Low-Energy Ion-Molecule Reactions and Chemiionization Kinetics***
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Crossed ion-beam–neutral beam reactive scattering experiments are being performed with the goal of using product quantum state distributions, energy disposal measurements, and state-resolved angular distributions to extract dynamical information on collision mechanics and features of the potential surface mediating the reaction. Attention has been focused on hydrogen atom transfer reactions of O^- with D_2 and CH_4, where either complete or partial vibrational state resolution of the products has been accomplished. In the $O^- + D_2$ systems, product vibrational states of OD^- up to v' = 4 are resolved over the full collision energy range from 0.25 eV to 1.2 eV. The extent of product vibrational excitation increases with increasing collision energy, and vibrational surprisal plots are consistent with a negative vibrational temperature that decreases in magnitude with decreasing collision energy. In conjunction with angular distributions that become more symmetric with decreasing energy, the data are consistent with incipient statistical behavior at the lowest energies. The $O^- + CH_4$ reaction forming OH^- shows that the product is sharply backward scattered with significant vibrational excitation at 0.34 eV, with the products maintaining their vibrational excitation but becoming forward scattered with increasing collision energy. A series of experiments on O^- with vibrationally excited molecules prepared by laser excitation is planned.

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Department of Chemistry

247. ***Reactions of Atoms and Radicals Using Pulsed Molecular Beams***
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Unimolecular and bimolecular reaction dynamics of atoms and small radicals are being studied using pulsed molecular beams. Exothermic and endothermic reactions of atomic carbon in its ground electronic state are examined using laser ablation of graphite. Endothermic hydrogen transfer reactions of $C(^3P)$ induced by translational energy with H_2, HCl, HBr, H_2S, CH_3OH, CH_3OD, C_2H_2 and CH_4 yield CH radicals. Center-of-mass collision energies with all species except H_2 peak at ~ 2 eV but can exceed 6 eV. The rotational distributions with all reactants are rather similar and can be fit to temperatures in the range 1500-2200 K. In the reaction with methanol there are two reaction sites, methyl and hydroxyl. In the reactions studied so far, the spin-orbit and the Lambda-doublet ratios are statistical. Mechanisms are discussed using the detailed calculations available for the $C + H_2$ system, which indicate that an insertion route is open for these reactions with no or only a small barrier. The reaction with chloroform is being studied as a prototype of a system in which both exothermic and endothermic channels (yielding CCl and CH products, respectively) are open at the employed collision energy. Only a very small CH signal is detected, but large signals from CCl are readily observed. In preparation for the studies of free radicals decomposition, an ion imaging detector has been introduced into a crossed molecular beams TOF machine. With this technique the product state distributions of one product correlated with a specific quantum state of a second product can be determined. Preliminary images of NO from the photodecomposition of nitrogen dioxide and H and CO from the decomposition of isocyanic acid were obtained.

248. *The Stabilization Theory of Dynamics*

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We have developed a new method of carrying out computations on complex systems as HO_2 and NO_2. The former we have published on and the latter we are working on. They are complex because once the first fifty or so vibrational states are exceeded all eigenfunctions (both bound and resonance) become very topologically complex and seemingly unassignable because of the same reasons that cause classical chaos in these energy and configuration regions. For HO_2 the chaos is caused by pure mode coupling. For NO_2 the same reason exists but in addition, chaos and complexity caused by the surface crossing and the conical intersection occurs. The complexity translates into the need to use for eigenfunction representation, very dense and large basis sets or grids. This in turns causes the Hamiltonian matrix to be so large that it cannot be fit into core memory as required by standard methods of diagonalization. We have developed a new iterative recursive polynomial method to compute the action of the Green function on a vector which avoids storing the Hamiltonian matrix in the core. This is what is needed to compute bound, resonant and scattering information. The method is extremely powerful and can be used on present day work stations. Armed with this formalism we developed a two part computational program and we worked on the important to combustion, HO_2 molecular species. We have computed its bound vibrational states, many of its resonant states (with lifetimes), its' density of states and its' total photoadsorption cross section and its' recombination rate. These calculation used our Green function computational scheme in a mode that generates a greatly reduced basis which then uses conventional diagonalization to finish the problem. This not only yielded bound and resonant states but gave a spectral representation that enable us to compute the other mentioned properties. Additionally, we have made a breakthrough in the interpretation of complex spectra. By applying a scaling technique we are able to construct the bifurcation diagram directly from quantum spectra and to compare the results with classical calculations. The method allows the identification of important motions. More diverse systems of greater complexity and dimensionality will be investigated in the future.

249. *Reactions of Small Molecular Systems*

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The focus of this work is complex reaction mechanisms of prototypical molecules and radicals that display phenomena important in combustion chemistry. In the case of NO_3, a detailed understanding is sought for the two unimolecular reaction pathways: $NO + O_2$ and $O + NO_2$, both separately and in competition with one another. This is a case of nearly identical energy thresholds and qualitatively different transition states (i.e., tight versus loose). For the $NO + O_2$ channel, which has a tight transition state, tunneling will also be examined. The main experimental tools are double-resonance and time-resolved pump-probe methods, detecting NO_3 and NO via LIF. C_2H_2 experiments will examine the threshold region, specifically, the roles of intersystem crossings and reactions via zeroth-order triplet versus singlet surfaces. For the case of C_2HD, the H/D ratio provides a good diagnostic. In this case H atoms are detected via 1+1 photoionization or by using the high-n Rydberg time-of-flight (HRTOF) method. With the latter, detailed product state distributions are obtained from the c.m. translational energy distributions, and high sensitivity and good resolution have been demonstrated. Photolytically prepared radicals such as C_2H are also examined.

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Department of Mechanical Engineering

250. *Spectroscopy and Kinetics of Combustion Gases at High Temperatures*

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This program involves two complementary activities: (1) development and application of cw laser absorption methods for sensitive detection of species and measurement of fundamental spectroscopic parameters at high pressures and temperatures; and (2) shock tube studies of chemical reactions relevant to combustion. Species of interest in the spectroscopic portion of the research include OH, HO_2, CO_2 and CH_3. Recent shock tube studies of reaction kinetics have been focused on the reactions $HNCO + OH \rightarrow CO_2 + NH_2$, $HNCO + OH \rightarrow$ products, $H + O_2 \rightarrow HO_2$, and $CO + OH \rightarrow CO_2 + H$.

State University of New York at Stony Brook
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Department of Chemistry

251. *Ionization Probes of Molecular Structure and Chemistry*

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Ionization processes in intense, wavelength-tunable laser fields are being used in new spectroscopic techniques to investigate the spectroscopy and photochemistry of ions and molecules. Resonant multiphoton ionization, laser threshold ionization spectroscopy, and photoinduced Rydberg ionization (PIRI) spectroscopy provide sensitive tools for the detection of transient species and for examining the excited state structure and dynamics of molecules. These methods also provide means for the detection and identification of minute quantities of molecular species in difficult environments such as the mixtures produced in combustion reactions. Newly developed primary tools in these studies are mass analyzed threshold ionization spectroscopy (MATI), which provides high resolution ion vibrational spectra of selected molecules, and PIRI, which gives access to the excited states of ions. In MATI the various ionization thresholds that mark the energy states of an ion in transitions from a neutral state are measured by using the fact that very highly excited neutral states near each threshold can be ionized by an electric field. In PIRI the final ionization is accomplished by the absorption of a further photon. The ions produced in either method are sent through a mass spectrometer so the optical spectrum of each mass is obtained with high sensitivity. These techniques are being used to refine our knowledge of the molecular orbital structure of benzene and substituted benzenes, molecules which play an important role in many combustion processes.

University of Utah
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Department of Chemistry

252. ***Thermochemistry and Reactivity of Transition-Metal Clusters***
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The objective of this project is to obtain information regarding the thermodynamic properties of transition metal clusters, their binding energies to various ligands, and their reactions by using a metal cluster guided ion beam mass spectrometer and a cluster ion photodissociation spectrometer. Recent progress includes studies of the reactions of vanadium, chromium, and iron cluster ions with D_2 and O_2. In the D_2 reactions, metal cluster monodeuteride ions are observed as the major product for all systems. The kinetic energy dependence of these reaction cross sections is analyzed to yield cluster ion-deuterium atom bond energies. Larger cluster ions also react with D_2 to form dideuteride cluster ions in what is believed to be an activated dissociative chemisorption process. In the O_2 reactions, cluster dioxide product ions are formed efficiently in exothermic processes for all three metal systems examined. Less abundant are cluster monoxide product ions which are formed in endothermic reactions. Analysis of the kinetic energy dependence of these reactions is particularly complicated, but thermodynamic information about the binding energies of one and two oxygen atoms to the clusters can be obtained. The trends in this thermodynamic information provide clues regarding the geometric and electronic structures of the bare clusters.

253. ***Spectroscopy of Polyatomic Transition Metal Clusters and Unsaturated Transition Metal-Ligand Complexes***
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In this project we use electronic spectroscopy to investigate the chemical bonding and electronic structure of unsaturated transition metal-ligand complexes and polyatomic transition metal clusters. Our aim is to develop an experimental knowledge base which will elucidate the chemical bonding and electronic structure of these species, enabling a correlation between electronic structure and reactivity to be drawn. A second aim is to investigate several molecules in sufficient detail to provide stringent tests of theoretical calculations on these computationally challenging molecules. Throughout this grant we have used pulsed laser ablation in a supersonic expansion of helium along with resonant two-photon ionization spectroscopy to investigate species formed when metal is ablated in the presence of methane. Our spectra of RuC have led to a definitive identification of its ground state along with 9 excited electronic states. Our spectra of MoC have enabled its ground state symmetry and bond length to be determined, and studies of FeC have permitted many excited states to be characterized. Most interesting, however, is our observation of complex organochromium molecules which are formed in the chromium-methane laser-induced plasma. In some, such as $CrCH_3$ and CrCCH, chromium replaces hydrogen in an otherwise stable molecule. Others have a more complicated structure, as in $CrCH_2$ and CrC_3H_2. Work is in progress to completely analyze the spectra of these organochromium species.

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Department of Chemistry

254. ***Photon and Electron Stimulated Surface Dynamics of Single Molecules***
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The aim of this proposal is to initiate fundamentally new studies of the surface dynamics of individual molecules. Recent technological advances in the field of low temperature scanning tunneling microscopy (STM) have made it possible to image and even manipulate single molecules adsorbed on metal surfaces. Thermal drift problems inherent to the construction of STMs from piezoelectric materials have impeded the development of low and variable temperature STMs which might be able to follow the kinetics and possibly the dynamics of thermally activated processes of single adsorbates in real time. Rather than studying thermally activated processes, we propose to examine the dynamics of photon and electron induced chemistry of single molecules using low temperature STM. The ability to study individual events occurring for molecules absorbed at specific surface sites or next to coadsorbed molecules with specific relative stereochemical geometries provides us with radically new dynamical information which is unattainable from conventional studies involving ensembles of molecules. The specific goals of our project are to examine, at the level of individual molecules, (1) the photodissociation dynamics of adsorbates whose photofragments remain trapped on the surface, (2) the dynamics of localized adsorbate chemistry induced by electrons emitted from the STM tip, (3) bimolecular photoreactions between coadsorbed molecules with prearranged relative stereochemistry. The results of our work should improve our fundamental understanding of surface chemistry and the technological prospects for spatially localized processing of materials by photons from focused laser beams and electrons emitted from STM tips.

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Department of Chemistry

255. ***Atomic Probes of Surface Structure and Dynamics***
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In the last year, we have extended our reversible work-based formulation of transition state theory (TST) for calculating transition rates in multidimensional systems. One important challenge has been to extend TST to systems with quantum degrees of freedom. The most commonly used quantum TST has been the centroid density formulation originally suggested by Gillan. This had been tested and found to work well for symmetric transitions. We have, however, found that the centroid density approximation does not work well for asymmetric systems at low temperature when tunneling becomes an important transition mechanism. We have formulated a new quantum transition state theory where the transition state is defined as a NP-1 dimensional cone in the space of all closed Feynman paths represented by P beads, rather than a surface in classical N-dimensional space of the system coordinates. The free energy barrier is evaluated by reversible work in this `action-space' and we refer to the method as Reversible Action-space Work Quantum Transition State Theory (RAW-QTST). It has been found to work well on test problems, including asymmetric transitions at low temperature. We have also applied the method to a very large system, H_2 desorption from Cu(110) surface, where the two H atoms and eight Cu atoms where treated fully quantum mechanically and about 200 Cu atoms were included classically. In a harmonic limit, applicable at very low temperature, the theory reduces to so called instanton theory. At high temperature, above the crossover temperature for tunneling, the theory reduces to the centroid density approximation and in the classical high temperature limit the classical variational TST is recovered. This work is carried out in collaboration with Dr. Greg Schenter and Dr. Bruce Garrett at the EMSL of Pacific Northwest National Laboratories.

University of Wisconsin at Madison Madison, WI 53706

Department of Chemistry

256. *Vibrational State Control of Photodissociation*
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The fundamental and practical importance of highly vibrationally excited molecules in combustion processes, atmospheric chemistry, plasmas, and a host of other environments motivates their detailed experimental investigation. This research uses a combination of laser excitation to prepare highly vibrationally excited molecules with single-quantum-state resolution, and spectroscopic detection to monitor the excited molecule or its decomposition product, in studies of the unimolecular reaction, photodissociation, and bimolecular reaction dynamics of vibrationally energized molecules. A collection of state preparation and detection techniques gives these measurements broad scope. The excitation approaches are vibrational overtone excitation, stimulated emission pumping, and stimulated Raman excitation, and the detection methods are UV and VUV laser-induced fluorescence and laser-induced grating spectroscopy. By selectively preparing vibrational states and subsequently dissociating or reacting them, these experiments explore normally inaccessible regions of both the ground and electronically excited potential energy surfaces. These approaches have even achieved laser control of the course of a chemical reaction. The experiments provide new insights into the structure and dynamics of vibrationally excited molecules, which play an important role in fundamentally and practically important processes.

257. *Spectroscopy Studies of Methyl Group Internal Rotation and of Organic Free Radical Vibration*
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One long-term goal of this work is to develop new techniques for measuring vibrational spectra of polyatomic neutral-free radicals. Toward that end, an optical parametric oscillator (OPO) has been constructed based on the crystal KTP and pumped by the second harmonic of an injection-seeded Nd:YAG laser to provide tunable near-IR. Testing of this device is underway. IR absorption will be detected by depletion of laser-induced fluorescence from $v = 0$ radicals formed by photolysis of suitable precursors upstream in a pulsed nozzle expansion. In addition, work will be initiated to address the spectroscopic problem of internal rotation of methyl and silyl groups attached to aromatic rings. Statistical modeling of chemical reactions of molecules that include methyl rotors requires good intuition about whether internal rotation is nearly free or hindered. Internal rotors present relatively tractable examples of noncovalent interactions that determine the energetics of different molecular conformations as well. Such rotors also accelerate intramolecular vibrational redistribution and alter photochemical pathways. From a combination of spectroscopic experiments and ab initio calculations, an understanding is developing of the pattern of rotor barriers vs. electronic state and also the effects of chemical substitution at different locations on the benzene ring. The result is a growing intuition about the mechanism by which noncovalent interactions within a molecule determine the potential energy function for internal rotation.

Atomic, Molecular, and Optical Physics

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Division of Physics, Mathematics, and Astronomy

258. *Spectroscopy with Nonclassical Light*
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Radiative interactions of simple atomic systems with light, which is manifestly quantum or nonclassical in its characteristics, will be investigated. Examples of nonclassical radiative fields include squeezed states of light and states that exhibit photon antibunching and sub-Poissonian photon statistics. Frequency tunable sources of such fields are being developed in the laboratory with the objective of exploring a variety of applications in atomic spectroscopy. From the perspective of quantitative spectroscopic analysis, squeezed light offers the potential for enhanced sensitivity beyond the usual quantum limit set by the vacuum fluctuations of the electromagnetic field (the so called coherent-state or shot-noise limit). However, in addition to the possibility for improved measurement sensitivity, the coupling of atoms to squeezed, antibunched, or sub-Poissonian fields should lead to fundamentally new atomic radiative processes relevant to diverse problems in optical physics, including resonance fluorescence and laser operations. Apart from the scientific objectives, the research program should make important contributions to a number of areas of technological significance, including spectroscopic detection of weakly absorbing or transient species and efficient harmonic generation from the near infrared into the blue.

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Department of Physics

259. ***Few-Body Coulomb Systems***
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Advances in bright, high-energy light sources have promoted double photoionization as a fundamental technique for studying the few-body Coulomb problem, including double escape near threshold. We have extended our fourth-order Wannier description of the unstable equilibrium in the three-body potential, or "Wannier saddle," to include non-zero total angular momentum. A key element is the electron-pair center-of-mass momentum, which is fully represented by the momentum of the recoiling ion. We have thus derived general and Wannier-theory predictions for recoil-ion angular distributions in good agreement with recent experimental observations. In a related project, we have analyzed antiproton impact ionization of hydrogen near threshold from the point of view of an unstable dynamical equilibrium. We show that the instability is displaced from the potential saddle–the center of charge of the antiproton and the electron–with the proton on the line between the negative pair but about six times closer to the proton than to the electron. We have derived the threshold law and considered possible negative-ion probes of these fundamental Coulomb instabilities.

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Department of Physics

260. ***Studies of Photon and Electron Interactions with Atoms and Ions***
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Electron and photon interactions with ground and excited atoms, ions and molecules of importance in lasers, astrophysical, and laboratory fusion plasmas are studied to understand the underlying physics, and the results are used to guide both theory and measurements. Two new theoretical methodologies have been developed for small-angle electron DCSs for optically allowed transitions in atoms, ions and molecules and used successfully. They provide a stringent test of both theory and experiment and are utilized to assist measurements and calculations obtain reliable small-angle, particularly at zero degree, DCSs for optically allowed transitions. The first method is a dispersion relation for the electron DCSs in the momentum transfer squared, K^2, at fixed energy E, which leads to a complex angular momentum Regge pole representation. This description, which embeds the more reliable large scattering angular measurements, allows an accurate extrapolation of the generalized oscillator strength (GOS) down to $K^2 = 0$, yielding the optical oscillator strength (OOS). This method has been employed to justify the successful universal extrapolation method. The second method is the recently developed theory of the GOS for forward electron scattering for optically allowed transitions in atoms, molecules and ions. The method provides a unique path to reach the OOS at $K^2 = 0$ without traversing the nonphysical region and reveals the wide range of applicability of the first Born Approximation for small-angle electron scattering. The R-matrix method is used with extensive configuration interaction target wave functions that account for correlation and core-polarization effects. It is used to calculate integral and differential cross sections. Detailed multistate phototoinization calculations are performed for ground and innershell excited states to investigate and understand recent predictions and experimental measurements demonstrating strong enhancement of shake-up satellites and many-electron effects in sodium and potassium.

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Department of Physics

261. ***Ion/Excited-Atom Collision Studies with a Rydberg Target and a CO_2 Laser***
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A series of experiments will study collisions between multiply-charged ions and highly-excited neutral atoms. The highly-excited "Rydberg target" is formed by laser excitation of a Rubidium atomic beam. The multiply-charged ions are obtained from the CRYEBIS ion source at Kansas State University, where these experiments will be carried out. The studies will determine both the total charge capture probability and the distribution of internal energy in the highly-excited ions formed by charge capture.

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Department of Physics

262. ***Physics of Correlated Systems***
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The theoretical studies of this project focus on the description of quantum mechanical correlations in a number of different systems in atomic physics. We focus on correlations, or coupling between different degrees of freedom, because these are responsible for all forms of energy transfer from one type of motion into another. One arm of the present research effort strives to understand the behavior of open-shell atomic systems in regimes that are not readily handled by conventional theoretical methods based on an independent electron approximation. Substantial headway made by this project has now given us the capability to calculate complex resonant photoionization spectra even for transition metal atoms such as titanium, reproducing the bulk of experimental observations. The theoretical description of negative ion photodetachment has also progressed to allow the treatment of far more challenging species and energy regimes. More recently, we have begun a new thrust to explore the collisions among three identical bosons, which could be either in free space or else confined in a trap. This has already elucidated some issues relevant to recent experimental observations of Bose-Einstein condensation. This work will continue as we investigate the many-body excitations which occur when a condensate of trapped atoms is driven by a periodic perturbation.

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Department of Physics

263. ***Experiments in Ultracold Collisions***
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Laser-cooled atoms are being used to investigate atomic collisions at temperatures below 1 mK. These extremely low energy collisions are of interest because of the large collisional deBroglie wavelength, the dominant role played by the long-range interatomic potentials, and the fact that spontaneous decay can occur during the course of the slow collision. Applications of laser cooling generally require high density. Under these conditions, collisions can be an significant loss mechanism. Understanding and/or control of these collisions will be important for future progress. In the experiments, diode lasers are used to confine rubidium atoms at high density in a magneto-optical trap. Inelastic trap-loss collisions are observed by measuring the ejection rate of atoms from the laser trap. The dependence of the trap-loss collision rate on parameters of the laser trap has been investigated in detail. Suppression (or shielding) of inelastic collisions with laser light has been demonstrated. A cooperative effect involving collisions induced by two separate lasers has been observed and explained in terms of a collisional flux enhancement. Efficient excitation to the highly-excited 5D level has been achieved using pulses of diode laser light in the counterintuitive order. This will allow collisions of Rb 5D atoms to be investigated.

Cornell University
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School of Applied and Engineering Physics

264. ***Interactions of Highly Charged Ions with Atoms at keV Energies***
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This is an experimental project to investigate interactions between very highly charged ions and atoms at kinetic energies characteristic of thermonuclear fusion and astrophysical plasmas. The fundamental processes studied include single and multiple-electron capture, target ionization, and de-excitation of the highly excited projectile states formed in collisions with free atoms and atoms on surfaces. The data obtained are useful for modeling plasma behavior and contribute to the general understanding of low energy atomic collisions. Highly charged ions are produced by the Cornell superconducting solenoid, cryogenic electron beam ion source, CEBIS. The ions extracted from CEBIS are charge-selected and decelerated to energies around 100 qeV (where q is the ion charge). The q+ ions interact with either a gas or a Si(111) target. High resolution electron spectra in coincidence with recoil target ions for $Ar^{(q+)}$ ($8 \leq q \leq 16$) projectiles incident on Ar and other gas targets provide information on the multi-electron capture process. Energy gain spectra measured at different scattering angles are used to obtain a more detailed picture of highly charged ion-surface interactions.

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265. ***Theoretical Investigations of Atomic Collisions***
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Collisions at ultralow temperatures are under investigation as a source of information about the interactions between atoms at large distances.Theoretical methods for the calculation of atomic interactions are being developed. A new procedure for incorporating the effects of correlation in multiple ionization events is being explored. The charge transfer cross sections for doubly-charged nitrogen ions in helium are determined using a close-coupling formalism.

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Department of Physics

266. ***Atomic Physics of Strongly Correlated Systems***
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This research program focuses on the physics of strongly correlated atomic systems. The hyperspherical method is being developed for studying three-electron atomic systems, with the main emphasis on doubly and triply excited states. For doubly excited states the goal is to develop hyperspherical close coupling method to obtain accurate positions and widths and photoabsorption cross sections. For triply excited states the goal is to analyze the correlation patterns of these states in order to find new classification schemes. Studies in general three-body systems will focus on higher energy regions where three-body breakup channels are open and on systems where the interaction potentials are not restricted to Coulomb interactions. In ion-atom collisions the close coupling method using two-center atomic orbitals have been reexamined with the aim of achieving benchmark results for simple systems. This is achieved by optimally choosing the basis functions on one center or another. Work is being undertaken also in the study of differential cross sections and coherent parameters in ion-atom collisions, focussing on weak channels. We also continue theoretical developments in providing tools for analyzing recoil-ion momentum spectra and ejected electron spectra in response to the recent experimental activities in this area.

267. *Atomic Physics with Highly Charged Ions*

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The primary goal of the project is to understand at the most basic level binary collisions involving highly charged ions and individual targets and to provide conceptual frameworks and descriptions useful in understanding interactions of highly charged ions with matter in more complex situations. The facilities used include: (a) a cryogenic electron beam ion source (CRYEBIS) capable of delivering highly charged ions up to bare argon and Xe^{46+} at velocities between 0.1 and 2.0 a.u., (b) a tandem-LINAC accelerator delivering fast beams with specific energies up to 4 MeV/amu in charge states up to, for example, hydrogen-like chlorine, and (c) an ion-ion collision facility. The targets used include neutral gases, ions, Rydberg atoms, clusters, and solid surfaces. Quantities measured include electron spectra, both characteristic and continuum; differential and total cross sections for electron transfer, excitation, and ionization; and recoil momentum distributions. Recent experiments focus on the role of quasi-free electron scattering in ion-atom collisions, and the relationship between electron-ion and atom-ion scattering. Saturation effects in ionization of light targets by very highly charged projectiles are studied through total cross-section measurements. An atomic hydrogen target is in use for the study of continuum electrons produced by fast ion bombardment, and a supersonic cold He gas jet is in use for high resolution recoil momentum spectroscopy in fast-ion/He collisions. The first measurements of absolute differential cross sections for inelastic electron scattering from ions were obtained from ion-atom scattering and compared to a close coupling R-matrix calculation. The study of the effective threshold for direct ionization in collisions of slow bare nuclei with neutral targets, in competition with well understood electron capture, is continuing. Measurements of electron capture from Rydberg targets by highly charged projectiles are being carried out, and efforts to characterize the final states populated are in progress. The mechanisms for the breakup of molecules by fast ion bombardment and the importance of the alignment of the molecule with respect to the beam are under study. Interactions of slow, highly charged ions with graphite and mica surfaces are underway. All projects are part of a joint experimental/theoretical study, and the development of theoretical techniques, models, and conceptual frameworks is an integral part of the program.

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Department of Chemistry

268. *Atomic Physics in Strong Fields*

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New nonperturbative theoretical formalisms and accurate and efficient numerical techniques are being developed for ab initio studies of several atomic and molecular processes in intense laser fields of current significance. In particular, a generalized complex-scaling pseudospectral technique along with non-Hermitian Floquet formalism has been developed for the exploration of (i) above-threshold multiphoton detachment of (H^-) in two-color laser fields: angular distribution and partial rates and (ii) two-color phase control of high-order harmonic generation. Further, we have performed the first theoretical study of the chemical bond hardening and molecular stabilization of diatomic molecular ions in one- and two-color laser fields. Finally, a new adiabatic approach has been developed for the treatment of multiphoton dynamics driven by intense laser pulses.

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Department of Physics and Astronomy

269. *The Dynamics of Weakly-Bound States in Collisions and Fields*

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Several processes associated with the dynamics of weakly bound atomic electrons in time-dependent external fields and in ion-atom collisions are investigated. The first of these, selective-field ionization (SFI), is a widely used experimental diagnostic of Rydberg state populations. A new theory of SFI involves the coherent time evolution of many interacting states, requiring numerical studies of the effects of ramped electric fields on state mixing and ionization as well as the development of analytical methods for handling linearly varying fields. In the case of oscillatory applied fields, a new discrete-time representation of Floquet analysis is applied to the microwave spectroscopy of Rydberg states, including a study of ionization probabilities of nonhydrogenic atoms. A discrete-time approach is also being developed for charge-transfer collisions involving highly excited target atoms. This approach extends the applicability of eigenchannel R-matrix methods to the evolution of Rydberg states in dynamic two-center fields.

270. *Coherent Excitation of Autoionizing Resonances*

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Atomic ionization by electron impact is being investigated by (e,2e) spectroscopy. Experiments with a cadmium target have observed interference effects between partial waves of differing multipolarity. The technique measures (e,2e) energy spectra for carefully chosen ejected-electron directions and makes use of the fact that dipole ionization in cadmium is due almost entirely to autoionization in the ejected-electron energy range of interest. A comprehensive set of measurements has been carried out for an incident beam energy of 150eV and scattering angles between 2° and 18° which covers the range of momentum transfer 0.2 to 1 au. A comparison between the experimental results and a plane wave Born approximation calculation enables two important conclusions to be drawn. Firstly, the calculated monopole and quadrupole phases (relative to the dipole) are incorrect by $+/-\pi/4$. It is found that a simple constant correction is valid over the entire momentum transfer range investigated. Secondly, contrary to expectations, the calculated magnitudes result in better agreement between theory and experiment as the momentum transfer increases. Thus a factor of two correction for the monopole and quadrupole magnitudes, which is necessary at the smallest momentum transfer, is unnecessary for momentum transfer ≥0.5. Present experiments in cadmium are investigating post-collision interaction effects; the Coulomb interaction between the fast and slow outgoing electrons results in an autoionizing resonance position and line shape that depends on the ejected-electron direction; preliminary experiments have found such effects. A second (e,2e) spectrometer is being configured for experiments in helium.

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Department of Physics

271. ***Hydrogen Atom and Molecule Collisions***
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Radiative collisions involving excited states of atomic and molecular hydrogen are being studied with optical, vacuum ultraviolet, and laser spectroscopy. The shock wavefront produced when a Q-switched laser is focused into H_2 heats a small volume of the gas, dissociating the molecules and leaving in its wake a dense atomic gas which provides a source of hydrogen atoms for these experiments. Well-defined conditions are selected by varying the time delay from the arrival of the laser pulse. Current work includes the measurement of fluorescence near Lyman-alpha, and theoretical analyses of H–H and H–H^+ collisions at densities high enough to observe several atoms interacting simultaneously with the radiator. Observations of the spectral line profiles from Na atoms added to the source probes radiative collisions of unexcited atomic H with excited Na. In other experiments, a short wavelength excimer laser pulse focused into H_2 produces H^- through multiple photon processes. The details of this and the subsequent interaction of the H^- with ions such as Al^+ to produce population inversion and laser are also under study.

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Department of Physics

272. ***Theoretical Hyperfine Structure Constants and Lifetimes for Transition Metal Atoms and Ions***
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Transition metal atoms are technologically important for plasma diagnostics, catalysis, deep level traps in semi-conductors, hydrogen storage and astrophysics. Their properties often involve large correlation and substantial relativistic effects which we treat using relativistic configuration interaction methods, which we have developed. We are now concentrating on improving our hyperfine structure accuracy by including more core-valence and second-order correlation effects (triple and quadruple excitations). In particular, in the isoelectronic Cs II and Ba III ions, we have found important contributions from 4d electrons, for the first time, and pointed out the need for (re-) measurement of many of the hfs constants. We have extended our work to include a lifetime study of Nb II 4d3 5p levels; we find our length and velocity values bracket the measurement, with a spread of 10%. Our second lifetime study will be on La II; we are already finding the presence of 4f electrons in the excited states requires the presence of additional core correlation. Finally, we have upgraded our computer hardware (to an Alpha 250 4/266) and our software; the total efficiency gain is a factor of 20. Runs on complicated species like U, now take 3 hours instead of 50 hours.

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Center for Ultrafast Optical Science

273. ***Atomic Processes in High-Energy-Density Plasmas***
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The plasmas that can be produced by a new generation of ultrashort-pulse-duration lasers have unique, and independently controllable, parameters, such as electron density, temperature, excited-state populations, and ionization stages. Atomic processes in plasmas–which are usually complicated functions of several of these parameters–may thus be studied in a controlled manner. By investigating the phenomenon of continuum lowering, this project addresses the question: at what point is an electron bound to an ion? A bound state for an isolated ion is predicted to be a free state in a high-density plasma. The bound-state series-limits of various ions are being measured by use of high-spectral-resolution and short-wavelength absorption- or emission-spectroscopy. High temporal resolution is obtained with a laser-produced–continuum-radiation source and/or a streak camera, both of which are synchronized with the laser-plasma interaction and provide picosecond temporal resolution. By use of these ultrashort time scales, highly ionized plasmas, with electron densities held constant (near-solid density), are studied over a range of electron temperatures from a few electron volts to a kilovolt. The results of experiment are compared with the predictions of current theoretical models by means of both computer simulation and analysis.

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Department of Physics and Astronomy

274. ***Dynamics of Collision Processes***
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This project seeks to obtain a unified point of view for understanding the dynamics of a number of collision processes involving electron-alkali systems, specifically, single- and multiphoton detachment of negative alkali ions, low-energy electron alkali scattering, and collisional detachment of negative alkali ions. Emphasis is placed on discovering propensity rules and characteristics of highly excited, correlated-electron states produced in these processes. Eigenchannel R-matrix methods will be used to perform the numerical calculations proposed. Recent work has focused on highly excited, correlated two-electron features in Li^- and Na^- photodetachment processes. Calculated predictions have been compared and contrasted with similar calculated results for the negative hydrogen ion.

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Department of Physics

275. Screening Resonances in Plasmas
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The interaction potential between atomic ions and electrons in plasmas has consistently been modified to include short-range order and dynamical screening effects introduced by neighboring ions and fast electrons. These modifications determine one-electron properties (e.g. spectral lines which serve as key quantities in plasma diagnostics) as well as more-electron properties (e.g. dielectronic recombination rates which account for plasma losses). So far, the applications have been restricted to the usual Debye-Hückel theory which has been used to extend standard and non-standard atomic structure programs. Furthermore, the approach to screening has been generalized to encompass also dynamic screening effects in order to account for ion motions. The approach allows the simultaneous evaluation of level broadening and continuum threshold lowering. Basic features of line broadening have been incorporated into the theory while line splitting (due to deviations of the immediate ion environment from sphericity) is presently being programmed. Calculations for the important case of a hydrogen plasma exhibit an unexpectedly high abundance of negative hydrogen ions in a variety of plasma conditions and even the possibility of excited states of this ion. The main focus of this study, the occurrence and stability of the negative hydrogen ion in plasmas, has so far been of interest for astrophysical plasmas, this ion being the main contributor to the opacity of white dwarf stars and one of the main contributors to the opacity of the solar chromosphere. The present findings indicate, however, that the opacity of a broader range of plasmas may be affected also, e.g. laboratory plasmas and, possibly, even fusion plasmas.

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276. H^- Spectroscopy
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Experimental studies are being continued on the spectroscopy of the negative ion of hydrogen. Earlier work on this project has been done on an 800 MeV H^- beam at LAMPF using laser beams Doppler-shifted into the vacuum ultraviolet. The last measurement made before the high-energy beam line closed was a study of the interaction of the H with a series of thin foils and a determination of the branching ratios for the production of parabolic substates of the hydrogen atom as a function of foil thickness. The carbon foils used, ranging in thickness from 10 to 500 $\mu g/cm^2$, were considered to cause sub-femtosecond perturbations of the negative ion. The fourth paper on the foil measurements is nearing completion. A series of experiments to study excess photon detachment of electrons from H^- using a 35 keV beam at Los Alamos is underway. Our observation of the lowest singlet D resonance in H^- using a two-photon process from the ground state has demonstrated the feasibility of using lasers to address other dipole forbidden states in this ion. In current measurements a seeded YAG 1.06 pulsed laser beam is focussed on the H^- beam and the energy spectrum of the detached electrons observed. Two electron energy groups, separated by the energy of a single light quantum, are observed in the photodetachment continuum. From the angular distributions the ratio of S to D production can be deduced. An experiment using the same basic apparatus to observe the region of the Feshbach and shape resonance in H^- under high resolution with a tunable VUV laser beam developed at Los Alamos is under construction. In these measurements the singlet P Feshbach resonance will be viewed with unprecedented resolution, and an accurate measurement of the branching ratio of the shape resonance will be made.

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Department of Physics

277. Molecular Structure and Collisional Dissociation
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Electron collision techniques are used to probe the structure and the collisionally induced break-up of various technologically important species. We studied the electron-impact ionization and dissociative ionization of SO_2, CH_4, and the free radicals CH_3, CH_2, and CH. Work on the silane radicals $SiH_x$and on NH_x (x=1-3) is in progress. The work involving CH_x, SiH_x, and NH_x is motivated (i) by data needs for fundamental processes in low-temperature plasmas and the further development and quantitative interpretation of plasma diagnostics techniques (e.g., threshold ionization mass spectrometry) and (ii) by fundamental aspects (comparison of measured data with calculations and establishment of scaling laws and data trends for targets of similar structure). Simultaneously, we continue work on the extension of a semi-empirical method of calculating electron-impact ionization cross sections of atoms to calculations of ionization cross sections for hydrogen-, helium-, and lithium-like ions, for the multiple ionization of atoms, and for the ionization of molecules, radicals, clusters, and fullerenes.

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Department of Physics

278. *Atomic Structure of Highly-Charged Ions*

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Atomic properties of multiply-charged ions are investigated using excitation of energetic heavy-ion beams. Spectroscopy of excited atomic transitions is applied from the visible to the extreme ultraviolet wavelength regions to provide accurate atomic structure and transition rate data in selected highly ionized atoms. High resolution position-sensitive detection has been introduced for measurements in the extreme ultraviolet region. The detailed structures of Rydberg states in highly charged beryllium-like ions are measured as a test of long-range electron-ion interactions. The measurements are supported by multiconfiguration Dirac-Fock calculations and by many-body perturbation theory. Additional studies of high-angular-momentum Rydberg transitions are being performed to establish reference wavelengths and improve the accuracy of ionization energies in highly charged systems. Precision wavelength measurements in highly charged few-electron ions are underway as tests of the most accurate relativistic atomic structure calculations. Precision lifetime measurements in laser-excited alkali atoms have been initiated to establish the accuracy of relativistic atomic many-body theory in many-electron systems.

279. *Precision Measurements of Atomic Lifetimes in Alkali Like Systems*

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This project focuses on precision measurements of excited state lifetimes in neutral alkali and alkali like charged systems. Scientists in astrophysics, geophysics, and plasma fusion depend on such lifetime measurements as means for calibrating relative values of oscillator strengths. From a theoretical point of view, alkali like atoms provide the simplest open shell systems for detailed comparisons between experiment and theory. In addition, the interpretation of parity nonconservation experiments requires accurate knowledge of atomic structure including radial matrix elements. The goal of this project is to address these needs experimentally and provide tests for atomic theory. An apparatus has been constructed for measuring atomic lifetimes by laser-excitation of a fast-atomic beam. This technique is extremely versatile and can be applied to a wide variety of atomic systems. The experiments are being carried out in the new Atomic Physics Accelerator Laboratory at Notre Dame (APALaND).

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Department of Physics

280. *Electron Transfer, Ionization, and Excitation in Atomic Collisions*

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The processes of electron transfer, ionization and excitation in intermediate- and high-energy ion-atom and ion-molecule collisions are studied theoretically. Recently, proton and alpha-particle collisions with sodium atoms have been treated for energies ranging from 1 to 100 keV per amu. A coupled-channel approach using Sturmian pseudostates has been employed to account for the strong interaction among the transfer, ionization and excitation channels. Generally, very good agreement with experiment is found. The double excitation of helium atoms in collisions with protons has also been studied using this approach. A channel-distorted strong-potential-Born (perturbative) approach has been applied to electron transfer by protons from the K shell of atomic negative ions and targets along a sequence, for example, isoelectronic or involving various stages of initial target ionization. Scaling rules have been determined. Additional studies involving excited states have also been carried out. The second-order Faddeev and Born approaches have been applied to electron transfer in collisions of protons with spatially oriented hydrogen molecules and molecular ions at collision energies in the range of 0.5 to 10 MeV. Interference effects deriving from the two target nuclei have been studied.

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Department of Physics and Astronomy

281. *Amplitude Modulation of Atomic Wavefunctions*

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This project uses a novel laser excitation method in conjunction with the electron-electron interaction in a multi-electron atom to modulate the electronic wavefunction of a single electron within an excited atom. Using this method, many bits of digital information can be stored within a single atom. This project will provide experimental confirmation of this process. Methods will be investigated to retrieve the stored information, and the limits of the information storage capacity will be explored. These novel wavefunctions are expected to have significant effects on other radiative processes, which should be important for the development of new coherent radiation sources. These radiative effects will be examined. Current progress includes the development and characterization of a high-power, short-pulse blue laser and the construction of an interferometer for encoding time information onto the laser. Initial, low-power experiments have shown that the atom recognizes the laser pulses' timing. Our first high power experiments have now shown that the excitation technique can be accomplished with at least 60%

efficiency. Future experiments will include further improvements of the laser system to make the excitation even more efficient, and the use of a different atomic system (strontium) to enhance the modulation efficiency.

282. *Behavior of Atoms in a Strong Radiation Field*
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This project is a theoretical study of the interaction of an atomic system with a strong (synchrotron or laser) radiation field. Atomic systems containing two electrons, e.g., helium and the negative hydrogen ion, are of primary interest. Among the processes being explored, double ionization is of special interest. Double ionization is challenging not only because of the importance of the electron-electron correlation but also because the boundary conditions for two-electron escape are complicated. We have developed and successfully applied a method for calculating differential cross sections for double ionization by one photon, and we have compared our results favorably with data from several recent experiments. We are currently extending these calculations to include absorption by more than one photon. Our eventual goal is to treat the radiation field nonperturbatively.

University of Tennessee at Knoxville
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Department of Physics and Astronomy

283. *The Production and Destruction of Metastable Negative Ions*
Pegg, D.J. **$102,000**
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We continue to investigate the structure of few-electron atomic negative ions and the manner in which they interact with electromagnetic radiation via the process of photodetachment. The primary motivation for the work is to gain an improved understanding of the role played by correlated electron motion in atomic structure. The results also find practical application in the diagnostics of laboratory and astrophysical plasmas. In one series of experiments, a crossed laser-ion beam apparatus is used to make energy- and angle-resolved measurements of the detached photoelectrons. The spectra provide information on photoelectron kinetic energies, yields, and angular distributions. Electron affinities, asymmetry parameters and cross sections have been determined from the measurements. Recent experiments include an investigation of the cross section for photodetachment of the excited negative ion of carbon and the angular distribution of the photoelectrons detached in the process. In other experiments we have studied structures in detached electron spectra arising from ion-atom collisions. These structures have been identified with shape resonance states in negative ions of lithium and boron. Feshbach resonances arising from the autodetaching decay of doubly excited states of the lithium negative ion produced following uv absorption have also been investigated in high resolution using a very sensitive collinear beam apparatus.

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Department of Physics

284. *State-to-State Energy Transfer in Atomic Collisions*
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Experiments studying the radiative collision $Xe + Cl_2 + 2\ h\nu \rightarrow Xe^+ + Cl_2^-$ have been completed. Measurements have been made of the v,J energy disposal in XeCl*(B,C) following breakup of the triatomic reaction complex. Fully quantal calculations are used to model the bound-free fluorescence of XeCl*(B). The energy disposal following the radiative collision has been measured for laser wavelengths from 280–310 nm. The experiments have been compared with a numerical solution of an impulsive release model for the dynamics of the breakup. Measurements of state-to-state energy transfer rates for Xe (5d,5d',6d) states in collisions with other rare gases are continuing. These results are relevant to kinetic models of excimer lasers and the nuclear pumped, infrared xenon laser. In many previous experiments, strong coupling to these states through avoided crossings with Xe (6p, 6p', 7p) were suggested, but not confirmed, because the dynamics of Xe(nd) could only be indirectly observed. The 5d excited states fluoresce in the far infrared, where detectors are too slow for studies of dynamics, but the dynamics can be studied using two-color, pulse-probe laser induced fluorescence. The results will be compared with recent theory by Hickman, Huestis, and Saxon.

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Department of Physics and Astronomy

285. *Semiempirical Studies of Atomic Structure*
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The properties of highly-ionized many-electron atoms are studied through the use of semiempirical data systematizations, experimental measurements, and theoretical computations. Time-resolved measurements are made through the use of fast ion beam excitation methods, which are combined with wavelength data from laser- and tokamak-produced plasmas, astrophysical sources, and conventional light sources. The experimental studies are supported and interpreted through ab initio calculations, and large blocks of data are systematized and parametrized. During the past year lifetime measurements were made with the Toledo Heavy Ion Accelerator for levels of B II in the Be sequence, N III in the B sequence, Cd III and In IV in the Pd sequence, Tl II, Pb III and Bi IV in the Hg sequence, and Bi II in the Pb sequence. Spectroscopic classification studies of Cl V, Kr XXIV and Mo XXX in the Al sequence were made using the sliding spark source at the University of Lund and the JET tokamak at Abingdon. Relative intensity anomalies were studied for eight selected Al-like ions from Si II to Ni XVI using the accelerators at Lund and Bochum. Theoretical calculations and predictive data-based systematizations were also made in a number of these isoelectronic sequences, using our new measurements and our critically evaluated data base.

Department of Physics and Astronomy

286. ***Negative Ion-Atom Collisions***
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This research project concentrates on the measurement of cross sections for various scattering processes in few-electron negative ion-atom collision systems in order to provide increasingly stringent tests of our understanding of the physics of ion-atom collisions at intermediate energies. Studies of single- and double-electron detachment have been recently completed for H^-+(He, Ne, Ar, CH_4) systems. Preliminary results have been obtained this past year for the measurement of target excitation to the n=2 states in H^-+He collisions. These results with be compared with similar measurements in the H^++He collision system to aid in the understanding of the excitation process. The ion energy-loss spectroscopy (IELS) experimental technique is used to obtain these measurements. IELS permits the determination of absolute cross sections for the direct excitation of discrete target states, as well as target ionization processes. Current research involves expanding on the preliminary results for n=2 excitation obtained this year in H^-+He collisions by studying excitation and ionization to more states in additional collision systems, as well as obtaining a more precise value for the n=2 cross section in H^-+He collisions.

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Department of Physics

287. ***Dynamics of Multielectron Systems Interacting with Matter and Light***
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One of the central questions of science is: how are complex things made from simple things? In biology and chemistry the issue is how to understand large molecules in terms of atoms. The general theme of our work in atomic collisions is interdependency of electrons in atomic systems. Specifically, we study the dynamics of electron correlation by studying reactions in which electron correlation is dominant. This occurs in few electron transitions in fast collisions of photons and charged projectiles with atoms and molecules. Using synchrotron radiation one may observe both single and double ionization of simple atomic systems. Calculations are done using many body perturbation theory specifying the nature of electron correlation in terms of initial and final state correlation. We also study two and few electron transitions in interactions of atoms and simple molecules with charged projectiles. Two center correlation is studied in systems in which projectile electrons interact with target electrons. Using first order perturbation theory we have been able to relate cross sections for charged particle impact to Compton scattering by photons. These relations are now being tested experimentally and are providing an emerging picture of mechanisms for the dynamics of electron correlation.

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Department of Computer Science

288. ***Theoretical Studies of Atomic Transitions***
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Atomic structure calculations are being performed for properties associated with energy transfer mechanisms in atoms. Properties of particular interest are energy levels, transition probabilities, autoionization rates, and photoionization cross-sections. Recent interests are the nuclear effects of hyperfine interaction and isotope shifts on transition energies and decay processes that may be hyperfine induced. An atomic structure package has been developed based on the multiconfiguration Hartree-Fock (MCHF) method, modified for distributed, parallel computing. Through the use of independently optimized wave functions, accurate transition probabilities, both allowed and spin-forbidden, will be determined for lines in complex spectra, particularly those of astrophysical interest. A similar technique can be applied to autoionization. Fully relativistic codes, more appropriate for study of the heavy elements, such as the lanthanides, are also being modified for independent optimization and large-scale studies. They will be applied to the study of transitions in magnesium-like systems and other heavy atoms.

University of Virginia
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Department of Physics

289. ***Studies of Autoionizing States Relevant to Dielectronic Recombination***
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Two electron processes in excited atoms are of practical importance in dielectronic recombination as occurs in fusion plasmas and in short-wavelength lasers, and this program is focused on such processes. The experimental approach employed involves multistep laser excitation of the two valence electrons in alkaline earth atoms to doubly excited states, which decay by autoionization. This laser excitation process is the inverse of dielectronic recombination and gives detailed information about both autoionization and dielectronic recombination rates. Omnipresent electric fields alter dielectronic recombination rates and the distributions of final states. Measurements in the past year of Ba 6snk-6pnk spectra in electric fields indicate that the population after dielectronic recombination is spread over more states in a field than it is in zero field. Due to the smaller energy spacing of the field states, the energy spread is no larger. Thus, the most significant effect of the field is the change in the rate, not the final state distribution. Measurements of autoionization rates in circularly polarized electric fields, which mimic ionic collisions, show very low autoionization rates, suggesting that ionic collisions in plasmas mix m states and increase recombination rates.

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Department of Physics

290. Near Threshold Excitation and Ionization of Atoms
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The primary emphasis of our work is to probe and identify many-body effects due to electron correlations with unprecedented level of detail, focusing on phenomena near thresholds since there electron-electron correlation are the strongest. Our aim is to study these fundamental aspects by using photoexcitation and photoionization processes. This is achieved by conducting high resolution measurements on rare gases and open-shell atoms using time-of-flight spectrometry coupled with high brightness and high resolution third generation photon sources. New results have been obtained for studies involving 1) angle resolved Auger Resonant Raman spectroscopy to study the angular distribution of the Xe $4d_{5/2} \rightarrow 6p$ decay spectrum, 2) Compton scattering of He, 3) high resolution studies in laser-excited hollow Lithium. Present activities include 1) photoexcitation and ionization of Cl, 2) extending the resonant Raman technique to study in detail Ar and Kr, 3) continue our effort in laser excited targets and 4) construct a new electron spectrometer that will complement our time-of-flight spectrometers.

291. Synchrotron Radiation Atomic Physics Facility
Berrah, N. **$94,832 Operating**
616-387-4938 **$205,165 Equipment**
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A three year project supported under the Scientific Facility Initiative to introduce a synchrotron radiation-based capability to conduct high-resolution, extreme ultraviolet and soft x-ray spectroscopy at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory for research in atomic, molecular and optical physics was initiated. New experimental stations on an undulator beamline at the ALS with a capability for high-resolution measurements dedicated to the study of photon prompted multielectron processes in atomic and molecular systems will be established. The experimental stations will include state-of-the-art electron spectrometers with the highest energy resolution currently available, a recoil ion spectrometer and an ion beamline for photoionization studies of ion targets. Coupled with a phase-shifting optical device to produce circularly polarized light, these experimental stations will permit study of gas phase electron microscopy with both linearly and circularly polarized light. A few quantum mechanically complete experiments will also be performed. This experimental device will be accessed initially by participator research team members including those from the National University of Mexico/Cuernavaca. European collaborators and independent investigators will also be granted access.

292. Correlated Charge-Changing Ion—Atom Collisions
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Experimental investigations of atomic interactions in collisions of few-electron ions with neutral gas targets or electrons are conducted. Interactions involving excitation, ionization, and charge transfer (capture) are studied. The primary emphasis of this work is the study of two-electron processes, and in particular, those collision processes for which the electron-electron interaction (i.e., electron correlation) is important. This work centers around three general areas of investigation: (1) emission of electrons along the beam direction which travel with the beam velocity, i.e., cusp-electron production, (2) double (or multiple) ionization of helium or other targets, and (3) resonant recombination involving either resonant transfer excitation (RTE) or dielectronic recombination (DR). Specific collision processes are isolated and identified, for the most part, using coincidence techniques in which projectile charge-changing events are associated with electrons, recoiling target ions, or x-rays. Measurements are conducted using accelerators at Western Michigan University, Indiana University, Kansas State University, Lawrence Livermore National Laboratory, and Michigan State University.

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Department of Physics

293. Negative Ion Detachment Cross Sections
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The general goal of this experimental research project is to develop an understanding of the collisional dynamics for systems where negative and positive ions collide with atoms or molecules in the gas phase as well as with atoms which may be absorbed to a well-characterized metallic or metal-oxide surface. The gas phase experiments focus on the determination of two-body collision cross sections while the aim of the surface experiments is to examine the collisionally induced desorption of electrons and negative ions from surfaces. The collision energies for each of these experiments range from a few electron volts up to about 0.5 keV. In the gas phase experiments, cross sections for collisional and associative electron detachment, charge transfer, and negative ion-molecule reactions are determined for a variety of reactants; in the surface experiments, both the absolute anion and electron sputtering yields are determined along with the kinetic energy spectra of each sputtered species. In both cases the fundamental microscopic measurements are ultimately used as input for modeling macroscopic gaseous discharges or plasmas where the cross sections for gas phase collisions and the yields for surface collisions determine the equilibrium concentrations.

Chemical Energy

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Department of Chemistry

294. ***A Model Approach to Hydrodenitrogenation Catalysis***
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Despite the importance of removing nitrogen from petroleum feedstocks to providing more processable and environmentally sound fuels, the mechanisms of metal-catalyzed, hydrodenitrogenation (HDN) reactions are not well understood. We are continuing studies of soluble model compounds that mimic HDN substrate-catalyst interactions and demonstrate purported HDN reactions. Our primary focus is on the six-membered heterocyclic compounds such as pyridine and its derivatives. Recent studies allow us to support the following conclusions: 1. The η^2(N,C) binding mode renders a pyridine ligand susceptible to nucleophilic attack and results in C–N bond cleavage. 2. The overall reaction between an η^2(N,C) pyridine complex and an attacking nucleophile can be partitioned into two stages: nucleophilic attack at the metal center followed by ligand migration to the η^2 ligand. 3. In our model system, ligand migration is rate-limiting and the ligand migrates to the substrate as a σ nucleophile. 4. The C–N bond scission appears to be driven by the formation of a strong metal-nitrogen multiple bond and made possible by the reduction in pyridine C–N bond order that arises from η^2 coordination. 5. Carbon-carbon bond scissions of a ring-opened pyridine ligand are possible at the same metal site when the pyridine is highly substituted. 6. Although the first step of quinoline HDN involves hydrogenation to tetrahydroquinoline, tetrahydroquinoline has not been induced to bind in the η^2(N,C) mode. These results offer new, significant insight into HDN related processes, including the manner by which nitrogen heterocycles may be further degraded after C–N bond cleavage.

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Department of Chemistry

295. ***High-Temperature Chemistry of Aromatic Hydrocarbons***
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This work focuses on the fundamental molecular processes involved in the rearrangements and interconversions of polycyclic aromatic hydrocarbons (PAHs) under conditions of thermal activation. PAH ring systems figure prominently in the molecular architecture of coal, but prior to this systematic program of study, little was known about the chemical transformations that PAHs undergo at high temperatures, such as those employed in the uncatalyzed gasification and liquefaction of coal. This year several additional examples of fullerene fragment formation from bay region PAH at high temperatures have been discovered, e.g., the production of cyclopent[cd]fluoranthene from benz[a]anthracene, dicyclopenta[cd,fg]pyrene from benz[e]pyrene, inter alia. The possible intermediacy of bay region diradicals in such processes is supported by the generation of pyracylene from cyclopent[def]phenanthrenone by decarbonylation-rearrangement. Isotopic labelling experiments with $^{13}C_2$-picene further support our proposed unified mechanism for high temperature transformations of this type. The spectacular triple cyclodehydrogenation of decacyclene to triacenaphthotriphenylene, a 36-carbon bowl-shaped fullerene fragment, has also been observed at 1200–1300°C. The long-range objectives of this research are to uncover all the principal reaction channels available to PAHs at high temperatures and to establish the factors that determine which channels will be followed in varying circumstances.

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Department of Chemistry

296. ***Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds***
Bercaw, J.E. **$148,000**
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The objectives of this research program are (1) to discover new types of chemical transformations between hydrocarbons and transition-metal compounds; (2) to investigate their mechanisms; and (3) to explore the possibilities of coupling these transformations with others to catalyze chemical reactions for the preparation of fuels, commodity chemicals, and polymeric materials. A current focus is the catalytic polymerization of olefins. Ziegler-Natta catalysis is a well-established and commercially very important process; however, it is clear that new (and superior) polymers with different microstructures and new homo-block copolymers could be made from the same readily available monomers if sufficient control over the catalytic process could be achieved. C_2-symmetric yttrocene derivatives with linked cycopentadienyl ligands have been prepared. The alkyl and hydride derivatives function as well-defined, single component, isospecific alpha olefin polymerization catalysts well suited to mechanistic investigations. A ligand capable of affording only one enantiomer of a chiral catalyst has been synthesized. The absolute facial preferences for olefin insertion into Y–H and Y–C bonds has been established for a chiral, highly deuterated olefin using NMR methods. Recently a new class of zirconocene catalysts have been developed that produce highly syndiotactic poly alpha-olefins. A modified version allows the preparation of polypropylenes with tacticities varying from isotactic to syndiotactic.

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Department of Chemical Engineering

297. ***Effects of Supports on Metal Complexes and Clusters: Structure and Catalysis***
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The research is a fundamental investigation of the effects of supports on the structure and catalytic properties of metal complexes and clusters. The metals are Rh and Ir. The supports are MgO, γ-Al_2O_3, and zeolite LTL. The former are used as high-area powders and as ultrathin layers on metal single crystals. Like the oxides, the zeolite is basic, incorporating K^+ and Ba^{2+} exchange ions. With precursors such as $[Ir(CO)_2(acac)]$, metal subcarbonyls such as $[Ir(CO)_3(OMg)_3]$ are formed (where the braces around MgO denote groups terminating the MgO). With precursors such as $[HIr_4(CO)_{11}]^-$ and $[Ir_6(CO)_{15}]^{2-}$, supported clusters such as Ir_4 and Ir_6 are formed. The supported species are being characterized structurally with IR, EXAFS, and NMR spectroscopies, TPD, H_2 chemisorption, and imaging methods. The samples are being tested as catalysts for ethylene hydroformylation toluene hydrogenation, and n-butane hydrogenolysis. The goals are to determine how the support structure and composition affect the structure of the well-defined supported metal complexes and clusters and their reactivities and catalytic properties. For example, tetrairidium clusters on MgO were oxidized to give iridium oxide clusters of nearly 4 atoms each, and these were reduced in H_2 to give back Ir_4. These latter clusters on MgO catalyze toluene hydrogenation, and the catalytic reaction rate depends only modestly on the MgO surface hydroxyl content.

University of California, Irvine
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Department of Chemistry

298. ***Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes***
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The purpose of this project is to study the chemistry of complexes of yttrium and the lanthanide metals, a series of 15 metals readily available in the United States, so that the special properties of these metals can be utilized in energy-saving optical and magnetic materials and in the catalysis of conversions of abundant low-value substrates such as CO and CO_2 into more useful chemicals. To achieve this goal, more information is needed on ligands which solubilize the metals as complexes, which allow full characterization of the chemistry, and which are compatible with the practical applications. Alkoxide and aryloxide ligands have been found to be effective in making polymetallic complexes including soluble manipulatable complexes which have interior structures similar to metal oxides. The nitrogen analogs of aryloxides, arylamido ligands, have also been found to be valuable ligands for these metals providing a wide range of structural types. Investigation of "dehydrated" $CeCl_3$ extensively used in organic synthesis for its unique reactivity in alkylations as $CeCl_3$/RLi has shown that this ligand system is not as simple as previously assumed. The "dehydrated" material is actually $[CeCl_3(H_2O)(THF)]_n$, a fact which requires reevaluation of reaction mechanisms for this popular reagent.

University of California, Riverside
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Department of Chemistry

299. ***Study of the Surface Chemistry of Hydrocarbon Radicals and of Carbonium Ions on Metal Oxide Surfaces***
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This project focus on the development of two separate directions related to the characterization of the surface chemistry of hydrocarbons on metal oxide surfaces. In the first, the oxidation of nickel surfaces to form thin nickel oxide films spectroscopies is been investigated. In particular, the effect of argon ion bombardment on the oxidation of nickel films was studied by using X-ray photoelectron spectroscopy (XPS). In the absence of any ion beams, exposure of nickel surfaces to an oxygen atmosphere leads to the moderately rapid formation of a thin (3–5 monolayers thick) nickel oxide overlayer. At room temperature the oxygen uptake stops once this limit is reached, but at higher temperatures the slow growth of a thicker oxide is seen. The diffusion coefficient for oxygen through the forming NiO film was determined to be on the order of 2×10^{-18} cm^2/s at 625 K. The simultaneous impingement of argon ions on the surface during oxygen exposures was found to enhance the oxidation process. Indeed, ion beam current densities as low as 0.01 $\mu A/cm^2$ were found to be sufficient to induce nickel oxidation past the 3-5 ML limit even at room temperature. The oxidation rate was found to be roughly proportional both to the ion flux and to the square of the oxygen pressure. The build-up of a NiO film during this Ar^+-ion/oxygen treatments was also found to slow down at higher temperatures, presumably because of the combined effect of a higher probability for desorption of molecular oxygen from the surface and a higher atomic oxygen mobility into the bulk. The oxide films prepared at low temperatures appear to be quite disordered, and display an extra feature in the Ni 2p XPS spectra around 853.2 eV which could be assigned to partially reduced nickel. Annealing of those films to temperatures above 400 K leads to the possible ordering of the surface and to the disappearance of the signal for the Ni^{+x} species in the XPS, and further heating above 600 K leads to the diffusion of oxygen atoms into the bulk and to the partial reduction of the surface nickel to its metallic state. Finally, the presence of water in the gas phase during the nickel Ar ions/oxygen treatment was seen to result in the production of a surface hydroxyl layer, the same as when the oxidation is carried out in the absence of ion excitation. The second direction of this project has been to study the conversion of alkyl groups chemisorbed on the oxide surfaces prepared as described above. On clean nickel surfaces, alkyl species decompose via a combination of beta-hydride and reductive elimination steps to yield a mixture of alkanes and alkenes. On the other hand, most of the surface reactivity is inhibited by the presence of surface oxygen, and only the products of total oxidation reactions, namely, CO, CO_2 and H_2O, desorb from fully oxidized surfaces under vacuum. The interesting aspect of this research is the fact that formation of acetone, a partial oxidation product, was observed for the reaction of 2-propyl iodide with low oxygen precoverages. The desorption temperature of that partial oxidation reaction, when compared to the desorption of acetone from Ni(100), suggests that its formation is reaction limited. The experimental results obtained so far suggest that alkyl halides adsorb and dissociate on the nickel atoms first, forming the desired alkyl groups. At slightly higher temperatures, around 200 K, most of those moieties undergo the beta-hydride and reductive elimination reactions to alkenes and alkanes, respectively, typical of the metallic function, but a small fraction migrates to the oxygen functionality and to form alkoxy groups, which then dehydrogenate above 300 K to produce the ketone.

University of California, Santa Barbara Santa Barbara, CA 93106

Department of Chemical and Nuclear Engineering

300. Alkane Activation and Reactivity on Iridium, Platinum, and Ruthenium Surfaces

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The research objective is to quantify alkane activation on various transition metal surfaces including Ir(110) and Ir(111). We have employed molecular beam techniques to investigate the molecular trapping and trapping-mediated dissociative chemisorption of perhydrido- and perdeutero-ethane and propane, as well as $c\text{–}C_3H_6$ on Ir(110) at low beam translational energies, $E_i \leq 5$ kcal/mol, and surface temperatures, T_S, from 85 to 1200 K. In each of these cases, the cleavage of C–H (C–D) bonds through the trapping-mediated mechanism is unactivated with respect to a gas-phase energy zero, i.e., the activation energy for reaction from the physically adsorbed state, E_r, is less than the activation energy for desorption, E_d, from this state. We have also measured the initial adsorption probability of CH_4 and CD_4 on Ir(111) under both low pressure ($< 10^{-3}$ Torr) and high pressure (1 Torr) conditions. Under low pressure conditions trapping-mediated chemisorption is the dominant mechanism of methane dissociation with activation energies of 16.0 and 17.0 kcal/mol for CH_4 and CD_4. By diluting the methane in argon at a total pressure of 1 Torr, we have also examined the direct activation of methane. Under these conditions the translational energy of the methane is characterized by a Maxwell-Boltzmann distribution at the surface temperature. For this case the apparent activation energies of methane activation are 17.0 kcal/mol for CH_4 and 17.9 kcal/mol for CD_4. For both CH_4 and CD_4, the rate of reaction is greater for the high pressure experiments than the low pressure experiments.

Department of Chemistry

301. Studies Relevant to the Catalytic Activation of Carbon Monoxide

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This research is concerned with quantitative investigations of fundamental reactions relevant to the catalytic activation of carbon monoxide and other C_1 compounds. New carbonylation catalysts based on rhodium(III) heterogenized on polyvinyl pyridine polymers have been developed and these are active in Reppe type hydroformylation and hydrogenation of alkenes. In addition, exploratory studies have been carried out to use sodium formate as the reductant in the catalytic reduction of chlorinated organic compounds. Time resolved spectral techniques have been used to prepare and to investigate the spectra and dynamics of organometallic intermediates relevant to the activation of hydrocarbon C–H bonds and to formation of carbon-carbon bonds via CO migratory insertion into metal-alkyl bonds. The latter is the key reaction in the carbonylations of various organic substrates. The goals are to delineate the quantitative details of these fundamental processes, to understand chemical principles relevant to the activity and selectivity of molecular catalysts for activating hydrocarbons and C_1 compounds such as CO, and to define guidelines for designing new, environmentally friendly and more efficient applications of energy and chemical feedstocks.

Carnegie-Mellon University Pittsburgh, PA 15213

Department of Chemical Engineering

302. H_2SO_4-Modified ZrO_2 and ZrO_2/SiO_2 Aerogels as Solid Superacids

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Manipulation of sulfate content, silica content, and activation temperature provided the means for controlling the strength of surface Brønsted acid sites in the zirconia-silica-sulfate system. This approach allowed the development of an acid strength hierarchy, based on the adsorption of pyridine and isomerization of 1-butene and n-butane, as a rational basis for acid catalyst design. Introduction of silica into zirconia-sulfate co-gels also provided insight into the activation behavior of this important class of materials. Silica retarded sintering upon heat treatment, thereby delaying crystallization of zirconia to higher temperatures. Activation of sulfate to a form capable of catalyzing the isomerization of n-butane was also delayed to higher heat treatment temperatures, confirming the role of crystallization in initiating the activation sequence.

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Department of Chemistry

303. *Polyoxoanion-Stabilized Transition Metal Nanoclusters: Soluble Analogs of Heterogeneous Catalysts*
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The first examples of a new type of metal-particle catalyst, polyoxoanion and Bu4N$^+$-stabilized transition-metal nanoclusters, were discovered recently under our DOE grant support. Presently, the following knowledge is being gathered, information necessary to construct a paradigm covering their catalytic applications: an understanding of what gives rise to their stabilization and isolability, an understanding of how this stabilization can be enhanced to generate higher temperature-stable nanocluster catalysts, and an understanding of the nanocluster's catalytic reactions and their underlying mechanisms. Ultimately, our goal is a full understanding of the strengths and weaknesses of this exciting new subclass of soluble metal-particle catalysts.

304. *Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylenes*
Norton, J.R. **$122,535**
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Protonation of mono- and dinuclear dialkyl and olefin osmium complexes gives cationic alkyl, alkylidene, and olefin complexes. In the case of $Os(CO)_4(C_2H_4)$, both the kinetic and thermodynamic sites of protonation are Os, but C_2H_4 inserts into the Os–H bond in the presence of as weak a coordinating ligand as Et_2O. We have examined the reactivities of these cationic Os complexes toward olefins, alkynes, and CO, and have found insertion reactions but no utility as polymerization catalysts. In collaboration with Elliott Burnell of the U. of British Columbia, we have rethought our analysis of the structure of the parent diosmacyclobutane from nematic phase NMR data. We have prepared diosmacyclobutanes from strained olefins such as norbornene and cyclobutene. We will now assess (1) the effect of ring strain on the relative binding affinities and (2) the potential for strained diosmacyclobutanes to cleave C–C and Os–Os bonds to form tethered alkylidene complexes: $(CO)_4Os{=}CHR{-}RHC{=}Os(CO)_4$.

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Department of Chemistry and Biochemistry

305. *Syntheses and Reactions of Pyrrole and Indole Complexes*
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The objectives of the project are (1) to synthesize new transition metal pyrrole and indole complexes and (2) to investigate how the metal ion coordination affects the reactivity of the heterocycle. An understanding of how coordinated heterocycles might be activated toward reduction, ring opening, or nucleophilic addition reactions may provide a basis for understanding basic mechanisms of the hydrodenitrogenation catalysts. A series of new η^5 pyrrolyl complexes of ruthenium(II) have been synthesized, and the heterocyclic ligand was found to be activated toward nucleophilic substitution reactions at the alpha carbon atom. Reactions with alkyl and aryl lithium reagents and with amide nuleophiles led to the preparation of new derivatives with substituted pyrrolyl ligands. 2,5-Disubstituted pyrroylyl ligands have also been prepared in some cases. The new pyrrole ligands can be readily displaced from the ruthenium ion by protonation reactions, and the free ligands have been isolated. The results demonstrate that these reactions have potential useful applications for the preparation of new substituted pyrrole rings. In a related project η^5 -tetramethylpyrrole, η^6 -indole, η^6 -indolyl, and η^6 -indoline complexes of pentamethylcyclopentadienyl Ir(III) have been synthesized. Reactions of these complexes with nucleophiles and reducing agents have been studied. For example, $[(\eta^5\text{-- }HNC_4Me_4)Ir(C_5Me_5)](OTf)_2$, **1**, undergoes a quasi-reversible two-electron reduction at - 1.34 V vs Fc. Reaction of **1** with a hydride donor resulted in a reduced Ir(I) product in which nucleophilic hydride addition to the Cp* ligand had occurred. In contrast reactions of the indole and indoline complexes with nucleophiles resulted in attack on the carbocyclic ring of the heterocycle. Further studies of these systems are in progress.

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Department of Chemistry

306. *Model Studies in Hydrocarbon Oxidation*
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The research performed during the last grant period has continued with an investigation of the chemistry of molecular terminal chalcogenido complexes. By studying the chemistry of a series of complexes with M=O, M=S, M=Se, and M=Te bonds, it is hoped that this research will provide results that are relevant to systems concerned with both hydrocarbon oxidation and hydrodesulfurization processes. For example, we have synthesized the first series of oxo, sulfido, selenido, and tellurido derivatives of hafnium $Cp^{\dagger}_2Hf(E)(NC_5H_5)$ (E=O, S, Se, Te), and the first mononuclear telluroformaldehyde complex of tantalum $Cp^*_2Ta(\eta^2{-}TeCH_2)H$. Studies on these complexes have revealed interesting differences in the chemistry of the systems as a function of the chalcogen. For example, coupling and cleavage reactions play an active role in a variety of important transformations. However, in spite of the potential importance of reactions involving the interconversion of $[M](E)_2$ and $[M](\eta_2{-}E_2$ moieties, relatively few well-characterized examples of such transformations have been described. Significantly, we have reported the first examples of such transformations for tellurium, thereby suggesting that such reactions are more facile for tellurium than its lighter congeners. We have also compared the ability of molybdenum and tungsten centers to activate C–H bonds and have demonstrated that the hexakis(trimethylphosphine)molybdenum complex only forms aryloxy-hydride complexes in its reactions with phenols, whereas the corresponding tungsten complex undergoes intramolecular C–H bond activation. Nevertheless, although C–H bond activation by the molybdenum center is thermodynamically unfavored, magnetization transfer studies demonstrate that it is kinetically capable of such reactions.

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Department of Chemistry

307. ***Synthetic Todorokite: Preparation, Characterization, and Applications***
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The goals of this project are to prepare new octahedral molecular sieve (OMS) and octahedral layer (OL) materials by several methods including sol-gel, reflux, autoclave methods; to prepare and characterize isomorphously substituted OMS and OL materials; to develop new characterization methods for OMS and OL systems such as diffuse reflectance UV-visible spectroscopy; and to optimize catalytic properties of OMS and OL for dehydrogenation of alkanes to terminal olefins and oxidation of alkanes to terminal alcohols. Materials with transition metals substituted into framework or tunnel sites of OMS and OL have been prepared. Characterization of such systems will be done with a variety of methods in order to study structural, compositional, surface, electronic, electrical, morphological, thermal, magnetic, electron transfer, redox, and catalytic properties. Characterization of changes in the OMS and OL catalysts during reaction are being studied. Some reactions of interest are oxidative dehydrogenation of cyclohexane, decomposition of hydrogen peroxide, and styrene formation.

University of Delaware
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Center for Catalytic Science and Technology

308. ***Synthetic Reactions of Oxametallacycles and Related Intermediates on Transition Metal Surfaces***
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The goal of this research is to identify the requirements for and competition between activation of C–H, C–C, and C–O bonds in the synthesis and decomposition of oxygenates on transition metal surfaces. Current research is focused on surface oxametallacycle chemistry. These intermediates are implicated in a variety of reactions in homogeneous catalysis, heterogeneous catalysis and surface science, including epoxide synthesis and carbonylation and decarbonylation processes. However, spectroscopic evidence for oxametallacycles is generally lacking and the patterns of reactivity of these intermediates are not well established. We are employing both experimental techniques (Temperature Programmed Desorption, High Resolution Electron Energy Loss Spectroscopy, and X-ray Photoelectron Spectroscopy) and theoretical methods (Density Functional Theory) in these studies. A primary goal is to demonstrate the synthesis of surface oxametallacycles, and thus to determine the factors which control their formation and the selectivity of their reactions, and to identify new reactions with ramifications for catalysis. Our research has produced the first evidence for the participation of oxametallacycles in higher alcohol chemistry on certain transition metal surfaces, and most recently it has produced the first evidence both for stable oxametallacycle formation and for novel cyclization chemistry of these intermediates. This work holds the potential of establishing new principles for surface organic syntheses, of discovering new chemistry, and thus of providing guidance for the development of new catalysts and processes for oxygenate synthesis.

Department of Chemistry and Biochemistry

309. ***Oxidation Catalysis with Tris(pyrazolyl)borate Metal Complexes***
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This project involves the development of catalysts for the oxidation of organic substrates using dioxygen as the source of the oxygen. In particular, the approach involves coordination and symmetric cleavage of the O_2 molecule into two reactive metal-oxo moieties by hindered tris(pyrazolyl)borate complexes of late transition metals. The feasibility of this scheme has been previously demonstrated using a set of cobalt complexes. In the initial phase of the research the mechanism of the cobalt mediated stoichiometric reaction will be elucidated in detail, and some reactions of the cobalt system [$Tp^{t\text{-}Bu,Me}Co$, $Tp^{t\text{-}Bu,Me}$ = hydridotris (3-t-butyl-5-methylpyrazolyl)borate] related to oxidation catalysis will be investigated. Building on this, the metal complexes will be modified to facilitate catalytic turnover. To this end the ligands must be "hardened" against oxidative degradation. This will be done by appropriate substitution of the ligand and/or the metal. In the long term, catalytic oxidations of various substrates as well as the design of ligands for regio- and stereo-selective oxidations will be investigated.

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Department of Chemistry

310. ***Bimetallic Complexes as Methanol Oxidation Catalysts***
McElwee-White, L. **$332,000**
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The project involves preparation of bimetallic Pt/Ru and Pt/Mo complexes as catalysts for the electrooxidation of methanol. The currently accepted mechanisms for methanol oxidation at Pt/Ru anodes involve C–H activation at Pt and "active oxygen transfer" from Ru. Since these reactions are known individually for mononuclear complexes, the catalysts are designed to mimic the anode behavior. Design features of the complexes include bridging ligands such as 1,10-phenanthrolinedione or bidentate phosphines to prevent dissociation of the metal centers, low-valent starting materials that allow a series of oxidation states for each metal to be generated during oxidation studies, and incorporation of ligands that are relevant to the methanol oxidation process. Both chemical and electrochemical oxidation of the complexes are being examined and reaction of the oxidized species with methanol is being investigated. The complexes whose solution electrochemistry is most promising for methanol oxidation will be deposited on electrodes for studies of electrocatalysis under the aqueous conditions found in direct methanol fuel cells.

Harvard University
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Department of Chemistry

311. ***Model Microcrystalline Mixed-Metal Oxides for Partial Oxidation and Desulfurization***
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The broad objective of this proposal is to investigate how the constituents of bimetallic materials function in important catalytic processes. We are currently investigating the activity of mixed Co-S and Co-O phases supported on Mo(110) for hydrocarbon oxidation, deoxygenation and desulfurization. A general method for synthesizing small (~100 angstroms) metal clusters on Mo(110) has been devised, allowing us to compare the chemistry of small particles to that of uniform films. The reactivity of the small Co clusters is substantially different than a uniform monolayer. For example, methanol does not react on the Co clusters whereas it decomposes to CO and dihydrogen on the uniform monolayer at ~375 K. Currently, the reactions of methyl radicals with adsorbed oxygen and hydroxyl are being investigated on the uniform phases and Co clusters with the goal of synthesizing methanol. Scanning tunneling microscopy and theoretical studies are planned to develop an understanding of the contributions of geometric and electronic structure effects in determining the reactivity differences. These studies have broad significance in that they serve as a test of aspects of the cluster-surface analogy and may provide a means of manipulating product distributions in catalytic processes via variation in particle sizes.

University of Illinois at Urbana-Champaign
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School of Chemical Sciences

312. ***Electron Transfer Activation of Coordinated Thiophene***
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The presence of organic sulfur compounds in fossil fuels poses very serious environmental and engineering challenges. The most effective method for addressing these problems is through the hydrodesulfurization (HDS) process whereby the sulfur is removed by hydrogenolysis of C–S bonds in the fossil fuel matrix. The project objectives are threefold: (1) elucidate mechanisms for metal-catalyzed HDS, (2) develop new methods for desulfurization of fossil fuels, and (3) develop new uses for organosulfur components of fossil fuels. Most of these studies employ thiophenes as representative substrates. Experiments focus on HDS pathways that involve electron transfer to a metal-thiophene ensemble followed by protonation, i.e., heterolytic hydrogen activation. The stereochemistry and energetics for individual steps are examined for model systems based on ruthenium complexes. New desulfurization methods and new uses for the organosulfur components in fossil fuels are developed through the addition of nucleophiles to metal thiophene ensembles.

Indiana University
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Department of Chemistry

313. ***Chemical Principles Relevant to Materials Precursor Design and Synthesis***
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The project objective is to determine, by a series of case studies, which chemical routes are particularly facile for the conversion of mixed-metal alkoxides to solid-state oxide materials. The transformation from molecule to infinite lattice solid will be effected by thermolysis, hydrolysis, and plasma treatment. The groups L to be considered include simple hydrocarbon-derived alkoxides, heavily fluorinated alkoxides, and vicinal diolates. These are chosen to incorporate progressively more complex chemical features, each of whose typical reaction patterns are well-established. Chemically-facile routes are expected in certain cases because elimination of known neutral organic molecules can be envisioned. Such "weak" bonds will cause the precursor-to-product process to occur under very mild conditions. This research involves establishing whether such expectation will be realized under CVD processing conditions. Incorporation of mobile protons will also be considered as a "trigger" for precursor processing at especially low temperatures. In every case, mechanistically diagnostic experiments will be executed in order to allow generalization of these results to make more rational the design of effective molecular precursors to technologically-valuable solid materials.

314. ***Alkoxide Ligands in Organometallic Chemistry and Catalysis***
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Alkoxide and related aryloxide and siloxide ligands are hard π-donor ligands and complement the now traditional soft π-acceptor ligands such as tertiary phosphines, carbonyls and π-hydrocarbyl ligands. We are using the former with hard metals such as early transition elements, lanthanides and group 2 and 3 main group elements as ancillary ligands for the development of a new field of organometallic chemistry. Current areas of research include (i) the development of selective hydrogenation catalysts for conjugated dienes employing W2(OR)6 compounds; (ii) the use of bidentate and tridentate diols and triols to impose specific coordination geometries at the metal atoms; (iii) studies of opening of sulfur, nitrogen and oxygen containing aromatic rings as models for steps in HDS, HDN and HDO catalysis and (iv) the development of single site metal alkoxide catalysts for the ring-opening of epoxides and strained cyclic esters.

315. A Model Approach to Vanadium Involvement in Crude Oil Refining

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The project is directed toward characterizing the initial fate of crude oil vanadyl impurities under the reducing and sulfur-rich conditions of industrial hydrodemetallation (HDM) and hydrodesulfurization (HDS) processes. The impurities are ultimately converted to insoluble vanadium sulfides (primarily V_2S_3 and V_3S_4), which lower the activity of, and eventually poison, the Mo heterogeneous catalyst. Recent work has concentrated on detailed characterization of various V/S clusters that represent models for intermediate stages of V sulfide polymer growth. A number of di- and trinuclear species have ben prepared and studied by a range of techniques, including x-ray crystallography, VT magnetic susceptibility measurements, VT ^1H NMR studies, and EHT MO calculations. Selected complexes under study include $[V_3Cl_6(SCH_2CH_2S)_3]^{3-}$, $[V_2(SCH_2CH_2S)_4]^{z-}$ (z=1 or 2) and $[V_xO_y(pyt)_z]$ (pyt=pyridine-2-thiolate), which represent models of small V species adsorbed on the surface of the growing V_2S_3/V_3S_4 phases. The V/pyt complexes have been investigated by EI mass spectrometry, the observed MS fragmentation patterns (C–S and C–N bond cleavage) being employed as a model system for the fragmentation pathways of organovanadium impurities during the high temperature conditions of crude oil refining. The work has most recently been extended to include a variety of V/O/carboxylate clusters; the latter organic functionality is common in crude oils. A number of tetranuclear and pentanuclear species have been prepared and characterized by crystallographic and physical methods, including magnetochemistry. Aggregation methodology has been developed for the stepwise conversion of mononuclear vanadyl species to penta-, ennea-, and pentadecanuclear products, and all these species have undergone detailed characterization. The reaction of such species with H_2S is also being investigated as a model system for V sulfide polymer formation under refining conditions.

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Department of Chemistry

316. Synthesis and Chemistry of Cationic d^0 Metal Alkyl Complexes

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The objective of this research is to design and synthesize new types of electrophilic organometallic complexes for use in fundamental studies of olefin polymerization and C–H activation chemistry, and for exploitation in catalysis. Earlier studies of $Cp_{p2}Zr(R)(L)^+$ complexes identified the key features required for high insertion reactivity in early metal systems: an electrophilic metal center, a d^0 metal electron configuration, and one or more vacant (or virtual) coordination sites cis to the M–R ligand. Current work is directed to the development of new classes of cationic early metal alkyls, which incorporate these features in non-Cp_2M ligand environments. A series of Zr and Hf alkyl complexes $(N_4\text{–macrocyle})M(R)_2$ (R = CH_3, CH_2Ph, CH_2SiMe_3) containing dianionic tetra-aza macrocycles (N_4–macrocycle = Me_8-taa, Me_4-taen) in place of Cp ligands has been prepared. The pockets of these macrocycles are too small to accommodate the large group 4 metal ions, so the metal sits out of the N_4–plane and cis structures are imposed. Base-stabilized cations [*cis*-$(N_4\text{–macrocycle})M(R)(L)][BPh_4]$ (L = THF, RCN, PMe_2Ph), and base-free cationic systems $[(N_4\text{–macrocycle})M(R)][B(C_6F_5)_4]$, have been prepared by protonolysis routes. The base-free systems are moderately active ethylene polymerization catalysts. One example, $(Me_8\text{–taa})Hf(CH_3)+$, also undergoes clean single insertion of vinyltrimethylsilane, and clean double insertion of dimethylacetylene. Ortho C–H activation of 2-methylpyridine and vinyl C–H activation of 2-vinylpyridine have also been observed with these cationic systems. Cationic alkyls based on tetradentate Schiff base ligands, e.g., $(F_6\text{–acen})Zr(R)+$, have been prepared more recently. These systems are active olefin polymerization catalysts in the presence of AIR_3 cocatalysts. Chiral analogues catalyze the stereoselective polymerization of propylene to isotactic polypropylene. Current efforts are focused on more highly electron-withdrawing chelating ligands, which should maximize the electrophilicity of the metal center in these systems and thus increase reactivity. Additionally, studies of other ligand systems, including bidentate O,N donors and chiral chelating bis-amide ligands are being pursued.

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Department of Chemistry

317. Homogeneous Models of Ammoxidation Catalysis

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We continue to exploit the discoveries of simple and efficient routes to a wide variety of organoimido-substituted derivatives of the hexamolybdate cluster, $[Mo_6O_{19}]^{2-}$. Since the hexamolybdate displays an MoO_6 coordination environment conspicuously similar to that within the ammoxidation catalyst component MoO_3, attention has focused on the preparation of benzyl- and allylimido-hexamolybdates, which would represent the closest approximation yet available of purported ammoxidation surface species. Reaction of the hexamolybdate with the benzylimido delivery reagent $Ph_3P{=}NCH_2Ph$ in acetonitrile in fact yields benzonitrile in 37% yield, presumably through the intermediacy of the benzylimido hexamolybdate $[Mo_6O_{18}(NCH_2Ph)]^{2-}$, thus providing the first example of a functional ammoxidation mimic. This reaction also produces a substantial amount (34%) of $PhCH{=}NCH_2Ph$; this product derives from reaction of benzyl amine, which itself arises as a result of unwanted hydrolysis of the benzylimido ligand. The intermediates in this ammoxidation mimicry are being sought and attempts are underway to transfer this chemistry into solvents which can be dried more efficiently.

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Department of Chemical Engineering

318. Molecular Structures and Reactivity of Mixed Metal Oxide Monolayer Catalysts
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Metal oxide monolayer catalysts, supported metal oxide catalysts possessing the active metal oxide components as a surface phase, find extensive applications in the energy industries of petroleum refining, pollution control from power generation plants, and automotive pollution control. To help bridge the knowledge gap between model and industrial metal oxide monolayer catalysts, a fundamental research program will address the relationships between the molecular structures and surface acidity and the molecular structures and surface redox chemistry of mixed metal oxide monolayer catalysts. For the fundamental surface acidity portion of the research program the alumina-supported tungsten oxide system will be the focus of the investigation, and for the fundamental surface redox chemistry portion of the research program the alumina-supported vanadium oxide system will be the focus. The influence of secondary metal oxides upon the molecular structures and reactivity of these systems will be investigated. The molecular structures will be primarily determined with in situ Raman spectroscopy, but complementary structural spectroscopies (solid state nuclear magnetic resonance (NMR) and extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES)) will also be applied. The surface chemistry will be probed by surface acidity and surface redox measurements. This fundamental information should allow better understanding of the synergistic interactions that occur in mixed surface metal oxides.

Department of Chemistry

319. Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane
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The general objectives addressed in this research are: the mode of methane activation on metals, the structure-sensitivity of the C–H bond activation, the nature of surface species originating from methane, oxygen, and dopants, the relationship between surface structure and dynamics of elementary catalytic steps, and the controlling characteristics of partial oxidation of methane. Palladium is the metal of choice because of its ability to activate methane at relatively low temperatures and a weak Pd–O surface bond. Methane was found to dissociatively chemisorb on Pd surfaces at <400K with an observed structure sensitivity of Pd(679) >Pd(311) >Pd(111). New fundamental methodology involving angle-resolved X-ray photoelectron spectroscopy (ARXPS), surface core level shifts, and X-ray photoelectron diffraction (XPD) at high energy resolution and valence band (VB) spectroscopy has also been developed. It was shown from XPD behavior of O/Pd surface core level shifts that O induced Pd surface states to exponentially decay to 5 subsurface layers. The resultant model of angular dependence in the photoelectron intensity attenuation has been extended to other overlayer systems (i.e. CO, S, Cl, and NO on Pd[100]), as well as to studies of the initial state atomic orbital character of trigonal prismatic layered MoS_2. Upon doping the $MoS_2(0002)$ surface with Cs, no Cs-induced surface relaxation was observed, but a new photoemission peak 1.6 eV above the VB edge of MoS_2 was observed corresponding to an electron donor-acceptor surface complex (*J. Phys. Chem.* **1996**, *100*, 10739). Hartree-Fock and density functional theory calculations are being performed on model Pd surfaces to better understand the Pd-adsorbate bonding interactions. Computational efforts to elucidate the electronic structure of MoS_2 and Cs/MoS_2 are also in progress.

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Department of Chemistry

320. Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Models and Precursors for Fullerenes
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The remarkable discovery that buckminsterfullerene or "buckyball," C_{60}, is a stable molecule has led to a flood of research focused on this new family of three-dimensional carbon cages known as fullerenes. These unique structures can be produced by laser vaporization of graphite or coal. Metal derivatives show promise as superconductors. This program deals with the synthesis, structural analysis, and chemistry of polynuclear hydrocarbons with carbon frameworks represented on the buckminsterfullerene surface ("buckyball" fragments referred to as "buckybowls"). These curved-surface hydrocarbons are expected to serve as models for the fullerenes in some of their chemical and physical properties. The simplest example of such a hydrocarbon is corannulene, $C_{20}H_{10}$, which represents the polar cap of buckminsterfullerene. However, corannulene undergoes rapid bowl-to-bowl inversion that may lessen its utility as a fullerene model. Consequently, a goal of this program was to produce a "locked" bowl-shaped hydrocarbon; this was accomplished by the addition of a second five-membered ring to corannulene to afford cyclopentacorannulene. More recently, this program produced the first semibuckminsterfullerenes ($C_{30}H_{12}$) representing half of the C_{60} surface. In theory, the $C_{30}H_{12}$ with 3-fold symmetry might be dimerized to produce buckminsterfullerene itself, and this exciting reaction is being explored. The synthesis of additional fullerene related hydrocarbons is a current goal of the program.

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Department of Chemistry

321. Metallocarboxylate Chemistry
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Compounds having a carbon dioxide ligand bound to a metal center are models for surface-bound CO_2 in catalytic processes. Our work is centered on the synthesis and characterization of such compounds, especially those with carbon dioxide bridged between two metal centers. In the present period, new compounds of the symmetric μ_2–η^3 type have been structurally characterized; these, together with others of the same type, allow correlation of the IR ν_{asym} band of the ligated CO_2 to be made with the coordination geometry of the metal center which binds the carboxyl oxygens. The ν_{sym} band varies only slightly with changes in the metallocarboxylate. New synthetic routes have been established for compounds having the carboxyl oxygens bound to zirconium by using transmetalation reactions of related tin complexes. A further new direction involves the synthesis and chemistry of ruthenium complexes with chelating nitrogen ligands (bipyridyl, terpyridyl, etc.) that also bear C_1 ligands; such compounds are little-known but are implicated as intermediates in reductions of CO_2 catalyzed by ruthenium complexes. Thus, the reaction of $Ru(bpy)_2(CO)(CHO)^+$ PF_6^- with water in the presence of oxygen leads to the corresponding μ_2–η^2 CO_2-bridged complex; furthermore, the reaction can be photoassisted.

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Department of Chemistry and Biochemistry

322. Odd-Electron Organometallic Chemistry of Relevance to Hydrocarbon Functionalization
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Investigations of transition metal hydride complexes that are potential precursors to highly unsaturated odd-electron organometallics has continued. The structure of $Cp^*MoH_3(dppe)$ has revealed an unexpected and unprecedented pseudo-trigonal prismatic geometry, while a product of protonation, $[Cp^*MoH(MeCN)_2(dppe)]^{2+}$ shows the expected pseudo-octahedral structure. These studies, as well as a structural study on $CpMoH_3(PMe_2Ph)_2$ and parallel theoretical investigations, have allowed a better understanding of the mechanism of hydride fluxionality in these trihydride complexes of Mo(IV). The electrochemical oxidation of $Cp^*MoH_3(dppe)$ affords the EPR active 17-electron $[Cp^*MoH_3(dppe)]^+$, which decomposes over several hours at room temperature. The decomposition involves reductive elimination of H_2 and trapping by a donor solvent to afford a stable $[Cp^*MoH(S)(dppe)]^+$ radical, which has been isolated and is currently being characterized. The radical can be reversible deprotonated by a number of bases. The deprotonated radical, presumably $[Cp^*Mo(S)_2(dppe)]^+$, has also been isolated. The decomposition of $[Cp^*MoH_3(dppe)]^+$ using nondonor solvents, which presents the potential of generating highly reactive 15-electron $[Cp^*MoH(dppe)]^+$ or $Cp^*Mo(dppe)$ species, will be a subject of future investigation. The generation of such intermediates in the presence of substrates whose C–H and C–C bonds can be selectively activated will be a particular focus of our research. Further knowledge has been gained on the role of external bases for the mechanism and stoichiometry of oxidation/deprotonation of transition metal hydrides. The ubiquitous external base for bulk electrochemical oxidations of hydride complexes is water. Investigation of oxidations of $CpMoH(L)(CO)_2$ ($L = PMe_3$ or PPh_3) and $CpMoH(PMe_3)_3$ in the presence or absence of water has revealed: (i) the action of the base as a "proton shuttle", featuring proton capture from the 17-electron hydride cation and later delivery to the 18-electron hydride precursor, followed by irreversible elimination of H_2; (ii) formation, isolation, and crystallographic characterization of a Mo(III) hydroxo complex, $[CpMo(OH)(PMe_3)_3]^+$ and a Mo(IV) oxo complex, $[CpMo(O)(PMe_3)_2]^+$.

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Department of Chemistry

323. High-Pressure Heterogeneous Catalysis in a Low-Pressure, Ultrahigh Vacuum Environment
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The major thrust of this project is to carry out high-pressure, heterogeneous catalytic reactions in a low-pressure, ultrahigh vacuum environment. These studies have now become possible because of the culmination of several investigations in the laboratory over the last five years resulting in the development of new physical processes and techniques: collision-induced absorption; collision-induced recombinative desorption; bulk vibrational spectroscopy; and the synthesis of adsorbed, reactive intermediates by translational and collision-induced activation. These new processes allow the simulation of a high-pressure environment while maintaining the single-collision conditions in which microscopic reaction steps and intermediates can be elucidated and detected by molecular beam scattering coupled with high-resolution electron energy loss spectroscopy. Results to date show that bulk H is the reactive species in the high pressure reaction involving the hydrogenation of C_2H_4.

324. Controlled Synthesis of Polyenes by Catalytic Methods
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A way has been found to synthesize totally new polyenes in a controlled living fashion from dipropargyl derivatives employing well-characterized alkylidene complexes of the type $M(CHCMe_2R)(NAr)(OR')_2$ (M = Mo or W, R = Me or Ph, Ar = 2, 6 diisopropylphenyl, R' = $OCMe_3$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, or various phenoxides) as catalysts. Dipropargyl derivatives of the type $HC\equiv CCH_2XCH_2C\equiv CH$ (X = NR, O, $C(CO_2R)_2$, $SiMe_2$, and so forth) are cyclopolymerized to give soluble polyenes that contain either six-membered rings (head-to-tail cyclopolymerization) or five-membered rings (tail-to-tail cyclopolymerization). The reaction can be controlled by varying the solvent and the type of catalyst so that "dangling" chains resulting from simple insertion of one of the propargyl groups are absent. Addition of one of the acetylene bonds to an alkylidene to yield a new disubstituted alkylidene normally would essentially terminate polymerization, since the disubstituted alkylidene would not react readily with more terminal acetylene. This problem is avoided by the speed of the intramolecular cyclization reaction to give a five-membered ring and a new monosubstituted alkylidene. This new polymerization reaction will lead to a large number of new materials since the conditions of polymerization are relatively mild (versus Ziegler-Natta conditions) and many functionalities therefore tolerated. In addition to investigating the scope and details of this new controlled cyclopolymerization reaction, the properties (nonlinear, conductivity, electrochemical, and so forth) of these new materials as a function of chain length will be studied, a fundamental question that remains largely unresolved in the area of unsaturated polymers (polyanilines, polythiophenes, polyparaphenylene, and so forth). It seems possible that, owing to the control exercised in their preparation, a wide variety of new materials will become available that may rival the more established unsaturated polymers in applications, as well as in fundamental research. A catalyst has now been prepared that cyclopolymerizes dipropargyl diethylmalonate to only six-membered rings, and another that polymerizes o-trimethylsilyphenylacetylene in a living manner to give low polydispersity polyenes that contain between 10 and 100 double bonds. Nonlinear optical measurements on both types of polymers are being carried out in order to correlate β and γ with chain length and structure.

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Department of Chemical Engineering

325. *Zeolite Characterization and Dynamics: The Effect on Molecular Transport and Catalyst Selectivity*
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Zeolitic materials are most often crystalline alumina-silicates with microporosity (less than 20Å) created by interconnected ring-like structures. These channels give sorbing molecules access to the intraparticle surface where chemisorption and reactions occur. Since the channels within the lattice are similar in size to sorbing molecules, the term "configurational diffusion" has been used to describe intraparticle transport. The limited size of the products for the reactions of hydrocarbons, selective sorption, and selectivity in isomerization and trans-alkylation reactions have been ascribed to this "shape selectivity." This research focuses on three related aspects of zeolites: the mutual interactions between adsorbing molecules and the zeolite lattice, the nature of the pore structure of the zeolite characterized during adsorption, and the influence of extreme steric constraints on cracking and isomerization reactions for cycloalkanes. Earliest perceptions of the pore structure within a zeolite have depended on the visualization of the Si(Al)-oxygen crystalline bond network. This representation and analysis depends upon an image of a fixed pore configuration based primarily upon X-ray diffraction (XRD) studies of the solid structure. Recent studies employing solids nuclear magnetic resonance (NMR) and in situ XRD have documented that the shape of the adsorbing pores can change on adsorption. More recently, detailed spectroscopic studies of adsorption and of adsorbing molecules have begun to provide a picture of the pore structure and the sorbing species during sorption. In situ infrared spectrometry (specifically far-FTIR) and thermal or gravimetric analyses (DTA and TGA) can also be employed to understand the dynamic configurational changes in the sorbing species and the energetics of these interactions. Several of these techniques have been developed, and each will be used in concert to understand the effects of the interactions between adsorbing molecules, their transport, and their reactivity. Specifically, ^{29}Si, ^{129}Xe, and ^{15}N NMR will be employed in conjunction with high resolution adsorption, HR–S, with DTA-TGA, and with FTIR for the initial studies of the adsorption of C6 and C7 cycloalkanes within ten- and twelve-member ring zeolites. In addition, the rate of adsorption/diffusion will be quantified by solids-gas chromatography (SGC). The cracking and isomerization reaction of these cycloalkanes will be studied to understand the symbiotic relationship between dynamic pore/adsorbate interactions and the resultant reactions of these cycloalkanes.

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Department of Chemistry

326. *Towards Computer Aided Catalyst Design: Three Effective Core Potential Studies of C-H Activation*
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We have focused on methane activation. Study of this reaction also provides the impetus for improved modeling of inorganic systems. Research has focused primarily on methane activation by transition metal (TM) imidos (L_n M=NZ), and mercury complexes. Since hydrocarbons other than methane are present in natural gas, a conversion catalyst must operate in a multisubstrate environment. To complement experiments by Wolczanski, we studied CH activation of hydrocarbons larger than methane by Zr-imidos. This work provides new insight into substrate effects in CH activation allowing us to address questions relevant to selectivity. A major question of interest in catalysis involves modifying a complex to make it more active. Previous work has focused on the role of metal and ancillary ligands in methane activation. Our most recent research indicates it is difficult to tailor imido reactivity through electronic modification of imido substituents (Z), because most substituents studied are found to exert their influence primarily through inductive effects localized on the sigma framework. This suggests several profitable areas to be pursued. Hg(II) and complexes of related electrophilic, late TMs have attracted much experimental interest. A main impediment to their development is lack of an intimate understanding of the CH activation mechanism. Our objective is to study how prototypical hard and soft anionic ligands control the kinetics and thermodynamics of methane activation by Hg(II) complexes. The great sensitivity shown by these systems to ligand modification suggests that these ligands can be modified to effect lower CH activation barriers. This research suggests several logical extensions to greater activity including replacing mercury with related metals and going to cationic complexes.

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Department of Chemistry

327. ***The Role of Hydrogen in C-N, C-C, and C-S Bond Activation on Ni and Pt Surfaces***
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C–N, C–C, and C–S bond activation reactions play an important role in catalytic processes used in both the fuels and chemical industries. We are examining the role of hydrogen in bond activation reactions on Ni and Pt surfaces in order to establish a basic understanding of the primary factors which control bond activation. The primary methods include spectroscopic characterization of adsorbed intermediates using a combination of surface spectroscopies and transient kinetic studies of stoichiometric surface reactions. Over the year we have focused our research primarily on developing a fundamental information regarding two reaction systems on nickel. Phenylthiolate is the dominant intermediate independent of hydrogen availability during C–S bond activation in phenylthiol. Hydrogen appears to be directly involved in C–S bond activation on Ni. For C–S bond activation, tilted orientations of the adsorbed phenylthiolate intermediates appear to be most favorable for hydrogenolysis. Adsorption in perpendicular or nearly perpendicular orientations limits bond activation as well as interactions with the attached phenyl group. Coadsorbed hydrogen does not activate C–C bonds in small hydrocarbons. However, we have found that energetic forms of hydrogen activate strained C–C bonds in cyclic hydrocarbons at low temperature. After initial atomic hydrogen addition from the gas phase to form an adsorbed alkyl group, coadsorbed hydrogen adds to form the alkane. Efforts to activate C–C bonds in unstrained ring systems like cyclohexane, cyclohexene, and toluene were unsuccessful suggesting that even these reactions are kinetically controlled on the surface. These studies establish a method of probing hydrogen induced C–C bond activation and also provide a new approach for preparing adsorbed alkyl species on Ni. In summary, over the past year we have developed substantial new understanding of the role of hydrogen in C–S and C–C bond activation reactions on Ni.

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Department of Chemical Engineering and Materials Science

328. ***Homogeneous–Heterogeneous Combustion: Chemical and Thermal Coupling***
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The roles of homogeneous and heterogeneous reactions in catalytic oxidation processes are being studied experimentally and theoretically by measuring rates and concentration and temperature profiles near reacting surfaces and by calculating these profiles for known kinetics. Laser-induced fluorescence methods are being developed to measure the concentrations of free-radical intermediates near reacting surfaces for several combustion reactions on polycrystalline platinum and rhodium as functions of surface temperatures and reactant composition, pressure, and temperature. Concentrations of stable and radical intermediates with and without homogeneous reaction will be measured directly. Concentration and temperature profiles are also being calculated for various reaction processes and flow conditions. Of particular interest is the occurrence of multiple steady states and oscillations for various models of homogeneous-heterogeneous processes. Reaction rate expressions for individual surface and homogeneous reactions are used to simulate the experimentally observed behavior. Particular interest centers on the selectivity of partial oxidation reaction such as production of CO and hydrogen from methane oxidation, olefins by oxidative dehydrogenation of alkanes, and oxygenates by oxygen addition to alkanes. The objective of this research is to understand the contributions of each type of reaction in practical situations in catalytic reactors and combustors in order to determine their implications in reactor selectivity for chemical synthesis and for pollution abatement.

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Department of Chemistry

329. ***Late Transition Metal Oxo and Imido Complexes***
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This project involves the exploration of the chemistry of late-transition metal oxygen and nitrogen bonds and is of relevance to catalytic processes in chemical manufacturing and pollution control. Recent highlights include the chemical and structural characterization of the only model for the binding of dinitrogen inside the nitrogenase Mo/Fe cluster, the synthesis and characterization of a dioxo centered M/Au (M = Rh, Ir) clusters with square pyramidal coordination geometry about oxygen stabilized by Au–Au and Au–M bonds, and the synthesis and characterization of unexpectedly stable dppm and dppm-H imido complexes. The nitrogenase model complex is our previously synthesized gold complex $[(LAu)_3N_2(AuL)_3]^{2+}$ ($L = PPh_3$). Our recently completed structural characterization of this complex reveals that it contains a dinitrogen unit inside a cluster of six Au atoms. Each nitrogen atom is bonded to three metal atoms as has been proposed by Rees and others for the bonding of dinitrogen inside the Mo/Fe cluster of nitrogenase. Reduction of $[(LAu)_3N_2(AuL)_3]^{2+}$ in the presence of a proton source produces ammonia indicating that $[(LAu)_3N_2(AuL)_3]^{2+}$ structurally and chemically models nitrogenase. The dioxo clusters $[(COD)_2M_2(O)_2(AuL)_4]^{2+}$ (M = Rh, Ir; L = PPh_3) were prepared by the reaction of $[(LAu)_3(O)]+$ and $[(COD)MCl]_2$ and contain oxygen atoms in an usual square pyramidal coordination geometry. These clusters are related to a class of complexes containing all-gold metal atoms which are stabilized by "aurophilic" Au–Au bonds. Our dioxo clusters contain not only stabilizing Au–Au bonds but also stabilizing Au–M bonds indicating the likely existence of a new class of complexes related to the all-gold complexes. Finally, we have succeeded in expanding our previously reported dimeric Pt oxo complexes $[L_4Pt_2(O)_2]$ (L = a phosphine) to the analogous imido complexes. However, while the oxo complexes were prepared for a large variety of phosphine ligands the only effective phosphine for the imido complexes is dppm and dppm-H. This unique ability of the dppm and dppm-H ligand to stabilize the imido complexes is not understood at this time.

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330. *Mechanistic Studies of Transition Metal-Catalyzed Alternating Copolymerizations of Carbon Monoxide with Olefins*

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Polyketones are a significant new class of polymers prepared from alternating copolymerization of CO and olefins. The basic objective of the program is to elucidate the fundamental mechanisms of these copolymerization reactions catalyzed by Pd(II) and Ni(II) species. Well-defined Pd(II) catalysts of the type $(N\text{-}N)PdCH_3(solv)^+ BAr'_4{}^-$ (N–N = bipyridine, phenanthroline; Ar' = $3,5\text{–}(CF_3)^2\text{–}C_6H_3\text{–}$) have been prepared. A highly detailed mechanism of copolymerization of ethylene and CO has recently been reported (*J. Am. Chem. Soc.*, **1996**, *118*, 4746–4764). All potential intermediates in the catalytic cycle have been independently generated including the alkyl ethylene complexes $(N\text{–}N)Pd(C_2H_4)R^+$, alkyl carbonyl complexes $(N\text{–}N)Pd(CO)R^+$, acyl carbonyl complexes $(N\text{–}N)Pd(CO)COR^+$, acyl ethylene complexes $(N\text{–}N)Pd(C_2H_4)COR^+$ and chelate complexes $(N\text{–}N)PdCH_2CH_2COR^+$ and $(N\text{–}N)PdC(O)CH_2CH_2COR^+$. Migratory insertion rates for all carbonyl and olefin complexes have been measured as well as relative binding affinities of ethylene and CO to key species. This kinetic and thermodynamic data has been combined to provide a detailed picture of the mechanism of copolymerization and which intermediates are of significance in the catalytic cycle. The data obtained accurately predicts the observed turnover frequency and the observed kinetic dependence (first-order in ethylene, inverse order in CO). Work has continued on the development of chiral bis-oxazoline-based Pd(II) catalysts for synthesis of isotactic, optically active polyketones based on styrenic monomers. Unique ligand exchange processes have been developed which provide a new method of synthesis of stereoblock polyketones and a deeper understanding of chain-end versus enantiomorphic site control of polymer microstructure. A fundamental study of substituent effects on migratory insertion rates in a series of substituted styrene complexes $(phenantroline)Pd(CH_3)(CH_2 = CHC_6H_4X)^+$ (X = H, CF_3, Cl, CH_3, OCH_3) has been completed (*J. Am. Chem. Soc.* **1996**, *118*, 2436–2448). These studies clearly show that ground state energies are more sensitive to substituent variation than transition state energies and electron-donating substituents stabilize the ground state and thus retard the overall rate of migratory insertion. Work is in progress on the complete mechanistic analysis of copolymerizations catalyzed by bidentate phosphine-based systems and the development of new bidentate ligands for use with both Pd(II) and Ni(II) systems.

331. *Reductive Coupling of Carbon Monoxide to C_2 Products*

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A variety of synthetic routes to tungsten nitrene complexes have been developed. Nitrene transfer from cationic tungsten nitrene monomers to trimethylphosphine has been achieved, and a copper catalyst for nitrene transfer from PhINTs to olefins has been prepared. These results are encouraging for developing systems that will transfer the neutral nitrene NR fragment to electron-rich olefins to form aziridines. Another result in M–N–C chemistry is the selective regiochemistry for electrophile addition to $W{=}N\text{–}CR_2$ units. With an ancillary alkyne ligand in the coordination sphere, a coordinated imine ligand forms $(M\text{–}NH{=}CR_2{}^+)$. The regioselectivity of proton addition is reversed when the nitrogen lone pair is involved in a simple 2-center-2-electron bond as protonation then occurs at carbon to form a nitrene ligand $(M{=}N\text{–}CHR_2{}^+)$. The $Tp'(CO)_2W$ fragment avidly seeks three electrons, and the stability of six-coordinate monomers incorporating a three-electron donor into the sixth site has allowed us to isolate analogous N, NH^+, and CH complexes. In addition to the CH carbyne complex, alkyl carbyne derivatives $Tp'(CO)_2WCCH_2CH_2R$ and their vinyl and allyl isomers have been prepared. By combining complementary carbyne reagents, $Tp'(CO)_2MoCCl$ and deprotonated $Tp'(CO)_2WCCH_3$, dimers containing the CCH_2C linkage can be synthesized. These dimers are susceptible to deprotonation and oxidation to form simple CCC bridged dinuclear products.

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Department of Chemical Engineering

332. *Solid-State, Surface, and Catalytic Studies of Oxides*

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Multicomponent oxides are catalysts for a number of technologically important reactions, including the selective conversion of low-priced saturated hydrocarbons by oxidation (selective oxidation) to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher value, and for the removal of nitorgen oxides, which is an atmospheric pollutant from exhausts of lean-burn, gasoline engines (lean NO_x conversion). The emphasis of this project is to identify the properties of oxidic catalysts that determine their catalytic properties in these reactions. In selective oxidation, it was found that modification of a silica-supported vanadium oxide catalysts with phosphorus resulted in significant increases in the selectivity for the formation of maleic anhydride. Spectroscopic characterization of the samples suggested that the high selectivity could be correlated with the formation of a phosphorus-vanadium oxide compound. Indeed, impregnation of a solution of this compound onto a silica support produced a catalyst of high selectivity close to a commercial sample. The vanadium ions in this sample were in a lower average oxidation state than for the less selective samples. In lean NO_x reduction, it was found that effective catalysts contained transition metal oxides highly dispersed in an inert matrix. The desired catalytic properties could be correlated with the inability of the catalyst to activate oxygen rapidly. Thus, alumina-supported Au and Ag catalysts could also be made effective for NO^x reduction when the crystallite size of Au or Ag particles was such that the sample did not activate oxygen rapidly.

Department of Chemistry

333. *Organometallic Adsorbates and Models Chemistry, Spectroscopy, and Catalysis*

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The project goal is to characterize chemisorptive processes responsible for dramatic enhancements in catalytic activity when actinide, lanthanide, and early transition element organometallic complexes are adsorbed on Lewis acidic surfaces. Surface reaction chemistry is studied by chemical and spectroscopic techniques, while catalytic properties (e.g., olefin hydrogenation) are characterized by kinetic measurements, isotopic labeling, product stereochemistry, and spectroscopy. On Lewis acid supports, Cp_2MR_2 complexes (Cp = cyclopentadienyl-type ligand; M = Th, U, Zr; R = alkyl group) undergo R^- abstraction to yield electrophiles, highly electrophilic Cp_2MR^+ species, which are shown to be active catalytic centers by CPMAS NMR spectroscopy. Importantly, these species can be spectroscopically, structurally, and functionally modeled in solution by isolable $Cp_2MR^+ X^-$ complexes, where X^- is a weakly coordinating fluroarylborate anion. The chemisorptive process as well as the pathway by which methylalumoxane, "$[Al(CH_3O]_n$" activates organo-group 4 complexes for industrial scale olefin polymerization processes can be modeled using fluroarylborane organo-Lewis acids as abstraction reagents. Finally, these catalysts can be employed to produce completely new types of functionalized polyolefins via a ring-opening processes in which exo-methylene substituted cycloalkanes open to yield exo-methylene substituted polyethylenes.

334. *Chemical Interactions in Multimetal—Zeolite Catalysts*

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The problem of changing the selectivity of Rh catalysts in CO hydrogenation from hydrocarbon production to synthesis of oxygenates by "promoting" the catalyst with manganese has been addressed. By using zeolite supported samples, it was possible to synthesize samples with identical Rh content but with the manganese being present either as Mn^{2+} ions or as MnO particles. In the former case, no oxygenates were formed; in the latter case a high yield of ethanol and ethyl acetate was obtained, suggesting that acetate ions are primary products. Subsequent catalyst characterization revealed that MnO and Rh clusters are located inside zeolite cavities and in direct physical contact with each other. Research towards zeolite supported acids, such as sulfated ZrO_2, has been initiated.

335. *Organometallic and Surface Chemistry of Mixed-Metal Systems*

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Our research focuses on the reactions of ligands attached to clusters and the relation of these reactions to reactions on metal surfaces. Because of their importance in surface chemistry and catalysis, most of this research concerns carbonyl, sulfur dioxide, oxo, sulfido, carbido, and hydrido ligands and their derivatives. We have demonstrated that bridging CO in clusters can be attached by electrophiles and subsequently converted to C, CCO, C_2, and C_4 ligands in polymetal clusters. Similarly, the attack of nucleophiles on SO_2 bound to metal clusters and the conversion of coordinated SO_2 to coordinated S or SO was demonstrated. We are currently studying the relative reactivities of bridging CO and SO_2 ligands and extending vibrational spectroscopic characterization of the products. The latter information is relevant to the identification of ligands on metal surfaces. Recent studies center on the reaction of the SO_2 analog OSNPh with either $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(NCCH_3)_2$. Products from these reactions include $Ru_3(CO)_9(\mu_3\text{-NPh})$, $(\mu_3\text{-S})$, Ru_4, $\eta^2SnPh)(\mu_4\text{-S})$ and $Ru_4(CO)_{11}(\mu_4, \eta^2\text{-SNPh})(\mu_4\text{-NPh})$, which have been structurally and spectroscopically characterized.

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336. *Transition Metal-Mediated Thermal and Photochemical Carbon Dioxide Activation*

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The overall goals of this project are to elucidate the patterns of reactivity, both thermal and photochemical, of coordinated CO_2 and to develop catalytic processes based on these patterns. Activities during the past year have been focused in two areas: 1) attempts to produce the first cis, bis- CO_2 complex as a potential precursor to oxalate derivatives via C–C bond formation and 2) exploratory studies of transition metal-mediated insertion of CO_2 into C–C and C–H bonds. Regarding (1) we have sought to prepare cis-(tetraphos)$Mo(CO_2)_2$. In several experiments an unstable compound (IR: 1700, 1620 cm^{-1}), believed to be the desired CO_2 adduct has been isolated, but we have been unable to obtain it in pure form. Towards (2) we have initiated CO2 reactivity studies of a metallacyclobutane complexes [$L_nM= L_2Cl_2Pt, L_2Ni, Cp^*Rh(PMe_3)$], derivable from cyclopropanes, to model prospective systems for catalytic cyclopropane carboxylation. While several Pt(IV) derivatives failed to react with CO_2, insertion has been observed with some of the Ni- and

Rh-derivatives; characterization and reactivity studies of the resulting metallalactone complexes are underway. We are also investigating the possibility of CO_2 trapping of reactive metallacycles generated in metal-catalyzed isomerization of strained hydrocarbons, e.g. quadricyclane→norbornadiene. We have also been examining the interaction of CO_2 with several systems known to activate C–H bonds (e.g. Rh(I), Mo(O), Cu(I), and Ru(O) complexes) with the potential for effecting hydrocarbon carboxylation. Finally, our study of the reactivity and mechanism of the thermal decarbonylation of a set of $Cp'_2Nb(CO_2)R$ complexes, the first systematic reactivity study of a set of related CO_2 complexes, has been published.

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Department of Chemical Engineering

337. *Activity and Selectivity Enhancements in Liquid-Phase Reactions by Metal-Support Interactions*

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The project objectives are to study metal-support interactions that have a pronounced influence on adsorption and catalytic behavior and to use these effects to alter hydrogenation reactions such as those involved in fine chemicals production. In addition to determining kinetic behavior, emphasis is on characterizing adsorbed molecules as well as the chemical and physical state of the metal and support. Benzaldehyde hydrogenation on Pt/TiO_2 was found to have turnover frequencies 10–100 times greater than those on Pt/SiO_2 and Pt/Al_2O_3 while benzyl alcohol hydrogenation was inhibited. This resulted in a 100% selectivity to the desired intermediate–benzyl alcohol–up to conversions above 80%. Special sites formed at the Pt-TiO_2 interface are proposed to explain this behavior. As a test of this hypothesis, TiO_2 was placed on the surface of UHP Pt powder and the improvements in activity and selectivity were replicated. A reaction model was proposed which fit the kinetic data well. Turnover frequencies for phenylacetaldehyde hydrogenation were measured and again the most active Pt/TiO_2 catalyst gave values 2–5 times higher than typical supported Pt catalysts. At conversions up to 60%, this catalyst also gave the highest selectivity to phenylethanol (70%) compared to 0–30% for the other Pt catalysts. A study of the hydrogenation of benzene/toluene mixtures over supported Pd showed that the ratio of rates in an equimolar mixture, R_{Tol}/R_{Bz}, was consistently near 0.65 and thus favored benzene. This ratio was essentially independent of support, pretreatment temperature, or reaction temperature. A detailed kinetic analysis revealed that previous interpretations of rate parameters were inappropriate and an improved reaction model was proposed. A new high-pressure reactor system has now been constructed to allow the study of liquid-phase hydrogenation reactions. Reactants to be initially examined include an organic acid, an aromatic hydrocarbon, and a conjugated aldehyde. Acetic acid adsorbed on Pt and TiO_x-covered Pt surfaces is concurrently being studied by HREELS, XPS, AES and TPD.

Department of Chemistry

338. *Transition-Metal-Mediated Transformations of Small Molecules*

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Catalytic transformations by transition metals and their compounds is of fundamental scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands usually associated with such systems. The current research is focused on transition metal catalyzed polymerizations. The study specifically encompasses homogeneous metal catalyzed systems for the synthesis of several different kinds of copolymers incorporating the carbonyl functionality in the backbone. The carbonyl functionality is derived form carbon monoxide, an inexpensive monomer. Such polymers are of great current interest because of their photodegradability and because they are precursors to a wide range of functionalized polymers. The principal research goals are: (a) the design of living copolymerization systems that would allow the directed synthesis of block terpolymers involving the copolymerization of two different olefins with carbon monoxide, as well as block polymers incorporating polyolefin and olefin-carbon monoxide blocks, (b) the synthesis of regiospecific, stereospecific and, ultimately, chiral alternating olefin-carbon monoxide copolymers using appropriate catalysts, (c) the synthesis of star, comb, and graft polymers with alternating olefin-carbon monoxide segments, (d) the synthesis of alternating copolymers of functionalized olefins with carbon monoxide, and finally (e) the direct synthesis of polycarbonates and polyoxalates from carbon monoxide and diols.

Intercollege Materials Research Laboratory

339. *Carbon Deposition and Deactivation of Metallic Catalysts*

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The overall objective of this program is to achieve conditions where it is possible to control the catalytic properties of a given metal by inducing geometric and electronic perturbations to the reactive surfaces of the crystallites. One of the consequences of such an action would be to enable one to alter the catalytic reactivity in such a manner so as to optimize the performance for a desired reaction pathway, while simultaneously suppressing the rate of detrimental side reactions, such as certain forms of carbon deposition. Our strategy has centered around a study of the effect of introducing selected adatoms into the host metal and using the decomposition of ethylene to probe the manner by which the chemistry of the various faces of the crystallites is modified. It is well known that iron, cobalt and nickel undergo rapid deactivation when heated in hydrocarbon environments at temperatures in excess of 500°C, and this is believed to be due to the formation of graphite overlayers. In the current program we are endeavoring to prevent premature catalyst deactivation by forcing the carbon species to follow an alternative route. Instead of accumulating on the metal surfaces where reactant molecules undergo dissociative chemisorption, the carbon species are diverted from these faces and following diffusion through the metal crystallites, eventually precipitate at other faces to form a nanofiber structure. Under such circumstances the active faces remain relatively clean and available to perform the desired hydrocarbon conversion reactions. We have demonstrated that this condition can be achieved by the introduction of a small amount of selected adatoms, including copper, silver or tin, into the ferromagnetic metal. While the total amount of carbon deposited during reaction was increased significantly with the bimetallics, the growth features were such that it did not interfere with the desired reaction and as a consequence, catalytic activity of the particles was maintained for prolonged periods of time. The modification in the carbon depositing characteristics of the metal are rationalized according to the notion that the presence of the additive promotes surface atom reconstruction of particles and also induces electronic perturbations in the catalyst system.

Department of Materials Science and Engineering

340. Determination of the Distribution of Hydrogen in Coal by Fourier Transform Infrared (FTIR) Spectroscopy
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The purpose of this research is to determine the role of hydrogen-containing functional groups in coal. Work in the last year has focused predominantly on measuring parameters that describe the strength and extent of hydrogen bonding interactions using FTIR. By studying model phenolic systems we have found that intramolecular interactions play a key role. These parameters are then used in a model that describes coal swelling and its relationship to structure (cross-link density, etc.) Our previous work has demonstrated that present theories need to be modified to account for the high degree of cross-linking found in coal and we have developed a new theory based on a non-Gaussian model in order to address this problem.

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Department of Chemical Engineering

341. Support Effects Studied on Model Supported Catalysts
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We are studying support effects associated with precious-metal catalysts, with particular application to automotive emissions control. In automotive catalysis, the oxide support plays an important role in maintaining oxygen stoichiometry through the use of a reducible oxide(ceria). We have shown that this appears to occur through an oxygen transfer from the ceria to the precious metal, which can be observed through TPD experiments with CO (which desorbs as CO_2) and through steady-state CO oxidation measurements, where a second reaction mechanism is observed. Large crystallites and single crystals of ceria are not able to transfer oxygen, demonstrating structure sensitivity of the ceria. To study the structure sensitivity, we are using simulated annealing studies of small ceria clusters and oxygen TPD experiments. Difficulties associated with growth of ceria crystallites are avoided in real catalysts through the use of ceria-zirconia mixtures. Therefore, we are also studying the effect of mixed oxides to determine the way in which stabilization occurs.

Department of Chemistry

342. Inorganic Polymers and Materials
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This project is focused on the development of new polymeric-precursor synthetic routes of technologically important ceramics in processed forms. Current studies are conducted on the syntheses, properties, ceramic-conversion reactions, and applications of new boron-based polymers, including polyvinylborazine, polyborazylene, borazine-modified polysilazanes, and both decaborane and carborane-based polymers. In addition, investigations are being conducted on the use of these polymers as reagents for the synthesis of a wide range of metal boride, metal nitride, and metal silicide ceramics. Major achievements of the last year have included the development of melt-spinnable polymeric precursors to both BN and composite SiNCB ceramic fibers and a new efficient synthetic route to lanthanum metal boronitride intermetallics, such as the $La_3Ni_2B_2N_3$ superconductor. The continued development of the fundamental synthetic methodology needed to produce new inorganic monomers and polymers is also a key component of this project.

343. Catalytic Hydrogenation of Carbon Monoxide
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Central objectives for this program encompass the development of new strategies for conversion of carbon monoxide and hydrocarbons into organic oxygenates at mild conditions of pressure and temperature. A primary focus is placed on designing transition metal complexes with thermodynamic properties and potential mechanistic pathways that promote the formation and transformation of intermediates that determine the selectivity and rate for substrate reactions. The seminal observation that rhodium porphyrin complexes have the unusual thermodynamic capability to produce metalloformyl (M–CHO) species at low pressures of H_2 and CO is utilized in guiding the design of metal complexes that have both the thermodynamic and kinetic properties necessary for catalytic CO hydrogenation. Production of formyl species from H_2 and CO has now been shown to be a general property for rhodium complexes of nitrogen donor macrocycles and has also recently extended to complexes of nonmacrocyclic tetradentate ligands with both nitrogen and oxygen donors. Structurally flexible nonmacrocyclic ligand complexes manifest reaction pathways excluded to macrocyclic ligand complexes, and have the capability of achieving oxidative addition, reductive elimination, and migratory insertion steps integral to selective CO hydrogenation to alcohols. An alternate reaction pathway to form organic oxygenates that occurs through initial CO reductive coupling has been observed for rhodium porphyrins and the scope of rhodium complexes that can reduce and couple CO is currently being evaluated. New materials are also being designed to achieve simultaneous activation of CO and CH_4 to give organic formyl and acyl functional groups.

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344. *Fundamental Aspects of Selective Reduction of NO_x and Low Temperature Methane Activation Catalyzed by Zeolites*

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Medium pore-sized zeolites containing a wide variety of charge-compensating cations are active catalysts for selective reduction of NO by hydrocarbons and for low-temperature activation of CH_4 by NO. The objective of the proposed research is to develop a fundamental understanding of the surface chemistry which governs both of these chemical processes. Metal-loaded zeolites will be prepared by ion exchange under controlled conditions which will be systematically changed in order to vary the type and concentration of metal species. The catalysts are to be characterized by a variety of techniques including FTIR, MAS-NMR, temperature-programmed reactions with probe molecules, and isotopic exchange reactions. Fundamental information regarding the individual steps involved in the reaction mechanism and which of these steps are rate limiting will be developed by isotopic transient investigations. The role of parameters such as zeolite acidity, structure, and the reducibility of the charge-compensating cations will be probed through reaction studies and catalyst characterization, and relationships will be developed between these catalyst properties and key reaction steps such as the activation of methane. Moreover, the importance of components such as H_3CNO_2 and NO_2 in forming a N–N bond in these systems will be investigated.

Department of Chemistry

345. *Vibrational Spectroscopic Studies of Surface Chemical Interactions in Chemisorption and Catalysis*

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Catalytic reactions are being studied using vibrational spectroscopy methods coupled with electron and photon stimulation of the reactions. The vibrational spectroscopic methods include Fourier transform infrared reflection absorption spectroscopy (IRAS) on model single-crystal catalysts and transmission infrared spectroscopy (TIR) on high area powdered catalysts. Current problems include: (1) study of the role of defect sites on catalytic reactions; (2) study of the activation of chemical bonds by coordinatively unsaturated surface sites on supported metal catalysts; and (3) study of the dynamical motion of adsorbates on single-crystal surfaces and the anisotropic nature of these motions. For project (3) the ESDIAD (electron stimulated desorption ion angular distribution) method is employed. A particularly important goal of project (2) is to learn how to thermally activate C-H bonds in alkanes. Following up on our photochemical work in which coordinatively unsaturated $Rh(I)CO/Al_2O_3$ species were found to activate C-H bonds, a study of the thermal activation of alkanes on these sites is underway.

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Department of Chemistry

346. *Novel Intrazeolite Metal-Oxo Catalysts and Alloy Clusters*

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The focus of this project is the design of novel catalysts based on transition metal complexes and oxo species encapsulated in the cages of zeolites. These systems are expected to offer both improved control over the active species in heterogeneous catalysis and novel reactant and product selectivities. We combine the catalytic activity of transition metal catalysts with the shape selectivity and well-defined pore structure of zeolite pores. Recent work has focused on intrazeolite manganese triazacyclononane chelate complexes and their activity in highly selective olefin epoxidation and other reactions. The selectivity of these catalysts exceeds that of many previous zeolite/metal complex-based epoxidation catalysts. Furthermore, we are also exploring homogeneous oxidation catalysis with this family of complexes as a basis for the design of future hybrid catalysts, and we have substantially improved the activity of the complexes compared to previous work. Molybdenum oxo species encapsulated in zeolite hosts were also found to be highly selective epoxidation catalysts. First successful developments in the design of asymmetric, zeolite-encapsulated epoxidation catalysts have been achieved. Using chiral Mn-salen complexes in large-pore hosts such as EMT, asymmetric epoxidation of cis-olefins has been observed. We perform comprehensive characterization with spectroscopic and structural techniques including EXAFS (Extended X-Ray Absorption Fine Structure) spectroscopy utilizing synchroton radiation, in situ FT-IR coupled to thermodesorption, Micro Raman, UV-NIR, and ESR spectroscopies. Catalytic studies of hydrocarbon conversions address issues such as the location of catalytically active sites, stability against migration, and shape selectivity.

347. *Catalytic Arene Hydrogenation Using Early Transition Metal Hydride Compounds*

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During the last year a concerted effort has been focused on gaining a better understanding of the mechanism of arene hydrogenation catalyzed by Group 5 metal hydride compounds. The kinetics of the hydrogenation of aryl-phosphines (e.g., PPh_3, $RPPh_2$), etc. by niobium aryloxide systems has been studied and successfully modeled. The stereochemistry of the reactions have been explored by a variety of methods and shown to occur in a predominantly all- *cis* fashion. The stoichiometric reaction of tantalum polyhydrides, $[Ta(OAr)_2(Cl)(H)_2(L)_x]$ (x=1,2) and $[Ta(OAr)_2(H)_3(L)_2]$ with cyclohexene, cyclohexadiene and related olefinic substrates has been surveyed. The organometallic products obtained are found to be highly dependent on the nature of the aryloxide ancillary ligation. The mechanism of styrene hydrogenation by $[Ta(OAr)_2(Cl)(H)_2(PMe_2Ph)_2]$(OAr=2,6-diphenylphenoxide) is being studied. The regio and stereoselectivities of various surface supported Group 5 metal species are also being evaluated. In particular, the nature of the oxide support on the hydrogenation of arene substrates is being studied.

348. Fundamental Studies of Reactive Intermediates in Homogeneous Catalysis

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Mass spectrometry and gas-phase ion chemistry techniques are employed to investigate the thermodynamics and intrinsic reactivity of organic and organometallic models for reactive intermediates in combustion and homogeneous catalysis. Energy-resolved collision induced dissociation (CID) in a flowing afterglow-triple quadrupole apparatus has been used to determine M–CO bond dissociation energies for a series of homoleptic metal carbonyl anions. We have now completed measurements and analyses of the sequential M-CO bond strengths in a series of cyclopentadienyl (Cp) metal carbonyl ion complexes, $CpM(CO)_n^{+/-}$($Cp=c\text{-}C_5H_5$). These data provide an instructive picture of the variable influence of this important polydentate organic ligand on M-CO bonding. Moreover, the trends exhibited by the bond strengths in isoelectronic $CpM(CO)_n^+$, $CpM(CO)_n$ and $CpM(CO)_n^-$ complexes provide quantitative insights into the interplay between back-bonding and M–CO bond strengths. Unlike the $M(CO)_n^-$ ions, which display remarkably constant M-CO bond energies around 40 kcal/mol, the $CpM(CO)_n^-$ ions show spectacular variations in their sequential M–CO bond strengths, which range from about 24 kcal/mol for the "slipped" η^3–$CpCo(CO)_2^-$ ion to more than 70 kcal/mol for η^5–$CpCoCO^-$. Energy-resolved CID has also been used in conjunction with other gas-phase ion experiments to determine absolute heats of formation for organic fragments such as phenyl radical, the isomeric benzynes, cyclopropenylidene, the isomeric dehydrotoluenes and phenyl carbene. These data are being used to derive sequential C–H bond energies for simple hydrocarbons such as benzyne, toluene and cyclopropane. Construction is nearly completed of a new flowing afterglow-guided ion beam instrument, which will be use for refined measurements of thermodynamic data for a wider variety of organic and organometallic intermediates. We have developed a new method for preparing negative ions of biradicals in the gas phase, and have used this method in collaboration with the Lineberger group in Boulder to determine electron affinities and singlet-triplet splittings for trimethylenemethane, meta-benzyne and para-benzyne. We have successfully developed an electrospray ionization (ESI) source for our flowing afterglow-triple quadrupole apparatus. The ESI source is being used to examine the properties and reactivity of massive transition metal complexes transported from polar solutions directly into the gas-phase flow reactor. A preliminary value for the Ru-bipy (bipy=2,2'-bipyridine) bond dissociation energy in $Ru^{2+}(bipy)_3$ of 46 kcal/mol has been determined from energy-resolved CID. The tandem ESI-flowing afterglow-triple quadrupole instrument will ultimately be used to examine directly the components of catalytically-active homogeneous solutions.

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349. I. Metal Carbonyl - Hydrosilane Reactions and Hydrosilation Catalysis; II. Catalytically Relevant Chemistry of (η^5-Indenyl) Ru Alkyl Complexes.

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The reactions of hydrosilanes [e.g., Me_2PhSiH, Ph_2SiH_2] towards manganese p-substituted benzoyl complexes $(CO)_5MnC(O)C_6H_4Y$ (Y =H, Me, OMe, t-Bu, CF_3) provided either $ArCH_2OSiMe_2Ph$ (90%) and variable amounts of $(CO)_5MnSiMe_2Ph$ or exclusively $(CO)_5MnCH(OSiHPh_2)Ar$. Similar studies with $(L)(CO)_4MnCOAr$ and (L)$(CO)_4$MnCOCH3 [L =PPh_3, PMe_3, $P(OMe)_3$] were thwarted by facile decarbonylation reactions for the former and ill-defined degradation reactions for the latter. In particular, the acetyl complexes yielded mostly disiloxanes: 2 equiv. of Me_2PhSiH consumed L =$P(OMe)_3$ (all-cis, in 15 min.), PPh_3 (50%-cis, 45 min), and PMe_3 (all-cis, 3 days). These Mn complexes and $(L)(CO)_4MnH$ [L =CO, $P(p\text{-tolyl})_3$, $P(OMe)_3$] were surveyed as hydrosilation precatalysts (Me_2PhSiH, Ph_2SiH_2) towards acetone or ethyl acetate. The manganese acyls $L(CO)_4MnC(O)R$ [L =CO, R =CH_3, Ph; L =PPh_3, R =CH_3] also catalyzed the $PhSiH_3$ hydrosilation-reduction of $Cp(CO)_2FeC(O)CH_3$ to give $[FpCH(CH_3)O]_{3-x}H_xSiPh$ [x =0-2] and $FpCH_2CH_3$. The $PhSiH_3$ (1.6 equiv) / $RhCl(PPh_3)_3$ (3%) system, however, converted Cp(L)(CO)FeC(O)R to their alkyl derivatives, $Cp(L)(CO)FeCH_2R$ (49 to 87% isolated yields), plus some vinyl complexes $Cp(L)(CO)FeCH{=}CH_2$: [FpC(O)R, R =Me, Ph, i-Pr, t-Bu; $Cp(L)(CO)FeC(O)CH_3$, L =PPh_3, $P(OMe)_3$, and $P(OPh)_3$]. The facile carbonylation of (Ind)Fe(CO)(L)R apparently entails η^5-η^3 indenyl ring slippage commensurate with stereospecific, backside association of CO prior to the alkyl-CO migration. Thus, $[Fe^{13}]CH_3$ and CO provided only $[Fe^{13}]COCH_3$, where $[Fe^{13}]$ =Cp or (Ind)Fe(^{13}CO)(PPh_3). Studies on the stereochemistry of carbonylation of optically active [Fe]Et to [Fe]COEt, [Fe] =CpFe(CO)(PR_3) and (Ind)Fe(CO)(PR_3), were initiated. Catalytic $PhSiH_3$ hydrosilation-reduction of resolved $[Fe]COCH_3$ (L = PPh_3) provided [Fe]Et, which underwent carbonylation (80 psig, 0°C) to give racemic [Fe]COEt. Epimerization of the CpFe and (Ind)Fe systems occurred under very mild conditions via the ethyl intermediates.

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350. Dimensional Effects in Controlled Structures Support Catalysts Derived from Layered Synthetic Microstructures (LSMs)

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A new class of supported catalysts has been produced using solid-state fabrication techniques typical of the microelectronics industry. Deposition of alternating, nanometer thick layers of catalyst and support on an inert wafer, followed by etching perpendicular to the flat surfaces to reveal only the edges of the layers, provides a catalyst surface in the form of nanometer-wide, micrometer-long lines (the edge of a thin plate). These Layered Synthetic Microstructures (LSMs), with Ni and silica as catalyst and support, duplicate the size effect ("structure sensitivity") which is observed during ethane hydrogenolysis on traditional silica supported Ni clusters of nanometer "diameter." In principle, any catalyst/support system can be manufactured so that the catalyst and support are uniform in size and geometry with arbitrary nanometer dimensions. Surface studies can be carried out on a totally accessible surface and one which behaves catalytically like a supported cluster. The objective of this research is to develop this new structure as a tool for understanding supported catalysts. LSMs (Ni/SIO$_2$) will be fabricated using ion milling to provide higher catalyst surface areas per unit wafer area. Other supports will be studied (Al$_2$O$_3$ carbon, MgO, and silica-alumina). The Ni/SIO$_2$ LSMs will be tested using other structure sensitive and structure insensitive catalytic reactions. These include the reaction of CO and H$_2$ which shows a rate maximum with 4 nanometer clusters; cyclopropane hydrogenation exhibits shows a rate maximum with 2 nanometer clusters; and benzene hydrogenation which is unresolved. Characterization will be carried out concurrently. TEM can be used to examine the edge array, Auger analysis will provide a spatially averaged composition, and both STM (AFM) and TPD will be used. Fabrication of Pt based LSMs will be carried out. Platinum catalyzed reactions which would be candidates for study include: hydrogen plus oxygen at 273 K since in excess hydrogen the rate is structure sensitive while in excess oxygen it is insensitive; the hydrogenation of cyclohexene which is structure insensitive; and skeletal isomerization of methylcyclopentane which exhibits selectivity changes (rather than rate changes) with cluster size greater than 2 nanometers.

Department of Chemistry

351. Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds
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The investigation of homogeneous C-H bond activation has been continued with a variety of metal complexes. The reactive fragment [Cp*Rh(PMe$_3$)] has been found to react with a variety of alkanes and arenes to give C-H oxidative addition products, and with fused polycyclic hydrocarbons to give eta-2 complexes and/or C–H bond activation products. The project has now been expanded to include C–C bond activation. Reaction of this same fragment with biphenylene results in aryl-aryl bond cleavage and the formation of rhodium biaryl complex. Mechanistic studies indicate that this product is a rhodium biaryl complex formed via initial aromatic C–H bond oxidative addition followed by intramolecular rearrangement to the C–C inserted product. A homogeneous catalyst has also been found for the hydrogenolysis of the aryl-aryl bond of biphenylene, giving biphenyl. C–C cleavage reactions of biphenylene have also been observed with other rhodium and cobalt complexes. Reactions of the related metal fragment tris-3,5-dimethyltrispyrazolylborate (Tp'Rh(CNR) where R = neopentyl) also show C–H activation reactions with of a variety of alkanes. Competitive activation of alkanes has been examined, showing that this fragment is more selective than either Cp*Rh(PMe$_3$) or Cp*Ir(PMe$_3$). Methane has been activated thermally at 2000 psi. Reaction with cyclopropane initially gives a C–H activation product, which then converts intramolecularly to a four-membered metallacycle product. Ethylene initially reacts by way of vinylic C–H activation, but then converts intramolecularly to an eta-2 ethylene complex. The secondary derivative Tp'Rh(CNR)(i-propyl)H has been prepared and observed to rearrange intramolecularly to Tp'Rh(CNR)(n-propyl)H. Work with the tris-3,5-dimethylpyrazolylborate complex Tp'Rh(CNR)(CH$_3$)H has provided kinetic evidence for an alkane complex being involved in C-H activation reactions. The deuterated analog Tp'Rh(CNR)(CD$_3$)H rearranges intramolecularly to give Tp'Rh(CNR)(CD$_2$H)D. The kinetics of the reaction of Tp'Rh(CNR)(CH$_3$)H with benzene has been found to be first order in metal complex and first order in benzene, and is interpreted in terms of an associative substitution on a methane sigma-complex.

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Department of Chemistry

352. Carbon-Hydrogen Bond Functionalization Catalyzed by Transition-Metal Systems
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A primary focus of this project is the development of homogeneous catalysts for the conversion of alkanes to the corresponding alkenes. Complexes of the form Rh(PMe$_3$)$_2$ClL have been discovered to catalyze efficient thermal (non-photochemical) alkane transfer-dehydrogenation under dihydrogen atmosphere. Apparently, the role of hydrogen is to add to the complexes, which then dissociate L to afford H$_2$Rh(PMe$_3$)$_2$Cl, which then reacts with hydrogen-acceptors to give the fragment Rh(PMe$_3$)$_2$Cl; the latter then reacts with alkanes. Recently, significant progress has been made toward the development of hydrogen-free catalytic systems. RhL$_2$Cl derivatives with L larger than PMe$_3$ were found to effect the stoichiometric dehydrogenation of cyclooctane. In the presence of hydrogen acceptors, catalytic transfer-dehydrogenation is observed. The efficiency of both the stoichiometric and catalytic reactions is limited by ligand degradation. A search for degradation-resistant ligands with suitable electronic and steric properties has revealed that the P(cyclobutyl)$_3$ complex, [RhL$_2$Cl]$_2$, gives clean and quantitative stoichiometric cyclooctane dehydrogenation, and fairly efficient catalytic dehydrogenation. Further, the catalyst decomposition product can be regenerated with hydrogen. A second objective of this project is the development of metal carbonyl catalysts for the deoxygenation of organoelement oxides using CO. Several such catalyst systems have been discovered and in all cases mechanistic studies have revealed an unanticipated pattern: the reaction proceeds via substitution of a ligand (either phosphine or halide) by CO to give a less electron-rich carbonyl. Although present in very minor concentration, the substitution product is the key species which reacts (via nucleophilic attack at CO and loss of CO$_2$) to deoxygenate the substrate (e.g. R$_2$SeO, R$_3$NO, R$_3$AsO).

Department of Physics and Astronomy

353. *Morphological Instability in Model Thin Film Catalysts: Structure, Reactivity and Electronic Properties*
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We are exploring new aspects of the relations between microscopic surface structure and chemical reactivity for model bimetallic catalysts, i.e., ultrathin films of metals on metals. Our focus is on atomically rough, morphologically "unstable" single crystal surfaces (e.g., bcc(111) and fcc(210)) that undergo massive reconstruction and faceting when covered by ultrathin films of metals or other adsorbed species (ca. 1 monolayer thick), upon annealing to elevated temperatures. We use a variety of ultrahigh vacuum (UHV) surface science methods, including atomic resolution scanning tunneling microscopy (STM) and catalytic studies in a high pressure reactor, (i) to study metal film induced on faceting atomically rough substrates of W, Mo, Ir, Pd, (ii) to use structure sensitive catalytic reactions, including hydrogenolysis of n-butane, and the cyclization of acetylene to benzene, to correlate surface morphology and reactivity, and (iii) to characterize the electronic properties of the bimetallic interfaces using synchrotron radiation. In recent UHV STM studies of Pd-covered W(111), we find that the surface becomes completely faceted to 3-sided pyramids upon annealing to $T>750K$. Atomic resolution images confirm that facet sides have {211} orientation. Faceting is observed to occur only for elements having Pauling electronegativity greater than 2.0, suggesting that surface electronic effects control morphological stability. Structure sensitivity in a model catalytic reaction, n-butane hydrogenolysis, is observed over planar and faceted Pt/W(111). We have also used synchrotron radiation methods to characterize Pt, Pd and Au on W(111), and we find substantial substrate core level shifts associated with interface formation.

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Department of Chemical Engineering

354. *New Heterogeneous Catalysts for Selective Reduction of NO_x Emissions to Improve Vehicular Transportation*
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The objective of the proposed research is the rational identification of new heterogeneous catalysts for the removal of nitrogen oxides (NO_x) from automobile tailpipe emissions through their selective catalytic reduction by hydrocarbons (hydrocarbon-SCR) under excess oxygen ("lean") conditions. The focus will be on noble-metal-based catalysts due to their high activity and hydrothermal stability. The proposed research will employ kinetic and microcalorimetric measurements, in-situ spectroscopic characterization, and kinetic analysis techniques to achieve this goal. It is anticipated that significant progress will be made towards understanding the fundamental surface chemistry of the hydrocarbon-SCR reaction. In particular, we expect to identify the important competing reactions, measure or at least estimate their rates, identify the nature of important reactive intermediates, and identify the active sites of the catalyst. Furthermore, we expect to apply this information towards the identification and synthesis of new generations of catalysts. If successful, the proposed research will have a significant impact in the area of emission control due to the high market potential of a commercially viable hydrocarbon-SCR catalyst. Such a catalyst would find a commercial use in several mobile emission control applications including diesel and "lean-burn" gasoline vehicles.

Department of Chemistry and Biochemistry

355. *Studies of the Transformations of Sulfur Containing Heterocycles by Transition Metal Cluster Compounds*
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Recent studies have focused on the activation of sulfur containing strained ring heterocycles, thiiranes and thietanes, by polynuclear metal complexes. The principal objective is to develop catalysts for the formation of polythioether macrocycles by ring opening cyclooligmerization reactions of the strained ring precursors. Goals include synthesis of new macrocycles and the development of more efficient routes to known ones. Studies of activation process and the mechanisms of the cyclooligomerizations are included. The ligand behavior of the macrocycles is also being investigated through the preparation and x-ray crystallographic characterization of new complexes containing these ligands.

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Department of Chemistry

356. *Chemistry of Bimetallic and Alloy Surfaces*
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The objectives of our research are to define the overall chemical reactivity of Pt–Sn alloys, clarify the role of a second metal in altering surface chemistry and catalysis on Pt bimetallic and alloy surfaces, and develop general principles for understanding the reactivity and selectivity of bimetallic and alloy catalysts. The surfaces studied are primarily the stable, ordered surface alloys of Sn with Pt, Ni, and Rh that can be prepared by the controlled vapor deposition of Sn onto single crystal metal substrates. Our recent ALISS studies on Pt(100) and Ni(100) have shown that the lattice mismatch between Sn and Ni or Pt completely controls the buckling distance of Sn in Pt–Sn or Ni–Sn alloys independent of the surface bonding geometry or coordination, and we are now exploring how this affects the site-blocking efficiency of Sn atoms in the surface layer. Through TPD studies of a series of hydrocarbons on the (2×2) $Pt_3Sn(111)$ and $(\sqrt{3} \times \sqrt{3})R30°$ Pt_2Sn surface alloys, we have found that upon increasing the Sn concentration within the surface layer on Pt(111), adsorption energies are reduced in the order: alkynes>aromatics>alkenes>alkanes. Sharper changes occur in the adsorption energies and dehydrogenation activities of the surfaces upon the elimination of the 3-fold Pt sites on the $(\sqrt{3} \times \sqrt{3})R30°$ Pt_2Sn surface alloy. We have determined that the sticking coefficients and saturation coverages of hydrocarbons on Pt–Sn alloys do not decrease nearly as sharply with Sn concentration as may be expected. The adsorption kinetics can be understood if the influence of a modifier precursor state is properly included. Secondly, reaction ensembles for hydrocarbon dehydrogenation on Pt–Sn alloy surfaces are quite small, at most a few (<5) Pt atoms, for a number of hydrocarbon reactions. Our current work is aimed at making detailed spectroscopic studies of hydrocarbon bonding on these surfaces. In parallel with these chemisorption studies, we are measuring catalytic reaction kinetics over these same surfaces at higher (1–760 torr) pressures to understand in detail how the composition and structure of Pt–Sn alloy surfaces affect catalytic activity and selectivity for hydrocarbon reactions.

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Department of Chemical Engineering

357. *The Dynamics of Adsorption on Clean and Adsorbate-Modified Transition Metal Surfaces*

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The objectives of this research are (1) to determine the probabilities of both dissociative and nondissociative adsorption of alkanes on clean and adsorbate-covered surfaces, (2) to gain an understanding of the molecular dynamics of the adsorption process via experiments and molecular dynamics simulations, and (3) to clarify the role of precursor states in adsorption. Model metal surfaces are studied under highly controlled conditions in ultrahigh vacuum to reveal the dynamical features of the adsorption process. Molecular beams of gases are directed at these surfaces and the dependence of the adsorption probabilities for reactive and/or nonreactive adsorption are measured directly. Stochastic simulations are combined with the experiments related to nondissociative adsorption to gain insight into the energy exchange processes that lead to trapping and adsorption. Recent focus has been on the molecular dynamics simulations to understand the dynamical differences in the adsorption of ethane, propane and methane on Pt(111). Using pairwise additive methyl-platinum potentials determined from fitting the dependence of the adsorption probability of ethane on Pt(111) on the incident energy and angle, the adsorption probabilities and the energy scaling determined experimentally for propane and methane on Pt(111) were predicted by simulations. These results indicate that molecular adsorption rates may be predictable from simple potentials. We have also examined the trapping of ethane on adsorbate-covered surfaces, both experimentally and theoretically. Generally, adsorbates increase the adsorption probability of ethane and render it nearly independent of the angle of incidence. Stochastic simulations show the origin of these effects to be increased corrugation of the surface; ie, microroughness of the gas-surface potential.

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358. *Photochemistry of Intermolecular C-H Bond Activation Reactions*

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Photoreactivity measurements have been carried out on the intermolecular C-H activating $(HBPz'_3)Rh(CO)_2$ (Pz'=3,5-dimethylpyrazolyl) complex in various hydrocarbon solutions at room temperature. In each case UV-visible and FTIR spectra recorded throughout photolysis illustrate that the parent dicarbonyl complex can be converted readily to the corresponding alkyl or aryl hydrido product complex. The photochemical reaction proceeds without interference from secondary or thermal reactions and the reactivity has been measured quantitatively in the form of quantum efficiencies for intermolecular C–H bond activation (ϕ_{CH}). The results show that the C–H activation proceeds very efficiently (ϕ_{CH}=0.13-0.32) on excitation at 366 nm but is much less effective (ϕ_{CH}=0.0059-0.011) on photolysis at 458 nm for each of the hydrocarbon substrates. The quantum efficiencies on UV irradiation are consistent with rapid CO dissociation and the formation of a monocarbonyl reaction intermediate prior to C–H activation. Significantly, the photoefficiencies are found to be unaffected on increasing the dissolved CO concentration, illustrating that the monocarbonyl intermediate is extremely short lived and is solvated before CO is able to coordinate. Additionally, the lack of a CO concentration dependence on ϕ_{CH} illustrates that the solvated intermediate is not subjected to a competitive back-reaction with CO prior to the C–H activation step. Hence, the quantum efficiencies for C–H activation appear to be determined solely by the branching ratio between the dissociative and nondissociative routes from the reactive excited state in the complex. The lower quantum efficiencies obtained on excitation at long wavelength may be the result of ineffective CO dissociation from a lower energy state, or may involve a η^3 to η^2 ligand dechelation mechanism. This aspect is still to be determined. At any particular excitation wavelength the photoefficiencies are observed to be similar across the series of alkanes studied but are significantly reduced for the aromatic solvents, even though the aryl hydrido photoproducts are found to be more thermodynamically stable. The differences in ϕ_{CH} are also rationalized in terms of the photophysical properties the reactive excited state and can be related to solvent effects on the nonradiative relaxation rates of the complex in the various hydrocarbon solutions.

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Department of Chemistry

359. *Mechanistic Examination of Organometallic Electron-Transfer Reactions*
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The goal of this research is to provide a mechanistic understanding of electron transfer processes between organometallic complexes to enable utilization of the reactivity of odd-electron complexes in catalytic reactions. It has been shown that metal carbonyl anions participate in single electron processes with a number of organometallic complexes and by two-electron processes with other complexes and have begun to gain an understanding of which process is expected. Reactions of metal carbonyl anions with Fischer-type carbene complexes, $M(CO)_5(C(OMe)Ph)$, M = Cr,W, have not shown carbene transfer reactions, but have shown a new site for nucleophilic attack (abstraction of methyl) on carbene complexes. Such reactions are two-electron processes (nucleophilic). In contrast, reactions of cationic carbene complexes of iron with metal carbonyl anions give evidence for single electron reactions. Reactions of metal carbonyl anions with $Os(CO)_4RR'(R,R'= H,Me)$ show a smooth deprotonation and lack of reactivity by the methyl. The same reactions under CO do not give formation of an acyl, but show interesting substitution behavior. These studies have provided a much clearer understanding of one- and two-electron processes in organometallic reactions. We are now exploiting this understanding to activate inert complexes in electron transfer catalyzed reactions.

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360. *Correlations between Surface Structure and Catalytic Activity/Selectivity*
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The project objective is to address those issues which are keys to understanding the relationship between surface structure and catalytic activity/selectivity. Of primary concern are those questions related to the origins of the enhanced catalytic properties of mixed-metal catalysts and the critical active site requirements for molecular synthesis and rearrangement. The experimental approach utilizes a microcatalytic reactor contiguous to a surface analysis system, an arrangement which allows in vacuo transfer of the catalyst from one chamber to the other. Surface techniques being used include Auger (AES), UV and X-ray photoemission spectroscopy (UPS and XPS), ion scattering spectroscopy (ISS), temperature programmed desorption (TPD), low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS), infrared reflection-absorption spectroscopy (IRAS), and scanning probe microscopies (STM/AFM). Currently the preparation, characterization, and determination of the catalytic properties of ultra-thin metal and metal oxide films are being explored. Specifically, the program is proceeding toward three goals: (1) the study of the unique catalytic properties of ultrathin metal films; (2) the investigation of the critical ensemble size requirements for principal catalytic reaction types; and (3) the modeling of supported catalysts using ultra-thin planar oxide surfaces.

361. *Solid-State NMR Studies of Zeolite Acidity*
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High-Resolution ^1H nuclear magnetic resonance (NMR) will be used to characterize hydrogen bonding to the Brønsted acid site and H–D scrambling. The latter study may lead to a new way to characterize Brønsted acidity in zeolites. Other experiments will seek to thoroughly understand the ^1H NMR properties of HZSM-5 including the effects of chemical exchange and diffusion. The second strategy will use in situ ^{13}C NMR to look for intermediates in acid catalyzed reactions in zeolites. A laser heating system will be built for temperature jump and quench experiments that are expected to yield higher concentrations of reactive intermediates than are observed in standard variable temperature experiments. The focus of this project is Brønsted acidity in zeolites rather than reaction mechanisms per se.

362. *Catalysts and Mechanisms in Synthesis Reactions*
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The objective of this research is to understand the role of surface-generated gas-phase radicals in the catalytic oxidation of hydrocarbons, with emphasis on the conversion of methane to more useful chemicals and fuels. Matrix isolation electron spin resonance (MIESR), variable ionization energy mass spectrometry (VIEMS) and laser-induced fluorescence (LIF) methods have been used to detect radicals that emanate from or react with metal oxide surfaces during a catalytic reaction. The detection of methyl radicals using the MIESR system has been effective in establishing the mechanism by which methane and ethylene react to form propylene. The technique has been used to demonstrate that methyl radicals react with adsorbed ethylene to form propyl radicals, which rapidly lose a hydrogen atom. The VIEMS system has been used to follow the role of methyl radicals formed over Ba/MgO catalysts during the selective catalytic reduction of nitric oxide to N_2. It has also been demonstrated that water and oxygen react over strongly basic oxides, such as lanthanum oxide, to form hydroxyl radicals in the temperature range 1200 to 1350 K. The hydroxyl radicals are believed to be formed by the abstraction of hydrogen atoms from water at reactive surface oxygen ions, and they may play an important role in catalytic combustion.

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Department of Chemical Engineering

363. *Catalytic Hydrocarbon Reactions over Supported Metal Oxides*

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The primary goal of this research program is to determine how catalyst composition, redox ability, structure, and neighboring sites control the catalytic properties of metal oxides. Molybdenum, tungsten, chromium, and vanadium cations are supported on silica using preparation methods that enable molecular control over the structure and oxidation state. Supported structures featuring crystallites, isolated cations, and dimers with either a metal-metal or bridging sulfur bond are used as model templates to investigate key steps in catalytic oxidation and hydrodesulfurization catalysis. The research effort focuses on reaction studies over the different structures. Reduction of the cation site and C–H abstraction are studied using oxidative dehydrogenation of butenes to butadiene and 1-butene isomerization to *cis*- and *trans*-2-butene. Differences in the rates of alkyl cation and allylic intermediate formation reveal information on how cations function in oxidation catalysis. Mechanisms and site requirements for selective hydrogenolysis of the C-heteroatom bond in thiophene hydrodesulfurization are studied. Cations, or ensembles of cations, that can undergo a four electron transfer are most active for hydrodesulfurization revealing key aspects of the catalytic mechanism.

Department of Chemistry

364. *Morphological Aspects of Surface Reactions*

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Our work examines substrate morphology and fragments synthesized on surfaces using thermal, electron, and photon activation techniques. Our goal is to acquire fundamental descriptions of heterogeneous chemical processes at gas-solid interfaces in selected systems that have controlled and characterizable morphology, are of catalytic significance, and are relevant to DOE missions. Solid surface morphology reaction intermediate preparation, and kinetic characterization of intermediates lie at the heart of our program. By electron irradiation of methane, weakly held on Pt(111), we have cleanly prepared chemisorbed methyl groups, a very important hydrocarbon fragment. The thermal reactions of these methyl groups among themselves and with coadsorbed deuterium have been studied. Similarly, activation of cyclopropane on Pt(111) to form metallocycles has been investigated along with companion work on other hydrocarbons containing three carbon atoms. By starting with cyclopropane and irradiating with electrons at low temperatures, we have prepared and kinetically characterized several interesting three-carbon intermediates.

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Department of Chemical Engineering

365. *The Formation of Silica, Alumina, and Zirconia: Supported High Surface Area Monometallic and Bimetallic Catalysts*

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A new generation of thermally resistant supported metal catalysts prepared by the sol-gel method is currently under development. These catalysts derive their superior thermal properties by minimizing sintering processes which occur through surface diffusion. Because surface diffusion is substantially decreased when metal particle size is matched to the average pore diameter of the support, synthetic procedures aimed at obtaining this match are under study. The resultant materials are being tested as catalysts in the oxidation of CO, the combustion of volatile organic compounds such as benzene, and the hydroisomerization of butane to isobutane by superacid catalysts. Finally, the development of catalytic ceramic membrane reactors to study the dehydrogenation of butane and i-butane is in progress. It is anticipated that the separation and catalytic properties of palladium and platinum can synergistically be used to improve olefin yields by shifting the position of equilibrium. Sol-gel synthesis of supported metal catalysts is performed by a one-step synthesis process. The metal, usually introduced as an acetyl acetonate precursor dissolved in acetone, is added to the appropriate alcoxide (tetraethoxysilane or aluminum tert-butoxide). The homogeneous mixture is then hydrolyzed through the addition of water. Important synthetic variables include the water/alkoxide ratio, the preparation pH and the reaction temperature. In particular, the pore size distribution is strongly related to the water/alkoxide ratio. Current research efforts in the area of the preparation of thermally resistant supported metal catalysts are focused primarily on Rh, Pd, and Pt supported on silica and alumina surfaces. The synthesis of sulfated zirconia catalysts using a two-step sol-gel method results in high surface area materials which are capable of isomerizing n-butane at low temperatures. Unfortunately, deactivation of these materials at relatively low times on stream is a major drawback to these very promising materials. Our current research effort is to understand the underlying causes of this deactivation. In particular, deactivation may occur as a result of the following: (i) loss in Brønsted acid site activity, (ii) partial reduction of sulfur, (iii) phase changes associated with zirconia, (iv) formation of coke, and (v) poisoning of acid sites. Several physical techniques are currently being used to provide an explanation for the deactivation. The formation of coke is under study using a combined TGA-mass spectrometer approach. Changes in acid site distribution are under study using a novel in-situ infrared diffuse reflectance cell, while changes in crystal morphology are being probed using x-ray diffraction. Ceramic membranes have the mechanical strength and permeability required for general use, but the pores are usually too large for selective gas separation. The sol-gel method of catalyst preparation is easily applied to membrane formation. The formation and stabilization of colloidal particles in aqueous media are important in the formation of very small pores. Efforts are under way to add a transition metal to the sol before coating. This will hopefully result in a thermally stable catalytic membrane. The dehydrogenation of n-butane is being studied as a probe reaction. The decrease in hydrogen concentration by diffusion through the membrane results in an increase in selectivity as result of the shift in equilibrium. The flux of hydrogen through the membrane is increased by reacting it with acetylene on the reverse side of the membrane. This reaction results in an increase in the concentration gradient across the membrane.

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366. Ligand Intermediates in Metal-Catalyzed Reactions

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The first goal of this project is the synthesis, isolation, and characterization of homogeneous transition metal complexes containing ligand types (–CHO, –CHOH, $-CH_2OH$, –C, $=CH_2$, $H_2C=O$, –OCHO, $-OCH_2R$, CO_2, etc.) intermediate in C_1/C_2 catalytic reactions. A second goal entails the characterization of ligand intermediates in other important feedstock conversions, and the identification of new types of binding modes and bond activation processes. A third, new goal involves the development of catalysts that can be immobilized in fluorocarbon solvents. Mechanistic understanding of key steps and insight for the design of new catalysts is sought. The following topics are under active investigation: (1) the determination of relative ligand binding affinities towards Lewis acidic metal centers, including divergent kinetic and thermodynamic O=C/C=C selectivities in bifunctional nonconjugated substrates; (2) the characterization of nonclassical metal C–H "sigma bond" complexes as reaction intermediates; (3) the synthesis, structure, electronic properties, and reactivity of complexes that contain unsupported and supported C_2 and C_3 linkages spanning two metals; (4) C–H bond activation reactions of aromatic nitrogen heterocycles such as pyrrole, and new HDN processes; and (5) hydrogenation reactions with Rh(I) catalysts bearing fluorinated phosphine ligands.

367. Carbon-13 NMR of Solid-State Hydrocarbons and Related Substances

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The objective of this project is the development of new nuclear magnetic resonance (NMR) techniques to study solid organic materials to gain structural and chemical information on model compounds and naturally occurring samples. The most important recent achievements have been: (1) the development of new spatial correlation techniques to measure ^{13}C chemical shift tensors in single crystals; (2) improved theoretical methods for the calculation of shielding tensors; (3) developing a new magic angle slow turning (MAT) method of obtaining two-dimensional solid-state NMR spectra of powdered samples where the isotropic shift is projected along one axis and the tensor powder patterns along the second axis; (4) extending the theoretical and experimental shift tensor work to nitrogen containing species; and (5) construction and utilization of a high pressure NMR sample cell for observing hydrocarbons dissolved in supercritical fluid CO_2. The single crystal correlation techniques completely characterize all six terms of the chemical shift tensor and its orientation in the molecular frame. The accuracy of the single crystal methods is sufficiently high that it may be used along with quantum mechanical methods to refine crystal structures of fused aromatic hydrocarbons. Considerable progress has been made in dealing with the single crystals of sufficient size to obtain high quality data in a reasonable period of time. A new icosahedral flipper probe has recently been constructed which has significantly reduced the size requirements for single crystals (e.g., 14 mg) on a 400 MHz spectrometer. Theoretical calculations have been extended to a wide range of polycondensed aromatic hydrocarbons and a number of corresponding heterocyclic (O, N, S) species. A major effort has recently been mounted to obtain ^{15}N chemical shift tensor data on heterocyclic compounds. Enriched compounds were initially employed for studying powder patterns in compounds containing one and two nitrogen atoms. Experimental and theoretical correlations have shown that the nitrogen shift tensors are extremely sensitive to intermolecular interactions. Powder pattern experiments carried out at high (400 MHz) have demonstrated that it is possible to obtain chemical shift tensor data at the natural abundance level on model compounds which have been doped with stable free radicals. The ^{13}C shift tensor data on model compounds have been extremely valuable in interpreting the MAT data obtained on several coal samples and the ^{15}N data will be evaluated to determine its value in identifying the types of nitrogen species present in coals. Use of supercritical fluid solvents is rapidly gaining importance in problems of environmental cleanup and as a method for providing alternative cleaning solvents for a variety of industrial and commercial uses. NMR shift and spin relaxation data provide details on the important solute-solvent interactions.

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368. Influence of Surface Defects and Local Structure on Acid/Base Properties and Oxidation Pathways over Metal-Oxide Surfaces

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The purpose of the project is to examine the effect of surface defects (primarily oxygen vacancies) and local structure on catalytic oxidation reactions over metal oxide materials. The $SnO_2(110)$ surface is being investigated because of the flexibility allowed in controlling surface cation coordination numbers, oxidation states, and the selective introduction of two different types of surface oxygen vacancies. The relative acidity/basicity of these two surface defects have been tested previously with probe reactions. Recently, the acid/base properties of these specific surface sites have been investigated using NH_3 and CO_2 as probe molecules. NH_3 chemisorption experiments demonstrate that four-coordinate Sn^{2+} sites at bridging oxygen vacancies are stronger Lewis acid sites than Sn^{4+} sites on the stoichiometric surface or more reduced sites around in-plane oxygen vacancies. These acidity measurements correlate with the activity of the specific cation sites for the dissociation and subsequent selective oxidation of alcohols (weak Brønsted acids). In contrast to the literature for SnO_2 powders, CO_2 shows no significant interaction (i.e., carbonate formation) over the different preparations of our extended single-crystal surface under conditions similar to those reported in the literature for carbonate formation on SnO_2 powders. New directions include the characterization of point defects with STM, and density functional calculations of defect geometry and electronic structure.

369. *Bimetallic Oxycarbides and Oxynitrides: A New Class of Hydrogenation Catalysts*

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Considerable work has been done with single-metal carbides and nitrides showing that they have high activity, selectivity, and life in catalytic reactions involving hydrogen transfer. This project deals with the study of a novel class of catalysts for the processing of petroleum and chemical feedstocks. The new materials are mixed-metal carbides and nitrides. The catalysts have multiple capabilities that include heteroatom removal, hydrogenation, and isomerization, and can lead to highly upgraded products. The resulting technology will improve the energy efficiency of refineries and produce cleaner-burning fuels for the automobile industry. Preliminary work indicates that the two metallic components give rise to enhanced catalytic properties. The new materials have higher catalytic activity in hydrodenitrogenation than the individual monometallic substances, and higher even than a commercial sulfided catalyst. The emphasis of this project will be on the synthesis and characterization of a homologous series of mixed metal carbides and nitrides. The ultimate objective is to understand the origin of the catalytic enhancement. Substantial effort will be placed on characterization of adsorbates by infrared and Raman spectroscopy.

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370. *Structure-Property Relationships for Binary Metal Oxide Catalysts*

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Alkali and alkaline earth oxides, both alone and on supports, are recognized as solid base catalysts. However, very little is known about these materials despite their potential for many industrially important reactions. In an attempt to explore solid base structure-property relationships, we have been using in situ x-ray absorption spectroscopy (EXAFS and XANES) to determine the atomic structure near rubidium and strontium supported on a variety of carriers. In addition, IR spectroscopy and stepwise desorption of adsorbed carbon dioxide have been used to characterize the basicity of these materials. Characterization results have been correlated to the activity of the catalysts for decomposition of 2-propanol to acetone and propene. The x-ray absorption studies were performed at the Rb K edge on 5wt% Rb supported on carriers of varying acidity, based on the Sanderson electronegativity scale. Analysis of the radial structure functions revealed that the Rb-O distance correlates roughly with support acidity. Additional in situ investigations were conducted in the presence of 2-propanol in the gas phase. Perturbations of the local structure due to adsorbed alcohol were observed. The rate of 2-propanol decomposition over the catalysts, normalized per base site counted by carbon dioxide chemisorption, varied dramatically as a function of support. Basic sites formed by Rb incorporation onto acidic supports were less effective for the reaction than sites formed on more basic supports. Results from x-ray absorption spectroscopy of supported Sr indicated that the carrier does not exert a strong influence on the supported alkaline earth compound, contrasting the results for supported alkali. These structural results were confirmed by reactivity trends for 2-propanol decomposition. Apparently the support plays a more crucial role in the formation of surface basic sites from alkalis than from alkaline earths. Ongoing work in the laboratory focuses on the structural determination of the active base sites for catalysis on these materials.

Department of Materials Science and Engineering

371. *Understanding and Controlling Metal-Support Interactions in Nanocrystalline Bimetallic Catalysts*

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Supported metal catalysts are vital for control of automobile emissions and to the chemical and petroleum industries. Issues such as loss of surface area due to the migration and coalescence of metal crystallites during service, thermal degradation of the support material or metal crystallites, the role of the support-metal interface and the segregation behavior of the metal crystallites are all critical to the functionality of the catalysts. The purpose of this research is to use high-resolution transmission electron microscope (HRTEM) techniques to analyze, understand and control the atomic and electronic structure, chemical composition, segregation behavior, wettability, thermal stability and catalytic properties of bimetallic nanocrystalline catalysts as a function of alloy composition and substrate reactivity. A field-emission gun HRTEM equipped with an energy-dispersive X-ray spectrometer and Gatan imaging filter will be used to image the atomic structures of nanocrystalline bimetallic alloys on different substrates with 0.14nm spatial resolution and simultaneously determine the chemical compositions and electronic properties of the crystals and support-crystallite interface with 0.5nm spatial resolution. This research will provide a fundamental understanding of phenomena such as: 1) the effect of support reactivity on the atomic structure, morphology and stability of bimetallic catalyst crystallites, 2) the effect of support reactivity on the surface and interfacial segregation behavior of bimetallic crystallites, 3) the effect of crystallite size on the morphology and segregation behavior of bimetallic particles, 4) the mechanisms and kinetics of nanocrystalline particle sintering as a function of alloy composition, substrate reactivity and temperature, and 5) the effect of all of the above on the resulting catalytic properties and stability of bimetallic crystallites.

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Department of Chemistry

372. *Oxide-Supported Metal Catalysts: Factors Controlling Particle Size and Chemisorption / Catalytic Properties*

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Many catalysts for energy technology consist of transition metal particles attached to oxide supports. Interactions at the interface between the metal and the oxide dictate the metal particle morphology, which in turn controls catalytic activity and selectivity, yet these interactions are poorly understood. This project involves experiments designed to clarify the geometric, dynamic and energetic factors which control the microstructure of the metal / oxide interface, and to rationalize the interplay between this microstructure and chemical reactivity. Specifically, the project goal is to determine how the number, dimensions and structure of metal particle are influenced by: oxide surface structure and defect density (on ZnO crystals), the choice of metal, temperature, coadsorbed chlorine and hydrogen, and high-pressure gases. The chemisorption and catalytic properties of ultrathin metal islands and isolated metal adatoms are studied, as well as the dependence of these upon the characteristics of the underlying oxide surface. For Pt particles, the reactions being studied are pertinent to hydrocarbon conversion catalysis. For Cu particles, they pertain to methanol synthesis and water gas shift catalysis. Recent research highlights demonstrate the structural sensitivity of Cu catalysts and the interesting role of ZnO in optimizing the activity of the Cu particles.

373. *Homolytic Activation of Hydrocarbons and Hydrogen by Persistent Metal Radicals*

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The binding and activation of hydrogen by cationic transition metal complexes such as $[RE(CNR)_3(PR_3)_2]^+$ is being explored. This highly reactive, coordinatively unsaturated rhenium complex actually binds dihydrogen in preference to more conventional ligands such as chloride. Abstraction of a Cl atom from methylene chloride to form the novel Re(II) chloride complex $[RE(CO)_3(PR_3)_2Cl]^+$ has also been observed. Structural investigations indicate that the Re–Cl bond is much longer in the Re(I) complex. In related chemistry, diactionic dihydrogen complexes of osmium have been prepared by protonation of cationic $[(bipy)(PR_3)_2Os(CO)H]^+$ using triflic acid. The resulting hydrogen complex is very thermally robust but is a strong acid, undergoing complete proton transfer to weak bases such as diethyl ether. Extension of this chemistry to lighter elements of the iron group is under investigation.

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Department of Chemical Engineering

374. *Thermodynamic and Kinetic Aspects of Surface Acidity*

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During the past year, most of our work on catalyst acidity has involved studies of sulfated-zirconia catalysts for isomerization of n-butane. We have found that whereas the heat of ammonia adsorption on our sulfated zirconia catalyst (calcined at 848 K and containing 2 wt.% sulfur) decreases from 160 to 80 kJ/mol as the adsorbate coverage increases to 250 micro-mol/g, only those sites with heats higher than about 130 kJ/mol (50 micro-mol/g) are active for butane isomerization at 423 K. These heats of ammonia adsorption are similar to those measured on various zeolites. The strong acid sites on sulfated zirconia must be present in the proper hydration state to show high catalytic activity for butane isomerization. For example, the initial catalytic activity decreases by over an order of magnitude as the temperature used for drying the catalyst (following initial calcination and exposure to air) is increased from 588 to 773 K. The higher catalytic activity can be restored for a catalyst dried at 773 K by exposure to water at a dosage of approximately 100 micro-mol/g. The heat of water adsorption on such a sample decreases from 200 to 140 kJ/mol as the coverage by water increases to the level of 100 micro-mol/g, and this same behavior is observed for adsorption of water on zirconia. These high heats are indicative of dissociative adsorption of water, as confirmed by infrared and NMR spectroscopic measurements. Spectroscopic measurements show that this level of water addition does not alter the number of Brønsted acid sites. Rather, the role of water is to promote the catalytic activity of the sites and/or to suppress the rate of catalyst deactivation. Reaction kinetics measurements were conducted at 423 K on optimally-dried catalysts for the isomerization of n-butane and the isomerization of isobutane. The reaction order with respect to the alkane reactant decreased and approached zero order as the pressure of the reactant increased from 0.1 to 1 atm. This behavior was also observed for the rate of butane disproportionation to form propane and pentane species, such that the isomerization selectivity was essentially independent of the alkane pressure. These data strongly suggest that butane isomerization takes place via an intermolecular process involving a C_8 intermediate. Studies of the rates of butane isomerization versus time on stream showed that deactivation constants were higher during isomerization of n-butane compared to isomerization of isobutane, and the deactivation constant increased linearly with increasing pressure of n-butane and is independent of the isobutane pressure. The rate of catalyst deactivation during n-butane isomerization can be decreased significantly by removing the impurity olefins from the alkane feed stream. Thus, a primary mode of catalyst deactivation is via decomposition of olefins on the active sites, and we have been able to operate sulfate zirconia catalysts for prolonged periods of time through the use of an appropriate olefin-trap.

Department of Chemistry

375. Organometallic Chemistry of Bimetallic Compounds

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Four different projects at the interface between organometallic chemistry and homogeneous catalysis are being pursued. All are designed to give increased understanding of the mechanisms of organometallic chemistry related to homogeneous catalysis. (1) Bimetallic catalysis has almost unlimited potential but very few systems are known in which there is direct evidence for involvement of a bimetallic compound. The hydrogenation of alkynes by $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ to give rhenium-alkene complexes suggests that it may be possible to develop a catalytic system based on more labile metal-alkene complexes. The unusual lability of indenyl(alkyne)$Re(CO)_2$ systems is being investigated. (2) Hydroformylation with chelating diphosphines with wide natural bite angles near 120° gives high regioselectivity for straight chain aldehydes. Attempts to explain this selectivity with steric effects have failed and the role of electronic effects of chelating ligands is being investigated. (3) $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ is a highly unusual and reactive dimer of a d^6-16e fragment. The diverse reactions of alkynes with this fascinating compound are being investigated. (4) The reaction of $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ with acetylene to produce the bis ethylidyne cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ is being investigated in detail with isotopically labeled materials. This reaction is interesting in relation to transformations on metal surfaces.

376. Mechanism and Design in Homogeneous Catalysis

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The principle goals of this proposal are the design, synthesis, characterization, and use of new ligand structures for controlling selectivity at transition metal centers. One synthetic effort concerns the (1) synthesis of novel chiral phosphite ligands containing aza-crown ether ligands, (2) demonstration of the ability of these ligands to coordinate to metal centers, (3) establishing the catalytic competence of complexes of these ligands in hydroformylation and hydrogenation reactions, (4) synthesis of a series of novel borate-functionalized chiral diphosphine ligands, and (5) demonstration that borate-functionalized diphosphines ligate transition metal complexes that are catalytically active in hydrogenation reactions. We have demonstrated that chiral aza-crown ether ligands can be readily synthesized, that these ligands form effective hydroformylation catalysts with catalyst precursors such as $Rh(acac)(CO)_2$, that these catalysts show significantly enhanced activity for the hydroformylation of allylammonium salts relative to simple phosphites, and that the hydroformylation products are enantiomerically enriched. We have also found that these catalysts demonstrate unusual phase separation behavior that may be exploited in simplified catalyst separation/recycling schemes. Our other synthetic effort concerns the synthesis of borate-functionalized diphosphines based on ferrocene. We now have both racemic and resolved versions of these novel diphosphines in hand, as well as crystallographic structures for several variations of these ligands. We have demonstrated that these ligands bind to Pt and Rh complexes to yield clean compounds. The rhodium complexes are catalytically active toward alkene hydrogenation. We are now poised to study the influence of the borate functional group on binding constants, catalytic rates, and catalytic selectivity. We also have made significant synthetic progress toward versions of this ligand that contain guanidinium functional group; this novel design should promote interactions with carboxylate-containing substrates.

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377. Aluminum Coordination and Active Catalytic Sites in Aluminas, Y Zeolites, and Pillared Clays

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The extension of the NMR REDOR technique to silicon from the proton of ammonia chemsorbed by acid zeolite has provided an important distinction between the silicon atoms bridged to the lattice aluminum by an OH. Those OH bridges which belong to a cluster Si-(OT_n), where T is another four-fold coordinated metal, here an Al, act as Brønsted sites if n=1. Their protons are transferred to NH_3 and NH_4^+ is formed. NH_4^+ enjoy a fast isotropic reorientation (at the NMR time scale at the room temperature). In a cluster with n>1, the bridging OH hydrogen bond NH_3 and is not a Brønsted site. The number of acid OH is between 30 and 60% of the number of framework aluminum in USY and dealuminated Y (DHY). It is about 75% FAl in dealuminated mordenite(DHM) and larger than 85% in DHZ. These are unexpected results and, among numerous consequences, they explain why poisoning a reaction occurring on Brønsted sites requires more molecules than calculated from FAl. The progress reported above has been made possible by the careful development of a quantitative IR method of measuring the number of NH_4^+ and NH_3 coordinated by the zeolite. It has been shown also that the dispersion of the Lewis sites on the non-framework aluminum (NFAl), that is, the ratio number of Lewis sites/NFAl is between 25 and 75%. The use of NH_3 as a probe has been definitely improved by using ^1H MAS NMR to assign the IR lines. Comparison of chemisorbed CO and NH_3 FTIR has shown that "high frequency" CO stretching integrated absorbance at 2173-77 cm^{-1} is proportional to the number of strong Brønsted sites. The latter are those in the cluster Si $^4Q(1Al)$ but with no next-nearest aluminum eighbors. These measurements were applied to fluorinated ultrastable Y. It has been shown that fluorination 1) dealuminates the zeolite and thus decreases the number of Brønsted sites, and 2) decreases the dispersion of Lewis sites. As a result the activity of the fluorinated USY vs. pentane transformation (isomerization essentially) decreases noticeably.

378. An Investigation of Molybdenum and Molybdenum Oxide Catalyzed Hydrocarbon Formation Reactions

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Model oxide olefin metathesis catalysts consisting of MoO_2, MoO_3, metallic molybdenum and oxygen overlayers on molybdenum were characterized using various surface sensitive techniques including X-ray and ultraviolet photoelectron, Raman and Auger spectroscopies and low energy electron diffraction and their activities tested using an isolatable, high-pressure reactor. It is found that MoO_2 mimics the activity and selectivity of alumina supported metathesis catalysts rather well for reaction below ~650 K and provides a good model for this system. Another, higher-temperature reaction regime is identified on the oxide with an activation energy close to that found for the metal (~65 kcal/mol) and where the reaction selectivity decreases with increasing reaction temperature. Reactions with ethylene on metallic molybdenum suggest that reaction proceeds, in this case, via reaction of surface C_1 species. In addition, the formation of 2-butene from propylene is found to be rather stereoselective with cis-2-butene being substantially favored over trans-2-butene. This effect is being investigated further. The presence of relatively thick carbonaceous layers is found during the catalytic conversion of hydrocarbons on both the metal and the oxide, and restart reactions indicate that catalysis proceeds in the presence of such layers. Raman spectroscopy reveals that these consist of both graphitic particles and a hydrocarbon layer. It is also found that hydrocarbon conversion rates are accelerated, both for olefin metathesis and palladium-catalyzed acetylene cyclotrimerization, if hydrogen is added to the reaction mixture even though hydrogen is not required for the reaction. A possible explanation for this effect is that hydrogen acts to remove these strongly bound hydrocarbons exposing more surface sites for catalysis. Unfortunately, the model MoO_2 catalyst is very unreactive in ultrahigh vacuum so that both ethylene and propylene merely adsorb and desorb molecularly on this surface. However, it is also found that oxygen overlayers on molybdenum effect their catalytic metathesis activity where the presence of about 0.6 monolayers of oxygen yields the largest enhancement. Although these surfaces are not as active as the oxides, they exhibit a rich chemistry in ultrahigh vacuum and allow the effect of oxidation to be scrutinized. Ethylene reacts on oxygen-covered Mo(100) to form both ethane by self-hydrogenation, and methane and photoelectron spectroscopy demonstrates that ethylene undergoes carbon-carbon bond scission on oxygen-covered Mo(100). Carbenes (CH_2) can also be grafted onto the surface by adsorbing methylene iodide on oxygen-covered Mo(100) and it is found that these react with adsorbed hydrogen to form methane. A similar reaction pathway involving carbene formation and hydrogenation is proposed for methane formation from ethylene. In this case, the methane yield increases with oxygen coverage up to a coverage of 0.6 monolayers and decreases thereafter in an activity pattern that mimics the variation in metathesis activity. Methane is similarly evolved in temperature-programmed desorption following adsorption of both propylene and 2-butene on oxygen-covered Mo(100). Reaction pathways are being investigated in these cases by grafting possible reaction intermediates by adsorbing halogenated precursors onto these surfaces. Initial work has been carried out to synthesize more realistic model metathesis catalysts by reacting molybdenum hexacarbonyl with planar alumina substrates in ultrahigh vacuum. It is found that carbonyls adsorbed at low temperatures desorb intact. Higher temperature adsorption results in complete carbonyl decomposition and the formation of a surface carbide. This suggests that the removal of the first CO in the carbonyl is rate limiting and, once decarbonylation is initiated, the remaining carbonyls are removed very rapidly. Heating the carbide-covered surface to ~1300 K removes all surface carbon and desorbs CO. It is shown, by synthesizing an oxide substrate using isotopically labelled oxygen that the carbon reacts with the alumina substrate. The carbide can be reformed by reaction with ethylene. Finally, as part of this project, we have been developing strategies for analyzing Near-Edge X-ray Absorption Fine Structure spectra (in collaboration with D.K. Saldin of the University of Wisconsin-Milwaukee) and angle-resolved X-ray Photoelectron Spectroscopy data (with D.K. Saldin and D. R. Mullins of Oak Ridge National Laboratories).

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379. Acidity and Effect of Acidity on Supported Metals
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We are investigating the effect of acidity and counter cation on the activity and selectivity of Pt or Pd supported in L-zeolites. The electronic state and the dispersion of the metal particles are determined by XANES and EXAFS, respectively, and the catalytic probe reaction is neopentane isomerization and hydrogenolysis. In the case of Pt/L-zeolite, Sn is added as a modifier to compare these catalysts with standard Pt-Sn/Al_2O_3 reforming catalysts. The physical state of both Pt and Sn is studied by X-ray absorption spectroscopy (XANES and EXAFS). n-Hexane is used as a model reactant for catalytic reforming and the chemical state of Pt is further catalytically probed by competitive hydrogenation of benzene and toluene at low temperature.

380. Pd Catalysts for Use in Vehicular Applications
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Pd-based catalysts are being widely developed for new automotive applications with special focus on fast light-off (including close-coupled convertors), enhanced hydrocarbon emission control, and lengthened warranty periods. Pd poses particular challenges for these applications because its physical and chemical state changes with temperature and reactant environment over the range of conditions experienced in vehicular applications. Interaction effects with the support, dopants and contaminants also affect Pd catalyst performance. In this research, we will study the behavior of Pd-based catalysts on a range of supports under typical vehicular reaction conditions. A simple in-situ technique based on UV-visible reflectance spectroscopy is being developed to monitor the Pd's chemical state and particle size under reaction conditions. (Chemical interactions of the Pd with other catalyst components will also be observed.) In earlier work, we used this technique to study changes in Pd and PdO abundance, as well as formation of an aluminate-like phase during the oxidation of methane. A variety of high-temperature supports will be used in this study, including low and high surface area aluminas, lanthanum aluminates and metal supports derived from etched, oxidized superalloys. Noble metal catalysts are often promoted with CeO_2, but the performance of the CeO_2 is affected by changes in catalyst state induced by the reaction environment. As reaction conditions are cycled over temperature and composition ranges to simulate vehicular operation, we will monitor the state and morphology of the Pd component of the catalyst, Pd-CeO_2 interactions, and the interactions of both the CeO_2 and the noble metals with the supports. Simultaneous measurements of reaction products and surface state will allow us to analyze the physical and chemical processes of catalyst activation and deactivation.

Department of Chemistry

381. Catalytic Oxidation of Hydrocarbons by Binuclear Fe Complexes
Caradonna, J.P. **$128,244**
203-432-5221
jpc@miles.chem.yale.edu

This project is investigating the ability of non-heme iron metalloenzyme reactivity models to catalyze the oxidation of alkane and arene molecules, including the conversion of methane and ethane to methanol and ethanol, respectively. The objective of this project is to characterize the electronic structure and reactivity properties of a series of non-heme mononuclear and dinuclear iron complexes, characterize any intermediates formed during oxygen atom transfer chemistry, and elucidate the mechanisms and specificity of the reactions. Comparisons to analogous heme-based chemistry will be made. A series of diferrous, ferric/ferrous, and diferric complexes were synthesized from simple polyamide and polycarboxylate ligands and spectroscopically characterized. The diferrous and mixed-valence compounds are capable of catalyzing the oxidation of alkanes, alkenes, arenes, and sulfides in the presence of oxygen atom donors. Oxidation occurs via pathways that do not involve freely diffusing hydroxyl radicals. Both intra- and intermolecular kinetic isotope effects are analogous to those reported for the enzymes methane monooxygenase and cytochrome P450. Intermediates observed during catalytic turnover and reactions with dioxygen are currently being examined.

382. Some C-X Bond Cleavage Chemistry
Crabtree, R.H. **$95,000**
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crabtree@minerva.cis.yale.edu

In the latest period, the CF bond breaking chemistry discovered right at the end of the previous period has provided some striking new results. In the most important one, we find that Freons such as CF_2Cl_2 in the vapor phase are quantitatively destroyed by a series of inorganic materials such as sodium oxalate to give carbon, sodium fluoride and sodium chloride. The Montreal Convention's limits on ozone-destroying freons means that convenient means of destroying CFC stockpiles could be of growing importance in the years to come. Our finding has attracted substantial interest from industrial companies and the press and broadcast media. The same series of materials also reacts with cyclic perfluoroalkanes to give perfluoroarenes in high conversion and yield. In other work, we find that $Hg/NH_3/hv$(254 nm) leads to the functionalization of teflon and a variety of perfluoroalkanes by a charge transfer reaction, followed by nucleophilic attack of NH_3 on the intermediate perfluoroalkene. We also find that ferrocenes react with perfluoroalkanes under visible light illumination in THF to give charge transfer. In the presence of lithium triflate, loss of LiF leads to the formation of perfluoroalkenes. These new reactions are of considerable mechanistic and practical interest and we are following them up in the current grant period.

Separations and Analysis

University of Alabama
Tuscaloosa, AL 35487-0336

Department of Chemistry

383. Clean Solvent Extraction Using Polyethylene Glycol-Based Aqueous Biphasic Systems
Rogers, R.D. **$311,000**
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Aqueous biphasic systems (ABS) consist of two immiscible phases formed when certain water soluble polymers are combined with one another or with certain inorganic salts in specific concentrations. As two-phase systems they are suitable for carrying out liquid/liquid separations of various solutes such as biomolecules, metal ions, and particulates. In ABS the major component in each of the two phases is water, and thus a liquid/liquid extraction technology can be envisioned which completely eliminates the use of volatile organic compounds (VOCs). Elimination of VOC's has the potential to revolutionize many industrial processes by drastically reducing potential downstream pollution while increasing safety. In addition, certain separations where traditional oil/water techniques are not applicable or perform poorly, may be successfully carried out utilizing ABS. The long range goal of this project is to obviate the need for VOC's in many separation and waste remediation technologies by the development of ABS into useful systems for the selective batch or chromatographic removal and recovery of solutes and particulates. This goal includes: a) development of a fundamental understanding of the factors governing solute partitioning in ABS, b) understanding phase behavior in ABS in order to attain the ability to fine-tune the PEG-rich phase and thus solute partitioning, b) expanding the uses of ABS by targeting applications suited to this technology, c) gaining an understanding of the relationships between liquid/liquid ABS separations and solid-supported chromatographic ABS separations, and d) full adaptation of ABS into both liquid/liquid and solid-supported aqueous biphasic extraction technologies.

University of Arizona
Tucson, AZ 85721

Department of Chemistry

384. Raman Spectroscopy of Reversed-Phase Liquid Chromatographic Alkylsilane Stationary Phases on Thin Silica Films
Pemberton, J.E. **$116,000**
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pembertn@u.arizona.edu

Reversed-phase liquid chromatography (RPLC) is the most popular mode of liquid chromatography used today. The stationary phase used for RPLC typically consists of silica gel onto which an alkylsilane layer has been covalently bound. Despite intense effort, a fundamental understanding of the molecular basis of the separation process has not been achieved. We are using Raman spectroscopy to characterize RPLC alkylsilane stationary phases at the molecular level with the intent of providing greater insight into the molecular basis of retention. Several types of stationary phase supports are currently being explored. The first type is a novel layered structure culminating with an outer thin silica film formed by spin coating a sol-gel solution. The sol-gel approach to the synthesis of these silica films is beneficial in that control over the microstructure of the silica layer can be achieved. This strategy will hopefully result in silica gel systems that are chromatographically relevant. A second type of stationary phase under investigation is a similar sol-gel thin silica film structure, but one that contains the RPLC stationary phase as an organic modifier. Finally, true modified-silica RPLC column packing materials commercially available for chromatography are being investigated. Studies are underway to further develop and refine the Raman spectroscopic characterization of these materials for chromatographically-relevant surface coverages of alkylsilanes, and to investigate the influence and interactions of mobile phase solvents and solutes on the structure, orientation, and order of alkylsilane bonded phases. This work should enable the first systematic Raman spectroscopic characterization of covalently-bonded alkylsilane stationary phase behavior at silica surfaces in environments relevant to true RPLC systems to be performed thus furthering our understanding of the molecular basis of retention in RPLC systems.

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

385. Interfacial Chemistry in Solvent Extraction Systems
Neuman, R.D. **$105,000**
334-844-2017
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The microscopic interfaces, i.e., association microstructures, in acidic organophosphorus extraction systems associated with Na^+, Co^{2+}, Ni^{2+}, Zn^{2+}, and UO_2^{2+} are being systematically investigated using various physicochemical, spectroscopic and scattering techniques in order to resolve the physicochemical nature and structure of reversed micelles of metal-extractant complexes, the thermodynamics of the formation and growth of reversed micelles, the effect of organic phase additives on the structure of reversed micelles, and the relationship between reversed micellar structure and selectivity. A new structural model–the "open water-channel" model–for reversed micelles and a quantitative model that relates the extractability and selectivity to the size of reversed micelles in solvent extraction systems have been proposed and are being experimentally verified. Advanced laser techniques (SLLS, LIF, FRAP) are being utilized to characterize the properties, structure, and dynamics of extractant-laden liquid-liquid interfaces. A molecular modeling effort has been initiated to examine metal-extractant species using geometry optimization and molecular dynamics simulations. This innovative research program continues to make significant contributions directly relevant to the science and technology of liquid-liquid extraction.

Brigham Young University
Provo, UT 84602

Department of Chemistry

386. Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport
Lamb, J.D.; Bradshaw, J.S.; **$102,000**
Shirts, R.B.; Izatt, R.M.
801-378-3145
john_lamb@byu.edu

The metal cation selectivity of macrocyclic ligands such as crown ethers and cryptands is applied to making cation separations in hydrophobic liquid membranes and other systems. Potential macrocyclic ligand carriers are designed and synthesized, then screened for cation binding characteristics using potentiometric titration, solvent extraction, calorimetry, NMR, and X-ray crystal structure determinations. Macrocycles which demonstrate potential for separations are then incorporated into liquid membrane systems. Focus is placed on the synthesis and characterization of new proton ionizable macrocycles that permit coupling of cation transport to the reverse flux of protons. Macrocycles containing acidic moieties within the macrocyclic ring structure are particularly emphasized. State-of-the-art molecular mechanics modeling techniques are used in the design phase of the project. Current focus is being given to a new type of polymer inclusion membrane for stable, long-term separations. Investigation is also under way on a novel method for mixing aqueous and nonaqueous phases in solvent extraction. This method exploits the unusual behaviour of some hydrophobic solvents which coalesce with the water phase upon heating, then separate on cooling. Selective extractions of metal cations using macrocyclic extractants can be carried out rapidly by this method.

Brown University
Providence, RI 02912

Department of Chemistry

387. Thermal Generation of the Photoacoustic Effect
Diebold, G.J. **$88,000**
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gerald_diebold@brown.edu

In our investigation of the photoacoustic effect in carbon suspensions, we have found that gas is produced and that since its molar volume is so large compared with that of water, a large acoustic wave is radiated. We plan to investigate the properties gas generation, with and to identify the gases and other chemical species that are produced. We believe that there is evidence for an unusual environment for chemical synthesis since the temperatures and possibly the pressures are high in the vicinity of the carbon particles. We plan to investigate some of the questions raised by gas generation. We are investigating the composition of the gases. Our procedure is to use gas chromatography to determine the composition of the gases. We believe that the fraction of energy that goes to chemical reaction can be determined from an analysis of the reaction products and a knowledge of the enthalpies of reaction for each of the products. In addition, we are using transmission electron microscopy to characterize the precipitate that is found in the suspension after irradiation. We are continuing experiments with reverse micelles in order to obtain statistics on the accuracy of the method we have been developing. According to the theory we have worked out, the photoacoustic experiment is capable of determining the thermal diffusivity, the thermal conductivity, and the diameter of micelles. The data analysis for the experiments has been difficult since the dependence of the signal on these quantities does not appear to be unique. We also are investigating the nonlinear response of the transient grating signal that we have found when a high power Nd:YAG laser irradiates water. The nonlinearity appears to be a result of the response of the grating itself; that is, the generation of higher harmonics in the signal comes from the large excursion in the index of refraction of the absorbing fluid induced by the laser.

University of California, Santa Barbara
Santa Barbara, CA 93106-5130

Materials Research Laboratory

388. *Halocarbon Separations with Zeolitic Materials*

Cheetham, A.K.	**$385,000**
805-893-8767	**(39 months)**
cheetham@iristew.ucsb.edu	

Two environmental pressures are driving the need to develop a better understanding of separation processes involving halocarbons. First, ozone-depleting chlorofluorocarbons (CFCs), which have been widely used for many decades in a diverse range of technologies, are being replaced under the Montreal Protocol by alternative halocarbons such as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). Second, there is an urgent need to remove halocarbon solvent residues (and other organics) from a large number of contaminated sites in the U.S.A. and elsewhere. Typically, the solvents are present in ground-water. Several pressing technical issues arise from these important trends; the focus of this project is in halocarbon separations. The demand for enhanced separation procedures is necessitated by the fact that halocarbon solvent residues are frequently encountered in complex mixtures. For example, many industries combine their solvent residues prior to returning them for reprocessing or disposal. On the other hand, many disposal routes, which include catalytic conversions to HCFCs, are highly specific for particular halocarbons, so that a preliminary separation of the CFCs, or a separation of the products, is required. Aluminosilicate zeolites and related molecular sieves, which are used extensively in hydrocarbon separation processes, offer a range of potential advantages over other media for such separations. The work will examine the behavior of a number of common halocarbons in a wide range of siliceous and aluminosilicate zeolite materials. Our research will span studies of adsorption selectivity, the structure and dynamics of carefully selected host-guest complexes, and computer modeling of these systems.

Carnegie Institute of Washington
Washington, DC 20015-1305

Geophysical Laboratory

389. *High-Pressure Synchrotron Infrared Spectroscopy: An Integrated and Dedicated Facility at the National Synchrotron Light Source*

Hemley, R.J.	**$67,925 Operating**
202-686-2410	**$205,637 Equipment**
ext.2465hemley@gl.ciw.edu	

A synchrotron facility dedicated to high-pressure infrared spectroscopy and micro-infrared spectroscopy is proposed. The facility will consist of a versatile and dedicated high-pressure beam line capable of a broad range of measurements from the far-infrared to the visible spectrum at the U10 beam line of the National Synchrotron Light Source (NSLS). This new facility will give significantly higher IR brightness, particularly at long wavelengths, in comparison to the existing, partially dedicated beam line (U2B). The addition of the dedicated beam line will allow a wide range of microspectroscopic studies at high (and ambient) pressure. A new FT-IR will be installed at the beam line along with a recently completed high-pressure (long working distance) microscope. Existing instrumentation at U2B will be upgraded with a commercial, high-magnification infrared microscope for micro-infrared measurements of 1-bar and low-pressure samples. With the existing high-pressure x-ray facility at the NSLS, the new instrumentation will permit synchrotron IR, synchrotron x-ray, and optical experiments on the same high-pressure samples. Systematic high-pressure measurements addressing a range of problems in condensed-matter physics and chemistry, earth and planetary science, and materials science will be performed. These studies include high-pressure studies of dense hydrogen and related planetary materials; minerals of the earth's crust, mantle, and core; geochemical reactions; glasses and melts; surfaces and interfaces; whole-rock samples; and new high-pressure technological materials.

University of Chicago
Chicago, IL 60637

Department of Biochemistry and Molecular Biology

390. *Development of a Fast X-ray Shutter*

Schildkamp, W.	**$33,660 Operating**
312-702-2118	**$264,000 Equipment**
wilfried@cars1.uchicago.edu	

Experiments which exploit the time structure of synchrotron radiation from the high brilliance Advanced Photon Source (APS) storage ring facility offer exciting new research opportunities in many areas of science. The spectral brilliance expected for a single pulse of x-rays emitted by an insertion device is sufficient to permit probing time domains in dynamic processes in a range of systems previously not accessible at second generation synchrotron facilities. Examples include x-ray scattering and spectroscopic techniques with nanosecond time resolution. However, in order to reach this time scale, a fast x-ray shutter mechanism capable of separating a single x-ray pulse from the pulse train originating from the circulating particle bunches in the storage ring is necessary. This selection is required since no x-ray detector presently available or planned is capable of readout times comparable to inter-bunch times. We propose to develop such a fast mechanical shutter system which will be capable of predictably isolating a single pulse of x-rays when the APS operates under normal storage ring conditions (18 equally spaced bunches separated by 204 nsec). The shutter will eliminate the need for single bunch operation which limits the total current in single bunch operation to 5 to 10% of the design current and limits the efficient use of the facility in single bunch mode. Partial funding of the shutter is provided by an existing grant from the National Institutes of Health for construction of the BioCARS Sector 14 beamlines at the APS.

Colorado School of Mines
Golden, CO 80401

Department of Chemical Engineering

391. A Mechanistic Study of Molecular Sieving Inorganic Membranes for Gas Separation
Way, J.D. **$89,000**
303-273-3519
dway@mines.edu

The objectives of this research are to investigate selective transport mechanisms in microporous, silica membranes and to examine the effects of membrane microstructure and surface chemistry on separation performance. A further objective is to use theoretical chemistry to simulate the adsorption and transport of penetrants in pores of molecular dimensions. In the past year we have investigated how both molecular size and adsorption influence the separation of hydrocarbons such as acetylene, ethene, ethane, and propane. Mixed gas ethene/ethane separation factors (ratio of permeabilities) measured at 20 bar feed pressure at temperatures up to 500 K were much larger than the pure gas values and ranged from 0.8 to 6.2. A local maximum was observed at higher temperatures. We were unable to measure the permeance (pressure normalized flux) of propane. However, the presence of ethane and propane reduced the permeance of other gases considerably, with up to a 44% decrease in CO_2 permeance from a 2% propane 98% CO_2 feed mixture. The fouling was shown to be reversible by desorption of the adsorbed hydrocarbons at lower pressures. FTIR studies and quantum simulations are in progress to determine the chemical nature of the adsorption site on the silica surface.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

392. A Multinuclear Magnetic Resonance Study of the Interactions of Pollutants with Major Soil Components
Maciel, G.E.; Lindsay, W. L.; Sutton, S. **$110,000**
970-491-6480
maciel@lamar.colostate.edu

This project will provide detailed information on the fundamental chemical-physical behavior (including chemical transformations) of certain organic contaminants with major soil constituents; specifically clays and humic materials. Chemical interactions and physical behavior will be studied via state-of-the-art nuclear magnetic resonance (NMR) experiments on solid and aqueous-solution samples. The specific tasks of this project are (1) to generate, or update and refine, the chemical-structural and NMR data bases of the specific clays and humics chosen for study; (2) elucidation of the behaviors of individual pollutants with these specific humics and clays; (3) study of the fundamental interactions in clay-humic "complexes"; (4) elucidation of pollutant mobility and diffusion in the specific humic and clay systems; (5) chemical structural characterization of ternary systems (pollutant-humic-clay); and (6) exploratory studies of pollutant/whole-soil systems. Results of this kind of study are needed in the long term for development of reliable and versatile soil-groundwater models of pollution. First-year activity included choosing, isolating/purifying and characterizing organic soil components (humic acid, fulvic acid, humin) and clays to be used as long-term stocks for most of the pollutant/soil and pollutant/soil-component experiments of this three-year project, and probably subsequently. The ^{13}C NMR spectrum of the raw soil, prior to any chemical treatment, was found to be surprisingly well defined in terms of a variety of peaks from contributing chemical structures and functionalities (probably because of low soil iron content). The organic samples isolated seem ideal for exploring the interactions of various pollutant species with a variety of organic-chemical functionalities. One of the most pervasive types of results that we have obtained in the first-year effort on this project is the almost universal absence of chemical transformations of any organic pollutants adsorbed on (in) soil components. While specific pollutant-substrate interactions can be established for certain organics, these interactions do not appear to lead to chemical transformations on a time scale of months (exception: acetone on a clay). This tentative result may have substantial significance for relying on the impact of microrganisms for converting toxic organics into less harmful species in soils. Very promising preliminary results have been obtained via ^2H wideline patterns of deuterium-labeled acetone, ethylene glycol and benzene adsorbed on whole soil, humic acid and Ca-montmorillonite. The lineshapes show evidence of both mobile and immobilized species. The lineshapes are being analyzed in terms of motional models and in terms of correlations between pollutants adsorbed on whole soils and pollutants adsorbed on soil components.

University of Delaware
Newark, DE 19716

Department of Chemistry and Biochemistry

393. Linear and Nonlinear Spectroscopic Probing of Solute Interactions with Chemically Modified Silica Surface
Wirth, M.J. **$85,000**
302-831-6771
mwirth@udel.edu

This research project investigates physically how charged species interact with chromatographic surfaces. The results will benefit efforts to remove heavy metal ions from water, analyze complex environmental samples, and characterize biopolymers for evaluating human health effects of radiation. The work specifically focuses on the implementation and characterization of ultrathin polymer films on silica. 1) Monolayers of polyethylenimine covalently attached to polysiloxanes promise to combine a high capacity for metal ions with the high hydrolytic stability required for large-volume pumping of contaminated water. 2) Ultrathin films of polymethacylate cross-linked to a self-assembled monolayer promise to eliminate electrostatic interactions between cations and silica, which enables more sensitive capillary electrophoresis of trace metal ions as well as biopolymers. The study of cationic interactions with each of these surfaces is being conducted using fluorescence spectroscopy and chemical force microscopy to study electrostatic interactions, solid-state NMR, ellipsometry and atomic force microscopy to characterize the polymer films, and near-field optical microscopy to probe topography and cation adsorptivity simultaneously.

Duke University
Durham, NC 27708

Department of Chemistry

394. ***Fluorescence Lifetime in Chemical Analysis: The Next Generation***
McGown, L.B. **$76,000**
919-660-1545
lbmcgown@chem.duke.edu

The two directions in this research are linked by the common thread of new multiharmonic fourier transform (MHF) technology for frequency domain fluorescence lifetime measurements. In the new technique of Total Lifetime Distribution Analysis (TLDA), the commercial MHF instrument provides rapid acquisition of "total" lifetime information over a broad spectral window, thereby replacing spectral resolution with lifetime resolution for fluorescence characterization and fingerprinting applications. Sensitivity benefits from inclusion of the majority of the total emission signal in the lifetime measurement. Data analysis using the self-modeling maximum entropy method (MEM) provides a complete lifetime distribution that is free from bias of an assumed decay model. Much of our attention is focused on detailed exploration of the strengths and limitations of the MEM approach. Strategies for improving the performance of MEM, in order to increase the accuracy and resolution of frequency domain lifetime analysis, are under investigation. The introduction of the MHF as a rapid, on-the-fly detector of fluorescence lifetime in capillary electrophoresis will increase the accuracy and sensitivity of laser excited fluorescence detection, providing universal applicability through the use of direct and indirect detection schemes without compromising the speed or resolution that make CE such a valuable technique. Current investigations emphasize the initial modification of a commercial CE system for MHF lifetime detection and optimization of S/N in the lifetime measurement.

University of Florida
Gainesville, FL 32611

Department of Chemistry

395. ***The Glow Discharge as an Atomization and Ionization Source***
Harrison, W. W. **$95,000**
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willard-harrison@ufl.edu

This research project focuses on fundamental and applied studies of the glow discharge as an analytical source for trace elemental analysis of solid samples by atomic spectroscopy, with primary emphasis on atomic emission and mass spectrometry. We are interested in both conducting and nonconducting sample materials, using dc and rf discharges respectively. A major change in instrumentation focus now finds our efforts directed to very fast pulsed discharges coupled to a time-of-flight (TOF) mass analyzer. The TOF is already in operation, although still undergoing fine tuning and refinement. For conducting materials, a microsecond regime pulsed glow discharge permits relatively high power, although low average power. The more intense conditions existing in the pulsed glow discharge plasma provide analytical advantages for both atomic emission and mass spectrometry. In addition, the pulsed discharge allows for temporal resolution to reduce or eliminate certain types of spectral background problems. Optimum utilization of time-resolved methods arises from the combination of a TOF mass analyzer with the pulsed discharge. A pulsed rf discharge in the millisecond range is also providing encouraging results for nonconductor materials. We plan to study thin film samples, as well as bulk materials, to determine the full capability of the pulsed discharge.

396. ***Development of Laser-Excited Atomic Fluorescence and Ionization Spectrometric Methods***
Winefordner, J.D. **$95,000**
352-392-0556
jdwin@chem.ufl.edu

The emphasis in this research is upon the development of new, sensitive, selective spectroscopic methods for trace elemental analysis. Several projects are ongoing that involve ionization, emission, and fluorescence in flames and glow discharges. Laser enhanced ionization (LEI) in a microflame is being studied with two means of sample introduction: ultrasonic nebulization, which will permit a thorough optimization of burner design and flame gas composition, and laser ablation, which will provide the capability of analyzing single small particles and for elemental mapping of surface and depth profiles. LEI is also being studied as a high resolution spatial spectroscopic probe for flame temperatures (via detection of OH fluorescence) and for the in situ detection of N_2 via measurement of Raman scattering. Glow discharge atomic reservoirs are also being studied using both emission spectrometry with a microcavity hollow cathode discharge and laser excited atomic fluorescence for a microplanar discharge. Both of these glow discharge systems accept small volume discrete samples. The emission system has multielement capability on subsample volumes, and the fluorescence system has the potential to approach single atom detection in a real sample.

The George Washington University
Washington, DC 20052

Department of Chemistry

397. ***New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission and Mass Spectrometry***
Montaser, A. **$99,000**
202-994-6480
montaser@gwis2.circ.gwu.edu

This research follows a multifaceted approach, from theory to practice, to the investigation and development of novel helium plasmas, sample introduction systems, and diagnostic techniques for atomic spectrometry and mass spectrometry. Four major sets of research programs are being conducted that each include a number of discrete but complementary projects. The first program is concerned with investigation of atmospheric-pressure helium inductively coupled plasmas (He ICPs) that are suitable for atomization and ionization of elements, especially those possessing high ionization energies, for the purpose of enhancing the detecting powers for a number of elements. The second program includes simulation and computer modeling of He ICPs. The aim is to ease the hunt for new helium plasmas by predicting their structure and fundamental and analytical properties, without incurring the enormous cost for extensive experimental studies. The third program involves spectroscopic imaging and diagnostic studies of plasma discharges to instantly visualize their prevailing structures, to quantify key fundamental properties, and to verify predictions by mathematical models. The fourth program entails development and characterization of new, low-cost, low-sample consumption nebulization devices. These efforts collectively offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition.

Hampton University
Hampton, VA 23668

Department of Chemistry

398. ***Use of Ion Chromatography–dc Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals***
Urasa, I.T. **$57,500**
804-727-5396
urasa@hamptonu.edu

The research has focused on studies of the solution chemistry and speciation of trace metals using chromatographic coupled with spectroscopic techniques. A new thrust in this work is directed towards incorporating solid phase extraction in metal speciation. Application of solid phase extraction in analytical measurements has several advantages, namely: isolation of the analyte from complex sample matrix; sample preconcentration which, for dilute samples, leads to improvement in measurement sensitivity; and the possibility of some separation of the chemical species present. The study is looking at several types of sorbent; including bonded reversed phase, bonded normal phase, naturally occurring polymers, and selected minerals. These materials are being investigated, developed, and characterized for the extraction of neutral, charged, and hydrated metal species in solution. The extraction mechanisms involved in each case will be elucidated. Attempts will also be made to modify sorbent functionality by derivatization, thereby placing on the adsorption site desired functionalities to achieve selectivity in the extraction and speciation process. Analytical separation of the extracted metal species will be achieved by coupling the extraction tube with an appropriate analytical column.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

School of Chemical Sciences

399. ***Molecular Aspects of Transport in Thin Films of Controlled Architecture***
Bohn, P.W. **$88,000**
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Localized vibrational spectroscopy is being coupled with measurements of plasmon surface polaritons (PSPs) in Ag- or Au-supported ultrathin ($d \leq 35$nm) organized molecular assemblies exposed to organic penetrants, with a special emphasis on understanding the role of film defects on macroscopic properties. Because defects likely control a wide variety of technically important properties of the films, understanding their structure, dynamics, and how they mediate transport in the assembly is critical. Measurements of shifts in PSP resonances are exquisitely sensitive, ultimately permitting changes in film thickness as small as $\Delta d \leq 0.01$ nm to be detected. These measurements allow us to build a detailed picture of the changes in the dielectric function of the molecular assembly as it interacts with the penetrant. Vibrational spectroscopy is used to probe the changes in molecular motions and relaxation which occur after penetrant interaction, and the PSP measurements give detailed information about the spatial distribution of penetrant molecules in the film. Using these coupled experiments, we are building a detailed picture of the nature of defects in these molecular assemblies.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

400. ***Multidimensional Hadamard Transform Spectrometry: A New Analytical Technique***
Hammaker, R.M.; Fateley, W.G. **$19,078**
913-532-1454

Multidimensional spectrometry is defined in terms of three spatial dimensions (x_i, y_i, z_i) and one spectral dimension (wavelength, λ_j or frequency, ν_j). The x_i and y_i or surface coordinates are accessed via a stationary two-dimensional (2-D) Hadamard encoding mask and the z_i or depth coordinate arises from using a photoacoustic detection system for depth profiling by optical modulation and phase-sensitive detection. Measurements utilizing two-dimensional and three-dimensional spectrometry are in print. Results for this program's first images and spectra from four-dimensional spectrometry are in press. Present efforts are focused on enhancement of capabilities for performing various multidimensional spectrometries. A multiwavelength acoustic-optic tunable filter (AOTF) for the spectral dimension is in its final testing. A new moving 2-D Hadamard encoding mask as a potential replacement for the stationary 2-D Hadamard encoding mask for the two surface dimensions has been obtained and is now being evaluated. Decoding the multiwavelength AOTF results by Hadamard methods gives a multiplex advantage in the spectral dimension. Using the multiwavelength AOTF without decoding will provide a multiplication advantage in images without spectral separation. The moving mask with completely open windows will allow access to any spectral region where appropriate sources, spectral separators, and detectors are available.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

401. ***Perforated Monolayers***
Regen, S.L. **$86,000**
610-758-4842
slr0@lehigh.edu

This program is aimed at preparing new classes of synthetic membranes that can be used to separate small molecules on the basis of their size, shape, and polarity. The general approach that is being taken is to fabricate composite membranes from "perforated monolayers" (i.e., monolayers that are assembled from "porous surfactants") plus highly permeable substrates such as cast films of poly[1-(trimethylsilyl)-1-propyne] (PTMSP). Research that has been carried out to date has led to the synthesis and characterization of a homologous series of calix[n]arene-based surfactants that differ in their internal diameter. Current efforts are now focusing on (i) the fabrication of composite membranes from such amphiphiles by use of Langmuir-Blodgett (LB), and self-assembly methods and (ii) the characterization of their barrier properties toward He and N_2.

Louisiana State University
Baton Rouge, LA 70803

Department of Chemistry

402. ***Novel Micellar and Calixarene Derivatives for Selective Luminescence Measurements***
Warner, I.M. **$96,000**
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Our research for this funding period has focused on continued studies of calixarenes as host molecules for analytical measurements. We continue to explore these molecules for their guest:host properties as related to analytical measurements. Our studies have also focused on the ternary complexes of these calixarenes. One goal of this component of our research is to examine the similarity of the calixarenes to the cyclodextrins in terms of their binding properties. In addition to solution studies, we propose to use the calixarenes for selective separations in the area of capillary electrophoresis. In regard to these latter studies, we have recently synthesized several novel chiral calixarenes by use of a novel synthetic scheme developed in our laboratory. Some of these calixarenes have been used as pseudophases in capillary electrophoresis to achieve selective chiral separations. Even more selective chiral separations are achieved when these chiral pseudophases are used in combination with achiral micellar media.

Michigan State University
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Department of Chemistry

403. ***Direct Examination of Separation Processes in Chromatography by Laser-Induced Fluorescence***
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Much of the present knowledge of chromatographic separation processes has been obtained from experimental data and theoretical models that reflect the macroscopic behavior of solute zones. Because the separation ultimately arises through the migration and interaction of individual molecules, however, a more detailed understanding is necessary to guide future improvements in chromatographic performance. This research program is concerned with two technological advances that enable this challenge to be addressed from a unique and promising new perspective. First, a novel detection system has been developed in our laboratory that allows the examination of separation processes in situ as the solute traverses the chromatographic column. This system employs laser-induced fluorescence detectors to measure the solute zone profile at several distinct points along an optically transparent column. By effectively isolating the regions of interest, this system enables an accurate measure of kinetic, thermodynamic, and hydrodynamic processes that was not previously possible. Second, a three-dimensional stochastic computer simulation has been developed and validated which provides a more detailed understanding of mass transport processes in chromatographic separations. In this simulation, the migration of individual molecules is established through diffusion and convection within a fluid phase that is in contact with a surface. Molecular interaction and, hence, retention may arise by partitioning into permeable surfaces or by adsorption at solid surfaces. The molecular distribution and the corresponding zone profile may be examined and characterized by means of statistical moments at any specified time or spatial position during the simulation. This simulation provides the opportunity to perform hypothetical experiments and to make observations that may not be possible in a real chromatographic system. During the present grant period, these advances in experiment and theory have been used to characterize the kinetics of solute distribution between the fluid and surface phases. The experimental studies were performed using octadecylsilica, the most common stationary phase for liquid chromatography. The rate constants for a homologous series of model solutes were determined as a function of temperature in the range from 10 to 70°C, pressure in the range from 400 to 4463 psi, and mobile-phase composition. The experimental rate constants correlate well with values predicted by the stochastic computer simulation for a partition mechanism under diffusion-limited conditions. From these results, it is apparent that kinetic processes are a significant contribution to zone broadening and must be minimized in order to improve chromatographic performance.

University of Missouri at Rolla
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Department of Chemistry

404. ***A New Class of Macrocyclic Chiral Selectors for Stereochemical Analysis***
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Halocarbons are usually separated using gas-liquid chromatography (GLC) using relatively long columns. Most of the more volatile chlorofluorocarbons can be better resolved by gas-solid chromatography (GSC), however, some of these compounds react with highly active stationary phases. Particularly reactive are the replacement chlorofluorocarbons that are not fully halogenated or fluorine substituted. A new, less-active GSC stationary phase was found to be sufficiently inert to effectively separate the lower molecular weight chlorofluorocarbons in addition to the large more polar halocarbons. These GSC columns also were used for analyses of the halocarbon content of refrigerator insulation. It was found that percent levels of specific halocarbons remained in the insulation decades after it was manufactured. Consequently, the destruction and disposal of old refrigerators could release significant quantities of halocarbons to the atmosphere. Commercial halocarbon preparations were sometimes found to contain significant quantities of other halocarbon impurities. Among the more prevalent chiral monoterpenoid compounds in conifers are α-pinene, β-pinene, and smaller amounts of camphene and limonene. The most prevalent chiral monoterpenoid compounds in fossilized resin (referred to as amber in this paper) appear to be borneol, isoborneol, and camphene. Most of these compounds have easily measured enantiomeric excesses. The borneol and isoborneol in some amber samples have pronounced enantiomeric excesses despite the fact that they are tens of millions of years old. The enantiomeric ratios of the monoterpenoids in different ambers vary tremendously and often are distinct. However, in any single amber sample, the stereochemistry (absolute configuration) of the excess monoterpenoid enantiomers appears to be identical. The camphene in amber may be a secondary reaction product formed over time, possibly from the dehydration of borneol. Although a compound's original stereochemistry can be preserved, it also may diminish with the number and type of chemical transformations over geological time. The monoterpene enantiomeric ratios in modern conifer resins vary tremendously. Future stereochemical studies are outlined that could provide the data necessary for more exact geochemical interpretations and possibly for obtaining pertinent paleobiological information.

University of North Carolina at Chapel Hill
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Department of Chemistry

405. ***Solid-State Voltammetry and Sensors in Gases and Other Nonionic Media***
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This project is based on using microelectrode voltammetry for design and application of quantitative electrochemical transport and kinetics experiments to semi-solid and solid redox phases. The experiments include transport and electron transfer reactions of electron donor/acceptor solutes and surfaces in polymeric solvents and liquid crystalline phases. The goals of this project include (i) developing the necessary miniaturized electrode methodologies, cells, and requisite theory for quantitative voltammetry in rigid media, (ii) exploring important characteristics of homogeneous and heterogeneous electron transfer reaction dynamics in rigid environments, in particular how the dynamics of "outer sphere" redox couples respond to rigidification of their surroundings, (iii) exploring polymer-phase transport, including polymer-in-polymer diffusion of redox-labelled poly-ethers, anisotropic transport in liquid crystalline phases and polymers, and coupling between slow diffusion and homogeneous electron transfers, and (iv) learning to dynamically manipulate diffusion rates of redox sites within polymer electrolytes so as to fashion ultrathin, electrically conducting mixed valent layers by freezing the concentration gradients that are electrolytically generated at electrodes. We have recently succeeded in fashioning an example of a frozen gradient system from a polyether-derivatized viologen.

Princeton University
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Physics Department

406. ***Pixel Array Detector for Time-Resolved X-ray Science***
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Our goal is to develop, test, and install a silicon-based Pixel Array Detector (PAD) for x-ray applications at synchrotron radiation sources. At present, there are no existing detectors capable of recording successive x-ray images at the megahertz rates made possible by sources such as the Advanced Photon Source. The PAD is designed to fill this need and is intended for time-resolved applications such as Laue crystallography, destructive analysis, materials failure, phase transition studies, etc. The PAD consists of a two-dimensional array of radiation sensitive pixels fabricated on a silicon wafer. Each pixel is connected to its own electronics cell, consisting of signal-conditioning and storage electronics. All pixels operate in parallel to integrate the incident signal in a way which allows very high count-rates.

Purdue University
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School of Chemical Engineering

407. *Fundamentals of Electric Field-Enhanced Multiphase Separations*

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The research is motivated by recent scientific and practical evidence that the use of electric fields offers a powerful means for enhancing the efficiency of and reducing waste generation in various unit operations that are used in the separation and purification of chemicals. Unfortunately, existing theoretical and experimental foundations of the effects of electric fields in multiphase separations are weak. The electric field-induced enhancement of the performance of separations processes dealing with fluid mixtures can be attributed to a variety of interactions between applied fields and the fluids and/or interfaces separating the fluid phases in multiphase systems. A central issue in electro-separations is the dispersion of one phase into another phase, which simply entails the creation of drops of the first phase in an otherwise continuous second phase, and is the subject of this research program. Particular attention will be paid in the present research to the development of a fundamental understanding of the factors that control the creation of satellite droplets during drop formation and a distribution of drop sizes during atomization. The latter phenomena can signal the death of practical processes not only in separations but in applications ranging from the synthesis of ceramic precursor powders to ink-jet printing. The goals of the research will be accomplished through an approach that places equal emphasis on theory and experiment. Theoretical and computational analyses will utilize large-scale computations with finite element, boundary element, and volume of fluid methods. The experiments will rely on visualization of sub-millisecond events such as the rupturing of fluid interfaces using ultra high-speed video photography at rates up to 40,000 frames per second and quantitative measurement of drop sizes and velocities using Phase Doppler Anemometry/Velocimetry.

Department of Chemistry

408. *Ion Trap Mass Spectrometry: Ion Motion, Reactions, and Applications*

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Fundamental understanding of ion motion in the quadrupole ion trap is being sought by (i) unique electrode configurations including moveable endcaps and a split ring and (ii) novel methods of manipulating ions, including phase-locked resonant excitation, dc pulse activation, parametric oscillation, and stored waveform methods of ion ejection. Simulations of the motion of ensembles of ions, which include collision effects and ion-ion interactions, are being refined through extension of our ITSIM program. Three-dimensional visualization of simulated trajectories are used to assist in elucidating the behavior of trapped ions and allowing for predictions to be made for procedures which minimize ion-ion interactions. Experiment and simulation are being applied: (i) to evaluate capabilities of measuring ion polarizability, (ii) to study electrical cooling using external quadrupolar DC pulses, (iii) to characterize mass shifts due to coulombic ion-ion interactions, (iv) to study the differences in ion mobility of ions arising from different collisional cross sections, (v) to characterize new methods of mass analysis including the use of quadrupolar dc ejection during activation. Fourier transforms of the induced image currents are being used to perform broad-band non-destructive ion detection. The thermochemical properties of tricyclo[3.3.3.0]undec-3(7)-ene, a pyramidalized alkene and typical chemical system of interest, are being determined by cluster ion dissociation.

409. *Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser Ionization: Fourier Transform Mass Spectrometry*

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The research group continues to use Fourier transform ion cyclotron resonance (FTICR) mass spectrometry to study the chemistry and photochemistry of metal-containing ions in the gas phase. Some areas of current interest are summarized here: (1) Infrared multiphoton dissociation studies on transition metal containing ions of the form $MC_nH_{2n}^+$ (M = Fe, Co, Ni; n = 2-5), as well as $MC_4H_6^+$ and $M(C_2H_4)(C_2H_2)^+$ isomers for M = Fe, Co, Ni are underway. Of particular interest are the observation of multiple products and the application of competitive dissociation for determining relative bond energies. (2) Detailed studies on Nb_n^+ (n = 2-15) clusters with C_nH_{2n} (n = 2-4) are underway providing detailed information on size, structure and reactivity relationships. Complete dehydrogenation of alkenes also connects with our interest in studying metallocarbohedrenes (met-cars) and related metal-carbon clusters. (3) Sequential reactions of metal clusters with CH_3I to generate $M_nI_x^+$are being probed as a means of characterizing the number of non-metal-metal bonded electrons, and the consequence of electronic structure on subsequent reactivity. (4) With the help of Professor Sabre Kais at Purdue, we have begun a vigorous ab initio program focusing on metal-containing ions. Currently we are calculating $Fe(CH_2S)^+$ and $Fe(CH_2O)^+$ structures to explain the interesting differences in their chemistry we observe. We have also begun to study Nb_n^+ to try to support the conclusions drawn on electronic structure obtained from the CH_3I reactions.

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Department of Chemical Engineering

410. *Chemical Interactions between Protein Molecules and Polymer Membrane Materials*

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These results represent the first measurements of intermolecular forces between adsorbed proteins and hydrophobic polymeric films. The intermolecular forces, including the adhesion forces between a model protein, hen egg lysozyme (Lz), and itself and a polymeric film made from poly(bisphenol-A-arylsulfone) (PSU) and deposited on molecularly smooth mica, were measured above, at and below the pI (10.8) of Lz. Buffer and Lz solutions similar to those used in the force measurements were filtered through commercial PSU ultrafiltration (UF) membranes in order to obtain measures of fouling and cleanability. Lz-Lz and Lz-PSU adhesion forces correlate inversely with fouling, cleanability and protein transport. This suggests that intermolecular forces between Lz-PSU, although important initially, play a lesser role once the membrane surface is fully covered with adsorbed protein, while those between Lz-Lz dominate long term filtration behavior. As with most studies with proteins and membranes, it is difficult to extrapolate these results to other proteins and membrane materials. We have also made progress with respect to the development of flexible and inexpensive techniques for modifying the surfaces of commercial membranes. As a complementary approach to the photochemical (ultraviolet radiation) method, we have investigated, as part of this project, the surface modification of polyacrylonitrile (PAN) and PSU by low temperature plasma. During the period of this grant, four publications have appeared in the literature and one publication is completed and will be submitted shortly while the last manuscript is in preparation. They are: a) Pincet, F., Perez, E. and Belfort, G., "Do Denatured Proteins Behave like Polymers?" *Macromolecules* **1994**, *27(12)*, 3424–3425, b) Pincet, F., Perez, E. and Belfort, G., "Molecular Interactions Between Proteins and Synthetic Polymer Films," *Langmuir* **1995**, *11(4)*, 1229–1235, c) Ulbricht, M. and Belfort, G., "Low Temperature Surface Modifications of Polyacrlonitrile Ultrafiltration Membranes - 1. Plasma Treatment Effects," *J. Appl. Polymer Sci.* **1995**, *56*, 325–343, d) Ulbricht, M. and Georges, B., "Surface Modification of Ultrafiltration Membrane by Low Temperature Plasma. II. Graft Polymerization onto Polyacrylonitrile and Polysulfone," *J. Membrane Sci.* **1996**, *111*, 193–215, e) Koehler, J.A., Ulbricht, M. and Belfort, G., "Intermolecular Forces Between Proteins and Polymer Films with Relevance to Filtration," in preparation, and f) Nabe, A., Staude, E., and Belfort, G., "Effects of Surface Modification of Polysulfone Ultrafiltration Membranes on Fouling by BSA Solutions," in preparation.

Rutgers, The State University of New Jersey
Piscataway, NJ 08855-0849

Department of Physics and Astronomy

411. ***High Resolution Upgrade for Core-Level Photoemission Spectroscopy***
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We are upgrading the present high resolution core-level photoemission beamline U4A at the National Synchrotron Light Source (NSLS), so that it will have higher resolution (~15–30 meV) over a broader spectral range (10–200 eV) than is currently available at any other photoemission beamline at NSLS. This will result in a beamline performance that is state-of-the-art for core-level photoemission. The present Toroidal Grating Monochromator (TGM) design with point to point focusing at three separate beamline positions will be replaced by a Spherical Grating Monochromator (SGM) design with only source to sample point focusing. These will improve both the resolution and the brightness at the sample so that photoemission microscopy in addition to high resolution core-level spectroscopy will be possible. Such an upgraded beamline should prove to be extremely useful in new studies of bimetallic systems and semiconductor interfaces. This upgrade will complement the other new beamlines at NSLS that are mainly at higher photon energy (100–1000 eV).

Stanford University
Stanford, CA 94305-2115

Department of Geological and Environmental Sciences

412. ***Detectors and Other Instrumentation for Research in Environmental Chemistry and Heterogeneous Catalysis at the Stanford Synchrotron Radiation Laboratory***
Brown, G.E., Jr.; **$404,000 Equipment**
Hedman, B.; Hodgson, K.O.;
Kendelewicz, T.; Leckie, J.O.;
Madix, R.J.; Parks, G.A.; Pianetta, P.
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The main objective of this project is to purchase two state-of-the-art X-ray detectors and associated instrumentation for use in synchrotron-based environmental chemistry and heterogeneous catalysis research at the Stanford Synchrotron Radiation Laboratory (SSRL). During the next year, we will test and purchase a 30-element Ge array detector with fast throughput JFET-based electronics for use in X-ray Absorption Fine Structure (XAFS) spectroscopy studies of the products of chemical interactions of metal and metal-ion adsorbates at less than monolayer coverages on oxide surfaces and at oxide-water interfaces in simplified model systems. Such reactions play a major role in determining the transport properties, toxicity, and ultimately the bioavailability of environmental contaminants such as toxic heavy metals and radionuclides; they are also of critical importance in heterogeneous catalysis. However, the pathways of these types of surface reactions are often poorly understood, particularly under reactive conditions, which limits efforts to remediate environmental contaminants or attempts to increase the efficiency of catalytic processes. We will also use XAFS spectroscopy and the new hard X-ray detector to study the chemical speciation and transformation of heavy-metal contaminants in more complex natural soils and in hyperaccumulating plants and organisms under different environmental conditions. The information provided by these studies is critical for developing robust and cost-effective strategies for chemical separations and remediation technologies. Two of the main limitations on current XAFS studies of the speciaton of heavy metal contaminants in environmental samples and of the nature of reactive metal sites on metal oxide substrates of catalytic importance are lack of sufficient X-ray flux and of sensitive, high-throughput detectors. The new hard X-ray detector, coupled with the new high-flux molecular environmental science beam line at SSRL, will increase the sensitivity of our XAFS studies by at least an order of magnitude. During the second year of this project, we plan to test and purchase a vacuum-compatible 13-element detector system for use in soft-x-ray/vacuum ultraviolet surface XAFS, photoemission, and x-ray standing wave studies of metal and metal-ion adsorbates on clean oxide surfaces. These studies are intended to provide fundamental information on the effects of adsorbates on the geometric and electronic structures of oxide surfaces.

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Department of Chemistry

413. ***Determination of Solvation Kinetics in Supercritical Fluids***
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This research program is directed toward several key aspects of supercritical fluid science and technology. The goals/subprojects are as follows. (1) Understanding the effects of neat and entrainer-modified supercritical fluids on solute-fluid dynamics. (2) Determining the effect of fluid density on the disposition of energy between a dissolved solute and the fluid bath. (3) Probing the effects of continuous phase density on the internal dynamics of reverse micelles formed in supercritical carbon dioxide. (4) Quantifying the behavior of polymers subjected to supercritical carbon dioxide in molten form and under infinite dilution conditions. (5) Quantification of solute-solute synergism and the origin of such. (6) Investigation of local density and composition surrounding a solute at an interface as such influences extraction and separation processes in supercritical fluid science and technology. Modern ps (and now fs) in situ optical spectroscopy are used in this work. To date this work has helped to better define and quantify how solvation occurs in supercritical fluid systems and how one can tailor a supercritical fluid for a particular "solvent" need. Overall, this work is providing a better molecular-level view of the unique chemistry of supercritical fluids and how one can control reactions and solute conformation by using a supercritical fluid.

State University of New York at Stony Brook
Stony Brook, NY 11794-3800

Physics Department

414. ***Enhancement of the Microscopy Facilities at the NSLS X1A***
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The project (expected to start in August 1996) is designed to open important new capabilities at the microscopy stations on the NSLS soft X-ray undulator beamline X1A. Both the Scanning Transmission X-ray Microscope, STXM, and the Scanning Photoemission Microscope, SPEM, use zone plates to form microprobes for imaging with elemental and chemical specificity. STXM is designed to study primarily biological and other organic specimens at 50 nm or better resolution. SPEM is designed to study surfaces at 150 nm or better resolution. Both instruments can take spectra from small specimen areas - absorption spectra on STXM, photoelectron spectra on SPEM. STXM will be made vacuum compatible to extend XANES microscopy capabilities to the nitrogen and oxygen edges, where even small amounts of residual air interfere with imaging and spectroscopy. At the same time the computer and software system will be brought up-to-date. The stage will be rebuilt using a new design for accurate linearity and orthogonality of the axes. SPEM will also have its stage rebuilt to improve reliability and reproducibility. Its computer/data acquisition/software system will be replaced with one that is compatible with STXM for improved speed, flexibility, and economy. These upgrades will be performed with minimal down-time by introducing new hardware and software during NSLS shutdown periods.

Syracuse University
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Department of Chemical Engineering and Materials Science

415. ***Mechanisms of Gas Permeation through Polymer Membranes***
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The objective of this study is to investigate the mechanisms of gas transport in polymers by molecular dynamics simulations. It is desired, in particular, to determine the effects of systematic changes in polymer structure on the gas transport. Accordingly, diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 in poly(dimethyl siloxane) (PDMS), poly(propyl methyl siloxane), poly(trifluoropropyl methyl siloxane), and poly(phenyl methyl siloxane) were calculated for a temperature of 300 K. The diffusion coefficients decrease with decreasing intrasegmental mobility of the polymer chains (i.e., with increasing bulkiness of side chains and increasing glass-transition temperature) as well as with increasing "kinetic" diameter of the penetrant molecules. The calculated values of the diffusion coefficients for all gas/polymer systems studied are consistent with experimental values within the expected error limits. An analysis of the trajectories of the penetrant molecules in the polymers revealed two types of motions: (1) "oscillating motions" inside cavities in the polymer matrix, and (2) "jumps" from one polymer cavity to another one. The lengths of the jumps are of the order of 8–10 Å, whereas the oscillating motions are of the order of <5 Å. The diffusion of gases in polymers is controlled by the fractional free-volume in the polymer, the free-volume distribution, and the dynamics of the free-volume. Preliminary simulations indicate that the most highly gas-permeable polymer, namely PDMS, has a larger mean free volume and a broader distribution of free-volume voids than the other poly(organosiloxanes) studied. As a result, PDMS also has the lowest selectivity for different diffusing gases. The above studies were concerned with the transport of light gases in silicone polymers, which are in the "rubbery" state at the temperature assumed for the molecular dynamics simulations (300 K). These studies have been extended to "glassy" polymers, since such polymers are being widely used as membrane materials for the separation of gases of industrial interest. Accordingly, values of diffusion and solubility coefficients for He, O_2, N_2, and CH_4 in glassy poly(methyl methcrylate), PMMA, have been estimated for the temperature of 308 K (35°C), at which experimental data for some of these gas/PMMA systems are available for comparison. The computations were based on a "transition-state" model developed by U. Suter and his coworkers at the Federal Swiss Institute of Technology, because the methodology used for silicone polymers is too time-consuming when applied to the estimation of diffusion and solubility coefficients of gases in glassy polymers. The estimated (computed) values of the diffusion coefficients for O_2, N_2, and CH_4 in PMMA agree within a factor of 4 or better with the experimental values (extrapolated to zero gas concentration in the polymer). The estimated value of the diffusion coefficient for CO_2 in PMMA is much lower than the experimental value; this is probably due to the fact that the computations used the Lennard-Jones size parameters of the penetrant gas molecules and did not take into account the shapes of the molecules. The estimated solubility coefficients for O_2, N_2, CO_2, and CH_4 are within a factor of 5 or better of the experimental values. No experimental diffusion or solubility coefficients for He in PMMA are available for comparison. All estimated values of the diffusion and solubility coefficients are averages for 5 different polymer microstructures. Clearly, the computational techniques available at present for the estimation of diffusion and solubility coefficients of gases in glassy polymers must be substantially improved. The computed solubility isotherms (i.e., plots of the gas solubility versus equilibrium pressure) for O_2, N_2, CO_2, and CH_4 in PMMA exhibit the expected nonlinear "dual-mode sorption" behavior; the solubility isotherm for He in PMMA is linear (i.e., obeys Henry's Law) due to the very low solubility of this gas in the polymer. The computed mean-square displacement, $<r^2>$, of the penetrant gas molecules in the PMMA microstructure exhibits three different dynamics as a function of time, t: at short times ($t < 1$ ps) the penetrant molecules have only local mobility; the molecules then exhibit an anomalous diffusion behavior, $<r^2$proportional to t^n, $n < 1$; after a longer time the penetrant molecules show the expected Einstein diffusion behavior, $<r^2> = 6\,Dt$, $n = 1$, where D is the diffusion coefficient. For He, the Einstein behavior is observed at much shorter times (10^{-9} s) than for the other gas molecules studied.

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Department of Chemistry

416. Polymer-Based Separations: Synthesis and Application of Polymers for Ionic and Molecular Recognition

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Our research is focused on the synthesis of polymer-supported reagents for application to selective metal ion separations and as highly efficient catalysts for organic reactions. In one example, earlier research has shown that the covalent immobilization of a diphosphonate ligand within a polymer support yields a polymeric reagent with very high affinities for radionuclides. Current research has just been published which details a new synthesis of diphosphonate ligands immobilized directly on to polystyrene. This synthesis widens the variety of methods that can be applied to the preparation of a family of polymers bearing diphosphonate ligands, each member of the family displaying different selectivities towards different metal ions. The source of these differences is the microenvironmental effect wherein the polarity surrounding a given ligand is modified through the presence of non-coordinating groups. This effect has also been found to allow for the synthesis of efficient catalysts for application to the Mitsunobu, aldol and Prins reactions.

417. Study of the Homogeneity of the Packing Density of Chromatographic Columns and its Effects on Column Performance

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Chromatographic columns are not homogeneous but exhibit important radial fluctuations of their packing density and of any property (porosity, permeability, efficiency, retention, saturation capacity) which is related to this density. Several authors have shown that the local velocity is typically 3–4% higher and the column efficiency 50–100% higher in the central core region than close to the wall for analytical columns. We have recently obtained similar results for preparative columns (2" i.d.). The lack of homogeneity of the column packings problem can be related to the important change in their apparent density which accompanies the consolidation of beds of particles. This phenomenon is well known in soil mechanics and in the manufacturing of pharmaceutical tablets. Because of the friction of the bed against the column wall during the bed consolidation, systematic radial fluctuations of the packing density take place. The aim of our research is to understand the phenomena which take place during column packing, the mechanism of bed consolidation and to improve the efficiency of columns.

418. Fundamental and Instrumental Development of Capillary Electrokinetic Separation Techniques for Energy Applications

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This multifarious research program is dedicated to the development of capillary electrokinetic separation techniques for energy related applications. Research is directed at (i) developing a fundamental understanding of pertinent separation and band dispersion mechanisms and (ii) developing and refining instrumentation and instrumental approaches for these techniques. (i) The fundamental work focuses on studies involving highly ordered assemblies as running buffer additives. These additives include macrocyclic compounds such as cyclodextrins (CDs) and calixarenes, micelles, and soluble (entangled) polymers and are employed in electrophoretic (e.g., capillary electrophoresis, CE) and/or electrochromatographic (e.g., micellar electrokinetic capillary chromatography, MECC, and capillary electrochromatography, CEC) modes of separation. In some cases, reasonable correlations between molecular modeling-based CD-solute interaction energies and retention behavior have been observed for mixtures of geometrical isomers and optical isomers. A dual-CD phase (charged and neutral) form of capillary electrochromatography (cyclodextrin distribution capillary electrochromatography, CDCE) has been demonstrated that offers advantages over the more established MECC technique. Since the CDs used in the CDCE technique effect solute retention independently, it is anticipated that molecular modeling techniques will eventually lead to the computational development of "designer" CDCE separation systems (simple-to-complex combinations of commercially available CDs) that meet many separation challenges.

A new class of macrocyclic phenolic compounds (calixarenes) have also shown some promise as reagents for CE separations. The mechanisms by which DNA restriction fragments migrate and disperse in size-selective CE separations employing entangled polymers as running buffer additives are also being studied using novel instrumentation (see below). (ii) Instrumental work includes efforts to extend the utility of laser induced fluorescence (LIF) and spectrophotometric detection in CE. Examples include the use of on-column complexation with Arsenazo III (for low ppb screening of uranyl) and with hydroxyquinolines (in conjunction with the sensing of metals, see below). A novel instrumental configuration that permits rapid and reproducible translation of the LIF detection zone along a CE capillary resulted in improvements in both separation and detection performance and facilitated certain fundamental studies. It should be possible to modify this instrumentation for field use. A prominent new area of research involves the development of separation-based fiberoptic sensors (SBFOSs). The introduction of CE methodologies into sensing provides a unique and powerful element of selectivity for remote analyses. Prototype SBFOSs have been fabricated and demonstrated for measurements of florescent dyes in a CE mode, metal ions in a CE mode with on-column chelation, and fluorescent toxins in an electrochromatographic mode. Incremental improvements in the design and function of the SBFOS are being implemented.

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Department of Chemistry

419. *Development of Laser-Ion Beam Photodissociation Methods*

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This research program focuses on numerous aspects of laser-mass spectrometry and fundamental gas-phase ion chemistry. Photodissociation methods are being developed to probe dissociation reactions of highly activated ionic systems. In addition, the potential analytical utility of laser-ion photodissociation for structural characterization of complex molecules is being evaluated. A tandem time-of-flight (tof/tof) photodissociation apparatus is now being used for a range of tandem mass spectrometry experiments. The ions are formed by pulsed UV laser desorption (matrix-assisted laser desorption ionization [MALDI]), and photodissociation of the mass-selected ion is performed by using a high-power, pulsed eximer, Nd:YAG or N_2 laser. The primary objective of this research is to improve the sensitivity of MS-MS experiments by 100 times (10 to 100 femtomole) and the mass resolution of MS-II by 5 to 10 times (1,000 to 10,000). The objective of the tof/tof experiment is to study the dissociation reactions of very large (>m/z 5000) molecules. In addition, laser-ion beam photodissociation methods are being used to examine ionic clusters that are important to matrix-assisted-UV-laser desorption ionization of polar, thermally labile biomolecules. In particular, studies are conducted on excited state H^+-transfer reactions and the way in which such reactions influence the dissociation chemistry of gas-phase ionic systems. These studies are performed on a home-built tof apparatus. Clusters of matrix and analyte are formed by a pulsed supersonic nozzle and the clusters are ionized by either 337 nm or 355 nm photoexcitation. The clusters can be formed with or without solvent, e.g., CH_3OH or NH_3. These studies are aimed at understanding both the mechanism of ion formation and the influence of solvent on the ionization process.

Texas Tech University
Lubbock, TX 79409

Department of Chemistry and Biochemistry

420. *Metal Ion Complexation by Proton-Ionizable Lariat Ethers and Their Polymers*

Bartsch, R.A. **$95,000**
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Goals of this research project are the synthesis of new metal ion complexing agents and chelating polymers and their applications in metal ion separation processes. Cyclic polyethers (crown ethers) which possess pendent, proton-ionizable groups are novel agents for metal ion separations by solvent extraction and liquid membrane transport processes. Movement of the metal ion from the aqueous phase into the organic phase does not require concomitant transport of an aqueous phase anion. This factor greatly increases metal ion extraction and transport efficiency for proton-ionizable lariat ethers compared with those of crown ethers and non-ionizable lariat ethers in separations involving metal chlorides, nitrates, and sulfates. New lariat ether carboxylic acids, phosphonic acid monoethyl esters, phosphinic, sulfonic, and phosphonic acids and N-(R)sulfonyl carboxamides are being synthesized and tested to probe the influence of structural variation within the ligand upon the selectivity and efficiency in separations of alkali and alkaline earth metal ions. Novel chelating polymers are being synthesized by condensation polymerization of proton-ionizable dibenzocrown ether monomers. In addition to ion-exchange sites, these resins provide crown ether units for metal ion recognition. Sorption behavior of these resins for a variety of alkali metal, alkaline earth, and heavy metal cations is being assessed.

421. *Separations on Water-Ice*

Dasgupta, P.K. **$93,500**
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Water-ice has many unusual properties some of which may be beneficial in separation problems. This project seeks to explore the merits of water-ice as a separation medium. Lessons learned from there would be used to investigate other related phases as separation media. Using finely powdered ice and using partially polar eluents such as ethyl acetate - hexane, we have successfully separated various test mixtures including plant extracts. However, pressure induced melting of ice limits the ultimate separation efficiencies that can be attained in such systems. Electrophoretic separations can also be carried out on planar ice surfaces. In that case, extremely high fields can be applied. Such separations are rapid but the difficulty of reproducing surfaces run-to-run limits overall reproducibility. Present work centers on open silica networks produced within capillaries by sol-gel approaches. Such structures are easily and inexpensively produced and appear to permit very high separation efficiencies, especially when used in conjunction with capillary based separation systems.

University of Texas at Austin
Austin, TX 78712

Department of Chemical Engineering

422. *Carbon Dioxide Based Solvents for Waste Minimization*
Johnston, K.P. **$382,000**
512-471-4617 **(39 months)**
kpj@che.utexas.edu

Our goal is to develop environmentally benign carbon dioxide-based solvent formulations to replace toxic organic solvents for chemical processing. The use of CO_2 could lead to large reductions in organic wastes to soil, water and air. Waste minimization is vital to the growth of the U.S. chemical industry. We propose to design surfactants to produce CO_2-based solvent formulations in the form of microemulsions, emulsions, and latexes. CO_2-based solvents offer exciting new opportunities in chemical manufacturing involving heterogeneous reactions (including polymerization), solvent free coatings, extraction of heavy metals including radioactive compounds from soils and wastewater, polymer processing, and separations processes including cleaning and purification. Because a CO_2 phase has such different properties than either hydrophilic or lipophilic phases, it may be considered to be a third type of condensed phase. An organic latex, polymethylmethacrylate, has been synthesized in CO_2 with a fluorocarbon homopolymer stabilizer, demonstrating the ability to disperse an organic phase. Recently, in an article in Science, we demonstrated that microemulsion droplets with "bulk-like" water properties may be formed in CO_2 with a relatively nontoxic ammonium carboxylate perfluoroether surfactant. The ability to design surfactants for the interface between organics and CO_2, or water and CO_2, and to understand the mechanisms of stabilization of microemulsions, emulsions and latexes in CO_2 are the keys to advancement in this field. Water-in-CO_2 emulsions would be particularly desirable as solvents for waste minimization. Because the van der Waals forces are so much weaker in CO_2 than in typical oils, and because supercritical fluids are highly compressible, totally new concepts will be required. Presently, the principles for designing surfactants for CO_2 are unknown.

423. *Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications*
Koros, W.; Paul, D. **$90,999**
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Formation and testing of highly aromatic membrane materials with hindered intrasegmental mobility and interchain packing are being pursued in this project. Such materials are good candidates to provide entropically and energetically selective diffusion media for separation of important gas pairs like oxygen and nitrogen. Currently, convenient solution-based processing of polymers allows producing economical asymmetric membranes with thin (1000Å) selective layers. Unfortunately, limitations limit the selectivity achievable with conveniently soluble polymers. Analysis of the deficiencies of such membrane materials suggested an approach to greatly improve their properties while maintaining compatibility with current commercial formation equipment. Specifically, an additional reactive step is being investigated to achieve the necessary rigidity for optimum membrane properties. This project seeks to continue to expand on past experience in tailoring properties while beginning to explore secondary steps to achieve truly superior separation properties. Thermal and chemical treatments to achieve this step are being investigated currently, since they are most easily implemented.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

424. *Spectroscopic Characterization of Intermediates in the Iron Catalyzed Activation of Alkanes*
Eyring, E.M. **$102,000**
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Infrared and Raman techniques are being used in time-resolved vibrational spectroscopic studies of the oxidation of organic compounds by hydrogen peroxide in liquid media. A focus of the work is the identification of hypervalent non-porphyrin iron species thought to be reactive intermediates in these oxidation reactions. Concurrently, high pressure kinetic techniques are being used to elucidate the entry of ligands such as dioxygen into the well-packed active site of a nonheme iron O_2 carrier called myohemerythrin. Peroxidase enzymes trapped in inorganic sol-gel films and monoliths show promise for bioremediation of waste sites. A carbon dioxide adduct of myoglobin encapsulated in such an inorganic sol-gel has been prepared using supercritical carbon dioxide and is being investigated by a combination of flash photolysis and mass spectroscopic techniques.

425. *Time-Resolved Analytical Methods for Liquid/Solid Interfaces*
Harris, J. M. **$95,000**
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Many chemical phenomena that occur at boundaries between insulating solids and liquids (adsorption, partition, monolayer self-assembly, catalysis, and chemical reactions) are critical to energy-related analytical chemistry. These phenomena are central to developing chromatographic methods, solid-phase extraction, immobilized analytical reagents, and optical sensors. The goal of this program is to develop surface-sensitive spectroscopies by which chemical kinetics at liquid/solid interfaces can be observed on timescales from nanoseconds to seconds. Temperature-jump relaxation measurements are used to probe adsorption/desorption kinetics at liquid/solid interfaces; kinetic barriers to adsorption of molecular ions onto alkylated silica surfaces are being investigated. The lateral surface diffusion of molecules at liquid/solid interfaces is being studied using fluorescence recovery after patterned photobleaching; these measurements are providing information about the structure of alklyated-silica surfaces. Surface heterogeneity of adsorption sites on silica has been examined by time-resolved fluorescence, and its chemical origins investigated by ^{29}Si nmr spectroscopy. Surface-enhanced Raman spectroscopy is being used to study adsorption and binding to silica surfaces, deposited as thin layers over silver- and gold-island films that enhance the Raman scattering of interfacial species. Molecular dynamics simulations have been carried out to help better understand kinetic barriers to adsorption. Stopped flow kinetic experiments, using dispersed, colloidal solids, are being developed to monitor irreversible adsorption kinetics on a millisecond time scale.

Department of Metallurgical Engineering

426. ***Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species***
Miller, J.D. **$102,000**
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Froth flotation is one of the most important examples of applied surface chemistry and this separation technology is used in the food, petroleum, pulp-paper, and mineral industries. Several novel experimental techniques such as in situ Fourier transform infrared (FTIR) internal reflection spectroscopy (IRS) with reactive internal reflection elements, multichannel laser Raman spectroscopy, nonequilibrium laser-Doppler electrophoresis, and atomic force microscopy for surface force measurements are being developed and/or used to analyze surfactant adsorption phenomena at mineral/water interfaces and to describe the impact of adsorption phenomena on the hydrophobic character of the surface. The nonsulfide flotation research includes the soluble salt, semisoluble salt, and insoluble oxide mineral systems. Atomic force microscopy in concert with FTIR/IRS techniques is currently being used to investigate the influence of the structure of interfacial water on the short-range interparticle forces responsible for the adsorption of surfactant colloids in soluble salt flotation. Significant progress has been made in understanding the nature of the forces responsible for heterocoagulation of oppositely charged particles at high ionic strengths by measuring interparticle forces using atomic force microscopy. Also, progress continues to be made in spectroscopic characterization of interfacial water at both hydrophilic and hydrophobic surfaces by depth profiling using in situ FTIR/IRS. In the category of semisoluble salt minerals, carboxylic acid adsorption by fluorite, calcite, and apatite minerals is being examined by FTIR/IRS using a polygon shaped IRE in order to obtain more reflections on a small crystal. Interaction forces have been measured by atomic force microscopy between insoluble oxide mineral systems such as silica/alumina at various pH values in order to understand the aggregation/dispersion behavior of the above mineral suspensions.The effect of surface hydration and interfacial water structure as determined from surface spectroscopy, on the interactions at high ionic strengths, will provide further information on the relationship between collector adsorption phenomena and hydrophobic state. The results obtained from this research program will provide the basis for new reagent schedules to improve flotation separation efficiency and to promote energy conservation.

Virginia Commonwealth University
Richmond, VA 23284

Department of Chemistry

427. ***Selective Methods for Quantification of Target Species in Complex Mixtures***
Rutan, S.C. **$82,000**
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The quantification of specific compounds in complex mixtures is a common goal in many analytical methods. Here, two experimental approaches are coupled with chemometric data analysis methods to explore the possibility of obtaining reliable, quantitative results subsequent to chromatographic separations. The first approach is liquid chromatography coupled with UV-visible diode array and mass spectral detection for the analysis of polyaromatic hydrocarbons, metabolites, and pesticide residues. Quantification will be achieved by using methods such as adaptive filtering, direct trilinear decomposition, and neural networks. Standard addition methods can be used for calibration. In the second experimental approach, thin-layer chromatography will be used to separate the analytes, and the kinetics of a subsequent derivatization reaction will be used to resolve and quantify the species of interest on the thin-layer plates. This novel approach has been applied successfully for the analysis of amino acids, and the trilinear decomposition method has given satisfactory results for the quantitative resolution of the severely overlapped amino acids, glutamine and glycine. Chemiluminescent-detection approaches based on these principles are also being investigated.

Washington State University
Pullman, WA 99164

Department of Physics

428. ***UV Laser-Surface Interactions Relevant to Analytic Spectroscopy of Wide Bandgap Materials***
Dickinson, J.T. **$85,000**
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This research focuses on basic studies of the laser desorption and ablation of materials, in particular those with bandgaps which exceed the photon energies of the incident light. The mechanisms of emission and formation of ground state and excited neutral species, ions, and free electrons are probed using time resolved optical spectroscopy, photoluminescence, charged particle energy analysis, and angular distribution measurements. The existence and production of point defects and their role in (a) photodesorption processes, (b) heating and vaporization, and (c) plasma formation is of particular interest. Current studies involve imaging and quantifying defect densities, the production of surface defects with particle bombardment and mechanical stimulation, modeling the role of anion vacancies in photostimulated emission of cations, and studies of laser interactions with inorganic solids containing covalently bonded anions which photodecompose. The latter include nitrates, carbonates, and phosphates with a number of cations such as alkali and alkaline earth metals. We have shown that photodecomposition of the oxyanion controls and strongly increases the coupling of UV laser light to these materials, thus generating highly non-linear responses. We also seek detailed understanding of the way electron bombardment and mechanical stimulation of the surfaces modifies the laser interactions with these materials, often enhancing emissions of charged particles and neutrals by several orders of magnitude. A new model for defect dominated laser plume formation from wide bandgap materials is under development and verification that excludes inverse bremstrahlung as a necessary mechanism for heating of electrons in the plasma

University of Wyoming
Laramie, WY 82071

Department of Chemistry

429. ***Solid-Matrix Luminescence Analysis***
Hurtubise, R.J. **$95,000**
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The development of a fundamental understanding of physicochemical interactions and photophysical aspects for the room-temperature fluorescence and phosphorescence of aromatic compounds adsorbed on solid matrices is the major goal of this project. Glucose, trehalose, cyclodextrins, sodium acetate, and filter paper are used as solid matrices. Silicone treated filter paper is employed to selectively remove polycyclic aromatic compounds from water and then the isolated compounds are determined by solid-matrix luminescence. Distribution constants are obtained for the compounds between the silicone treated filter paper and water, and they are used to investigate the selectivity of the compounds for the filter paper. Solid-matrix luminescence analytical data are obtained for several lumiphors in carbohydrate glasses. Also, phosphorescence lifetimes, intensity data, and luminescence quantum yields are acquired as a function of temperature for phosphors in glucose glasses with and without heavy atoms in the glasses to calculate photophysical rate constants and elucidate the physicochemical interactions of the phosphors in the glasses. The solid-matrix phosphorescence of perdeuterated phenanthrene adsorbed on silicone treated filter paper and a modified sample cell are used to develop a novel oxygen sensor. The sensor is employed over a wide range of oxygen concentrations, and it is very sensitive to oxygen in the presence of carbon dioxide. A new form of solid-matrix luminescence spectrometry is being developed in which the vibronic modes of the excited singlet state and excited triplet state of lumiphors are detected by a combination of infrared and luminescence spectrometry.

Heavy Element Chemistry

Florida State University
Tallahassee, FL 32306

Department of Chemistry

430. ***Research in Actinide Chemistry***
Choppin, G.R. **$123,000**
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choppin@chem.fsu.edu

This research emphasizes the basic studies of the behavior in solution of the actinide elements and of the chemically related lanthanide elements. The systems are chosen for investigation because the data can provide increased understanding of the principles governing the chemical behavior of the f-elements with a variety of complexing ligands, both organic and inorganic. The data may also be of direct value for modeling calculations of the behavior of actinides in environmental and waste repository systems or in improved separation schemes of these elements. Emphasis continues on the thermodynamic, kinetic, and spectroscopic (absorption and luminescence) studies of the complexation and redox reaction of the actinides. A major environmental ligand studied is humic acid to which binding of actinides in the III, IV, V, and VI states is very rapid while dissociation is much slower. Binding constants and kinetics of actinide complexation to humics for different sized fractions are being investigated by several radiotracer and spectroscopic techniques. A study of actinide complexation thermodynamics by potentiometry and calorimetry at 5, 25, 45 and 70°C. Hydrolysis of AnO_2^+ at these temperatures in different electrolytes has been measured. Actinide binding to large, soluble anionic polyoxometallates (e.g., $H_2P_2W_{12}O_{48-12}$) is being investigated as such anions may serve as a model for clay and colloid systems. Several ligands have been synthesized and are being studied by potentiometry, calorimetry, fluorescence, NMR, raman, IR, and visible spectroscopies to evaluate their value in actinide separations.

University of New Mexico
Albuquerque, NM 87131

Department of Chemistry

431. ***Preorganized and Immobilized Ligands for Metal Ion Separations***
Paine, R.T. **$106,000**
505-277-1661
rtpaine@unm.edu

The objectives of this project are to (1) design and synthesize new families of organic ligands capable of selective chelation of d- and f-block metal ions present in nuclear and industrial waste streams, (2) study the structural details of the ligand/metal complexes formed in order to improve the design and synthesis of chelators, and (3) prepare solid phase, immobilized chelators suitable for practical applications in the separations field. At the present time two classes of chelate systems are under examination: multidentate phosphonopyridine N-oxides and polyaminophosphonates. In the former group, aqueous soluble and organic solvent soluble ligands have been prepared and metal coordination chemistry has revealed key features that control metal ion selectivity. Radiochemical extraction studies have shown that these ligands are highly selective and powerful chelators for actinide (III) ions. In the case of polyaminophosphonates, water soluble reagents have been generated and the small molecule ligand properties are being used to devise approaches for the synthesis of cluster or dendritic polyaminphosphonates for colloid separations.

Ohio State University
Columbus, OH 43210

Department of Chemistry

432. ***The Electronic Structure of Heavy-Element Complexes***
Bursten, B. E. **$69,332**
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This project focuses on the use of advanced theoretical methods to calculate the electronic structure of organoactinide and related coordination complexes. The principal methodologies currently employed are the fully relativistic discrete variational $X\alpha$ (DV-$X\alpha$) method, analytical-basis-set density functional methods with relativistic effective core potentials, and ab initio methods. A number of interesting new results have resulted from these calculations in the past year. First, we have generated relativistic effective core potentials for trans-actinide elements through Element 118. We have used these potentials to initiate electronic structural studies of molecules of these elements. We are also continuing our studies of the structure, bonding, and reactivity of actinide-containing molecules, particularly organometallics. Systems currently under investigation include an extensive series of sandwich compounds of the type $(\eta^n\text{–}C_nH_n)^2An$ (An = Th, Pa, U, Np, Pu, Am; n = 6, 7, 8). We have also expanded our studies of organoactinide chemistry by examining those factors that lead to linear and bent AnL_2 moieties. These studies encompass new and exciting results by experimentalists on systems such as $(\eta^5\text{–}C_5Me_5)_2U(NR)_2$. Our results to date are consistent with the interplay of electronic effects involving both 5f and 6d orbitals of the actinide elements in determining the geometries and reactivities of these molecules.

Chemical Engineering Sciences

University of California, San Diego
La Jolla, CA 92093

Department of Applied Mechanics and Engineering Sciences

433. ***Premixed Turbulent Combustion***
Libby, P.A. **$55,000**
619-534-3168
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This project is primarily concerned with flames in stagnating turbulence. Such flames are rich in problems of fundamental interest, e.g., the extinction of turbulent flames under high rates of strain. As a consequence, there are five or six laboratories in Western Europe and several in the United States carrying out relevant experiments. Although our effort is primarily theoretical, we pay close attention to experimental results coming from these laboratories. In addition we have carried out and published in the proceedings of the Twenty-fifth Symposium (International) on Combustion the results of our own experiment on turbulent flames in impinging streams. Our principal focus during the past year has been on a Reynolds stress formulation for such flames. This configuration is the most widely studied experimentally but to date there has been no satisfactory theoretical treatment of them. Although totally convincing solutions have not to date been obtained, several important findings have resulted from this effort. In particular we have shown that the calculated mean axial velocity is in excellent agreement with data despite highly inaccurate predictions for the Reynolds stresses. The implications are that the mean velocities are determined by the mean pressure and that the Reynolds stresses are to be calculated in a known mean velocity field. In addition we have found that the models for pressure-rate-of-strain effects derived for constant density flows must be altered to account for the variations of density associated with heat release. This effort is continuing. During the past contract year we have published three journal articles related to analyses of highly idealized flames in a channel, of laminar Couette flow involving premixed combustion and of the extinction of premixed turbulent flames under nonisenthalpic conditions.

Colorado School of Mines
Golden, CO 80401

Department of Chemical Engineering and Petroleum Refining

434. ***Composition of Dependence of Fluid Thermophysical Properties Theory and Modeling***
Ely, J.F. **$116,500**
303-273-3885
jely@mines.edu

The objective of this research is to develop high accuracy predictive models that describe the physical property behavior of complex mixtures. The work is currently progressing along three fronts: (1) development of improved corresponding states models for asymmetric mixtures through reference fluid equation of state design and improved mixing rules; (2) investigation of the phenomenological behavior of the viscosity of molecular (e.g., structured) mixtures through nonequilibrium computer simulation techniques; and (3) development of ultrahigh accuracy equations of state for complex fluids and fluid mixtures through the use of stepwise regression and simulated annealing optimization. The ultimate goal of this research is to develop improved computer-based models for process design that provide accurate predictions of phase transitions and bulk-phase properties in systems that have large size and/or polarity differences. Current work is focused on non-equilibrium simulations of large structured molecules and their mixtures. The ultimate goal of this part of the study is to develop improved predictive models for the viscosity of high molecular weight fluids.

Colorado State University
Fort Collins, CO 80523

Department of Chemical Engineering

435. *Study of Improved Methods for Predicting Chemical Equilibria*
Lenz, T.G. **$90,000**
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The primary goal of this project is to develop an accurate, yet inexpensive, molecular-based computational model for predicting thermodynamic properties of nontrivial molecules. Accomplishments to date have included accurate prediction of chemical equilibria for a wide range of hydrocarbons as well as very accurate prediction of the heat capacities for heteroatomic alternative refrigerants. Software developed within this project has been provided to the Quantum Chemistry Program Exchange, and is available as programs QCPE593 and QCMP145. The computational model within these programs is based on molecular mechanics. A consistent force field is the heart of this molecular mechanics program (QCFF), and substantial effort has been devoted to parameterization of this force field. Several experimental studies have been undertaken within this project to provide structural information for the force field parameterization. The most recent experimental studies have dealt with lactic acid. This work has involved isolation and characterization of the d and l enantiomers of lactic acid, as well as the racemic mixture of this molecule. The structure of l-lactic acid has been obtained using single-crystal x-ray crystallography, and a similar study for the racemic material is currently in progress.

Cornell University
Ithaca, NY 14853

School of Chemical Engineering

436. *Simulation of Fluid Behavior in Well-Characterized Porous Materials*
Gubbins, K.E. **$227,000**
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KEG@CHEME.CORNELL.EDU

This work is developing new and rigorous theoretical and simulation methods for the study of the adsorption behavior of fluids in well-characterized porous materials. In particular, fluids in porous carbons, aluminosilicates (particularly MCM-41), aluminophosphates, and buckytubes are being studied. Simulations of carbon dioxide/methane and nitrogen/methane mixtures in zeolites have been carried out, and are being compared with experimental data; in both of these mixtures inversion of selectivity has been found in certain materials. Both selective adsorption and melting/freezing studies have been made for a range of gases adsorbed in buckytubes and MCM-41. Both increases and decreases of melting temperature have been observed, depending on the material and conditions. Studies of the adsorption and filling behavior of water and water/hydrocarbon mixtures in activated carbons are being carried out. The Presence of active chemical sites on the carbon surface has been shown to give rise to a completely different pore filling mechanism from that for simple fluids, and to lead to continuous filling as opposed to the capillary condensation observed for more simple systems.

437. *Molecular Simulation of Phase Equilibria for Complex Fluids*
Panagiotopoulos, A.Z. **$132,000**
607-255-8243
azp2@cornell.edu

The objective of this project is the investigation of phase equilibria for complex fluids using molecular simulation techniques. The long-range goal is development of improved modeling techniques for rational design of efficient industrial chemical processes. Current research encompasses three main classes of systems, namely polymeric, surfactant, and ionic systems. A major methodological development during the past year has been the introduction of histogram reweighting Monte Carlo sampling methods. The methods allow significantly more accurate determination of phase coexistence properties than previously available techniques. They also can be used to locate critical points for strongly interacting fluids with high precision. We are presently applying these methods to polar and polarizable fluids, primitive electrolyte models, and lattice models for surfactants and polymers. For surfactant systems, the methods allow determination of aggregation properties in addition to transitions between structured phases. A related method, Hamiltonian-Scaling Gibbs ensemble Monte Carlo, has been developed to allow determination of properties for a series of related models from a single simulation.

Department of Mechanical and Aerospace Engineering

438. *Reaction and Diffusion in Turbulent Combustion*
Pope, S.B. **$101,000**
607-255-4314
pope@mae.cornell.edu

Fundamental processes in non-premixed turbulent combustion are being studied using direct numerical simulations (DNS). Previously, we have performed studies (on grids up to 128^3) of reactions in homogeneous turbulence, over a broad range of Damkohler numbers and reaction-zone thicknesses. In the last year, three aspects of the project have come to fruition. First, the DNS code has been implemented to run in parallel on the IBM SP2. This allows grid sizes up to at least 256^3, and hence a wider parameter range. Second, we have completed a comprehensive and fundamental study of the mixing of two passive scalars. This study extends in a significant way an earlier study of the mixing of a single scalar which, for the last decade, has served as a standard test case. Third, as a prelude to studying reaction in inhomogeneous turbulence, we have completed a study of the mixing of a passive scalar with an imposed mean gradient. In progress is work on reactive scalar mixing layers, and periodic reaction zones. These studies are providing essential information for the construction and testing of models of turbulent combustion that are applicable to practical devices.

University of Delaware
Newark, DE 19716

Department of Chemical Engineering

439. *New Generation of Group Contribution and Equation-of-State Models*
Sandler, S.I. **$114,000**
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SANDLER@che.UDEL.EDU

To make intelligent, cost-effective decisions for the design of new chemical processes, for the development of synthetic fuels and other new technologies, and for estimating the environmental fate and bioaccumulation of chemicals, accurate methods of predicting and correlating thermodynamic properties and phase equilibria are needed. The research being conducted under this grant addresses this problem from three different directions. First, the Wong-Sandler mixing rules, which have greatly expanded the range of application of equations of state to highly nonideal mixtures, are being further developed to apply to collections of mixtures that previously could not be accurately described over large ranges of temperature and pressure. This includes hydrogen-containing mixtures and mixtures with strongly polar compounds. The second area of research is the use of ab initio molecular orbital calculations to compute the effect of hydrogen-bonding and other strong association phenomena. The results of these calculations have been incorporated into equations of state to reduce the number of adjustable parameters that must be used. Following completion of the EOS work, the quantum mechanically-derived information will be used in the development of a new generation of group contribution methods (such as UNIFAC) to improve the accuracy of these important prediction methods. We have also been using computer simulation and statistical mechanical theory to develop an accurate thermodynamic description of long chain hydrocarbons, polymers, and mixtures involving these components.

University of Illinois at Chicago
Chicago, IL 60680

Department of Chemical Engineering

440. *Computer Simulation of Osmosis and Reverse Osmosis in Solutions*
Murad, S. **$85,000**
312-996-5593 **(15 months)**
MURAD@UIC.EDU

Computer simulation studies are being carried out to study the phenomena of osmosis and reverse osmosis in solutions. These studies have been carried out using both a molecular dynamics method recently developed by us, as well as a modified Gibbs ensemble Monte-Carlo (GEMC) method. Both gas mixtures and liquid (including aqueous) solutions are being investigated, since reverse osmosis is considered an attractive technique for separations in these systems. Our results show that computer simulations could prove to be a useful tool for determining the feasibility of reverse osmosis as a possible technique for many industrial separations problems. Our studies on aqueous electrolyte solutions have also suggested a new mechanism for reverse osmosis separations of salts from aqueous solutions. It was previously thought that ions are prevented from crossing the semi-permeable membrane, despite their smaller size (compared to water), because of surface interactions between the membrane and the ions. Our work seems to suggest that water molecules strongly cluster around the ions, thus effectively increasing their size and preventing them from permeating the semi-permeable membrane. We are also studying the phenomenon of electro-osmosis at the molecular level using the method of molecular dynamics in an effort to better understand it. This will ultimately allow separations carried out using these techniques, to be carried out more efficiently.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemical Engineering

441. *Prediction of Thermodynamic Properties of Complex Molecules*
Donohue, M.D. **$89,000**
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donohue@jhu.edu

The goal of this research program is to improve our understanding of the factors that cause deviations from ideal behavior in complex fluids (i.e. molecules whose size, shape, or interaction energy cause them to behave differently from spherical, non-polar molecules). We are particularly interested in understanding the properties of mixtures of such molecules. Our program includes a combination of theory, molecular simulations, and experiments. In the past, most of our work was concerned with developing equations of state for spherical molecules and molecules that can be considered strings or chains of spherical molecules. Being able to predict the properties of such molecules is important because most organic molecules are chain molecules. While we have continued to work in this area, our work has broadened considerably. In particular, we have put considerable effort into understanding how small molecules interact with polymers and how small molecules interact with surfaces. We also have tried to develop a much deeper understanding of how macroscopic properties depend on the detail of molecular packing and geometry. For example, a 2-D hexagonal lattice has the same coordination number as a 3-D cubic lattice, but they have different energies. We have developed a new theory that can predict the energetic differences as a function of both coordination number and lattice structure. Future work will be directed at generalizing this theory to polymer solutions.

University of Maryland at College Park
College Park, MD 20742

Institute for Physical Science and Technology

442. ***Thermophysical Properties of Fluids and Fluid Mixtures***
Sengers, J.V. **$135,000**
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Critical fluctuations affect the thermodynamic and transport properties of fluids and fluid mixtures in a wide range of temperatures and densities. Equations that incorporate the effects of these critical fluctuations on the thermodynamic and transport properties are being developed. Specifically, we are investigating the crossover from Ising-like to mean-field critical behavior in fluids and fluid mixtures including ionic systems. We are developing and applying a general isomorphism approach to describe thermodynamic properties of mixtures with complex phase diagrams. We are in the process of extending the theory to high-temperature aqueous salt solutions. We are also developing equations for the transport properties of mixtures like carbon-dioxide+ethane and methane+ethane by extending the mode-coupling theory to include the nonasymptotic critical behavior of the transport properties.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

443. ***Theoretical Studies of Solid-Fluid Phase Equilibria***
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In this project statistical thermodynamics is applied to the calculation of solid-fluid phase equilibrium. In our recent work a study of solid-fluid equilibrium for flexible chain molecules has been initiated. A method for calculating the free energy in Monte Carlo simulations of chain molecules in the solid phase has been developed. This method has been used to calculate the solid-fluid phase diagrams of freely jointed chains of tangent hard spheres. The methodology is being extended to the case of chains with bond angle constraints and torsional intramolecular potentials. The results of this work will be used to analyze the solid-fluid equilibrium in chain molecules, such as the normal alkanes, from a corresponding states perspective, and to develop generalized van der Waals theories of solid-fluid equilibrium. In our work on mixtures we have shown that hard sphere mixtures exhibit five of the six most important classes of solid-fluid phase behavior for binary organic mixtures. Theoretical results for hard sphere mixtures have also been used to assess some methods from classical thermodynamics that are commonly used to estimate solid-fluid phase diagrams for mixtures. We have extended our theory of solid solutions to the treatment of attractive intermolecular interactions. The predictions of the theory agree quite well with experimental data for binary mixtures involving argon, krypton and methane.

North Carolina State University
Raleigh, NC 27695

Department of Chemical Engineering

444. ***Theoretical Treatment of the Bulk and Surface Properties of Fluids Containing Long, Flexible Molecules***
Hall, C.K. **$104,000**
919-515-3571
hall@turbo.che.ncsu.edu

This research program is designed to enhance understanding of the behavior of fluids and fluid mixtures containing chain-like molecules. The objective is to develop a theory that is capable of predicting the experimentally observed thermophysical properties, including phase equilibria and transport properties, of fluids and fluid mixtures containing chain-like molecules ranging in length from alkanes to polymers. Highlights of this year's accomplishments include: (1) the extension of the Generalized Flory Dimer theory to fluids containing hard heteronuclear chains, i.e. block, alternating and random copolymers, (2) the completion of a very large scale simulation of the dynamics of very long (n=192) polymer melts and analysis of evidence for knot formation, (3) simulation of the static and dynamic properties of double-tethered chain molecules at interfaces, and (4) the simulation of the sorption and diffusion of model penetrants into model polymer membranes (including facilitated transport membranes) in the presence of a chemical potential gradient. Work is continuing on extracting activity coefficients from the Generalized Flory Dimer theories, with the aim being to use this as a basis for developing a new group contribution approach to estimate the properties of mixtures when experimental data are unavailable.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemical Engineering

445. ***Molecular and Polymeric Fluids in Microporous Media***
Glandt, E.D. **$100,956**
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The distribution of dissolved macromolecules between a bulk solution and the interior of a porous substrate occurs in a variety of technologically important systems. The partition coefficient K, which is the ratio of concentration in the pores to that in the bulk, is primarily determined by the effective size of the polymer molecules. For dilute solutions, K decreases rapidly as the effective polymer dimensions exceed the average pore size. We have used liquid-state theory to construct a rigorous integral equation model for the structure of concentrated flexible linear polymers in the presence of a rigid matrix of discrete repulsive obstacles. We have used the structural information to calculate the thermodynamic properties of the polymer in these model porous materials. In particular we have been able to calculate the partition coefficient as a function of concentration. The model provides good agreement with thermodynamic properties obtained from previous computer simulations of bulk polymer solutions, as well as with our own simulations of polymers in porous materials.

Princeton University
Princeton, NJ 08544

Department of Chemical Engineering

446. Computational and Theoretical Studies of Homogeneous Nucleation in Supercritical Fluids

Debenedetti, P.G. **$72,000**
609-258-5480
pdebene@pucc.princeton.edu

We have studied the influence of fluid-phase non-idealities on the precipitation of solids from ternary supercritical mixtures. We are also investigating, theoretically and computationally, the properties of fluids under extreme temperatures and pressures. Water can form two glassy phases that are separated by an apparently first-order phase transition. This unusual phenomenon is known as polyamorphism. We developed a microscopic model of a network-forming fluid that exhibits polyamorphism. We are testing this theoretical prediction by computer simulation. We showed that the simplest explanation of the anomalous properties of supercooled water does not require the existence of spinodal curves or metastable critical points. We have measured the evaporation rates of amorphous and crystalline water at 150K, and used this to estimate the entropy difference between vitreous and crystalline water. We showed that glassy water is connected to ordinary liquid water by a thermodynamically reversible path at atmospheric pressure. We are studying the potential energy hypersurface of superheated liquids, and find that even at the triple-point density, local potential energy minima (inherent structures) contain very large voids. The equation of state of the superheated liquid is highly sensitive to the maximum size of voids that can form in the inherent structure.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

447. Fundamental Studies of Fluid Mechanics and Stability in Porous Media

Homsy, G.M. **$80,000**
415-723-2419 **(18 months)**
bud@chemeng.stanford.edu

This research project treats flow and transport problems in porous media, which are of interest in energy recovery processes. Both macroscopic Darcy scale and pore scale flows are studied. In the former case, current work is focused on the interactions between fingering instabilities and flows driven by permeability heterogeneity. Current Darcy scale analyses are devoted to analyzing the fingering process in the presence of strong permeability heterogeneity. Current pore-scale work focuses on the propagation of interfaces of wetting and nonwetting viscoelastic fluids. Theory shows that the instability of interface propagation depends on contact angle dynamics, capillary number, and Weissenberg number. Perturbation theory for small Weissenberg numbers has shown how viscoelastic thin-film dynamics differs from the Newtonian case. In the wetting case, the hydrodynamically entrained film is thinner due to the increased resistance to elongational flow, and viscoelastic forces destabilize the interface. In the nonwetting case the main effect of elasticity is to stabilize the dynamic contact line against rivulet formation. The stabilization mechanism is related to the increased resistance to streamwise acceleration accompanying the rivulet formation. Recent experimental studies on the instability of dynamic contact lines have demonstrated that elasticity is a stabilizing force, in agreement with the theoretical predictions. Some ancillary studies of the effect of chaotic mixing in viscoelastic liquids were also undertaken and have been recently published.

State University of New York at Buffalo
Buffalo, NY 14260-4200

Chemical Engineering Department

448. Molecular Simulation of Phase Coexistence, with Application to Ordered Phases

Kofke, D.A. *$65,000*
716-645-2911

The aims of this research are the development of simulation tools that can be used by researchers in molecular thermodynamics, and the application of these tools to understand phase equilibria involving ordered phases, particularly solids. Phase equilibria play a central role in modern technology–particularly in the development, manufacture, and performance of materials–and as a consequence the study of phase coexistence occupies the activities of a wide array of engineers and scientists. Empirical, phenomenological modeling of these phenomena long ago reached its limits, and modern approaches employ a molecular viewpoint. Model substances, defined in terms of molecular interactions, are used to understand complex phenomena observed in real substances. Accurate evaluation of phase equilibria properties in model substances requires computer simulation. This has proved a difficult prospect, particularly in connection with ordered phases such as solids and liquid crystals. Thus there is a great need to develop new simulation techniques that can treat these systems. In this work two approaches are being developed to extend our abilities to evaluate coexistence by molecular simulation. The first method employs thermodynamic integration in new ways and with great efficiency. The second represents a significant departure from standard practice in simulation, and in fact constitutes something of a hybrid of simulation and numerical technique. The first method is well-grounded in theory, and has proven effectiveness; the second is more tentative, and requires significant development before it may be used routinely. Thus this research strikes a balance between incremental and radical advances in technique. The methods developed in this work are used to study phase equilibria of ordered phases. Phase diagrams describing coexistence between fluids, liquid crystals, plastic crystals, and oriented crystals are computed to examine the effects of a wide array of basic molecular features: composition, polydispersity, electrostatics, shape, and flexibility.

State University of New York at Stony Brook
Stony Brook, NY 11794

Department of Chemistry

449. ***Thermophysical Properties of Fluids and Fluid Mixtures***
Stell, G.R. **$120,000**
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Theoretical research continues on the thermophysical properties of fluids using a statistical mechanics-based approach to do molecular modelling. Current emphasis is on the study of phase separation in ionic fluids, on fluids of associating particles, and on fluids in porous media. The work on ionic fluids includes studies in which the assumptions of the mean spherical approximation are augmented by new treatments of ionic association to yield phase diagrams in which the location of phase separation is more accurately predicted. The work on association includes studies of dimerization and polymerization in model liquids of reacting atoms in which the core volume of the product molecules is considerably smaller than the sum of the core volumes of the reacting monatomic particles. The work on fluids in porous media includes a general study of thermodynamic relations for a simple fluid in such a medium that is assumed to have a realistically irregular pore structure, in contrast to earlier studies of fluids in single pores of a particular shape. In addition to the above, new work on colloidal systems has begun.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemical Engineering

450. ***Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems***
Cummings, P.T. **$149,021**
423-974-0227
ptc@utk.edu

The objective of this project is to develop fundamentally-based predictive theories for the thermodynamic properties and phase equilibria in mixed solvent electrolyte systems and supercritical aqueous solutions. During the current year, a new model for water has been under development in our research group. The model features polarizability and has the property that the isolated water molecule has the bare dipole moment of water (1.85D) unlike almost all other models for water. The goal of this model is to reproduce the properties of water over wide ranges of density and temperature, so that it will yield an accurate vapor-liquid phase envelope, as well as be effective in the high-temperature, high-pressure supercritical regime. We have also developed a molecular dynamics simulation of water/alcohol/tetrabutylammonium halide salt systems. We are performing simulations with this code to probe the molecular basis of experimental measurements of phase equilibria and densities in alcohol/water/organic salt systems performed in our laboratory. Many of the simulation codes written in our group for this project have been developed to run on the massively parallel supercomputers in the Center for Computational Sciences at Oak Ridge National Laboratory.

Yale University
New Haven, CT 06520

Department of Mechanical Engineering

451. ***Computational and Experimental Study of Laminar Premixed and Diffusion Flames***
Smooke, M.D.; Long, M.B. **$206,000**
203-432-4344
smooke%smooke@biomed.med.yale.edu

Our research has centered on an investigation of the effects of complex chemistry and detailed transport on the structure and extinction of hydrocarbon flames in coflowing axisymmetric configurations. We have pursued both computational and experimental aspects of the research in parallel. The computational work has focused on the application of accurate and efficient numerical methods for the solution of the boundary value problems describing the various reacting systems. Detailed experimental measurements have been performed on axisymmetric coflow flames using two-dimensional imaging techniques. Spontaneous Raman scattering and laser-induced fluorescence are used to measure the temperature, major and minor species profiles. Our goal is to obtain a more fundamental understanding of the important fluid dynamic and chemical interactions in these flames so that this information can be used effectively in combustion modeling.

Advanced Battery Research

Arizona State University
Tempe, AZ 85287

Department of Chemistry

452. ***Novel Electrolytes for Rechargeable Alkali Batteries***
Angell, C.A.; Xu, K. **$137,000**
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caa@asu.edu

An extension of our original program on "ionic rubber electrolytes" is in progress. The ion-plasticized salt/polymer complex, which constitutes the ionic rubber, is being further plasticized by additives of various types to explore a wide range of possible high conductivity, high cation transport number, rubbery electrolytes. Additives under study are inorganic quasi-salts, which are resistant to attack by Li and are stable to one volt negative with respect to Li^+/Li, boroxy-based Lewis acid molecular solvents, which solvate anions and form Li^+-conducting protective films on lithium metal, and inorganic molecular liquids. Some of these systems are suitable for rechargeable Li cell construction. New polymers which are compatible with Li chloroaluminates are being sought.

California Institute of Technology
Pasadena, CA 91125

Department of Materials Science

453. Design of Metal Hydride Alloys for Battery Electrodes with High Cycle Lifetimes
Fultz, B.; Ratnakumar, B.V. **$175,451**
818-395-2170
btf@hyperfine.caltech.edu

This program is addressing basic questions that underlie the design of new metal hydride alloys for service as negative electrodes in nickel - metal hydride battery cells. Ternary solutes from the groups IIIB, IVB, VB of the periodic table are being substituted for Ni in $LaNi_5$ in a systematic way and in dilute amounts to preserve the single-phase $CaCu_5$ -type crystal structure. We are correlating the thermochemical properties of the solute atoms to their effects on the cyclic lifetime of the metal hydride electrodes, both during electrochemical cycling and during gas-phase cycling. The microstructural changes resulting from the degradation processes of the electrodes are being analyzed by x-ray diffractometry and transmission electron microscopy. Effects of temperature and electrical parameters during charge/discharge cycling are also being used to test ideas about the mechanisms of electrode deterioration. Additional studies of engineering importance for metal hydride electrodes include measurements of thermodynamic and kinetic properties of hydrogen absorption in different alloys.

Case Western Reserve University
Cleveland, OH 44106-7078

Chemistry Department

454. Applications of In-Situ and Ex-Situ Spectroscopic Techniques for the Study of Electrode Materials with Relevance to Energy Generation and Energy Storage
Scherson, D.A. **$149,999**
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Electronic and structural aspects of a MnO_2 electrode in a rechargeable MnO_2/Zn battery have been examined in situ as a function of the state of charge by Mn K-edge X-ray absorption fine structure (XAFS). All data were acquired in a sandwich-type spectroelectrochemical cell which employs the same electrode materials found in commercial MnO_2/Zn rechargeable batteries. The main conclusions emerging from this study may be summarized as follows: (i) The relative amplitudes of the three major Fourier transform shells of the extended X-ray absorption fine structure (EXAFS) function of the MnO_2 electrode in the undischarged state are very similar to those found for ramsdellite, a MnO_2 polymorph with substantial corner-sharing linkages among the basic MnO_6 units. (ii) An analysis of the background-subtracted pre-edge peaks and absorption edge regions for the net 1-e^- discharged electrode yielded Mn^{3+} as the predominant product. (iii) An analysis of the spectral data revealed that the full recharge of MnO_2, which had been previously discharged either by 1-e^- or 2-e^--equivalent electrons, generates a material with decreased corner-sharing linkages compared to the original undischarged MnO_2. Insight into the nature of the species generated by the discharge and recharge of pyrite (FeS_2) in non-aqueous electrolyte was gained from the analysis of XAFS data recorded in situ. Measurements were obtained using a carefully designed sandwich-type FeS_2/Li spectroelectrochemical cell consisting of a thin film (1.5 mil) of $LiClO_4$-doped poly(ethylene oxide) (PEO) solid polymer electrolyte, an FeS_2 cathode formed by spreading finely ground, naturally occurring pyrite directly onto the polymer electrolyte, using a gold sputtered Ni foil as the current collector, and a lithium strip placed on the other side of the electrolyte serving as a counter-reference [C/R] electrode. The analysis of the in situ extended X-ray absorption fine structure (EXAFS) yielded an Fe-S distance for a cell which had been first fully 4-e^- discharged, and, subsequently, 2-e^- recharged, remarkably similar to that found for pyrite. Furthermore, the features observed in the X-ray absorption near edge region (XANES) were similar to species in which the iron is present in a tetrahedral environment. Both these findings are not consistent with Li_2FeS_2 as being present in these electrodes, as has been proposed in the literature.

Clark University
Worcester, MA 01610

Department of Chemistry

455. Novel Aluminum and Sulfur Batteries
Licht, S.
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Work is actively proceeding on development of a new battery, the aluminum sulfur battery. Each storage cell contains an aluminum anode, a solid sulfur, and/or aqueous polysulfide cathode and operates at or near room temperatures. Both the very high discharge domain (over 10 mA/cm^2) and the low discharge domain (less than 0.1 mA/cm^2) of the cell are being studied and optimized. Development includes optimization of the aluminum anode and of the sulfur cathode through electrochemical, spectroscopic, and potentiometric measurements in a variety of temperature, concentration, and partial discharge domains for the combined solid sulfur-aqueous polysulfide system. Measurements of aluminate, hydroxide, and solution additive concentrations during anode discharge are being studied to improve anodic utilization efficiencies under a variety of discharge conditions. Cells incorporating the most promising modifications are being tested. From these discharge tests, high energy capacity cells will be designed and tested with a 250-Wh/kg objective.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

456. Nanomaterials in Secondary Battery Research and Development
Martin, C.R. **$80,000**
970-491-0271 **(15 months)**
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Li-ion batteries are one of the most promising technologies for the development of a new generation of high energy-density, light weight portable power sources. For this reason a substantial research effort is currently being devoted to development of new electrode materials and electrolytes for such batteries. Surprisingly, however, very little work is being devoted to optimization of the electrode morphology - specifically optimal particle shape and size for the Li-insertion material that makes up the battery electrode. The reason this area has been neglected is that, prior to our work, there have been essential no methods that allow for synthesis of Li-insertion materials with tailored particle sizes and shapes. We have developed a novel approach for preparing monodisperse nanoscopic particles of nearly any desired material. This method, called "template synthesis" produces nanoscopic tubules and fibers of the desired material. The objective of this work is to use the template approach to prepare high density ensembles of tubular and fibrilar Li-insertion materials and then to show that these nano-engineered battery electrodes can out-perform electrodes, of the same material, that have been prepared via conventional routes. In particular, we would like to show that the nano-engineered tubular and fibrilar battery electrodes can deliver higher capacity, at high discharge currents, than conventional battery electrodes. We have already proven that this concept works. In collaboration with Professor Hiroshi Yoneyama at Osaka University, we prepared nanoscopic tubules of the cathode material $LiMn_2O_4$. A high density ensemble of tubules in which the tubules protruded from a substrate current collector surface like the bristles of a brush was prepared. The tubules had an outside diameter of 200 nm and a wall thickness of ca. 50 nm. Constant current charge and discharge experiments were conducted on these tubular electrodes and on a conventional thin film electrode composed of the same material. Both the tubular and thin film electrodes contained 0.75 mg of $LiMn_2O_4$ per cm^2 of Pt current-collector surface area. We found that the tubular electrode delivered greater capacity than the thin film electrode and that the ratio of the tubule capacity to the thin film capacity increased with increasing current density. At a current density of 1.0 mA per cm^2, the tubular electrode delivered an order of magnitude higher capacity than the thin film electrode, even though both electrodes contained the same amount of $LiMn_2O_4$.

University of Minnesota
Minneapolis, MN 55455

Corrosion Research Center

457. *Characterization of Insertion Electrodes in High-Energy Cell*

Smyrl, W.H. **$275,625**
612-625-0717 **(15 months)**
smyrl001@maroon.tc.umn.edu

The objective of the research is to perform the enabling materials research necessary for the development of a battery oriented to the consumer market. Special requirements, in terms of safety, cycling life, and high energy and power densities are necessary for this class of batteries. The discovery in our laboratory of a novel V_2O_5 material that has a high capacity for Mg^{+2} insertion (4 equivalents of Mg^{+2} per mole of V_2O_5) opens the way for its use as a 'universal' host for intercalation of divalent and trivalent cations. Magnesium, zinc, and aluminum are being studied because of their high energy, combined with their availability, low-cost, and increased safety over lithium-based systems. With the introduction of the lithium-ion concept that avoids the problem of safety hazards of lithium metal anode batteries, the area of nonaqueous high-energy, rechargeable batteries offers promise for portable consumer products. A second approach is to develop battery systems of other energetic materials. The present research is directed to the synthesis of high-capacity, reversible aerogels of V_2O_5 materials for Mg^{+2}, Zn^{+2}, and Al^{+3} battery systems.

School of Physics and Astronomy

458. *Modeling of Transport in Lithium Polymer Electrolytes for Battery Applications*

Halley, J.W. **$100,302**
612-624-0395 **(15 months)**
woods@jwhp.spa.umn.edu

The goal of this research is to provide new insight into the mechanism of ionic conduction in Li polymer electrolytes and the electrolyte-electrode interface using a combination of new and powerful simulation techniques that have not previously been applied to these materials. A molecular dynamics model for amorphous polyethylene oxide has been developed, using a unique approach in which the model is developed by simulating a polymerization process, starting with liquid dimethyl ether. This has significant advantages over starting a molecular dynamics simulation in the crystalline phase. We are using the molecular dynamics model to evaluate solvation and hopping activation free energies for Li^+ ions and various cations. This output from the molecular dynamics studies will be used to construct lattice models of the system at larger length and longer time scales appropriate to the transport problem and to evaluate various suggestions concerning the nature of the ionic transport in these electrolytes. Later, the models will also be used to study the electrode-electrolyte interface.

Moltech Corporation
Tucson, AZ 85747-9108

459. *New Materials Technology For Rechargeable Lithium Batteries*

Skotheim, T. **$143,000**
520-799-7500
skotheim@moltech.com

Rechargeable batteries with high specific energy are of critical importance for applications where portability is an issue. The objective of this program is to develop significantly improved polymer technology that will be incorporated into thin film rechargeable lithium cells, which have the potential to leapfrog existing technologies. We are currently developing advanced battery technologies and materials for high-capacity, long-cycle-life lithium polymer batteries. Our work on high-capacity organo-sulfur polymer cathode materials has made significant progress, including synthesis and characterization of all materials made in-house. Processing techniques for polymer cathode are being determined and/or improved, resulting in better performance of our laboratory test cells.

University of Nevada at Las Vegas
Las Vegas, NV 89154

Department of Physics

460. ***Long-Ranged Polymer Dynamic Behavior and Conductivity in Battery Polymer Electrolytes: Poly(ethylene oxide)/Salt Systems***
Selser, J.C. **$20,000**
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selser@physics.unlv.edu

In this project, light scattering–principally the noninvasive dynamic light scattering technique known as photon correlation spectroscopy–is being used to study long-ranged, slow relaxations of poly(ethylene oxide) (PEO) in methanol solutions and in the melt both with and without lithium perchlorate. The purpose of this work is to reveal how long-ranged PEO relaxations in PEO solid polymer electrolytes are related to lithium ion conductivity in these electrolyte systems. Following the project plan outlined in the FY 1995 project summary, the first phase study of the effects of lithium ions on PEO global behavior in methanol solutions has been completed and the results reported in the literature (P.A. Banka, et al, *Macromolecules* **1996**, *29*, 3956-3959). Briefly, it was found that repulsive interactions between lithium ion/PEO oxygens complexes caused PEO coils to swell in solution resulting in the conversion of PEO to a polymer electrolyte and the "salting in" of PEO in methanol. Significantly, it was shown that repulsively interacting complexes were not uniformly distributed along PEO chains, but were instead concentrated in coil outer portions. The study of the effect of lithium ions on PEO coil internal motions is also progressing but completion of this portion of the project awaits delivery of a satisfactory high molecular weight, narrow molecular weight distribution PEO sample. Significant progress has also been made on the second phase of the project dealing with melt PEO samples. Development of a procedure for preparing optically clear melt samples is close to completion and light scattering measurement capability has been extended by the purchase of a second light scattering photometer, modification of the existing photometer, development of light scattering measurement methodology and on improved data analysis.

City University of New York (CUNY), Hunter College
New York, NY 10021

Department of Physics and Astronomy

461. ***Magnetic Resonance and X-Ray Absorption Studies of Materials for Advanced Batteries***
Greenbaum, S.G.; denBoer, M.L. **$202,000**
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A comprehensive three-year program of spectroscopic investigations of secondary lithium battery materials is proposed. All three components of cells under development for high energy density lithium ion batteries will be studied: lithiated carbon anodes, polymer electrolytes, and transition metal oxide cathodes. The proposed research will involve close interactions with Cambridge Battery Associates, Inc. (A subsidiary of Arthur D. Little, Inc.), E.I.C. Laboratories, Inc., and the U.S. Army Power Sources Laboratory (ARL), as well as other groups. The mode of collaboration includes provision of (electrochemically) well-characterized samples for our studies in return for spectroscopic feedback to be utilized in continued materials development and, of course, joint publications of scientific results. We propose ^{7}Li nuclear magnetic resonance measurements to provide information on the local environment and dynamics of mobile Li^+ in cathodes and electrolytes. Complementary information on the geometric and electronic environment of the transition metal ion will be obtained by x-ray absorption spectroscopy, both near-edge and extended fine structure, and corresponding soft x-ray absorption measurements of the C 1s level in the lithiated carbon. The x-ray measurements will be supplemented by electron paramagnetic resonance measurements, which yield knowledge of spin densities and symmetries. In situ x-ray absorption and synchrotron infrared techniques will also be developed and implemented.

North Carolina State University
Raleigh, NC 27695

Department of Chemical Engineering

462. ***Composite Polymer Electrolytes Using Cross-Linked Fumed Silica Fillers in Low Molecular Weight Polyethylene Oxides: Synthesis, Rheology and Electrochemistry***
Khan, S.A.; Fedkiw, P.S.; Baker, G.L. **$165,626**
919-515-4519
Khan@che.ncsu.edu

The objective of this project is the synthesis and evaluation of a composite polymer electrolyte system for use in rechargeable lithium batteries. Based on surface-modified, cross-linked fumed silica and low molecular weight polyethylene oxide/glycols, this new approach should yield low-cost, processable solid electrolytes with conductivities that rival gel electrolytes. The principal features of the new system include: (i) exceptional processability; the composite is processable as a viscous fluid using standard techniques but can set to give a solid with a yield point, (ii) dimensional stability; the fumed silica can be cross-linked by UV, thermal, or other curing methods to improve the mechanical properties and ensure dimensional stability, (iii) good conductivity; room temperature conductivities for electrolytes containing lithium salts should easily reach 5×10^{-4}S/cm, (iv) low cost; this is a consequence of simple processing and the ready accessibility of the materials, and (v) inherent safety; cured composite electrolytes should have the electrochemical stability typical of solid polymers. Current efforts have focused on the synthesis of surface-modified fumed silica and understanding the processing/rheological behavior of fumed silica composites. Two different types of surface-anchored groups have been attached to commercial fumed silica; these materials are being characterized to determine and optimize their surface coverage. Electrochemical and rheological studies have been undertaken on composite polymer electrolytes consisting of surface modified fumed silica with octyl groups, methyl-capped polyethylene glycol and lithium imide salts. Our results show these materials to exhibit room temperature ionic conductivities higher than 10^{-3} S/cm and improved electrochemical stability. In addition, they exhibit mechanical strength with modulus similar to some elastomers, $\sim10^6$ dynes/cm^2. These properties, together with the processability ease of these systems, show great promise for fumed silica composite electrolytes.

Pennsylvania State University, University Park
University Park, PA 16802

Center for Advanced Materials

463. ***Development of Novel Strategies for Enhancing the Cycle Life of Lithium Solid Polymer Electrolyte Batteries***

Macdonald, D.D.; Allcock, H.R.; Urquidi-Macdonald, M. **$231,000**
814-863-7772
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A wide range of substituted polyphosphazenes that can serve as the bases for solid polymer electrolytes (SPEs) have been synthesized during the past three years of the project. The conductivities of SPEs formed from these polyphosphazenes and lithium triflate ($LiSO_3CF_3$) have been measured, and many are found to be greater than 10^{-5}S/cm at 25°C. Most importantly, we have established correlations between the substituent properties and the conductivity that will guide future synthetic efforts. We have also paid attention to the rheological properties of the polymers, with the goal of identifying systems that would not require crosslinking, because this adds an additional step in any manufacturing process and hence increases the cost. Finally, we have fabricated prototype batteries of the type Li/SPE/TiS_2, which are found to have open circuit voltages of 2.8–3.02V, but in-depth performance studies have yet to be performed. In parallel with the synthetic work outlined above, we have developed a combined impedance/dilatometry system for exploring the cycling performances of laminates that have been fabricated using the substituted polyphosphazenes. By using the Pt/SPE/Pt laminate, we have shown that the impedance of the system can be delineated into interfacial and bulk electrolyte components, as determined from the effect of pressure. Increasing pressure is found to decrease the interfacial resistance but to increase the bulk resistivity, with the latter being attributed to a decrease in the free volume. The cycling behavior of Li/SPE/Li has also been explored, in terms of changes in impedance and laminate thickness, as lithium (6 mA. hrs) is electrochemically pumped from one side to the other. We find no degradation (increase) in the impedance as the system is cycled at a current density of 6 mA/cm^2 for more than 500 cycles. This finding suggests that, although irreversible changes occur at the Li/SPE interface, and perhaps in the bulk electrolyte as well, the metallic lithium/SPE interface should not be the limiting factor in cycle life performance, at least for laminates based on substituted phosphazenes. This is in contrast to other SPEs, where lithium "powdering" has been implicated in a sudden increase in cell (Li/SPE/IC) resistance and hence to failure. Finally, based on our impedance studies, we have derived physical models for the interface, including an electrical analog and a model based on the interstitial conduction of Li^+ through a reaction product layer at the Li/SPE interface. We have also developed an Artificial Neural Network (ANN) model for Li/SPE/IC batteries, based on data taken from the literature. This model shows that the charge/discharge rate and depth of discharge, amongst other factors, are important parameters in determining cycle life.

Rutgers, The State University of New Jersey
Piscataway, NJ 08855

College of Engineering

464. ***Solid Electrolyte-Electrode Interfaces: Atomistic Behavior Analyzed Via UHV-AFM, Surface Spectroscopies, and Computer Simulations***

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908-445-2216
shg@rutile.rutgers.edu

UHV-AFM, STM, and XPS surface analyses and molecular dynamics computer simulations have been used to examine the structural and dynamic properties of the cathode/electrolyte interface in solid-state oxide thin-film batteries. In the experiments, the electrolytes have included lithium-containing borates, phosphates, and phosphorous oxynitride ion conducting (IC) glasses and Li and V_2O_5 as the cathode/electrode materials. Lithium silicates and WO_3 and V_2O_5 have been studied in the simulations. Lithium migration into the oxide cathode during formation of the interface between the cathode and the IC oxide glasses has been evaluated using XPS and the simulations. Results show significant lithium migration across the interface during interface formation in both the experiments and the simulations. In the XPS studies, V_2O_5 was deposited in situ onto lithium borate, lithium phosphate, and lithium phosphorous oxynitride glass substrates using RF sputtering. The thickness of the IC glass substrates was varied from 50Å to 750Å. The Li concentration in the cathode was measured as a function of cathode overlayer thickness on each glass electrolyte. A correlation between electrolyte thickness and Li penetration in to the cathode was observed. However, this migration could be controlled under appropriate conditions. In the molecular dynamics simulations, new potentials were generated to give stable crystalline forms of vanadia and tungsten oxide and γ-lithium vanadate and lithium tungsten bronze. Valence change of the cathode cations as a function of Li intercalation was employed to mimic the real situation. The simulations showed penetration of Li from the IC glass into the cathode, with different penetration occurring as a function of crystal orientation. The amorphous form of the cathode also behaved differently than the crystalline forms, consistent with experimental data. Importantly, Li intercalation from the glass electrolyte into the vanadia showed the appropriate phase change to the δ form of lithium vanadate, even though the potentials were not designed for this phase. This shows the robustness of the potentials used here. Also, a channeling of Li occurred in the glass in contact with the WO_3 crystal as the Li migrated into the crystal. Finally, UHV-AFM force distance studies using a lithiated electrolyte glass and an oxidized tungsten tip indicated the ability of using this approach to determine transport characteristics on a nanometer scale.

University of South Carolina
Columbia, SC 29208

Department of Chemical Engineering

465. ***Synthesis, Characterization, and Testing of Novel Anode and Cathode Materials for Li-Ion Batteries***
White, R.E.; Popov, B.N.; Ritter, J.A. **$200,000**
803-777-3270
rew@sun.che.sc.edu

The primary objectives of this proposed research are to synthesize and characterize novel compounds with high energy density and cycle life to be used as the cathode and anode materials in Li-ion cells with the following characteristics: (i) high reversibility of the Li-ion insertion/deinsertion reaction, (ii) high thermal stability and chemical compatibility of the electrodes with the electrolyte, (iii) good electronic conductivity of the electrodes, and (iv) high diffusivity of the Li-ion in the solid, active portion of the electrodes. These compounds will have higher capacities and energy densities than the materials that are used currently for Li-ion cells. In addition, the objectives include developing the ability to control and ultimately predict the microstructure of these cathode and anode materials by tailoring the chemistry and engineering history of the material, and to relate the macroscopic performance of the material to its microstructure (i.e., to develop structure-property relationships). The ultimate objective of this work is to use a priori knowledge to engineer the microstructure of a material to achieve optimal performance of a Li-ion battery.

Texas A & M University
College Station, TX 77843

Center for Electrochemical Systems and Hydrogen Research

466. ***Cell Components with Emphasis on Hydride Electrolytes for Nickel/Metal Hydride Batteries***
Srinivasan, S. **$118,500**
409-845-8281
b-mahan@tamu.edu

Hydride electrodes, using active materials prepared by mixing AB_5 and AB_2 (1:1) alloys, show better rate capabilities and cycle life behavior than electrodes using the individual alloys as active materials - mainly due to the higher chemical stability of the mixed alloys. The detailed mechanisms responsible for this better behavior are the subject of our on-going investigations. Addition of Zn or Pd to the metal hydride alloy decreases the capacity fading rate of the hydride electrode. Zinc addition to the electrolyte seems to be more advantageous than its inclusion in the alloy because in the former case, Zn is regenerated on the surface during charging of the electrodes. The changes in morphology, structure and composition of metal hydride electrodes, after charge/discharge cycles, were determined using scanning electron microscopy and energy dispersive X-ray analysis techniques. Capacity degradation after charge/discharge cycling and rate capability measurements of the hydride electrodes were also evaluated and correlated with these characteristics. Results showed that Al in an alloy enriches on the surface of alloy particles and causes its dissolution. Such a break-down of alloy particles enhances the electrode kinetics of the hydriding reaction and hence the rate capability of the hydride electrode.

Tufts University
Medford, MA 02155

Electro-Optics Technology Center

467. ***Reseach on Advanced Thin Film Batteries***
Goldner, R.B. **$20,000**
617-627-3136
rgoldner@pearl.tufts.edu

Affordable, high energy and power density rechargeable batteries are needed for powering portable electrical and electronic equipment for medical and consumer applications; and they are needed also for electrical vehicle and power load levelling applications. Most of the applications require voltages >3 Volts. Inorganic thin film lithium-ion rocking-chair cells are particularly attractive candidates for these batteries. To assist U.S. industry in their development of such advanced batteries, the Tufts University Electro-Optics Technology Center, (in collaboration with the Eveready Battery Company, Oak Ridge National Laboratory, Physical Sciences Inc., and Rome Air Force Laboratory), proposes to continue a research program the objective of which is to obtain affordable and safe prototype inorganic thin film lithium-ion rocking-chair batteries that are: more durable, have higher voltages, and higher power and energy densities than can be obtained with commercially available rechargeable batteries.

Utah State University
Logan, UT 84322-0300

Department of Chemistry and Biochemistry

468. ***The Development of Conductive Diamond Thin Films as Advanced Battery Electrode Materials***
Swain, G.M. **$55,000**
801-797-1626 **(15 months)**
gmswain@cc.usu.edu

Synthetic diamond thin films possess several technologically useful properties including high chemical and thermal stability, excellent thermal conductivity, hardness, light weight and good electrical conductivity (doped form). One relatively unstudied application of this advanced material is the use of diamond thin films as electrode materials for advanced battery systems. The research being conducted in this project is focused on the growth and characterization of boron-doped(≥100 ppm B/C) diamond thin film electrodes for use in advanced batteries. Specifically, the performance characteristics of conductive diamond thin films, used as a support for the alkaline nickel hydroxide redox system, is being electrochemically, spectroscopically and microscopically evaluated. The research is being conducted in three parts. First, the coating of diamond on planar Ni and high surface area Ni FIBREX supports is being studied using microwave-enhanced chemical vapor deposition (CVD) as a function of the growth conditions (C/H ratio, pressure, temperature and plasma power). The objective of this phase of the research is to develop the conditions required to coat a continuous and conductive film on Ni and Ni FIBREX; the latter is a commonly used battery electrode material. The resulting films are fully characterized by SEM, AFM, Raman microprobe spectroscopy, XRD and AES. Second, the corrosion resistance of boron-doped diamond thin films, grown on planar Si substrates, is being tested in strongly alkaline electrolytes similar to those used in commercial batteries (≥5 wt.% KOH). The corrosion studies are being performed as a function of the diamond film properties, the electrolyte composition, solution temperature and cycle number or exposure time using cyclic voltammetry and ac impedance analysis. Once the conditions to coat diamond on Ni and Ni FIBREX have been developed, then the corrosion studies will utilize these materials. Third, $Ni(OH)_2$ films are being deposited on boron-doped diamond thin films, grown on planar Si substrates, and the electrochemical performance of the active material/diamond substrate is being studied during multiple charge and discharge cycles in 15 wt.% KOH. The active material is being deposited cathodically from $Ni(NO_3)_2$ solutions mixed with 50:50 ethanol and water. A novel feature of this phase of the research is the extensive use of in situ STM and AFM to examine the structural and electronic properties of the active material/diamond electrodes during different states of charge and discharge. This novel research may lead to the development of more durable and stable battery electrode materials exhibiting improved electrode reaction kinetics, coulometric efficiency, and performance lifetimes for the redox reaction of interest.

SPECIAL FACILITIES

The special facilities described on the following pages are supported wholly or partly by the Division of Chemical Sciences. They represent an assembly of unique and/or expensive equipment which would be costly to develop elsewhere. They represent research resources for the general Scientific community, and qualified scientists from laboratories outside the host laboratory are encouraged to make use of them. However, any activity that can be carried out through commercially available laboratories is not appropriate for these DOE-supported facilities.

The process by which an off-site scientist can use a facility is discussed in each facility summary. For the National Synchrotron Light Source, the Stanford Synchrotron Radiation Laboratory, and the Combustion Research Facility, see the section, "User Mode." For the remaining facilities, see "Collaborative Use," which describes the different procedures used at the individual facilities.

Each of the facility summaries also gives the names of individuals to contact for further information, a general description of the facility, and a list of technical data on the primary available instrumentation.

The Office of Basic Energy Sciences also supports other facilities not summarized here. Information concerning these can be obtained by contacting the Director of Materials Sciences, ER-13, U.S. Department of Energy, Germantown, MD 20874.

Budgets for the operation of those facilities specifically funded as Chemical Sciences Facilities (KC-03-01-04) are given below.

Location	Facility	Operating Funds
Brookhaven National Laboratory	National Synchrotron Light Source	$ 7,853,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	26,346,000
	Radiochemical Engineering Development Center	7,078,000
Sandia National Laboratories, California	Combustion Research Facility	4,307,000
Stanford University	Stanford Synchrotron Radiation Laboratory	13,390,000

PREMIUM COAL SAMPLE PROGRAM (KC-03-02-01)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The purpose of the Premium Coal Sample Program is to provide the coal science community with long-term supplies of a number of premium coal samples that can be used as standards in fundamental research. The premium coal samples distributed through this program are as chemically and physically identical as possible, have well-characterized chemical and physical properties, and are stable over long periods of time. The coals were mined, transported, processed into desired particle and sample sizes, and packaged in environments as free of oxygen as possible. The natural moisture content was also maintained in order to ensure that the coals are in as pristine and stable a condition as possible.

AVAILABILITY

Eight coal samples are available to research personnel at a nominal replacement cost. A limited quantity of large pieces, stored under similar inert conditions, is also available on special request. More than 800 shipments totaling over 22,000 ampoules have been made thus far. A Users Handbook is updated periodically and available upon request (see contact below) or on the World Wide Web at http://www.anl.gov/PCS/pcshome.html.

PERSON TO CONTACT FOR INFORMATION

Dr. Ken B. Anderson
Chemistry Division
Bldg. 200
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone: (708) 252-1928
Fax: (708) 252-9288

E-mail: kbanderson@anl.gov

#	Seam	State	C	H	O	S	Ash
1	Upper Freeport	PA	85.5	4.70	7.5	2.32	13.2
2	Wyodak-Anderson	WY	75.0	5.35	18.0	0.63	8.8
3	Illinois #6	IL	77.7	5.00	13.5	4.83	15.5
4	Pittsburgh #8	PA	83.2	5.32	8.8	2.19	9.2
5	Pocahontas #3	VA	91.1	4.44	2.5	0.66	4.8
6	Blind Canyon	UT	80.7	5.76	11.6	0.62	4.7
7	Lewiston-Stockton	WV	82.6	5.25	9.8	0.71	19.8
8	Beulah-Zap	ND	72.9	4.83	20.3	0.80	9.7

PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne electron pulse radiolysis facility has been and is being used for a wide variety of experiments. Although the accelerator was designed for chemical research, it has been used for a wide variety of experiments. Recent nonchemical experiments include the verification of radiation monitors under pulse conditions, the determination of cavity modes induced in cavities by a short pulse of electrons, the verification of the theory of wakefield acceleration, and the effect of high-energy electrons on material properties. For chemical experiments, the moderate energy of the electron accelerator (maximum energy of 21 MeV transient mode, 14 MeV steady state mode) generates transient species without excessive nuclear activation. The pulse width can be varied from 25 ps to 10 ms. In addition, a 5-ps pulse with the same peak current as the 25-ps pulse has been developed. In liquids, transient concentrations up to 20 mM can be generated with the 25-ps pulse and concentrations more than 10 mM can be generated with the longest pulse. Instrumentation for the measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. A 2-ps streak camera with custom software is available for fast emission measurements. Very high time resolution measurements that make use of the short pulse capability of the Linac can also be made. All data acquisition equipment is computer interfaced to provide accurate data reduction. Sample preparation and handling facilities are available for solid, and handling facilities are available for solid, liquid, and gaseous samples.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah   Phone: (708) 252-3471
Chemistry Division   Fax: (708) 252-4993
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Computer address: Jonah@Anlchm.bitnet
Alternative: Jonah@ANLCHM.CHM.ANL.GOV

TECHNICAL DATA

Energy	
Transient mode	21 MeV
Steady-state mode	14 MeV
Average current	200 μA (maximum)
Pulse repetition rate	Single pulse to 800 pps (800 pps not possible for all pulses)
Current/pulse	
Transient mode	20 A peak
Steady-state mode	1.5 A peak
Picosecond pulse	25 nC (charge per pulse)
Picosecond (5 ps)	6 nC
Pulse width	5 ps 25 ps. 4 to 100 ns } transient mode 0.5 to 10 μs steady state mode

NATIONAL SYNCHROTRON LIGHT SOURCE

Brookhaven National Laboratory
Building 725B, P.O. Box 5000
Upton, NY 11973-5000

The National Synchrotron Light Source (NSLS) is the largest facility in the U.S. dedicated to the production of synchrotron radiation. Funded by the Department of Energy as a user facility, construction on the NSLS began in 1977 with VUV Ring operation commencing in 1982 and X-Ray Ring operation in 1984. Since then, the facility has undergone a major 4-year upgrade and is continually improved to take advantage of the latest technology in storage rings, beamline optics, and insertion devices.

The NSLS operates two electron storage rings producing high brightness synchrotron radiation in the infrared, visible, ultraviolet, and x-ray regions of the electromagnetic spectrum. Insertion devices installed in the straight sections of the rings provide radiation that is anywhere from one to several orders of magnitude brighter than the radiation from bending magnets. The VUV Ring operates at 800 MeV with a critical energy of 486 eV. It has 17 beam ports split into 25 experimental stations, or beamlines, and also supports two insertion devices. The X-Ray Ring operates at 2.5 GeV, 300 mA, with a critical energy of about 5 keV. It has a total of 30 beam ports split into 60 beamlines and currently supports 5 insertion devices: two undulators, a superconducting wiggler, and two hybrid wigglers. There are also a number of beamlines devoted to machine diagnostics and R&D. The NSLS facility has user laboratories and a wide range of research equipment for basic and applied studies in condensed matter, surface science, photochemistry and photophysics, lithography, crystallography, small-angle scattering, metallurgy, x-ray microscopy, topography, etc. Detailed information about beamline research programs, experimental apparatus, and optical configurations is available from the NSLS User Administration Office.

USER MODES

Approximately 2300 scientists from more than 350 institutions came to the NSLS to perform research during 1994. The NSLS is a national user facility available without charge to university, industrial, national laboratory, and government users. In addition, a program is available to assist faculty/student research groups who have limited grant support and wish to defray travel expenses to the NSLS. Proprietary work can be done on a full cost recovery basis with the option to retain title to inventions resulting from research at the NSLS.

There are several ways of using NSLS experimental facilities. A large fraction of the beamlines have been designed and constructed by Participating Research Teams (PRTs). PRTs are comprised of one or more research teams from industry, universities, and other laboratories with large, long-range programs which have been approved by the NSLS Scientific Advisory Committee (SAC). The PRT members are given priority for up to 75% of their beamline's operational time, and their programs are reviewed by the SAC every three years. Peer-reviewed General User proposals are scheduled on both PRT beamlines and on beamlines built by the NSLS for the general community. The NSLS facility operates throughout the year with beam time scheduled in 4-month cycles. Deadlines for General User proposals are September 30, January 31, and May 31. Information about submitting research proposals, becoming a PRT, or applying for financial assistance may be obtained from the NSLS User Administration Office.

PERSON TO CONTACT FOR INFORMATION

Eva Z. Rothman,
User Administrator
NSLS Bldg. 725B
Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000

Phone: (516) 344-7114
Fax: (516) 344-7206

E-mail: ezr@bnl.gov
See also World Wide Web at:
URL = http://www.nsls.bnl.gov/

NSLS TECHNICAL DATA[*]

Storage Rings	Key Features
VUV	17 ports; E_c = 25.3 Å; 0.808 GeV electron energy
X-Ray	30 ports; E_c = 2.48 Å; 2.584 GeV electron energy

Research Area	Wavelength Range (Å)	Energy Range (eV)	Number of Beamlines
Absorption Spectroscopy	0.35 - 2480	5 - 35,000	24
Circular Dichroism	10.3 - 5904	2.1 - 1,200	2
High Pressure Physics	1 - 10,000 μm	0.124 - 1,240 meV	2
	WB[†]; 0.12 - 1.24	WB; 10,000 - 100,000	2
High Q-Resolution Scattering	WB; 0.12 - 6.20	WB; 2,000 - 100,000	15
Imaging:			
Medical	WB; 0.12 - 1.24	WB; 10,000 - 100,000	2
Tomography	WB; 0.12 - 3.10	WB; 4,000 - 100,000	3
X-Ray Microprobe	WB; 0.12 - 3.10	WB; 4,000 - 100,000	3
X-Ray Microscopy/Holography	10 - 80	155 - 1,240	1
X-Ray Topography	WB; 0.41 - 3.10	WB; 4,000 - 30,000	2
Infrared Spectroscopy	1 - 10,000 μm	0.124 - 1,240 meV	2
Lithography	124 - 4133	3 - 100	1
Nuclear Physics	—	80 - 400 MeV	1
Photoemission Spectroscopy	2.10 - 6200	2 - 5,900	19
Photoionization	2.10 - 4133	3 - 5,900	3
Protein Crystallography	WB; 0.41 - 3.10	WB; 4,000 - 30,000	6
Radiometry	WB; 8.27 - 248	WB; 50 - 1,500	1
Small Angle Scattering:			
Biology	0.66 - 5.90	2,100 - 18,800	2
Materials Science	0.36 - 6.20	2,000 - 34,000	4
Small Molecule Crystallography:			
Powder	WB; 0.12 - 3.10	WB; 4,000 - 100,000	4
Single Crystal	0.21 - 6.20	2,000 - 59,400	7
Standing Waves	WB; 0.62 - 6.89	WB; 1,800 - 20,000	2
Surface Scattering/X-Ray Reflectivity	WB; 0.48 - 6.20	WB; 2,000 - 26,000	10
Time Resolved Fluorescence	1393 - 5904	2.1 - 8.9	1
UV Reflectometry	WB; 8.27 - 6200	WB; 2 - 1,500	2
X-Ray Emission Spectroscopy	2.48 - 50	248 - 5,000	2

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[*] From 1993 NSLS User's Manual–BNL 48724.

[†] WB = White Beam.

JAMES R. MACDONALD LABORATORY (KC-03-01-03)

Department of Physics
Kansas State University
Manhattan, KS 66506

The laboratory operates a 7-MV tandem accelerator, a 9-MV superconducting linear accelerator (LINAC) and a cryogenic electron beam ion source (CRYEBIS) for the study of ion-atom collisions with highly charged ions. The tandem can operate as a stand-alone accelerator with six dedicated beam lines. The LINAC is operated as a booster accelerator to the tandem. The tandem-LINAC combination has four beam lines available. The CRYEBIS is a stand-alone facility for studying collisions with bare ions at low velocity. An ion-ion collision facility using the CRYEBIS and a new ECR ion source are under development. The laboratory has a variety of experimental apparatus for atomic physics research. These include recoil ion sources, Auger electron spectrometers, X-ray spectrometers, and a 45-inch-diameter scattering chamber. The laboratory is available to users who require the unique facilities of the laboratory for atomic collision experiments.

COLLABORATIVE USE

Users are encouraged to seek a collaborator on the staff or to submit a brief proposal to the Laboratory Director.

PERSON TO CONTACT FOR INFORMATION

Patrick Richard, Director Phone: (913) 532-6783
James R. Macdonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506-2604

E-mail: Richard@phys.ksu.edu

TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 7MV
Output currents	Up to 10 μA, depending on the ion species and the charge state
Repetition rate	DC or 3-ns pulses at rates up to 4 MHz, or 12 MHz operation
Magnet limitations	$ME/q^2 \leq 150$

LINAC Booster

Acceleration field	9 MV
Resonators	Split-ring, superconducting Nb, operated at 97 MHz
Beam repetition rate	12 MHz with 75% of beam bunched
Mass limitation	$M < 100\mu$ due to injection energy

CRYEBIS

Beams	Up to bare ions of C, N, O, F, Ne, Al, and Ar. Up to Kr^{36+} and Xe^{47+}, Fe beams under development
Beams energy	A few to 200 KeV/q
Output currents	10^5 to 10^8 parts/s

PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556-0579

The Notre Dame pulse radiolysis facility is based on a 2-100 ns electron pulse from an 8-MeV linear accelerator. It is fully instrumented for computerized acquisition of optical and conductivity information on radiation chemical intermediates having lifetimes of 5 ns and longer. An excimer laser/dye laser combination is available for use at the pulse radiolysis facility for double-pulse experiments involving photolysis of radiolytic transients. Energies of ~400 mJ at 308 nm and ~50 mJ at various near-UV and visible wavelengths are available. For typical absorption studies, where one produces 10^{-5} M of intermediates, spectral and kinetic information can be obtained on species having extinction coefficients in excess of 100 M^{-1} cm^{-1}. Conductometric methods in aqueous solution cover the pH range of 3 to 11. Data are recorded digitally and stored in magnetically readable form for rapid off-line examination of spectral and kinetic details.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

PERSON TO CONTACT FOR INFORMATION

J. Bentley Phone: (219) 631-6117
Assistant Director Fax: (219) 631-8068
Notre Dame Radiation Laboratory
Notre Dame, IN 46556

E-mail: bentley@vsmallv.rad.nd.edu

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	Workstation (DOS/Intel 486)
Pulse width	2–100 ns
Time resolution (RC)	2 ns
Pulse current	Up to 4 A
Repetition frequency	0.2 s^{-1}
Optical absorption measurements	
Spectral region	210 to 750 nm
Sensitivity	± 0.00002 absorbance
Conductivity	
pH range	3 to 11
Sensitivity	± 5 mhos/cm

HIGH FLUX ISOTOPE REACTOR (KC-03-01-04)

Research Reactors Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Since it began full-power operations in 1966, the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) has been one of the world's most powerful research reactors. A primary purpose of the HFIR is the production of ^{252}Cf and other transuranium isotopes for research, industrial, and medical applications. These materials are produced in the flux trap in the center of the HFIR fuel element where a working thermal-neutron flux of 2.5×10^{15} neutrons/cm^2·s) is available to irradiate the target material. Additional irradiation facilities are also provided in the beryllium reflector.

Beyond its contributions to isotope production, the HFIR also provides for a variety of irradiation tests and experiments that benefit from the exceptionally high neutron flux available. In the fuel element flux trap, a hydraulic rabbit tube provides access to the high thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. A modification of the flux trap experimental facilities in 1986 has provided two locations in the maximum flux region that can accommodate instrumental capsules and engineering loops. The beryllium reflector contains numerous experimental facilities with thermal-neutron fluxes up to 1.0×10^{15} neutrons/($cm^2 \cdot s$). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by ORNL or other qualified users.

Another major use of the HFIR is for neutron-scattering experiments to reveal the structure and dynamics of a very wide range of materials. The reactor has four horizontal beam tubes with inner diameters of 10 cm that extend outward from the reactor core at the midplane of the reactor. Beam tube HB-2 extends radially from the reactor centerline, and beam tube HB-3, which extends tangentially from the core, is offset 34 cm from the reactor center. A third tube is aligned on a tangential line 39 cm from the reactor centerline with both ends extending outward from the reactor to allow for the installation of two individual facilities. The two ends of this tube are designated HB-1 and HB-4. A scattering block of beryllium has been placed at the centerline between beam tubes HB-1 and HB-4, effectively making them into two tangential tubes.

The neutron-scattering instruments installed on the horizontal beam tubes are used in fundamental studies of materials of interest to solid-state physicists, chemists, biologists, polymer scientists, metallurgists, and colloid scientists. These instruments are open to use by university and industrial researchers on the basis of scientific merit, and about 150 to 200 researchers use the experiment facilities at the HFIR each year.

PERSON TO CONTACT FOR INFORMATION

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Research Reactors Division Fax: (615) 547-9175
Oak Ridge National Laboratory
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Oak Ridge, TN 37831

E-mail: leeje@ornl.gov

RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER (KC-03-01-04)

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The objective of the base program at the Radiochemical Engineering Development Center (REDC) is to supply transplutonium elements for use in research. The REDC is the distribution center for the DOE/ER heavy-element research program. Target rods are fabricated at REDC, irradiated in the High Flux Isotope Reactor (HFIR), and processed at REDC for separation, recovery, and purification of the heavy actinides up through ^{257}Fm. Since their construction in the mid-1960s, REDC and HFIR have provided the western world's supply of elements beyond curium (atomic number 96), either directly or by furnishing starting materials for further nuclear-synthesis reactions. The transuranium element isotopes produced in the REDC are used nationally and internationally to study the basic physics and chemistry of the transuranium elements. They are also being used in research and development, programs relating to environmental effects, biological effects, and waste isolation.

Similar radiochemical separations projects can be and are often carried out in the REDC for other DOE programs. Currently, transplutonium elements are being recovered from targets irradiated at Savannah River for Defense Programs. Also, ^{252}Cf portable neutron sources are prepared for a variety of radiography, activation analysis, and cancer treatment applications. REDC facility management is under the direction of the Assistant Secretary for Nuclear Energy. Base funding is provided by the Office of Energy Research and is supplemented by other agencies when their projects are carried out.

PERSON TO CONTACT FOR INFORMATION

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Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, TN 37831-6423

E-mail: wam@ornl.gov

COMBUSTION RESEARCH FACILITY (KC-03-01-04)

Sandia National Laboratories
Livermore, CA 94551-0969

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, research in fundamental chemistry in combustion, as well as analytical studies of reacting turbulent flows. (These programs are individually described elsewhere in this publication.) The active program of visitors to the facility, including senior researchers, graduate students, and postdoctoral researchers supported through the Chemical Sciences Division, is described below.

Facility support, through the Chemical Sciences Division, includes operation and continued development of the CRF central lasers. Several are available. The tunable dye laser (Diana) is used by Sandia staff and visiting scientists for single-shot temperature, density, and species concentration measurements, and for two- and three-dimensional imaging of turbulent flames. A multipurpose laser system (Sirius) consists of a frequency-doubled Nd:YAG laser and a pulse-amplified ring dye laser. When the Nd:YAG laser is operated in single-axial mode in combination with the ring dye laser, the spectral resolution for CARS and other nonlinear spectroscopy experiments (performed in any of the CRF laboratories via the beam distribution system) is as small as a few thousandths of a wave number. Sirius is used also for CARS measurements in flames with large luminous backgrounds (e.g., heavily sooting flames laden with coal particles). A third central laser (Dyeblaster) consists of a frequency-doubled Nd:YAG laser and is used routinely to pump dye lasers in user laboratories throughout the CRF.

In addition, DOE/Energy Efficiency and Renewable Energy sponsors programs at the CRF in combustion technologies and materials processing by design, DOE/Fossil supports programs in coal combustion and related diagnostics development, DOE/BES Engineering Science supports advanced analysis of turbulent flows and DOE/BES Materials Sciences support programs in combustion-related materials research.

Complete facilities for resident and visiting researchers are available: offices for 60 staff, a meeting room accommodating 250 people, a laboratory building housing 24 independent experiments, special facility laser systems, a network of computer workstations, and access to supercomputers.

In specific instances, proprietary research can be carried out at the CRF. For this type of work, the DOE will be reimbursed on a full cost recovery basis for the use of all CRF resources. Details of a DOE Class Waiver for patent rights are available.

USER MODE

Qualified scientists are encouraged to take advantage of the specialized resources available at the CRF. Prospective participants should submit a brief proposal to the laboratory director. Criteria for selection include technical merit, the extent to which CRF facilities are used, overlap with DOE program objectives, and the availability of specific equipment.

In general, the CRF will host visiting scientists to use the special-purpose lasers, work with resident staff, make use of computers and codes, and set up experiments. Visitors pay for their own salary, travel, housing, meals, and other local expenses. Facility lasers, apparatus, technicians, instrumentation, computers, and support-group services are provided without charge for research that is not proprietary. Research results from nonproprietary projects are expected to be published and disseminated.

For scientists with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are opportunities for faculty, postdoctoral scientists, and graduate students to obtain Sandia support for combustion-related research at CRF.

PERSON TO CONTACT FOR INFORMATION

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TECHNICAL DATA

Equipment	Key features	Equipment	Key features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2-μs pulse length 5 J/Pulse, 5 Hz Tunable 440 to 620 nm 0.3-nm bandwidth	Combustion bomb	Simulated constant-volume engine combustion
Multipurpose pulsed laser system	High peak power, high resolution double YAG and tunable dye lasers: Single mode capability 10 to 500 mJ/pulse 10 to 29 ns/pulse	Internal combustion research devices	Highly repeatable environment for homogenous charge, diesel combustion, and pulse combustion studies
Low-pressure flames	10 torr to 1 atm Mass spectrometer sampling probe LIF detection of radicals	Experimental diagnostics research	Nonlinear optical spectroscopy Laboratories
Atmospheric flames	Diffusion and premixed flames	Turbulent flame structure laboratory	Rayleigh, Mie, and Raman 2-D imaging
Vertical turbulent diffusion flame	Open-circuit, induced-draft with tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow	Burner Engineering Research Laboratory	Firing rates from 1 kW to 3 MW, capabilities for air/fuel preheat, fuel gas recirculation, and humidification. Continuous monitoring of flue gas O_2, CH_4, CO_2, CO, NO, and NO_2. Optical diagnostics for particle and species concentrations and temperature

STANFORD SYNCHROTRON RADIATION LABORATORY (KC-03-01-04)

Stanford Synchrotron Radiation Laboratory
MS 69, PO Box 4349
Stanford, CA 94309-0210

The Stanford Synchrotron Radiation Laboratory (SSRL) is a national user facility which provides synchrotron radiation, a name given to x-rays or light produced by electrons circulating in a storage ring at nearly the speed of light. These extremely bright x-rays can be used to investigate objects of atomic and molecular size, allowing a wide variety of research in basic and applied studies on the structure of matter. The facility, which provides 25 experimental stations on 21 beam ports as well as ancillary equipment, is used by researchers from industry, government laboratories and universities in many areas, including the fields of biology, chemistry, environmental molecular science, geology, materials science, electrical engineer, chemical engineering, physics, astronomy, and medicine.

Vacuum Ultraviolet Studies (VUV)

Research utilizing the VUV and soft x-ray radiation includes: (a) the determination of electronic states in metals, semiconductors, magnetic systems, superconductors and other interesting materials; (b) properties of ultra-thin layers and small clusters; (c) kinetic processes in a variety of materials; (d) lithography and dynamic process of chemisorbed gases.

Structural Molecular Biology

X-rays are used for research in structural molecular biology including: (a) protein structures and functions through diffraction studies in the crystalline state: (b) protein structures through extended x-ray absorption fine structures studies; (c) dynamic fluctuations in biological systems; (d) the nature of membrane and membrane protein interactions; and (e) the structure and function of metal sites in metalloproteins and metalloenzymes. Specialized facilities for protein crystallography are available. A new high brightness wiggler beam line with 3 experimental stations for structural molecular biology is under construction and will be commissioned in October 1996.

X-Ray Studies of Condensed Matter

Research utilizing x-rays for studies of condensed matter include the following areas: (a) structures of amorphous materials, catalysts and environmentally interesting systems; (b) structures of and phase transitions in surfaces and thin surface layers; (c) kinetics of structural changes in materials; (d) chemical reactivities in the gas phase; (e) nuclear resonant scattering; and, (f) fundamental x-ray scattering and absorption physics. A new beam line for environmentally-relevant studies is in the initial phases of construction.

Synchrotron Radiation Sources

Considerable research is also underway in the development of accelerators and devices inserted into the accelerators to produce more intense or brighter synchrotron radiation.

USER MODE

SSRL is currently used by approximately 950 scientists from over 100 US and foreign based institutions. Scientists gain access to the facility through a refereed proposal system. Proposals are due May 1 and October 1 each year. The booklet "User Guide" available from SSRL contains information pertinent to proposal submittal. To date, 2336 proposals for research have been received.

PERSON TO CONTACT FOR INFORMATION

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CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS

	Horizontal Angular Acceptance (mrad)	Mirror cutoff (keV)	Monochromator	Energy range (eV)	Resolution ΔE/E	Approximate spot size, hgt x wdth, mm	Dedicated Instrumentation
Insertion Devices Stations							
WIGGLER LINES—X-RAY							
End Stations							
4-2 (4 periods)							
Focused	2.0	10.2	Double Crystal	2400 - 10200	$\sim 5 \times 10^{-4}$	1.0 × 3.0	
Unfocused	1.0		Double Crystal	2400 - 45000	$\sim 10^{-4}$	2.0 × 20.0	
6-2 (27 periods)							
Focused	2.3	22	Double Crystal	2050 - 21000	$\sim 5 \times 10^{-4}$	1.0 × 4.0	
Unfocused	1.0		Double Crystal	2050 - 32000	$\sim 10^{-4}$	2.0 × 20.0	
7-2 (4 periods)							Six-Circle Diffractometer
Focused	2.0	10.2	Double Crystal	2400 - 10200	$\sim 5 \times 10^{-4}$	1. × 5.0	
Unfocused	1.0		Double Crystal	2400 - 45000	$\sim 10^{-4}$	2.0 × 20.0	
9-2 (8 periods)					*Under Construction*		
Focused	2.0	23	Double Crystal	4000 - 23000			Area Detector
White Light	0.5			4000 - 45000			
10-2 (15 periods)							
Focused	2.3	22	Double Crystal	2400 - 21000	$\sim 5 \times 10^{-4}$	0.6 × 4.0	
Unfocused	1.0		Double Crystal	2400 - 45000	$\sim 10^{-4}$	2.0 × 20.0	
Side Stations							
4-1	1.0		Double Crystal	2400 - 45000	$\sim 5 \times 10^{-4}$	2.0 × 20.0	
4-3							Two-Circle Diffractometer
Focused	1.0	Variable	Double Crystal	2400 - 20000	$\sim 10^{-4}$	0.15 × 20	
Unfocused	1.0		Double Crystal	2400 - 45000	$\sim 10^{-4}$	2.0 × 20.0	
7-1	1.0		Curved Crystal	6000 - 13000	$\sim 8 \times 10^{-4}$	0.6 × 3.0	Rotation Camera
7-3	1.0		Double Crystal	2400 - 45000	$\sim 10^{-4}$	2.0 × 20.0	
9-1	3.0	16	Curved Crystal	11500 - 13500	*Under Construction*		Rotation Camera
9-3					*Under Construction*		
Focused	2.5	23	Double Crystal	4600 - 23000			
Unfocused	0.7		Double Crystal	4600 - 40000			

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS (CONT.)

	Horizontal Angular Acceptance (mrad)	Mirror cutoff (keV)	Monochromator	Energy range (eV)	Resolution ΔE/E	Approximate spot size, hgt x wdth, mm	Dedicated Instrumentation
Insertion Devices Stations (Cont.)							
VUV/Soft X-Ray Stations							
5-3 multi-undulator	1.5		4 Gratings	10 - 450	$0.5\text{-}1 \times 10^{-3}$	≤ 1 mm^2	
5-2 multi-undulator	1.5		4 Gratings	10 - 1200	$0.5\text{-}1 \times 10^{-3}$	1 mm^2	
5-4			NIM	*Under Construction*			
10-1	2.0		6m SGM	250 - 1200	$\sim 2 \times 10^{-4}$	≤ 1 mm^2	
Bending Magnet Stations							
X-Ray							
1-4	2.0		Curved Crystal	6700 - 10800	4.0×10^{-3}	0.25×1.0	Small Angle Scattering Detector
1-5	1.0		Double Crystal	2400 - 30000	$\sim 10^{-4}$	2×17	Area Detector/CAD-4
2-1 (Focused)	4.8	8.9	Double Crystal	2400 - 8900	$\sim 5 \times 10^{-4}$	2×6	
2-2	1.0		None	3200 - 40000		4×22	
2-3	1.0		Double Crystal	2400 - 30000	$\sim 5 \times 10^{-4}$	2×20	
VUV/Soft X-Ray							
3-1	2.0		Grasshopper	24 - 1000	$\Delta\lambda = .05\text{-}2$ Å	1.0×1.0	
3-3	8-10	4.5	UHV Double Crystal (Jumbo)	800 - 4500	$\sim 5 \times 10^{-4}$	1.5×1.5	
3-4	0.6		Multilayer	0 - 3000	White or $\Delta\lambda/\lambda = .6\%$	2×8	Vacuum Diffractometer Lithography Exposure Station
8-1	12		6m TGM	8 - 180	$\sim 1 \times 10^{-3}$	≤ 1 mm^2	
8-2	5.0		6m TGM	150 - 1000	$\sim 1 \times 10^{-4}$	≤ 1 mm^2	
1-2	4.0		6m TGM	8 - 90	$\sim 1 \times 10^{-3}$	1.0×1.0	

FY 1996 EQUIPMENT FUNDS

Outlay funds of the Office of Basic Energy Sciences are divided among operating, equipment, and construction funds. Equipment funds are provided primarily to DOE laboratories. (Operating funds provided to other projects are used for all costs, including purchase of necessary equipment.) FY 1996 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment Funds
Ames Laboratory	$ 414,000*
Argonne National Laboratory	2,045,000*
Brookhaven National Laboratory	1,891,000
Idaho National Engineering Laboratory	37,000
E.O. Lawrence Berkeley National Laboratory	836,000
Lawrence Livermore National Laboratory	29,000
Los Alamos National Laboratory	108,000
National Renewable Energy Laboratory	226,000
Notre Dame Radiation Laboratory	418,000
Oak Ridge National Laboratory	1,491,000
Pacific Northwest National Laboratory	749,000
Sandia National Laboratory California	1,024,000
Sandia National Laboratories New Mexico	0
Stanford Synchrotron Radiation Laboratory	4,199,000

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*In addition to the amounts shown, funds for General Purpose Equipment are provided to these laboratories. The amounts are $150,000 for Ames Laboratory and $2,000,000 for Argonne National Laboratory.

SELECTED TOPICS OF GENERAL INTEREST

The numbered references below refer to abstract numbers, not to page numbers.

INSTITUTION INDEX

This index lists the institutions responsible for the projects cited in this publication. The references below indicate page numbers, not abstract numbers.

INVESTIGATOR INDEX

Investigators' surnames are indexed in the form appearing in the citation; given names generally have been reduced to initials. For projects with multiple investigators, each name is indexed. The references below indicate page numbers, not abstract numbers.