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Summaries of FY 1994 Research in the Chemical Sciences

SEPTEMBER 1994

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences

Prepared by
Office of Scientific and
Technical Information

ERRATA

For DOE/ER--0144/12

Under "SELECTED TOPICS OF GENERAL INTEREST," the following index headings are **reissued** to replace the entries under "SOLAR PHOTOCHEMICAL ENERGY CONVERSION" on pages 145 and 146. We regret any inconvenience caused by this error.

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Summaries of FY 1994 Research in the Chemical Sciences

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences

This report was compiled for the Office of Energy Research from project summaries contained in the Research-In-Progress (RIP) database of the Office of Scientific and Technical Information, Oak Ridge, Tennessee. The RIP database describes new and ongoing energy and energy-related research projects carried out or sponsored by the Department of Energy.

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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 five 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 headings, the "Selected Topics of General Interest" list, 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 its 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 on 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.

Another section of this publication includes summaries of projects funded during FY 1994 by the Small Business Innovation Research (SBIR) Program Office in response to technical topics submitted by the Division of Chemical Sciences to the annual SBIR Solicitation and the annual Small Business Technology Transfer Solicitation.

Questions about the details 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 be directed to the undersigned.

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

Chemical Sciences Division Organizational Chart

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Heavy Element Chemistry	
Dr. John L. Burnett	903-3182

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* On leave from Sandia National Laboratories, New Mexico
† On leave from the Los Alamos National Laboratory

Chemical Sciences Division
Office of Energy Research
U.S. Department of Energy
Washington, DC 20585

PROGRAM SUMMARIES

Each Branch 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 on page viii. 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 Materials Sciences Division. The Chemical Sciences Environment Safety and Health (ES&H) staff are also indicated on page viii.

Fundamental Interactions Branch (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 Physics (KC-03-01-03)

The Atomic Physics program supports experimental and theoretical 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.

Facility 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 Chemical Sciences 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 Materials Sciences Division, the National Synchrotron Light Source (NSLS) at Brookhaven. 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.

Processes and Techniques Branch (KC-03-02)

Chemical Energy (KC-03-02-01)

This 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 instrument 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) the chemistry of excited spectroscopic states, (3) thermochemistry of actinide elements and compounds, (4) the chemistry of actinides in near-neutral aqueous solutions and the reactions of aqueous actinide ions with various complexing agents, (5) the 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 Technology
(KC-03-02-04)

The Advanced Battery Technology Research and Development program supports research to develop new generic battery technology focused on the nonautomotive consumer market with emphasis on improvements in battery size, weight, life, and recharge cycles. Areas of research include materials development and characterization, battery component development and interactions, characterization methodologies, and systems development and modeling. 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 investigations of lithium cells, metal hydrides, bifunctional air electrodes, fundamental studies of composite electrode structures, failure and degradation of active electrode materials, and thin-film electrodes, electrolytes, and interfaces. Characterization and methodologies include problems of electrode morphology, zinc corrosion, separator/electrolyte stability, stable microelectrodes, and the transport properties of electrode and electrolyte materials and surface films. Investigations in computational chemistry, modeling, and simulations, including property predictions, phenomenological studies of reactions and interactions at critical interfaces, film formation, phase change effects on electrodes and 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.

AMES LABORATORY

Iowa State University
Ames, IA 50011

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SANDIA NATIONAL LABORATORIES, CALIFORNIA
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NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **$679,000**

1. ***Raman Spectroscopy of Model Photosynthetic Systems***
   Cotton, T.M.
   515-294-9887

The objective of this project is to prepare model photosynthetic systems that exhibit rapid and efficient electron transfer behavior. Monolayers and multilayers composed of donor (chlorophylls and porphyrins) and acceptors (viologens and quinones) species are prepared on various types of substrates by self-assembly and Langmuir-Blodgett techniques. This approach can be used to control the spacing between species within a multilayer assembly. The effect of orientation on electron transfer kinetics can be probed using spread monolayer films at an aqueous interface. Such information is important because vectorial charge separation in reaction centers isolated from photosynthetic membranes depends upon highly ordered structures. Following characterization of the monolayers, these are transferred to solid supports and their electrochemical and photochemical properties are investigated by voltammetric methods. A highly sensitive technique, surface enhanced Raman spectroscopy, is used to characterize the structural aspects of the model systems and to monitor the electron transfer process as well. For this purpose, the monolayer and multilayer systems are prepared on metal substrates. The use of a number of different types of donor molecules has shown that the metal plays an important role in the photochemical response of the system. Enhanced photochemistry occurs on metal substrates which exhibit optical absorption (surface plasmon resonances) in the visible region of the electromagnetic spectrum. The possibility for using plasmon resonances to enhance further the photochemical efficiency in model systems is under investigation. [1.75 FTE]

2. ***Laser Spectroscopy and Electronic Energy Transfer of Light Conversion Systems***
   Small, G.J.
   515-294-3859

Electronic energy and electron transfer processes in photosynthetic protein complexes are investigated in order to understand the structure-dynamics relationships that lead to the high solar energy conversion efficiency of photosynthesis. Particular attention is paid to characterizing the excited electronic states of the photocatalytic chlorophylls and other cofactors that are bound to the protein, understanding the manner in which low frequency protein vibrations mediate the transport of energy or charge, and the determination of the effect of the inherent glass-like structural disorder of proteins on the kinetics of transport. To this end, high resolution laser-based frequency domain spectroscopies (e.g., spectral hole burning) developed in this laboratory are applied. Currently, spectral hole burning is the most powerful method for the study of the above problems and has provided the first qualitative data on electron-vibration (protein) coupling and the glass-like disorder of proteins. These data are used to test existing theoretical models and to develop new ones. Because the understanding of energy/electron transport and solar energy conversion in the photosynthetic unit is of very considerable complexity, new experimental approaches are developed. Recently, a high pressure/variable temperature apparatus has been interfaced with the laser-spectroscopic system. [2.25 FTE]

3. ***Ultrafast Spectroscopy and Energy Transfer***
   Struve, W.S.
   515-294-4276

Time resolved fluorescence and pump-probe spectroscopies, on the ultrafast femtosecond time scale, are used to characterize electronic energy transport, vibrational cooling, and charge separation in photosynthetic systems. These investigations encompass both naturally occurring and artificial photosynthetic systems. Recent attention has focused on femtosecond energy transfer and coherence decay in green photosynthetic bacteria. In addition, antenna kinetics and vibrational coherences in chlorosomes from the green bacterium *Chloroflexus aurantiacus* have been studied. The bacterial chlorophyll c aggregates in these antennae are a potential model for efficient self-assembly of artificial antennae. Current issues include the extent of real-time exciton coherence in strongly coupled antennae and the extent which vibration thermalization of pigments in proteins contributes to femtosecond transient. An in-depth femtosecond analysis of vibrational cooling and dielectric relaxation of bacterial chlorophyll a in polar solvents has also been concluded recently. New studies are investigating energy transfer in monolayer and multilayer antenna systems in two-dimensional surfaces. An ongoing effort involves the formation and characterization of monolayer recognition template systems. [2.90 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division **$4,947,000**

4. ***Electron Transfer and Energy Conversion***
   Miller, J.R.; Meisel, D.
   708-252-3481

This program performs fundamental research on long-distance electron transfer reactions and redox catalysis in the condensed phase. Electron trasnfer rates are controlled by the nature and spatial orientation of molecular material between the electron donor and acceptor groups. Experimental measurements and ab initio theory are used to establish the role of the intervening structural elements. Electron pulse radiolysis provides a technique to examine this question as well as the effects of energy, polarity, ion pairing, and temperature on the rate of the process. Energetics of electron transfer at the surface of small semiconductor particles are altered by the sizes of the particles in the 10-100 Å range. Chemical alteration of their surfaces has marked effects on charge recombination processes of photoexcited particles. New research is under way on the photophysics and electron transfer of molecules that are attached to surfaces or tethered in novel ways. [6.2 FTE]

5. *Preparation and Photophysical Characterization of Photosynthetic Components*

Norris, J.R.
708-252-3544

The purpose of this work is to provide the necessary compounds, reagents, and components for unraveling the chemical machinery of natural and artificial photosynthesis. This work provides stable, nonabundant, isotopically labeled materials that are fully characterized in their physical and chemical properties. For example, fully deuterated reaction center proteins and fully deuterated chlorophylls and bacteriochlorophylls are biosynthesized, purified, and characterized by optical and magnetic resonance spectroscopies, mass spectrometry, and neutron diffraction. These fully deuterated materials are needed in order to track the chemical events of natural and artificial photosynthesis by state-of-the-art spectroscopic techniques. Also, fully deuterated material, including the reaction center protein, is necessary to probe the microscopic structure of the photosynthetic machinery with neutron scattering and diffraction. Finally, other fully characterized, isotopically labeled material containing carbon-13 and/or nitrogen-15 are available as required for magnetic resonance spectroscopies, and are invaluable analytical tools for probing the components, structure, and mechanisms of charge separation as performed by natural and artificial photosynthetic systems. [0.6 FTE]

6. *Photosynthesis Research*

Norris, J.R.; Thurnauer, M.; Tiede, D.M.; Tang, J.; Chen, L.X.
708-252-3544

This research is devoted to advancing the understanding of natural photosynthesis for application in artificial photosynthesis. This work explores the detailed mechanics of how an electron is pumped by light activation from the primary donor (bacteriochlorophyll special pair) to the primary acceptor (bacteriopheophytin). Why this natural chemistry appears to require 10 times less work by the surrounding medium than in artificial photosynthesis is explored by femtosecond optical spectroscopy in genetically modified bacterial reaction centers. Another major goal of this work is to establish the characteristics of the quinone photochemistry that result in long-lived charge separation. During the quinone activity, pairs of free radicals are created that can be probed by unique state-of-the-art time domain magnetic resonance techniques. Isotopically labeled material is required for these magnetic resonance experiments. Finally, a substantial theoretical component is devoted to both the primary charge separation events and to the state-of-the-art electron paramagnetic resonance characterization of charge separation across a membrane barrier. [5.3 FTE]

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

Trifunac, A.D.; Sauer, M.C., Jr.; Bartels, D.M.; Werst, D.W.; Jonah, C.D.
708-252-3483

Chemical transformations resulting from the interaction of ionizing radiation with condensed matter are examined. The goal is to provide a total description of chemical processes and reactive intermediates involved in "high-energy" chemistry and thus develop a state-of-the-art molecular mechanism of many processes that have widespread technological importance. This wide-ranging and comprehensive research effort utilizes specialized techniques and instruments (picosecond electron linear accelerator, ultrafast intense UV lasers, and time-domain optical and magnetic resonance methods) to discover and examine short-lived species. Studies of transient intermediates such as radical cations and electrons provide a basis for the understanding of chemical reactivity of reactive species that are important for describing molecular transformations occurring in chemical and biological uses of radiation. Several novel species and processes have been observed and characterized for the first time. A significant part of this research examines the role of solvent as the modulator of chemical reactivity of electrons and ions. Novel low-temperature matrix methods have been developed using zeolite "microreactors" to allow detection of very elusive radical ions and to develop strategies for control of ion-mediated chemical transformations. [8.9 FTE]

8. *Artificial Photosynthesis*

Wasielewski, M.R.
708-252-3538

The principal goal of the artificial photosynthesis 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. [2.8 FTE]

Energy and Environment Division $179,000

42. ***Combustion Chemistry***
Brown, N.J.
415-486-4241

Combustion processes are governed by chemical kinetics, energy transfer, transport, fluid mechanics, and the complex interactions among these. In all chemical changes, the pathways for energy movement and the competition among the pathways determine reaction rates, product yields, and product state energy distributions. Understanding the fundamental chemical processes offers the possibility of optimizing combustion processes. Recent research has been concerned with the application of functional sensitivity analysis to explore the relationships between dynamic observables and the potential energy surface structure. Functional sensitivity analysis has been applied to classical dynamics studies of energy transfer and to quantum mechanical studies of reactive scattering. New applications of the methodology will involve analyzing experimental/theory comparisons to assess specifically where a particular experimental result can be used to eliminate potential inaccuracies. The formalism will also be used in conjunction with a surface fitting exercise to assure that a high density of *ab initio* points is computed in regions that most influence the dynamics. New emphasis will be placed on using functional sensitivity analysis to provide a detailed map of the important regions of the potential energy surface that most strongly influence the calculation of the thermal rate coefficient. A second portion of the effort is concerned with modeling combustion chemistry with particular emphasis on treating problems that require parallel computing for a tractable solution. [1.0 FTE]

Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

Division of Applied Physics $39,000

43. ***Chemical Kinetics Modeling***
Westbrook, C.K.
415-422-4108

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 the overall 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 are combined together to validate the reaction mechanisms, including results from laminar flames, shock tubes, flow systems, detonations, and even internal combustion engines. Fuels to be studied next include chlorinated hydrocarbons characteristic of toxic wastes, aromatic hydrocarbon species, and smaller oxygenated hydrocarbons. [0.3 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Molecular Science Research Center $4,850,000

44. ***Chemical Structure and Dynamics***
Colson, S.D.
509-375-6882

This program will achieve a molecular level understanding of chemical reaction dynamics at condensed phase interfaces. The methods used for these studies include (1) the synthesis of unique surfaces and interfaces through controlled deposition of atoms, molecules, and clusters; (2) the synthesis of atomic and molecular clusters designed to mimic the structures of surface sites and of solvated species in solution and at interfaces (the structures and reaction dynamics of these clusters will provide unique insight into condensed-phase chemistry and can aid in developing and validating ab initio theories); (3) laser methods for the study of molecules in clusters, in solution, and at interfaces with sufficient time resolution to measure chemical processes in real time; (4) atomic-resolution surface mapping and analysis methods combined with reactive and nonreactive molecular scattering and diffusion studies, for chemical characterization of surfaces and interfaces; and (5) direct excitation of surfaces, interfaces, clusters, and molecules with electrons and photons to model chemical processes inherent in radioactive mixed waste storage (radiolysis) and in the energetic destruction of wastes. [10.8 FTE]

45. ***Molecular Theory and Modeling***
Dunning, T.H., Jr.; Garrett, B.C.
509-375-6863

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 with modeling of the complex molecular systems found in the environment. Five research areas are emphasized: (1) structure and properties of aqueous clusters and the energetics and dynamics of molecular processes involving such clusters; (2) structure of molecules and the energetics and dynamics of molecular processes in aqueous solutions; (3) structure and energetics of ion-ligand complexes (such as crown ethers) and the dynamics of complex formation in aqueous solutions; (4) binding of molecules to soil minerals and the dynamics of molecular processes at the interface of minerals and aqueous solutions; and (5) energetics and dynamics of molecular processes occurring at the interface between amorphous materials, e.g., glasses and aqueous solutions. This knowledge will further the development of new separations processes for the treatment of wastes, the construction of reliable models of contaminant transport and transformation in soils and groundwater, and the assessment of the stability of long-term waste storage forms. [8.3 FTE]

Sandia National Laboratories, California
Livermore, CA 94551

Combustion Research Facility $2,619,000

46. Turbulent Reacting Flow Research

Barlow, R.S.; Schefer, R.W.; Paul, P.H.; Chen, J.H.; Najm, H.; Koszykowski, M.L.
510-294-2688

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 flows are also studied computationally by direct numerical simulation (DNS), where all scales of fluid motion are computed. A current focus is the inclusion of realistic chemical kinetic mechanisms in the DNS calculations. [6.0 FTE]

47. Chemical Dynamics and Kinetics

Chandler, D.W.; Miller, J.A.; Rohlfing, E.A.; Hayden, C.C.; Durant, J.L.; Taatjes, C.A.
510-294-3132

The goal of this research is to understand the details of fundamental chemical processes that occur in combustion. Chemical kinetics experiments 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 OH + CH_4 and NH_2 + NO and the collisional quenching of electronically excited NO. 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 from the H + D_2 reaction and the speed and internal state distribution of the HI product from the H + HI reaction. Femtosecond time-resolved applications include investigations of internal conversion, vibrational energy redistribution, and dissociation. 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. [6.0 FTE]

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

Farrow, R.L.; Rakestraw, D.J.
510-294-3259

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) and resonant four-wave mixing techniques for combustion measurements. 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. Current 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, thermal-grating generation, and laser saturation effects. High-resolution pulsed laser systems, in both the UV and infrared wavelength regions, are used for detailed spectral studies. The experimental results are compared to theoretical calculations, with an important goal being the development of quantitative models for routine data analysis. (Computer codes for analyzing CARS and DFWM spectra are being developed and transferred to diagnostics and combustion researchers.) Polyatomic molecules have been detected by exciting infrared transitions, an approach that should dramatically widen the class of species detectable by DFWM. [3.0 FTE]

49. Flame Chemistry: Modeling and Experiments

Miller, J.A.; Kee, R.J.
510-294-2759

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 fluorescense 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.) [4.0 FTE]

50. Combustion Research Facility (CRF) Diagnostics Research: Novel Techniques and Strategies

Trebino, R.; Gray, J.A.; Paul, P.H.
510-294-2893

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. [3.0 FTE]

Atomic Physics

Argonne National Laboratory
Argonne, IL 60439

Physics Division $1,455,000

51. Accelerator Based Atomic Physics

Berry, H.G.; Dunford, R.W.
708-252-4039

In this project, details of atomic and molecular are studied structure using several different heavy ion accelerators in the Physics Division. The ATLAS heavy-ion accelerator provides an ion beam with low energy spread which makes it an attractive facility for studying the atomic physics of highly charged ions over the entire periodic table. The program includes studies of atomic structure as well as ion-atom collisions. The atomic structure work aims at precision tests of quantum electrodynamics, relativistic quantum theory, and the electroweak theory. The experiments measure sub-nanosecond lifetimes and soft X-ray wavelengths in 2- and 3-electron ions. The work on ion-atom collisions aims at understanding the dynamics of these collisions and has applications in fusion energy research, plasma physics, and astrophysics. Another area of investigation is the study of collisions between two very heavy nuclei (combined nuclear charge >173) at energies near the Coulomb barrier . At BLASE, laser spectroscopy with a low-energy (20 to 50 keV) ion beam is used to test ab initio theory of hyperfine structures in heavy open-shell ions. Lifetime measurements are used to provide precise tests of many-body perturbation theory, relativistic Hartree-Fock calculations, and as a study of the mixing of the weak and electromagnetic interactions. The fast molecular ion-beam experiments at the Dynamitron apply Coulomb-explosion imaging (CEI) to study vibrations in small diatomic and polyatomic molecular ions. Ongoing measurements in polyatomic ions reveal new many-body dynamics in these systems, unobservable using other techniques. [5.5 FTE]

52. Synchrotron Radiation Based Atomic Physics

Berry, H.G.; Kanter, E.P.; Young, L.
708-252-4039; 708-252-9647

The research program in atomic, molecular, and optical (AMO) physics using X rays from synchrotron radiation sources continues principally through experiments at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Beam line X24A is jointly operated in collaboration with the National Institute of Science and Technology. The primary goal of the program is to increase understanding of the structure and dynamics of atoms and molecules, with an emphasis on how these properties are influenced by multi-electron correlation effects, relativity, and quantum electrodynamics. Measurements include studies of absorption structures near the K-edges of atomic gases and vapors, ion yields at the same K-edges, and coincidence experiments of ions and Auger electrons liberated in high energy photoionization of atoms, molecules, and surfaces. Design work is under way for an atomic physics station at the Argonne Advanced Photon Source (APS). An undulator beam line with a cooled crystal spectrometer is being prepared for the turn on of the APS in FY 96. The system will allow new atomic physics experiments at higher energy than the work at the NSLS and which will also be able to utilize the much higher beam fluxes of the APS. [3.0 FTE]

Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, CA 94720

Chemical Sciences Division $851,000

53. High-Energy Atomic Physics

Gould, H.A.
510-486-7777

The goals of this program are to understand atomic collisions at relativistic energies, and to search for new physics beyond the standard model using the most advanced atomic physics techniques. Recent results include the discovery of a new recombination process: capture from pair production. In this process an electron is captured by a relativistic (bare) ion when the electron is produced as part of an electron-positron pair by the motional Coulomb fields of the relativistic ion passing within atomic distances of a target nuclei. The cross section for capture from pair production increases with energy at relativistic energies, and it is predicted to be a significant mechanism for beam loss at the Relativistic Heavy-Ion Collider under construction at Brookhaven National Laboratory. Present activities include (1) extending the measurement of capture from pair production to 10 GeV/n heavy ions, (2) developing calculations of capture from pair production, (3) developing a new experiment to search for physics beyond the standard model using trapping and cooling of francium, and (4) continuing to adhere to applicable standards for environment, health, safety, and procedure in all activities. [2.0 FTE]

54. Atomic Physics

Prior, M.H.
510-486-7838

This program conducts challenging studies of the structure and interactions of atomic systems in order provide the most detailed description of their behavior and to stimulate theoretical understanding of the observed phenomena. The approach to this work emphasizes research topics that are best addressed with unique tools and expertise available at Lawrence Berkeley Laboratory (LBL). Currently the program exploits the ability of two state-of-the-art, electron cyclotron resonance (ECR) ion sources at LBL to produce intense, highly charged beams for the conduct of low-energy ($v < 1.0$ au) ion–atom collision studies. Current emphasis is on multiple electron transfer to bare, one, and two electron ions. This includes measurement of magnetic substrates populated in double electron capture, and the production of low-energy (<20 eV) continuum electrons accompanied by transfer to bound projectile states in collisions with He and more complex targets. Auger electron spectra, and photon spectra from multiply charged ion–atom collisions are used to gain insight into population mechanisms and the structure of highly excited states. The program benefits substantially from collaborative efforts with colleagues from outside LBL. [1.5 FTE]

Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

Physics Department $200,000

55. Spectroscopy and Collision Studies with Highly Charged Ions Produced by Electron Beam Ion Traps

Schneider, D.; Knapp, D.; Beiersdorfer, P.; Marrs, R.
510-422-5940

The spectroscopy and interactions of highly charged ions produced in the LLNL Electron Beam Ion Traps (EBITs) are being studied. These devices produce stationary ions up to fully stripped Uranium ($U_{9}2+$). Spectroscopy studies feature high-resolution, high-accuracy measurements of transition energies in few-electron high-Z ions. These measurements allow the determination of nonperturbative QED corrections and nuclear size effects on energy levels in high-Z systems. The three main spectroscopic projects are the measurement of n=2-2 transitions in near-helium like ions, observation of optical hyperfine splittings in hydrogenic ions, and measurement of radiative recombination energies in bare and hydrogenic ions. Studies of electron-ion interactions are focused on dielectronic recombination and electron impact ionization. The dielectronic recombination measurements are focused on n=1 resonances in high-Z systems, where quantum interference between dielectronic recombination and radiative recombination has recently been observed. The electron impact ionization studies are primarily being carried out on helium like and hydrogenic high-Z ions, probing a region in which cross sections have traditionally been extrapolated from low-Z ions. [1.0 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Physics Division $1,650,000

56. Accelerator Atomic Physics

Datz, S.; Dittner, P.F.; Krause, H.F.; Vane, C.R.
615-574-4984

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 facilities used for this research are the EN Tandem Accelerator and the Holifield Radioactive Ion Beam Facility (HRIBF). Using heavy ions of different Z but the same charge state, the Z dependence of the energy shift of the Binary Encounter peak energy have been studied. In order to determine the relative importance of electron-electron vs. electron-nucleus interactions in excitation and ionization, neutral and charged ions 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, sulfur beams at energies of 6.4 TeV are being used to study lepton pair production cross sections as a function of angle, lepton energy, and target Z. Preparations for similar experiments with 33 TeV lead beams are under way. 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^+. [4.6 FTE]

57. Collisions of Low-Energy Multiply Charged Ions

Meyer, F.W.; Havener, C.C.
615-574-4705

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 cross sections in the energy range from 0.1 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. Exploratory experimental studies of the neutralization of multicharged ions during grazing interactions with metal surface are also in progress. The current emphasis is on characterizing the energy and angular distributions of ejected electrons, and on measuring the angular and charge state distributions of scattered ions 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. [0.9 FTE]

58. *Theoretical Atomic Physics*
Strayer, M.; Shultz, D.
615-574-4590

Computational and mathematical techniques are applied to interpret interactions between atoms, ions, electrons, and photons over a wide range of energies, from a few electron to ultrarelativistic energies. Emphasis is on processes involving highly charged ions of interest in fusion plasmas, X-ray lasers, and accelerator-based atomic collision experiments. The techniques used include numerical lattice solutions of the time-dependent Schrodinger and Hartree–Fock equations by basis-spline collocation methods, Monte Carlo evaluation of Feynman diagrams, and Born expansion and distorted wave techniques. Calculations using several large codes on a massively parallel computer are done routinely. Applications have been made to processes at nonrelativistic energies such as capture and ionization, in ion–atom collisions, and multiphoton ionization by intense laser beams. Recent studies include multiphoton and collisional ionization of helium atoms, and neutralization of slow, highly charged ions near a conducting surface. Successful interpretations have been provided for recent experiments on cusp electrons and post-collision effects in ion–atom collisions. The program on relativistic collision physics is focused on phenomena important in accelerator and detector design (e.g., pair production with capture and free pair backgrounds in heavy-ion colliders). Detailed comparisons have been made of perturbative and lattice treatments of pair production with capture. [1.0 FTE]

59. *EN Tandem Operations*
Vane, C.R.
615-574-4789

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. 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, silicon through chlorine, as well as beams of many heavier ions including nickel, iodine, gold, and uranium. A VAX-11/750 CAMAC-based data acquisition system, an Elbek magnetic spectrograph with position-sensitive detectors, a high-resolution electron spectrometer, Si(Li) detectors, and a curved crystal spectrometer are available to users. Recent major beam usage has included the channeling of carbon and nitrogen ions through thin crystals, angular distribution of Auger electrons following the collision of highly charged ions with several target gases, electron spectra as a function of projectile charge state for 1-MeV/u oxygen ions colliding with Argon gas, slow highly charged carbon ions (produced using a "hammer beam" from the EN Tandem) capturing electrons in collisions with helium, and high-resolution measurements of X rays accompanying ion collisions with silicon oxide. [1.3 FTE]

Sandia National Laboratories, New Mexico
Albuquerque, NM 87185

Department of Plasma Processing Science — $126,000

60. *Atomic Processes in Reactive Plasmas*
Riley, M.E.; Hebner, G.A.
505-844-3141

Low-temperature glow discharges are commonly used for processing materials (e.g., deposition of thin films, reactive ion etching, sputtering, etc.). The goal of this project is to gain an understanding of the fundamental electron-molecule and chemical mechanisms occurring in low-temperature glow discharges. Present work concentrates on 13.56 MHz, capacitively coupled and inductively coupled discharges in helium, argon, and chlorine. Microwave interferometry, atomic absorption spectroscopy, laser-induced fluorescence, and other techniques, both intrusive and non-intrusive, are used to measure spatially resolved electron and metastable densities. Additionally, measurements of Stark splitting of the Rydberg states are used to infer spatially and temporally resolved electric field strengths in the discharge sheath regions. Results of the experimental measurements are compared with numerical simulations of the plasma. The simulations are based on hybrid fluid-Boltzmann codes. The simulations are as ab initio as possible. The helium model has been chosen to include sufficient levels and transitions as well as processes including surface scattering of ions, electrons, and metastables. All cross sections are taken from published values in the literature. The simulations have been extended to include the DC discharge case in order to benchmark the plasma results with literature results for this difficult case. The combined results of the experimental and theoretical program provide extended and new insights into the electron and heavy particle kinetics of importance to the growing suite of models for materials processing. [1.0 FTE]

Chemical Energy

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program $1,153,000

61. *Organometallic Complexes in Homogeneous Catalysis*
Angelici, R.J.
515-294-2603

The aim of this research is to provide an understanding of the details of the process in which organosulfur compounds in petroleum feedstocks are desulfurized. This hydodesulfurization (HDS) reaction is practiced on a very large scale commercially worldwide. As increasingly stringent environmental regulations require further reductions of sulfur in petroleum-based fuel, modifications of the catalytic process are required. 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 bonding 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. These results rule out other mechanisms and provide a deeper understanding of the hydrodesulfurization process. [2.1 FTE]

62. *Chemical Kinetics and Reactivity of Transition Metal Complexes*
Espenson, J.H.
515-294-5730

The general goal of this project is to understand the homogeneous chemistry that underlies catalytic processes including fuel synthesis and selective oxidation of organic compounds. The concern for the environment and efforts to reduce chemical waste have provided a strong impetus for the development and exploration of new oxidation catalysts. An example is CH_3ReO_3, an excellent catalyst for the electrophilic activation of H_2O_2 in both aqueous and nonaqueous media. Studies of catalytic oxidations of metal thiolates, thiols, bromide ions, olefins, phosphines, and other interesting reagents are being carried out. The kinetics and mechanisms of such reactions are being examined with a particular emphasis on chemical composition, structure, and reactivity of the active form of the catalyst. The second area concerns metal radicals. These 17-electron organometallic species are produced photochemically, and their reactions with a variety of substrates are being studied by laser flash photolytic techniques. The major effort in this area is now directed toward catalytic reactions yielding non-thermodynamic products, an avenue of considerable potential interest in organometallic and organic synthesis. [4.3 FTE]

63. *Fundamental Investigations of Supported Metal Catalysts*
King, T.S.
515-294-9479

Small metal particles, on the order of 1 to 10 nm, supported on high surface area materials such as alumina, are an important class of catalysts that find numerous applications in various industries and in pollution control technology. These materials are important in commercial applications and the fundamental catalytic processes occurring at the surfaces of these small clusters of metal atoms present challenging scientific problems. This program is focused on elucidating adsorption and surface reaction behavior unique to highly dispersed metal particles. In this project a combination of solid-state NMR is used with various traditional catalytic experiments. The general approach taken in this work is to systematically vary composition and structure of working catalysts and correlate this information with catalytic performance. Current research is focused on silica-supported mono and bimetallic catalysts, alkali promoted ruthenium catalysts, and zeolite supported rhodium for several reactions including selective hydrogenations and Fischer-Tropsch synthesis. The experimental approach includes characterizing adsates and populations of adsorbed species via volumetric chemisorption, ^1H nuclear magnetic resonance spectroscopy (NMR), ^{13}C NMR, and Fourier transform infrared spectroscopy; investigating dynamics of surface phenomena (e.g., adsorption/desorption and surface diffusion) by 2-D and selective excitation NMR experiments; and monitoring catalytic behavior by steady state, microreactor experiments. [1.9 FTE]

64. *New Synthetic Routes to Layered Catalytic Materials: Organometallic Precursors for Chemical Vapor Deposition*
Miller, G.J.
515-294-6063

This research project involves exploration and development of alternative synthetic strategies and characterization of new solid-state materials that have potential technological applications as catalysts or electronic devices (sensors or switches). Current efforts include (1) synthesis of low-valent organometallic compounds of the early transition metals to act as precursors in subsequent thermal decomposition studies; (2) synthesis of transition metal cluster compounds with structural elements desired in the ultimate polycrystalline or thin film products (e.g., M_3 clusters); (3) metal organic chemical vapor deposition studies of binary and ternary transition metal compounds for eventual catalytic studies; and (4) synthesis of mixed metal chalcogenides, chalcogenide halides, and tellurosilicates using these precursors. The approach involves both solution and gas phase synthesis, evaluation of thermodynamic parameters, and characterizations via X-ray diffraction, electron microscopy, Raman spectroscopy, photoelectron spectroscopy, and magnetic susceptibility. Recent studies concern novel ternary niobium and tantalum chalcogenide halides containing Nb_3 clusters, which create possibilities for tunable band gaps under similar structural and chemical features and development of transition metal tellurosilicates containing ethane-type $Si_2Te_6^{6-}$ units. The goals of this research are (1) to find sources of activated metal atoms which may overcome the thermodynamic driving forces when traditional synthetic approaches are used; (2) to examine potential catalytic, chemical, and electronic properties of the product systems; and (3) to tailor the solid-state products by appropriate choice of precursor material. [0.75 FTE]

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

Schrader, G.L.
515-294-0519

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 chemical production. A complement of experimental approaches is being used to perform kinetic measurements and comprehensive catalyst characterization. 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 at the elevated temperatures and pressures typical of industrial processes. The goal of this research program is to provide fundamental relationships between structure, composition, oxidation state, or surface properties and catalytic activity and selectivity. [2.6 FTE]

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

Trahanovsky, W.S.
515-294-2886

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. [2.0 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemical Technology Division $695,000

67. *Fluid Catalysis*

Rathke, J.W.; Chen, M.J.; Klingler, R.J.
708-252-4549

This program uses an array of in situ high-pressure spectroscopic and kinetic techniques to explore new catalytic chemistry and catalytic reaction mechanisms for the transformation of simple precursor molecules that serve as raw materials for many industrial processes. Precursors of interest include those of the C_1, chemical industry, e.g., CH_4, CO, CO_2, and CH_3OH; the ammonia synthesis precursors, N_2 and H_2; and the ceramic precursors, e.g., $(CH_3)_4Si$, $(CH_3)_3B$, and $Al_2(CH_3)_6$. Programmatic activities encompass high-pressure NMR studies of homogeneous catalytic chemistry in supercritical fluids, catalytic and stoichiometric organometallic processes associated with the production of advanced materials, and catalytic processes for the selective functionalization of methane and other hydrocarbons. Recent research includes (1) the first in situ high-pressure NMR studies of the Shell Process for the hydroformylation of olefins, (2) the development of a new technique for investigating ceramic precursor processes that uses the rf field gradient within a toroid cavity to achieve NMR microscopy at high pressures, and (3) the synthesis of some highly electrophilic and unusually reactive polyfluorophthalocyanine complexes designed to achieve the controlled activation of hydrocarbons. [4.4 FTE]

Chemistry Division $1,891,000

68. *Premium Coal Sample Program*

Vorres, K.S.
708-252-7344; 708-252-4993

This program provides basic coal research scientists with the best available coal samples. The eight carefully selected samples are now available in glass ampoules in quantities to provide for 15 or more years' requirements. The samples have been kept in as pristine a condition as possible through careful control of the conditions in all stages from sample collection through processing and packaging. The samples have been characterized through the efforts of more than 60 laboratories, and additional characterization is being carried out. The sample stability is monitored through periodic gas analysis. The number of orders exceeded 795 and over 21,000 ampoules have been shipped. A Newsletter has been issued quarterly to give new information to all recipients of the samples. A new Users Handbook for the Premium Coal Sample Program provides a description of the program, analytical information, a bibliography of over 538 articles with author, subject, journal, and coal indices, as well as a literature summary. [0.5 FTE]

69. *Characterization and Reactivity of Coals and Coal Macerals*

Winans, R.E.; Dyrkacz, G.R.; Botto, R.E.; Carrado, K.A.; Stock, L.M.
708-252-7479

This program seeks to elucidate the chemical and physical nature of the Argonne Premium Coal Samples and selected maceral constituents. In these studies, physical separations and selective chemical degradation reactions are combined with a powerful array of instrumental techniques. The instrumental approaches feature laser desorption, high-resolution and tandem mass spectrometry, solid state and nuclear magnetic resonance (NMR) imaging, and neutron and synchrotron X-ray scattering and spectroscopy. Synthetic clays are being designed for the catalysis of large, coal-derived molecules. Statistically accurate, rank-dependent models are being developed for the Argonne Premium Coal Samples. The ultimate goal is to provide fundamental information that will assist in the development of advanced processes for coal utilization. [9.6 FTE]

Brookhaven National Laboratory
Upton, L.I., NY 11973

Department of Applied Science **$420,000**

70. *Metal Hydrides*

Reilly, J.J.; Johnson, J.R.
516-282-4502

Knowledge of the behavior and properties of hydrogen-metal systems is essential for the successful implementation of many energy related processes and applications. A prime concern of this program is to increase that store of knowledge through the determination of thermodynamic, kinetic, and structural parameters of their systems and to relate all pertinent data and hypotheses in order to develop a predictive capability regarding the behavior of any given system. This capability permits the synthesis of compounds having optimum properties for particular applications. Current areas of research, all of which involve collaborations with others and technology transfer activities, are kinetics of the formation and decomposition of hydride phases, electrochemical characterization of metal - hydrogen systems, the preparation of improved metal hydride electrodes for batteries, and the preparation and characterization of a new class of hydrogen bronzes prepared from complex oxides. The major experimental tools and/or techniques are equilibrium pressure - temperature - composition measurements, X-ray diffraction, electrochemical measurements, and the use of high pressure apparatus to study the kinetic behavior of metal hydride suspensions. [2.1 FTE]

Chemistry Department **$1,838,000**

71. *Structure and Reactivity in Catalysis and Advanced Materials*

Koetzle, T.F.; McMullan, R.K.; Andrews, M.A.; Bullock, R.M.; Hrbek, J.; Rodriquez, J.A.
516-282-4384

This program probes fundamental aspects of chemical catalysis from a multi-faceted perspective which includes homogeneous and heterogeneous catalytic systems, as well as investigations of advanced materials. Brookhaven National Laboratory's (BNL's) High Flux Beam Reactor (HFBR) and National Synchrotron Light Source (NSLS) play a key role in much of this research, often via collaborative efforts with scientists from other institutions. A central theme of the experimental work in homogeneous catalysis is the examination of transition-metal hydride complexes, which are of central importance in many catalytic processes. Neutron diffraction studies at the HFBR provide uniquely accurate structural data for these compounds that can then be correlated with their chemical reactivity. The reactivity studies are designed to elucidate the factors that determine the rates and mechanisms for cleavage of M–H bonds and their concurrent reactions with unsaturated organic substrates. The high selectivity of homogeneous catalysts is also being exploited to develop novel aspects of organometallic carbohydrate chemistry, including those that may ultimately lead to new approaches to the utilization of biomass organics. Heterogeneous catalysis studies that correlate structure with reactivity are also being undertaken. The structures of adsorbates on metal surfaces are being determined by a variety of methods including X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) at the NSLS, while their corresponding catalytic reactions are examined by ultra-high vacuum surface science techniques, infrared spectroscopy, and high-pressure kinetics. Emphasis is placed on understanding the effects of catalyst promoters and poisons at a molecular level, and on understanding the distinctive catalytic behaviors of bimetallic surfaces that may serve as models for industrial bimetallic catalysts. In the area of advanced materials, collaborative structural studies utilize both the HFBR and the NSLS to investigate a variety of systems including zeolites, buckminsterfullerene, biomaterials, and dielectrics. These investigations, which include novel *in situ* real-time studies of crystallization kinetics at the NSLS, are providing a foundation for understanding the special characteristics of these materials. [14.2 FTE]

Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, CA 94720

Chemical Sciences Division **$1,058,000**

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

Bartlett, N.
510-642-7259

The aim of this project is the synthesis and characterization of new materials that may have utility in efficient storage or usage of energy. The novel materials include 2-D networks of light π-bonding atoms (boron, carbon, and nitrogen) with structures akin to graphite. Of these, the more metallic have possible applications as electrode materials for high-energy-density batteries, and those that are semiconducting could be useful in converting light to electrical energy. Good ionic conductors are also being sought, with emphasis on lithium-ion and fluoride-ion conductors, because batteries based on lithium and fluorine would be unsurpassed in their energy-density features. In addition, new fluorides are being synthesized, some of which are thermodynamically unstable, and yield elemental fluorine with mild activation. Because the metal and fluorine atoms in these fluorides are of comparable electronegativity, they can be electronic conductors and, in some cases, even superconductors. Cationic fluorides high-oxidation-state metals promise to be oxidizers of extraordinary power. These in solution, in anhydrous hydrogen fluoride, should be efficient oxidative fluorinators, usable even below room temperature. [2.1 FTE]

73. *Catalytic Hydrogenation of Carbon Monoxide*

Bell, A.T.
510-486-7095

The purpose of this program is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide (or carbon dioxide) and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors that limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition–structure and performance. Investigations of methanol synthesis over copper have revealed that carbon dioxide undergoes hydrogenation to methanol much more readily than carbon monoxide. The pathway from carbon dioxide to methanol is found to proceed via the formation of formate, methylenebis(oxy), and methoxy species, all of which have been observed in situ by IR spectroscopy. The dynamics of elementary processes involved in the synthesis of normal olefins and alkanes over ruthenium have been studied using isotopic tracer techniques. A new mechanistic model has been proposed to interpret these results, which includes steps for the readsorption of olefins from a physisorbed layer and depolymerization of readsorbed ethylene. Rate coefficients for chain initiation, propagation, and termination, as well as ethylene depolymerization, have been determined from simulations of experimental data. [2.5 FTE]

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

Bergman, R.G.
510-642-2156

The goal of this project is the development of new chemical reactions in which transition metals interact with organic materials, and the understanding of how these reactions work and can be applied to the development of new potentially useful chemical transformations. Several years ago a major discovery on this project was that of the first alkane–transition-metal C–H oxidative addition reactions (C–H activation). Subsequent work has been directed at examining the scope and mechanism of the C–H activation reaction and working toward utilizing it 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) substitution of indenyl for pentamethylcyclopentadienyl ligands to facilitate migratory insertion reactions in the products of C–H oxidative addition reactions; (4) exploratory studies on the extension of C–H activation methods to C–F activation; and (5) 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. [5.0 FTE]

75. *Potentially Catalytic and Conducting Polyorganometallics*

Vollhardt, K.P.C.
510-642-0286

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. While much is known about how such clusters are assembled and disassembled, their chemistry is largely unpredictable and/or uncontrollable, and the compounds made present an opportunity to solve these problems. Recent advances include (1) the synthesis of various isomers or quatercyclopentadienyltetrametals and their redox chemistry along the tetrametallic chain, (2) the elucidation of the intricate dual mechanistic pathways by which a methyl to a carbonyl bond is formed in a dinuclear system exposed to either incident radiation or heat, (3) the synthesis of extended π-substituted metallocenes as building stones for supramolecular aggregates, and (4) theoretical and synthetic studies aimed at understanding and preparing "semibuckministerfullerence", a molecule that should allow the exploration of the endohedral chemistry of "buckyball" C_{60}. [2.7 FTE]

Los Alamos National Laboratory
University of California
Los Alamos, NM 87545

Isotope and Nuclear Chemistry Division — $376,000

76. *Transition Metal-Mediated Reactions of SO_2, H_2, and Other Small Molecules*

Kubas, G.J.; Burns, C.J.
505-667-5846

Studies of the binding and chemical conversions of environmentally and energy-related small molecules, e.g. SO_2, NO, and H_2, by transition metal complexes is the main goal of the program. Of major importance is delineating the reactivity patterns and ancillary ligand electronic effects of a wide variety of molecules on the 16-electron Group 6 complexes, $M(CO)_3(PR_3)_2$ and $Mo(CO)(diphosphine)_2$, as well as new systems such as $TcCl(diphosphine)_2$. Remarkably, these highly reactive species have now shown four different types of binding/reactivity at the same metal center site: 1, classical ligand binding, 2, nonclassical binding of H_2, 3, oxidative addition, and 4, free radical formation. Type 4 was recently found on reaction of $W(CO)_3(PR_3)_2$ with I_2 to give novel 17-electron $WI(CO)_3(PR_3)_2$, while type 3 occurs with H_2S but not H_2O, demonstrating the delicate electronic balance here. The ligand environments of these complexes will be fine-tuned to define the boundaries of the above reactivities, allowing further understanding of, for example, the reaction coordinate for H_2 cleavage on metals. The development of a catalyst for the conversion of acid-rain causing NO_x pollutants to benign species. Since SO_2 and NO are electronically similar, it is likely that NO can be catalytically reduced on the same molybdenum sulfide complexes (e.g., $Cp_2Mo_2S_4$) that disproportionate SO_2 and catalyze hydrogenation of SO_2. [1.4 FTE]

National Renewable Energy Laboratory
Golden, CO 80401

Basic Sciences Division $396,000

77. *Basic Research in Synthesis and Catalysis*

DuBois, D.L.; Curtis, C.J.
303-231-7371

The major objectives of research carried out by the Synthesis and Catalysis task are to develop new catalysts for electrochemical reduction of CO_2 and CO and new organometallic precursors for the synthesis of small semiconductor particles. $[Pd(triphosphine)(solvent)](BF_4)_2$ complexes have been shown to catalyze the electrochemical reduction of CO_2 to CO with high rates and selectivity. Mechanistic studies and structure-activity relationships are being used to improve the performance of these catalysts. Stoichiometric reduction of coordinated CO to a hydroxymethyl ligand with electrochemically generated metal hydride complexes has also been demonstrated. The overall process represents a conversion of CO_2 to coordinated hydroxymethyl. Current research is attempting to incorporate both proton reduction and CO activation capabilities in the same molecule and to achieve multi-electron reduction of CO_2 and CO at a single site. The second project involves the synthesis of new organometallic complexes and their evaluation as precursors for the production of small semiconductor particles and particle structures in solution. Correlations of precursor structure and reactivity with the quality of the material produced are being used to guide modification of the precursors to give better materials. [2.6 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemical Technology Division $530,000

78. *Kinetics of Enzyme-Catalyzed Processes*

Greenbaum, E.; Woodward, J.
615-574-6835

Isolated photosystem I (PSI) reaction center/core antenna complexes (PSI-40) were platinized by reduction of [PtCl6]2- at 20 °C and neutral pH. The presence of metallic platinum on PSI complexes was detected by its effect of actinic shading and electrostatic shielding on P700 photooxidation and P700′ reduction, in addition to direct visualization of the platinized PSI particles with scanning tunneling microscopy. The reaction centers (P700) in both platinized and non-platinized PSI-40 were photooxidized by light and reduced by ascorbate repeatedly, although with somewhat slower rates in platinized PSI due to the presence of platinum. The effect of platinization on the excitation transfer and trapping dynamics was examined by measuring picosecond fluorescence decay kinetics in PSI-40. The fluorescence decay kinetics in both platinized and control samples can be described as a sum of three exponential components. The dominant (amplitude 0.98) and photochemically limited excitation lifetime remained the same (16ps) before and after platinization. The excitation transfer and trapping in platinized PSI-40 was essentially as efficient as that in the control (without platinization) PSI. Also, studies were continued on the role of the cellulose-binding domain on the major cellulase enzyme components in cellulose hydrolysis. The kinetics of the cellulose-binding domain's ability to adsorb on tomicrocrystalline cellulose (Avicel) and its effects on the surface structure of the cellulose fibers were studied. The catalytic domain of *Trichoderma reesei* cellobiohydrolase I was rendered inactive by modification with a water-soluble carbodiimide. [4.0 FTE]

Chemical and Analytical Sciences Division $2,763,000

79. *Organic Chemistry and the Chemistry of Fossil Fuels*

Buchanan, A.C.; Britt, P.F.; Hagaman, E.W.
615-576-2168

The program objective is to conduct fundamental research that reveals new insights into the organic chemical structure and reactivity of coal. Solid-state NMR methods are being developed to obtain structure/reactivity information in chemically modified coals. NMR techniques under investigation include high resolution solid-state ^{19}F-NMR, and ^{13}C-NMR methods that utilize the ^{13}C-^{19}F dipolar interaction in ^{19}F-labeled organic molecules, polymers, and coals to reveal information on local structure. Fluorination chemistry under investigation includes conversion of carboxylic acids into acyl fluorides in low rank coals using diethylaminosulfur trifluoride and sulfur tetrafluoride, and fluorination of chemically generated carbanion sites in bituminous coals with N-Fluorobenzenesulfonimide. Reaction mechanisms that underpin thermal and catalyzed reactions of coal are being explored through the use of model compounds that represent organic structural features present in the coal macromolecule. Silica-immobilized compounds are employed to study the impact of restricted mass transport on free-radical reaction pathways. Current investigations focus on hydrogen transfer mechanisms in diffusionally constrained environments, and on retrogressive reaction pathways for silica-immobilized diphenylalkanes, phenethyl phenyl ethers, and phenyl benzyl sulfide. Polymers containing carboxylic acids are being prepared for investigation of reaction pathways associated with low temperature crosslinking events observed in the pyrolysis of low rank coals. Silica-immobilized organosulfur compounds are under investigation as calibrants for temperature programmed reduction studies of sulfur species in coals. This research will contribute to the scientific foundations required for the commercial development of novel processes for the conversion of coal into chemicals or fuels in an environmentally acceptable manner. [5.5 FTE]

80. *Basic Aqueous Chemistry to High Temperatures and Pressures*

Mesmer, R.E.; Holmes, H.F.; Palmer, D.A.; Simonson, J.M.; Ho, P.C.
615-574-4958

The goal of this research is the experimental study of aqueous solution chemistry of broad classes of solutes at high temperatures and pressures to establish basic principles governing thermodynamic properties of electrolytes and of chemical equilibria. The advancement of experimental methods and new models for representation and prediction of behavior over wide extremes of temperature and pressure is an important part of the program. A number of complementary techniques is developed and used up to and beyond the critical temperature of water and its solutions. Current research uses are flow calorimetry, densimetry, isopiestic apparatus, electrochemical cells, electrical conductance apparatus, vapor-liquid partitioning cells, and Raman spectroscopy. Chemical equilibria under study are ionization association, metal complexation, metal ion hydrolysis, solubilities, volatilities, and oxidation-reduction reactions. Reaction thermodynamic quantities, excess properties of electrolytes, and kinetic parameters 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. Computer simulations to relate macroscopic observations to microscopic quantities are being initiated. Results impact strongly the scientific communities in basic solution chemistry and hydrothermal geochemistry, steam generator technology, geothermal technology, environmental chemistry, and nuclear and hazardous waste disposal. [3.1 FTE]

81. *Heterogeneous Catalysis Related to Energy Systems*

Overbury, S.H.; Huntley, D.R.; Mullins, D.R.; Grimm, F.A.
615-574-5040

The objective of this program is to achieve a better understanding of how reactions occur on metal substrates, how surface reactivity is affected by structure, and how reactive species alter the structure and reactivity of the substrate. Major emphasis is placed upon the surface chemistry of organosulfur compounds, which is relevant to understanding many industrially and environmentally important catalytic processes. Substrates of interest are single crystals and films of metals found in hydrodesulfurization catalysts including Ni, W, and Ru. Reaction species include alkyl thiols, aryl thiols, thiophenes, and bi-functional molecules such as mercaptoethanol and hydrocarbon compounds related to these species. Since chemisorbed atomic S, C, and O are products of these reactions, their effects on reaction pathways are also of interest. The effects of metallic and non-metallic atomic adsorbates on the structure of the substrate is examined as well as their bonding geometry on the substrates. Kinetic parameters and mechanisms of reactions are determined by monitoring formation rates both of desorption products (detected by mass spectrometry) and of surface species (detected by electron energy loss and soft X-ray photoelectron spectroscopy). Structure of the adsorbate/substrate is determined by ion scattering and electron diffraction. Molecular orbital calculations and ion scattering simulations are performed as an aid in interpretation of experimental results. [3.5 FTE]

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

Sigman, M.E.; Dabestani, R.T.
615-576-2173

This research program constitutes a fundamental investigation into the influence of local chemical environment on the photochemical degradation of hazardous organics. Studies focus on photochemical events at interfaces, both solid/liquid and solid/gas, and on the aqueous photochemistry of hazardous organics. Current emphasis is on the photochemistry of aromatic hydrocarbons (ArH) and polynuclear aromatic hydrocarbons (PAHs). Product analysis and in situ spectroscopic techniques are the primary methods used in these investigations. This research is concerned with determining photochemical reaction mechanisms at interfaces and in aqueous solutions with an emphasis on elucidating contributions from electron transfer and singlet molecular oxygen pathways. Work in this laboratory has demonstrated the dramatic effect which a highly polar surface, such as that of SiO_2, can have on the photochemistry of weakly interacting organics, as typified by unsubstituted ArHs and PAHs. The studies of the mechanistic aqueous photochemistry of ArHs and PAHs, an area which has been virtually ignored in the past, have demonstrated the significant role of hydrophobic effect in controlling the observed photochemical behavior of these materials. Results from these studies will enhance the basic understanding of photochemical processes occurring in aqueous solutions and at industrially and environmentally important interfaces. Among other benefits to be derived from this research is a better understanding of those factors which control the environmental fate and residence times of anthropogenic materials which are generated through the production and consumption of fossil fuels. [2.2 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $664,000

83. *Free-Radical Chemistry of Coal*

Franz, J.A.; Alnajjar, M.S.; Autrey, T.; Linehan, J.C.
509-375-2967

This project studies properties of transient intermediates related to high temperature thermolytic conversion of hydrocarbon resources to fuels and chemicals. Thermodynamic properties of organic and organometallic free radicals, mechanisms of hydrogen transfer, molecular rearrangements and hydrocracking are examined using experimental kinetic, photoacoustic, and electrochemical calorimetric methods. Semi-empirical and ab initio computational approaches, including advanced post-SCF methods for open-shell molecules, are being applied to characterize energetics and potential surfaces of hydrogen transfer and molecular rearrangement reactions. The project is also involved in developing and applying solid state NMR techniques for characterization of carbon and heteroatom-containing structures in coal and related materials, and use of NMR methods for measurement of bond distances and enhanced structural resolution in heterogeneous materials and particle surfaces. [3.7 FTE]

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program **$1,111,000**

84. *Analytical Separations and Chemical Analysis*
Fritz, J.S.
515-294-5987

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. New resins and techniques are developed for solid-phase extraction and for chromatographic separations. Resins of small particle size are incorporated into membranes in order to obtain rapid mass transfer. Chelating reagents and resins are prepared and used for isolation of selected metal ions from aqueous solutions. [2.1 FTE]

85. *Analytical Spectroscopy*
Houk, R.S.
515-294-9462

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. [4.5 FTE]

86. *Chemical Analysis at Liquid-Solid Interfaces*
Porter, M.D.
515-294-6433

This project examines new avenues for the design, construction, and characterization of monomolecular films at liquid-solid interfaces. Efforts focus on (1) developing atomic-scale descriptions of the lateral packing of spontaneously adsorbed monomolecular films formed from alkanethiols at gold, silver, and copper surfaces; (2) probing solvent-monolayer interactions at such interfaces with in situ infrared reflection and Raman spectroscopies; and (3) examining the fabrication for molecular recognition monomolecular films formed from organosulfur derivatized cyclodextrins. The atomic-scale arrangements are probed by scanning tunneling, atomic force, and lateral microscopy. The molecular level descriptions are derived primarily from infrared reflection and Raman spectroscopies, optical ellipsometry, electrochemistry, and contact angle studies. The aim 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). The molecular recognition effort examines the incorporation of size selective channels in long alkyl chain monolayers as well as the synthesis and fabrication of organosulfur-derivatized cyclodextrin monolayers. [2.2 FTE]

87. *Lasers in Analytical Chemistry*
Yeung, E.S.
515-294-8062

The cental theme of this project is the identification, evaluation, and application of analytical concepts based on the most recent developments in spectroscopy, particularly laser technology. Solutions to a large number of chemical problems, especially those in environmental, clinical, and energy-related areas, are currently limited by the available analytical methodology. Attempts will be made to remove limitations by developing new techniques for measurements, by providing novel instrumentation, and by gaining an in-depth understanding of the fundamental physical and chemical principles behind the measurements. Specific studies include (1) atomic spectroscopy, particularly 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 biomolecules deposited or absorbed on surfaces of materials, for example by laser desorption; and (4) real-time spectroscopic probes of laser-initiated gas phase reactions relevant to photochemical vapor deposition and etching schemes. [4.7 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division **$1,039,000**

88. *Separations Science Related to Nuclear and Hydrometallurgical Technology*
Horwitz, E.P.; Gatrone, R.C.; Dietz, M.L.; Nash, K.L.
708-252-3653

The objectives of this program are (1) to develop new and improved reagents that may be applied to help solve major problems in environmental management and (2) 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 the physical properties of extractant systems; (2) the study of how small changes in the conformation of macrocyclic polyethers affect metal complex stability and macrocycle selectivity; (3) the design, synthesis, and characterization of new classes of macrocyclic compounds that show significantly improved selectivity for monovalent cations; and (4) the design, synthesis, and characterization of new classes of aqueous soluble nonphosphorus complexing agents that are capable of forming stable complexes with actinides in highly acidic media but will readily decompose under mild thermal oxidizing conditions to form environmentally acceptable species. All four objectives are directed towards application in nuclear technology, such as actinide separations, waste processing, by-product recovery from nuclear waste, and hydrometallurgical processing. [3.5 FTE]

Brookhaven National Laboratory
Upton, L.I., NY 11973

Department of Applied Science **$500,000**

89. *Structure and Function in Electrochemistry*

Adzic, R.
516-282-4522

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. Besides insights into fundamental surface electrochemistry and electrocatalysis, the results will have potential applicability in electrochemical energy conversion, electroorganic synthesis and electrochemical sensors. X-ray scattering (utilizing the National Synchrotron Light Source), scanning tunnelling microscopy, (non-enhanced) Raman scattering, and Fourier transform infrared spectroscopy will be the primary in situ probes. Specific studies will focus on establishing the correlation between the surface structure and electrocatalytic activity by in situ determination of the surface and foreign adatom structures, geometry of active sites, and identification of adsorbed intermediates; examining the reconstruction of stepped surfaces of gold and platinum; and exploring the new catalysts for methanol oxidation based on the platinum–metal oxide systems. Structures and electrosorption valencies have been determined for several metal and anion adsorbates on Au, Pt, and Ag single crystal electrode surfaces and the structure of the active sites for O_2 reduction has been determined for Au(111) and Au(100) modified by Tl adatoms. [1.3 FTE]

90. *Microparticle Analysis by Laser Spectroscopy*

Tang, I.N.; Fung, K.H.
516-282-4517

Many areas of scientific research and technological development pertaining to DOE's missions demand chemical characterization of aerosol particles so minute in size that conventional methods for bulk analysis are simply not applicable. This program focuses specifically on basic understanding and novel application of laser-based spectroscopic methods for *in situ* characterization of such suspended microparticles. During the past year, progress has been made in establishing the ultimate sensitivities that various Raman processes may achieve on microparticles. It is concluded that, while spontaneous Raman emission gives a sensitive detection limit in picograms, stimulated Raman emission, being a highly nonlinear process, is rather limited in its use in quantitative analysis. The single particle levitation technique, in conjunction with appropriate 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 ionic association and solute phase transformation at high concentrations otherwise unattainable in bulk solutions. Thus, the very existence of *new* solid metastable states in microparticles, but never in the bulk phase, has been discovered. This research will not only lead to a discovery and elucidation of heretofore unknown properties unique to microparticles, but also will provide the science and technology basis for advanced analytical instrumentation. [1.4 FTE]

Idaho National Engineering Laboratory
Idaho Falls, ID 83415

$306,000

91. *Negative Ionization Mass Spectrometry*

Delmore, J.E.; Appelhans, A.D.; Dahl, D.A.
208-526-2820

The elucidation of mechanisms for the formation of gas phase ions from high temperature inorganic matrices is the main thrust of this program. A tube ion source was 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 either be mounted in a mass spectrometer to analyze the emitted ions or imaged in the newly constructed ion source imaging instrument, or exchanged between the two. Gases can be diffused through the material in the tube so that high temperature gas/solid reactions can be studied in the mass spectrometer. The imaging studies have demonstrated that for the ion emitters studied to date the ions originate directly from the surfaces of the inorganic matrices and not from the refractory metal supports. This work indicates that the emitters are little chemical factories that produce the species needed for ion production, and in many cases preform the ion. This leads to methods for custom designing new emitters. New theories describing ion emission are currently being formulated to deal with these experimental findings. High temperature re-dox chemistry to pre-form the ion of interest is proving to be important in oxide based emitters. The most recent research involves cation and anion emission from liquid glass ion sources, and again re-dox is proving to play an important role. The next experimental thrust will utilize a pulsed ion source for determining the extent to which preformed ions are sufficiently stable to be stored on a surface by electrostatic repulsion, followed by electrostatic extraction. A major enhancement of ion current during the extraction cycle will demonstrate the role of pre-formed ions. To help develop a more complete understanding of the processes it is necessary to be able to model the motion of ions in electric and magnetic fields. A physical properties of extractant systems; (2) the study of how small changes in the conformation of macrocyclic polyethers affect metal complex stability and macrocycle selectivity; (3) the design, synthesis, and characterization of new classes of macrocyclic compounds that show significantly improved selectivity for monovalent cations; and (4) the design, synthesis, and characterization of new classes of aqueous soluble nonphosphorus complexing agents that are capable of forming stable complexes with actinides in highly acidic media but will readily decompose under mild thermal oxidizing conditions to form environmentally acceptable species. All four objectives are directed towards application in nuclear technology, such as actinide separations, waste processing, by-product recovery from nuclear waste, and hydrometallurgical processing. [3.5 FTE]

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Lawrence Berkeley Laboratory University of California, Berkeley Berkeley, CA 94720

Energy and Environment Division $208,000

92. *Repetitively Pulsed Laser/Material Interaction*
Russo, R.E.
510-486-4258

The repetitively pulsed laser material interaction is studied as a powerful approach for chemical separations and analysis. A pulsed, high-powered laser beam simply blasts constituent elements from any sample material into the vapor phase, which is analyzed by classical spectroscopic techniques. However, the explosive interaction is not fundamentally or experimentally defined for general application. The primary emphasis of the research is to understand the fundamental nature of the laser material interaction for chemical analysis. However, this knowledge base is also valuable in numerous other disciplines, including environmental, materials, medicine, and nonproliferation. The program has explored several real time analytical technologies for studying this interaction, including monitoring the ablated species using an inductively coupled plasma with a photodiode array spectrometer, monitoring the emission spectra from the laser induced surface plasma, and monitoring the acoustic energy in the target. Correlation of data from these techniques has provided important new information. An important result is that at a particular laser power density, the efficiency of energy coupling to the target declines. These data indicate that the laser energy becomes absorbed by the high electron-density plasma created by the laser at the surface. At this power level, the induced surface plasma heats and evaporates the sample material, a detrimental condition for chemical analysis. [1.7 FTE]

Oak Ridge National Laboratory Oak Ridge, TN 37831

Chemical Technology Division $1,303,000

93. *Chemical and Physical Principles in Multiphase Separations*
Byers, C.H.; Basaran, O.A.
615-574-4653

Electromagnetic fields can enhance drastically rates of transport of momentum, heat, and mass in fluids and thereby offer unparalleled opportunities for improving the efficiency of a wide variety of separation processes. Thus the main goal of this research is to explore by means of fundamental experimental, theoretical, and computational studies the effectiveness of electromagnetic fields in enhancing the efficiency of multiphase separations processes. The primary focus of the program is to develop a fundamental understanding of the effects of electric fields on liquid drops–a topic of great interest in diverse areas of science and technology–with the ultimate goal of using that understanding in devising novel means to dramatically improve transport rates in liquid-liquid systems. Hence, the first and dominant part of the program addresses such issues as (1) equilibria, shapes, and stability of drops, (2) free and forced oscillations of freely floating and supported drops, (3) fluid mechanics of drop formation, (4) breakup and atomization of drops, and (5) interaction and coalescence of multiple drops. A second developing thrust entails an exploratory study of the use of electric fields in enhancing liquid-vapor operations. This part of the program addresses such fundamental issues as (i) effects of external electric fields on bubbles, (ii) formation of bubbles in an ambient flow field, and (iii) free surface flows of multiphase fluids over complicated solid boundaries. Other externally applied force fields, e.g., due to rotation or acoustic fields, are sometimes used to aid the study or to enhance the effectiveness of externally applied electromagnetic fields on drops and bubbles. In addition to multiphase separations, the above-cited two thrusts have ramifications in areas of science and technology that range from cloud physics to ferrohydrodynamics to electrospraying of liquids. [2.8 FTE]

94. *Interactions of Solutes, Solvents, and Surfaces: Adsorption and Supercritical Extraction*
Cochran, H.D.
615-574-6821

Fundamental theoretical and experimental studies are aimed at understanding the striking properties of supercritical solutions in terms of the underlying fluid microstructure and molecular interactions. These solutions are important in novel separation technologies such as supercritical extraction and supercritical fluid chromatography and in other technologies as well. Codes are under development to perform a number of important types of molecular simulation calculations on massively parallel supercomputers, including studies of solutions in supercritical water and studies of interactions of supercritical fluids with polymers. These codes will enable study of questions previously beyond reach because of limited computational power. Small-angle and wide-angle neutron scattering studies of supercritical solutions of the noble gases have continued; reduced background of the instrument is an important indicator for success in these experiments. Applicability of the generalized quartic equation of state has been successfully broadened to include both polar and nonpolar fluids; critical temperature, critical volume, acentric factor, and dipole moment are the four fluid parameters required. This equation offers improved accuracy without qualitative increase in computational complexity compared with existing equations. Complementary applied programs are performed to support U.S. industry in areas such as hazardous waste processing, food processing technology, textile manufacturing, and petroleum production. [0.5 FTE]

95. *Chemistry of Actinides and Fission Products*

Toth, L.M.; Hunt, R.D.
615-574-5021

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). [1.5 FTE]

Chemical and Analytical Sciences Division $1,904,000

96. *Research Development and Demonstration of Advanced Chemical Measurement Techniques*

Ramsey, J.M.; Barnes, M.D.; Shaw, R.W.; Whitten, W.B.; Young, J.P.
615-574-5662

New laser-based chemical analysis techniques are the goal of this research project. State-of-the-art laser technology is applied to improve measurement sensitivity and/or specificity. Ultrasensitive fluorescence detection, resonance ionization initiated mass spectrometric methods, and nonlinear optics have been emphasized. Target application areas include biotechnology, environmental sciences, and materials processing and science. The ability to detect single molecules in droplets has been used to explore cavity quantum electrodynamic effects, including emission lifetime and quantum yield modification; the latter translates into even further detection sensitivity. Experiments are in progress to extend a single molecule detection method to the large family of nonemissive molecules via the use of labeled antibodies. A regeneratively amplified tunable laser system has been devised. With this system, ultrashort pulse (picosecond and femtosecond) near infrared and infrared spectroscopy becomes possible. Probing of surfaces and interfaces by nonlinear optical vibrational spectroscopy is the initial application of this unique system. Gas phase and surface spectroscopies have been utilized to understand chemical vapor deposition syntheses of thin films by spatial identification of process intermediates. The utility of practical semiconductor diode lasers has been investigated for isotopically selective resonance ionization mass spectrometry. [2.5 FTE]

97. *Mass Spectrometric R & D for Inorganic Analyses*

Smith, D.H.; Barshick, C.M.; Duckworth, D.C.; Riciputi, L.R.
615-574-2449

The generic goal of this FWP is to advance the state of the art in inorganic mass spectrometry. Both applied and fundamental issues are addressed. A continuing concern is to improve analytical methods with respect to sensitivity, accuracy, precision, and simplicity. Extending the field into areas previously closed to it is a constant goal. The measurement of isotopic ratios and their application to problems of concern to DOE is a long-standing interest. Much of the present effort is directed toward expanding, refining, and through studies of the fundamental processes, obtaining a better understanding of glow discharge mass spectrometry. An investigation of species unique to glow discharges (e.g., metal argides) has been initiated. The first efforts will be directed toward completing the thermodynamic cycle for species important in the glow discharge process. [1.5 FTE]

98. *R & D in Secondary Ion Mass Spectrometry*

Todd, P.J.; McMahon, J.M.; Short, R.T.
615-574-6824

The objective of this work is to cross barriers that limit the analytical applicability of secondary ion mass spectrometry (SIMS). This is mainly accomplished by first understanding the fundamental cause of the barrier, and the circumventing of it by instrumental or chemical development. For example, correlation for ion kinetic energy distribution for time-of-flight SIMS has been limited to the flight tube of the analyzer. In order to achieve high mass resolution for these instruments, ion sources are made very small and high acceleration voltages are used. Researchers developed a method of correcting for ion kinetic energy distributions in both the ion source and flight tube, thereby removing the severe restrictions on ion source design. As another sample, SIMS has met with limited success for analysis of insulators. By coordination of primary ion and electron flood gun currents with secondary ion source potentials, a compensation scheme has been developed that is generally applicable to imaging by SIMS microprobe of samples as large as 1 cm in diameter. Current research centers around extending charge compensation schemes, developing chemical preparation methods to enhance secondary ion emission from organic samples, and studying chemical damage to organic and inorganic samples by primary ions. Collaborative studies where SIMS is used for analysis are also conducted, and include geochemistry, materials science, biomedicine, and the Human Genome project. [2.2 FTE]

99. *Mass Spectrometry R & D for Organic Analysis*

VanBerkel, G.J.; Goeringer, D.E.; McLuckey, S.A.; Ramsey, R.A.
615-574-1992

The objective of this research program is to enhance organic mass spectrometry as an analytical tool via improved undertaking of the underlying chemical and physical processes involved. A remarkably wide 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 can occur as well as the wide variety of processes associated with ionization. Ionization by glow discharge, positron annihilation, laser irradiation, and electrospray are of primary interest in this program. Attention is currently heavily focused on reactions associated with electrospray ionization and with the combination of electrochemistry with electrospray. The behavior of gaseous ions under a wide variety of conditions has also been a longstanding interest. Research is presently concentrated on the behavior of gaseous ions in the quadruple ion trap operated with a relatively high buffer gas pressure. The goal of this work is to determine the extent to which ion internal and kinetic energies can be defined so as to improve the ion trap as a tool for deriving fundamental information from gaseous ions. This information includes structure, reactivity, and energetics. Current efforts include modelling the collisional activation process as well as the kinetics of decomposition. Experimental measurements allow for refinement of the models which may then become powerful predictive tools. The results of these efforts should enhance both the analytical figures of merit of the ion trap as a mass spectrometer as well as its ability to provide high quality structural and energetic information. [1.6 FTE]

Chemistry Division $911,000

100. *Chemical and Structural Principles in Solvent Extraction*

Moyer, B.A.; Sachleben, R.A.; Bonneson, P.V.
615-574-6718

Crown ethers, lariat ethers, and related compounds synthesized and studied in this program effect highly selective separations of metal ions from aqueous solution. These metal-specific ligands are being examined to elucidate the principles of thermodynamics and structure that govern chemical recognition in liquid-liquid extraction processes. Questions being addressed entail the influence of preorganization, metal-ligand complementarity, lipophilicity, inductive effects, and steric factors on extraction selectivity and behavior. Neutral and ionizable functionalities have been combined in single macrocyclic molecules as represented by the class of ionizable dibenzo-14-crown-4 lariat ethers, selective extractants for small alkali metal cations. Alternatively, neutral macrocycles are used alone or in synergistic combination with cation-exchange extractants to achieve novel systems for selective separation of alkali, alkaline-earth, and transition metals. In particular, systems selective for lithium, sodium, cesium, manganese, and copper cation have been elucidated. Structural aspects are probed extensively by the methods of X-ray structure determination of crystalline model compounds, molecular mechanics, and spectroscopy (e.g., FTIR, NMR, and UV/vis). Thermodynamic aspects are probed by distribution measurements, titration calorimetry, potentiometry, and other physical measurements. Multiequilibrium modeling techniques employing the program SXLSQA aid interpretation of extraction results. [3.3 FTE]

Chemistry and Analytical Science Division

101. *Advanced Spectroscopic Methods for Chemical Analysis*

Hulett, L.D., Jr.; Dale, J.M.
615-574-8955

The present program makes use of positrons for studies of gases and solids. Both experimental and theoretical work has been done on the ionization of organic molecules. Positrons with energies above thresholds of 2-3 eV extract electrons from the molecules to form positronium, leaving ions with minimal degrees of fragmentation. Positrons with energies below the 2-3 eV positronium formation threshold will also produce ions, but for certain molecules extensive fragmentation occurs. These effects have been studied as functions of molecular structure and bond type. Measurements of optical fluorescence, induced from solids by positron impact, have begun. Equipment for the studies of Auger electron spectra, induced by slow positrons has been put under construction. Defect structures in iron-aluminum alloys have been studied by means of positron lifetime spectroscopy. An industrial application of positron spectroscopy to weathering assays of protective polymer coatings, funded through a small CRADA, has been a byproduct of this FWP. More spinoff of this type is expected. Future work will be directed toward inorganic and polymer solids, applying knowledge gained from the molecular studies. Collaborations involve the ORNL Health and Safety Research Division, Vanderbilt University, the University of Texas at Arlington, Bell Laboratories, Brookhaven National Laboratory, and the Masonite Corporation. [1.1 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $878,000

102. *Sources in Analytical Spectrometry*

Gordon, R.L.; Styris, D.L.
509-376-2540

This research facilitates the direct analysis of solid samples by elucidating the nature of the interactions between trace level analytes and environmental matrices. Speciation of trace elements in and on environmental matrices is determined with X-Ray absorption spectroscopy (XAS). Chemical species information is then used, in conjunction with mass spectrometry, to identify chemical and physical processes which will permit efficient, reliable, and direct atomization and/or ionization of analytes from solid samples for purposes of analytical spectroscopy. Complicated and costly pre-analysis chemical processing will therefore be avoided. The research also endeavors to extend XAS to include quantitative speciation in mixtures. Another activity seeks to develop the fundamental physics and chemistry of three innovative ion sources for mass spectrometry. The first seeks to understand and exploit observed major enhancements in the electron capture cross section to excited states of large organic molecules. The second uses an electrothermal source which, without complexities introduced by plasmas, permits analysis of microliter samples. The third source directly introduces powder samples for analysis by inductively coupled plasma mass spectrometry. [2.0 FTE]

103. Fundamentals of Phase Partitioning in Supercritical Fluids
Yonker, C.R.; Fulton, J.L.
509-372-4748

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 (1) simple bi-molecular solute/solvent interactions to (2) more complex multi-molecular clustering, chelation, and micellization phenomena as well as (3) fluid/liquid interfacial phenomena. Understanding these phenomena will lead to new supercritical fluid separation and reaction processes, and provide a basis for improving existing processes. Molecular level studies in supercritical fluids also provide an improved understanding of condensed phase interactions by bridging the gap between the gaseous and liquid states. The approach entails the use of spectroscopic techniques such as FT-IR, Raman spectroscopy, NMR, EXAFS, small angle X-ray scattering (SAXS), and dynamic fluorescence quenching. Concurrent are efforts at modelling the fluid structure and predicting intermolecular and interaggregate attractive potentials. The program focuses on the fundamental chemistry that controls the behavior of complex molecular organization in supercritical fluids through experimental and theoretical investigations. These investigations involve probing the underlying chemistry of solute/solvent intermolecular interactions in supercritical fluids and expanding the spectroscopic methods for their characterization. Further studies seek to characterize angstrom- to micron-sized molecular assemblies in supercritical fluids, e.g., alcohol aggregates, chelates, reverse micelles, and microemulsions. It is anticipated that this program will provide the basis for new and improved analytical separations (i.e., extractions and chromatography) and for larger scale separations and reactions, as well as an expanded understanding of solvation and structure in both the supercritical and liquid phases. [1.6 FTE] [1.6 FTE]

Materials and Chemical Sciences Department

104. Laser-Based Analytical Techniques
Bushaw, B.A.
509-375-2699

Laser ablation techniques have received renewed interest for possible chemical analysis because of their potential to perform direct, fast sample interrogation without chemical pretreatments. Unfortunately sample matrix effects have still not been adequately understood or controlled. Universal dissolution of heterogeneous samples is sought so that the ablation plume is representative of the samples being studied. One issue of continued interest has been the role that the electronic distribution, both in the sample and ablation plume, plays in determining the efficiency of ablation and ionization. In general, large differences of ablation and atomization efficiencies have been observed between metal, semiconductor, and insulator samples. These striking changes have been attributed to the nature of the electronic distribution, but only superficial correlations are currently known. In an effort to make laser ablation and laser induced emission spectroscopy a better analytical method, new efforts will be devoted to studying the specifics of the ablation and atomization dynamics. This work is a follow-up to the FY 93 efforts to develop and validate a double-pulse laser-ablation-ionization scheme for use with simple optical emission spectroscopies. A new magnetic lens system will be investigated in FY 94 and 95 to enhance the direct emission of the post-ionized plume, and possibly increase conveyance of ions to additional ion optics and mass spectrometer systems. [0.8 FTE]

Heavy Element Chemistry

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $1,743,000

105. Heavy Element Chemistry Research
Nash, K.L.; Morss, L.R.; Appelman, E.H.;
Beitz, J.V.; Soderholm, L.
708-252-3581

This program probes the basic physical and chemical properties of the lanthanides and actinides in solution and in the gaseous and solid states. Parallel research efforts address f-element coordination chemistry in solution and solid phases, spectroscopy of the metal ions in various coordination environments, and the influence of f-electrons on the electronic and cooperative properties of solids. Investigations of coordination chemistry focus on the design and characterization of new chelating agents exhibiting selectivity for these metal ions by combining hard and soft donor atoms in appropriate coordination geometries. Heavy element photophysics and photochemistry studies provide a predictive understanding of the consequences of electronic excitation of heavy element compounds with particular emphasis on optically detected nuclear magnetic resonance, photodestruction of complexants, and photoseparation of volatile metal fluorides. Studies of f-electron interactions target development of a predictive understanding of the influence of these ions on bulk properties, such as the interactions between f-ions and transition metals that produce valence instabilities in the solid state. Such materials are candidates for technological applications including catalysts, switches, and sensors. Throughout this research, the role of basic science in solving problems of critical national interest is always considered to be of prime importance. [7.5 FTE]

Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, CA 94720

Chemical Sciences Division $1,465,000

106. Actinide Chemistry
Edelstein, N.M.
510-486-5624

Future processes for the use, safe handling, storage, and disposal of actinide materials rely on further development of basic actinide chemistry and the availability of trained personnel. This research program is a comprehensive approach to the exploration of actinide chemistry and to student training. Research efforts include synthetic organic and inorganic chemistry for the development of new chemical materials, their chemical and physical characterization, and thermodynamic and kinetic studies for the evaluation of complex formation. One aspect is the development of complexing agents that specifically sequester actinide ions, which are intended for the decorporation of actinides in humans and the separation of actinides in the environment. Extensive studies are under way to prepare organometallic and coordination compounds of the f-block elements to show differences and similarities among the f-elements, and between the f- and d-transition elements. Optical and magnetic studies on actinides provide information about electronic properties as functions of atomic number. Synchrotron radiation investigations of actinide materials with hard X rays have begun for determining chemical oxidation states and short-range structural information in both solutions and amorphous materials. Efforts to realize the construction of a dedicated actinide facility at the Advanced Light Source are continuing. [11.0 FTE]

Nuclear Science Division $129,000

107. Chemistry of the Heaviest Elements

Hoffman, D.C.; Gregorich, K.E.
510-486-4474

The objectives of this project are to investigate the chemical properties of the heaviest elements (1) to determine the architecture of the periodic table of the elements at its furthest reaches, and (2) to make detailed comparisons of the chemical properties of the heaviest elements with those of their lighter homologs. The actinide series ends with lawrencium (Lr, element 103), and the change in chemical properties in going to the transactinide and seaborgium (Sg, element 106) is especially important. The chemical properties of elements 102–106 can be investigated even though only small numbers of atoms with half-lives near one minute or less can be produced. Aqueous phase chemical separations have been used to determine the most stable oxidation states of elements 102–105 to determine or confirm their periodic table positions. Measurements of the formation and strength of halide complexes of these elements in the aqueous phase, and comparisons with similar properties of their lighter homologs are being used to obtain detailed information on the chemical properties of the heaviest elements. Isothermal gas phase chromatography is used to compare the volatilities of halides of elements 104 and 105 with those of the lighter group 4 and 5 halides. These gas-phase studies allow modeling of the chemical properties in an environment free of complex solvent interactions. While the most basic chemical properties of elements 102–106 (such as their most stable oxidation states) can be understood on the basis of simple periodic table extrapolations, more detailed chemical properties (such as the aqueous complexing strengths or gas-phase volatilities of halides of these elements) show anomalous trends which cannot be easily understood on the basis of classical periodic table extrapolations. The recent observation of longer-lived isotopes of element 106 will allow the first measurements of its chemical properties. Attempts are continuing to try to produce and identify new, longer-lived isotopes of the heaviest elements that will permit more detailed studies of chemical properties. [1.0 FTE]

Los Alamos National Laboratory
University of California
Los Alamos, NM 87545

Isotope and Nuclear Chemistry Division $260,000

108. Actinide Organometallic Chemistry

Burns, C.J.
505-665-1765; 505-665-3688

Studies of the non-aqueous coordination and organometallic chemistry of the actinides are being conducted to uncover fundamental differences in the chemical behavior of these elements with respect to the lanthanides and transition metals. Through the use of non-classical coordination environments, new insight can be gained into the bonding in these species. A thorough understanding of the chemical, structural, and physical properties of complexes of the actinides is critical in evaluating and predicting the behavior of these elements, and supports the development of new technologies to solve problems in chemical processing and waste treatment. During the past year, general synthetic methods were developed for the introduction of ligands capable of engaging in multiple bonding to metal centers (oxo and imido ligands). These ligands are capable of stabilizing unusual oxidation states and coordination environments, as evidenced by novel reactions like the unprecedented two-electron cleavage of hydrazine at an actinide center. Other developments include (1) greatly improved synthetic methods for the preparation of complexes of the formula(Me{5}C{5}){2}AnMeAr (An = U, Th), which have been used to generate highly reactive "benzyne", or o-phenylene complexes and (2) investigations of the chemistry of mixed halide-aryloxide complexes of uranium, which point to significant differences between aryloxide groups and other supporting ligands in their ability to sterically and electronically stabilize an actinide metal center. [0.55 FTE]

109. Actinide Chemistry in Near-Neutral Solutions

Clark, D.L.
505-665-4622

The project objective is to provide fundamental physicochemical knowledge pertinent to the behavior of plutonium and other actinides under environmental and physiological near-neutral pH conditions. The early actinides (U, Np, Pu, Am, Cm) constitute a long term hazard because of their high radioactivity and long half-lives. Consistent activation parameters for carbonate ligand exchange on U(VI), Np(VI), Pu(VI), and Am(VI) have been obtained through variable temperature ^{13}C NMR spectroscopy, and support a uniform mechanism for carbonate ligand exchange for light actinide complexes. Advances continue in the application of ^{17}O NMR as a speciation tool for study of hydration number, hydrolysis, and complexation of light actinides (U, Np, Pu, Am, and Cm) in near-neutral solution. This has lead to new electrochemical preparative procedures for isotopic labeling of actinyl ions AnO_2^{n+} (n = 1 or 2) with NMR active isotopes, and to the direct observation of and NpO_{22+} containing species by ^{17}O NMR. ^{17}O and ^{13}C NMR was used to map out the stability fields of monomeric and polymeric uranyl carbonate complexes in near-neutral solution. Researchers have successfully used ^{13}C NMR to map out the stability fields of monomeric and polymeric neptunyl carbonate complexes in near-neutral solution. This work demonstrates the applicability of multinuclear NMR in transuranic chemistry and will allow extraction of thermodynamic binding constants for the neptunium system. Applications of NMR spectroscopy will provide badly needed data to help define thermodynamic databases for performance assessment models for high level nuclear waste management, and fate/transport models that may be used to support regulatory compliance at Federal facilities. [0.4 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemistry Division $1,272,000

110. *Chemistry of Transuranium Elements and Compounds*
Haire, R.G.; Gibson, J.K.; Johnson, E.; Krause, M.O.; Peterson, J.R.
615-574-5007

The program's primary objective is to promote the chemistry, physics, and material science of the actinides and their compounds through systematic investigations. This goal is pursued by determining experimentally thermochemical, structural, and electronic properties and is supplemented by theoretical calculations. Results are frequently interpreted as a function of electronic configurations, which permits an understanding in terms of the framework of the entire periodic table. Studies may include the 4f elements, or selected transition elements, for comparative purposes or when they are incorporated in compounds or alloys with the actinides. Overall, the intent is to fundamentally define and understand actinide science, to establish important scientific databases, and to provide information that is relative to a diversity of technological areas. The latter includes various aspects of nuclear waste disposal, environmental assessments, as well as transmutation technologies. Examining the high-pressure behavior of the actinides yields unique information concerning bonding, phase behavior, and critical atom–atom separations. Thermodynamic information for the actinides is acquired via high-temperature mass spectrometry, differential thermal analysis, theoretical calculations, and so forth. The high-temperature vaporization of oxides and metals is pertinent to both fundamental and practical questions. Relativistic calculations provide information on ionization potentials, electronic structures, radii, and so forth, which aids in establishing a fundamental understanding of these elements. Solid-state spectroscopy (Raman, luminescence, fluorescence, absorption) studies are used to define structural environments, electronic energy levels, and transitions in actinide materials. These spectral techniques provide sensitive investigative tools that complement X-ray analysis. New thrusts in the program include defining the electronic structure and dynamics of free actinide atoms and molecules via electron spectroscopy and conducting photoionization studies of actinides via mass spectrometry in conjunction with tunable lasers. [6.2 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, CA 94720

Chemical Sciences Division $164,000

111. *Molecular Thermodynamics for Phase Equilibria in Mixtures*
Prausnitz, J.M.
510-642-3592

Phase equilibria are required for design of efficient large-scale separation processes in the chemical and related industries. 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 development of molecular thermodynamics for interpretation and correlation of reliable experimental data toward confident prediction of phase equilibria for engineering. The correlations are expressed through semitheoretical physicochemical models in a form suitable for computer-aided design. These models are suggested by theory and, in some cases, supplemented by molecular simulations. Particular attention is given to traditional or novel materials that may be useful for innovative low-energy consuming separation processes such as polymers and gels and micellar systems with possible applications in biotechnology. However, attention is also devoted to conventional materials for applications in fuel technology, salt production, and for recovery of solutes from wastewater. 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 design. [1.75 FTE]

Energy and Environment Division

112. *Turbulent Combustion*
Talbot, L.; Cheng, R.K.
415-642-6780

The overall objective of this program is to investigate, primarily experimentally, the interaction and coupling between turbulence and combustion. The processes are complex and are characterized by scalar and velocity fluctuations with time and length scales spanning several orders of magnitude. The approach is to gain a fundamental understanding through detailed investigation of idealized laboratory flames. The flame configurations which been have developed are accessible to both laser diagnostics and numerical models. The research emphasis is to obtain a physical understanding of the effects of combustion heat release on turbulence characteristics, and to quantify the relationship between turbulence intensity and the burning rate. The major effort is concentrated on investigating flames with moderate turbulence intensity where chemical reaction rates are not significantly affected by turbulence mixing. The turbulent burning rate can be determined from the flame front topology (i.e., the flamelet geometry) which can be compared to the turbulence characteristics. The investigation of flames with intense turbulence has also been initiated for a closer simulation of the combustion processes in practical systems. Intense turbulence may alter the reaction rates, cause flame quenching, and affect the formation of pollutants. In situ measurement of the local burning rate will be carried-out by the use of laser induced fluorescence techniques. The work on flames with intense turbulence will be guided by the results of flames with moderate turbulence. [1.8 FTE]

Los Alamos National Laboratory
University of California
Los Alamos, NM 87545

Theoretical Division $84,000

113. *Thermophysical Properties of Mixtures*
Erpenbeck, J.J.
505-667-7195

The thermophysical properties of mixtures of particles interacting through simple interaction potentials are evaluated, using both equilibrium Monte Carlo (MC) and molecular dynamics (MD), 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. MCMD calculations for equimolar, binary, hard-sphere mixtures having mass ratio 0.03 and diameter ratio 0.4 (similar to helium-xenon) have previously been reported (including rather precise corrections for large-system size and Green-Kubo time) for all but the highest fluid densities. The possibility of a fluid-fluid demixing phase transition in this mixture is currently being investigated through Monte Carlo calculations in the constant-pressure Gibbs ensemble. Calculations for systems of 216 particles suggest the presence of such a transition for a rather narrow range of pressures, distinctly below those for which constant-volume ensemble calculations indicate the occurance of a fluid-solid transition. However, constant-volume ensemble calculations also demonstrate the presence of large finite-system effects at the high densities involved. It is therefore essential that full account be taken of possible finite-system effects in the Gibbs ensemble as well by studying the same pressure range for larger numbers of particles; such calculations are now in progress. [0.5 FTE]

Sandia National Laboratories, California
Livermore, CA 94551

Combustion Research Facility $414,000

114. *Analysis of Turbulent Reacting Flows*
Ashurst, W.; Kerstein, A.R.; Barr, P.K.
510-294-2274

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 new model of premixed flame propagation has been developed. The model is based on previous simulations and new experimental data which indicates a dependence upon the vortical flow structure. Flame propagation within an engine chamber may show interaction with the unburnt gas vortical structure in a manner that enhances the flame-vortex interaction. This possible effect will be strongest while the flame size is small compared to the chamber volume. The structure of a nonpremixed methane-air flame, which has a parabolic shape, has been computed using two and three-step reduced kinetic mechanisms, and the curvature effects upon flame temperature and the production of oxides of nitrogen have been estimated. 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 effect of molecular transport on turbulence-chemistry interactions in nonpremixed combustion. [1.7 FTE]

Advanced Batteries

Ames Laboratory
Iowa State University
Ames, IA 50011

Department of Materials Science and Engineering

115. *Design and Processing of High Purity and Ultrafine Electrodes for High Performance Nickel/Metal Hydride Batteries*
Ellis, T.W. **$150,000**
515-294-1366; 515-294-3709

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) cell has emerged as one of the most promising environmentally acceptable substitutions for current Ni/Cd rechargeable batteries in non-automotive 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 purity level) and electrode fabrication technique for the negative electrode centered on the AB_5 (based on $LaNi_5$) compound. The objective of this work will be to greatly reduce self-discharge and to double cycling life characteristics of this electrode material over the competing AB_2 compounds. Also, focus will be on development of a unique processing approach for the NiOOH positive electrode that will permit fabrication of new ultra fine pitch electrodes. Such an ultra fine 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 will be done with intimate contact between the Ames Laboratory and Harding Energy Systems Inc., an emerging domestic battery manufacturer.

Argonne National Laboratory
Argonne, IL 60439

Chemical Technology Division

116. Ion Transport Properties Determined by In-Situ NMR Spectroscopic Imaging

Klingler, R.J. **$150,000**
708-252-4356; 708-252-9373

The goal of this program is to use *in situ* magnetic resonance imaging (MRI) to better define electrode-electrolyte interfaces and solid-state ion transport mechanisms. Work will be conducted using a modification of the toroid cavity probe that was designed at Argonne National Laboratory (ANL). Based on past performance, the proposed MRI technique should provide high-resolution NMR spectroscopic information while simultaneously resolving distances on the micron scale in a working electrochemical cell. This new spectroscopic technique will be used for the *in situ* analysis of the chemical composition at the electrode-electrolyte interface, ion concentration gradients within solid state batteries, conformational dynamics of polymeric electrolytes, and ion penetration depths within graphite insertion electrodes. In addition, the electrochemical-MRI technique should be of general use for the investigation of reactive intermediates within the diffusion layer of electrocatalytic systems. Special emphasis will be placed on lithium-polymer electrolyte batteries. Lithium ion transport numbers will be measured from the ion concentration gradients under various conditions to aid in the design of prototype lithium-polymer electrolyte batteries that are being developed at ANL in collaboration with workers at 3M Corporation. These experimental lithium ion transport numbers will be used to evaluate the merits of various theoretical mechanisms that have been proposed to describe ion transport in lithium-polymer electrolytes. The lithium foil anodes, as well as the lithium-polymer electrolyte interface, will be investigated by a combination of ^7Li, ^1H, ^{13}C, and ^{17}O NMR spectroscopy. The resulting NMR chemical shift information will be used to probe the chemical composition and factors that influence the growth of films at the electrode-electrolyte interface. In addition, the NMR spectral properties of the polymer electrolyte will be probed with distance across the lithium ion concentration gradient established in a working electrochemical cell to search for specific ion-polymer interactions during the ion transport process. The factors that influence dendrite formation on the lithium anodes will be probed in a working secondary battery by imaging the surface with ^7Li NMR spectroscopy.

Chemistry Division

117. Template Mediated Synthesis of New Carbon Negative Electrodes

Winans, R.E.; Carrado, K.A. **$150,000**
708-252-7479; 708-252-9288

This proposed study addresses one of the limitations of lithium secondary batteries, which is the performance of the negative electrodes. A designed synthetic approach to preparing carbon electrode materials with properties appropriate for an electrode in lithium rechargeable batteries is described. A unique templating method that is derived from our work with pillared clays should produce useful porous carbon structures. The carbons will be characterized for their physical and potential electrode properties by several methods based on our own experiences and those of two collaborators. The unique carbons which will be prepared could lead to better lithium secondary batteries and a better understanding of the chemistry and physics of the negative electrode.

Brookhaven National Laboratory
Upton, L.I., NY 11973

Department of Applied Science

118. Synthesis and Characterization of Metal Hydride Electrodes

McBreen, J.; Reilly, J.J. **$180,000**
516-282-4513

The purpose of this work is to elucidate the structural parameters that affect the thermodynamics, kinetics, and stability of alloy hydrides in electrochemical applications. The goal is to use this information in the development of new high capacity, long life hydride electrodes for rechargeable batteries. The project is a coordinated team effort between BNL, Texas A&M Univ., Hughes Aircraft Corp. and LANL. Work at BNL focuses on alloy development and the application of *in situ* methods, at NSLS, such as X-ray absorption (XAS), X-ray diffraction (XRD) and X-ray tomography, to elucidate the hydride phases and the role of the alloying elements in hydrogen storage and corrosion inhibition. *In situ* XAS measurements have been made on several AB_5 alloys, including $La_{0.8}Ce_{0.2}Ni_{4.8}Sn_{2.5}$, that were prepared at BNL. In addition *ex situ* measurements were made on similar electrodes that had been cycled at Texas A&M University and on alloys prepared by ball milling at LANL. XAS studies were done at the Ni K edge and at the La and Ce L_3 edges. The electronic effects of hydriding could be determined from the near edge spectra (XANES). The extended fine structure (EXAFS) indicated the formation of $Ni(OH)_2$ on cycling. Thus the ability of XAS to follow the chemistry of the hydriding process and the corrosion of individual components has been demonstrated. [1.8 FTE]

Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, CA 94720

Chemical Sciences Division

119. Characterization of the Li–Electrolyte Interface

Ross, P.N., Jr. **$173,000**
510-486-6226

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. [3.0 FTE]

Energy and Environment Division

120. Application of Pulsed Laser Deposition to the Study of Rechargeable Battery Materials

Cairns, E.J. **$59,000**
510-486-5028

Complex metal oxide powders are used as the electronically active materials in a wide range of rechargeable batteries, including zinc/air and lithium/metal oxide types. Previous performance studies of these high-surface-area powders have been limited by uncertainties in the solid/electrolyte interfacial area. In this research program, dense electrocatalytic metal oxide films with perovskite and pyrochlore structures are prepared by pulsed laser deposition onto conductive polycrystalline substrates. Well-defined mechanistic studies of O_2 reduction and evolution reactions on these films are then carried out. Films of the spinel structure for studies of electrolyte stability and Li intercalation reactions are also prepared. Initial experiments to produce polycrystalline $La_{0.6}Ca_{0.4}Co0_3$ perovskite films on glassy carbon substrates have been performed. Films produced to date are less dense than expected due to corrosion of the glassy carbon during the ablation process. Film-covered electrodes have been mounted in the tip of a rotating disk electrode. Preliminary electrochemical measurements and post-test analyses indicate that the perovskite films are quite stable in highly alkaline electrolytes. Voltametric studies of the $La_{0.6}Ca_{0.4}Co0_3$ films in 30wt% KOH show at least one redox process occurring in the film, and the films show catalytic activity for both the evolution and reduction of 0_2. Optimization studies of the ablation process to produce films of other metal oxides and to improve density are underway. [1.1 FTE]

121. Fundamental Characterization of Carbon-Based Materials for Electrochemical Systems

Kinoshita, K. **$107,000**
510-486-7389

Carbon-based materials have many desirable physicochemical properties for electrochemical systems such as batteries, fuel cells, capacitors, etc. They have excellent corrosion resistance in many electrolytes, acceptable electronic conductivity, good thermal conductivity, and they are available in a host of physical structures. Despite these attractive features, and their widespread usage, there still exists a lack of full understanding of how to control and modify the physicochemical properties of carbon-based materials by chemical or thermal treatments. Lawrence Berkeley Laboratory (LBL) is preparing samples of carbonaceous materials which will be studied by FTIR spectroscopy to identify surface groups which may influence electrochemical reactions. An electrochemical cell with rotating ring disk electrode utilizing these carbonaceous materials is being set up to investigate the kinetics of oxygen reduction.

Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

Department of Chemistry and Materials Science

122. Effects of Chemical Doping and Carbon Structure on Lithium Intercalation in Advanced Batteries

Pekala, R.W. **$97,000**
510-422-0152; 510-423-4897

This research project examines the synthesis and processing conditions necessary to tailor the local structure and composition of porous carbons for potential applications in energy storage devices (i.e., batteries, capacitors). Carbon aerogels are being formed from resorcinol-formaldehyde and phenolic-furfural precursors. These porous carbons have low electrical resistivity, an ultrafine pore size distribution, high surface area (400 to 1100 square meters per gram, roughly the size of one or two basketball courts), and a solid matrix composed of interconnected particles or fibers. Preliminary data show that these materials are attractive electrodes for double layer capacitors. Carbon foams derived from the phase separation of polyacrylonitrile/solvent mixtures are being investigated as lithium intercalation anodes for rechargeable lithium-ion batteries. These carbon foams differ from aerogels in that they have much larger pore sizes and one or two orders of magnitude lower surface area. High capacity and good cycleability are observed during lithium intercalation experiments. These materials can potentially lead to new batteries with energy densities that are approximately four times greater than conventional nickel-cadmium batteries. In summary, this research project investigates the sol-gel polymerization of multifunctional organic monomers, the phase separation of polymer/solvent mixtures, the formation of porous composites, intrinsic chemical doping, and pyrolysis in controlled atmospheres. A variety of characterization tools are being used to study the structure and properties of porous carbons. The overall objective is to develop a fundamental understanding of how morphology, chemical composition, and local order affect the electrochemical performance of porous carbons. The potential payoff from this research is the development of new energy storage devices with superior performance.

Los Alamos National Laboratory
University of California
Los Alamos, NM 87545

Center for Materials Science

123. *Development of Materials for Advanced Ni/Metal Hydride Cells*
Schwarz, R.B. **$121,250**
505-667-8454

This research investigates 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 hydrogen absorption–desorption cycles. [1.3 FTE]

National Renewable Energy Laboratory
Golden, CO 80401

Basic Sciences Division

124. *Microstructure and Ion Transport in Vanadium Oxide Electrodes for Rechargeable Batteries*
Turner, J.A.; Zang, J.-G. **$100,000**
303-384-6667; 303-384-6655

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 will investigate the fundamentals of ion transport, charging/discharging and the failure mechanisms in these vanadium oxide electrodes, and gain a better understanding of the factors which affect the performance, lifetime, and safety of related rechargeable batteries. Both conventional thermal decomposition and novel sol-gel techniques will be employed to prepare the vanadium oxide electrodes. The correlation between the fractal structure/morphology of the electrodes and their performance will be studied. These results will allow the prescription of improved preparation conditions loading to optimal thin film morphologies. In collaboration with an industry partner, investigations will be on the limiting mechanisms of the charging/discharging process in V_6O_{13}. The deterioration mechanisms of these electrodes in the cycling process will also be examined. Based on both the kinetic data and a new theoretical model/calculation algorithm developed recently in our laboratory, the ion transport processes will be stimulated in a solid state battery. For a given thin film combination chosen by the industry partner, the optimum thicknesses of the component layers will be predicted, both for maximizing performance and minimizing 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 expertise in the charging/discharging processes of electrochromic materials is expected to provide cross-fertilization and new insights into the ion insertion kinetics of vanadium oxide and other components of lithium rechargeable batteries.

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Solid State Division

125. *Rechargeable Thin-Film Lithium Batteries*
Bates, J.B. **$194,000**
615-574-6280

The purpose of this program is to conduct the research needed for further improvement and commercialization of thin-film rechargeable lithium batteries developed at the Oak Ridge National Laboratory. These batteries have potentially many applications as small power supplies that can be fabricated directly onto chips or circuit boards. Several important issues addressed in this research are crucial to the commercialization of this technology. These include long-term cycle testing, determining cell performance as a function of temperature and discharge current density, and devising a reliable method for fabricating stacked, bipolar multicell batteries. Methods for utilizing the lithium phosphorus oxynitride electrolyte discovered at ORNL for improving the performance of existing rechargeable lithium-solid polymer electrolyte batteries are also investigated. Part of this research is carried out under a Cooperative Research and Development Agreement with a commercial firm. Joint research is also conducted with the University of Minnesota Corrosion Research Center on the possible use of V_2O_5 films prepared by sol gel methods as the cathodes for thin-film rechargeable lithium batteries. [1.4 FTE]

Sandia National Laboratories, New Mexico
Albuquerque, NM 87185

Exploratory Batteries Department

126. Doping of Lithium Manganese Oxide for Improved Battery Performance

Doughty, D.H.; Levy, S.C. **$150,000**
505-845-8105

Lithium ion rechargeable batteries (LIRBs) hold the potential to be the inexpensive, long lived portable power source of the future. Some projections show LIRBs replacing Ni/Cads because of improved performance and significantly lower environmental impact. Cathode performance is critical to overall LIRB technology and influences some of the most important challenges in the development of commercial batteries, namely energy density, cycle life, and rate capability. This investigation focuses on the influence of doping lithium manganese oxide ($Li_xMn_2O_4$) cathode materials on the fundamental properties that control cathode performance. The program has three components: solid state molecular modeling of doped $Li_xMn_2O_4$, synthesis of materials based on predictions of the model, and electrochemical evaluation of the newly synthesized materials. While the effects of surface area, pore volume, and gain size can be manipulated in several ways, only doping the crystalline material can change the bulk properties of a given phase of $Li_xMn_2O_4$. Substitutional and interstitial doping of various metals to adjust the crystal lattice and spinel framework of $Li_xMn_2O_4$ will modify the diffusion of ions and the ability of the lattice to accommodate expansion and contraction that occurs during lithiation. There has been success in modeling the insertion and deinsertion of lithium into the spinel phase of undoped $L_xMn_2O_4$. Improved agreement with observed lattice expansion upon lithiation will be achieved by refining the Mn(IV) potential functions. Comparing the effect of the addition of dopants in $Li_xMn_2O_4$ on lattice energy and lattice parameters is under way. Furthermore, proof-of-concept has been demonstrated on a new non-aqueous precipitation method for lithiated manganese oxides. The goal is to exploit the power of state-of-the-art atomistic modeling to direct the synthesis experiments in much the same way that pharmaceutical research is guided by molecular modeling of drug precursors. [1.2 FTE]

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Akron
Akron, OH 44325

Department of Chemistry

127. ***Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion***
Lim, E.C. **$101,850**
216-972-5297

The primary objective of the research is to gain fundamental understanding of the factors governing the efficiency of charge 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 for covalently bonded diaryl compounds in solution and for van der Waals complexes in supersonic free jets, using laser-based techniques. Where appropriate, and feasible, quantum chemical methods are also used to gain theoretical understanding of the energetics of charge transfer processes.

University of Alabama
Tuscaloosa, AL 35487

Department of Chemistry

128. ***Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids***
Kispert, L.D. **$89,240**
205-348-7134

The current goal is to study the role of a host matrix in the mechanism of carotenoid cation radical formation and decay and to determine the special properties of carotenoids that enable them to serve both as antennae and as photoprotective agents in photosynthesis 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 isomer, that the solid host can stabilize higher energy cis isomers. All trans or cisoidal carotenoid cation radicals can exist on solid supports and possibility 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 measured proton couplings indicating a planar configuration for the polyene chain. Attempts are under way to manipulate the host matrix in such a manner as to understand the carotenoid function (i.e., protection, quenching, energy transfer, and antenna) and to ultimately develop predictive mechanisms for directing the outcome of photochemical events.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

129. ***Supramolecular Structures for Photochemical Energy Conversion***
Gust, J.D., Jr.; Moore, T.A.; **$208,000**
Moore, A.L. **(15 months)**
602-965-4547

Photosynthetic solar energy conversion is the ultimate energy source for essentially all life, and one of the most durable and efficient solar conversion "technologies." The goal of this project is to synthesize artificial photosynthetic reaction centers which employ the basic chemistry and physics of photosynthesis to help meet the 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 charge-separated state with a quantum yield close to unity. Another 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. A third investigation deals with new methods for the stabilization of charge separation through intramolecular proton transfer.

Boston University
Boston, MA 02215

Department of Chemistry

130. ***Study of Intermediates from Transition Metal Excited-State Electron-Transfer Reactions***
Hoffman, M.Z. **$105,730**
617-353-2494

The electron-transfer quenching of the excited states of transition metal coordination complexes results in their one-electron oxidation or reduction, generating complexes with the metal center in unusual oxidation states or containing coordinated radicals, and the corresponding reduction or oxidation of the quencher. The major objective of this research, which utilizes the techniques of time-resolved spectrofluorimetry, cyclic voltammetry, and continuous and pulsed photolysis and radiolysis, is to gain an understanding of the parameters that govern the efficiencies of formation of energy carriers from the quenching reactions. The dependencies of the kinetics and efficiencies of all the mechanistic steps of the overall redox reactions on the temperature and the nature of the solution medium are also being examined. Concern is directed as well toward the properties and reactivities of the excited states of the photosensitizers and the reduced and oxidized species. During the past year, the following projects have been investigated: (1) the reductive quenching of the excited states of Ru(II)-tris-homo- and heteroleptic complexes that contain 2,2′-bipyridine, 2,2′-bipyrazine, and 2,2′-bypyrimidine; (2) the photochemistry and photophysics of Cr(III)- polypyridyl complexes; (3) the photophysics of Ru(II) complexes in the presence of organic solvents and solutes; and (4) the photosensitized oxidation of phenols via electron transfer and singlet oxygen mediation.

131. ***Photoinduced Electron Transfer in Ordered Polymers***
Jones, G. **$105,000**
617-353-2498

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 a number of chemical bond lengths. 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 along the axis of an [alpha] helix. Systems that have been prepared include di- and tripeptides that have been modified by attachment of pyrene and xanthene dye chromophores and other photoactive groups. A family of new chromophores based on the acridinium ion has been synthesized. On photoexcitation these structures engage in intramolecular charge separation and give rise to chemically reactive radical pair states within picoseconds. 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. Current work also includes the synthesis of amphipathic helices that will potentially provide protein "bundles" for assembly of synthetic reaction centers. Methods that are employed include peptide synthesis, laser flash photolysis and fast kinetics, fluorescence probes of polymer microdomains, 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.

Brandeis University
Waltham, MA 02254

Department of Chemistry

132. ***Mechanistic Studies of Excited State Chemical Reactions***
Linschitz, H. **$87,300**
617-736-2506

This research seeks to clarify the thermodynamic and kinetic factors which govern the efficiency of endergonic photochemical processes. Dissipative vs. reaction pathways in various donor-acceptor systems are studied in homogeneous solutions using nanosecond laser flash photolysis to identify excited states and transient reaction (radical) intermediates. Quantum yields are measured by energy-transfer and/or actinometric techniques. Particular emphasis is given to reductions by simple anions, for which Marcus reorganization energies may be obtained from spectroscopic data. Also, energy-flow patterns and related properties of charge-transfer excited states of porphyrins and other systems are being studied to establish general trends in these photosensitizers. In the above context, problems of major concern include the mechanisms of very fast singlet to ground state interval conversion and the anomalous fast rates observed in anion quenching reactions with highly unfavorable ΔG^{o*} values.

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

133. ***Picosecond Dynamic Studies of Electron Transfer Rates at III–V Semiconductor/Liquid Interfaces***
Lewis, N.S. **$175,000**
818-395-6335 **(14 months)**

Work in this laboratory is focused on elucidating the processes involved in charge transfer in photoelectrochemical solar cells. An understanding of these processes is important in solar energy conversion devices, the study of corrosion at semiconductor surfaces, and in further development of the theories of electron transfer at solid–liquid interfaces. The goal of this project is to use time-resolved measurements to obtain the desired kinetic information on these energy conversion systems. The semiconductor liquid junction is treated as a donor–acceptor system in which charge transfer to an acceptor is probed by observing the time-resolved decay kinetics of the initial photogenerated electron. In the specific case being studied in this laboratory, the "donor" is an epitaxial layer of GaAs, and the acceptor is the selenide ion in aqueous 1 M KOH. Excess holes and electrons are created by a picosecond light pulse and then recombine by various pathways, including the one of primary interest—interfacial charge transfer. The entire kinetic scheme is monitored by the decay of light emission from the semiconductor. A computer model is then used to extract values for the heterogeneous charge transfer rates. GaAs surfaces treated with complexes of ruthenium, cobalt, and osmium have been found to yield faster luminescence decay rates than unmodified samples in contact with the same electrolyte. This corresponds to faster charge transfer from the semiconductor to the redox species and in agreement with earlier work done in this laboratory. Modeling work is now being performed to more quantitatively describe these results in terms of specific heterogeneous electron transfer rate constants. While it might be expected that these rates could also be obtained from measurements of light-induced current decays, the effects of RC shaping on these electrical signals must be considered. Work has been completed on semiconductor liquid systems demonstrating that the form of these decays is not sensitive to the interfacial kinetics, and can be adequately predicted from equilibrium properties of the semiconductor and solution.

University of California, Berkeley
Berkeley, CA 94720

Department of Chemistry

134. Theoretical Studies of Electron Transfer in the Photosynthetic Reaction Center

Chandler, D. **$121,251**
510-643-6821

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.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

135. Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin

El-Sayed, M.A. **$130,950**
310-825-1352

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 in bacteriorhodopsin (bR) present in *Halobacterium Halobium.* In both systems, solar energy is first converted into electric energy and then into chemical energy stored in the form adenosine triphosphate (ATP) chemical bonds. The final step in the solar to electric conversion involves the formation of proton gradients. In both systems, the conversion of the proton gradients into ATP is the same while the conversion of the solar energy into the 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, 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. The 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? (2) What role do metal cations play in the proton pump? Researchers are presently determining the femtosecond photoisomerization time of retinal and its modified derivatives in bR and some of its mutants in which charged and hydrogen bonding residues in the retinal cavity are individually replaced by neutral nonhydrogen ones. 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 made to locate the position of these two metal cations by use of anomalous X-ray and extended X-ray absorption fine structure techniques.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemistry

136. *Photochemistry of Chelated d^6 and d^8 Metal Silyls*

Watts, R.J. **$92,150**
805-893-2032

Organometallic sensitizers based upon metal-silicon bonded complexes are being studied for their photoconversion potential. The specific effects of metal silicon bonds upon those excited state properties which include photoconversion are a focal point of the research. Ligands that are capable of binding metal centers through a combination of N- and Si- coordinating sites have been designed, prepared, and characterized as a starting point for the research. The metal–silicon bond, like a metal–carbon bond, is capable of promoting photochemical reduction of substrates, but it is distinct in its tendency to labilize under circumstances where a comparable metal–carbon bond is inert. The current research employs laser-induced transient absorption spectroscopy as a means to characterize electron distributions and photochemical processes following absorption of light in metal–silicon bonded complexes. Absorption transients in N_2 versus CO_2 saturated solutions are monitored in order to establish cases where CO_2 might bind the complex following excitation. Studies of interactions of several different disastereomeric species with solvents as well as CO_2 as substrates are being used to assist in identification of specific active sites within the metal complexes. The research program seeks to establish cases where the metal–silicon bonds in these complexes are cleaved by light, and to take advantage of the potentially high reactivity of these products in activating normally inert materials, such as CO_2, as a segment of a photoconversion cycle.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

137. *Photoinduced Charge Separation in Linked Donor-Acceptor-Chromophore Systems*

Elliott, C.M. **$106,700**
303-491-5204

The work included in this study is directed at gaining a better understanding of intramolecular electron transfer reactions. Molecular assemblies consisting of a photoexcitable chromophore, an electron acceptor, and/or an electron donor comprise the central focus of this work. In one part of the study the electron acceptors and donors are each organic moieties attached by saturated, flexible alkyl linkages. These types of systems have several advantages. First, they are modular, and thus easy to modify. The acceptor- and donor-containing ligands are synthesized separately and used to assemble the chromophores as a final step. Second, the energetics of the electron transfer processes can be controlled and varied in straightforward ways through the ligand synthesis. Finally, the connectivity between the various donors and acceptors can be controlled through easy variations in the synthesis. A disadvantage of the above systems is that the exact distance and conformation at the instant of the electron transfer event cannot be known. A series of triply bridged, rigid heterodinuclear metal complexes has also been prepared where one metal complex serves as the chromophore and the other serves as the acceptor or donor. These complexes are potentially excellent systems for probing the extent to which the sigma bonding framework participates in electron transfer in intramolecular assemblies.

138. *In situ Scanning Tunneling Microscopy Imaging of Dye Sensitization Processes at Layered Chalcogenide Semiconductor Electrodes*

Parkinson, B.A. **$114,430**
303-491-0540

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 photocurrent generated at photon 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 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 photo-induced 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.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

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

Koval, C.A. **$106,700**
303-492-5564

The goal of this research is a better understanding of how solar energy can be utilized in photoelectrochemical cells and facilitated transport membranes. Reactions of "hot" electrons that are created by light absorption in a semiconductor electrode have the potential to increase the efficiencies or to alter the product distribution in photoelectrochemical cells. By studying this process with rotating ring-disk electrodes immersed in solutions containing several electron acceptors, hot electron reaction can be observed at the indium phosphide-acetonitrile interface. Current investigations involve defining the surface chemistry of indium phosphide that produces high fractions of hot electron photoproducts and measuring hot electron transfer kinetics. In addition, the rotating ring disk electrochemical methods utilized for indium phosphide are being adapted to study the wavelength dependence of photoreduction due to size quantization at superlattice electrodes. The ability to use photochemistry to transport chemical species against their concentration gradients could, in principle, be useful in a variety of contexts ranging from environmental restoration to energy storage. Liquid and polymer 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 and photoefficiency of photochemically controlled membrane transport.

Columbia University
New York, NY 10027

Department of Chemistry

140. Charge Generation and Separation at Liquid Interfaces

Eisenthal, K.B. **$116,400**
212-854-3175

Femtosecond second harmonic (SH) and picosecond sum frequency (SF) generation reveal novel static and dynamical properties of interfacial systems. As a prototype, the orientation and ground state recovery of electronically excited Malachite Green, a triphenylmethane cation, was investigated (SH) at aqueous/solid, liquid and vapor interfaces. Both the recovery time, an order of magnitude slower than in water (0.7 ps), and orientation are apparently determined solely by the aqueous component. The unique interfacial environment also clarifies mechanisms of bulk phenomena, here providing evidence that only the partially charged dimethylaniline groups, and not the hydrophobic phenyl group of this molecule are implicated in the relaxation. The structure and spectroscopy of soluble CD_3CN and insoluble $CD_3(CH_{12})_{19}CN$ at the air/water interface was probed by a nonlinear surface vibrational technique (SF) allowing both head (-CN) and tail ($-CD_3$) group behavior to be differentiated. These apparently dissimilar systems both display a sharp phase transition, characterized by sharp changes in -CN orientation and vibrational frequency indicating a loss of hydrogen bonding between the water and -CN at high surface density. The change in orientation of the $-CD_3$ moiety of $CD_3(CH_2)_{19}CN$ is more gradual.

141. Theoretical Studies of Electron Transfer and Optical Spectroscopy

Friesner, R.A. **$109,544**
212-854-7606

In a first project, the empirical pseudopotential model has been used to calculate bandgaps in small semiconductor particles to within ~0.1 eV as a function of particle size for three materials: CdS, CdSe, Si. Calculations of the absorption spectrum and the homogeneous zero phonon linewidth for CdSe particles, the result for which can be compared with the experiments of Brus, Bawendi, Alivisatos, and coworkers, are currently in progress. The model for CdSe particles developed during these studies will be used to determine the dynamical behavior of the excited electron, including trapping in surface state. A second project involves development of methods for quantum dynamical calculations on complex systems and applications of the method to electron transfer through DNA. Development of computational methodology to efficiently solve the Redfield relaxation equation for hundreds of quantum levels has been completed; methodology to derive the appropiate Redfield equations from a microscopic Hamiltonian using canonical transformations to render the perturbatively treated part of the Hamiltonian small is in progress. Simulations of electron transfer in DNA predict that long range transfer should be quenched at low temperature; this prediction can be tested experimentally.

Department of Electrical Engineering

142. Translational-Energy-Resolved Studies of Photogenerated Carrier-Induced Reactions on UHV Semiconductor Surfaces

Osgood, R.M., Jr. **$60,000**
212-854-4462

Photodissociation of CH_3Br, CH_3Cl, and CH_3I on GaAs(110) using time-of-flight (TOF), temperature programmed desorption (TPD), and photoluminescence (PL) in ultrahigh vacuum (UHV) has revealed several photochemical processes on semiconductor surfaces. For example, photogenerated substrate electron-hole pairs promote adsorbate dissociation of the methyl halides by electron attachment. This mechanism applies to the C–X (X = Br, Cl, I) bond cleavage in the first layer. In CH3Br, dissociation by electrons at the conduction band minimum (CBM) or hot electrons is observed with distinct energies for the ejected methyl fragments. Wavelength variation indicates a threshold at the band gap in the first case and a 3.5-eV threshold in the second. The CBM process exhibits self-quenching behavior due to electron recombination via Br-induced surface states. This is confirmed by PL yield, which decreases upon irradiation. Above one monolayer, the methyl halides dissociate by hot electrons or direct absorption. In the most recent analyses, the correlation of results from NEXAFS and TOF measurements, along with insights gained from the modeling of TPD spectra have provided insight into the structure of methyl halides on the GaAs(110) surface and demonstrated the ability to obtain structural information from the TOF measurements of photoinduced dissociation. NEXAFS experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory to probe the σ^* state of the C–X bond and show that the molecules in the first layer are inclined at ~45° from the surface normal in the [0] direction for a coverage of 0.8 ML. Furthermore, the NEXAFS results show that molecules in the second layer are inclined in the opposite direction. Modeling of the TPD data demonstrates the importance of intra-absorbate interactions based on the dipole nature of the methyl halides and also provides some insight into the differences in interactions between the adsorbate and substrate for varying coverages from 0.5 to 1 ML. The preferred angle of ejection of methyl radicals from the attachment of hot electrons varies slightly (~ 5°)with coverage, becoming more normal with increasing coverages between 0.5 and 1 ML, as would be expected from theory. More recent results have shown that surface adsorption can be significantly altered by surface bromination of, most probably, the inwardly rotated Ga atom.

Dartmouth College
Hanover, NH 03755

Department of Chemistry

143. *Photoinduced Dipoles and Charge Pairs in Condensed Phase*
Braun, C.L. **$97,000**
603-646-2500

The project objective is to understand photoionization in liquids and solids comprised of 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 revealed that the dipole moments of excited molecules in solution could be measured with the same techniques. This new dipole moment technique (transient photoinduced polarization) is being developed toward better sensitivity and time resolution. In another system, solute molecules dissolved in liquid hexane are photoionized by two-photon absorption from a picosecond laser pulse. The geminate electron–cation pairs that result usually recombine on the picosecond time scale, but occasionally they escape to form high-energy products. The recombination kinetics depend sensitively on the radii of the distribution of geminate pairs. Measurement of the geminate pair distributions will prove useful to the understanding of condensed phase ionization whether by UV photons or by ionizing radiation such as X-rays.

University of Houston
Houston, TX 77204

Department of Chemistry

144. *Charge Separation in Photoredox Reactions*
Kevan, L. **$116,400**
713-743-3250

This research is directed toward a better molecular understanding of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies including reverse micelles, vesicles, polymer matrices, and microporous oxides. Control of the location of an electron donor will be achieved by attachment of variable length alkyl chains to phenothiazine and porphyrins. Photoyields will be monitored by electron spin resonance and the photoproduced cation location will be assessed by deuterium electron spin echo modulation and matrix proton electron nuclear double resonance. The results will help determine the structural requirements for optimizing photoinduced charged separation for the storage of light energy.

Marquette University
Milwaukee, WI 53233

Department of Chemistry

145. *Photophysical and Photoredox Studies of Transition Metal Complexes and Zeolite-Entrapped Assemblies*
Kincaid, J.R. **$87,300**
414-288-3539

The general goals of this research program are to develop a reliable interpretive framework for analysis of the resonance Raman (RR) and time-resolved resonance Raman (TR^3) spectra of potential photosensitizers based on transition-metal complexes of polypyridines and phthalocyanines and related ligands and to apply these techniques to elucidate the photophysical and photoredox properties of such species both in solution and in various organized assemblies. In an extension of earlier work on zeolite-entrapped complexes, current attention is focussed on the synthesis and characterization of complexes whose inherent photophysical properties are expected to be most significantly altered upon entrapment within the zeolite supercage. In addition, progress is being made in the development of molecular assemblies based on the organized Y-zeolite framework. Specifically, synthetic methods have been developed which facilitate the construction of sensitizer/donor dyads which are fixed in adjacent zeolite supercages. The purity of these new materials is confirmed by spectroscopic and chromatographic methods of analysis, and preliminary studies of photophysical properties provide encouraging evidence for an electronic interaction between the components of the dyad. To the extent that such interactions are significant, these materials may provide the basis for an effective strategy to achieve substantial gains in net charge-separation upon photoexcitation.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

146. *Photochemical Approaches to Conversion of Light to Electricity or Fuel*
Wrighton, M.S. **$232,800**
617-253-1597

The objective of this research is to design, synthesize, characterize, and demonstrate interfacial systems for the conversion of light to electricity or chemical fuel. Areas to be investigated include (1) semiconductor surface chemistry (to improve efficiency and durability of photoconversion systems); (2) multicomponent redox molecules (to mimic the essential functions of natural photosynthesis of light absorption, charge separation, and charge transport); (3) surface modification reagents (to tailor the properties of electrodes used in photoconversion processes); and (4) molecular materials as photoconductors (to be fabricated into photoelectrodes). Unique surface chemistry of semiconductors has led to efficient photoconversion devices. Preliminary results show promising leads in molecular approaches to photoconversion which theoretically will be no less efficient than semiconductor-based devices. Molecular systems under study include donor-chromophore-acceptor molecules such as covalently linked ferrocene-porphyrin-viologen systems capable of being linked to electrode surfaces.

University of Massachusetts-Boston
Boston, MA 02125

Department of Chemistry

147. *Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions in Homogeneous and Heterogeneous Media*

van Willigen, H. **$107,670**
617-287-6147

The project is concerned with the study of the factors that affect the kinetics and efficiency of photoinduced electron transfer reactions with time-resolved electron paramagnetic resonance (TREPR) techniques. The time evolution of the TREPR spectra gives information on the kinetics of the formation and decay of the transient free radicals formed in the electron transfer process. In addition, chemically induced electron polarization (CIDEP) effects give an insight into the mechanism of the electron transfer process. The work during the past year has been concerned with the study of the singlet and triplet excited state reaction of acetone with the donor triethylamine. A second area of investigation is the study of reductive and oxidative quenching reactions of C60 in the photoexcited triplet state. Of interest are the kinetics and mechanisms of the reactions in homogeneous as well as heterogeneous media. Studies are being performed as well on the photooxidation of porphyrins adsorbed in the pores of silica gel by quinones. The unique spatial distribution of reactants and products in the pores of silica gels may promote forward electron transfer while the energy wasting back electron transfer process may be inhibited. Finally, measurements are performed on semiconductor suspensions in aqueous solutions. Of interest is to use time-resolved EPR to get information on photoinduced electron transfer reactions taking place at the surface of the semiconductor particles.

University of Minnesota
Minneapolis, MN 55455

Department of Chemistry

148. *Ultrafast Studies on Intermolecular Electron Transfer in Contact and Solvent-Separated Ion Pairs*

Barbara, P.F. **$116,400**
612-625-0064

This research involves two projects: (1) the novel application of femtosecond and subpicosecond spectroscopy to the study of the early events in photoinduced intermolecular electron transfer on well-defined model systems comprising two reactants that are in contact and (2) ultrafast experiments on the solvated electron in water and alcohols. The bromide/benzene cation contact ion pair was prepared in benzene solution by ultrafast excitation of the bromine atom/benzene molecule charge transfer complex. Bromine atoms were prepared in situ by photolysis of α-bromoacetophenone. Various issues of the dynamics involving the dimer cation and the ion pair have been investigated. Ultrafast near infrared-pump/variable wavelength probe transient-absorption spectroscopy has been performed on the aqueous solvated electron. The photodynamics of the solvated electron excited to its p-state are qualitatively similar to previous measurements of the dynamics of photoinjected electron dynamics as having a rate-limiting bottleneck at low energies presumably involving the p-state.

149. *The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems*

Lipsky, S. **$120,000**
612-624-9581

Photophysical properties of simple organic liquids are being studied that have relevance in determining their behavior when subjected to high-energy radiation. Recent work includes (1) determination of the ionization threshold of neat liquid benzene and estimation of its ionization efficiency and electron range distribution function from dependence of photocurrent on photon energy and on strength of applied electric fields; (2) determination of the ionization thresholds of some saturated hydrocarbon liquids and estimation of their electron range distribution functions from the effect of a magnetic field to enhance the recombination fluorescence of dissolved low concentrations of aromatic molecules or, in some cases, to effect the recombination fluorescence of the neat liquid itself; and (3) Measurement of the fluorescence action spectrum of benzene as a function of benzene concentration in various saturated hydrocarbon and perfluorocarbon solvents over an excitation energy interval from 120 nm to 250 nm. This work is designed to characterize the "channel 3" behavior in the condensed phase and to unravel peculiar effects of increasing benzene concentration to inhibit "channel 3" in certain spectral regions.

National Institute of Standards and Technology, Gaithersburg
Gaithersburg, MD 20899

Chemical Kinetics and Thermodynamics Division

150. *Pulse Radiolytic Studies of Electron Transfer Processes and Applications to Solar Photochemistry*

Neta, P. **$200,862**
301-975-5635

The pulse radiolysis technique is applied to the study of electron transfer and other processes involving reactive intermediates. Complementary experiments are carried out with excimer laser flash photolysis. These studies are concerned with mechanisms, kinetics, and thermodynamics of reactions of organic and inorganic radicals and unstable oxidation states of metal ions. Reactions are studied in both aqueous and non-aqueous solutions. The studies focus on the unique ability of pulse radiolysis to provide absolute rate constants for reactions of many inorganic radicals and organic peroxyl radicals, species that are key intermediates in many chemical processes. Recent measurements have focused on solvent effects on the rate constants for reactions of peroxyl radicals with several compounds, including porphyrins. A special concern of this work is the study of electron transfer reactions of porphyrins and metalloporphyrins, which permits evaluation of these molecules as 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. Currently under study is the reduction of carbon dioxide by reduced forms of metalloporphyrins and the possibility of carbon dioxide insertion into alkyl-metal bonds.

University of New Orleans
New Orleans, LA 70148

Department of Chemistry

151. *Electronic and Nuclear Factors in Intramolecular Charge and Excitation Transfer*

Piotrowiak, P. **$82,450**
504-286-6840

This project concentrates on the understanding and the possible future utilization of two aspects of photoexcited charge separation and recombination processes: (1) the role of the molecular orbital and vibrational mode symmetry in determining the electronic coupling between the donor and acceptor and (2) the dynamics and energetics of ion pairing processes and their influence on the efficiency and lifetime of intramolecular charge separation. On the first topic, high resolution molecular laser studies have lead to a very interesting observation of mode-specific vibronic donor-acceptor coupling in a family of spirobifluorenes. This is an unusual finding in molecules as large as these (MW >300), especially since the mode-specific coupling is observed up to high vibrational excitation levels ($\sim$ 600 cm^{-1}). Further molecules are being prepared and a computational analysis of the results is currently in progress. These results may have an implication in the design of new materials exhibiting directional charge and excitation transfer properties. On the second topic, p-aminonitrobiphenyl and p-aminonitroterphenyl are being utilized as sensitive probes of ionic association in a variety of media. The transient charge transfer absorption bands of the molecules are very sensitive to the polarity of the medium and to the presence of counterions. Spectral shifts as large as 7000 cm^{-1} have been recorded. These dynamic spectral shifts allow one to monitor simultaneously both the dynamics and the energetics of the ion association process. Since the lifetime of these charge transfer states is very long (several μs), a much broader range of timescales can be explored if then it is possible when the time dependent fluorescence shifts are studied. The details of the interplay between the ionic association and the intramolecular electron transfer are being presently investigated.

University of North Carolina at Chapel Hill
Chapel Hill, NC 27599

Department of Chemistry

152. *Excited State Processes in Transition Metal Complexes: Redox Splitting in Soluble Polymers*

Meyer, T.J. **$145,500**
919-962-6319

Polypyridyl complexes of Ru(II), Os(II), and Re(I) are being investigated for applications in molecular-level energy conversion processes. The photochemical and photophysical properties of these complexes are well understood and provide a basis for predicting light absorption and excited state stabilities and lifetimes. Based on this knowledge, synthetic procedures are being developed for the preparation of a new family of black absorbers which absorb light efficiently throughout the near-UV visible. These molecules emit in the near infrared, are photochemically stable, and have excited states whose lifetimes are sufficiently long to be accessible. In this class of complexes, emission and resonance Raman spectroscopies are being used to explore the roles of electronic structure, molecular vibrations, and the medium on properties and lifetimes. Synthetic methods have been developed based on ether or amide links for attaching derivatives of these complexes to soluble polymers along with organic groups that can act as electron or energy transfer donors or acceptors. Photophysical studies on the resulting molecular assemblies show that soluble polymers can be designed in which photoinduced electron or energy transfer can be initiated and controlled on single polymeric strands. The goals of this work are to mimic the light harvesting, electron transfer abilities of the reaction center of photosynthesis and to study long-range electron and energy transfer.

Northwestern University
Evanston, IL 60208

Department of Chemistry

153. *Dynamic Structural Studies of Light-Induced Charge Transfer and Electronic Localization/Delocalization Phenomena in Metal-Based Molecular Systems*

Hupp, J.T. **$135,000**
708-491-3504

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, flow and laser studies of somewhat slower electron transfer in thermodynamically well-defined, ligand-bridged redox systems; and 4, resonant vibrational characterization of delocalized intervalence transitions. The combination of 2 and 3 has now yielded data that spans more than 11 orders of magnitude in intramolecular electron transfer reaction rate. Current experiments at the rate extremes (i.e., ultrafast and moderately slow) are yielding important new information concerning the role of solvent and internal modes, including (1) vibrational coherence in back electron transfer reactions and (2) possible direct coupling of intermediate frequency solvent modes to the electron transfer reaction process. New results from area 4 are being used to explore the efficacy of primitive "molecular wires" in long-range charge separation.

154. *Vibrational Dynamics in Photoinduced Electron Transfer*

Spears, K.G. **$102,130**
708-491-3095

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 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 electron transfer that is dependent on vibrational quantum number, and is very sensitive to solvent polarity. The ion pair formed after the electron transfer has up to four quanta of the CO stretch mode, and the energy relaxation rate was measured. New theoretical models have been developed that incorporate all the energy relaxation and electron transfer rate competitions.

Ohio State University
Columbus, OH 43210

Department of Chemistry

155. *Photochemistry in Constrained Spaces: Zeolites and Layered Double Metal Hydroxides*

Dutta, P.K. **$101,850**
614-292-4532

Constrained heterogeneous systems offer opportunities for stabilizing redox products formed by photochemical reactions. The interior cages of zeolites and the interlayer space of layered double metal hydroxides are being investigated for arrangement of photoactive molecules. In the case of zeolites, $Ru(bpy)_3^{2+}$ is entrapped in the supercages, and surrounded by ion-exchanged N,N′-tetramethylene-2,2′-bipyridinium ion and placed in an aqueous solution containing propyl viologen sulfonate. Directional electron transfer from the ruthenium species in the zeolite to the viologen in solution is observed upon visible excitation. The efficiency of this process increases as the zeolite crystals get smaller, indicating that interfacial zeolite-solution electron transfer is important. Strategies for reduction of the Ru^{3+} species by water, along with oxygen evolution has been designed. The second class of materials under study involves layered double metal hydroxides. Long chain fatty acids have been incorporated into the interlayers. These materials have properties characteristic of membranes and act as a partition medium for hydrophobic molecules. The interlayer is used as a site for generating small crystals of titanium dioxide. These have been sensitized with zinc porphyrins and the photochemical properties are being explored.

University of Oregon
Eugene, OR 97403

Department of Chemistry

156. *Photochemical Water-Splitting Using Organometallic Oxides as Sensitizers*

Tyler, D.R. **$74,663**
503-346-4649

The project objective is to split water photochemically into hydrogen and oxygen using homogeneous molybdenum oxide catalysts. The project will be divided into four parts. In the first part, water-soluble catalysts will be synthesized and developed. In part two, the mechanism of oxygen evolution will be investigated. Part three is concerned with the mechanisms of hydrogen evolution, and in part four, the oxygen and hydrogen producing schemes will be combined into a complete cycle that splits water photochemically. An important early goal is to establish that both oxygen and hydrogen can be generated from water using the same catalyst system. Mechanistic investigations are a key part of each section because the information obtained will be used to optimize the efficiencies of the hydrogen and oxygen producing reactions.

Pennsylvania State University, University Park
University Park, PA 16802

Department of Chemistry

157. *Electron Transfer Reactions in Microporous Solids*
Mallouk, T.E. **$125,850**
814-863-9637

This project employs solid state materials, such as zeolites and lamellar oxide semiconductors, as organizing media for artificial photosynthetic systems. The microporous solid organizes photoactive and electroactive molecules in space via ion-exchange equilibria, size exclusion effects, and selective adsorption reactions. The goals of the project are to develop design principles for hybrid organic/inorganic electron transport chains, to understand the factors that control intermolecular electron transfer rates in these systems, and to prepare functional materials that convert light efficiently to stored chemical energy. Supramolecular electron transport chains, organized at the zeolite/solution interface, contain up to five electroactive components and are being studied by flash photolysis/transient absorbance techniques. Internally platinized layered metal oxide semiconductors are sensitized by adsorption of ruthenium polypyridyl complexes and produce hydrogen photochemically from nonsacrificial electron donors such as iodide. Photochemical charge separation is being studied in related materials, in which photosensitizer and electron relay molecules are intercalated between sheets of oxide semiconductors such as $K_4Nb_6O_{17}$ and $KTiNbO_5$. A new technique has been developed for growing lamellar heterostructures consisting of photoactive and electroactive polycations interleaved with two-dimensional polyanions. The latter are layered metal oxide semiconductors and insulating metal phosphates. The factors that control structure, charge separation, and recombination in these composite materials are currently being studied.

158. *Polar Solvation and Electron Transfer*
Maroncelli, M. **$106,700**
814-865-0898

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.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemistry

159. *Evaluation of Electronic Coupling in Photoinduced Electron Transfer Reactions*
Therien, M.J. **$125,000**
215-898-0087 **(15 months)**

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
Pittsburgh, PA 15260

Department of Chemistry

160. *Time-Resolved Optical Studies of Charge Relaxation and Charge Transfer at Electrode Interfaces*
Waldeck, D.H. **$92,150**
412-624-8430

The aim of this project is to develop a quantitative understanding of the kinetics of photogenerated carriers in semiconductor electrodes and at the semiconductor–electrolyte interface. Previous studies elucidated the important features that are needed in a quantitative description of the carrier dynamics and relaxation. Recent efforts have developed a perturbative model that includes effects from "bimolecular" recombination, and it was shown experimentally that time-resolved fluorescence can study the carrier dynamics in the low-injection regime as well as the high-injection regime. Present efforts are aimed at including the space charge potential in the treatment of the carrier motion explicitly. Chemical derivatization of the interface is used to gain a measure of control over the energetics of the surface and to modify the recombination pathways at the interface. Recent studies have shown that silane compounds modify the recombination rate significantly, but have little effect on the electrical properties of the interface. Present studies are aimed at preparing better defined interfaces so that important features of the relaxation can be evaluated quantitatively.

Portland State University
Portland, OR 97207

Department of Chemistry

161. *Asymmetric Polymeric Porphyrin Films for Solar Energy Conversion*
Wamser, C.C. **$92,150**
503-725-4261

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 CH_2Cl_2 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.

Princeton University
Princeton, NJ 08544

Department of Chemistry

162. *Resonance Raman Spectroscopy of Photoreaction Centers*
Spiro, T.G. **$116,400**
609-258-3907

Resonance Raman spectroscopic techniques are applied to investigation of vibrational spectra of the chromophores in the electron transfer chain of the reaction center of the photosynthetic bacterium *Rhodobacter sphaeroides*. Preliminary experiments indicate distinct differences between the spectra of the two bacteriopheophytin chromophores, one of which is on the electron transfer pathway and the other of which is not. The temperature variation of these spectra is being examined to investigate the nature of the protein structure change associated with the temperature variation of the electron transfer rate. The nature of the recently discovered low-frequency modes of the special pair is being investigated by using depolarization measurements, which may help to distinguish between intramolecular and intermolecular vibrations. Transient resonance Raman spectroscopy will be used to study the role of protein dynamics via the evolution of the vibrational spectra of the electron transfer intermediates.

University of Rochester
Rochester, NY 14627

Department of Chemistry

163. *Photochemistry of Dithiolate Complexes of the Platinum Group Elements*
Eisenberg, R. **$106,700**
716-275-5573

Emissive complexes of the platinum group elements are under investigation in the context of light to chemical energy conversion. These complexes contain a dithiolate ligand and have the general formula PtLL′ (S-S) where L and L′ are neutral monodentate ligands or parts of a bidentate ligand such as a diolefin, diphosphine, or a diimine. All of the complexes are emissive at 77 K, and for the diimine derivatives, the complexes luminesce in fluid solution at 298 K. This property, in conjunction with the coordinative unsaturation of square planar complexes, make these Pt(II) systems of interest for their potential photochemistry. The nature of the emission varies with the dithiolate ligand, being ^{3}MLCT for complexes where L and L′ are phosphine or olefin donors and/or the dithiolate is maleonitriledithiolate and multiple emitting states for Pt(diimine)(ecda) where ecda = ethyl-2-cyano-3,3-dithioacrylate (a 1,1-dithiolate). For the complexes containing diimine ligands, a strongly solvatochromic absorption band exists which is assigned to a mixed metal/ligand-to-ligand′ charge transfer (MMLL′ CT). The range of luminescent platinum complexes has been extended during the past year through the synthesis and characterization of new systems containing quinoxalinedithiolate (qdt) and toluene-3,4-dithiolate (tdt). For the tdt complexes, variation of the diimine ligand yields a correlation consistent with the LUMO in these complexes being strictly π^*_{diimine}. The qdt complexes $(TBA)_2[Pt(qdt)_2]$ and Pt(phen)(qdt) are solution emissive (Φ_{em} of 10^{-5} and 10^{-3}, respectively) and both show significant Ph dependent changes in absorption and emission spectra resulting from protonation of the qdt ligands. For $Pt(qdt)_2{}^{2-}$, single protonation leads to a large red-shift of the low energy MLCT absorption band and emergence of a new red-shifted emission. In solutions below pH 6, a second protonation takes place, yielding $Pt(Hqdt)_2$. The ground-state basicity constants for the two qdt protonations have been determined from spectrophotometric titrations, and efforts have been made to determine the excited state $pK_b{}^*$ for this system.

164. *Ultrafast Optical Studies of Surface Reaction Processes at Semiconductor Interfaces*

Miller, R.J.D. **$135,000**
716-275-4079

This work exploits semiconductor liquid junctions as an optical switch. These systems are extremely efficient at charge separation (photocurrent quantum yield $\sim$ 1) and can exhibit solar energy conversion efficiencies approaching those of the best solid state devices. The most tantalizing feature of these systems is, theoretically, they are capable of attaining nearly twice the solar energy conversion efficiencies of solid state semiconductor systems. Due to the discrete nature of molecular acceptors it is possible to avoid energy conversion losses through lattice heating in the junction. However, to achieve this goal, interfacial charge transfer must be made sufficiently fast to compete with carrier thermalization. Whether or not this is possible is an important issue as it determines the level of theoretical modeling needed to properly treat the electronic coupling between the highly delocalized states of the solid state and the molecular acceptors across the interface. To this end, a number of non-linear optical methods have been conducted to arrive at a real time view of interfacial charge transfer processes at GaAs(100)/($Se^{-2/-1}$) aqueous liquid junctions. This system is expected to show some of the most rapid interfacial charge transfer dynamics and may serve as a test case for the hot carrier model for optimized solar cell design. Studies of interfacial hole transfer dynamics, field accelerated transport, and dynamic studies of the water response function have shown that interfacial charge transfer can occur near strong coupling limits. Assuming bulk studies of carrier relaxation are applicable at surfaces, this work illustrates that a significant fraction of the carriers undergo interfacial transitions prior to thermalization. A direct observation of the carrier thermalization at the surface is needed to solidify this statement, and ongoing femtosecond photoemission experiments along this line will prove a final test for the concept.

165. *Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Solutions*

Whitten, D.G. **$130,950**
716-275-1858

This work involves a study of light-induced electron transfer reactions in solution and in the solid state and focuses on the potentially useful net chemical conversions that can occur as a consequence of single electron transfer quenching of excited states. Typically, these reactions are initiated by photoexcitation of visible or near ultraviolet light absorbing electron acceptors (or donors) and subsequent quenching by single electron transfer. In the cases examined in these studies, the quencher does not absorb light in those regions and typically contains a potentially fragmentable bond. The fragmentation, however, is only accessible in the radical ion due to a drastic and selective reduction of bond dissociation energies which can occur for different species upon one electron oxidation or reduction. Donors which can be fragmentable from their radical cations include amines, diamines, aminoketones, and aminoalcohols. Acceptors which can undergo corresponding fragmentation include organic halides, ethers, and esters. Focus has been on understanding structural features in reactive donors and acceptors which accelerate fragmentation rates so that they become competitive with rapid return electron transfer in photogenerated radical ion pairs. Polymeric systems containing photoexcitable acceptors and fragmentable donors which can be reacted in both solid state and in solution have been designed and synthesized. Interestingly, fragmentation (and concurrent depolymerization) is observed even in the solid state where the lack of solvent and diffusional processes might be expected to significantly retard net photochemical electron transfer reactivity.

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

Department of Chemistry

166. *Intramolecular Electron Transfer Across Synthetic Peptides: Effects of Structural Constraints, Secondary Structure, and Polarizable Side Chains*

Isied, S.S. **$87,300**
908-932-3764

This project addresses the question of the understanding and the control of long range electron transfer in proteins. In this research, well defined, rigid peptide systems, where metal donors and metal acceptors are covalently attached at the peptide terminals, are assembled. Examples of these bridging peptide networks include oligoproline units, cyclic peptides, and peptides with α-helical structures. Results from this work have clearly indicated that the connectivity of the donor to the acceptor (i.e., the number and type of covalent bonds connecting the donor and the acceptor) can play an important role in increasing the distance across which long range electron transfer can be observed. For example, rapid electron transfer is observed across rigid helical peptides consisting of nine proline units, which is approximately equal to the diameter of a small protein. New experiments emphasizing the electronic interaction across hydrogen bonding networks are currently being carried out to test their effectiveness as electron transfer mediators.

Stanford University
Stanford, CA 94305

Department of Chemistry

167. *Energy Transfer Processes in Solar Energy Conversion*

Fayer, M.D. **$152,290**
415-723-4446

Photoinduced electron transfer and electronic excitation transport are being studied in complex molecular systems experimentally and theoretically. Of particular interest are situations in which the molecular structure of the system or dynamics in the system play a significant role in the electron and excitation energy transport. Experimental methods include picosecond transient absorption and picosecond fluorescence. Recently the first theoretical description of electron transfer and geminate recombination for a donor and any number of acceptors distributed on the surface of a spherical micelle was obtained. This is a complex problem that required the determination of the radial distribution function of hard disks on the surface of a sphere to properly include excluded volume in the calculations. Both analytical theory and Monte Carlo simulations were used. Excitation energy transport in complex polymer systems has been studied. By properly processing polymeric solid samples it is possible to create nano-domains of chromophore tagged chains embedded in a photoinactive polymer host. The number of tagged chains in the nano-domains can be controlled. These clustered chromophore systems exhibit very rapid energy transport. Theory to describe excitation transport among systems of interacting polymer chains and interacting chromophore containing micelles was also developed and applied to experimental systems. In addition, experiments and theory on photoinduced electron transfer and geminate recombination in liquid and solid solutions were used to understand the role of molecular diffusion one electron transfer dynamics in liquids.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

168. *Studies of Radiation-Produced Radicals and Radical Ions*

Williams, T.F. **$130,000**
615-974-3468

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 form the adsorption 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 1 electron is delocalized over two non-adjacent 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 in rigid matrices proceeding by hydrogen transfer, ring opening, ring closure, and sigmatropic shifts. There is 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 Austin
Austin, TX 78712

Department of Chemistry and Biochemistry

169. *Vectorial Electron Transfer in Spatially Ordered Arrays*

Fox, M.A. **$195,000**
512-471-1811

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.

170. *Photoredox Processes at Polymer–Water Interfaces*

Webber, S.E. **$97,000**
512-471-3633

This research concerns chromophores covalently attached to amphiphilic polymers, with the underlying idea that the combination of hydrophobic compartmentalization and aqueous medium will help solvate the ion-pairs produced in photoredox reactions and enhance charge separation. In recent work, polyethylene oxide has been end-tagged with aromatic chromophores, and the adsorption of these hydrophobically modified polymers onto polystyrene latexes has been studied by light scattering and fluorescence. Photoinduced electron transfer from these species has been investigated both in homogeneous aqueous solution and adsorbed at the interface of water-soluble polystyrene latexes. Charge separation following singlet- and triplet-excited state quenching was found for polyethylene oxide-anthracene and polyethylene oxide-pyrene both in H_2O homogeneous solution and H_2O/latex biphasic systems. The efficiency of charge separation for triplet state is high (ca. 0.6-1.0) and is relatively insensitive to environment because the back electron-transfer reaction is spin-forbidden. For the singlet state, the efficiency of charge separation is lower (ca. 0.2-0.3) and is relatively sensitive to the environment. In all cases the ion pairs have a long lifetime, in excess of 1 ms. Diblock polystyrene-blk-poly(methacrylic acid) polymers have been synthesized using anionic polymerization techniques incorporating an average of one naphthalene/polymer at either the beginning of the polystyrene block or at the junction between the polystyrene and polymethacrylic acid blocks. These polymers form stable micelles in pure water. Photophysical techniques and SEM images demonstrate that the intact micelles adsorb onto the polystyrene surface and can achieve a nearly close packed monolayer coverage. This represents a new strategy for modifying polymer films with photoactive groups.

Tulane University
New Orleans, LA 70118

Department of Chemistry

171. Photoinduced Energy Transfer in Transition Metal Complex Oligomer
Schmehl, R.H. **$92,150**
504-865-5573

This research involves the synthesis and spectroscopic examination of polymeric transition metal complex sensitizers which exhibit vectorial energy migration. Such polymers can be used for light harvesting applications in artificial photosynthetic devices. The polymers are prepared from bridging ligands having two covalently linked 2,2′-bipyridyl (bpy) chelates (bpy-R-bpy). Each metal center of the polymer contains two bis-bipyridine ligands and a third bidentate chelating ligand which serves to tune the electronic properties of the complex (the repeating unit for a homopolymer is $[(\text{bpy-R-bpy})\,\text{ML}(\text{bpy-R-bpy})\text{L}]_x$). Simple synthetic methods were developed for the preparation of bis-bipyridines having a variety of R moieties such as R=phenyl (bpy-ph-bpy) and R=ethyl (bpy-et-bpy). In addition complexes have been prepared in which two metal centers with different tuning ligands are linked together: $[\text{L}_2\text{M}_1(\text{bpy-ph-bpy})\text{M}_2\text{L}'_x]$ where M=Os, Ru, L represents a combination of other diimine ligands and L′ represents a combination of diimine and other ligands such as CN^-. By using time resolved luminescence techniques, rate constants for energy migration between adjacent metal centers can be determined. Changes in rate constants brought on by variations in R are related to changes in the electronic interaction between neighboring metal centers. Data from a limited number of complexes allows optimization of bridging ligand design. Further, investigation of energy transfer rate constants as a function of the free energy difference between excited states of neighboring metal centers allows determination of intramolecular and solvent reorganizational barriers to energy migration.

Washington State University
Pullman, WA 99154

Department of Chemistry

172. Investigations of Charge-Separation Processes in Metal Complexes
Crosby, G.A. **$108,723**
509-335-5605

The research is directed toward the fundamental problem of charge separation at the molecular level. The intent is to identify the structural determinants of the barriers to charge separation by exploiting model compounds. Current efforts are focused on metal complexes of Rh(III), Pt(II), and Re(I) containing aromatic heterocyclic ligands. Analyses of luminescence spectra and decay times monitored as a function of temperature provide the physical parameters of the excited states. For Rh(III) complexes solid-state photochemistry is being quantified by monitoring the spectra of both reactant and product. Data are providing Arrhenius activation barriers that can be related to the energy gaps separating excited states of disparate orbital parentages and reactivities. Concomitant with the spectroscopic measurements extensive many-electron calculations are being performed in order to quantify the orbital natures of the spectroscopic states monitored at low temperature. The ultimate goal of this research is to arrive at a degree of understanding of these systems such that new complexes exhibiting excited state charge separation can be designed at the molecular level and synthesized in the laboratory.

173. Membrane Based Photochemical Systems as Models for Photosynthetic Cells
Hurst, J.K. **$48,500**
509-335-7848

The objectives of this research are to examine how microphase compartmentation can be used to control chemical and photochemical dynamics and to develop integrated chemical systems based upon ultrathin membranes that perform useful solar-driven work. Two projects are currently being pursued: (1) investigating the potential use of 1-methyl-4-cyanopyridinium ion and surface-active analogs as combined oxidative quenchers and membrane relays for use in vesicle-based systems for solar photoconversion, and (2) investigating mechanisms of water oxidation by a series of dimeric ruthenium μ-oxo coordination complex ions. The impetus for these latter studies is the need for effective methods to close the oxidative half-cycle in water photolysis. Recent work has been directed at structurally characterizing the higher oxidation states by resonance Raman and EPR spectroscopies and at applying steady-state initial velocity kinetic methods to determining whether or not they are involved in catalysis.

University of Washington
Seattle, WA 98185

Department of Biochemistry

174. Femtosecond Spectroscopy of Energy Transfer Dynamics in Photosynthetic Antennas
Nagarajan, V. **$78,000**
206-543-1788

The goal of this project is to elucidate the pathways and mechanisms of electronic excitation transfer (EET) among the "antenna" complexes of photosynthetic bacteria, by the use of femtosecond pump-probe spectroscopy. The antennas are large arrays of pigment-protein complexes that collect light energy and transfer it efficiently to the "reaction center", where a series of electron-transfer steps is initiated eventually culminating in the production of ATP. Each of the major antenna complexes has a distinctly different absorption spectrum. Transient absorption spectra acquired following excitation of specific antenna complexes are analyzed globally, with the goal of extracting a comprehensive picture of the EET process. The dynamics of intracomplex EET are probed by transient absorption anisotropy.

Wayne State University
Detroit, MI 48202

Department of Chemistry

175. Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates

Endicott, J.F. **$195,000**
313-577-2607

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 excited state 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 the donor-acceptor coupling inferred from electrochemical measurements is consistently much larger than that inferred from a Hush-type of interpretation of the spectroscopic measurements. The possibility that the conventional interpretation of the transition moment may be in error is being examined, since the results suggest that details of the donor-acceptor coupling mechanism may be more important than usually assumed. Series of complexes with different bridging ligands, and with different donor-acceptor coupling mechanisms are being examined in order to evaluate the evolving concepts.

Wichita State University
Wichita, KS 67260

Department of Chemistry

176. Mixed-Metal, Multielectron Photocatalysts for Solar Energy Conversion

Rillema, D.P. **$130,000**
316-689-3120 **(16 months)**

The design and synthesis of potential solar energy photocatalysts is the focus of the investigation. A number of platinum(II) biphenyl complexes of the form $Pt(bph)L_2$, where bph is the 2,2′-biphenyl dianion and L_2 is CO, bis(diphenylphosphino)ethene, bis(diphenylphosphino)methane, cyclooctadiene, bipyridine and CN-, have been isolated. An X-ray structure of $Pt(bph)(CO)_2$ indicates that the Pt–C(bph) bond distance is 2.04 Å; the Pt–C(CO) bond distance is 1.98 Å. The complex crystallizes in the space group Cmcm and views along the a, b, and c axes indicate that the complexes stack with Pt–Pt distances of 3.2 Å. The emission properties of the complex differ in a 4:1 ethanol-methanol glass compared to the observed behavior in the solid state. In the glass at 77 K, structured emission is observed attributable to emission from a ^{3}LC state. The emission maximum is located at 499 nm. In the crystal, the emission spectrum is broad and the maximum is located at 730 nm at 298 K, but red shifts to 865 nm at 77 K. The source of the emission is assigned to a ^{3}MLCT state and the red shifts to 865 nm at 77 K. The source of the emission is assigned to a ^{3}MLCT state and the red-shift is related to interactions of the d_{z^2} orbitals of the stacked platinum complexes raising its energy above the d_{xy} orbitals. In solution at room temperature, the emission spectrum is more structured in 4:1 ethanol-methanol than in methylenechloride. These results indicate that the ^{3}LC and ^{3}MLCT states are in close proximity and may account for the difference in behavior between the solid state and glass emission properties.

Chemical Physics

Aerospace Corporation
Los Angeles, CA 90009

Space and Environment Technology Center

177. A Shock Tube Study of the Reactions of Hydroxyl Radicals with Combustion Species

Cohen, N.; Koffend, J.B. **$83,902**
310-336-7427

The project objective is the measurement of rate coefficients for reactions of OH radicals necessary for understanding and predicting oxidation and combustion kinetics of hydrocarbon fuels and anthropogenic industrial pollutants. The experiments are being performed in a shock tube under combustion conditions (near 1200 K and 1 atmosphere pressure). Under such conditions, reactions with OH radicals are often the most important step in the decomposition process. Transition-state theory (TST) calculations are also being carried out to relate the measurements to other data at lower temperatures so that reliable temperature dependences of the rate coefficients under study can be established. The calculations also assist in the formulation of semiempirical rules for predicting the rate coefficients of species for which no data are available. Experimental measurements were completed for a series of hydrocarbons; since then the shock tube facility has been completely renovated and newly instrumented. Calibration measurements are nearly complete. TST calculations have since been carried out for a series of twelve halogenated alkanes that are of environmental concern; the predicted rate coefficients will shortly be verified by shock tube measurements.

University of Akron
Akron, OH 44325

Department of Chemistry

178. *Generalizations Concerning Vibrational and Rotational Energy Redistribution within Polyatomic Molecules*

Perry, D.S. **$94,864**
216-375-6825

This project employs high resolution infrared 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.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

179. *Electronic Structure and Reactivities of Transition Metal Clusters*

Balasubramanian, K. **$95,060**
602-965-3054

The objective of this research is to seek answers to fundamental and intriguing questions pertinent to the electronic structure and reactivities of 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. Mixed coinage metal clusters are also studied. 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, ρ_e). Computations on the potential energy surfaces are undertaken to shed light on the reactivity of these species. Spectroscopic constants of several low-lying electronic states of PtN, WN, and other transition metal nitrides and hydrides are computed including spin-orbit effects. The observed spectra are too complex to explain without theoretical studies. Comparisons with observed spectra are made. Systematic studies of Pt_3Au_2 found in inorganic complexes as well as Pt_3Ag_2 are being made. The properties Pt_3Au, Pt_3Ag, and Pt_3Cu are computed. Likewise, computations on Pd_3Au will be undertaken to gain insight into the nature of mixed-metal bonds. The potential energy surfaces of transition metal dimers with ethylene and butadiene will be computed to gain insight into the nature of organometallic ring closure reactions. Specific reactions planned are W_2 + Butadiene, W_2 + ethylene, Ta_2 + Butadiene and Nb_2 + Butadiene. The metal + CO interactions for M = Au, Os, Re, Ru, and Ta are studied. The atom-atom potentials will also be developed for molecular dynamics studies. Transition metal carbides such as TaC, WC, ReC, IrC, and PtC are studied. These studies use complete active space MCSCF (CASSCF) followed by multi-reference configuration interaction (MRCI) computations which include several million configurations. Spin-orbit effects are included using the relativistic configuration interaction (RCI) method.

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

Steimle, T.C. **$68,092**
602-965-2636

The oxidative addition of transition metal atoms by simple molecules such as CH_4, NH_3, and H_2O is studied using a laser ablation/reaction source, the products of which are skimmed to produce a well collimated molecular beam. The sample is interrogated by near natural linewidth limited laser induced fluorescence spectroscopy, recorded in the presence of a variable static electric field. In addition, the pure rotational spectra of the ground electronic state is recorded using a pump/probe microwave optical double resonance technique. The permanent electric dipole moments, magnetic hyperfine interactions, and fine structure parameters have been determined for PtN, MoN, NbN, and TiN, and the results have been interpreted in terms of plausible molecular orbital bonding descriptions. The optical spectra of the Pt/NH_3 and Nb/NH_3 products exhibit band systems that are associated with polyatomic molecules and which are currently being analyzed.

University of Arizona
Tucson, AZ 85721

Department of Chemistry

181. *Chemical Activation of Molecules by Metals; Experimental Studies of Electron Distributions and Bonding*

Lichtenberger, D.L. **$106,700**
602-621-4749

The continued purpose of this research program is to obtain detailed experimental information on the different fundamental ways metals bond and activate organic molecules. The approach is to 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. During this period of the project researchers have (1) characterized the electronic features of cis and bidentate phosphines in their coordination to metals, and identified a metal-phosphine twist mechanism that relieves steric strain without significantly weakening the bond, (2) extended theoretical investigations of the orbital characteristics and bonding capabilities of C_{60} to transition metals, with emphasis on osmium and platinum complexes, (3) developed a detailed description of the π conjugation of long chain acetylides with iron and ruthenium metal centers, including metals that are linked by an acetylide function, (4) examined the relationships between the ionization energies, electron transfer kinetics, and ion solvation thermochemistry of decamethylmetallocenes, and (5) improved the instrumentation for gas phase photoelectron spectroscopy, particularly with respect to the digital data acquisition and analysis.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

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

Felker, P.M. **$93,120**
310-206-6924

The project objectives are two-fold. 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 ultra-cold supersonic molecular-beam samples. In the past year progress was made in one area in particular. Specifically, it was shown that mass-selective ionization-detected stimulated Raman spectroscopies (IDSRs) are widely applicable to the study of intermolecular vibrational transitions in molecular clusters. This fact means that one now has a new, prolific source of information on intermolecular potential energy surfaces. To date the intermolecular vibrations of complexes of benzene with water, carbon dioxide, nitrogen, argon, and krypton, of fluorobenzene with argon and krypton, and of fluorene with argon and benzene have been studied, in a species-selective way. Such data has also been obtained on benzene$_\eta$ clusters (η = 2 to 5) and benzene-water$_\eta$ clusters (η = 2 to 7) and isotopomers thereof.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemistry

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

Wodtke, A.M.; Auerbach, D.J. **$100,000**
805-893-8085

This project will involve a series of exploratory experiments to study the interaction of highly vibrationally excited molecules with single-crystal metal surfaces. Stimulated emission pumping will be used to prepare single quantum states of vibrationally excited molecules in a beam incident upon a single-crystal surface within an ultrahigh vacuum surface-science chamber. This technique will allow study of the interactions of molecules in a single quantum state and with up to several hundred joule per mol of vibrational energy. Auger electron spectroscopy, temperature programmed desorption, X-ray photoelectron spectroscopy, and time resolved mass spectroscopy will be used to map out the relative reaction probability as a function of the reactant vibrational quantum numbers. The studies will be perhaps the first surface reactive studies done with beams prepared in individual quantum states and the first studies of molecules in highly excited vibrational states and promise to advance knowledge of how reactant vibrational energy influences (1) activated dissociative adsorption, (2) non-dissociative or molecular adsorption, and (3) direct ("Eley-Rideal") reactions between incident and absorbed species. The proposed studies require a combination of techniques from the fields of surface science, molecular beams, and laser spectroscopy. The experiment will be a collaborative effort between the University of California-Santa Barbara (Wodtke) and IBM Almaden Research Center (Auerbach).

Catholic University of America
Washington, DC 20064

Department of Chemistry

184. *Studies of Combustion Kinetics and Mechanisms*

Slagle, I. **$124,000**
202-319-5383

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 1000 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 20 torr) and, when possible, the primary reaction products are determined and their branching fractions measured. These experimental studies are coupled, where possible, 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 on the reactions of atomic oxygen with radicals (CH_3 + O and CH_2OH + O) and the unimolecular decomposition of free radicals (t- and s-C_4H_9).

University of Chicago
Chicago, IL 60637

James Franck Institute

185. *Bond Selective Chemistry beyond the Adiabatic Approximation*
Butler, L.J. **$97,000**
312-702-7206

The series of experiments pursued for this project develop a unified understanding of bond-selective molecular dissociation processes important in combustion. To investigate how local electronic excitation of a polyatomic molecule can result in selective decomposition channels over other energetically allowed ones, this work utilizes photofragment velocity and angular distribution analysis in a crossed laser-molecular beam apparatus. Polarized emission spectroscopy provides complementary information by probing the early dissociation dynamics. Work this year included emission spectroscopy to probe the dissociation dynamics of H_2S from a conical intersection in the Franck–Condon region to the H + SH product exit channel; a collaborative theoretical project which compares the adiabatic prediction for the branching ratio between C–S and S–H bond fission in CH_3SH excited in the first ultraviolet absorption band with experimental results; an experiment which demonstrates how to calibrate the absolute photoproduct branching ratios using mass spectrometric detection when the ion fragmentation patterns of the radical products are unknown (the C–C:C–Cl branching ratios in bromoacetone and chloroacetone photolysis by calibrating the signal intensities at X^+ and CH_2CO^+ using acetyl chloride photodissociation); and a study of the competition between H_2 elimination and C–N, C–H bond fission in methyl amine at 222 nm.

186. *Quantum Dynamics of Fast Chemical Reactions*
Light, J.C. **$97,000**
312-702-7197

This research is focused toward the direct and accurate quantum evaluation of thermal rate constants for elementary bimolecular reactions in the gas phase. In addition, state-to-state cross sections for reaction and for photodissociation will be determined. 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 discrete variable representation) and from the cumulative reaction probability, N(E). Recently it was shown that the use of an imaginary absorbing potential in the region outside the activation energy barrier region was useful in making the calculations more efficient and robust. The dynamics of electronically nonadiabatic collisions are now being treated using the two diabatic surfaces, together with an appropriate interaction term. Real nonadiabatic effects are common in photodissociation and in some chemical exchange reactions. An additional use for the nonadiabatic approach is to permit an adiabatic reaction rate to be generated as the net result of transitions from a reactant to a product electronic energy surface. This “fictional” nonadiabatic approach simplifies the treatment of reactant and product coordinates, thus simplifying the calculation of state-to-state probabilities and rate constants. Most recent focus has been on the development of a “quantum transition state theory” based on operator expressions for N(E) with semiclassical log derivative boundary conditions. Applications to real 3-D reactions are in progress.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

187. *Laser Photoelectron Spectroscopy of Ions*
Ellison, G.B. **$102,278**
303-492-8603

This enterprise uses photoelectron spectroscopy to study the properties of negative ions and radicals. The essence of the experiment is to cross a 0.6 keV mass-selected ion beam (M^-) with the output of a CW laser, $\hbar\omega$. The resultant detached photoelectrons with kinetic energy, KE, are energy analyzed by means of a set of electrostatic hemispherical analyzers, $M^- + \hbar\omega \rightarrow N + e^-$ (KE). Analysis of the photoelectron spectra enables us to extract molecular electron affinities, vibrational frequencies, and electronic splittings of the final radical, M, as well as the relative molecular geometries of ions (M^-) and radicals (M). A critical review of three different experimental methods used to measure bond energies, radical kinetics, gas phase acidity cycles, and photoionization mass spectroscopy has been published. These experimental techniques are currently in use to measure the bond energies of a large number of molecules. The basic premises of each of these experiments are discussed and the strengths and weaknesses of each method are identified. These procedures have been compared using a set of about 30 molecules. These three different techniques have only a few disagreements among them; the case of ethylene being the most serious. For the overwhelming number of studies, all measurements lead to bond energies within each other's error bars. Tables of ionization potentials, electron affinities, and heats of formation for about 40 important organic and inorganic radicals were included as were bond energies for the parent molecules at 0 K and 298 K.

188. *Time-Resolved FTIR Emission Studies of Laser Photofragmentation and Chain Reactions*
Leone, S.R. **$99,910**
303-492-5128

Current research involves two major thrusts. One is to develop methods for studying radical-radical reactions and the other is to study single collision energy transfer and reactive dynamics. Both methods utilize time-resolved Fourier transform infrared emission, which combines a commercial FTIR spectrometer with a high repetition rate excimer laser. The study of radical-radical reactions is somewhat difficult, since two very short-lived species must be produced in well-characterized and well-defined quantities. Using high energy laser pulses and a fast flow reactor, a series of radical-radical processes have been studied and detailed analyses of product states completed, including $Cl + C_2H_5$, $O + CH_3$, $H + CF_3$ and $CF_3CH_2 + D$. A vibrationally and rotationally resolved study of collisions of fast H atoms with HF, which produce both inelastic T-V excitation transfer as well as the H atom exchange reaction, has also been completed. The exchange channel is directly probed by the D + HF and H + DF collision systems. Detailed comparisons of the experimental and theoretical results for these systems provide one of the most exacting tests of vibrational and rotational dynamics in a system with competing pathways.

Columbia University
New York, NY 10027

Department of Chemistry

189. Energy Partitioning in Elementary Gas-Phase Reactions

Bersohn, R. **$94,090**
212-854-2192

Research is centered on the important combustion reaction of oxygen atoms with acetylene and the reaction of atoms with vibrationally excited molecules. The reaction of $O(^3P)$ atoms with acetylene molecules has two sets of products: (1) $O(^3P) + HCCH \rightarrow {}^3B_1CH_2 + CO$ and (2) $O(^3P) + HCCH \rightarrow H + HCCO$. To study the dynamics of the reaction the hydrogen atom and CO products of this reaction were probed by laser induced fluorescence. When C_2D_2 reacts with O atoms more hydrogen (D) atoms and fewer CO molecules are produced than with C_2H_2. The explanation is that the simple channel (2) has a loose transition state and the complex channel (1) has a tight transition state which is harder for the D atom to cross. There are two surprising aspects to the CO state distribution. The CO is rotationally and vibrationally cold although the CO producing reaction is 47.6 kcal/mol exothermic. The absence of rotational energy release implies that at the instant of dissociation the heavy atoms are essentially colinear. Future plans include a similar study of the reaction of O atoms with propyne. $H_3C^{13}CCH$ will be synthesized to determine which carbon atom is the source of the CO. Efforts will be made to devise a vuv probing technique for$(^3B_1)CH_2$.

190. Laser-Enhanced Chemical Reaction Studies

Flynn, G.W. **$125,000**
212-854-4162

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 collisions between cool bath molecules and vibrationally hot molecules with chemically significant amounts of energy in an effort to investigate the quenching mechanism for unimolecular chemical reactions. In particular, quantum state and velocity distributions have been determined for carbon dioxide molecules recoiling from pyrazine molecules containing chemically significant amounts of vibrational energy (5 eV). This work has led to the surprising discovery that long range collisions appear to dominate the production of bath molecules which become vibrationally excited during this quenching process. In addition, experiments of this type are providing first glimpses of the separate behavior of the translational and rotational degrees of freedom of the recoiling bath molecules during the relaxation of highly vibrationally excited donors. Experiments designed to verify the presence of "super collisions" in the quenching of highly vibrationally excited molecules are being pursued with the intent of determining the vibrational, rotational, and translational energy distributions resulting from these remarkable energy transfer events. Finally, the detailed chemical dynamics of a number of gas phase reactions are being studied using infrared diode lasers to probe the reaction products and their energy distributions. 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, in assessing the role of statistics in the determination of quantum state product distributions, and in providing an improved understanding of combustion and atmospheric chemical processes.

191. Single-Collision Studies of Hot Atom Energy Transfer and Chemical Reaction

Valentini, J.J. **$92,000**
212-854-7590

This research project addresses the dynamics of chemical reactions that are important in combustion processes, or that serve as prototypes of important combustion reactions. The reactions being studied now involve free radical species, such as H, OH, and CH_3, reacting with hydrocarbons, such as CH_4. The major issue of interest is whether the dynamics of atom + polyatom reactions, which involve the concerted motion of many atoms in the polyatom reactant, are like those of the well understood and much simpler atom + diatom reactions. Both experimental and computational studies are employed to answer this question. The experiments use laser pulses to create the free radical reactant via photolysis, while other laser pulses characterize the energy distributions in the products, under single-collision conditions. The computational simulations are quasi-classical trajectory calculations. State-to-state reactive cross sections are revealed by the experiments and used to provide a rigorous test 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 will help develop models of these reactions that have significant predictive power.

Cornell University
Ithaca, NY 14853

Department of Applied and Engineering Physics

192. Resonance Ionization Spectroscopy of Combustion Radicals

Cool, T.A. **$67,900**
607-255-4191

Fundamental research on the combustion of halogenated organic compounds with emphasis on reaction pathways leading to the formation of chlorinated aromatic compounds and the development of continuous emission monitoring methods will assist in DOE efforts in the management and disposal of hazardous chemical wastes. Selective laser ionization techniques are used in the laboratory for the measurement of concentration profiles of radical intermediates in the combustion of chlorinated hydrocarbons. Concentration profiles of radical species in premixed hydrocarbon and chlorocarbon flames are measured with a flame sampling VUV photoionization mass spectrometer to assist in the development, refinement, and verification of chemical kinetic models. Low pressure $CH_4/O_2/N_2$ and $H_2/O_2/N_2$ base flames seeded with CH_3Cl and CCl_4 are currently under study. A second continuing objective is the development of resonance ionization detection schemes for in situ monitoring of flame species concentration profiles. Concentration profiles of Cl, ClO, CCl, CCl_3, CH_2Cl, CCl_2H, HCl, H, O, HCO, C_2H_3Cl, CO, N_2, and NO measured by resonance ionization complement additional species profiles determined by both VUV photoionization and electron-impact ionization methods in the flame sampling mass spectrometer. Finally, comprehensive studies have been completed of molecular quantum beat phenomena in cyanogen, C_2N_2, a highly toxic thermally stable species of interest in the development of laser-based diagnostics for studies of the thermal destruction of hazardous species.

Laboratory of Atomic and Solid State Physics

193. Photochemical Dynamics of Surface-Oriented Molecules

Ho, W. **$110,000**
607-255-3555 **(15 months)**

The main objective of the project is to understand the dynamics of surface photochemistry. The experimental procedure lies in measuring the velocity distributions as a function of angle of molecules produced in photochemically induced reactions on solid surfaces. An ultrahigh vacuum apparatus has been designed and constructed to couple to a nanosecond-femtosecond laser system. The desorption of O_2 and the production of CO_2 from O_2 coadsorbed with CO on Pt(111) at 80 K have been studied. The photoyields with femtosecond pulses show highly nonlinear dependence on fluence, large production branching ratio when compared to desorption and reaction by nanosecond pulses. A model based on multiple electronic excitation of the adsorbed molecules by the photogenerated hot carriers is found to be successful in explaining these differences. It has also been observed that velocity distributions of molecules desorbed by manifestly nonthermal mechanisms in many cases resemble thermal distributions. This striking fact was accounted for by using a simple model within the framework of generally accepted models of desorption induced by electronic transitions.

Department of Chemistry

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

Houston, P.L. **$104,691**
607-255-4303

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 will be 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.

Emory University
Atlanta, GA 30322

Department of Chemistry

195. Theoretical Studies of Combustion Dynamics

Bowman, J.M. **$90,156**
404-727-6592

The objective of this research project is to carry out detailed calculations, from first-principles, of dynamical processes in gas-phase combustion. The emphasis is on bimolecular chemical reactions of polyatomic molecules, and unimolecular reactions of importance in the formation and destruction of key radicals in combustion. In addition to their importance in combustion, the systems chosen for study are also being studied in detailed experiments. Reaction cross sections and rate constants for the atom-triatom reactions $H+H_2O$,H+HOD, have been calculated and compared to experiment. It appears that the only available potential surface for this reaction has a slightly small barrier, and an adjustment to it needs to be done, or, preferably, a new potential surface needs to be calculated. Resonance energies and widths of HCO have been calculated using a new method employing complex L^2 basis functions. The results compare reasonably with preliminary experiments from three groups. Final rotational distributions of the CO fragment were also calculated. Finally, the rate constant for the $D+H_2$ reaction has been recalculated at high temperatures and the agreement with experiment is quite good.

196. Kinetics and Mechanisms of Reactions Involving Small Aromatic Reactive Intermediates

Lin, M.-C. **$93,120**
404-727-2825

The kinetics and mechanisms of reactions of C_6H_5, C_6H_5O, and C_6H_4 are being investigated by resonance absorption (RA) and resonance-enhanced multiphoton ionization (REMPI) techniques using tunable dye lasers. For studies with the RA method, electronic transitions in the visible region are used to monitor these radicals in a reactor with a multiple-reflection cavity. For studies with the REMPI technique, the spectroscopy and kinetics of these radicals will be investigated in the UV/VUV region by means of one-, two-, or three-photon enhancement. Significant progress has been made in the kinetics of phenyl radical reactions, using the RA method. Temperature-dependent rate constants have been measured for the reactions with acetylene, nitric oxide, isobutane, cyclopentane, and cyclohexane. Additionally, the dynamics of photofragmentation of nitrosobenzene adsorbed on $Al_2O_3(11\bar{2}0)$ surface has been studied.

University of Georgia
Athens, GA 30602

Department of Chemistry

197. Spectroscopy at Metal Cluster Surfaces

Duncan, M.A. **$81,816**
706-542-1998

Metal clusters composed of a variety of pure component systems and metal mixtures are produced and studied in a molecular beam environment. The same methods are used to produce metal complexes, which have small molecules or rare gas atoms "physisorbed" on the metal cluster "surface." Electronic spectroscopy is applied to these clusters and complexes to investigate the fundamentals of metal-metal and metal-adsorbate bonding. These studies produce vibrational frequencies, bond distances, and bond energies for small cluster systems (metal dimers and trimers). Recently studied systems include Ag-K, Ag-Li, Ag-Al, and Ag_2-RG. Larger pure metal clusters and metal-compound clusters (i.e., metal-carbon, or "met-cars" clusters) are investigated with mass-selected photodissociation. Cage-like structures and microcrystalline structures are suggested for certain systems from these studies. Overall, these measurements of the fundamental interactions exhibited by clusters are used to evaluate their potential as models for bulk surface chemistry and catalysis.

Center for Computational Quantum Chemistry

198. Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions

Schaefer, H.F., III **$92,549**
706-542-2067

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. Reactions being studied using ab initio theoretical methods include the $C_2H_5 + O_2$ system, a number of carbyne (monovalent carbon) reactions, the varied unimolecular rearrangements of ethylnitrene, the cyclopropene - methylacetylene isomerization (for which methylvinylidene is a suggested intermediate), the glyoxal - dioxetene rearrangement, the isomerization of ketene to hydroxyacetylene, and the fragmentation of tetrahedrane. Other problems of current interest include the structure and energetics of singlet and triplet isocyanomethylene, the characterization of singlet biradical trimethylenemethane, and a theoretical examination of the hexamethyltungsten compound and its prototype CrH_6.

Harvard University
Cambridge, MA 02138

Division of Applied Sciences

199. Fundamental Spectroscopic Studies of Carbenes and Hydrocarbon Radicals

Thaddeus, P.; Gottlieb, C. **$78,500**
617-495-7340

The purpose of this project is to provide identification, accurate spectroscopic constants in the lowest vibrational states, and reliable structures of small reactive radicals and carbenes that may be key intermediates in the steps leading to cyclization in hydrocarbon combustion. The reactive species are produced in concentrations of a few ppm or less in either low pressure discharges or by H abstraction from stable organic molecules. Detection of reactive species by millimeter-wave rotational spectroscopy establish their existence in cases where the only prior information is often only theoretical (i.e., ab initio calculation). Accurate structures, determined from measurements of rotational spectra of isotopically substituted species, allow kineticists to estimate bond dissociation energies and heats of formation and to access the importance of key reaction mechanisms in hydrocarbon fuels. Molecules whose structures have been determined, or are in progress, include the cumulene carbenes H_2CCC and H_2CCCC and the HCCCO radical. Experiments with isotopically enriched starting gases can also be used to test reaction mechanisms, as illustrated by measurements of the yield of isotopically substituted HCCCO in various mixtures of carbon-13 enriched C_2H_2 and CO which support the conclusion that HCCCO is produced in the 3-body addition reaction of CCH with CO. The HCO, HCCO, and HCCCO radicals are now well characterized spectroscopically, but little is known about the analogous sulfur bearing radicals HCS, HCCS, and HCCCS. Theory predicts that the most stable isomer of HCCCS is bent, but millimeter-wave measurements helped establish that HCCS has a linear ground state. Vibrationally excited molecules currently being studied include HCCCS, C_6H, and HCCN. In HCCN, a fruitful interaction with IR spectroscopists allowed the barrier to linearity to be estimated.

Department of Chemistry

200. Laser Spectroscopy of Hydrocarbon Radicals

Chen, P. **$97,970**
617-495-1842

Supersonic jet flash pyrolysis of a variety of organic precursors to radicals, biradicals, and carbenes is used to prepare cold reactive intermediates in a skimmed molecular beam for spectroscopic studies. Resonant multiphoton ionization (MPI) spectroscopy with mass and photoelectron detection, VUV photoelectron spectroscopy, and zero-kinetic-energy (ZEKE) photoelectron spectroscopy are employed in this study. Ionization potentials are measured for inclusion in thermochemical determinations building on the earlier C_3H_2 studies. Quantitative modeling of polyatomic Franck–Condon factors allows the deconvolution of the badly congested photoelectron spectrum of dichlorocarbene, CCl_2, and a determination of a reliable adiabatic ionization potential. The Franck–Condon modeling was also used to establish the structure of reactive intermediates, with bond lengths determined to within 2%. A full analysis of 1 + 1 resonant MPI spectrum of C_3H_5 and C_3D_5 radicals finds three electronic states that are strongly coupled by vibronic interactions. The lowest Rydberg state is found to be nonplanar at its equilibrium geometry, as evidenced by the observation of inversion-doubled vibronic levels. The first rotationally resolved photoelectron spectrum of a polyatomic radical was also reported.

University of Illinois at Chicago
Chicago, IL 60680

Department of Chemical Engineering

201. Kinetics of Combustion-Related Processes at High Temperature

Kiefer, J.H. **$98,000**
312-996-9430

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. Current work includes 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 small unsaturated hydrides has been developed and applied to HCN and C_2H_2.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Mechanical and Industrial Engineering

202. Investigation of Saturated Degenerate Four-Wave Mixing Spectroscopy for Quantitative Concentration Measurements

Lucht, R.P. **$74,511**
217-333-5056

Degenerate four wave mixing (DFWM) is a promising combustion diagnostic, but the present lack of detailed models for line shapes and signal intensities has impeded the quantitative application of the technique. In this project, a combined experimental and theoretical approach will be used for the development and evaluation of strategies for quantitative measurements in flames. The theoretical approach is to solve the time-dependent density matrix equations for the DFWM process by direct numerical integration. The major theoretical tasks to be performed in this project are (1) to extend previous two-level DFWM modeling to the study of multi-level molecular (or atomic) systems and multi-frequency-mode lasers, (2) to develop a systematic and accurate means of calculating DFWM signal strengths and detection limits, (3) to evaluate strategies such as saturation or the use of picosecond lasers for quantitative measurements in flames, and (4) to incorporate the results of the theoretical modeling into the Sandia DFWM fitting code. Experimentally, DFWM measurements of OH and NO will be compared with quantitative laser-induced fluorescence (LIF) measurements over a wide rage of flame pressures and stoichiometries for comparison with the theoretical calculations for DFWM signal level, saturation intensities, and detection limits.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemistry

203. Theoretical Studies of Nonadiabatic and Spin-Forbidden Processes: Investigations of Reactions and Spectroscopy of Radical Species Relevant to Combustion Reactions and Diagnostics

Yarkony, D.R. **$132,000**
410-516-4663

A unique system of electronic structure programs is employed to consider spin-forbidden and electronically nonadiabatic processes involving radical species relevant to combustion reactions and combustion diagnostics. These programs (1) characterize the surface of intersection of two potential energy surfaces of either distinct spin-multiplicity or (see below) the *same symmetry*, (2) treat the spin-orbit interaction within the Breit-Pauli approximation, and (3) determine the interstate derivative couplings $fs(IJ,a)(R) = <Y_I(\mathbf{r;R})— \partial/\partial R_a —Y_J(\mathbf{r;R})>$ that result in the breakdown of the single surface Born-Oppenheimer approximation permitting questions basic to the understanding of elementary combustion processes not tractable using more standard quantum chemistry codes to be addressed. The aspect of the current research effort with potentially the most far reaching impact is the development of an algorithm for the systematic determination of points on the surface of intersection of two potential energy surfaces of the same symmetry and the role of conical intersections of two states of the same symmetry in the photodissociation of dimethylsulfide (CH_3 - S - CH_3). Other representative projects include spin-orbit induced perturbations in the B^2A' state of HCO. The CH radical is important for the chemistry of combustion processes, playing a key role in the formation of HCO^+ in the combustion of hydrocarbons by the reaction CH + $O(^3P)$ $\rightarrow HCO^+ + e^-$. For this reaction there is evidence that not only the X^2P ground state but also the metastable a^4S^- state may be involved. No previous determinations of the radiative lifetime of $CH(a^4S^-)$ have been reported. To address this deficiency lifetimes for the *spin-forbidden* radiative decay process $(a^4S^-,v) \rightarrow X^2P$ were determined and found to be quite long, on average being 12, 10,and 8 s for v = 0, 1, 2 respectively.

Johns Hopkins University
Laurel, MD 20723

Applied Physics Laboratory

204. *Q-Branch Raman Scattering and Modern Kinetic Theory*
Monchick, L. **$92,150**
301-953-6226

Rarefied gas dynamic techniques that have been used to generate solutions of modern quantum kinetic analogs of the Boltzmann equation to arbitrary degrees of approximation will be used to calculate Q-branch Raman scattering line shapes of D_2 in He. The current program has generalized the quantum kinetic equations to include off-energy-shell scattering (incomplete collisions), mixtures with finite radiator–scatterer concentrations, and open shell molecules. One rarefied gas dynamics method, the quantum analog of the BG-K approximation, has been applied to their solution. The result is rather more complex than the equivalent approximation devised for the Waldmann–Snider generalization because of the occurrence of the Fano collision operator rather than the on-energy-shell counterpart. A collocation method, which depends on a transformation of the kinetic equation into a Fredholm integral equation, has been worked out for the Waldmann-Snider equation, and is being studied for the Fano collision operator. It is further proposed to investigate the approximate methods, such as the Born approximation, of solving molecular off-energy-shell scattering equations, and to apply the results to the calculation of Q-branch Raman scattering in several systems of interest to anti-Stokes Raman spectroscopy (CARS) characterization of high-temperature, high-pressure gases.

University of Kentucky
Lexington, KY 40506

Department of Chemistry

205. *Laser Spectroscopy and Dynamics of Transient Species*
Clouthier, D.J. **$74,000**
606-257-1790

The goal of this program is to study the vibrational and electronic spectra and excited state dynamics of a number of transient sulfur and oxygen species. A variety of supersonic jet techniques, as well as Fourier transform infrared (FT-IR) and intracavity dye laser spectroscopy, have been applied to these experiments. High-resolution FT-IR spectra of formyl chloride (HCOCI and DCOCI) have been obtained and several bands have been rotationally analyzed to provide a detailed description of the ground state rovibrational energy levels. The v_5 and v_9 bands of sulfine (H_2CSO), a transient molecule of importance in sulfur-containing combustion systems have also been recorded. In a study of the reactions of molecular fluorine with hydrogen sulfide, carbonyl sulfide, and carbon disulfide, the FS_2 free radical has been detected for the first time. A strong laser induced fluorescence spectrum was recorded under jet-cooled conditions in the 700 - 485 nm region. A vibrational and rotational analysis of the spectrum, in conjunction with high quality ab initio calculations, proves that the spectrum is the $\tilde{A}^2A'$ - $\tilde{X}^2A''$ band system of FS_2 with the following structural parameters r(S-F)=1.651 Å,r(S-S)=1.865 Å, and <(FSS)=109.1° in the ground state and r(S-F)=1.642 Å,r(S-S)=2.09 Å and <(FSS)=97.1° in the excited state. Other work is continuing on small sulfur allotropes (S_3 and S_4), thioformaldehhyde, and formic acid.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemical Engineering

206. *Aromatics Oxidation and Soot Formation in Flames*
Howard, J.B. **$115,430**
617-253-4574

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

207. *Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules*

Field, R.W.; Silbey, R. **$143,560**
617-253-1489

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, which are suited to 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. 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 $E_{\text{vibration}}$. 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. The SEP study of the electronic ground state potential surface of the formyl radical (HCO) has been completed. The SEP spectra sample the rotation-vibration structure and dissociation lifetimes of vibrational resonances at energies up to 5000 cm^{-1} above the lowest dissociation limit.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

208. *Probing Flame Chemistry with MBMS, Theory, and Modeling*

Westmoreland, P.R. **$81,000**
413-545-1750 **(18 months)**

Elementary reactions in combustion are studied using molecular-beam mass spectrometry (MBMS) of free-radical and stable species in flames, new kinetics from reaction theories, and tests of mechanisms using whole-flame modeling. Work in the third year has focused on modeling low-pressure propene and ethene flat flames. Comparing predictions for a lean propene flame (ϕ = 0.229) to this project's measurements of 31 species, modeling of allyl was the major previous inadequacy. New reactions with H, O, and OH were predicted theoretically and tested in the model, improving allyl predictions but not enough. A new reaction of allyl+0_2 dominated allyl destruction with a rate constant of $(3\pm1)\text{x}10^{12}$ at 1000–1700 K, probably forming propenal+OH. Reactions of C_2H_4+O and C_2H_3+O_2 are also crucial uncertainties. The ethene submechanism was tested using the limited literature on ethene flame structure, revealing that these reactions are crucial uncertainties in those flames as well. Modeling comparisons, BAC-MP4 transition-state modeling, and reaction theories are being used to study these reactions. Planned experiments include study of propadiene-doped flames and ethene flames.

Department of Chemistry

209. *Theory of the Dissociation Dynamics of Small Molecules on Metal Surfaces: Finite Temperature Studies*

Jackson, B.E. **$80,510**
413-545-2583

Realistic theoretical models are used to examine the dynamics of some elementary 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. Three molecular degrees of freedom are treated quantum mechanically, and the other three classically. The dissociation dynamics on highly reactive Ni and weakly reactive Cu surfaces were compared. The importance of averaging over impact sites was demonstrated. Dissociation probabilities were computed for many initial translational, rotational, and vibrational states, and combined to simulate hot-nozzle and seeded beam experiments. 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. Simple collinear models have been used to understand isotope effects and product vibrational excitation. Observed activation energies have been explained in terms of enhanced reactivity due to adsorbate vibrational excitiation. A fully 3D model now allows for the calculation of reaction cross sections and time-of-flight and final state distributions.

University of Michigan
Ann Arbor, MI 48109

Department of Atmospheric, Oceanic, and Space Sciences

210. *Energy-Transfer Properties and Mechanisms*

Barker, J.R. **$179,450**
313-763-6239

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. In the experiments, the population distributions of the excited molecules are monitored with various techniques, including time- and wavelength-resolved IR emission and resonance-enhanced multiphoton ionization. The aim is to assemble a reliable data base and to develop a workable theoretical model for prediction of energy transfer properties. Another important objective is to determine the disposal of energy in translational, rotational, and vibrational degrees of freedom as highly excited molecules are deactivated. In the modeling effort, collisional/reaction master equation formulations are used to investigate the effects of the energy transfer properties on chemical reaction systems of interest in combustion and in other systems that experience temperature and pressure extremes.

University of Minnesota
Minneapolis, MN 55455

Department of Chemistry

211. *State-to-State Dynamics of Molecular Energy Transfer*

Gentry, W.R.; Giese, C.F. **$105,730**
612-625-2894

The goal of this research program is to elucidate the elementary dynamical mechanisms of vibrational and rotational energy transfer between molecules at a quantum-state resolved level of detail. Molecular beam techniques are used to isolate individual molecular collisions, and to control the kinetic energy of collision. Lasers are used both to prepare specific quantum states prior to collision by stimulated-emission pumping (SEP), and to measure the distribution of quantum states in the collision products by laser-induced fluorescence (LIF). The results are interpreted in terms of dynamical models, which may be cast in a classical, semiclassical, or quantum mechanical framework, as appropriate.

212. *Variational Transition State Theory*

Truhlar, D.G. **$101,850**
612-624-7555

This project involves the use of variational transition state theory (VTST) and semiclassical transmission coefficients for calculating rates of gas-phase reactions. The work involves development of the theory and of practical techniques for applying the theory to various classes of transition states, including new methods for interfacing reaction-path dynamics calculations with electronic structure theory and applications to specific reactions. The primary kinetic isotope effect for the [1,5] sigmatropic rearrangement reaction of *cis*-1,3-pentadiene has been studied using the direct dynamics methods with the new centrifugal-dominant small-curvature tunneling method. Rate constants and secondary kinetic isotope effects for the gas-phase S_N2 reaction $Cl^-(H_2O) + CH_3Cl$ were calculated based on a new chloride-water potential energy function that was specifically developed for heavy-water isotope effects. The kinetics of the reactions of OH with CH_4, CD_4, and C_2H_6 were calculated over wide temperature ranges by using interpolated canonical variational transition state theory and the centrifugal-dominant small-curvature tunneling approximation. The kinetic isotope effect of the reaction $CF_3 + CD_3H$ has been calculated by a large-reaction-path-curvature semiclassical method that gives insight into the corner-cutting nature of tunneling paths for hydrogen atom transfer.

National Institute of Standards and Technology, Gaithersburg
Gaithersburg, MD 20899

Chemical Science and Technology Laboratory

213. *Optically Driven Surface Reactions State-Resolved Probes of Surface Dynamics*

Cavanagh, R.R.; King, D.S. **$87,300**
301-975-2368

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 nonequilibrium 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 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) 7 x 7], 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. The reactivity of oxygen containing adsorbates (N_2O, NO_2, O_3, O_2, etc.) and the energy disposal in CO reaction products are being investigated.

214. *Kinetics Database for Combustion Modeling*

Tsang, W. **$98,940**
301-975-2507

The computer simulation of combustion based processes represents a technology with great potential for energy efficiency and pollution minimization through the reduction of the need for direct physical testing. A key ingredient necessary for the development of this technology is the availability of correct inputs of fundamental kinetic data on the thermal reactions which are the controlling processes during combustion. The goal of this project is to fulfill this need through the development of a data base of evaluated and estimated chemical kinetic rate constants. The strategy has been to start with methane and then add increasingly complex fuel molecules such as the larger alkanes, alkenes, alkynes and aromatics. Since it is unrealistic to cover every possible fuel molecule or its decomposition products, the strategy has been to select molecules containing specific functional groups as that the recommendations can be used as a basis for estimates and the setting of limits. Present work is now concentrated on small aromatic compounds including benzene, toluene, and phenol and initial decomposition products such as phenyl and benzyl. Altogether, the data base now contains recommendations for over 1000 reactions. Future work will capture for the data base larger aromatics such as napthalene and those containing a number of functionalities such as styrene.

Physics Laboratory

215. *Spectroscopic Investigation of the Vibrational Quasi-Continuum Arising from Internal Rotation of a Methyl Group*
Hougen, J.T. **$72,750**
301-975-2379

This project studies the vibrational quasi- continuum in acetaldehyde, methanol, hydrogen peroxide and related molecules because internal rotation is important in promoting intramolecular vibrational relaxation (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. All torsion-rotation levels below the barrier in acetaldehyde are now understood experimentally and theoretically; future plans for the molecule include double-resonance quantum number labeling of torsion-rotation levels above the barrier. Good progress has been made towards a global understanding of torsion-rotation states below the barrier and just above the barrier in methanol; future plans include an attempt at global understanding of the extensive existing data set for two additional torsional levels above the barrier. Concerning traditional vibrational states, a number of fundamental bands in acetaldehyde are now in the process of analysis and/or publication of results. Future plans for acetaldehyde and methanol include attempts to understand and quantify the interactions (perturbations) already observed between fundamentals and various continuum-precursor dark states.

University of New Orleans
New Orleans, LA 70148

Department of Chemistry

216. *Identification and Temporal Behavior of Radical Intermediates Formed during the Combustion and Pyrolysis of Gaseous Fuels*
Kern, R.D., Jr. **$85,000**
504-286-6847

An efficient reaction pathway for the formation of benzene, a key step in pre-particle soot formation, involves dimerization of propargyl radicals (C_3H_3). Using a shock tube coupled to a time-of- flight mass spectrometer to dynamically sample the reflected shock zone, dilute mixtures of propargyl chloride with and without hydrogen were analyzed for their kinetic behavior over the temperature range 1350-1600K. In the absence of hydrogen, propargyl chloride decomposition produces only minor amounts of benzene in contrast to a 26% yield of benzene observed in the presence of hydrogen. These surprising results are interpreted by proposing the reactive intermediate c-C_3H_2, singlet cyclopropenylidene, which is formed as a result of the molecular elimination of HCl from propargyl chloride. Subsequent reactions of c-C_3H_2 with H_2 to form thermally activated C_3H_4 ultimately produces C_3H_3 radicals which in turn dimerize to form benzene. Complementary experiments employing laser schlieren densitometric measurements of the rates of allene and propyne decomposition reveal that the formation of c-C_3H_2 appears to be the primary dissociative pathway. The subsequent reactions of c-C_3H_2 particularly with regard to benzene formation are the object of continuing investigations.

New York University
New York, NY 10003

Department of Chemistry

217. *Accurate Polyatomic Quantum Dynamics Studies of Combustion Reactions*
Zhang, J.Z.H. **$90,000**
212-998-8412

This project embarks on a new theoretical undertaking in computational studies of polyatomic reaction dynamics. The main objective of the project is to develop accurate yet practical computational methods for studying polyatomic reactions beyond the atom-diatom systems. Special emphasis is given to applications of new numerical methods to combustion reactions that involve more than three atoms. A time-dependent quantum wave packet method for computing reaction probabilities and cross sections of polyatomic reactions is being developed and applied to accurate full-dimensional numerical calculations for several important four-atom combustion reactions including the benchmark $H_2 + OH \rightarrow H_2O + H$. This time-dependent approach is shown to be a powerful tool for accurate and fast computation of polyatomic reactions, and further development and application of it to more complex reactions are in progress.

University of North Carolina at Chapel Hill
Chapel Hill, NC 27599

Department of Chemistry

218. *The Energetics and Dynamics of Free Radicals, Ions, and Clusters*
Baer, T. **$108,815**
919-962-1580

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. A recent study of the butene ion dissociation has permitted the analysis of three very different dissociation reactions (the loss of H CH_3 and CH_4) by a combination of ab initio molecular orbital and RRKM statistical theory calculations. The aim is to develop simple methods for calculating dissociation rates with the statistical theory. The role of angular momentum in slowing down the reaction rates is also determined. Measurements of dissociation onsets have yielded new values for heats of formation of unstable species, including the t-butyl ion. Present experiments are designed to measure the onsets for the loss of neutral free radicals from dimer ions. Among the reactions being investigated are those that produce the neutral t-butyl free radical. These experiments are made possible by the narrow TOF distributions achieved with the cold molecular beam. It permits distinguishing dimer ions formed from the photoionization of neutral dimers from those produced by dissociative ionization of neutral trimers.

University of Oregon
Eugene, OR 97403

Department of Chemistry

219. ***Dynamical Analysis of Highly Excited Molecular Spectra***
Kellman, M.E. **$90,613**
503-346-4196

A framework based on nonlinear dynamics theory for the analysis of highly excited vibrational states of polyatomic molecules is investigated. The goal is classification and investigation of patterns of spectra from experiments on molecules excited to the regime of "chaotic" dynamics. Three research areas are being investigated with application to species and methods of interest in combustion processes. The first is bifurcation analysis applied to spectra of triatomic molecules with classically chaotic dynamics involving all three coupled oscillators. 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 this bifurcation analysis and a Husimi phase space analysis of the quantum wavefunctions is being investigated. The second area is semiclassical analysis of experimental quantum spectra of acetylene. The third 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
University Park, PA 16802

Department of Chemistry

220. ***Metal Cluster Alloys and Oxides Elucidating Structural and Electronic Effects in Governing the Reactivity and Catalytic Role of Matter in Finite Dimensions***
Castleman, A.W., Jr. **$123,580**
814-865-7242

The physical basis for catalysis is poorly understood and the motivation for the present research is to provide a basis for understanding the role which composition, morphology, and electronic states have on the functioning of a catalyst for various classes of reactions. In order to separate the influence of the substrate from the supported particle, work is under way to investigate unsupported clusters comprised of metal alloys, oxide and mixed-metal oxides, and metal-carbon (Met-Car) clusters. Particular attention is being devoted to oxidation reactions involving nitrogen oxides and CO which are the products of combustion reactions, as well as reactions of simple alkanes and alkenes. Work is also in progress to study the absorption of various molecules on these clusters as well, and to determine mechanisms of reactions such as the extent of carbon-hydrogen bond activation for the case of small hydrocarbons. Unraveling the influence of charge states is an important aspect of the work, and in this context investigations of the reactions of appropriate catalytic materials in the neutral, cationic, and anionic state are pursued. A particularly exciting development has come from recent work showing that binary metal Met-Cars can also be formed and hence the promise of being able to tailor make catalytic materials with preselected electronic properties.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemistry

221. ***Spectroscopy and Reactions of Vibrationally Excited Transient Molecules***
Dai, H.-L. **$110,580**
215-898-5077

The energy transfer properties of highly vibrationally excited molecules are characterized through a combination of efficient, laser-based excitation techniques and efficient detection of IR emission with frequency and time resolution. Specifically, a time-resolved Fourier transform IR emission spectroscopy technique has been developed for monitoring the energy content of the highly excited molecules, populated by internal conversion following pulsed laser excitation of an excited electronic state, during collisional deactivation. As a demonstration, collisional deactivation of NO_2 excited at 21,000 (60 kcal/mole) cm^{-1} by a variety of molecules has been characterized. Several important factors, such as intramolecular vibrational mixing at high energies and the strength of the vibrational transition dipole, in influencing the energy transfer behavior have been identified. In particular, vibronic mixing causes the electronic transition moment to contribute to the vibrational transition dipole and greatly enhance collisional energy transfer. For example, NO_2 excited below 13,000 cm^{-1} loses <50 cm^{-1} per collision, but at energies greater than 13,000 cm^{-1} where vibronic coupling occurs, large energy transfer occurs during the collision. At 20,000 cm^{-1} more than 1500 cm^{-1} is transferred per collision. These experiments generate detailed information characterizing the behavior of a highly excited molecule during a collision and helps the understanding of the dynamics of molecules with sufficient vibrational energy for chemical reactions.

222. ***Intermolecular Interactions of Hydroxyl Radicals on Reactive Potential Energy Surfaces***
Lester, M.I. **$99,910**
215-898-4640

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 and various collision partners. This is accomplished by aggregating the collision partners in a weakly bound complex and probing these binary complexes through spectroscopic measurements and half-collision dynamical studies. The OH-Ar system has proven to be a prototype for examining the interaction potential of an open-shell system since it is amenable to experimental investigation and theoretically tractable from first principles. Experimental identification of the bound states supported by the Ar + OH (X $^2\Pi$) and Ar + OH (A $^2\Sigma^+$) potentials has made it feasible to derive realistic potential energy surfaces for this system in the attractive well regions. Observation of metastable levels which lie above the OH (X $^2\Pi$, A $^2\Sigma^+$) + Ar dissociation limits enables the repulsive wall region of the interaction potential to be probed at energies relevant to thermal collisions. Current work is aimed at understanding the OH (A $^2\Sigma^+$) + N_2 system and the origin of the surprisingly large quenching cross section measured for this collision partner.

Princeton University
Princeton, NJ 08544

Department of Chemistry

223. *Analysis of Forward and Inverse Problems in Chemical Dynamics and Spectroscopy*

Rabitz, H.A. **$101,850**
609-258-3917

This research is concerned with a quantitative exploration of the relationship between structure in intermolecular potential surfaces and resultant observable laboratory behavior. The research has two components. The forward aspects of the research aim at analyzing the potential-observable inter-relationships through the use of functional sensitivity analysis techniques. The ultimate goal is an understanding of how macroscopic laboratory observables are influenced by detailed structure in the underlying fundamental molecular potentials. The forward research also provides a basis to establish a practical and numerically stable algorithm for inverting laboratory data back to the sought-after potential. This inverse algorithm development constitutes the second aspect of the research. In particular, the forward sensitivities generated for analysis may be used to form the kernel of an interative inversion process. The technique is specifically designed to be stable and capable of yielding a potential surface without imposing model potentials, although known asymptotic limiting forms can be included. These new tools are being applied to study several systems, encompassing molecular beam scattering data and vibration-rotation spectra. The stable inversion of actual laboratory data is being accomplished in tri-atomic systems, yielding excellent results. Both forward as well as inverse simulations are being performed.

Department of Mechanical and Aerospace Engineering

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

Dryer, F.L. **$129,510**
609-258-5206

This program addresses improving understanding of combustion chemistry through experimental flow reactor studies in the temperature range 550–1200 K, the pressure range 1–20 atmospheres, and with characteristic reaction times from 10^{-2}–3 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 and acetaldehyde), simple olefins (especially ethene), 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.

225. *Aromatic-Radical Oxidation Kinetics*

Glassman, I.; Brezinsky, K. **$91,561**
609-258-5199

The primary focus of the program is the elucidation of the mechanistic details of the oxidation of aromatic rings. Phenyl radical ring rupture and the subsequent oxidation of the C_5 ring and the C_4 ring fragments have been the subject of plug flow reactor studies. Studies of cyclopentadiene oxidation have revealed, among other details, the formation of carbon dioxide is concomitant with the production of carbon monoxide and that the carbon dioxide is produced early in the reaction sequence, before the cyclopentadiene has undergone the majority of its oxidative decay. The oxidative decay of all other olefinic and aromatic hydrocarbons that have been studied in the flow reactor at one atmosphere pressure exhibit a reaction sequence in which the majority of the fuel decays before carbon monoxide is oxidized to form carbon dioxide. The seemingly anomalous early formation of carbon dioxide during the oxidation of cyclopentadiene has prompted a number of additional flow reactor studies in previous years to elucidate the mechanistic details. The research effort in the last year has continued the pursuit of the elucidation of the mechanism through the flow reactor examination of the pyrolysis and oxidation of anisole and through further systematic studies of the experimental parameters that affect the formation of the early carbon dioxide.

Rice University
Houston, TX 77251

Department of Chemistry

226. *Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals*
Curl, R.F., Jr.; Glass, G.P. **$91,000**
713-527-4816

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. In the oxidation of ammonia and hydrazine and in the combustion of N-containing fuels, competitive reactions of NH_2 determine the relative yields of the final nitrogen containing products N_2 and NO. A reaction of importance in such systems is that between NH_2 and atomic oxygen. The room temperature overall rate constant for this reaction was measured as 6.5×10^{-11} cm^3 s^{-1}. The main channel yields HNO + H. A minor channel leading to NH + OH also exists and was observed, but determined to account for only about 8% of the NH_2 reacting. The rate constant for the reaction NH + O was determined from fitting the NH time profile to be 6.6×10^{-11} cm^3 s^{-1}. Several additional hot bands of the CH stretch of HCCN needed for determination of the HCC bending potential of this quasilinear radical have been assigned. The production of soot and aromatics in flames may be initiated by the recombination of propargyl ($HCCCH_2$) radicals. This recombination rate was measured as 2.4×10^{-10} cm^3sec^{-1} at 295 K. The CH stretch of HCCN near 3247 cm^{-1} was observed and analyzed by IR laser kinetic spectroscopy at Doppler limited resolution. On the basis of the intensity of the lowest excited state with angular momentum about the a-axis, this triplet species is postulated to be a quasilinear molecule. Measurements of the rate of the reaction of ethynyl (C_2H) with H_2 over the temperature range 295–875 K were carried out. The rate constant of this reaction at elevated temperature is crucial to a critical evaluation of the mechanism of acetylene pyrolysis. These measurements provide an extrapolated rate of 5.3×10^{-11} cm^3sec^{-1} at 2000 K.

227. *Supersonic Bare Metal Cluster Beams*
Smalley, R.E. **$106,700**
713-527-4845

Transition metal clusters of size between one through several hundred atoms are the focus of this research due to their importance in heterogeneous catalysis. They are produced and studied in vacuum, levitated in magnetic fields, and their catalytic reactivity measured and correlated with electronic and geometric structure. A major new aspect begun extensively this last year is the development of carbon (fullerene-like) encapsulating supports for these bare metal catalysts so that their catalytic activity may be studied and optimized in real-world conditions.

University of Rochester
Rochester, NY 14627

Department of Chemistry

228. *Low-Energy Ion–Molecule Reactions and Chemiionization Kinetics*
Farrar, J.M. **$137,740**
716-275-5834

Crossed ion-beam–neutral beam reactive scattering experiments are being performed with the goal of using energy disposal measurements and angular distributions to extract dynamical information on collision mechanics and features of the potential surface mediating the reaction. Attention has been focused on the proton and hydrogen atom transfer reactions of O^- with HF and D_2, where vibrational state resolution of the products has been accomplished. Over the collision energy range from 0.40 to 0.60 eV, the O^- + HF system shows an increasing tendency to partition excess reagent translation into product translation. Such behavior represents a transition toward repulsive energy release as the collision system samples the low energy repulsive wall with both O-H and H-F bonds compressed. In the O^- + D_2 system, product vibrational states of OD^- up to $v' = 3$ are resolved. The reaction dynamics are direct at all energies, with available energy partitioned preferentially into product vibration, particularly for forward scattered products. Interesting and unusual rapid variations in the product state angular distributions near a collision energy of 0.30 eV are being examined for resonance behavior. A series of experiments on O^- + HF, H_2O, and NH_3, in which vibrationally excited molecules are prepared by laser excitation is planned.

University of Southern California
Los Angeles, CA 90089

Department of Chemistry

229. *Reactions of Carbon Atoms Using Pulsed Molecular Beams*
Reisler, H. **$95,060**
213-740-7071

The reaction dynamics of carbon atoms in their ground state are being studied using crossed pulsed molecular beams. A beam of carbon atoms is prepared by laser ablation of graphite and crosses a molecular beam containing a second reactant. Products are detected state-selectively. The effects of translational and internal energy on enhancing reactivity are being studied. The role of translational energy on the product state distribution in the reaction of atomic carbon with nitrous oxide has been examined. The newly formed CN bond is highly internally excited and its excitation is not affected significantly by translational energy. In contrast, the "old" NO product is formed internally cold at low translational energies and its vibrational and rotational energies increase with increasing collision energy. These results indicate a direct reaction mechanism. Translational energy also enhances endoergic reactions of atomic carbon with H-containing molecules such as methanol and hydrogen bromide. The effect of vibrational energy on reactivity is being studied using infrared radiation to excite the reactants to overtone and combination bands. In addition, a new pulsed radical source has been constructed for studies of reactions of free radicals.

230. *The Stabilization Theory of Dynamics*

Taylor, H. **$75,000**
213-740-4112

The project objective is to develop, test, and integrate into existing programs for computing dynamic quantities, a new L^2 "stabilization theory of dynamics." This theory computes (1) microcanonical and canonical, unimolecular and reaction rates; (2) cross sections for photoabsorption to the continuum (photoionization and photodissociation); (3) state-to-state cross sections in full or half scattering processes (reactive photodissociation, inelastic, etc.); and (4) resonance parameters. In short, a new conceptually simple and perhaps computationally economic way of computing first, the spectral density, and second, when necessary, the full Green's function for atomic and molecular systems is presented. The theory, which works simultaneously at many energies is different from previous L^2 theories in that it does not use complex rotation, analytic continuation, imaging, polynomial or numerical grid methods, nor absorbing potentials even when it treats problems that do not require full asymptotic specification. The input to the methods is the eigenvalues and eigenfunctions of the system enclosed in a box of size L, given as a function of L. For state-to-state processes, single channel distorted waves and distorting potentials are required.

231. *Reactions of Small Molecular Systems*

Wittig, C. **$111,550**
213-740-7368

This program examines fundamental processes relevant to hydrocarbon combustion. The main issues are mechanisms, rates, dynamics, etc. for unimolecular and bimolecular reactions. Emphasis is placed on a sophisticated experimental technique: high-n Rydberg time-of-flight (HRTOF) spectroscopy. Specialized laser equipment is also used: a tunable, high-energy, narrow-bandwidth parametric oscillator (to vibrationally excite reactants) and a femtosecond resolution pump-probe system. Ties are maintained with theoretical efforts dealing with the same systems. The scientific goals include (1) experimental studies of the HOCO radical intermediate: microcanonical k(E) values from threshold to several thousand wavenumbers above threshold; an accurate measurement of the HOCO well depth; CO_2 vibrational distributions from the H + CO_2 channel, which helps to establish transition state properties and the barrier height; overtone spectra below and above threshold; resonances above threshold; (2) unimolecular decomposition of radicals such as CH_3O and C_2H_5: spectra below and above threshold; product vibrational resolution via HRTOF, which helps establish transition state properties; and (3) photodissociation studies using the HRTOF method: development of a source of monoenergetic atomic hydrogen at energies betweeen 4000 and 8000 cm^{-1}; bond dissociation energies for radicals and stable molecules; preparation of radical–molecule complexes such as CH_3O–C_2H_2 by photoejecting hydrogen from a weakly bound complex.

Stanford University
Stanford, CA 94305

Department of Mechanical Engineering

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

Hanson, R.K.; Bowman, C.T. **$130,950**
415-723-1745

This program involves two complimentary activities: (1) development and application of cw ring dye laser absorption methods for sensitive detection of radical species and measurement of fundamental spectroscopic parameters at high temperatures and (2) shock tube studies of reaction kinetics relevant to combustion. Species under recent investigation in the spectroscopic portion of the research include NO and CH_3; this work has necessitated continued refinement of the intracavity frequency-doubled, cw ring dye laser. Shock tube studies of reaction kinetics include: $CO + OH \rightarrow CO_2 + H$; $H + HO_2 \rightarrow 2\ OH$ and $H + O_2 + M \rightarrow HO_2 + M$; and reactions of CH_3 radicals.

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

Department of Chemistry

233. *Ionization Probes of Molecular Structure and Chemistry*

Johnson, P.M. **$87,300**
516-632-7912

Ionization processes in intense wavelength- tunable laser fields are being used to investigate the spectroscopy and photochemistry of ions and molecules. Resonant multiphoton ionization, multiphoton laser threshold ionization spectroscopy, and multiphoton fluorescence 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 of the detection of minute quantities of molecular species in difficult environments such as the mixtures produced in combustion reactions. A primary tool in these studies is threshold ionization spectroscopy, which provides high resolution ion vibrational spectra akin to a photoelectron spectrum. A version of this method which incorporates mass resolution is being developed. In this technique the various ionization thresholds which mark the energy states of an ion in transitions from a neutral ground state are measured by using the fact that very highly excited neutral states near each threshold can be ionized by an electric field. The ions produced in this way are sent through a mass spectrometer so the optical spectrum of each mass is obtained with high sensitivity. This technique is being applied to the photochemical oxidation reactions of mixed clusters such as benzene-O_2.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

234. *Thermochemistry of Transition-Metal Clusters*

Armentrout, P.B. **$128,900**
801-581-7885

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. Progress to date includes complete collision-induced dissociation (CID) measurements of the binding energies of the cluster ions up to about 20 atoms of titanium, vanadium, chromium, iron, cobalt, nickel, and preliminary work on copper. Photodissociation studies of several cluster ions, Ti_2^+, V_2^+, Co_2^+, and Co_3^+, yield dissociation thresholds that are in good agreement with but much more precise than the CID results. Studies of the energetics and dynamics of reactions of clusters have been initiated. Ongoing results include the reactions of vanadium, chromium, and iron cluster ions with O_2 and with D_2.

University of Washington
Seattle, WA 98195

Department of Chemistry

235. *Atomic Probes of Surface Structure and Dynamics*

Jonsson, H.; Heller, E. **$109,000**
206-685-1804 **(15 months)**

This project involves theoretical calculations of atomic and molecular interactions with surfaces. A wide range of techniques are used and developed to address the various aspects of the problem. A reversible work based transition state theory has been developed to estimate transition rates in multidimensional systems, including quantum degrees of freedom. This has been applied to a fully quantum and thermally averaged H_2 molecule on a Cu(110) surface. Also, a method for finding the minimum energy path for a transition in a multidimensional system has been developed and applied to this problem. The scattering of atoms, in particular, He atoms, from overlayers and defects on metal surfaces, such as steps and adatoms has been studied by time-independent scattering calculations as well as time-dependent Gaussian wavepacket calculations. The calculations aid the interpretation of experimental measurements taken by others on atomic structure and kinetic processes at surfaces, such as diffusion, annealing, and growth. A new semi-classical technique, "Cellular Dynamics," is being developed and will allow faster and more accurate atom scattering calculations, not only of diffractive scattering, but hopefully also the selective adsorption resonances which can provide very useful information about atom surface interactions.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemistry

236. *The Photodissociation and Reaction Dynamics of Vibrationally Excited Molecules*

Crim, F.F. **$117,370**
608-263-7364

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.

237. *IR Spectroscopy of Organic Free Radicals Important in Combustion Processes*

Weisshaar, J.C. **$90,000**
608-262-0266

The primary long-term goal of this work is to develop new techniques for measuring vibrational spectra of polyatomic neutral free radicals. Such spectra would help the development of laser diagnostics for combustion kinetics research. A variation of resonant two-photon ionization (R2PI) will use tunable xIR to excite the radical vibrationally and xUV to selectively ionize only the vibrationally excited molecules. The spectroscopic problem of internal rotation of methyl and silyl groups attached to aromatic rings is another topic under active investigation. Internal rotors present tractable examples of non-covalent interactions that determine the energetics of different molecular conformations. Such rotors also accelerate intramolecular vibrational redistribution and alter photochemical pathways. Experiments have resolved internal rotor states in parent cations of aromatic molecules for the first time. Two-color resonant two-photon ionization (R2PI) with x1 tuned to various S1-S0 bands, x2 scanned, and detection of the electrons formed by pulsed field ionization (PFI) provides cation-S1 spectra with $\sim 2\ cm^{-1}$ resolution. The relative intensities of transitions to the 3a1″ and 3a2″ rotor levels reveal the sign of V6 (sixfold barrier height) and thus the conformation of minimum energy. Thus far, all measured values of V6 are small in magnitude. In all the *neutral* states studied thus far, including S0 p-fluorotoluene and S1 toluene, p-fluorotoluene, and phenylsilane, the conformation of minimum energy is staggered V6 < 0). In the corresponding cations, the minimum is eclipsed (V6 > 0). Computational work shows that modest *ab initio* calculations typically make a clear prediction of the minimum energy conformation and yield new insights into the nature of the intramolecular forces.

Atomic Physics

California Institute of Technology
Pasadena, CA 91125

Division of Physics, Mathematics, and Astronomy

238. Spectroscopy with Nonclassical Light
Kimble, H.J. **$99,000**
818-395-8340

A research program is proposed to investigate the radiative interactions of simple atomic systems with light which is manifestly quantum or nonclassical in its characteristics. Examples of nonclassical radiative fields include squeezed states of light and states which exhibit photon antibunching and subPoissonian 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 subPoissonian 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.

California State University, Fullerton
Fullerton, CA 92634

Department of Physics

239. Few-Body Coulomb Systems
Feagin, J.M. **$61,110**
714-773-3366

The semiclassical Wannier theory of threshold three-body Coulomb breakup from second to fourth order in internal coordinates including full angular momentum coupling has been extended. An asymptotic solution of the resulting coupled differential equations in six unknowns for large interelectronic separation and small excess system energy has been constructed. A correction to the Wannier threshold index which is linear in E has been obtained and shows that the Wannier threshold law dominates the cross section to at least a few eV above threshold. The resulting square-integrable wavefunction in the internal coordinates permits a realistic prediction of the momentum distribution of the outgoing particles. In addition, new complex-coordinate techniques have been used to derive corrections to the cross section that give agreement with experiment up to 8 eV above threshold. The formalism is being applied to an analysis of angular distributions. In a related project, numerically propagated two-electron wavepackets in helium and H^- in time have been used to develop a proper representation of the Coulomb singularities and the long-range boundary conditions. The approach allows broad application. Besides three-body breakup, the characteristics of an impurity atom in a quantum wire as well as the response of a hydrogen atom to an intense electric field have been examined.

Clark Atlanta University
Atlanta, GA 30314

Department of Physics

240. Studies of Photon and Electron Interactions with Atoms and Ions
Msezane, A.Z. **$97,038**
404-880-8663

Photon and electron interactions with ground and excited atoms and ions of importance in lasers, astrophysical, and laboratory fusion plasmas are studied using the R-matrix method and the NIEM Program of Henry et al. to understand the underlying physics and to guide measurements. Extensive configuration interaction target wave functions that take into account correlation and core-polarization effects are used to calculate integral and differential cross sections. Detailed multistate photoionization calculations are performed for excited states from innershell to investigate and understand the recent predictions and experimental measurements of strong enhancement of shake-up satellites and many-electron effects in sodium and potassium. Rigorous bounds were used to investigate the limiting behavior of the generalized oscillator strength as the momentum transfer squared approached zero to establish the limit theorem and to obtain an expression to normalize experiments. The analytic properties of the electron differential cross sections in the complex K-plane together with Pade Approximations are used to recompute inelastic and elastic cross sections and optical oscillator strengths.

University of Colorado
Boulder, CO 80309

Department of Physics

241. Physics of Correlated Systems
Greene, C.H. **$101,904**
303-492-4770

Several nonseparable or correlated atomic systems are being studied using theoretical quantum mechanics. This research attempts to understand the behavior of open-shell atomic systems in regimes that are not readily handled by conventional theoretical methods. This project started with photoionization calculations for some open shell atoms belonging to the fluorine and carbon groups of the periodic table. This effort progressed far enough to permit a highly detailed treatment of scandium, the lightest transition metal atom, which shows some features common to all heavier open shell atoms. A collaborative project is also underway to sort out the physics of very high two-electron excitations of the alkali negative ions. Studies will continue on these strongly correlated ions, and other two- and three-electron species that continue to pose extreme difficulties for atomic theory.

University of Connecticut
Storrs, CT 06269

Department of Physics

242. *Experiments in Ultracold Collisions*
Gould, P.L. **$89,169**
203-486-2950

The goal of this project is to investigate atomic collisions at extremely low energies (i.e., temperatures below 10^{-3} K). Such collisions exhibit several unique features: large collisional de Broglie wavelength, sensitivity to interatomic potentials at long-range, and the possibility of spontaneous decay during the course of the slow collision. Applications of laser cooling require an understanding of the collision since they are an important loss mechanism for high density samples. Ultracold atoms are prepared using laser cooling techniques. Rubidium atoms are cooled, compressed, and confined in a magneto-optical trap using diode lasers. Inelastic collisions which convert internal energy into kinetic energy are observed by measuring the ejection rate of atoms from the trap. Properties of the trap (e.g., restoring force) and the trapped sample (e.g., temperature and excited-state fraction) are being investigated as these are required in the interpretation of collision experiments. Current efforts are attempting to elucidate the rôle of excited-state hyperfine structure in these collisions and to measure the temperature dependence of the collisional rate. Experiments are also under way to directly detect, via state-selective ionization, products of specific collisions such as those which change hyperfine state of fine-structure state. Experiments involving collisions of cold atoms in highly excited Rydberg states are also planned.

243. *Plasma Density and Field Effects on Atomic Reactions*
Hahn, Y. **$84,955**
203-486-4469

A systematic theoretical study of the plasma environmental effects on atomic collision rates for high temperature fusion plasma is carried out. The atomic reaction rates modified by the plasma field are needed in plasma modelling and diagnostics. A comprehensive theory of spectral intensities and broadening has been formulated, based on the conventional pressure broadening theory and the rate equation approach. It involves three main steps: (a) An effective plasma potential $V_p(t)$ is constructed which contains all the 'slow' part of the plasma perturbations and depends explicitly on the plasma parameters, such as the plasma density and temperature. (b) The ionic states distorted by V_p are generated, in the quasi-adiabatic approximation, and the various atomic rates of the 'fast' perturbations are evaluated using these distorted states. (c) Finally, a set of discrete-continuum form of coupled rate equations is constructed, which provides the population density of ionic excited and charge states. The theory is being applied in detail to the hydrogen plasma, and will be extended to include impurity ions such as C, Si, and Fe. In the course of this study, a phenomenon of momentum coherence effectwas discovered, in which the time dependent external field can coherently interfere with moving electrons to enhance rates of processes in which they participate. The experimental consequences of such enhancement are being estimated, and its possible application to the tokamak divertor cooling problem is being addressed.

Cornell University
Ithaca, NY 14853

Nuclear Science and Engineering Program

244. *Interactions of Highly Charged Ions with Atoms at keV Energies*
Kostroun, V.O. **$300,000**
607-255-4991

The goal of this experimental project is to investigate interactions between very highly charged ions and atoms at kinetic energies characteristic of controlled thermonuclear fusion and astrophysical plasmas. The fundamental processes studied include single, double, and multiple electron capture by the projectile, target ionization, and de-excitation of the highly excited projectile states formed in collisions. The data obtained are useful for modeling plasma behavior and contribute to a general understanding of atomic collisions. Of particular interest are Ar^{q+} ($8 \leq q$ 16) on H_{2t} He and Ar collisions at 30 to 100 qeV incident energy. The highly charged argon ions are produced by the Cornell superconducting solenoid, cryogenic electron beam ion source, CEBIS. Ions extracted from CEBIS are charge selected, decelerated to low energies, and crossed with a gas target. Angular distributions of scattered projectiles associated with definite Q values, (changes in the total kinetic energy of the collision system that accompany electron capture) together with high resolution ($\Delta E/E = 0.005$) projectile energy gain spectra, measured at different scattering angles are used to unravel the details of the collision. Investigations of fundamental interactions are accompanied by precise measurements of total and partial cross sections for various processes.

Georgia Institute of Technology
Atlanta, GA 30332

School of Physics

245. Statistical Fluctuations in Lasers

Roy, R. **$90,117**
404-894-5265

Previous experiments on the phase-locking of Nd lasers with overlapping electric fields have been extended to obtain a significant new result—the synchronization of intensity fluctuations of two chaotic lasers. These novel experiments may have future applications to encoding signals in a background of chaotic fluctuations followed by real time decoding at the receiver. The synchronization of lasers at a distance and multiple element laser arrays will be studied in the near future. A series of careful experiments have has been performed to trace the evolution of pump waves and sidebands generated due to nonlinearities in an optical fiber. These waves interact through multiple four-wave-mixing processes and can exchange power with each other in a variety of simple periodic and complex patterns of spatial evolution. the role of stochastic processes on the power exchange has been examined, and the emergence of a stable spectrum with propagation has been found, contrary to predictions of conventional models. Experiments on an erbium doped fiber laser are in progress and the standard deviation of the intensity fluctuations of the laser have been measured as a function of pump excitation and display a rapid growth above threshold. Atom-atom interactions may play an important role in the destabilization of the macroscopic intensity of the laser light.

Harvard University
Cambridge, MA 02138

Harvard-Smithsonian Center for Astrophysics

246. Theoretical Investigations of Atomic Collisions

Dalgarno, A. **$135,800**
617-495-4403

Collisions at ultralow temperatures are under study. Cross sections have been calculated for the collisions of lithium atoms and of sodium atoms. The extreme sensitivity of the cross sections to the details of the interaction potentials has been demonstrated. The influence of the retardation corrections on the dispersion forces has been explored. Methods for determining long-range forces between ions and their parent atoms have been developed and applied to resonance charge transfer in ion-ion collision. An interesting oscillation structure in the variation of the cross sections with energy was found. Two-electron photoionization has been explored and cross sections obtained at threshold energies. Various multiphoton processes are also being investigated.

Kansas State University
Manhattan, KS 66506

Department of Physics

247. Atomic Physics of Strongly Correlated Systems

Lin, C.D. **$147,000**
913-532-1617

This project is aiming at the understanding of Coulomb three-body systems in atoms and molecules, including excitation and rearrangement collision processes. Using hyperspherical coordinates the photoabsorption spectra of helium atoms to highly excited states have been accurately calculated and photoabsorption spectra from the metastable states of helium have been predicted. The positronium formation cross sections in positron-hydrogen atom collisions have been calculated in the Ore gap. Electron capture cross sections from oriented circular and elliptic Rydberg states are also calculated. The latter were obtained using two-center atomic orbital expansion method and propensity rules for electron capture processes in ion-atom collisions have been derived, which are used to interpret experimental results from collisions with Rydberg atoms.

248. Atomic Physics with Highly Charged Ions

Richard, P. **$1,509,320**
913-532-6783

This project investigates the physics of collisions of highly charged ions with neutral gases, surfaces, clusters, electrons, and ions. The goal of the project is to elucidate the underlying processes for electron capture, ionization, and excitation in such collisions and to explain spectral features from the decay of ions and atoms so produced. Accelerated highly charged ions of a wide range of charge state and species up to Xe^{46+} are produced from a cryogenic electron beam ion source (CRYEBIS) and a tandem-LINAC accelerator. The ion velocities range from 0.1 to 20 a.u. Quantities measured include electron spectra, including both continuum and Auger electrons; momentum transfer spectra, obtained from angular scattering of the projectiles and from the recoil ion momenta; and charge state mass distributions of both projectile and recoil. Cross sections differential in all of the above quantities are measured and interpreted. The range of targets has now been expanded to include systems with structural characteristics ranging well beyond neutral atoms. For example, electron capture from laser-excited Rydberg targets is being pursued, which will allow the study of electron capture by highly charged ions at velocities from below to well above the velocities of the active targets electrons. A new ion-ion collision facility is under construction which will be used to study electron transfer between highly charged ion and multiply charged targets. Collisions of highly charged ions with fullerene (C_{60}) targets, which are intermediate between macroscopic surfaces and atomic targets, are being studied. Particular mechanisms recently emphasized include diffraction effects on continuum electron production in the scattering of quasi-free electrons by multiply-charged non-Coulombic ion potentials, and the role of hard electron-electron collisions in excitation and ionization of highly charged beam ions by light targets. In addition, the mass and charge distribution of molecules dissociated by fast ions are under investigation. All of the above collisions are part of a joint theoretical-experimental study, and the results of the experiments are used to help guide the development of detailed theoretical frameworks for description of the collision processes.

University of Kansas
Lawrence, KS 66045

Department of Chemistry

249. Atomic Physics in Strong Fields
Chu, S.-I. **$89,240**
913-864-4094

New nonperturbative theoretical formalisms and accurate computational methods are being developed for ab initio comprehensive investigation of intense-field multiphoton and nonlinear dynamical processes of current significance. The following projects are being studied (1) Development of a new complex-scaling generalized pseudospectral method for the treatment of (a) multiphoton detachment of H^- in strong laser fields and (b) laser-induced chemical bond "hardening" and "softening" and stabilization of small molecules in intense laser fields, a novel high-intensity phenomenon uncovered recently. (2) Development of time-dependent propagation method in the "interaction" representation for the study of multiphoton and above-threshold ionization of atoms and stabilization of negative ions in intense short laser pulses. (3) Relativistic generalization of Floquet theory for the treatment of atomic processes in superintense laser fields.

University of Kentucky
Lexington, KY 40506

Department of Physics and Astronomy

250. The Coherent Evolution of Weakly Bound States in Collisions and Fields
Cavagnero, M.J.; **$101,850**
Harmin, D.A.
606-257-6733

The dynamics of weakly bound atomic electrons subjected to time-dependent electric and/or magnetic fields is investigated. A theory is being developed of the fundamental atomic processes which underlie the experimental technique of Rydberg state detection known as selective field ionization. This study involves interference effects associated with the coupling of overlapping Stark manifolds. Its analysis involves the solution of the time-dependent Schroedinger equation using a novel kicked-interaction approach. A second investigation centers on the mixing of Rydberg states by the electromagnetic field produced by an ion in a collision process. This problem has been formulated in terms of a Floquet analysis similar to that used in the calculation of atomic transitions in strong laser or microwave fields.

251. Coherent Excitation of Autoionizing Resonances
Martin, N.L.S. **$77,600**
606-257-5840

(e,2e) spectroscopy is being used to investigate fundamental interference effects in the electron impact ionization of atomic cadmium. For small scattering angles, these interference effects are due to the coherent excitation of J=0,1,2 autoionizing levels and continua. The experiments probe both the magnitude and phase of excitation amplitudes. Experiments carried out at small momentum transfer have shown that plane wave Born approximation calculations using pseudo-relativistic Hartree-Fock wavefunctions, which might be expected to describe accurately the ionization process under these conditions, incorrectly predict both the magnitudes and phases of these complex amplitudes. The experimental phase discrepancies are similar to other workers' calculated phase differences between the Coulomb-Born and Plane Wave Born approximations, and the experimental magnitude ratios are about a factor of two different from the calculated values. Experiments are now in progress to observe the interference effects at larger scattering angles. Measurements to date lead to the somewhat surprising conclusion that the plane-wave Born approximation predictions get better, rather than worse, with increasing scattering angle. It is found that more partial waves are required to describe the ionization process; calculations have been carried out for J=0 to 7. One interesting prediction of the Born calculations is currently being experimentally investigated: for a momentum transfer of 1 a.u. the octupole transition to the J=3 levels of the main autoionizing configuration should become comparable in importance to the dipole transition to the J=1 levels.

University of Louisville
Louisville, KY 40292

Department of Physics

252. Hydrogen Atom and Molecule Collisions
Kielkopf, J. **$81,500**
502-852-5990

The fundamental processes which occur during low energy collisions involving excited states of atomic hydrogen are being studied with optical, vacuum ultraviolet, and laser spectroscopy. The profile of Lyman-alpha, for example, is sensitive to both the simple binary interaction of excited neutral hydrogen atoms with another atom or a proton, and to many-body collisions in which several other atoms interact simultaneously with the radiator. Spectroscopic measurements are made of the cold, dark, neutral atomic gas which follows by a few microseconds the production of a plasma in high pressure molecular hydrogen with focused light from a Q-switched laser. The conditions in this source are determined by spectroscopic diagnostics, time-resolved imaging, and hydrodynamic models to permit an analysis of the Lyman-alpha profile. Studies of excited state interactions of hydrogen with other atoms are also under way. These include observations of the continua emitted during the half-collision that marks radiative dissociation of selected excited states in OH, and an analysis of the development of a population inversion and lasing following charge neutralization collisions of the negative hydrogen ion and positive metal ions.

Michigan Technological University
Houghton, MI 49931

Department of Physics

253. ***Theoretical Hyperfine Structure Constants for Transition-Metal Atoms and Ions***
Beck, D.R. **$65,212**
906-487-2019

Accurate values for properties of transition metal atoms and positive ions important for plasma diagnostics, catalysis, deep level traps in semiconductors, hydrogen storage, astrophysics, etc., are determined. Hyperfine structure which can exhibit large many body and relativistic effects are calculated. The theoretical treatment involves the development of relativistic configuration interaction algorithms, which just have become as robust as the nonrelativistic equivalents. This includes the development of an automated data preparation algorithm which enables porting data sets along isoelectronic series, to homologous states, including changes in J, with fair ease. Previously, accurate (>17% error) first order hyperfine constants, and energy differences (>0.075 eV error) for lighter transition metal Sc II, Y II and Zr II) states, whose independent particle results sometimes had the wrong sign, or energy errors as large as 1 eV were obtained. This year, heavier, more complicated species (V II and Nb II) were investigated and an exploration of second order effects (in La I) began. Agreement with experiment is good. Simultaneously, treatment of core-valence many body effects, were extended to improve accuracy.

University of Nebraska at Lincoln
Lincoln, NE 68588

Department of Physics and Astronomy

254. ***Dynamics of Collision Processes***
Starace, A.F. **$64,000**
402-472-2795

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 multi-photon detachment of negative alkali ions, low-energy electron alkali scattering, and collisional detachment of negative alkali ions. Emphasis will be 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.

University of Nevada at Reno
Reno, NV 89557

Department of Physics

255. ***Screening Resonances in Plasmas***
Winkler, Peter **$44,581**
702-784-6792

The study of plasmas consisting of positive atomic ions and electrons as well as of the atomic processes which happen under plasma conditions is of particular interest for technological applications in materials sciences, computer chip design, fusion energy research, and also for astrophysical research. The present project focusses on the modifications that occur in atomic processes due to the plasma environment. The force between the charged particles is known to be significantly modified because of short-range order effects and static and dynamical screening potentials. 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 are the cause of plasma losses). As an extension of the usual Debye-Hueckel treatment of plasma screening, simulations of the complicated conditions in a real plasma have been performed employing approximate plasma models of various degree of sophistication. In previous research periods the existence of low-lying electron scattering resonances has been established for static plasma models. During the present period this research is mainly concerned with the extension to stochastic fluctuations of the plasma. This step takes the plasma model one step closer to the true conditions. The two most typical features of plasmas—the lowering of the continuum threshold and the line-broadening—have been included in one and the same model that leaves room for further extensions, e.g., the inclusion of non-spherical effects. The stochastic effects are presently evaluated and compared to both results from elaborate molecular-dynamicscalculations and of experiments. The comparison to other theoretical methods is valuable because here one has full control of the prevailing plasma conditions. In comparison to experimental studies the determination of the plasma parameters depends in part on the particular theoretical model with which plasma diagnostics is being perfomed, i.e., one of the main objects of the present research is involved right from the start. A fully self-consistent solution is being pursued.

University of New Mexico
Albuquerque, NM 87131

Department of Physics and Astronomy

256. ***H^- Spectroscopy***
Bryant, H.C. **$121,250**
505-277-3044

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 this 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. This extensive data set is currently under analysis. An experiment to study excess photon detachment of electrons from H^- using a 35 keV beam at Los Alamos is currently being designed and built. In this experiment, a seeded YAG 1.06 pulsed laser beam is focussed on the H^- beam and the energy spectrum of the detached electrons observed. A series of energy peaks, separated by the energy of a single light quantum, are expected to appear. An experiment 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 and using this same apparatus is being planned. Design work is proceeding for a 400 MeV H^- beam at Fermilab which will allow the continuation of the high energy work begun at LAMPF. Planning is also underway for a collaborative study of two-electron systems on the U8 beam line at the Advanced Light Source at Lawrence Berkeley Laboratory.

City College of New York
New York, NY 10031

Department of Physics

257. *Molecular Structure and Collisional Dissociation*

Becker, K.H. **$85,000**
212-650-5613

Electron collision techniques are used to probe the structure and the collisionally induced break-up of various technologically important species. Electron-impact ionization and dissociative excitation and ionization of (1) tungsten hexafluoride, sulfur hexafluoride and of the free radicals WF_x and SF_x (x=1-5) which play an important role in the plasma etching of tungsten and tungsten silicide films by SF_6-containing feedgas mixtures, of (2) BCl_3 and BCl which play an important role in the etching of Al, Al_2O_3 and III-V compounds, and of (3) various other chlorine-containing molecules and radicals which are used in the processing of Si, SiO_2, GaAs, GaAlAs and other Ga-based compounds will be studied. The results from these studies will provide information regarding the structure and the collisionally induced break-up of various technologically relevant species in the area of plasma-assisted materials processing.

University of Notre Dame
Notre Dame, IN 46556

Department of Physics

258. *Rydberg States in Multiply Charged Ions*

Livingston, A.E. **$71,683**
219-239-7554

The excitation, structure, and decay characteristics of highly charged ions in Rydberg states are investigated using excitation of energetic heavy-ion beams. Spectroscopy of excited atomic transitions is applied in the visible to the extreme UV wavelength regions to provide access to a wide range of selected atomic states in highly ionized atoms. Experiments are in progress to determine the structures of Rydberg states in high-Z beryllium-like ions. The measurements are supported by multiconfiguration Dirac Fock calculations. These studies reveal the effects of configuration mixing perturbations and core polarization contributions in the higher angular momentum (L) Rydberg levels. The measured highest-L structures also provide tests of new relativistic many-body perturbation theory calculations for highly excited states. Additional experiments are planned for the measurement of high-l Rydberg transition wavelengths in other ions for improving the accuracy of ionization energy values and for establishing reference wavelengths.

Pennsylvania State University, Lehman
Lehman, PA 18627

Department of Physics

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

Winter, T.G.; Alston, S.G. **$70,810**
717-675-9278

Theory is used to study electron transfer and ionization for intermediate- and higher energy ion-atom collisions. At intermediate energies (e.g., proton energies of about 100 keV), many electronic states are usually strongly coupled, and coupled-state approaches are then required. Recently, electron transfer and ionization from the K shell of neon have been treated using a coupled-Sturmian-pseudostate approach; the calculated cross sections agree well with experimental results. Secondly, as a more exacting test of theoretical methods, differential cross sections for electron transfer as well as elastic scattering in collisions between protons and singly ionized helium have been determined using both (double-center) Sturmian-pseudostate and triple-center approaches; the agreement between the two sets of results is outstanding for all energies and scattering angles. For charge-asymmetric systems at intermediate energies, a channel-distorted expansion of the single-electron capture amplitude in the strong potential gives cross sections in good agreement with experiment and with the above noted coupled Sturmian results. Applications of a second-born treatment at higher energies have revealed novel two-center interference effects superimposed on an atomic-like Thomas double-scattering peak in the differential cross section.

Rice University
Houston, TX 77005

Department of Space Physics and Astronomy

260. *Quantum Properties of Strongly Magnetized Plasmas*
Weisheit, J.C. **$65,000**
713-527-4654

The goal of this research program is to study effects of intense magnetic fields on atomic quantities, such as electronic structure, transition rates, and lineshapes, that are needed to determine quantum transport coefficients and equations of state. Strong fields ($B > 10^7$ Gauss) arise in a variety of transient laboratory environments, z-pinches, many laser-produced plasmas, and even some chemical explosions as well as certain kinds of stars. In work to date, which has focused on the structure of many-electron atoms and ions in high magnetic fields, the point of departure is Kadomtsev's generalization of the Thomas-Fermi equation. A nonlinear, second-order partial differential equation for the charge density n(r) has been derived; correct axial symmetry is imposed at the onset by way of a partial factorization ansatz for n(r). Numerical results have been obtained for helium and carbon atoms in megagauss to gigagauss fields. Computed charge densities exhibit features consistent with earlier, heuristic predictions and with published hydrogenic distributions. Use of a virial theorem for matter in strong fields enables atomic binding energies to be computed, too. Deformed atoms are much more tightly bound that those described by Kadomtsev's spherical model.

University of Rochester
Rochester, NY 14627

Department of Physics and Astronomy

261. *Study of Atoms Exposed to Intense Laser Pulses*
Eberly, J.H.; Meyerhofer, D.D. **$116,400**
716-275-3288

High-intensity laser–atom interactions are studied both theoretically and experimentally. Theoretical work will use supercomputer solutions of Schrodinger's wave equation to predict the behavior of atoms and electrons in intense laser fields. The wave functions obtained will be used to study multiphoton ionization. The calculations will focus on short-pulse laser fields similarly strong as those employed in the experimental program. The principal experimental tool is the Table Top Terawatt laser system, which has recently been upgraded to produce intensities in excess of 10^{18} w/cm^2 at a wavelength of 1μm. The ionization of atoms and ions in these intense fields will be studied, as will the effects of laser pulse duration and temporal shape on the ionization mechanisms.

University of Southern California
Los Angeles, CA 90089

Department of Physics and Astronomy

262. *Amplitude Modulation of Atomic Wavefunctions*
Cooke, W.E. **$89,240**
213-740-1128

This project will use a novel laser excitation method in conjunction with the electron–electron interaction in a multielectron atom to modulate the electronic wavefunction of a single electron within an excited atom. Using this method, bits of digital information can be stored within a single atom. This project will (1) provide experimental confirmation of this process, (2) investigate various ways to retrieve the stored information, and (3) explore the limits of the information storage capacity. These novel wavefunctions are expected to have significant effects on other radiative processes that should be important for the development of new coherent radiation sources, and this project will also explore these radiative effects.

263. *Behavior of Atoms in a Strong Radiation Field*
Shakeshaft, R. **$100,880**
213-740-7888

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., He and H^-, are of primary interest. Among the processes being explored, two are of special interest: double ionization and stabilization is challenging not only because of the importance of electron-electron correlation, but also because the boundary conditions for two-electron escape are complicated. The stabilization of a one-electron atom against ionization can occur in a strong high-frequency field, at least within the dipole approximation. However, it is not yet known to what extent stabilization persists when correlation in a two-electron atom, and corrections to the dipole approximation, are included.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Physics and Astronomy

264. *The Production and Destruction of Metastable Negative Ions*
Pegg, D.J. **$97,000**
615-974-7831

The structure of few-electron atomic negative ions and the manner in which they interact with electromagnetic radiation via the process of photodetachment are investigated. The primary motivation for the work is to gain an understanding of the role of correlated electron motion in atomic structure. The work also has a potential application in areas involving cold plasmas such as those used in the processing of materials. Thus far, the negative ions of the first six elements of the periodic table have been studied. A crossed laser-ion beam apparatus is used to make energy- and angle-resolved measurements on 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 the first investigation of the angular distribution of photoelectrons detached from the excited negative ion of carbon and the first observation of a Feshbach resonance in the cross section for the photodetachment of the negative ion of lithium. The resonance is associated with the autodetaching decay of the doubly-excited (3s3p)3P state of the ion.

University of Texas at Austin
Austin, TX 78712

Department of Physics

265. *State-to-State Energy Transfer in Atomic Collisions*
Keto, J.W. **$116,400**
512-471-5029

Rare gas excimers dissociating to Xe*(5d) and Xe*(6p) were studied in supersonic beams. Bound states of these excimers were previously observed in supersonic jets using two-photon resonance photo ionization but the spectra could not be assigned. Experiments just completed to observe the bound-free fluorescence spectra of laser selected states of the excimers have shown that these states predissociate to Xe*(6s[1/2]$_1$) at avoided crossings with the O$_g$+ repulsive potential. Fluorescence observed in gas cells must result from different molecular configurations. Measurements of state-to-state energy transfer rates for Xe*(5d,5d$'$) states in collisions with other rare gases are being pursued. These results are relevant to kinetic models of 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*(5d) could only be indirectly observed. These states only fluoresce in the far infrared, where detectors are too slow for studies of dynamics. Experiments are now being attempted to observe the dynamics of states of Xe*(5d) using two-color, pulse-probe laser induced fluorescence.

University of Toledo
Toledo, OH 43606

Department of Physics and Astronomy

266. *Semiempirical Studies of Atomic Structure*
Curtis, L.J. **$67,000**
419-537-2341

The goal of the project is to develop a precise, comprehensive, and reliable base of atomic structure data for complex atomic ions through the use of precision experimental measurements, sensitive semiempirical data systematizations, and specialized theoretical computations. The properties studied involve both primary data (wavelengths, frequency intervals, relative intensities, production and decay rates, etc.) and derived structural parameters (energy levels, ionization potentials, electric polarizabilities, lifetimes, transition probabilities, excitation functions, etc.). Measurements are made primarily through the use of fast ion beam excitation methods, which are combined with available data from laser- and tokamak-produced plasmas, astrophysical observations, and conventional light sources. Large blocks of data are systematized and parametrized along isoelectronic, homologous, isoionic, Rydberg, and yrast sequences and series. Examples of investigations conducted during the past year include (1) experimental lifetime measurements in very heavy ions such as Hg II and III, Au II, and Y III; (2) predictive systematizations which combine energy level and lifetime data to comprehensively specify transition probabilities for resonance and intercombination transitions in the Zn, Cd, and Hg sequences; (3) the development of a technique for branching ratio measurements in highly ionized atoms using efficiency-calibrated X-ray detectors; and (4) the use of simultaneous multiplexed measurement of decay curves to determine relative lifetimes to high precision.

267. *Negative Ion–Atom Collisions*
Kvale, T.J. **$63,883**
419-537-2980 **(18 months)**

The motivation in this series of measurements involving fundamental negative ion - atom systems is to provide increasingly stringent tests of the understanding of intermediate energy, ion - atom collisions. Absolute measurements of total cross sections for both the single- and double-electron detachment processes occurring in intermediate energy collisions between H$^-$ ions and the target atoms of helium, neon, and argon were submitted for publication this year. In those measurements, the secondary emission coefficient γ for energetic H^0 atoms striking a copper surface in the neutral detector was observed to be slightly target species dependent. A preliminary explanation of this effect may involve the population of excited H^0 states and a series of experiments are planned to study this effect. Having completed electron detachment total cross section measurements, the current experiments are the H$^-$ ion energy-loss spectroscopy measurements for the direct target excitation and ionization processes in which H$^-$ survives the collision. To date, there are no other measurements or theoretical calculations for these inelastic processes in these collision systems in intermediate energy region. Modifications to the accelerator for the angular differential cross section (ADCS) measurements are also in progress and work toward their implementation will continue this year.

Tulane University
New Orleans, LA 70118

Department of Physics

268. *Few Electron Transitions in Atomic Collisions*
McGuire, J.H. **$60,140**
504-865-5520

Describing reactions involving more than one electron requires information about the dynamics of few-electron phenomena, i.e., information required to describe how relatively complex many-body systems change. Theoretical techniques for calculating cross sections for multi-electron processes have been developed, which may be used to probe mechanisms for the dynamics of multi-electron effects. One method uses a Born expansion in the projectile interaction strength, Z_p, and incorporates all terms in the electron-electron interaction. The leading term in Z_p is reduced to a closed analytic form. The second order term is expressed as a one dimensional energy integral over a product of two off-energy-shell first order amplitudes, and so on. This method has been used to calculate cross sections for double excitation of helium to the n = 2 levels of helium by the impact of protons, ions, electrons and antiprotons. Cross sections have been analyzed for ionization plus excitation by charged particle impact in helium. Many body perturbation theory has been used to calculate cross sections for double and single ionization in helium by photon impact. Preliminary calculations for two electron transitions in collisions of charged particles with molecules have also been performed.

Vanderbilt University
Nashville, TN 37235

Department of Computer Science

269. *Theoretical Studies of Atomic Transitions*

Fischer, C.F. **$141,000**
615-322-2926

Atomic structure calculations are being performed to predict properties such as energy levels, binding energies, transition probabilities, lifetimes, hyperfine structure, isotope shifts, and photoionization cross-sections. Accurate computational procedures are being devised so that properties can be predicted even when they cannot be obtained from experiment, and to assist in the identification of observed data. The method used is the multiconfiguration Hartree-Fock (MCHF) method, optionally corrected for relativistic effects in the Breit-Pauli approximation. Fully relativistic Dirac-Fock calculations also are performed using the GRASP code. Recent calculations have stressed the application of systematic procedures which allow an estimate of the uncertainty in a predicted result. Intercombination lines have been investigated in C III and C II in the Breit-Pauli approximation. Results for C III were checked using GRASP and extended to the isoelectronic sequence. Accurate isotope shift and hyperfine structure in Boron (B II) have been reported. Also under development are new algorithms using spline basis methods suitable for cases such as highly interacting Rydberg series where the above procedures do not perform well.

University of Virginia
Charlottesville, VA 22901

Department of Physics

270. *Studies of Autoionizing States Relevant to Dielectronic Recombination*

Gallagher, T.F. **$113,185**
804-924-6817

This program is focused on studies of two electron processes in excited atoms. Examples of practical importance are dielectronic recombination in fusion plasmas and the use of doubly excited states in short wavelength lasers. The approach employed is 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. Recent measurements of the spectra in electric fields of doubly excited states converging to the well separated $6p_{1/2}$ and $6p_{3/2}$ limits of Ba^+ show that, contrary to expectation, the observed spectra can be described by a theory based on channels interacting only through a single continuum, with excitation to only one channel. In contrast, in Mg, in which the $3p_{1/2}$ and $3p_{1/2}$ Mg^+ limits are close together, no such simple picture describes the spectra in electric fields. Finally, time resolved excitation from the singly excited Mg 3snd to the doubly excited 3pnd state has shown that the observed spectrum depends strongly on the spatial location of the spectator nd electron.

Western Michigan University
Kalamazoo, MI 49008

Department of Physics

271. *Near Threshold Excitation and Ionization of Open-Shell Atoms*

Berrah, N. **$97,000**
616-387-4955

The objective of this research is to probe fundamental processes of atomic structure and the dynamics associated with the interaction of synchrotron radiation with open-shell atoms. The research aims at investigating, in atomic innershells, many-body effects due to the electron–electron interaction. Near-threshold photoexcitation-photoionization experiments will be performed to study electron correlation satellites in rare gases first and then open-shell atoms. Quantitative studies of such processes are expected to yield important information about interaction mechanisms, providing benchmarks for developing theoretical models. Current activities are focused on investigating electron correlations in rare gases, and in particular in He. Measurements of double to single ionization between 280 and 1210 eV have been performed at the BESSY synchrotron facility. These measurements when compared with the most recent calculations show the importance of initial-state correlations and final-state correlations.

272. *Correlated Charge-Changing Ion–Atom Collisions*

Tanis, J.A. **$97,970**
616-387-4941

Experimental investigations of fundamental 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 occurring in atomic collisions, and, additionally, the determination of whether the two electrons act independently of one another or if the electron-electron interaction is important. This work centers around three general areas of investigation: (1)

emission of electrons along the beam direction and traveling 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 X-ray emission, recoiling target ions, or electrons. Measurements are conducted using accelerators at Western Michigan University, Indiana University, Lawrence Livermore Laboratory, Michigan State University, and the Institute of Nuclear Research, Debrecen, Hungary. Work at Kansas State University is planned.

The College of William and Mary
Williamsburg, VA 23187

Department of Physics

273. *Negative Ion Detachment Cross Sections*

Champion, R.L.; **$119,113**
Doverspike, L.D.
804-221-3510

The goal of this research project is to develop an understanding of the collisional dynamics of systems in which negative ions collide with atoms and well-characterized surfaces and their adsorbates. The current experimental studies are designed to investigate both gas-phase, two-body collisions as well as the mechanisms that are associated with the collisionally induced desorption of negative ions and electrons from surfaces. The collision energies for these experiments range from a few electron volts up to several hundred electron volts. Cross sections for collisional and associative electron detachment, charge transfer, and negative ion–molecule reactions are currently being measured for collisions of O^-, S^-, and halogen anions with ozone. Future studies will include observing collisions of negative ions with atomic oxygen, chlorine and fluorine. Experiments to be performed will investigate the detailed dynamics of negative ion sputtering from surfaces and the related secondary electron emission resulting from the impact of atomic species with collisions energies below 500 eV. Both metallic and semiconductor surfaces are being studied. The role of sputtered negative ions, some of which subsequently autodetach, is currently being examined as a potential tool for surface analysis.

Chemical Energy

University of Arizona
Tucson, AZ 85721

Department of Chemistry

274. *A Model Approach to Hydrodenitrogenation Catalysis*

Wigley, D.E. **$109,107**
602-621-4118

Despite the importance of removing nitrogen from petroleum feedstocks to providing more processable and environmentally sound fuels, the mechanisms of these metal-catalyzed, hydrodenitrogenation (HDN) reactions are not well understood. The development of soluble, model compounds which simulate HDN substrate/catalyst interactions is continuing. Efforts are focusing on the polyaromatic heterocycles containing six-membered pyridine rings, prototypically quinoline and its derivatives, bound to high oxidation state early transition metal centers. Specifically, these studies have uncovered the following: (i) The first examples of C–N bond scission in $\eta^2(N,C)$-pyridine complexes by *alkyl migration* from a tantalum center to the Cα of an $\eta^2(N,C)$- pyridine ligand has been discovered. This result suggests the extent to which a metal can moderate C–N cleavage includes both substrate activation of the nitrogen heterocycle (leading to a reduced C–N bond order in the $\eta^2(N,C)$ binding mode) and *metal-mediated nucleophile transfer* to the substrate (leading to C–N scission). (ii) Since under industrial HDN conditions the heterocyclic ring is saturated before C-N bonds are cleaved, the development of new tetrahydroquinoline *amido* complexes like $\mathrm{Ta}[\eta^1(N)\text{-}\mathrm{C_9H_{10}N}]_4\mathrm{Cl}$ and $\mathrm{Ta}[\eta^1(N)\text{-}\mathrm{C_9H_{10}N}]_2(\mathrm{O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2})_2(\mathrm{CH_3})$ has been effected. These compounds will serve as precursors to $\eta^2(N,C)$ bound saturated heterocycles which constitute extremely accurate models of an HDN metal-substrate complex. These studies are significant in providing precedent for the long-standing, unresolved mechanistic problems in HDN catalysis concerning how the strong C–N bonds in heterocyclic compounds are cleaved.

Boston College
Chestnut Hill, MA 02167

Department of Chemistry

275. *High-Temperature Chemistry of Aromatic Hydrocarbons*

Scott, L.T. **$111,300**
702-784-6683

This work focuses on the fundamental molecular processes involved in the rearrangements and interconversions of polycyclic aromatic hydrocarbons (PAHs) at high temperatures. This year, an important and seemingly general new thermal transformation of simple PAHs has been discovered that shares several features with the production of fullerenes under high energy conditions, e.g., in flames. In this new transformation, exemplified by the conversion of chrysene to benzopyracylene, at least one benzene ring in the starting PAH is always ruptured, two new unsaturated five-membered rings are formed, the total number of rings increases, and the carbon/hydrogen ratio increases. In other recently completed experiments, a multi-step synthesis and detailed study of 13C-labeled pyracylene has unequivocally shown that this ring system does not undergo the 1,2-bond switching reaction at 1100 °C that has been suggested for pyracylenes embedded in fullerenes. The long-range objectives of this research are (1) to uncover all the principal reaction channels available to PAHs at high temperatures, (2) to establish the factors that determine which channels will be followed in varying circumstances, and (3) to use these high temperature reactions for the preparation of new and unusual PAHs.

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

276. Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds

Bercaw, J.E. **$143,972**
818-395-6577

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 recent 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. Racemic yttrocene and scandocene derivatives with linked cyclopentadienyl ligands have been prepared. The alkyl and hydride derivatives function as well-defined, single component, isospecific a olefin polymerization catalysts. Synthetic strategies to more active single component, isospecific catalysts are being developed. Well defined, syndiospecific catalysts are also being pursued. There has been very recent success in preparing a ligand capable of affording only one enantiomer of a chiral catalyst. Asymmetric catalytic transformations are being investigated with these optically active compounds. Moreover, polymerizations with racemic and optically active monomers are being examined to establish the enantiofacial preferences for olefin insertion reactions.

University of California, Davis
Davis, CA 95616

Department of Chemical Engineering

277. Characterization of Metal–Support Bonds in Supported Metal Catalysts

Gates, B.C. **$84,390**
916-752-3953

The goals of this research are to characterize structure, bonding, and catalytic properties of metal complexes and clusters of metals including Re, Ir, and Pt on the surfaces of MgO, γ–Al_2O_3, La_2O_3, and zeolites. Some of the metal oxide supports are high–surface area powders and some are thin layers on single crystals of Mo. The surface species are synthesized from organometallic precursors to give supported metal carbonyls, which are treated to form highly dispersed metal clusters. The surface species are investigated with EXAFS, temperature-programmed desorption, hydrogen chemisorption, infrared, Raman, and NMR spectroscopies; some experiments are done with ultrahigh vacuum techniques. Clusters as small and well defined as Ir_4 and Ir_6 have been formed on the supports, and the metal–support interface has been found to be characterized generally by a metal–oxygen distance of about 2.1 Å and a metal-oxygen distance of about 2.6 Å. The shorter distance is observed for all known metal subcarbonyls on metal oxide support interface. The longer distance is not a bonding distance; its presence is correlated with the presence of hydrogen in the sample. It may indicate the interaction of zerovalent metal atoms with oxygen ions with intervening hydrogen in the interface. Extremely small clusters of Tr and of Pt have also been prepared from salt precursors in zeolite L and used to catalyze η-hexane conversion; the results demonstrate connections between the samples prepared from organometallic precursors and those prepared conventionally.

University of California, Irvine
Irvine, CA 92717

Department of Chemistry

278. Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes

Evans, W.J. **$112,900**
714-856-5174

The objective of this research program is to investigate the special properties of complexes of yttrium and the lanthanide metals so that the chemical and physical properties of these inexpensive metals which are available in quantity in the United States can be optimally exploited. The research involves the synthesis of new classes of complexes, the determination of their ability to transform small molecule substrates into more valuable chemical products, and the development of new routes to energy saving materials which contain these metals. Recent studies of alkoxide-ligated yttrium and lanthanide complexes with alkylaluminum reagents have shown for the first time how these large metals can be combined with small ligands for form soluble complexes. In the past, such complexes containing these large metals and small ligands were either insoluble or unstable, and hence were not available for chemical transformations. Using aluminum or gallium reagents, stabilized forms of a variety of new metal ligand combinations can be accessed. The synthetic and structural information obtained so far suggests that these complexes will have interesting reactivity. In addition, the synthesis of these complexes represents a new route to molecular compounds containing various combinations of yttrium and the lanthanides with main group metals.

University of California, Riverside
Riverside, CA 92521

Department of Chemistry

279. ***Study of the Surface Chemistry of Hydrocarbon Radicalsand of Carbonium Ions on Metal Oxide Surfaces***

Zaera, F. **$137,000**
909-787-5498 **(15 months)**

In this project the surface reactions of saturated hydrocarbons on metal oxides are being studied by using a combination of surface sensitive techniques. The main long term goal is to obtain specific relations between the reactivity of the oxides and the structural details of their surfaces. Given that the main difficulty in pursuing this kind of research has proven to be the low probability for the initial dissociative absorption of the hydrocarbon molecules, that step will be bypassed by exposing oxide surfaces directly to species resembling those expected to form on the surface after activation, that is, to moieties in either radical or ionic states. The relevant metal oxide surfaces will be characterized, which are prepared either by cleaving oxide single crystals or by growing films in situ via the oxidation of metal surfaces under vacuum, using X-ray photoelectron spectroscopy (XPS), ion scattering (ISS), and low energy electron diffraction (LEED) in order to determine the stoichiometry, oxidation state of the constituent elements and degree of crystallinity of the solids. The chemistry of hydrocarbon moieties either in the form of radicals or as carbonium ions will later be studied on those oxide surfaces. Radicals will be prepared in one of two ways, either by thermal or photolytic excitation of suitable absorbed precursors (alkyl halides of azo compounds), or by direct pyrolytic decomposition of those precursors in the gas phase. The cationic species will also be made in the gas phase by ionizing hydrocarbon molecules, mass filtering the ions of interest, and decelerating them to low kinetic energies (1-10 eV). The species formed on the surface will be characterized by combining results from experiments using reflection-absorption infrared (RAIRS) and static secondary ion mass (SSIMS) spectroscopies, and the charge transfer between the absorbed moieties and the oxides will be measured directly by using XPS. Finally, the chemistry of these systems will be studied by using thermal desorption techniques.

University of California, San Diego
La Jolla, CA 92093

Department of Chemistry

280. ***New Molecular Precursors for Low-Temperature Routes to Oxide Materials***

Tilley, T.D. **$97,918**
619-534-6159

Advanced solid-state materials with useful properties increasingly involve intricate 3-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. The approach involves use of synthesis, coordination chemistry, and condensation reactions to build novel 3-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.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemical and Nuclear Engineering

281. *The Activation and Decomposition of Alkanes on Group VIII Transition Metal Surfaces: Dynamics, Kinetics, and Spectroscopy*

Weinberg, W.H. **$103,970**
805-893-8528

In this project, the dynamics and kinetics of molecular trapping, trapping-mediated activation, and direct dissociation of methane, ethane, propane, i-butane, and cyclopropane on the Ir(110)–(1 x 2), Ir(111), Pt(110)–(1 x 2), and Ru(001) surfaces will be studied. Both supersonic molecular beam scattering and "bulb" (microreactor) measurements will be made with evaluation of the reaction rates by mass spectrometry, Auger electron spectroscopy, and X-ray photoelectron spectroscopy. The rate coefficients of the elementary surface reactions (dehydrogenation, carbon–carbon bond cleavage, and hydrogenation with coadsorbed atomic hydrogen) will be quantified spectroscopically. The (vibrational) spectroscopies to be used are Fourier transform reflection-absorption IR and high-resolution electron energy loss spectroscopies. These results will provide a valuable quantification of both the reactivity and the selectivity of C–H bond activation for both trapping-mediated and direct dissociative chemisorption as a function of electronic and geometric structure within the Group VIII transition metals. During the past year, the kinetic rate parameters, preexponential factors and activation energies, for selective C–H, C–D,and C–C bond cleavage have been quantified on the Ir(III) surface for the molecules: di-1, 1-^{13}C-C_2H_6, C_2D_6, C_3H_8, $CH_3CD_2CH_3$, C_3D_8, n-C_4H_{10}, i-C_4H_{10}, i-$(CH_3)_3CD$, i-$(CD_3)CH$, and $(CH_3)_4C$. In addition, the activation of di-1, 1,$^{-13}$C-C_2H_6 at defect sites has been examined. It was found that C–H bond activation, with activation energies between 10.4 kcal/mol for ethane and 11.4 kcal/mol for higher alkanes, is favored by 0.44 - 0.63 kcal/mol over C–D bond activation for primary, secondary, and tertiary C–H (C–D) bonds. Selective activation of secondary and tertiary bonds is manifested by activation energies that are 300 cal/mol and 100 cal/mol less than for primary C–H bonds. The activation energy of carbon–carbon bond cleavage in C_3H_6 and $(CH_3)_2CD_2$ is 18.4 kcal/mol, but it is 19.1 in C_3D_8. In i-C_4H_{10}, and i-$(CH_3)_3CD$ the activation energy of C–C bond cleavage is 17.47, while for i-$(CD_3)CH$ it is 18.0 kcal/mol. In neopentane, C–C bond cleavage has a 16.1 kcal/mol barrier. The observed secondary kinetic isotope effect in C–C bond activation for these alkanes reflects the required bending deformation of the methyl groups to allow for the proper coordination of the surface Ir atom to the C–C bond.

Department of Chemistry

282. *Studies Relevant to the Catalytic Activation of Carbon Monoxides*

Ford, P.C. **$135,000**
805-893-2443

This research is concerned with quantitative investigations of fundamental metal complex reactions relevant to the homogeneous catalytic activation of carbon monoxide and other C_1 compounds. Among these are mechanistic studies of new carbonylation catalysts heterogenized on polystyrene based polymers and exploratory studies to apply water gas shift catalysts to the destruction of persistent pollutants. Also under study are applications of fast reaction techniques to prepare and to investigate reactive organometallic intermediates relevant to the activation of hydrocarbons toward carbonylation and to the formation of carbon–carbon bonds via the migratory insertion of CO into metal alkyl bonds. The goals are to delineate the fundamental principles of catalytic processes for the activation of C_1 compounds such as CO and of hydrocarbons and other substrates in order to establish guidelines for the design and engineering of new chemical systems for more efficient and environmentally friendly applications of energy and chemical feedstocks.

Carnegie-Mellon University
Pittsburgh, PA 15213

Department of Chemical Engineering

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

Ko, E. **$85,464**
412-268-3857

Sol-gel synthesis, along with supercritical drying, was used to prepare high-surface-area zirconia-silica aerogels with different molar ratios and varying degrees of molecular mixing. Because the two precursors, zirconium isopropoxide and tetraethylorthosilicate (TEOS), have very different reactivities (the former is more reactive), strategies were explored for minimizing their mismatch: (1) by prehydrolyzing TEOS, (2) by using tetramethylorthosilicate instead of TEOS, (3) by modifying the zirconium isopropoxide with acetylacetone (acac), and (4) by lowering the synthesis temperature from room temperature to 273 K. A series of zirconia-silica aerogels containing 5 mol% silica was characterized. The first finding was that even such a small amount of silica retarded the sintering of zirconia, as shown by increases in both BET surface area and pore volume over a temperature range of 373-1173 K. X-ray diffraction results showed that silica also delayed the transformations of zirconia from X-ray amorphous to tetragonal and tetragonal to monoclinic to higher temperatures. Matching precursor reactivity did improve homogeneity in these mixed oxide aerogels, as shown by specific activities of 1-butene isomerization. In sum, a positive correlation between molecular mixing and catalytic activity was established.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

284. Polyoxoanion-Mediated Methane Activation and Functionalization: Molecular Design of New Homogeneous and New Solid-State/Heterogeneous Catalysts

Finke, R.G. **$115,512**
503-491-6381

A primary goal of this research is to develop a chemical paradigm for polyoxoanion supported transition-metal catalysis, with an emphasis on small molecule (H_2, O_2, H_2O_2, CH_4) catalytic activation and functionalization (CH_4, RH). Again this past year, several projects were completed and the results published, specifically: (i) a patent recently issued on the oxidation of cyclohexene using the $[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ catalyst precursor and the preferred oxidant oxygen–the first bona fide polyoxoanion-supported catalyst system; (ii) also published were 3 papers describing the synthesis and characterization of the new polyoxoanions, $(1,5\text{-COD})Ir \cdot SiW_9Nb_3O_{40}{}^{6-}$,$Si_2W_{18}Ti_6O_{77}{}^{14-}$, and the all Na+ (and thus water-soluble) salt of $P_2W_{15}Nb_3O_{62}{}^{9-}$, plus a paper describing the use of fast-atom-bombardment mass spectroscopy to characterize massive polyoxoanions such as $P_2W_{15}Nb_3O_{62}{}^{9-}$. However, the most exciting development this past year was the discovery of reproducible size and reproducible activity Ir~ 300 and Ir~ 900 nanocluster catalysts that are stabilized by polyoxoanions such as $P_2W_{15}Nb_3O_{62}{}^{9-}$ and their associated Bu_4N+ counter cations. These new catalyst materials can be isolated and redissolved; this unusual property for nanocluster or colloidal catalysts, plus their high catalytic reactivity, offer many possibilities for new catalyst materials with potential applications in energy-related processes, manufacturing, or in energy-intensive environmental remediation.

285. Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylenes

Norton, J.R. **$115,537**
303-491-5609

It is known that olefin exchange with diosmacyclobutanes occurs through a ring-opened intermediate, with the leaving olefin coordinated to only one of the two osmiums. The product ratio, in the presence of fixed amounts of methyl acrylate and dimethyl fumarate, will be examined when the departing olefin is ethylene, propene, trans-2-butene, and isobutylene; a constant ratio will indicate a dissociative mechanism for exchange with the ring-opened intermediate, and a variable one an associative mechanism. Cationic osmium alkyl complexes $[Os(CO)_4R]^+$, and their dinuclear analogues $[Os_2(CO)_8R]^+$, will be prepared by protonating dialkyl complexes as well as olefin ligands; their reactivity toward olefins, acetylenes, and CO will be investigated. It appears that osmium is the kinetic site of protonation of $Os(CO)_4(C_2H_4)$, and the ethylene carbons are the thermodynamic site—a result that contrasts with that expected from the strength of the Os–H bond. The incorporation of cyclobutene into a diosmacyclobutane will also be attempted. The resulting ring system should be strained and may cleave into tethered monoosmium carbene complexes.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

286. Syntheses and Reactions of Pyrrole Complexes

DuBois, M.R. **$84,765**
303-492-5039

The objectives of the project are (1) to synthesize new transition metal pyrrole complexes and (2) to investigate how the metal ion coordination affects the reactivity of the heterocycle. An understanding of how coordinated pyrrole ligands might be activated toward reduction, ring opening, or nucleophilic addition reactions may provide a basis for understanding basic mechanisms of the hydrodenitrogenation catalysts. The characterization of p-cymene ruthenium(II) and osmium(II) complexes containing the tetramethylpyrrole or pentamethylpyrrole ligand have been completed. The complexes undergo stereoselective nucleophilic addition reactions which are directed by the charge of the pyrrole ligand. For example, the complexes $[(\text{p-cymene})M\text{-}(NC_4Me_4)]OTf$ (M = Ru, Os) underwent nucleophilic addition at the cymene ligand to form products with substituted η^5-cyclohexadienyl ligands. In contrast the complexes $[(\text{p-cymene})M(MeNC_4Me_4)](OTf)_2$ underwent nucleophilic addition at the α-carbon of the pentamethylpyrrole ligand. The resulting product when the nucleophile = hydride was characterized by an X-ray diffraction study and found to contain and η^4 non-planar nitrogen heterocycle. Further reaction of this product with protic acid led to further reduction and dissociation of the pyrrole ligand to form a cyclic iminium ion. Complexes of p-cymene ruthenium(II) containing indole or indolyl ligands have also been synthesized. Reversible conversion between coordinated indole and indolyl ligand has been effected by sequential addition of base and acid to the complexes. A comparison of bonding modes and reactivities of the indole and indolyl complexes is in progress.

Columbia University
New York, NY 10027

Department of Chemistry

287. Model Studies in Hydrocarbon Oxidation

Parkin, G. **$106,753**
212-854-8247

Research has centered on an investigation of the chemistry of molecular terminal oxo complexes with a view to providing results that are relevant to systems concerned with hydrocarbon oxidation. Transition metal complexes that contain terminal sulfido, selenido, and tellurido ligands have also been studied, since a knowledge of the chemistry of the heavier congeners of this group will help provide a more complete understanding of the chemistry of transition metal oxo complexes. For example, the first complete series of terminal chalcogenido complexes of the transition metals, $C_p{}^{Et+}{}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te), has been synthesized and structurally characterized.

University of Connecticut
Storrs, CT 06269

Department of Chemistry

288. *Synthetic Todorokite: Preparation, Characterization, and Applications*

Suib, S.L. **$82,000**
203-486-2797 **(15 months)**

The goals of this research program are to prepare, characterize, and study applications for synthetic todorokite materials. These materials are octahedral molecular sieve (OMS) systems consisting of manganese oxide octahedra linked by edges and vertices. The synthesis of a large pore 6.9 Å tunnel structure materials OMS-1 having the todorokite structure has recently been reported. The synthetic, thermal stability, acidity, adsorption, electrochemical, and oxidation catalysis properties of OMS-1 have recently been described in detail. Phase diagrams, transmission electron microscopy, surface studies, and bulk analytical spectroscopies have been used to characterize the OMS-1 material. The corresponding OMS material having the hollandite structure (OMS-2) has been synthesized by reflux methods which leads to a high surface area (up to 250 m^2/g) material with a 4.6 tunnel size that can be used in adsorption and catalytic applications. Both OMS-1 and OMS-2 materials are good electrical conductors and these systems have been investigated with cyclic voltammetry to understand more about the diffusion of cations in and out of these tunnel structures. Oxygen mobility occurs in OMS systems as evidenced by temperature programmed reduction, oxidation, and desorption studies. Cu, Ni, Co, and other transition metals can be substituted into the tunnels of these systems. In addition, substitution into framework sites may be done by incorporating transition metal dopants into the sol precursor which initially precipitates a layer structure (OL-1). Both the selective oxidation and total oxidation capabilities of the OMS materials are currently under investigation.

University of Delaware
Newark, DE 19716

Center for Catalytic Science and Technology

289. *Chemistry of Oxygenates on Transition Metal Surfaces: Activation of C–H, C–C, and C–O Bonds*

Barteau, M.A. **$61,110**
302-831-8905

The goal of this research is to understand, by means of surface science studies, the elementary processes involved in the synthesis of oxygen-containing fuels and chemicals on transition metals, and the dependence of these processes upon the nature of the surface. This research utilizes Temperature Programmed Desorption (TPD), High Resolution Electron Energy Loss Spectroscopy (HREELS), and X-ray Photoelectron Spectroscopy (XPS) as its principal tools. Application of these techniques has identified pathways, kinetics, and reaction intermediates relevant to the catalytic chemistry of oxygenates, and has revealed a surprising divergence of higher oxygenate pathways and product selectivities between rhodium and palladium surfaces. The current research is examining the chemistry of epoxides, halohydrins, and esters on transition metal surfaces in order to isolate and to characterize key oxametallacycle intermediates, to explore the reactions which compete with them (and to develop linear free energy relationships to account for this competition where possible), to examine the regioselectivity of bond-making and bond-breaking processes of these oxygenates on metal surfaces, and to connect these observations to established and emerging examples in homogeneous and heterogeneous catalysis. 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

290. *Oxidation Catalysis with Tris(pyrazolyl)borate Metal Complexes*

Theopold, K.H. **$84,000**
302-831-1546

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′Co,Tp′ = 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 binding equilibrium for O_2 must be shifted, and 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.

Harvard University
Cambridge, MA 02138

Department of Chemistry

291. *Mo-Catalyzed Heteroatom Removal Reactions: Effects of Promoters on Mechanism*

Friend, C.M. **$70,810**
617-495-4052

The mechanisms of desulfurization and deoxygenation reactions on clean and modified molybdenum surfaces have been deduced. General trends in reactivity have been identified so as to predict product distributions and relative kinetic parameters for processes related to catalytic hydrodesulfurization and deoxygenation. Structural tools have been developed as part of this project. The structures of intermediates such as 2,5-dihydrothiophene and methoxy adsorbed on Mo(110) have been derived from both vibrational and near edge X-ray absorption fine structure data. The comparison studies are important for establishing the validity of approximations used in determining the orientation of intermediates base on vibrational intensities. Analogous reactions understand the role of Co, which is used as a promoter in hydrodesulfurization catalysts. Recent efforts to understand the role of sulfur in these reactions have indicated that S inhibits dehydrogenation. The sulfur also forms S-S linkages with incoming reactants so that blocking of the surface by the sulfur does not substantially inhibit the reaction.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Chemical Engineering

292. Selective Carbon Oxygen Bond Scission during Reactions of Oxygenates on Single Crystal Catalysts
Masel, R.I. **$88,000**
217-333-6841

All of the previous studies of the decomposition of alcohols on single crystals of group VIII metals have shown that the carbon–oxygen bond stays intact during the decomposition process. However, in previous work it was found that the C–O bond breaks on (1x1)Pt(110). During the last three years there have been efforts to identify the active site for C–O and C–C bond scission. methanol, ethanol, and ethylene decomposition on hexPt(511), (1x1)Pt(511), Pt(331), Pt(210), (2x1)Pt(110), and Cu(210) have been examined with TPD and EELS. The first three of these surfaces are active and C–O and C–C bond scission while the next three are not. Such results are difficult to explain theoretically. However, it appears that a delicate balance between bond scission and dehydrogenation determines the rate of bond scission.

School of Chemical Sciences

293. Electron Transfer Activation of Coordinated Thiophene
Rauchfuss, T.B. **$108,000**
217-333-7355

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
Bloomington, IN 47405

Department of Chemistry

294. The Molecular Precursor Strategy for the Production of Superconducting Oxides
Caulton, K.C. **$115,000**
812-855-4798

The mechanism by which volatility is increased by CF_3 substituent groups has been investigated for copper-containing chemical vapor deposition (CVD) precursors. Syntheses of $Na_2Cu[OCH(CF_3)_2]_4(THF)n(n = 0$ and $4)$ have been developed and the molecular structure of both compounds shows intramolecular Na/F bonds. However, when n=O, there are also intermolecular Na/F bonds, thus creating a chain polymer. However, it is remarkable that polymer formation does not significantly suppress volatility, as gauged by thermogravimetry. This has been traced to intramolecular compensation as the polymer goes into the vapor phase as monomeric units, additional fluorines within the molecule can bind to Na^+, thus decreasing the heat to vaporization. Support for this hypothesis comes from synthetic and structural studies of $Na_2Cu_2[OC(CH_3)CF_3)_2]_6$ and $Na_2Cu_2[OC(CH_3)_2(CF_3)]_6(THF)_2$ which show very similar volatility in spite of intermolecular Na/F bonding (thus polymeric character) only in the former case. The CVD behavior of $Na_2Cu[OCH(CF_3)_2]_4$ has been further studied in the past year, with the result that the previously recognized NaF and Cu metal products are accompanied by $Cu[OCH(CF_3)_2]$. The detection of a monovalent copper compound reveals that the segregated deposition of NaF and Cu metal products is not simply dissociation of the heterometallic cluster, but involves redox chemistry at the copper center

295. Metal Alkoxides Models for Metal Oxides
Chisholm, M.H. **$123,000**
812-855-6606

Following on from recognition of the fact that alkoxide-supported clusters of molybdenum and tungsten have central M_xO_y cores that mimic the structures of ternary metal oxides of those metals, an extensive organometallic chemistry associated with these species was discovered. These molecular species provide models for catalytic reactions involving these metal oxides. Within the last 12 months, researchers have discovered what appears to be the first members of an extensive class of polynuclear polyhydrides supported by alkoxide ligands $W6(\mu\text{-}H)_4(H)(\mu\text{-}OPr^i)_8(OPr^I)_5$, $Mo_4(\mu\text{-}H)_2(\mu_3\text{-}H)(OBu^t)_7(HNMe_2)$, $[Mo_4(\mu_4\text{-}H)(OCH_2B\mu^t)_{12}]^-$, $W_4(H)_x({}^iOPr)_8(Me_2(PCH_2PMe_2)_3$, and $W_4(H)(p\text{-}tolyl)(OPr^i)_{10}$. The disposition of the hydride ligands in these clusters reveals a preference for metal-hydrogen and metal-oxygen rich domains. The reactivity of hydride ligands in the simplest of tungsten clusters,

$[W_4(H)(OR)_7]_2$, has been investigated toward C–C, C–N, and C–O double bonds as well as toward alkynes. Ethene inserts to give *cis*-ethyl-ethylene complexes $W_2(OR)_7(\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ but other α-olefins react only slowly to give products of olefin isomerization. In the presence of added hydrogen, α-olefins are catalytically and selectively (compared to internal olefins) hydrogenated. Ketones and aldehydes react to give alkoxide-ketone adducts, e.g., $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{ -}O\text{-}c\text{-}C_5H_8)$ or, in the case of benzophenone, a 1:1 adduct having a cis terminal hydride and an η^2-ketone $W_2(OPr^i)_7(H)(\eta^2\text{-}OCPh_2)$. Organic nitriles are coupled and partially hydrogenated and allene and butadiene are hydrogenated by intermolecular processes. The compound $W_2(O\text{-}c\text{-}C_5H_9)_8(\mu\text{-}C_3II_4)$ has been fully characterized. The attachment of thiophenes to $M_2(OR)_x$ centers has been found to lead to the stepwise activation of the aromatic ring, and in the presence of hydrogen, provides insight into the plausible mechanisms of hydrodesulfurization in heterogeneous catalysis.

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

Christou, G. **$52,500**
812-855-2399

The project is directed towards identifying the initial fate of crude oil vanadyl impurities under the reducing and sulfur-rich conditions of industrial hydrodemetallation (HDM) and hydrodesulfurization 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 characterization of discrete V/S clusters that represent models for intermediate stages of V sulfide polymer growth. The complex $V_2O(SPh)_4(bpy)_2$ (bpy = 2,2′-bipyridine) contains a $[V_2(\mu\text{-}O)(\mu\text{-}SPh)_2]^{2+}$ core and contains both a V–V single bond and antiferromagnetically coupled electrons. It has been studied by VT magnetic susceptibility, VT 1^H NMR studies, and EHT MO calculations. The related anion $[V_2(SCH_2CH_2S)_4]^{2-}$ has been identified as also possessing a V–V bond and antiferromagnetically coupled electrons and has been studied similarly. In contrast, $[V_3S(S_2)_3(bpy)_3]^+$ is diamagnetic, the first V/S cluster to be so, and represents a model for the currently unidentified, diamagnetic V/S species that have been detected by ^{51}V NMR on the surface of partially spent Mo catalysts. Other complexes under study include $V_3O_2Cl_2(SCH_2CH_2S)_2(bpy)_2$, $V_3OCl_3(SCH_2CH_2S)_2(bpy)_2$, and $[V_6O_2S_4(SCH_2CH_2S)_6]$, which represent discrete models of vanadyl units adsorbed on the surface of the growing V_2S_3/V_3S_4 phases.

University of Iowa
Iowa City, IA 52242

Department of Chemistry

297. Synthesis and Chemistry of Cationic d⁰ Metal Alkyl Complexes

Jordan, R.F. **$90,000**
319-335-2212

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^o 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 $[cis\text{-}(N_4\text{-macrocycle})M(R)(L)][BPh_4]$ (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. 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.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

298. Homogeneous Models of Ammoxidation Catalysis

Maatta, E. **$104,000**
913-532-6687

Significant progress has been achieved in the discoveries of simple and efficient routes to a wide variety of organoimido-substituted derivatives of the hexamolybdate cluster, $[Mo_6O_{19}]^{2-}$. Singly functionalized complexes $[Mo_6O_{18}(NR)]^{2-}$ have been prepared for R = n-Butyl, cyclohexyl, and various aryl groups. Single-crystal X-ray diffraction studies have been performed on three of these species. Multiple functionalization has been achieved in the case of R = 2,6-diisopropylphenyl. Hexamolybdate derivatives bearing 1, 2, 4, 5, and 6 (NAr) ligands have been prepared and four X-ray structures have been determined within this series. Cyclic voltammetric studies reveal a monotonic progression of the first reduction potential for these homologues toward increasingly negative potentials, clearly indicating the superiority of the arylimido ligand as an electron donor in comparison to the oxo ligand. This enhanced electron donation may render the imido-hexamolybdates sufficiently basic so as to react with electrophiles. Indeed, the hexakis(arylimido) derivative $[Mo_6O_{13}(NAr)H]^-$ is protonated at a bridging oxo site. Efforts are under way to incorporate other electrophiles into these "imido-activated" clusters, and to extend the methodologies to the preparation of allylimido analogues.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

299. *Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane*
Klier, K.; Simmons, G.W.; Herman, R.G. **$116,400**
215-758-3577

The general objectives addressed in this research are: the mode of methane activation on metals, 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 was the metal of choice because of its ability to activate methane at relatively low temperatures and a weak Pd–O surface bond. Both single crystal and dispersed microcrystalline forms of the metal have been studied, and diagnostics developed using single crystals have been applied to the examination of surface chemistry on the more complex polycrystalline forms of the metal. New fundamental methodology involving photoelectron diffraction at high energy resolution and valence band spectroscopy have also been developed.

Louisiana State University
Baton Rouge, LA 70803

Department of Chemical Engineering

300. *Gallium Zeolites for Light Paraffin Aromatization*
Price, G.L. **$77,600**
504-388-3068

The structural and chemical details of gallium loaded zeolites (which are useful for light paraffin aromatization) are under investigation. Current research work is focussing on the fate of zeolitic protons when gallium is added and catalysts are converted to an active state via hydrogen reduction. Thermal analysis of 1-propanamine has been extremely successful in probing the cation content of MFI zeolite and results have shown that protons are replaced by gallium during the reduction process. A new mode of 1-propanamine adsorption, distinct from adsorption at proton sites, has been discovered for zeolitic cations which applies not only to gallium but also to copper and indium cations. Further characterization with X-ray diffraction, FTIR, and catalytic reactor studies are underway.

Department of Chemistry

301. *Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Models and Precursors for Fullerenes*
Rabideau, P.W. **$97,000**
504-388-8859

The remarkable discovery that buckminsterfullerene, C_{60}, is a stable molecule has led to a flood of research focused on this new family of three-dimensional carbon compounds. These "fullerenes" are produced by laser vaporization of graphite or coal, and their metal derivatives show promise as superconductors. This program deals with polynuclear hydrocarbons whose carbon frameworks are represented on the buckministerfullerene surface (i.e., convex hydrocarbons), and, as such, serve as models for fullerenes. Program objectives are: (1) synthesis of convex hydrocarbons, and (2) investigation of chemical and physical properties, especially addition of metals. 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 compromises its properties as a convex hydrocarbon. This program produced the first "locked" bowl-shaped hydrocarbon by the addition of a second five-membered ring to corannulene, and quite recently, the first synthesis of a semibuckminsterfullerene ($C_{30}H_{12}$) representing half of the C_{60} surface. A second "semifullerene" synthesis now appears possible that will produce an isomeric $C_{30}H_{12}$ with a structure that could, in theory, be dimerized to buckminsterfullerene; this exciting reaction is being explored.

University of Louisville
Louisville, KY 40292

Department of Chemistry

302. *Metallocarboxylate Chemistry*
Gibson, D.H. **$94,000**
502-588-5977

Efforts to use carbon dioxide as a building block in organic synthesis depend upon finding catalytic methods for its fixation. Since effective catalytic methods will likely involve transition metals, the organometallic chemistry of CO_2 is receiving much attention. One area of investigation is the study of CO_2-bridged bimetallic complexes in which the metal centers have widely differing electron-donor and electron acceptor properties to facilitate binding of the CO_2 ligand. A new μ_2-η^2-CO_2-bridged complex, $CpFe(CO(PPh_3)$-$(CO_2)Re(CO)_4[P(OEt)_3]$, was recently prepared, and its thermolysis reactions were studied. At low temperatures a new μ_2-η^3 complex, $CpFe(CO)(PPh_3)(CO_2)Re(CO_3[P(OEt)_3]$, was formed; this compound has been structurally characterized and shows facial geometry at the rhenium center and an anti arrangement of the phosphorus ligands on the two metal centers. Heating the first compound at higher temperatures leads, through a series of intermediate compounds including the second complex, to a μ_2-η^3-CO_2-bridged complex in which the phosphorus ligands have exchanged metal centers. The sequence of reactions is believed to result from O–Re bond breaking in some of the μ_2-η^3 complexes leaving a coordinatively unsaturated rhenium center which reorganizes by facial to facial rearrangement or ligand migration. The reactions demonstrate the robust nature of the binding of the CO_2 ligand between the two metal centers. New CO_2-bridged complexes of the μ_2-η^3 type have been synthesized from reactions of the rhenium metallocarboxylic acid $Cp^*Re(CO)(NO)COOH$ in combination with Ph_3SnCl or *cis*-$Re(CO)_4(PPh_3)(F\text{-}BF_3)$. Both bimetallic compounds have been characterized by X-ray crystallography and are structurally distinct; the bridging CO_2 ligand is symmetrically bound in the Re-Re complex and unsymmetrically bound in the Re-Sn complex. Also, the characterization work on the iron and rhenium bimetallic complexes shows that the ^{13}C chemical shift of the carboxyl carbon is very sensitive to changes in the internal O–C–O bond angle in the compounds.

University of Maryland at College Park
College Park, MD 20742

Department of Chemistry and Biochemistry

303. Odd-Electron Organometallic Chemistry of Relevance to Hydrocarbon Functionalization

Poli, R. **$72,602**
301-405-1809

The general objective of this project is to test the feasibility of C–H functionalization by organometallic radicals. A variety of precursor molecules have been synthesized and their transformation to the radicals investigated by electrochemical techniques. The class of pentamethylcyclopentadienylmolybdenum (IV) trihalides has been thoroughly examined. Mixed-halide systems have been obtained by conproportionation of Cp^*MoX_4 and $[Cp^*MoY_2]_2$, and their investigation has allowed the complete elucidation of the mechanism of formation and complex equilibria between various forms of these materials. The oxidation of trihydride complexes of formula $CpMoH_3(dppe)$ and $CP^*MoH_3(dppe)$ in an EPR spectroelectrochemical cavity has afforded relatively stable paramagnetic hydride complexes, the nature of which is still under investigation. The oxidation of monohydride systems of formula $CpMoH(CO)_n(PMe_3)_{3-n}$ ($n = 0,2$) is highly dependent on the value of n. Whereas for $n = 2$ no paramagnetic intermediate is observed at temperatures as low as 193 K, for $n = 0$ the relatively stable $[CpMoH(PMe_3)_3]^+$ radical is observed. Chemical oxidation studies of these materials have been carried out with ferricinium and with Ag^+ and the products of these processes have been isolated and characterized. The stereochemical outcome of the reaction with Ag^+ demonstrates that this reagent unexpectedly functions as a hydride abstractor in this reaction and not as an oxidizing agent. Current and future efforts are directed at the generalization of the results of these chemical and electrochemical oxidation processes to other mono- and polyhydride systems.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

304. High-Pressure Heterogeneous Catalysis in a Low-Pressure, Ultrahigh Vacuum Environment

Ceyer, S.T. **$103,790**
617-253-4537

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.

305. Controlled Synthesis of Polyenes by Catalytic Methods

Schrock, R.R. **$132,886**
617-253-1596

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 a wide variety of new materials will become available that may rival the more established unsaturated polymers in applications, as well as fundamental research, because of the control exercised in their preparation. 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 y with chain length and structure.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

306. *Zeolite Characterization and Dynamics: The Effect on Molecular Transport and Catalyst Selectivity*
Conner, W.C.; Laurence, R.L.; Ragle, J.L. **$160,000 (20 months)**
413-545-0316

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(1). 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 a negative image of the pores 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, 29Si, 129Xe, and 15N NMR will be employed in conjunction with high resolution adsorption, HRADS, 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.

University of Memphis
Memphis, TN 38152

Department of Chemistry

307. *Towards Computer Aided Catalyst Design: Three Effective Core Potential Studies of C-H Activation*
Cundari, T.R. **$19,199**
901-678-2629

C–H activation is of fundamental importance in catalytic conversion of hydrocarbons such as methane into more useful functionalized products. The research applies the latest in computational methods and technology to study problems in C–H activation chemistry that are of interest to experimental researchers. These problems are currently under investigation. Methane activation by model multiply bonded Group IVB complexes ($L_2M=E$, L=ligand; M=Ti, Zr, Hf; E=O, NH, CH_2) is being studied. Methane is activated by 1,2-addition across the multiple bond so that its polarity and π-bond strength have been suggested as important factors in determining C–H activating ability. By methodically varying metal and activating ligand (E) the response of methane activation to these changes in the chemical environment can be probed. Π-loading has been suggested as a potential route to more potent methane activators. Through computation, methane activation by model amido (amido) complexes $M(NH)_x(NH_2)_{3x}$ is studied. Replacing an amido (NH_2) with an imido (NH) ligand makes the metal more π-loaded and thus calculation of the various potential energy surfaces allows to evaluate π-loading as a strategy for designing better methane activators. The third component to this research entails development of computational approaches for the lanthanides and then using the study of methane activation to test the efficiency and accuracy of the methods. Degenerate methane activation by lanthanide-methyl complexes also allows investigate the effects of the metal on the course of the reaction while separating kinetic from thermodynamic considerations.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

308. *Hydrogen Induced C–C, C–N, and C–S Bond Activation on Pt and Ni Surfaces*
Gland, J.L. **$109,610**
313-764-7354

Hydrogen induced reactions in absorbed organic molecules and intermediates containing C–S and C–N bonds on the Ni(100), Ni(111), and Pt(111) single crystal surfaces are the focus of this program goal. Simple surfaces like (111) and (100) have been selected so that the surface reactions kinetics for a single dominant bonding type can be studied. These studies have included both low pressure hydrogenolysis studies using TPD and vacuum spectroscopies, and in situ synchrotron based soft X-ray hydrogenolysis studies in the 0.01 torr range. In the third year of this program substantial progress has been made in the understanding of thiol and aniline hydrogenolysis on the Ni(100) and Ni(111) surfaces. Thiol hydrogenolysis is substantially more rapid on nickel than on platinum. The dominant intermediates are thiolates for methanethiol and phenylthiol on Ni. The orientation of absorbed aniline appears to be the dominant controlling factor for hydrogenolysis on both platinum and nickel. Hydrogenation of the aromatic ring appears to facilitate hydrogenolysis of the C–N bond on nickel, while on platinum direct hydrogenolysis of the C–N bond in an aromatic intermediate appears to be dominant. The reactivity studies for metastable subsurface hydrogen with a series of simple absorbed hydrocarbons has demonstrated that hydrogenolysis is not observed for several simple hydrocarbons even with energetic hydrogen atoms coming out of the bulk; instead, selective low temperature hydrogenation reactions appear to be dominant when reaction does occur. In situ ultra soft X-ray absorption above the carbon K edges has been used to characterize the rates of several hydrogen addition processes primarily in amines over the past year. Temperature programmed measurements have proved particularly useful for studying the factors which control the selectivity of surface reactions over a broad range of temperature. Detailed in situ spectroscopic studies are used to characterize the surface intermediates under reaction conditions.

University of Minnesota
Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

309. Homogeneous–Heterogeneous Combustion: Chemical and Thermal Coupling

Schmidt, L.D. **$130,000**
612-625-9391

The roles of homogeneous and heterogeneous reactions in combustion 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. The concentrations and internal temperatures of OH, NH, CN, and other 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 H_3 from methane oxidation and production of formaldehyde from methanol oxidation. 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 and pollution abatement. Rates and selectivities in reactions over Pt to produce OH and HCN have been compared over ceramic and metal monoliths.

University of Missouri at Columbia
Columbia, MO 65211

Department of Chemistry

310. Late Transition Metal Oxo and Imido Complexes

Sharp, P.R. **$112,789**
314-882-7715

The synthesis and reactions of late transition metal complexes containing metal–oxygen and metal–nitrogen bonds (e.g., oxo, imido, nitrido, hydrazido, dioxygen, and nitrosoarene complexes) are being studied. The goal is to develop the chemistry of these complexes as an aid to understanding the many important reactions involving late transition metal–oxygen and –nitrogen interactions and as new methods for the formation of C–N and C–O bonds. The recent synthesis of $[(COD)_4Pt_4(O)_2(OH)]^{3+}$ has provided the first example of an isolated late transition metal oxo complex capable of transferring an oxygen atom to unactivated alkenes. Major effort will be directed towards the optimization of this system and the elucidation of the requirements for transfer. It was also recently discovered that gold oxo complexes are excellent precursors to gold clusters. Of particular note is the unusual cluster $[L_6Au_8]_{2+}$, isolated from the CO reaction of oxo complex $[(LAu)_3O]$+. Structural characterization revealed a novel tetradedral core structure with two core Au atoms side-bonded to Lau-AuL units. Finally, bridging O_2 and PhNO complexes have been prepared as model precursors for the dissociative adsorption of O_2 on late transition metal surfaces. Efforts to take these final steps to oxo/imido complexes are under way.

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Department of Chemistry

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

Brookhart, M. **$148,750**
919-962-0362

The basic objective of this program is to elucidate the fundamental mechanisms of Pd(II)- and Ni(II)-catalyzed alternating copolymerizations of carbon monoxide with olefins. Specifically, well-defined organometallic precursors which yield active catalyst systems will be investigated to determine the catalyst resting state, details of the carbon–carbon coupling processes, the kinetics of the chain growth, and the modes of chain termination and chain transfer. Transient intermediates in the catalytic cycle will be sought by low temperature studies and through independent low temperature synthesis. Aspects of the migratory insertion reactions responsible for carbon–carbon bond forming reactions will also be probed using model compounds. The variation in mechanism as a function of the monomer, the ligand set, and the metal will be investigated. These catalytic systems have been chosen for study since they provide an opportunity to study the most fundamental details of carbon–carbon bond formation via migratory insertion reactions and because insights gained should guide the design of new catalysts for this potentially important class of polymers. A second objective of this program is to devise a new catalyst for the synthesis of new copolymers based on mechanistic information acquired. Specifically, the unsolved problem of copolymerizing polar olefins such as methyl acrylate with CO will be addressed along with the synthesis using chiral catalysts of optically active polymers possessing main chain chirality.

312. Reductive Coupling of Carbon Monoxide to C_2 Products

Templeton, J.L. **$101,150**
919-966-4575

Coupling reactions in the coordination sphere of d4 tungsten monomers have been induced with amine reagents. For [Tp'(CO)3W(N≡CMe)]$^+$ the result is a metallacycle with the H2NR reagent providing the NR unit which zips together carbon atoms from the nitrile ligand and a carbon monoxide. When an alkyne ligand is present in the coordination sphere primary amines react with the coordinated nitrile ligand by addition of the NHR and H entities across the triple bond to form amidine ligands. When ammonia is the base added to [Tp'(CO)(PhC≡CH)W(N≡Cme)]$^+$ a metallacycle results as the nitrogen from ammonia links carbons from the acetonitrile and the terminal alkyne to form a six-membered ring. Amine addition to the thermal alkyne carbon in [Tp'(CO)2W (RC≡CH]$^+$ is followed by rearrangement to form neutral vinyl amido complexes of the type Tp'(CO)2W(NR'CH≡CHR). Hydride removal from the coordinated nitrogen yields a cationic vinyl nitrene complex which can add nucleophiles at the vinyl terminus to form azavinylidene products.

Northwestern University
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Department of Chemical Engineering

313. Solid-State, Surface, and Catalytic Studies of Oxides

Kung, H.H. **$122,220**
708-491-7492

Selective conversion of low-priced saturated hydrocarbons by oxidation to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher value is of great technological importance. For practical purposes, it is important to produce only one desired product among many possibilities, some of which are extremely thermodynamically favorable. The emphasis of this project is to identify the properties of oxidic catalysts that determines such selective conversions. It has been demonstrated that the selectivity for oxidative dehydrogenation of butane to butenes and butadiene was much higher on a silica-supported vanadium oxide sample of low vanadium loading than on one with high vanadium loading. The difference could be attributed to the different structures of the vanadium oxide species, which was illustrated by their Raman spectra. Upon addition of a very small amount of cesium ions, the selectivity for oxidative dehydrogenation increased significantly for the high vanadium loading sample without any evidence of changes of the vanadium oxide crystallites. However, the catalyst became more resistant to reduction, and there were indications that cesium segregated to the vanadium oxide crystallite surface. Addition of phosphorus instead of cesium resulted in the formation of a vanadium phosphorus oxide compound, which produced maleic anhydride quite selectively.

Department of Chemistry

314. Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, and Catalysis

Marks, T.J. **$152,811**
708-491-5658 **(15 months)**

The project objective is to elucidate those chemisorptive processes responsible for dramatic enhancements in catalytic activity when actinide, lanthanide, and early transition element hydrocarbyls are adsorbed on certain inorganic surfaces. Surface reaction chemistry is studied by chemical and spectroscopic techniques, while catalytic transformations (e.g., olefin hydrogenation) are studied 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 electrophilic, highly reactive Cp_2MR^+ species, which are shown to be active catalytic centers by CPMAS NMR spectroscopy. These species can be spectroscopically, structurally, and functionally modeled in solution by $Cp_2MR^+ X^-$ complexes, where X^- is a weakly coordinating anion such as $B(C_6F_5)_4^-$. The adsorption process as well as the means by which methylalumoxane, "$[Al(CH_3O]_n$" activates organo-group 4 complexes for industrial scale homogeneous olefin polymerization can be modeled using $B(C_6F_5)_3$ and other organo-lewis acids as an alkide abstraction reagents. Finally, these results also led to study of the adsorption of $Th(\eta^3\text{-allyl})_4$ on Al_2O_3. This process yields arene hydrogenation catalysts rivalling or surpassing conventional platinum metal catalysts in activity, and which also effect the rapid exchange of saturated hydrocarbon C–H bonds with D_2.

315. Chemical Interactions in Multimetal-Zeolite Catalysts

Sachtler, W.M.H. **$107,670**
708-491-5263

The bimetallic system (Rh+Mn)/NaY stands for a group of important catalysts for which the selectivity is dramatically changed by a promoter. Unpromoted Rh/Y converts $CO+H_2$ quantitatively to hydrocarbons, manganese can change this selectivity to higher alcohols and other oxygenates. The objective is to understand this chemistry. EPR, FTIR, TPR, EXAFS, XPS, and catalytic tests are used. It was found using EPR how to determine and control the position of Mn^{2+} ions: in small zeolite cages or supercages. Preparation conditions were elaborated to control the chemical state of Mn after reduction: either Mn^{2+} ions or MnO particles. It was found that no oxygenates are formed when the proton concentration inside the zeolite is appreciable and/or when Mn is predominantly present as Mn^{2+} ions. High selectivity to oxygenates was, however, achieved in proton-free samples when Mn was present as MnO particles. Major products are ethanol and ethyl acetate. This surprising result suggests that formate ions on MnO particles and CH_x groups on Rh clusters might interact with each other when oxygenates are formed. This hypothesis will be tested; if confirmed it will be used to design more selective catalysts for higher alcohol synthesis.

316. Organometallic and Surface Chemistry of Mixed-Metal Systems

Shriver, D.F. **$112,000**
708-491-5655 **(18 months)**

This research is focused 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. It was demonstrated that CO bound to clusters can be converted to C, CCO, C_2, and C_4 ligands. Similarly, the chemistry of SO_2 in metal clusters was developed and the conversion of coordinated SO_2 to coordinated S or SO was demonstrated. The vibrational frequencies of these ligands in clusters was pursued to provide information for their identification on surfaces.

University of Oklahoma
Norman, OK 73019

Department of Chemistry and Biochemistry

317. Transition-Metal-Mediated Thermal and Photochemical Carbon Dioxide Activation

Nicholas, K.M. **$106,950**
405-325-3696

The primary objective of this project is to define the fundamental reactivity patterns of coordinated carbon dioxide; a secondary emphasis is on the study of new catalytic reactions involving CO_2 fixation. Efforts to promote migratory insertion of $(MeC_5H_2Nb(\eta^2 = CP_2)CH_2)CH_2SiMe_3$ (1) have revealed that a variety of Lewis acids react with 1 to promote rapid decarboxylation with production of various novel adducts–derivatives of the Lewis acid with Cp'_2 Nb(O)R. The unstable intermediate in the reaction of 1 with $ZnCl_2$ has the CO_2 ligand bridging between Mo and Zn. While studying the potential intermediacy of Cp'_2 Nb (CO) R (2) complexes in the thermolyses of C'_2 Nb (CO_2) R, it was discovered that 2 [and $(C_5\ H_5)_2$ Mo (CO) (3)] react rapidly with molecular oxygen to produce the corresponding CO_2 complexes $(\eta^5\text{-}C_5\ H_4\ CH_3)_2$ Nb $(\eta^2\text{-}CO_2)$ (4). These findings offer the first examples of aerobic oxidation of coordinated CO to CO_2, a generally assumed step in homogeneous and heterogeneous catalytic CO oxidation. Important extensions of this chemistry have revealed that (1) oxidation of CP'_2 NbCO (H) produces Cp'_2 Nb $(O)(\eta^1\text{-}OCOH)$, the apparent result of CO oxidation and subsequent migratory insertion and (2) CO complex 2 is transformed by the action of S_8 to the novel C,S-bonded complex, Cp'_2 Nb $(\eta^2\text{-}COS)$. In the catalytic area, solutions of $\{(PhMe_2\ P)_3\ Rh\ (NBD)\}\ BF_4$ (5) in THF under 20–100 atm of 1:1 CO_2/H_2 were found to catalyze the selective production (and decomposition) of formic acid at 20–40 °C with turnover numbers of 30–150/day. Kinetic and in situ IR and NMR studies provided evidence for a catalytic process involving formation of rhodium dihydride complexes $[H_2\ Rh\ (PMe_2\ Ph)_3\ (S)\ BF_4$ (6) S = H_2O, THF) that insert CO_2 to give formato species $\{HRh\ (S)\ (PMe_2\ Ph)_3,\ (\eta^1\text{-}OCHO)\}\ BF_4$ and $\{HRh\ (S)\ (PMe_2\ Ph)_2\ (P\eta^2\text{-}OCHO)\}\ BF_4$, which in turn, reductively eliminate formic acid. In the course of conducting control experiments on the above system it was discovered that in the presence of Rh(I) complexes, mixtures of CO_2 and O_2 oxidize a variety of ethers, producing formic acid (partly from CO_2) and esters (lactones) in a novel CO_2 - mediated process.

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College of Science

318. Highly Nucleophilic Acetylide, Vinyl, and Vinylidene Complexes

Geoffroy, G.L. **$116,151**
814-865-9591

The overall goal of this research is to develop a detailed understanding of the manner in which small organic ligands can be elaborated into more complex ligands by a variety of metal-mediated carbon–carbon, carbon–nitrogen, and carbon–oxygen bond forming reactions using highly nucleophilic acetylide, vinyl, and vinylidene complexes. The anionic acetylide complexes $[Cp(CO)(PPh_3)Mn\text{-}C{\equiv}CR^-]$ undergo a series of unusual addition and cycloaddition reactions with heterocumulenes, vinylketones, and epoxides. The acetylide complex is chiral, and the stereochemistry at the metal has been observed to influence the stereochemistry of the new organic ligand formed in these transformations strongly. These studies are being extended to an examination of the reactivity of the acetylide complex with an extensive variety of other organic substrates and also to explorations of its reactivity with a series of electrophilic organometallic complexes. Other studies in progress are aimed at developing new addition and cycloaddition reactions of manganese and rhenium vinylidene and vinylcarbyne complexes.

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Department of Chemical Engineering

319. *Enhancement of Activity and Selectivity by Metal-Support Interactions*

Vannice, M.A. **$122,220**
814-863-4803

The project objectives are (1) to study the creation of metal-support interactions that have a pronounced influence on adsorption and catalytic behavior, (2) to use these effects to alter hydrogenation reactions such as those involved in fine chemicals production, and (3) to enhance low-temperature CO oxidation activity. Focus is on characterizing adsorbed molecules as well as the chemical and physical state of the metal and support. Results for acetophenone hydrogenation over Pt show enhanced selectivity to phenylethanol (from 70% with Pt/SiO_2 to over 95% with Pt/TiO_2). Turnover frequencies were similar. Special active sites at the metal-support interface are proposed to explain this behavior. Au/TiO_2 catalysts have been found to be excellent CO oxidation catalysts at 273 K and lower. The preparation of 5 nm Au crystallites on TiO_2 has produced a more active catalyst. It was found that eliminating Cl does not increase activity while the presence of H_2O vapor reversibly decreases activity, and it was shown that UHP Au powder has no detectable activity at these conditions. Researchers are now conducting in situ FTIR measurements and examining various reaction models. An ultrahigh vacuum (UHV) system with high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), and a high-pressure reaction chamber has been used to investigate CO and acetone adsorbed on an UHP Pt foil. Both η^1 (end-on bonding) and η^2 (side-on bonding) species are present and, in contrast to Pt(111), a significant decomposition channel exists for the two species that produces H_2, CO, and surface carbon. Acid sites on the support supplied by spilled-over hydrogen from Pd or Pt crystallites have been proposed to explain higher observed specific activities obtained with acidic supports. The hydrogenation of mixtures of polyaromatic hydrocarbons is now being investigated to determine if the presence of these acid sites can alter the selectivity during the hydrogenation of benzene/toluene feed mixtures.

Department of Chemistry

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

Sen, A. **$100,000**
814-863-2460

Catalytic transformations by transition metals and their compounds is of great scientific, as well as practical importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The current research is focused primarily on transition metal catalyzed polymerizations. Specifically the study 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 from 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; and (c) the synthesis of alternating copolymers of functionalized olefins with carbon monoxide.

Intercollege Materials Research Laboratory

321. *Carbon Deposition and Deactivation of Metallic Catalysts*

Baker, T.K. **$127,423**
814-863-1439

The current program is focused on the manner by which various adatoms including metals and non-metals influence the deposition of carbon on nickel, cobalt, iron, and platinum during reaction in hydrocarbon environments. In addition to following changes in both the gas and solid phase product distributions as a function of adatom concentration, temperature, and reaction time, researchers are examining the relationship between the structural and morphological characteristics of the carbon deposits and that of the modified metal catalyst particles. A combination of experimental techniques including controlled atmosphere electron microscopy coupled with in situ electron diffraction, thermogravimetry, temperature programmed desorption, and flow reactor studies are being used in these investigations. Although it is generally recognized that sulfur can have devastating effects on the catalytic activity of metal particles, it was found that a careful and well controlled addition of small amounts (4–50 ppm) of sulfur to either Co, Ni, Fe, or Pt can produce a dramatic increase in the formation of filamentous carbon when these metals are reacted in a carbon containing gas at temperatures over the range 500 to 750 °C. If the presulfidation step was conducted at much higher H2S concentrations (>500 ppm), then on exposure to the hydrocarbon environment carbon deposition was initially suppressed; however, after a period of time on stream the optimum catalytic activity was eventually attained. It is suggested that the most active state of the catalyst is associated with the creation of a metal surface which contains a residual sulfur coverage of about 0.25 of a monolayer. The addition of sulfur into the melts was also observed to induce significant structural changes in the morphological appearance of carbon filaments, which constituted a major fraction of the solid deposit. In the case of Co, the filaments grown on the pure metal were highly graphitic in nature, and the degree of structural perfection decreased as sulfur was added to the system. With pure Ni the filaments were relatively smooth and did not contain any distinguishing features, whereas those produced on sulfur contaminated particles acquired a regular coiled form. This difference in structural conformation is attributed to modifications in particle geometry induced by the presence of sulfur, which has a direct impact on the diffusion of carbon species through the catalyst particle.

Department of Materials Science and Engineering

322. *Determination of the Distribution of Hydrogen in Coal by Fourier Transform Infrared (FTIR) Spectroscopy*
Painter, P.C. **$99,910**
814-865-5972

The purpose of this research is to determine the role of hydrogen-containing functional groups in coal. The work consists of two interrelated parts: (1) the quantitative determination of the aliphatic and aromatic CH content by Fourier transform infrared (FTIR) spectroscopic measurements and (2) the application of a newly developed thermodynamic model that describes the role of hydrogen-bonding interactions. This research is aimed at providing a knowledge of coal structure both at the level of local composition and at the larger scale of the effect of the balance of intermolecular forces on solution and swelling behavior. In recent work a new model for swelling has been developed that discards the affine deformation assumption of the old Flory-Rehner approach and uses the blob model of DeGennes to obtain an expression for the free energy. Spectroscopic measurements are being developed to determine coal/solvent interaction parameters and these will be applied to the determination of the phase behavior of coal/solvent gels, which in turn will provide fundamental information on the character of the network structure of coal.

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Department of Chemical Engineering

323. *Support Effects Studied on Model Supported Catalysts*
Gorte, R.J. **$90,210**
215-898-4439

The research is aimed at understanding metal–support interactions, especially those associated with noble metals on ceria and lantana, for applications in automotive, emissions-control catalysis. It is divided into three areas: (1) studies of Co-oxidation kinetics on ceria-supported catalysts, (2) TEM and ion-scattering studies of metals films on a CeO_2 single crystal, and (3) studies of particle-size and support effects for model, Pd catalysts. Particular attention is being given to understanding the apparent oxygen-migration phenomenon that has been observed on ceria-supported metals and to understanding why there are differences between the nobel metals and their interactions with ceria.

Department of Chemistry

324. *Catalytic Synthesis of Silicon Carbide Preceramic Polymers: Polycarbosilanes*
Berry, D.H. **$94,000**
215-898-2705

Polycarbosilanes are the most successful and widely studied class of polymer precursors for silicon carbide, but traditional methods for their synthesis are inefficient and nonselective. Ruthenium complexes $(Me_3P)_3Ru(H)_3(SiR'_3)$ catalyze the dehydrogenation of tertiary silanes at 150° to produce a distribution of linear and branched carbosilanes. The key C-H functionalization step is achieved by β-hydrogen elimination from silyl ligands to generate transient metal silaolefin complexes of the type $L_nRu(\eta^2\text{-}R_2Si{=}CR'_2)$. A stable silene complex, $(Me_3P)_3(H_2)Ru(\eta^2\text{-}Me_2Si{=}CH_2)$, has been prepared and characterized in solution, and found to react rapidly with $HSiR_3$ to stoiciometrically yield carbosilanes. In the presence of hydrogen acceptors such as t-butyl ethylene catalytic dehydrocoupling is rapid at 80–100 °C. Secondary silanes such as Me_2SiH_2 undergo 1,1-dehydrogenative coupling in the presence of hydrogen acceptors to yield oligomeric polysilanes of composition $(Me_2Si)_n(MeHSi)_m$. A new class of catalyst, $(\eta^6\text{-arene})Ru(SiR_3)_2(H)_2$, has also been synthesized and characterized and shown to be active for the catalytic dehydrogenative cross-coupling of Si–H and Ar–H bonds to yield aryl silanes. Current studies are aimed at increasing the selectivity of Si–C and Si–Si bond forming processes, and understanding reactions which lead to catalyst degradation.

325. *Inorganic Polymers and Materials*
Sneddon, L.G. **$108,000**
215-898-8632

This project is focused on the development of new polymeric-precursor synthetic routes that enable the formation of a variety of nonoxide ceramics in processed forms. Current studies are conducted on the syntheses, properties, ceramic-conversion reactions, and applications of boron-based polymers, including polyvinylborazine, polyborazylene, borazine-modified polysilazanes, and decaborane-based polymers. In addition, investigations are 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. The continued development of the fundamental synthetic methodology needed to produce new inorganic monomers and polymers is also a key component of this project.

326. *Catalytic Hydrogenation of Carbon Monoxide*
Wayland, B.B. **$124,000**
215-898-8633

A central objective of this program is to explore and develop new strategies for reduction and hydrogenation of carbon monoxide at mild conditions of pressure and temperature. One prominent pathway for hydrogenation of CO to form organic oxygenates passes through a metalloformyl intermediate that is a participant in the subsequent rate limiting process. Metalloformyl species (M-CHO) are generally thermodynamically unfavorable relative to the metal hydride (M-H) and CO precursors and thus very high pressures of CO are required to form finite quantities of this central intermediate. The seminal observation that rhodium porphyrin complexes have the thermodynamic capability to produce formyl 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 most recently also observed for non-macrocyclic tetradentate ligands with both nitrogen and oxygen donors.

Structurally flexible non-macrocyclic 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 also been observed for rhodium porphyrins and the scope of rhodium complexes that can reduce and couple CO is currently being evaluated.

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Department of Chemistry

327. *Studies of Supported Hydrodesulfurization Catalysts*

Hercules, D.M. **$82,450**
412-624-8300

Activation of supported Mo catalysts prepared by conventional methods (e.g., pore volume impregnation) often leads to the formation of mixed Mo oxidation states (e.g., reduction of Mo^{6+} to Mo^{5+}, Mo^{4+}, Mo^{3+}, etc.). As a result, direct correlation between the nature and abundance of supported species and catalytic activity is often difficult to establish. One objective of this research is to synthesize supported Mo catalysts containing discrete Mo oxidation states. Kazansky and coworkers reported the formation of a single Mo oxidation state (in this case Mo^{4+}) upon photoreduction in CO at room temperature of oxidic Mo/SiO_2 catalyst prepared by incipient wetness impregnation. Evidence for the presence of Mo^{4+} was primarily based on the average oxidation state estimated from CO_2 formation and, more recently, from IR results. The purpose of the study is to authenticate the postulated formation of a discrete Mo oxidation state upon photoreduction of Mo/SiO_2 catalyst. In this study, an allyl-based Mo/SiO_2 catalyst prepared by the sublimation of $Mo(\eta^3\text{-}C_3H_5)_4$ onto SiO_2, was analyzed by ESCA following oxidation at 500 °C and photoreduction in CO at room temperature. Following two hours of photoreduction, ESCA studies indicated a well defined Mo 3d doublet characteristic of a single Mo oxidation state, with Mo $3d_{5/2}$ binding energy of 232.1 eV. From the comparison between ESCA results and stoichiometric studies, this binding energy was assigned to Mo4^{+}.

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

Yates, J.T., Jr. **$156,170**
412-624-8320

This research is concerned with the use of vibrational spectroscopy and electron stimulated desorption for the study of elementary surface processes of importance in understanding catalysis by metals and by chemically modified metal surfaces. The vibrational spectroscopic methods employed include Fourier transform-infrared reflection absorption spectroscopy (FT-IRAS), high-resolution electron energy loss spectroscopy (HREELS), and transmission IR spectroscopy, with the latter method being employed to study actual high surface area catalysts. Current problems include (1) fundamental studies of the role of atomic steps on Pt single crystals on chemisorption and catalytic reaction; (2) fundamental studies of the metal–support interaction on both real and model metal catalysts supported on Al_2O_3 and SiO_2; (3) dynamical studies of the motion of adsorbed molecules on single crystal surfaces and of anisotrophy in these motions.

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Department of Chemistry

329. *Anchoring Strategies for Bimetallic Species in Zeolites*

Bein, T. **$89,240**
317-494-5495

The focus of this project is to develop novel hybrid catalysts based on organometallics encapsulated in zeolite cages. In combining the catalytic activity of the transition metal complex with the size- and shape-selectivity of the zeolite host, novel catalysts with unique performance and stability are created. A major emphasis is on utilizing intrazeolite protons as reactive sites for the attachment and stabilization of the precursors. Intrazeolite reactions of bimetallic organometallics with reactive ligands have been explored, including Ge- and Sn-transition metal complexes. For example, the reactivity and hydrogenation activity of trimethylstannyl tricarbonylcyclopentadienyl molybdenum in mesoporous MCM-41 host was recently studied. Thermolysis of this and related systems leads to interesting sub-nanometer alloy clusters stabilized in the zeolite pores. Furthermore, the reactions of vanadyl complexes with various zeolite hosts were examined, and high catalytic activity for the oxidation of alcohols was discovered. The versatile catalyst methyltrioxorhenium was reacted with different hosts. The resulting hybrid systems are active as selective olefin metathesis and oxidation catalysts. A comprehensive combination of analytical techniques is being used to probe local structural changes at the molecular level. These techniques include EXAFS spectroscopy utilizing synchrotron radiation, in situ FT-IR coupled to thermodesorption, Micro Raman, UV-NIR, and ESR spectroscopies.

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

Rothwell, I.P. **$94,500**
317-494-7012

The project continues to evaluate the use of early d-block metals (particularly niobium and tantalum) for carrying out the catalytic hydrogenation of arene rings. Recent results involve the development of new methods for the synthesis of hydrido, aryloxide compounds using reagents such as Bu^N_3SnH as the hydride source. These new metal hydrides such as $[Ta(OAr)_2(H)_x(Cl)_{3-x}(L)_y]$ ($x = 1, 2, 3$; $y = 1, 2$) function as highly regio and stereoselective arene hydrogenation catalysts. Mechanistic insight into the reactivity is being obtained by studying the stoichiometric reaction of these reagents with unsaturated substrates such as olefins, alkyne and conjugated dienes. The synthetic utility of these catalysts for carrying out the hydrogenation of aryl-phosphine compounds and other heteroatom containing substrates is being pursued. The addition of the alkylidyne bridged dimer $[(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2\ M(CH_2SiMe_3)_2]$ (M = Nb, Ta) to oxide supports such as silicane generates an extremely active arene hydrogenation catalyst precursor. The kinetics, regio- and stereochemistry of these heterogeneous catalyst systems is being determined for comparison with their homogeneous counterparts. The nature of the surface supported precursor and catalyst is being investigated by techniques such as infra-red spectroscopy and solid state NMR methods.

331. Fundamental Studies of Reactive Intermediates in Homogeneous Catalysis

Squires, R.R. **$96,690**
317-494-7322 **(24 months)**

The properties and reactivity of organic and organometallic species involved in combustion and homogeneous catalysis are being investigated with the use of a selected ion flow tube-triple quadrupole apparatus. Collision-induced dissociation threshold energy measurements are being used to determine sequential M–CO bond strengths in transition metal carbonyl ions. Methods have been developed for including metastable ion lifetime effects in the data analysis. Measurements of the sequential M–CO bond dissociation energies in 19 different $M(CO)_n^-$ ions have been reported, and the periodic trends in the data have been discussed. Currently, these measurements are extended to cyclopentadienylmetal carbonyl ions, $CpM(CO)_n^{+/-}$ (Cp = c- C_5H_5). An extraordinarily wide range of M–CO bond energies are evident, from 27 kcal/mol for $D[CpMn(CO)^-\text{–}CO]$ to 45 kcal/mol for $D[CpFe(CO)^-\text{–}CO]$. An electrospray ionization source has been constructed for use in examining catalytically active homogeneous solutions, and its performance is currently being optimized. The design of a new flowing afterglow-guided ion beam instrument employing a tandem quadrupole-octopole-quadrupole analyzer has also been completed, and the construction of this device is now in progress.

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Department of Chemistry

332. Selective Transformations of Carbonyl Ligands to Organic Molecules

Cutler, A.R. **$125,130**
518-276-8447

Results of a kinetics study on the $(CO)_5Mn$(p-toluoyl)-catalyzed SiH/SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ established a second-order isotope exchange equilibrium in which a ping-pong bi-bi mechanism requires coordinatively unsaturated manganese silyls, $(CO)_4MnSiR_3$, as active catalysts. These manganese silyls sequentially add one substrate silane and then release a product silane. The same active catalyst evidently operates during autocatalytic hydrosilation of $(CO)_5MnC(O)CH_3$ with $HSiR_3$. The resulting mixtures of $(CO)_5MnCH(OSiR_3)CH_3$ and $(CO)_5MnC(OsiR_3)=CH_2$ are accommodated by an intermolecular mechanism in which the active catalyst and substrate afford $(CO_5)MnC(CH_3)(OSiMe_2Ph)Mn(CO)_4$ as the key intermediate. Silane addition affords the former product whereas β-deinsertion produces the latter. The active catalyst originates via independently studied silane-induced degradation of manganese complexes. A similar mechanism operates when manganese complexes $(CO)_5Mn\text{-}Y[Y{=}C(O)R$, R, Br - but not $SiMe_3$ or $Mn(CO)_5]$ are used as efficient hydrosilation precatalysts for nonlabile iron acyls Cp(CO)(L)FeC(O)R. These reactions gave $Fp\text{-}CH(OSiR_3)CH_3$ under conditions where typical Rh(1) hydrosilation catalysts are inactive. These manganese complexes and hydrosilanes also afford extremely active catalysts for hydrosilane alcoholysis, silation of carboxylic acids, hydrosilation of organic aldehydes and ketones, and hydrosilation-reduction of organic esters. Carbonylation driven isomerization of $(\eta^5$-indenyl)(L)(CO)Ru-alkyl complexes occurs under mild conditions. For example, carbonylation of $(Ind)(L)(CO)Ru\text{-}CH(OR)CH_3$ gave $(Ind)(L)(CO)Ru\text{-}C(O)CH_2CH_2OR$, not $(Ind)(L)(CO)Ru\text{-}C(O)CH(O)CH_3$, under conditions where isomerization of α-alkoxyethyl to β-alkoxyethyl ligands was not detected. Results of mechanistic studies are consistent with carbonylation driving alkyl deinsertion equilibria involving $(\eta^3$-indenyl)(L)(CO)Ru$(CH_2{=}CHR)$H intermediates, R^1 = Me, Et, Ph, OR.

University of Rochester
Rochester, NY 14627

Department of Chemical Engineering

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

Saltsburg, H. **$170,000**
716-275-4582 **(18 months)**

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_2O_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

334. *Transition Metal Activation and Functionalization of Carbon–Hydrogen Bonds*

Jones, W.D. **$115,700**
716-275-5493

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. Mechanistic studies indicate that this product is 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. Reactions of a series of trispyrazolylborate complexes of rhodium have also been examined. The alkane and arene activation products [HB(3,5-dimethylpyrazolyl)3]Rh(CNR)(R′)H_2 where R = neopentyl have also been studied. 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. Independent synthesis of the methyl deuteride complex is being used to probe for the existence of a 'methane complex' prior to C–H activation.

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

Department of Chemistry

335. *Carbon–Hydrogen Bond Functionalization Catalyzed by Transition-Metal Systems*

Goldman, A.S. **$90,000**
908-932-5232

Significant progress has been made toward the goal of efficient transition-metal catalyzed alkane functionalization, particularly dehydrogenation. $Rh(PMe_3)_2(CO)Cl$, previously found to catalyze alkane photodehydrogenation, has been discovered to effect thermal (non-photochemical) alkane transfer-dehydrogenation under hydrogen atmosphere. Based on the results of mechanistic studies of this system, much more efficient catalysts for alkane dehydrogenation have been developed, including $Rh(PMe_3)_2(P^iPr_3)Cl$ and $[Rh(PMe_3)_2Cl]_2$. Apparently, the role of hydrogen is to add to the complexes which then dissociate to afford $H_2Rh(PMe_3)_2Cl$ which then reacts with alkanes. In part because the presence of a hydrogen atmosphere results in the hydrogenation of several mol acceptor per mol dehydrogenated product, the development of hydrogen-free systems has been attempted. $Rh(P^iPr_3)_2Cl$ was found to react in cyclooctane solution to give $H_2Rh(P^iPr_3)_2Cl$ (ca. 60% yield) and cyclooctane. In the presence of hydrogen acceptors, catalytic transfer hydrogenation is observed. The efficiency of both the stoichiometric and catalytic reactions of $Rh(P^iPr_3)_2Cl$ is limited by ligand dehydrogenation reactions. Future work will focus in part on the development of complexes RhL^2Cl where L has properties similar to that of P^iPr_3 but is more resistant to dehydrogenation. High level ab initio MO calculations have been successfully used to model the effect of varying ligands on the thermodynamics and kinetics of H_2 addition to late transition metal complexes; the results should be applicable to a wide range of catalytic reactions including, but much broader than, RhL_2Cl-catalyzed alkane dehydrogenation.

Department of Physics and Astronomy

336. *Morphological Instability in Model Thin Film Catalysts: Structure and Reactivity*

Madey, T.E. **$101,850**
908-932-5185

Model bimetallic catalysts (i.e., ultrathin films of metals on metals) are being studied to probe the relationship between microscopic surface structure and chemical activity. Recent studies have centered on the structure and reactivity of W(111) and Mo(111) surfaces covered with ultrathin films of various transition metals. First, a new ultrahigh vacuum scanning tunneling microscope has been used to examine the microscopic details of Pd-induced faceting of W(111): the Pd-coated surface is completely covered with facets ((112)-oriented pyramids) in the range 750 to 1100 K. The maximum facet dimensions are ~10nM. There is no evidence for surface alloying: the Pd film that causes faceting of the W substrate "floats" on the surface. Second, low energy electron diffraction (LEED) has been used to determine the morphological stability of Mo(111) covered by ultrathin metal films. The results are remarkably similar to W(111): on Mo(111), metals having Pauling electronegativity greater than 2.0 (Rh, Pd, Pt, Au) induce faceting, while those with electronegativity less than 2.0 (Ti, Fe, Ni, Cu, Ag) do not. Third, the catalytic reactivity of planar and faceted Pt/W(111) is being characterized using the hydrogenolysis of n-butane as a model reaction. The reaction is studied as a function of facet size, Pt coverage, and reaction temperature. There is a striking structural sensitivity in the reaction rates and products.

University of South Carolina
Columbia, SC 29208

Department of Chemistry

337. *The Transformations of Organic Amines by Transition Metal Cluster Compounds*
Adams, R.D. **$115,000**
803-777-7187

Research is being conducted on the coordination and ring opening transformations of strained cyclic hydrocarbons containing four carbon atoms or less and cyclic thioethers by metal cluster complexes. The principal objectives are to establish (1) the modes of coordination of the rings to groups of metal atoms and (2) the mechanisms of ring opening by the metal atoms whenever this occurs. Investigations of the insertion of alkynes into metal–metal bonds in metal cluster complexes containing two or more metal atoms and the reactions of these alkyne containing products with small organic molecules are also being conducted. In addition, studies of the potential of metal cluster complexes to capture and store visible and ultraviolet radiation by rearrangement of the metal–metal bonding of the complexes are also being performed.

University of Southern California
Los Angeles, CA 90089

Department of Chemistry

338. *Chemistry of Bimetallic and Alloy Surfaces*
Koel, B.E. **$97,000**
213-740-4126

The discovery of methods to prepare stable, ordered surface alloys of Sn and Pt, Pd, and Ni provides an enormous opportunity to make fundamental advances in understanding how chemistry is controlled on bimetallic and alloy surfaces. Angle-resolved, low-energy alkali ion scattering studies are being used to elucidate the detailed geometric structure of these surface alloys. Hydrocarbon chemisorption studies probe the reactions that occur on these surfaces. Initial focus is on the chemistry of Sn/Pt(111) surface alloys, where examinations are conducted on the changes that occur in dehydrogenation selectivity for the series Pt(111), (2 x 2) $Pt_3Sn(111)$ which contains 3-fold Pt sites, and ($\sqrt{3}$ x $\sqrt{3}$)R30° Pt_2Sn which only has 2-fold Pt sites. Later, the chemistry of Sn/Pt(100) surface alloys will be explored and compared, and also the analogous Sn/Pd and Sn/Ni single crystal surface alloys will be studied. In parallel with chemisorption studies in UHV, hydrocarbon conversion reaction kinetics and mechanisms will be investigated over these surfaces at higher pressures, including in situ observations of catalytic reaction intermediates by Fourier transform infrared (FTIR). This work will aid in developing a basic chemical foundation for Pt/Sn reforming catalysts and may be helpful in the design of new catalysts.

Southern Illinois University
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Department of Chemistry

339. *Studies of the Stabilities and Reactions of Solution-Phase Organic Radicals*
Bausch, M.J. **$96,030**
618-453-6461

Research in this project aims to develop a more complete understanding of the stabilities and reactions of organic reactive intermediates (including radicals and radical ions) of interest to a broad spectrum of chemists. Of particular focus are investigations of the thermodynamic strengths of chemical bonds found in small to medium sized organic reactive intermediates, as well as studies of the kinetics of the reactions of some of these reactive intermediates. Techniques used include micro-electrode based fast scanning cyclic voltammetry (FSCV) and photomodulated voltammetry (PMV); both are useful in examinations of the redox properties of novel species (including various phenalenes, perimidines, and corannulenes) as well as in examinations of the properties of electrochemically and photochemically generated products. The effects of β-substituents on the kinetic and thermodynamic stabilities of organic radicals are currently being investigated, in additional attempts to more accurately rationalize the formation and subsequent reactions of organic radicals, and add new insights into the understanding of chemical reactions pertinent to fossil fuel chemistry.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

340. *The Dynamics of Adsorption on Clean and Adsorbate-Modified Transition Metal Surfaces*
Madix, R.J. **$143,560**
415-723-2402

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 understanding of the molecular dynamics of the adsorption process, 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 studies of the adsorption of ethane on Pt(111) and Pt(110) surfaces to determine the effects of the microroughness of the (110) surface. The molecular adsorption probabilities of ethane, propane, and xenon were determined incident along both the (100) and (110) azimuths as a function of translational energy and incident polar angle at a surface temperature of 95 K using molecular beams.

Along the (110) direction the adsorption probability increases with increasing angle of incidence, whereas along the (100) direction it decreases with angle. To understand these observations stochastic simulations were performed. Ethane was treated as a pseudodiatomic molecule, and the solid was represented by a three to five layer slab of at least 108 platinum atoms coupled to a heat bath by friction and random forces. The methyl–methyl and the methyl–platinum forces were calculated using pairwise Morse potentials, and the platinum–platinum force constants were calculated from bulk and surface Debye frequencies. Morse parameters of $D_e = 2.3$ kJ/mol, $R_o = 3.1$ A, and $B = 1.3$ A^{-1} gave an excellent fit. The stochastic trajectory simulations predicted the magnitude of the adsorption probability to within 20% at all incident angles and energies as well as the different dependence of the adsorption probability on polar angle at the two azimuths studied. Examination of the energy flow during the trapping process shows that excitation of rotational energy into cartwheeling motion can assist trapping, if the excitation is not excessive. The simulations suggest that ethane trapping on Pt(110) (2x1) is enhanced relative to Pt(111) because the stronger corrugation of the Pt(110) (2x1) surface allows for more conversion of normal momentum to parallel momentum. Initial results suggest that the adsorption probabilities and the energy scaling determined experimentally for propane on Pt(111) are predicted by simulations using the Morse potential parameters determined from the ethane/Pt(111) system. Experiments and simulations are also planned to determine the energy scaling and activation energies for alkane activation on iridium surfaces, with emphasis on the precursor-dominated routes to reaction.

State University of New York at Binghamton
Binghamton, NY 13902

Department of Chemistry

341. Photochemistry of Intermolecular C–H Bond Activation Reactions

Lees, A.J.
607-777-2362

Measurements of the quantum efficiencies for the C–H bond activation are continuing and proving to be fruitful, not only because absolute values for photochemical conversion are determined but because information about the reaction intermediates and mechanisms is being obtained in systems where the key intermediates are extremely short lived. During the past year the research has concentrated on studying the photochemical and photophysical events in the $HB(Pz^*)_3Rh(CO)_2$ (Pz^* = 3,5-dimethylpyrazoylyl) complex, a known C–H bond activator. Absolute quantum efficiencies for intermolecular C–H bond activation have been determined in room-temperature hydrocarbon solutions by monitoring FTIR and electronic absorption spectral changes throughout photolysis and by integrating the varying light absorption over time. Photolyses at several excitation wavelengths have been performed and the subsequent quantum efficiency data indicate that there are two different electronic excited states responsible for the observed photochemistry. These two energy levels are assigned to be ligand field transitions. Significantly, population of the upper excited state gives rise to efficient C–H bond activation [$\Phi CH^{(366nm)} = 0.32$ in n-pentane] whereas irradiation into the lower excited state is relatively ineffective [$\Phi CH^{(458nm)} = 0.011$ in n-pentane]. It is believed that the lowest energy excited level gives rise to $\pi^3 \rightarrow \pi^2$ interconversions and that C-H bond activation occurs from a $HB(Pz^*)_3Rh(CO)$ intermediate produced mainly from the higher energy excited state. Quantum yields measured in a variety of hydrocarbon solvents reveal some important differences, being significantly lower in aromatic media [$\Phi CH^{(366nm)} =$ 0.12 (benzene), 0.14 (toluene), 0.17 (p-xylene) and 0.22 (mesitylene)]. An π_2-coordination complex is thought to occur in the aromatic hydrocarbon solutions prior to the C–H bond activation step. Further studies under way include measurement of the absolute quantum efficiencies of metal complexes in triethylsilane solutions.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

342. Mechanistic Examination of Organometallic Electron-Transfer Reactions

Atwood, J.D. **$83,614**
716-829-2122

Studies of the reactivity of metal carbonyl anions have demonstrated that single-electron processes through odd-electron intermediates and two-electron processes involving transfer of groups are possible. This research has also provided mechanistic criteria to distinguish between the two mechanistic types. Single-electron processes (1) give products typical for odd-electron complexes, (2) show only minor rate differences as the metal carbonyl anion is varied, and (3) show opposite phosphine ligand effects. Transfer of groups (1) occurs with no evidence for odd-electron complexes, (2) are very rapid reactions, and (3) have large variations of rates with variation of metal carbonyl anion. The single-electron studies have direct applications to electron transfer catalysis and reactivity of organometallic radicals. A possible role for proton transfer in activation and functionalization of carbon–hydrogen bonds is under examination. Reactions between metal carbonyl dianions and alkylidene complexes are being studied as a possible route to study alkylidene transfer reactions. Halogen transfer reactions occur, but do not subscribe to relative Marcus theory. Nucleophilic attack at the carbon of a cis CO is most probable. These studies have provided a much clearer understanding of one- and two-electron processes in organometallic reactions.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering and Materials Science

343. *The Relationship between Hydroxyl Groups on Oxide Surfaces and the Properties of Supported Metals*

Schwarz, J.A. **$80,510**
315-443-4575

Supported metal catalysts are commonly prepared by depositing catalytic precursors from aqueous solutions of electrolytes onto high-surface-area oxides. This impregnation step has been the focus of a number of recent studies from this laboratory that seek to relate the effect of formulation procedures on the catalytic properties of supported metal catalyst systems. A general conclusion of previous studies was that the performance of the finished catalyst depends on the characteristic properties of the hydroxyl inventory on the surface of the oxide support, in wet and in (pseudo)-dry conditions. Hydroxyl groups serve as adsorption or exchange sites during catalyst preparation. On the other hand, the configuration of hydroxyl groups still remaining on oxides after dehydration determines the acid-base characteristics of the catalyst, which is a major catalytic property. The purpose of the present investigation is to characterize the relationship expected to exist between the complex hydroxyl inventory at the oxide–solution interface and the intrinsic acid/base properties of partially dehydroxylated oxides. It is assumed that the same structural models are operational in describing the local configuration of hydroxyl groups on (pseudo)-dry oxides as well as at the oxide–solution interface. This allows extension of the concept of intrinsic heterogeneity of (pseudo)-dry oxide surfaces to the oxide–solution interface. The consequences of that heterogeneity upon the impregnation step during catalyst preparation are being examined.

Texas A & M University
College Station, TX 77843

Department of Chemistry

344. *Correlations between Surface Structure and Catalytic Activity/Selectivity*

Goodman, D.W. **$203,700**
409-845-0214

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 modelling of supported catalysts using ultra-thin planar oxide surfaces.

345. *Catalysts and Mechanisms in Synthesis Reactions*

Lunsford, J.H. **$101,850**
409-845-3455

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. Both matrix isolation electron spin resonance (MIESR) 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 particularly effective in establishing the mechanism by which methane is converted to ethane and ethylene. Reactions of $CH_3\cdot$ radicals with metal oxide surfaces are being examined to determine reactive sticking coefficients and to follow their role in the conversion of methane to methanol and formaldehyde. It has been demonstrated using LIF that methane and molecular oxygen react over lanthanum oxide and neodymium oxide in the temperature range 1200 to 1350 K to form hydroxyl radicals which emanate into the gas phase. The less basic cerium oxide forms no detectable hydroxyl radicals. When methane is replaced by a comparable amount of water, the concentration of hydroxyl radicals increases. It is concluded that the surface-catalyzed equilibrium reaction between water and oxygen is responsible for the formation of hydroxyl radicals with both methane and water as reagents. Hydroxyl radicals are believed to be formed by the abstraction of hydrogen atoms from water at reactive surface oxygen ions. These hydroxyl radicals may play an important role in catalytic combustion.

University of Texas at Austin
Austin, TX 78712

Department of Chemical Engineering

346. *Catalytic Hydrocarbon Reactions over Supported Metal Oxides*

Ekerdt, J.G. **$80,510**
512-471-4689

This research involves the use of oxide overlayers to model and study oxide catalysis and is directed toward developing a fundamental understanding of how catalyst composition, redox ability, and structure control the catalytic properties of metal oxides. Molybdenum and tungsten oxide systems are employed that permit examination of the role of metal oxide cations separately and in pairwise combinations. Specific projects are organized around two themes. The first deals with catalytic properties of fully oxidized cations in oxidation reactions and the second examines the catalytic properties of reduced oxidation state cations in carbon-carbon coupling and hydrogenation reactions. The research program also involves characterization of the processes used to prepare the catalysts and characterization of the resulting oxides using spectroscopic techniques. A variety of methods are used to prepare the overlayers on silica, alumina, and titania supports that include the use of organometallic precursors to direct the cation structure and selective photoreduction to generation cations with discrete and well-defined oxidation states.

Department of Chemistry

347. *Morphological Aspects of Surface Reactions*

White, J.M. **$106,700**
512-471-3704

This work focuses on substrate morphology and on fragments synthesized by thermal, electron, and photon activation. One aspect of the present work involves morphological studies of Rh on planar TiO_2 surfaces using scanning tunneling microscopy and scanning electron microscopy. The objective is to measure, in some cases in real-time, how the surface morphology changes as oxidation and reduction processes are carried out. Using a newly installed environmental scanning electron microscope, changes of the morphology of gold samples deposited on glass are studied as a function of temperature and gas phase environment. These preliminary experiments serve as a baseline for more detailed work using more active metals, such as rhodium, on catalytically important supports, such as silica and alumina. By exposing physisorbed methane to controlled doses of low energy electrons, spectroscopically significant concentrations of methyl groups have been prepared on Pt(111). Thermal reactions (kinetics) of these fragments are under investigation, in the presence and absence of coadsorbates such as atomic deuterium. On Ag(111), amino groups have been prepared by electron irradiation of adsorbed ammonia. The reactions of these with methyl groups has been examined with the goal of establishing the activation energy and pre-exponential factor for the formation of methyl amine.

Tulane University
New Orleans, LA 70118

Department of Chemical Engineering

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

Gonzalez, R.D. **$80,707**
504-865-5772

The potential advantages of sol-gel processing are being studied. These include purity, homogeneity, and controlled porosity combined with the ability to form large-surface-area materials at low temperatures. Because porous structures created in solution are preserved, this leads to applications in filtration, insulation, separation, sensors, and antireflective devices. An application of the method to catalysis is that a solid can be prepared from a homogeneous solution that includes not only the metal precursor, but also the support precursor. It is expected that supported metal catalysts prepared by sol-gel processing will be superior to catalysts prepared by traditional impregnation or ion-exchange methods for the following reasons: they should sinter less readily; metal loss should be minimized; and they will produce less coke and will, therefore, deactivate at a lower rate. Sol-gel processing leads to the formation of more homogeneous materials with a uniform distribution of particle sizes. The emphasis of this research is to prepare supported metal catalysts for the following applications: (1) catalytic reforming of petroleum crudes (supported Pt-Re-alumina); (2) supported multimetallic catalysts for use in the control of auto emissions; and (3) high-surface-area promoted zirconia and zirconia-titania mixed oxide catalysts with superacid properties for use in octane enhancement. In order to reduce deactivation, sulfur promoted zirconia catalysts are promoted through the addition of Pt. BET surface areas in excess of 1000 m^2/g have been obtained for Pt/SiO_2, 500 m^2/g for Pt/Al_2O_3, and 250 m^2/g for zirconia. By controlling the water/support precursor ratio it is possible to control the pore-size distribution. When the metal particle size coincides with the pore diameter of the support a very high resistance to sintering is obtained. Studies on thermally stable Pt/SiO_2 and Pd/SiO_2 have been completed. In order to stabilize the high-surface-area amorphous phase of alumina and zirconia, small quantities of a second oxide are being added.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

349. *Ligand Intermediates in Metal-Catalyzed Reactions*

Gladysz, J.A. **$120,000**
801-581-4300

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. The second goal entails the characterization of ligand intermediates in other important feed stock conversions, and the identification of new types of binding modes and bond activation processes. 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 kivergent kinetic and thermodynamic O=C/C=C selectivities in bifunctional non-conjugated substrates, (2) the characterization of nonclassical metal C–H "sigma bond" complexes as reaction intermediates; (3) unusual base-induced vinylic carbon–hydrogen bond activation reactions of alkene ligands; (4) the synthesis, structure, electronic properties, and reactivity of complexes that contain unsupported and supported C_2 and C_3 linkages spanning two metals; (5) carbon-hydrogen bond activation reactions of alkoxide complexes, and their application in new catalytic reactions; and (6) the synthesis, structure, and reactivity of CO_2 complexes in coupled redox states.

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

Grant, D.M.; Pugmire, R.J. **$114,000**
801-581-8854

The project objective is to develop new nuclear magnetic resonance (NMR) techniques to study solid organic materials applied to gain structural and chemical information on model compounds and natural samples. The most important achievements have been (1) developing new spatial correlation techniques to measure 13C chemical shielding tensors in single crystals; (2) improving theoretical methods for the calculation of shielding tensors; (3) developing a new magic angle slow turning (MAT) method of obtaining 2-D solid state NMR spectra where the isotropic shift is projected along one axis and tensor powder patterns along the second axis; (4) applying these 13C shielding tensor methods in the characterization of coals of all ranks. The single-crystal correlation techniques characterize 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. The various NMR spectroscopic methods provide carbon-13 NMR shielding tensors for a variety of polycyclic aromatic systems and hydroaromatics such as acenapthalene, perylene, triphenylene, and several naphthalene derivatives. Emphasis is on structural details in these hydroaromatics because of their importance in fossil fuels. Theoretical calculations have been extended to these model compounds to explain and support the experimental conclusions. Spectroscopic analyses of non-prontated to protonated aromatic carbons agree with elemental analyses and dipolar dephasing NMR techniques. The new 2-D methods are useful for analyzing the structure of coals of various ranks; the fraction of condensed carbons obtained may be used to estimate overage clutter size in condensed polyaromatic hydrocarbons, and these data have provided key parameters for use in coal devolatilization theories being developed in concert with work in the advanced combustion research institute.

Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

Department of Chemical Engineering

351. *Influence of Surface Defects and Local Structure on Oxygenate Reaction Pathways over Metal-Oxide Surfaces*

Cox, D.F. **$64,020**
703-231-6829

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 SnO2(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 effect of surface properties on the reaction pathways of oxygenates being examined. Previous results have shown that the dissociation of Bronsted acids (formic acid, methanol, water) can be alternately controlled by either the acidity of the molecules or the surface condition. Weaker acids dissociate more readily in the presence of cations with a reduced coordination relative to the stoichiometric surface, i.e., the nature of the surface cations (acid sites) controls the activity. However, this effect is limited to a specific range of surface compositions. The most highly defective surface exhibits the lowest probability for dissociate adsorption. The relative acidity/basicity of the two specific surface defects are currently being tested with probe reactions. New directions include the study of the effects of surface condition on the selective oxidation of propene and the characterization of point defects with STM.

University of Washington
Seattle, WA 98195

Department of Chemistry

352. *Model Oxide-Supported Catalysts for Energy Technologies*

Campbell, C.T. **$93,120**
206-543-3287

This project will identify the active form of surface Cu in the methanol synthesis reaction over Cu/ZnO catalysts and elucidate the influence of ZnO on the morphological and chemical properties of supported Cu films. The kinetics of methanol synthesis over vapor-deposited Cu thin films on ZnO single-crystal faces are compared with those over industrial Cu/ZnO catalysts. The growth kinetics, structure, annealing behavior, and chemisorption properties of thin Cu films on several ZnO single-crystal faces are also being studied using surface spectroscopies. The goal here is to clarify the geometric, dynamic, and energetic factors that control the microstructure of the metal/oxide interface, and to rationalize the interplay between this microstructure and chemical reactivity. Copper can form two-dimensional islands on the oxygen-terminated ZnO(0001) face that are only one atom thick. Surprisingly, these ultrathin islands behave chemically much like Cu(110), which is one of the most catalytically active bulk Cu faces. One goal is to see how the substrate geometry influences the morphology, stability, and chemical properties of such thin Cu particles. This Cu/ZnO system serves a very important role as a prototype for many metal/oxide catalysts where the choice of support is critical.

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

Heinekey, M. **$78,000**
206-543-7522

Preparation of highly reactive, coordinatively unsaturated rhenium cation of the form $[Re(CO)_3(PR_3)_2]^+$ (R = cyclohexyl, isopropyl, phenyl) has been carried out by protonation of the corresponding neutral methyl complexes with $H(Et_20)_2B(Ar')_4(Ar' = 3,5-(F_3C)_2Cx_6H_3)$. An X-ray study of the PCy_3 complex reveals that the coordinative unsaturation of the formally sixteen electron complex is relieved by coordination of one of the C–H bonds of the cyclohexyl group to the metal in an agostic interaction. The cationic complexes can be reduced by one electron using sodium metal to form the corresponding seventeen electron neutral radical species. This reaction represents the first practical preparation of these radical species. The sixteen electron cations are very electrophilic and react with a number of small molecules including H_2 and N_2. The resulting H_2 complexes are isolable and have properties comparable to the neutral tungsten analogs. Rapid exchange of coordinated H_2 for external D_2 has been observed, in addition to fast atom exchange to afford HD. The mechanism of this novel reaction is being investigated.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemical Engineering

354. *Thermodynamic and Kinetic Aspects of Surface Acidity*

Dumesic, J.A. **$103,499**
608-262-1092

This project involves the characterization of catalyst acidity and basicity, using microcalorimetric measurements, infrared spectroscopic studies, ^{2}D NMR studies of Bronsted acid/base sites, and reaction kinetics studies of acid-catalyzed reactons. The objectives of the work are to understand the factors that control the acid/base properties of surfaces and to quantify the kinetic aspects of the catalytic cycles in which these sites participate. For example, the surface acid/base properties of g-Al_2O_3 were recently investigated following addition of K_2O, MgO, La_2O_3, SnO, and SnO_2. Addition of basic metal oxide cations at loadings less than 200 mmol/g converted the stronger acid sites (heats of ammonia adsorption from 140–160 kJ/mol) to sites of intermediate strength (100-140 kJ/mol). Strong basic sites (heats of carbon dioxide adsorption from 140–160 kJ/mol) were formed at higher loadings of basic oxides on alumina. The effectiveness of basic metal oxides to neutralize acid sites and to generate basic sites on alumina can be related to the electronegativities of these oxides. Kinetic studies have focused on the quantitative aspects of acidity for isobutane and isoheptane cracking and for methylamine syntheses from ammonia and methanol. Work is currently being extended to super-acidic materials, such as antimony halides and oxides of iron, tin, and zirconium treated with sulfur oxides. ^{57}Fe, ^{121}Sb, and ^{119}Sn Moessbauer spectroscopy are utilized to characterize these materials.

Department of Chemistry

355. *Organometallic Chemistry of Bimetallic Compounds*

Casey, C.P. **$126,600**
608-262-0584

The organometallic chemistry of bimetallic compounds is being investigated in an effort to discover new heterobimetallic compounds that can serve as catalysts for CO hydrogenation. 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 bimetallic compound. The discovery that $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ hydrogenates alkynes to give rhenium-alkene complexes provides a rare example of bimetallic catalysis amenable to detailed kinetic and mechanistic studies. To make the reaction catalytic in both metals, more labile metal alkene complexes are needed. Mn-Pt compounds will be explored since Mn-alkene complexes are liable. The use of indenyl ligands and of more labile Mn complexes is being explored. (2) The recent discovery of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ and of its reversible reaction with H_2 to produce $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ have opened a new area of research. The reactions of Re=Re with alkynes are being studied and a variety of novel bimetallic complexes are being characterized. (3) Reinvestigation of a spurious report of $Cp^*Co{=}CoCp^*$ led to the discovery of the paramagnetic cobalt cluster $Cp^*_3Co_3(\mu\text{-}H)_4$. The reaction of this cluster with acetylene to give μ-alkylidyne complexes is being studied in relation to heterogeneous catalysis. (4) Chelating diphosphines with wide natural bite angles near 120° will be used to make catalysts in which phosphine ligands are constrained to diequatorial positions in trigonal by pyramids. The effect of chelate bite angle on the regioselectivity of Rh-hydroformylation catalysts is being studied.

University of Wisconsin at Milwaukee
Milwaukee, WI 53201

Department of Chemistry

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

Fripiat, J. **$85,000**
414-229-5852

The application of ^{27}Al cross-polarization from the protons of chemisorbed ammonia has been extended to zeolites (ultrastable Y and dealuminated mordenites). As in plain aluminas, the non-framework alumina moieties contain two kinds of Lewis sites, namely a distorted tetrahedral site and a site with pentahedral coordination. These sites have been identified by FTIR spectroscopy of CO thermodesorption from 140 K to room temperature, as giving rise to stretching bands at $\sim$2190 cm^{-1} (distorted tetrahedral) and at $\sim$2220 cm^{-1} (pentahedral). Since CO chemisorption is easily quantified, the amounts of the two kinds of sites are now known for different aluminas and zeolites. It has been shown that the initial rate of n-pentane isomerization per Brönsted site is proportional to the number of Lewis sites (sum of the two kinds of sites) in dealuminated zeolites. Such a relation suggests the existence of the suspected synergy between Brönsted and Lewis sites, and it is on this aspect that the outcoming research will be focused.

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

Tysoe, W.T. **$92,270**
414-229-5222

Various model oxides catalysts synthesized in situ have been tested for their activity for olefin metathesis and it is found that MoO_2 forms the most active catalyst while metallic molybdenum is the least active. Measurement of the temperature dependence of the MoO_2-catalyzed reaction reveal two distinct reaction regimes; a low temperature regime where the activity resembles that of supported molybdenum oxides with high loading and a high temperature regime with kinetics similar to those when the reaction is catalyzed by metallic molybdenum. Reaction of ethylene catalyzed by metallic molybdenum in the high-temperature regime results in the formation of higher hydrocarbons with a distribution consistent with polymerization of surface C_1 species suggesting that high-temperature metathesis proceeds via an associative mechanism where surface carbenes combine to form metathesis products. This chemistry is consistent with surface science results for the adsorption of alkenes on metallic molybdenum. Efforts are currently focussing on elucidating the nature of the reaction pathway at low temperatures on MoO_2 as well as further clarifying the nature of the high-temperature reaction. In addition, it has been found that the addition of small amounts of hydrogen to the alkene ($\sim$ 2%) results in a substantial increase in the rate of formation of metathesis products. Analysis of the catalyst after reaction reveals that metathesis proceeds in the presence of a thick carbonaceous layer so that it is suggested, as a working hypothesis, that the role of the hydrogen is to titrate away some of the surface hydrocarbon species to facilitate access to the metal sites below. An increase in the formation rate of higher hydrocarbons supports this view and this phenomenon is being investigated in greater detail.

Yale University
New Haven, CT 06520

Department of Chemical Engineering

358. Acidity and Effect of Acidity on Supported Metals

Haller, G.L. **$112,250**
203-432-4378

A new class of silica-alumina mesoporous molecular sieves is under investigation. These materials have very narrow and variable pore size distributions, variable silica/alumina ratios, and are pseudo-crystalline (diffract X-rays, but lack three-dimensional crystallinity). These materials are solid acids which may have acid sites with strength between that of amorphous and crystalline (zeolite) silica-aluminas. The structure of these materials will be studied with solid state NMR to determine their acid strength quantitatively and to use them as reference materials to test hypotheses about the structure/acidity correlations of amorphous silica-aluminas of variable composition and acidity. Amorphous, mesoporous/pseudo-crystalline and crystalline (zeolite) silica-aluminas will be used as supports for Pt and Pd particles and the relative effect of the acidity of the supports on the activity and selectivity of several probe catalytic reactions will be determined. The structure and interaction of the metal particles with the acid sites will be studied by X-ray absorption. The objective is to better understand the mechanism of metal-acidic support interaction and to distinguish between three different proposed mechanisms of interaction: activated hydrogen spillover and reaction with hydrocarbon adsorbed on support acid sites; formation of metal-proton adducts with direct participation of adduct proton with reaction intermediates; and perturbation of metal particles by the global acidity of the support.

Department of Chemistry

359. Catalytic Oxidation of Hydrocarbons by Binuclear Fe Complexes

Caradonna, J.P. **$106,560**
203-432-5221

This project is investigating the ability of nom-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 compounds, which are all powerful reductants, heterolytically decompose peracids and are capable of acting as oxygen atom transfer catalysts when reacted with oxygen atom donor compounds and simple olefins, yielding both allylic oxidation and epoxidation products. An isostructural dicobalt(II) compound gives rise to only epoxidation products. Intermediates observed during catalytic turnover and reactions with dioxygen are currently being examined.

360. Alkane Photoreactions with Mercury Vapor

Crabtree, R.H. **$92,150**
203-432-3925

In the last period, the use of Hg^*/NH_3 ($Hg^* = \{^3P_1\}Hg$) for the conversion of alkanes including methane was reported. These studies have now been extended to other alkanes, and similar results are formed. It was believed that H atoms and NH_2 radicals were the reactive species in the vapor. Conversations with Bill Chupka, a physical chemist in the Department, led to consideration of the possibility that the NH_4 neutral molecule might be present. If so, its very low IP, comparable with Na or K might make it a very powerful reducing agent. Therefore, fluorocarbons such as CF_4 might react. Perfluoroalkanes have few or no reactions other than with the alkali metals, and these are not controllable. The reaction of Hg^*/NH_3 gives NH_4F and fluoroimines in a very controllable and reproducible way. The selectivity shown for perfluorodecalin suggests preferential 3° attack, followed by subsequent allylic imination at the 1 and 8 positions. This shows chelate control operates and suggests that NH_4 H bonds to the preexisting imine N and gives electron transfer to the nearby CF_2 group. The mechanism of this remarkable reaction will be studied in the next grant period. In addition, there has been further progress with defining conditions under which arenes react.

Separations and Analysis

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

361. ***Interfacial Chemistry in Solvent Extraction Systems***
Neuman, R.D. **$77,120**
205-844-2017

The microscopic interfaces, i.e., rodlike reversed micelles and other association microstructures in acidic organophosphorus extraction systems associated with Na^+, Co^{2+}, Ni^{2+}, Cu^{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 relationship between reversed micellar structure and selectivity, and the effect of organic phase additives on the structure of reversed micelles. A new structural model—the "open water-channel" model–for rodlike reversed micelles and a quantitative model which relates the extractability and selectivity to the size of reversed micelles in solvent extraction systems are being experimentally verified. Advanced laser techniques (SLLS, LIF, FRAP, SHG, and SFG) are to be utilized to characterize the properties, structure, and dynamics of extractant species. In particular, association microstructures, has been initiated using a novel experimental approach in order to provide pioneering information on interfacial/transport phenomena within supported liquid membranes (SLMs). A state-of-the-art surface force apparatus also will be employed to further examine adsorption behavior and molecule-pore wall interactions in SLMs. This innovative research program will make significant contributions to the science and technology of traditional liquid-liquid extraction and supported liquid membranes.

Brigham Young University
Provo, UT 84602

Department of Chemistry

362. ***Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport***
Lamb, J.D. **$95,997**
801-378-3145

The metal cation selectivity of macrocyclic ligands such as crown ethers and cryptands is applied to making cation separations in hydrophobic liquid membrane and other systems. Potential macrocyclic ligand carriers are designed and synthesized, then screened for cation binding characteristics using potentiometric titration, extraction, calorimetry, NMR, and X-ray crystal structure. 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 the effect of temperature on separation systems. A high temperature calorimeter is being used to study the binding of macrocycles to metal cations at high temperatures.

Brown University
Providence, RI 02912

Department of Chemistry

363. ***Thermal Generation of the Photoacoustic Effect***
Diebold, G.J. **$81,480**
401-863-3586

This research is directed towards investigation of the mechanism of generation of sound waves in dilute suspensions of particles. Micelles and other particles that act as spherical heat sources and whose dimensions are small enough so that heat conduction determines the properties of the photoacoustic wave will be studied. Sound generation is modelled where absorption of the optical radiation takes place inside the particle only. The particle is taken to have a negligible thermal expansion coefficient. Sound is generated only in the fluid surrounding the particle after heat diffuses from the particle. Experiments will be done using the transient grating technique. Calculations show that the acoustic wave has a distinct character when it is produced by the thermal conduction mechanism. The preliminary model indicates that the radius, thermal diffusivity, and thermal conductivity of the particle can be determined from the shape of the transient grating signal. Besides this work, investigation of the effects of viscosity and heat conduction on the time profiles of the photoacoustic waveforms that have been previously studied here will be carried out. In addition, the origin of the nonlinear effects that have been recorded in several experiments with particulate matter will be sought.

Colorado School of Mines
Golden, CO 80401

Department of Chemical Engineering

364. ***A Mechanistic Study of Molecular Sieving Inorganic Membranes for Gas Separation***
Way, J.D. **$84,390**
303-273-3519

The objectives of the research are to investigate the transport mechanism in microporous, metal oxide membranes and to examine the relationship between the membrane structure, the membrane surface chemistry, and separation performance. An example of a membrane material under investigation is the PPG hollow fiber membrane. A further objective is to use quantum mechanics and molecular dynamics to simulate the adsorption and transport of penetrants in pores of molecular dimensions. A mean pore size of 11.2 Å was calculated assuming the pores are perfect cylinders from physical adsorption of Ar at 87 K. The mean pore size from physiosorption agreed well with a pore size of 13 Å from small angle X-ray scattering. The effect of surface chemistry, specifically surface hydroxyl groups, on the transport of gases will be independently studied using FT-IR spectroscopy to measure the concentration of surface hydroxyl groups as a function of temperature and pressure. Very high mixed gas separation factors have been measured at 298 K and 21.7 bar feed gas pressure of 11.5 for O_2/N_2 and 250 for CO_2/CH_4. Mixed gas separation factors are up to 20% larger than the values obtained from pure gas measurements.

University of Delaware
Newark, DE 19716

Department of Chemistry and Biochemistry

365. *Linear and Nonlinear Spectroscopic Probing of Solute Interactions with Chemically Modified Silica Surface*

Wirth, M.J. **$76,630**
302-831-6771

An understanding of chemical basis of chromatographic separation is essential to the improvement of this important technology. This research effort employs novel techniques possible through the use of laser spectroscopy to probe the interactions between adsorbates and chromatographic surfaces. These are the interactions that underlie chromatographic separations. Specifically, the orientation and reorientation of adsorbed molecules on chromatographic surfaces is probed to determine both the geometry of the adsorbate-surface interaction and the dynamics of the adsorbate. For hydrophobic adsorbates, the solvation state of the octadecylsiloxane surface is revealed for the many types of chromatographic conditions. Study of the geometry and dynamics of adsorption of amino acids yields rich insight into the factors that control the adsorption of peptides and proteins. Other types of chromatographic surfaces, including shorter chain alky siloxanes as well as hydrophilic siloxanes are being studied. For all types of surfaces, the role of surface silanols in the adsorption process is being investigated.

Duke University
Durham, NC 27708

Department of Chemistry

366. *Studies of Multifrequency Phase-Resolved Fluorescence Spectroscopy for Spectral Fingerprinting*

McGown, L.B. **$68,840**
919-660-1545

This project explores the use of fluorescence lifetime techniques for chemical analysis. Phase-modulation spectrofluorometry is used to acquire fluorescence spectral and lifetime information in new approaches to the characterization of complex environmental and biological samples. The multiple dimensions of fluorescence information allows researchers to take full advantage of the high sensitivity of the fluorescence process to the microenvironment of the emitting molecules, in order to exploit the uniqueness of complex samples in their native matrices for sample characterization, classification, and fingerprinting. Dynamic, intermolecular interactions such as aggregation, macromolecular association, collisional quenching, and excited state complexation, are manifested as changes in fluorescence lifetime as well as spectral peaks, intensity, anisotropy, and vibronic band ratios. Lifetime resolution can be used to provide distributions of these spectral characteristics of a sample that reflect not only the various chemical components in a sample but also their distribution among different chemical microenvironments in a heterogeneous sample matrix. Such information is not available from separation-based techniques that employ chromatography or extraction to remove the components from the sample matrix. The self-modeling maximum entropy method has recently been introduced into this work as a new approach to distributional analysis of fluorescence lifetime data that provides a more detailed and accurate picture of the complex, heterogeneous systems under investigation. These include coal liquids, humic substances, and human serum. A recent development is the lifetime synchronous spectrum, or LiSS, which provides lifetimes and intensity as a function of synchronously scanned excitation and emission wavelengths. The LiSS shows promise as a fingerprinting tool because of its ability to indicate those spectral regions that are best for discriminating among different samples.

University of Florida
Gainesville, FL 32611

Department of Chemistry

367. *The Glow Discharge as an Atomization and Ionization Source*

Harrison, W. **$88,270**
904-392-0780

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 emission, atomic absorption, atomic fluorescence, and mass spectrometry. Of special interest is the use of a radiofrequency discharge for nonconducting samples, thus eliminating the need to mix metal matrices with nonconducting materials to permit dc discharge operation. There is also interest in the chemical plasma reactions that occur under the influence of an rf discharge compared to the dc mode. Complementary techniques of atomic absorption and atomic emission are used to obtain information about sputtering and excitation mechanisms. The influence impurity species have on the analyte and discharge gas species with respect to the atomization, excitation, and ionization processes is being characterized by two methods: (1) cryogenic cooling of the plasma to "freeze out" the impurities and (2) addition of impurities to study gas phase chemistry. Research continues in the investigation of the ionization mechanisms responsible for the signal anomalies occurring in pulsed dc glow discharges. The work with continuum source atomic fluorescence is aimed at developing a methodology that will permit simple multi-element trace element analysis. A xenon arc lamp has been coupled with the glow discharge to study the associated fluorescence spectra. Experimental conditions are being developed to optimize signal to noise ratios in the post-discharge period, after the normal glow discharge emission has ended. By pulsing the lamp at this time, a spectroscopically quiet region is accessed. Temporal profiles of fluorescence signals indicate optimum conditions for analytical work.

368. *Development of Laser-Excited Atomic Fluorescence and Ionization Spectrometric Methods*

Winefordner, J.D. **$93,120**
904-392-0556

The emphasis in this research is upon the development of new, sensitive, selective spectroscopic methods for trace elemental analysis. Several projects are ongoing which 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 N2 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 micro-planar discharge. Both of these glow discharge systems accept small volume discrete samples. The emission system has multi-element capability on sub-sample 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

369. *New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission and Mass Spectrometry*

Montaser, A. **$75,175**
202-994-6480

This research follows a multi-faceted approach, from theory to practice, to the investigation and development of novel helium plasmas, sample introduction systems, and diagnostic techniques for atomic and mass spectrometries. 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 of 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 sample introduction systems. 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

370. *Use of Ion Chromatography–dc Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals*

Urasa, I.T. **$27,160**
804-727-5398 **(6 months)**

The research has focused on studies of the solution chemistry and speciation of trace metals using chromatographic coupled with spectroscopic techniques. The new thrust is directed towards incorporating solid phase extraction in metal speciation. Application of solid phase extraction in analytical measurements has several advantages, including: 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. Several sorbents, including bonded reversed phase, bonded normal phase, and naturally occurring polymers will be studied 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. While limited separation can occur on the solid phase extraction tube, analytical separation of the extracted metal species will be achieved by the elution of the extracted species on a chromatographic column connected to the extraction tube.

University of Houston
Houston, TX 77204

Department of Chemical Engineering

371. *Mechanisms of Thickening, Cake Filtration, Centrifugation, Expression, and Ceramic Processing*

Tiller, F.M. **$95,642**
713-743-4322

This program has been directed toward development and verification of theory related to filtration, sedimentation, washing, and centrifugation. New theoretical equations have led to a better understanding of the relative performance of sedimenting and filtering centrifuges. CATSCAN studies of transient phenomena in sedimentation and filtration have revealed information which requires changes in existing theory. Revised equations indicate that errors in excess of 100% can be expected when the effect of sedimentation on filtration on horizontal surfaces is neglected. A new revolving laboratory filter with a vertical surface for cake deposition has been built to eliminate sedimentation.

University of Idaho
Moscow, ID 83843

Department of Chemical Engineering

372. ***Drop Oscillation and Mass Transfer in Alternating Electric Fields***
Carleson, T.E.; Budwig, R. **$39,470**
208-885-7652

The final year of this project involved the construction and operation of a system to visualize flow and mass transfer to a suspended droplet in an alternating field. A drop of sugar/water was maintained stationary in an octanol/freon continuous phase. The amount of sugar or octanol was adjusted to provide density and refractive index matching for the two phases. The drop was maintained stationary by means of a standing acoustic wave. The drop was also caused to oscillate by acoustics and the flow field in and around the drop determined by high speed video images of latex particle traces. Mass transfer experiments were conducted by mixing Rhodamine B fluorescent dye with the drop phase. A sheet of laser light was used to cause the dye to fluoresce in a narrow band through the drop and continuous phase. The concentration of the dye was determined by high speed video camera images which were digitized with respect to the light (i.e., fluorescence) intensity. Dye concentrations were determined from the digitized images. Mass transfer experiments with a stationary, still drop and a stationary, oscillating drop were conducted. The experimental results for the still drop were compared to theoretical predictions obtained with FIDAP software.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

School of Chemical Sciences

373. ***Molecular Aspects of Transport in Thin Films of Controlled Architecture***
Bohn, P.W. **$81,480**
217-333-0676

Work in this project is focused on understanding the molecular details of transport in modified and unmodified synthetic chemical microstructures. The experimental approaches must be able to extract signal from a specific restricted spatial regime, in the presence of background from portions of the sample many orders of magnitude larger, which requires response to molecular parameters, nanometer-scale spatial discrimination, and excellent sensitivity. Specifically the spatial localization of the electric field in thin Ag or Au layers, interspersed at different points within a polymer, is used to study the changes in chain structure associated with solvent swelling in Case II diffusion processes. Raman scattering from the molecular segments in close proximity (< 100 A) to the metal particles is used to characterize segments of the film undergoing swelling. Using deuterated solvents allows the solvent and polymer motions to be monitored separately. Studies of CH3OH permeation in poly(methyl methacrylate) indicate large changes in the ester side chain orientation associated with the glassy-to-rubbery transition which is the rate-limiting step in determining the permeant front velocity. Current studies are focusing on detailing the structural rearrangements in the plasticization step in this system.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

374. ***Multi-Dimensional Hadamard Transform Spectrometry: A New Analytical Technique***
Hammaker, R.M.; **$72,994**
Fateley, W.G.
913-532-1454

Emphasis has shifted from application of Hadamard transform techniques to visible and near-infrared Raman spectrometry to multidimensional spectrometry. 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, v_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 reported in the literature. The next efforts will include (1) development of four-dimensional spectrometry for the analysis of heterogeneous materials, (2) consideration of acousto-optic tunable filters (AOTFs) as spectral separators in multidimensional spectrometry, (3) development and application of new proprietary Hadamard encoding masks, and (4) enhancement of the capabilities for performing various multidimensional spectrometries.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

375. ***Perforated Monolayers***
Regen, S.L. **$74,000**
610-758-4842

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) methods, (ii) the characterization of their barrier properties toward He, N_2, and SF_6, and (iii) the clarification of the importance of transfer speed and surface pressure (during LB deposition) on the permeation selectivity (permselectivity), and reproducibility of these composite membranes.

Louisiana State University
Baton Rouge, LA 70803

Department of Chemistry

376. *Sensitized Luminescence in Organized Media*
Warner, I.M. **$93,000**
504-388-2829 **(15 months)**

This research is currently focusing on two key areas of study: (1) the use of micelles to enhance the selectivity of sensitized luminescence measurements and (2) the use of calixarenes to improve analytical measurements through guest–host interactions. Both areas are key to the development of novel methodologies for sensitized luminescence measurements in organized media. The first research area employs newly synthesized surfactants that contain lanthanide counterions as acceptors, for determination of non-luminescent organic compounds. When used in reverse micelles, the luminescence quantum yields of these novel surfactants is dramatically enhanced in the presence of various polar aromatic compounds. Some of these compounds are potential pollutants and carcinogens. The approach has led to a more than 500-fold enhancement of the normally observed sensitized luminescence. In addition, the lanthanide surfactant solution has been used as a mobile phase additive in high performance liquid chromatography (HPLC) separation and determination of various compounds of clinical interest. The coupling of HPLC and sensitized luminescence is attractive because this combination yields the powerful selectivity of HPLC and the excellent sensitivity and specificity of lanthanide luminescence detection. The second research area involves the synthesis and characterization of calixarenes for improved analytical measurements and separation through new guest–host chemistry. The 4-, 6-, and 8-sulfonated calixarenes have been synthesized and characterized by use of absorption, fluorescence, and nuclear magnetic resonance techniques. These compounds have also been used in energy transfer studies from the host calixarenes to the guest fluorescent compounds. Another aspect of the research in this area is the use of calixarenes as organic additives for improved measurements in capillary electrophoresis. These compounds are expected to improve the separation of drugs and aromatic compounds through use of capillary electrophoresis.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemical Engineering

377. *Solubilization of Trace Organics in Block Copolymer Micelles for Environmental Separations Using Membrane Extraction Principles*
Hatton, T.A. **$87,203**
617-253-4588

Block copolymer micelles are being investigated as versatile solvents for the removal and/or recovery of organic contaminants from aqueous solutions. The work consists of (i) development of a comprehensive data base on the solubility enhancements for a range of volatile organics of environmental interest, (ii) characterization of these micelles using light scattering, UV/Vis and fluorescence spectroscopy, densitometry, surface tensiometry, and titration, perfusion and differential scanning calorimetry, (iii) Monte Carlo numerical simulation of the effects of solutes on the structure of the micelles, and (iv) a demonstration of the effectiveness of this approach using hollow fiber membrane contactors. The engineering aspects of the proposed separations scheme is a major focus, with both experimental studies and an engineering economic evaluation. Regeneration of the block copolymer micellar solutions using temperature swings to disrupt the micelles, followed by steam stripping, is currently being explored, and the results are to be included in an economic evaluation of the overall process. Acrylic polyampholytes are a new class of polymers that will be investigated as they have the potential to be regenerated by pH swings rather than by thermal means.

Michigan State University
East Lansing, MI 48824

Department of Chemistry

378. *Direct Examination of Separation Processes in Chromatography by Laser-Induced Fluorescence*
McGuffin, V.L. **$80,025**
517-355-9715

The objective of this research program is to improve the understanding of fundamental hydrodynamic and physicochemical phenomena in chromatography and related separation methods. During this period, detailed studies have been performed to characterize the thermodynamic behavior of octadecylsilica, the most common stationary phase for liquid chromatography. The behavior was examined as a function of temperature (10–70 °C), pressure (400–4463 psi), and bonding density of octadecylsilane on the silica surface (2.7–5.4 umol/m2). The stationary phases with higher bonding density appear to undergo a second-order phase transition within the normal range of operating conditions. Solute retention is dominated by enthalpic processes in the liquid-like region, whereas entropic processes become more significant in the solid-like region. In both of these regions, the molar enthalpy and entropy remain relatively constant with temperature and pressure. Within the transition region, however, the balance of enthalpic and entropic forces changes in a progressive and discontinuous manner. Because this phase transition has a significant effect on solute retention and selectivity, it has important implications for both theoretical and practical applications.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

379. High Definition Raman Imaging

Morris, M.D. **$97,000**
313-764-7360

High definition Raman imaging is performed with a microscope/microprobe, using a tunable dual birefringent Fabry-Perot filter in the imaging mode and a spectrograph in the microprobe mode. The system provides complete three-dimensional and multispectral capability at 512 x 512 pixels per image and 25 cm^{-1} resolution, as well as confocal Raman microspectroscopic capability. In the imaging mode, failure mechanisms of composite materials are studied by means of mapping local compositions. The system is also used for mapping component distribution at dental adhesive/dentin interfaces, a model system for adhesion mechanisms generally. The microprobe mode is used to measure heat transport in electrophoresis capillaries. It also is employed with electrochemically machined probes for surface-enhanced Raman spectroscopy (SERS) with micron resolution. The first target system is ATP release in chromaffin cells, but the technology is useful in limited volume systems generally.

University of Minnesota
Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

380. Continuous Reaction Chromatography

Carr, R.W. **$84,099**
612-625-2551, 612-626-7246

Experimental and theoretical investigations of the simulated countercurrent moving bed chromatographic reactor (SCMCR) are being conducted. The SCMCR is a novel separative catalytic reactor design for which theory predicts that equilibrium limited and low conversion reactions may proceed to very near completion. Experimental implementation of this reactor scheme results in great improvements in product purity and in conversion when compared with the same reactions carried out in conventional reactors. The SCMCR takes advantage of reaction chromatography for increased conversion and product purity due to separation of products from reactants, and the simulated countercurrent moving bed principle for continuous processing and to avoid the solids handling problems of true countercurrency. In the hydrogenation of 1,3,5-trimethylbenzene at 200 °C, where the equilibrium conversion in a non-separative situation is 40%, a mathematical model predicts 97% conversion via the SCMCR, and 98% purity of the product, 1,3,5-trimethylcyclohexane. The experiment shows that 83% conversion and 96% purity can be attained. The difference can be explained by the heterogenous nature of adsorption on the chromatographic adsorbent, which is not taken into account in the calculations. The SCMCR has also been applied to the oxidative coupling of methane to ethane and ethylene (C_2). Interest in converting large reservoirs of natural gas to more valuable feedstocks has spurred extensive investigations of this metal oxide catalyzed reaction in laboratories around the world. In fixed bed and fluidized bed reactors, the large CH_4 to O_2 ratio necessary for high C_2 selectivity limits CH_4 conversion, hence C_2 yields, which are at most 20-25%, while commercialization requires >30% C_2 yields. A SCMCR that is extensively modified to accommodate the high temperatures required for this reaction gives CH_4 conversions of up to 65%, and C_2 yields of more than 50%.

University of Missouri at Rolla
Rolla, MO 65401

Department of Chemistry

381. A New Class of Macrocyclic Chiral Selectors for Stereochemical Analysis

Armstrong, D.W. **$53,835**
314-341-4429

New analytical approaches were developed for the analysis of gases and light hydrocarbons as well as naturally occurring chiral hydrocarbons and other enantiomers. Alpha and beta cyclodextrin were chemically bonded to porous layer fused silica open tubular columns and used as gas-solid chromatographic (GSC) stationary phase for the separation of C_1 to C_6 hydrocarbons and a variety of inorganic gases. In general, these cyclodextrin PLOT columns were superior to the analogous packed columns. The capillary columns show similar selectivities with an increase in efficiency and number of theoretical plates over the packed columns. The cyclodextrin stationary phases show good selectivities toward the light hydrocarbons and inorganic gases on capillary columns as short as ten meters. Subambient temperatures allow the baseline resolution of oxygen from nitrogen. These columns have been effectively utilized at temperatures up to 260 °C without loss of efficiency or degradation of selectivity. Complex natural samples must be fractionated before enantiomeric analysis. Centrifugal partition chromatography (CPC) was used to fractionate a catalytic-cracking feedstock (i.e., catalytic cracker feed) into 16 separate fractions in the descending mode and 5 fractions in the inverse or ascending mode. Each fraction was analyzed by UV, fluorescence, and synchronous luminescence (SL) spectroscopy as well as by gas chromatography/mass spectrometry (GC/MS). CPC can be used to fractionate larger samples of this type and with a greater degree of selectivity than previously reported preparative HPLC approaches. The SL spectra tended to be much more useful and information-rich for these complex mixtures as compared to UV or fluorescence spectra. CPC effectively separated catalytic cracker feed into fractions by polarity, aromaticity, and alkyl substitution patterns. Fractionation by heteroatom type and of homogues was observed. The aromatic content found by gravimetry after CPC separation matched well with the aromatic content measured by UV spectrometry. The enantiomeric separation of hydrocarbons by reversed phase LC is described. Chiral recognition results largely from "shape-selectivity" (i.e., the tight fit abstract of a hydrophobic moiety into a hydrophobic cavity) with few other substantial contributing interactions. Small amounts of methyl-tert-butyl ether greatly enhanced the separation efficiency. All commercial samples contain significant quantities of enantiomeric impurities. Approximately 90 chiral compounds were resolved by capillary GC on three different cyclodextrin-based, wall-immobilized capillary columns. Despite similarities in their structure and make-up, these stationary phases often displayed different enantioselectivities. Also their selectivities were different from wall-coated varieties of neat alkyl or alkyl-acyl derivatives of cyclodextrin. The immobilization chemistry affects selectivity as well as stability and efficiency. The practical result is a net increase in the number and types of compounds that can be resolved as well as their expanded usefulness in other capillary techniques.

National Institute of Standards and Technology, Gaithersburg
Gaithersburg, MD 20899

Chemical Kinetics and Thermodynamics Division

382. *Ion Kinetics and Thermochemistry Pertinent to Direct Mass Spectrometric Organic Speciation*
Sieck, L.W. **$144,500**
301-975-2563

This project involves the measurement of fundamental properties of gas phase ions. The National Institute of Standards and Technology (NIST) pulsed electron beam mass spectrometer (MS) is the prime experimental facility, and a Fourier transform ion cyclotron resonance (FTICR) instrument and triple MS system are also available. Emphasis is in two areas. One area is definition of the thermochemistry of associated and cluster ions via variable-temperature equilibrium measurements. Correlation lines, which express the dependence of bond strengths upon the differences between the acidities or proton affinities of the two interacting partners, are then developed for predictive purposes for use in experimentally inaccessible systems. These investigations are augmented by collaborative efforts involving the study of intracluster ion–molecule chemistry occurring after ionization of neutral organic clusters produced in expansion beams. The second area involves extension and clarification of earlier kinetic studies from other laboratories to provide a more accurate database for gas phase ion and neutral thermochemistry. Currently, research includes extensive measurement of proton transfer equilibria as a function of temperature to provide interlocking thermochemical ladders which, when referenced to primary standards, provide absolute proton affinity and acidity scales. Related studies include ion pyrolysis and ion kinetics pertinent to plasma etching and electric breakdown in gaseous dielectrics.

University of North Carolina at Chapel Hill
Chapel Hill, NC 27599

Department of Chemistry

383. *Solid-State Voltammetry and Sensors in Gases and Other Nonionic Media*
Murray, R.W. **$75,175**
919-962-6296

This project is based on design and application of quantitative electrochemical voltammetry, largely with microelectrodes, to investigate diffusion, electrochemical reactions, and electron transfer reactions of electron donor/acceptor solutes dissolved in rigid, typically polymeric, solvents. The goals of the project are (i) to develop miniaturized electrodes and electrochemical cells, electrochemical methodologies, and requisite theory that allow quantitative voltammetry in the rigid polymeric media, (ii) to explore important characteristics of homogeneous and heterogeneous electron transfer reaction dynamics in rigid environments, (iii) to explore polymer-phase transport processes, 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) to learn how 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.

Purdue University
West Lafayette, IN 47907

Department of Chemistry

384. *Ion Trap Mass Spectrometry: Ion Motion, Reactions, and Applications*
Cooks, R.G. **$150,000**
317-494-5262 **(18 months)**

Fundamental understanding of ion motion in the quadrupole ion trap is being sought by (i) laser tomography experiments which yield temporal and spatial resolution, (ii) dc pump/laser probe experiments for accelerating ions and characterizing their motion, and (iii) novel methods of manipulating ions, including phase-locked resonance excitation, dc pulse activation, and stored waveform methods of ion ejection. Simulations of the motion of ensembles of ions, including collision effects and ion-ion interactions, are being developed to supplement the experimental data. This information is being applied : (i) to evaluate capabilities for measuring ion polarizability, (ii) to characterize the neutral products resulting from positive ion/negative ion recombination, and (iii) to attempt to disperse ion by differences in ions mobility arising from different collision cross sections. In addition, improvements in analytical applications of this type of mass spectrometer, including improved mass resolution and improved mass measurement accuracy, are being sought through accurate descriptions of ion motion. Particular chemical systems of interest include (i) the fullerenes, where Diels-Alder and other ion/molecule reactions are of interest; (ii) multiply charged quaternary polypyridyl salts; and (iii) phenoxyl and other free radicals, the thermochemical properties of which are being measured by cluster ion dissociation.

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

Freiser, B.S. **$97,000**
317-494-5270

Studies continue on the chemistry and photochemistry of metal-containing ions in the gas phase by Fourier transform mass spectrometry (FTMS). Three areas of current interest are summarized here: (1) Researchers have previously generated some externally bound transition metal C_{60} ions in the gas phase, MC_{60}^+, and are particularly interested in the effect of C_{60} as a ligand on metal ion reactivity and whether the derivatization of C_{60} can be catalyzed by the metal center. One interesting case is the reaction of CoC_{60}^+ with cyclopropane in which a series of metallated and unmetallated alkyl derivatives are observed. (2) Studies of small metal cluster ions are under way with one focus being on bimetallic species synthesized in situ. In light of published results on Fe_n^+, the effect of systematically varying one of the metal atoms in the cluster is studied. (3) Metal ions hold promise as selective chemical ionization reagents. A particularly good application of this methodology has been to take advantage of the regio- and stereo specific reactivity of selected metal ions to determine the isotopolog and isotopomer distributions of partially deuterated aromatic compounds. This method is found to be far superior over high resolution NMR analysis.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemical Engineering

386. Chemical Interactions between Protein Molecules and Polymer Membrane Materials

Belfort, G. **$88,000**
518-276-6948 **(9 months)**
$64,018 aft

The molecular interactions between a layer of protein (hen egg-white lysozyme) and a Langmuir–Blodgett layer made from an organic silane (hexadecyltriethoxysilane, HTE) were measured using the Surface Forces Apparatus (SFA). HTE is used as a model hydrophobic surface since it readily forms a smooth Langmuir–Blodgett layer and has been shown to be extremely apolar. SFA measurements were also obtained between a lysozyme layer and an HTE layer coated with a hydrophobic membrane polymer (polysulfone, PSu). The HTE and PSu surfaces were characterized using Electron Spectroscopy for Chemical Analysis (ESCA) and Atomic Force Microscopy (AFM) to determine the actual coverage of the surfaces. The results of this study are relevant to a better understanding of the mechanism of protein interactions with hydrophobic materials. This is important in trying to understand the complex phenomena of membrane fouling from protein adsorption.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

387. Determination of Solvation Kinetics in Supercritical Fluids

Bright, F.V. **$93,000**
716-829-3615

This project is directed toward determining the effects of supercritical fluids on solvation and chemical reactions. The main sub-projects are (1) understanding the effects of neat and entrainer-modified supercritical fluids on solute-fluid interactions; (2) determining the influence of supercritical solvents on the energetics and dynamics of solute conformation; and (3) probing the effects of continuous phase density on the *internal* dynamics of reverse micelles formed in supercritical fluids. In order to follow these fast molecular-level processes, modern picosecond in situ optical spectroscopy is being used. To date this work has (1) helped define how "diffusion controlled" reactions proceed in supercritical fluids; (2) determined how and on what time scale entrainers preferentially solvate solutes in the near-critical region; (3) shown that the conformation (i.e., reactivity) of flexible solutes can be altered easily with fluid density; (4) studied how lateral diffusion within reverse micelles (formed in supercritical alkanes) is affected by the continuous phase density; and (5) begun to probe how the conformation of polymers can be controlled with supercritical fluids. This new information is leading to a better molecular-level understanding of the unique chemistry of supercritical fluids.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering and Materials Science

388. Mechanisms of Gas Permeation through Polymer Membranes

Stern, S.A. **$88,270**
315-443-4469

The objective of the present study is to investigate the mechanisms of gas permeation through polymer membranes. This information is required for the development of new, energy-efficient membrane processes for the separation of gas mixtures of industrial interest, as well as for increasing the efficiency of extant processes. The permeation of gases through polymer membranes occurs by a "solution-diffusion" mechanism, the diffusion of the penetrant gas inside the polymer matrix being rate-controlling. The development of fast computers has made possible the prediction of diffusion coefficients for small gas molecules in polymers via molecular dynamics simulations. A research effort has been initiated in this field and diffusion coefficients are being calculated for several light gases in poly(organosiloxanes). A supercomputer facility is being used for this purpose. So far, diffusion coefficients of O_2, N_2, CO_2, and CH_4 in poly(dimethyl siloxane) at 300 K have been calculated by the molecular dynamics technique. The value of each diffusion coefficient was taken as the average of five different microstructures of this polymer. The calculated and experimental values of the diffusion coefficients have been found to agree within 10%. The effects of substituting different functional groups in the side chains or backbone chains of poly(dimethyl siloxane) on the gas diffusion coefficients is presently under investigation.

University of Tennessee at Knoxville Knoxville, TN 37996

Department of Chemistry

389. *Polymer-Based Separations Synthesis and Application of Polymers for Ionic and Molecular Recognition*

Alexandratos, S.D. **$84,390**
615-974-3399

The synthesis of bifunctional polymers to study the synergistic interaction of supported ligands required new preparative techniques due to the limited number of reactions that could immobilize well-defined pairs of ligands on polymers. The development of bifunctional interpenetrating polymer networks (IPNs) was an important part of the research during the current period. Initial results show that the bifunctional IPNs offer a different binding environment to metal ions than the monofunctional analogues for example, as the imidazole:carboxylate ratio changes along the series 1:0, 0.5:0.5, 0:1, binding constants for Cu(II) at pH 5 are 3130, 1556, and $77N^{-1}$, while for Co(II) are 294, 189, and $26N^{-1}$, respectively. The effect of the microenvironment surrounding the imidazole ligand on its ability to complex metal ions was probed with a series of poly (N-vinylimidazole-co-ethyl acrylate) IPNs, with imidazole being replaced by increasing levels of weakly coordinating carboxylate ester moieties. The strength of the imidazole - ion interaction is found to be sensitive to the polymer microenvironment. Solid state ^{13}C NMR spectroscopy was introduced as a technique which could refine the understanding of the structure of the bifunctional IPNs. Network differences in the crosslink level and swelling characteristics allow two different types of solid state NMR techniques to be used in a complementary manner for identifying both networks. Combining the spectra with wet chemical analyses allows for an unambiguous determination of the ligands and their microenvironment.

390. *Study of the Surface Properties of Ceramic Materials by Chromatography*

Guiochon, G. **$83,420**
615-974-0733

Many properties of powders depend on the surface properties of their particles. The aim of this project is the characterization of powders by the adsorption energy distributions of a number of selected probe compounds. The procedure followed involves the determination of the adsorption isotherms of the probes and the calculation of the adsorption energy distribution from this isotherm. Adsorption isotherms are measured by a chromatographic procedure (elution by characteristic points), using open tubular columns whose walls are coated by a layer of the powder. This method permits an accurate determination of the isotherms. The adsorption energy distribution is derived from the isotherm by numerical solution of an integral equation relating it to the local adsorption isotherms and to the measured isotherm. Classical procedures are inaccurate because they introduce bias and artifacts. A new procedure has been developed which avoids these errors. Simulations of the measurement process have shown that the isotherms must be determined in an unusually wide range of partial pressures. This causes experimental problems which are being solved. Measurements are carried out using silica powders and various silica surfaces modified by chemical reactions. Diethylether, methanol, and methylene chloride are used as probe compounds.

391. *Capillary Electrokinetic Separations with Optical Detection*

Sepaniak, M.J. **$76,630**
615-974-8023

This multifarious research program is dedicated to the development of capillary electrokinetic separation techniques and associated optical methods of detection. Currently, research is directed at three general objectives. First, fundamental studies of pertinent separation and band broadening mechanisms are being conducted, with the emphasis on understanding systems that include highly ordered assemblies as mobile phase additives. The additives include cyclodextrins, affinity reagents (e.g., immunochemicals), soluble polymers (as size-sieving reagents), and fullerenes and are employed in electrophoretic (e.g., capillary zone electrophoresis (CZE)) and/or electrochromatographic (e.g., micellar electrokinetic capillary chromatography (MECC) and capillary electrochromatography (CEC)) modes of separation. The utility of molecular modeling techniques for predicting the effects of highly ordered assemblies on the retention behavior of isomeric compounds is under investigation. Reasonable correlations between computationally derived cyclodextrin–solvate interaction energies and retention behavior have been observed for certain mixtures of geometrical isomers and optical isomers. In addition, nonaqueous CEC separations of common fullerenes have been performed for the first time. Second, the analytical methodologies associated with these capillary separation methods are being advanced through the development of retention programming (with simplex optimization) techniques and new strategies for performing optical detection. With regard to the latter, the advantages of laser fluorimetry are extended through the inclusion of fluorogenic reagents in the mobile phase. These reagents include oligonucleotide intercalation reagents for detecting DNA fragments. Chemiluminescence detection using postcapillary reactors–flow cells is also in progress. It is expected that this work will provide a suitable background for performing detection using electrokinetic flow multiplexing. Third, successful development of these separation and detection systems will fill current voids in the capabilities of capillary separation techniques. In particular, it should be possible to perform highly efficient and selective separations of hydrophobic compounds (e.g., higher MW polycyclic aromatic hydrocarbons), mixtures of chiral compounds, DNA fragments, and fullerene mixtures.

Texas A & M University
College Station, TX 77843

Department of Chemistry

392. Development of Laser-Ion Beam Photodissociation Methods

Russell, D.H. **$83,420**
409-845-3345

The objectives of this research program include numerous aspects of laser-mass spectrometry and fundamental gas-phase ion chemistry. Photodissociation methods are being developed for probing the dynamics of dissociation reactions of highly activated ionic systems. In addition, the potential analytical utility of laser-ion beam photodissociation for the structural characterization of large biomolecules is being evaluated. A second-generation photodissociaton apparatus is now completed and used for a range of tandem mass spectrometry experiments. The instrument consists of a magnetic sector (Kratos MS-50) as MS-I and a high-sensitivity/high-resolution reflectron time-of-flight instrument as MS-II. The ions are formed by Cs^+ ion secondary ion mass spectrometer (SIMS) (dry or liquid matrix) and/or pulsed UV laser desorption, and photodissociation of the mass-selected ion is performed by using a high-power, pulsed excimer, Nd:YAG or N_2 laser. The primary objective of the current 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 studies are being expanded to include tandem time-of-flight (TOF/TOF) instruments. 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 photodissociaton 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.

Texas Tech University
Lubbock, TX 79409

Department of Chemistry and Biochemistry

393. Metal Ion Complexation by Ionization Grown Ethers

Bartsch, R.A. **$90,210**
806-742-3069

Objectives of this research are the preparation 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 functional groups are novel agents for metal ion separations by solvent extraction and liquid membrane transport processes. Movement of the metal ion from an 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 compared with that of structurally related non-ionizable crown ethers in separations involving metal chlorides, nitrates, and sulfates. New crown ether carboxylic acids, phosphonic acid monoethyl esters, phosphonic acids, and sulfonic acids 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 prepared by condensation polymerization of proton-ionizable dibenzocrown ether monomers. In addition to ion-exchange sites, these resins also provide crown units for metal ion complexation. Sorption behavior of these resins for a variety of alkali metal, alkaline earth, and heavy metal cations is being assessed.

University of Texas at Austin
Austin, TX 78712

Department of Chemical Engineering

394. Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications

Koros, W.; Paul, D. **$86,330**
512-471-5866

This project has evolved greatly and has had a significant influence on the development of advanced materials now being employed in second generation industrial gas separation membranes. Moreover, the third generation of materials and processes for their formation are beginning to be researched, and the goal is to establish guiding principles for these materials. The characterizations of sorption and diffusion coefficients governing the permeability and permselectivity of important gas pairs (H_2/CH_4, CO_2/CH_4, and O_2/N_2) are ongoing. Elevated temperature studies (>200 °C) are being performed on attractive candidates for new applications such as membrane-assisted reactors that benefit from this high temperature operational ability. This work is being extended to include actual implementation in butane dehydrogenation reactors with an industrial cooperative partner. The next generation of gas separation membrane materials are likely to be increasingly rigid and difficult to process solely via traditional means. Crosslinking and the introduction of long flat packable units in the backbone structure are being pursued as a way to increase the size and shape selective natures of the materials. Moreover, chemical reactive treatments, such as fluorination and bromination, are being investigated as avenues to increasing selective layer rigidity while minimizing processing into a useful membrane form.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

395. Laser Flash Photolysis, EPR, and Raman Studies of Liquids at Elevated Pressures

Eyring, E.M. **$80,000**
801-581-8658

The focus of this research is the determination of rates and mechanisms of chemical reactions in liquid solutions and in molecular sieves utilizing high pressure stopped-flow spectrophotometry, laser flash photolysis, EPR, and Raman techniques. Reaction rates are measured at pressures ranging from one atmosphere to 1500 atmospheres in order to determine volumes of activation. Volumes of activation are then combined with enthalpies and entropies of activation to obtain a clarification of reaction mechanisms. Reactions in which an arsenazo III ligand is displaced by diethylenefriaminepentacetate (DTPA) or by ethylenediaminetetraacetate (EDTA) in the first coordination sphere of trivalent europium, gadolinium, and terbium ions are being studied in aqueous solutions. A thermal ring closure reaction involving a molybdenum hexacarbonyl complex and 1,10-phenanthroline is being investigated in liquid carbon dioxide and in supercritical carbon dioxide. Changes with temperature and pressure in the volume of activation for this ring closure reaction in supercritical carbon dioxide are very large. A collaboration with another research group has demonstrated the usefulness of two of these high pressure techniques for elucidating the behavior of the binuclear Fe-O-Fe center in Myohemerythrin that reversibly binds molecular oxygen.

396. Time-Resolved Analytical Methods for Liquid/solid Interface

Harris, J.M. **$92,150**
801-581-3585

A number of chemical phenomena that occur at the boundaries between insulating solids and liquids (adsorption, partition, monolayer self-assembly, catalysis, and chemical reactions) are important to energy-related analytical chemistry. These phenomena are central to the understanding of chromatographic methods, solid-phase extraction techniques, immobilized analytical reagents, and optical sensors. In order to understand interfacial reaction mechanisms and dispersion in surface interactions, the goal of this program is to develop surface-sensitive spectroscopies by which chemical kinetics at liquid/solid interfaces can be observed on time-scales from nanoseconds to seconds. Several methods are being adapted to perturb interfacial chemistry including stopped-flow, temperature-jump, and photoexcitation techniques. The rates of relaxation of the surface chemistry to these perturbations are measured using fluorescence, surface-enhanced Raman, and infrared-reflectance spectroscopies. Surfaces under investigation include porous and fused silica, polymers, colloids in suspension, and thin insulating layers over metallic substrates. A variety of interfacial kinetic phenomena are being studied including transport of molecules at liquid/solid boundary and through porous solids, adsorption and desorption of molecules at surfaces, covalent-binding of molecules to surfaces, reorganization of surface-bound layers, interfacial charge-transfer, and metal ion complexation.

Department of Metallurgical Engineering

397. Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species

Miller, J.D. **$97,000**
801-581-5160

The objective of this research program is to develop fundamental understanding of surfactant adsorption phenomena at nonsulfide mineral surfaces in order to establish more energy efficient froth flotation separations. Froth flotation is one of the most important examples of applied surface chemistry and 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, Raman internal reflection spectroscopy, and nonequilibrium laser-Doppler electrophoresis are being developed to analyze surfactant adsorption phenomena at mineral/water interfaces and to describe the impact of the adsorption phenomena on the hydrophobic character of the surface. The nonsulfide flotation research includes the soluble salt, semi-soluble salt, and insoluble oxide mineral systems. A surface charge/collector colloid adsorption model has been substantiated to explain the flotation behavior of soluble salt minerals including alkali halides and double salts from their saturated brines. Atomic force microscopy in concert with FTIR and Raman IRS techniques is currently being used to investigate the influence of the structure of interfacial water on the hydration forces responsible for the adsorption of collector colloids in soluble salt flotation. In the category of semi-soluble salt minerals, carboxylic acid adsorption by fluorite and calcite minerals is being examined in situ by FTIR IRS and Raman spectroscopy. In addition, spectroscopic examination of transferred LB films is in progress to determine the nature and reactivity of adsorbed unsaturated carboxylates. Several insoluble oxide mineral systems including sapphire/sodium dodecyl sulfate and quartz/amine are being examined to describe collector adsorption phenomena with respect to adsorption density, adsorption state, and the order/conformation of adsorbed surfactant species. The effect of surface hydration and interfacial water structure as determined from surface spectroscopy will provide further information on the relationship between collector adsorption phenomena and surface hydrophobicity. 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

398. Selective Methods for Quantification of Target Species in Complex Mixtures

Rutan, S.C. **$59,655**
804-367-7517 **(9 months)**

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 hydrocarbon derivatives and metabolites. Quantification will be achieved by using methods such as rank annihilation, adaptive filtering, and residual bilinearization. Standard addition methods will be used for calibration. In the second experimental approach, thin-layer chromatography will be used to separate 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. Chemiluminescent detection approaches will also be investigated in this work. The application of the residual bilinearization method in the analysis of this type of data will also be explored. This novel approach will be applied to the analysis of amino acids.

Washington State University
Pullman, WA 99164

Department of Physics

399. UV Laser-Surface Interactions Relevant to Analytic Spectroscopy of Wide Bandgap Materials
Dickinson, J.T. **$109,620**
509-335-4914

This research emphasizes 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 emissions 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 current interest. In several materials, laser induced dislocation motion is a primary source of vacancy defects in the near surface region of several wide bandgap materials. Current studies involve imaging and quantifying defect densities, the production of surface defects with particle bombardment, modeling the role of anion vacancies in photostimulated emission of cation, and studies of laser interactions with inorganic solids containing covalently bonded anions which photodecompose.

University of Wyoming
Laramie, WY 82071

Department of Chemistry

400. Solid-Matrix Luminescence Analysis
Hurtubise, R.J. **$87,300**
307-766-6241

The major emphasis in this project is on the development of a basic understanding of the interactions that are needed for the room-temperature fluorescence and phosphorescence of aromatic compounds adsorbed on solid matrices. The solid matrices employed are trehalose, cyclodextrins, sodium acetate, and filter paper. Heat capacity data are acquired for sodium acetate, sodium acetate/sodium chloride mixtures, and cyclodextrin/sodium chloride mixtures over a wide temperature range. These data are related to the nonradiative transitions from the triplet state to the ground state of phosphors adsorbed on the solid matrices. With filter paper as a solid matrix, equations are developed that relate the Young's modulus of filter paper samples to moisture quenching of the phosphorescence of organic phosphors adsorbed on filter paper. A variety of photophysical data are compared for a filter paper. A variety of photophysical data are compared for a perdeuterated and undeuterated polycyclic aromatic hydrocarbon adsorbed on several solid matrices to determine the effects of deuteration on solid-matrix phosphorescence lifetimes. Also, photophysical data are acquired for eleven polycyclic aromatic hydrocarbons on different solid matrices and related to the energy-gap law. A new approach is developed for obtaining room-temperature solid-matrix luminescence from lumiphors in solid carbohydrates.

Heavy Element Chemistry

Florida State University
Tallahassee, FL 32306

Department of Chemistry

401. Research in Actinide Chemistry
Choppin, G.R. **$113,490**
904-644-3875

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. Binding of actinides in the III through VI oxidation states to humic acid is very rapid. Upon binding, most of the An is "weakly" bound and two days were found to be required to reach equilibrium between "strong" and "weak" binding. Binding studies of NpO_2^+ in humic acid solutions gave stability constants which had no dependence on pH in contrast to the behavior of the complexation of An(III), (IV), and (VI). Other systems under study at present involve actinide interaction with silicate ligands. The fluorescent half-life method has provided information on the residual hydration of the trivalent metals in a variety of complexes and in a number of systems used in solvent extraction separations of actinides. Studies on hydrolysis, carbonate, and phosphate complexation are also under way.

University of New Mexico
Albuquerque, NM 87131

Department of Chemistry

402. *Development of Immobilized Ligands for Actinide Separations*
Paine, R.T. **$94,090**
505-277-1661

The objectives of this project are to (1) design new families of organic ligands suitable for selective chelation of f-block element ions present primarily in complex liquid and solid-waste matrices, (2) examine the coordination chemistry and molecular structures of ligands in order to better understand ligand-metal binding, and (3) prepare solid-phase, immobilized chelators. The current efforts are specifically directed at the synthesis of novel phosphonopyridine N-oxide ligands that can display six, seven, and eight-membered chelate rings. These ligands are particularly robust and selective in their metal binding properties. The extraction properties of selected ligands are also characterized by radiochemical methods. Ligands that demonstrate favorable separations properties are then incorporated onto solid organic or inorganic supports, and the steric and electronic factors that subsequently influence the separation properties are examined.

Ohio State University
Columbus, OH 43210

Department of Chemistry

403. *The Electronic Structure of Heavy-Element Complexes*
Bursten, B.E. **$64,020**
614-292-1866

The focus of this project is to use 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 Xα (DV-Xα) method, and the relativistic ab initio methods in the COLUMBUS suite of programs. The V-Xα method has given excellent results with respect to the calculation of optical excitation energies in f^1 systems, such as the AnX_6^{q-} complexes (An = Pa, q = 2; An = U, q = 1; An = Np, q = 0; X = halide) and more complex f^1 organometallic complexes, such as $(\eta^8{-}C_8H_8)_2Pa$. Because the fully relativistic DV-Xα method provides information about the bonding in complexes that is hard to interpret, a quasirelativistic DV-Xα method, one that incorporates all of the major relativistic effects except for spin-orbit coupling, is also under development. This method will allow the results to be presented in the more familiar nomenclature of single groups rather than the double groups required for fully relativistic methods. Relativistic ab initio calculations are undertaken on a number of small model systems, such as UO_2Cl_2, UO_4^{2-}, and $U(NH)_4^{2-}$. These calculations will be used to determine whether these systems prefer planar structures, which might be expected from the geometry of the uranyl ion, or tetrahedral geometries. These results will be extended to studies of some novel new organometallic complexes, such as $Cp^*U(NR)_2$ ($Cp^* = \eta^5{-}C_5Me_5$).

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

404. *Physical–Chemical Studies of Transuranium Elements*
Peterson, J.R. **$150,350**
615-974-3434

This project provides training for pre- and postdoctoral students in chemical research with the transuranium 5f (actinide) and related 4f (lanthanide) elements. The goals of this project are to interpret and correlate the results of continuing investigations of the basic chemical and physical properties of these elements as related to general theories. Current research emphasis is on (1) characterization of f-element compounds by luminescence spectroscopy (extending experience and data base of optical probes of crystal structure); (2) study of energy upconversion processes in f-element-doped glass ceramics; (3) use of luminescence lifetimes to characterize f-element materials (and to determine the influences of various experimental parameters on them); (4) synthesis and characterization of mixed actinide-lanthanide titanates (for possible use to immobilize nuclear waste); (5) use of high pressure to alter the electronic structure about an f-element ion, to cause a phase transition in the material, to induce amphorization, or to determine the relationship with pressure of the several phases of an f-element material; (6) determination of the enthalpy of formation of selected lanthanide and actinide oxychlorides and the evaluation and applicability of predictive methods for estimating the thermodynamic properties of lanthanide and actinide materials; and (7) investigation of various techniques for preconcentration of technetium (Tc) in very dilute biological samples (e.g., human urine) in preparation for radiometric determination of Tc and optimization of equipment and procedures for the radiometric determination of Tc.

Chemical Engineering Sciences

University of California, San Diego
La Jolla, CA 92093

Department of Applied Mechanics and Engineering Sciences

405. *Premixed Turbulent Combustion*
Libby, P.A. **$53,909**
619-534-3168

In the past this project has involved several areas of research concerned with premixed turbulent combustion but during the past year efforts have focused on flames in stagnating turbulence. Such flames are rich in problems of fundamental interest, e.g., the problem of the extinction of turbulent flames. As a consequence, there are five or six laboratories in Western Europe and one in the United States carrying out relevant experimental investigations. The first two theoretical studies of these flames utilizing the K-ε theory of turbulence to characterize the fluid mechanics of the flow have been completed and published in

Combustion and Flame. A comparison of the theory and experiment for nonreactive impinging and counterflowing turbulent streams has been analyzed and four journal articles have been published on this work. Although the research is primarily theoretical in nature, a modest experimental effort on turbulent impinging reactant streams has been accepted for the Twenty-fifth Symposium (International) on Combustion. An important finding resulting from an effort to compare existing theory and experiment for flows involving combustion is the realization that heat release vitiates the assumption of a thin flame, the assumption employed in existing theory, and that an entirely new approach is called for, one treating the entire flow from one jet exit plane to the other, or from one exit plane to the wall. The approximate analysis is currently under way involving a Reynolds stress theory for the fluid mechanical treatment and the Bray-Moss-Libby theory for the aerothermochemistry. The study of highly idealized premixed combustion in a channel has been completed and submitted for possible publication.

Clarkson University
Potsdam, NY 13699

Department of Chemical Engineering

406. *Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures*
Lucia, A. **$54,805**
315-268-6674

The multicomponent multistage separation process analysis framework has been expanded. Global uniqueness of steady-state solutions has been rigorously established for separators involving ternary mixtures and fixed total vapor flow and pressure profiles. This set of specifications, which is called fixed molar overflow, represents a generalization of constant molar overflow and indirectly includes energy balances in the analysis. Recent "proofs" by other researchers in the field, based on extrapolations of infinite columns at infinite reflux, have been shown to contain contradictions, including violation of overall mass balance. Related research on feasibility for separation process design and simulation has been initiated and methods for computing singular points for defining either limits of feasibility or simply feasibility or infeasibility have been developed. All computer tools have been tested on a variety of separation process examples.

Colorado School of Mines
Golden, CO 80401

Department of Chemical Engineering and Petroleum Refining

407. *Composition of Dependence of Fluid Thermophysical Properties Theory and Modeling*
Ely, J.F. **$116,241**
303-273-3885

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 which provide accurate predictions of phase transitions and bulk-phase properties in systems that have large size and/or polarity differences.

Colorado State University
Fort Collins, CO 80523

Department of Chemical Engineering

408. *Study of Improved Methods for Predicting Chemical Equilibria*
Lenz, T.G. **$89,500**
303-491-7871

Thermodynamic data are of significant importance in designing new products and clean and efficient processes. A primary goal of this project is to provide an inexpensive yet accurate molecular-based computational model for predicting thermodynamic properties of hydrocarbons and heteroatomic molecules. Recent effort has involved parameterizing a molecular mechanics program (QCFF) for computation of standard enthalpies of formation ($\Delta H°_f$) and other thermodynamic quantities ($S°$, $C°_p$, and $H°_t$ - $H°_0$) for ethers and alcohols. Results have shown rms deviations between the QCFF calculated ($\Delta H°_f$) (298.15 K), $S°$ (298.15 K) and $C°_p$ (298.15 K), and the corresponding experimental values, for a group of ethers and alcohols, to be 0.53 kcal mol^{-1}, 0.54 cal mol^{-1} K^{-1}, respectively. The QCFF program was further employed to study the reaction equilibria for the dimerization of isoprene to two product isomers. One of these two isomers, dipentene, is a more useful industrial product. The QCFF study of this dimerization suggested that the formation of dipentene was likely controlled by kinetics rather than thermodynamics at low and moderate temperatures. This work thus emphasizes the power of QCFF, one of very few thermodynamic force fields available at present, in extending the thermodynamic force fields available at present, in extending the thermochemical database for heteroatomic molecules and studying reaction equilibria for industrially important reactions.

Cornell University
Ithaca, NY 14853

School of Chemical Engineering

409. *Simulation of Fluid Behavior in Well-Characterized Porous Materials*

Gubbins, K.E. **$227,217**
607-255-4385

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 pillared clays are being studied. The work may later be extended to other well-characterized materials. Studies in the first stage of the project have been on adsorption, heat of adsorption, phase changes, hysteresis, and diffusion for simple fluids (inert gases, methane, nitrogen) and their mixtures. Fluids of chain molecules (both alkanes and simple models of associating chain molecules) in carbons are also under study. As a second stage of the work, studies are under way on the behavior of water in carbons and aluminophosphates, which is quite different from that of the simple gases. The project includes experimental studies of adsorption in some of these materials, to provide data to test the models.

410. *Molecular Simulation of Phase Equilibria for Complex Fluids*

Panagiotopoulos, A.Z. **$125,000**
607-255-8243

The objective of this project is the investigation of phase equilibria for complex fluids using molecular simulation techniques. Current research encompasses three main classes of systems, namely polymeric, surfactant, and ionic systems. The first reported calculation of the phase coexistence envelope for a truly macromolecular continuous-space system was recently completed. The chain increment method developed in previous project periods was used for the calculation. Ongoing investigations in this area focus on testing engineering models for predicting activity coefficients in polymer/solvent systems. The second study area is block copolymeric surfactant solutions for which there is significant interaction between the formation of self-assembled microstructures and macroscopic phase equilibrium behavior. Finally, strongly interacting ionic systems are under study using specially developed cluster move algorithms and distance-biased pair transfers. These techniques were found to provide an efficient route to molecular simulation of the phase coexistence properties of ionic systems.

Department of Mechanical and Aerospace Engineering

411. *Reaction and Diffusion in Turbulent Combustion*

Pope, S.B. **$95,000**
607-255-4314

Direct numerical simulations (DNS) are being used to study fundamental processes in non-premixed turbulent reacting flows. A broad range of Damkohler number, Da, and reaction zone thicknesses are being studied, encompassing stable, near-equilibrium reaction; local extinction; and global extinction. A simple thermochemical model for one-step reversible reaction is employed, in which the state of the fluid is described by the mixture fraction $\varsigma(x,t)$ and the perturbation from equilibrium $y(x,t)$. A pseudo-spectral method, with grid sizes up to 128^3, is used to solve the Navier–Stokes equations and the conservation equations for ς and y. These equations are augmented with artificial forcing, so that the resulting velocity and mixture fraction fields are statistically stationary, homogeneous, and isotropic. At sufficiently high Damkohler number, the perturbation field is also statistically stationary, corresponding to stable reaction. But at lower Da, y increases without bound, corresponding to global extinction. The critical Damkohler number is Dacrit at which global extinction occurs, has been determined from the simulations, and is found to be significantly different from that predicted by simple models (flamelet, conditional moment closure, etc.). A simple statistical model has been constructed to show that the discrepancy can plausibly be explained by statistical variability. The simulation results are being used to assess the accuracy of simple models, especially for Damkoher numbers at which there is globally stable reaction, but significant local extinction.

University of Delaware
Newark, DE 19716

Department of Chemical Engineering

412. *New Generation of Group Contribution and Equation-of-State Models*

Sandler, S.I. **$103,472**
302-831-2945

To make intelligent, cost-effective decisions for the design of new 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 contract addresses this problem from three different directions. First, the recently developed Wong–Sandler mixing rules, which have greatly expanded the range of application of equations of state to highly nonideal mixtures, are being studied for collections of mixtures which heretofore 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 are being incorporated into a new generation of group contribution methods (such as UNIFAC), to improve the accuracy of these important prediction methods. The third area of research is to use computer simulation and statistical mechanical theory to develop an accurate thermodynamic description of long chain hydrocarbons, polymers, and mixtures involving these components. The Wong–Sandler mixing rules, discussed above to study solutions of these chain components in small molecule solvents, are also being used.

University of Illinois at Chicago
Chicago, IL 60680

Department of Chemical Engineering

413. *Transport Properties of Dense Fluid Mixtures Using Nonequilibrium Molecular Dynamics*
Murad, S. **$70,000**
312-996-5593

A new method, recently developed to study the behavior of fluids in confined geometries, has been extended to study the dynamic behavior of a solution separated from a pure solvent by a semi-permeable membrane. The membrane was designed to be impermeable to the solute molecules but permeable to the solvent molecules. Using this technique, it was possible to observe both osmosis and reverse osmosis in accordance with the Le-Chatelier's principle. This method has considerable promise for studying at the fundamental level, the phenomenon of reverse osmosis. Reverse osmosis can be used for many types of separations, including those important for waste water treatment, food purification and concentrations, etc. Computer simulations have been carried out using the method of nonequilibrium molecular dynamics to study the enhancement in thermal conductivity of simple fluids near the critical region. Results show that for system sizes larger than 10 molecular diameters, critical effects begin to be observed. These studies are continuing as well as a study of molecular fluids in the future.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemical Engineering

414. *Prediction of Thermodynamic Properties of Coal Derivatives*
Donohue, M.D. **$87,000**
410-516-7761

Changes in the chemical and petroleum industries have led to the need to predict properties for substances and mixtures that are complex in both their chemical structures and their intermolecular potential functions. This project uses a combination of experiments, computer simulations, and theory to better understand these systems. This experimental program includes spectroscopic measurements of specific molecular interactions, as well as spectroscopic measurements of local effects due to nonspecific interactions (i.e., non-random and density-dependent behavior). Computer simulations have been directed at understanding the effects of molecular geometry on both the equation of state and microstructure of the fluid. Theoretical work includes use of perturbation theories, integral equations (O-Z and RISM), and lattice theories. The comparison of spectroscopic measurements with the models that have been developed show good agreement for amphiphilic molecules and for polymer-solvent mixtures.

University of Maryland at College Park
College Park, MD 20742

Institute for Physical Science and Technology

415. *Thermophysical Properties of Supercritical Fluids and Fluid Mixtures*
Sengers, J.V. **$133,400**
301-405-4805

It has become evident that 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. The procedure is being used to develop accurate equations and tables for a number of important fluids including alternative refrigerants. The theory has also been extended to develop equations for the thermodynamic properties and transport properties of fluid mixtures like mixtures of carbon dioxide and ethane that have a continuous critical line. The theory is also being applied to renormalize practical chemical engineering equations of state for the effects of critical fluctuations.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

416. *Theoretical Studies of Solid–Fluid Phase Equilibria*
Monson, P.A. **$92,000**
413-545-0661

This project is concerned with the molecular theory of solid–fluid phase equilibria. Recent work on using molecular simulation and theory to investigate the influence of molecular shape upon solid–fluid equilibria to systems with effects of quadrupolar and dipolar interactions, and also to flexible chain molecules is being extended. The results of these studies will be used to analyze the solid-fluid equilibria in systems of nonspherical molecules such as the normal alkanes from a corresponding states perspective, and to develop generalized van der Waals theories of solid–fluid equilibria. A theory of solid solutions developed recently in this research group and successfully applied to the freezing of hard sphere mixtures into substitutionally disordered solids is being extended to the treatment of attractive intermolecular interactions and to the properties of substitutionally ordered solid solutions. The treatment of solid solutions of nonspherical molecules is also being considered.

National Institute for Petroleum and Energy Research
Bartlesville, OK 74005

Department of Fuels Research

417. Thermodynamic Properties for Polycyclic Systems by Noncalorimetric Methods

Steele, W.V. **$200,000**
918-337-4210

The main objective of this research project is the development of the thermodynamic properties for polycyclic molecules containing five-membered ring(s) via assigned spectra and statistical mechanics. A key goal is attainment of accord between spectroscopic and calorimetrically derived properties for temperatures approaching the critical. A consistent theoretical interpretation is sought for the vibrational modes for ring systems with as many as four rings. This will provide a more fundamental understanding of the foundation of estimation techniques such as group-additivity and molecular-mechanics. Highlights of the first year's research include: (1) For the first time, the fundamental vapor-phase vibrational frequencies were defined completely for furan, pyrrole, and thiophene. Ideal-gas thermodynamic functions were calculated. Anharmonic effects were shown to be negligible [*Spectrochemica Acta* **1994**, 59A, 765–795]. (2) Gas-phase vibrational spectra were obtained for 2-methylfuran, 2- and 3-methylthiophene. Agreement between calorimetrically derived entropies and values derived statistically was obtained for a narrow temperature range [*Spectrochemica Acta* **1994**, in press]. (3) Complete gas-phase frequency assignments were made for 2,3-dihydrofuran and 2,5-dihydrofuran [*Spectrochemica Acta* **1994**, in press]. (4) A paper, "Reconciliation of calorimetrically and spectroscopically derived thermodynamic properties at pressures greater than 0.1 MPa for benzene and methylbenzene; the importance of the third virial coefficient," was published [*Ind. Eng. Chem. Res.* **1994**, 33, 157–167]. (5) Papers describing the accord between spectroscopic and calorimetrically derived properties of indole, benzothiophene, benzofuran, benzoxazole, and benzothiazole will be submitted in early summer for peer review and subsequent publication.

National Institute of Standards and Technology, Boulder
Boulder, CO 80303

Thermophysics Divison

418. Integrated Theoretical and Experimental Study of the Thermophysical Properties of Fluid Mixtures: Properties of Mixtures Near a Phase Transition

Hanley, H.J.M.; Friend, D.G. **$290,000**
303-497-3320

A major objective of this research is to develop and refine theoretically based predictive models for the thermophysical properties of complex fluid mixtures. The effort focuses on the behavior and properties of fluids and mixtures near phase transitions: near the liquid–solid interface, in the region of liquid–liquid immiscibility, and near the gas–liquid critical locus. The three major components of the study comprise (1) an investigation of the structure factors and pair distribution functions of complex fluid systems using the scattering properties of cold neutrons, (2) theoretical and computer simulation studies of the solid-fluid transition, and (3) a study of the critical loci in mixtures using scaling theory for equilibrium processes and mode coupling approaches for dynamical phenomena. Partial structure factors have been obtained from neutron scattering experiments on colloidal systems of polystyrene mixtures in a partially deuterated solvent. The resulting data complement computer simulations of heterogeneous phases using ideas from density functional theory. Significant progress on estimating liquid–liquid phase behavior has been made. Work has started on understanding the behavior of amorphous mixtures.

North Carolina State University
Raleigh, NC 27695

Department of Chemical Engineering

419. Theoretical Treatment of the Bulk and Surface Properties of Fluids Containing Long, Flexible Molecules

Hall, C.K. **$100,000**
919-515-3571

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, 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 development of a Generalized Flory–Dimer theory for binary mixtures containing hard-chain molecules that differ in segment size, (2) the extension of the Generalized Flory theory to pure fluids containing heteronuclear hard chains, and (3) the determination, via molecular dynamics simulation, of diffusion coefficients, viscosities, and thermal conductivities of fluids containing hard-chain molecules with lengths comparable to alkanes. Work has begun on extending the Generalized Flory–Dimer theory to mixtures of square-well chains, to heteronuclear fluids, and to fused-hard-sphere-chain fluids. The aim here is to use this as a basis for developing a new group contribution approach to estimate the properties of fluids when experimental data is unavailable. The theories resulting from this research could eventually serve as the foundation upon which to build correlations of thermophysical properties of petroleum, natural gas, polymer solutions, polymer melts, and polymer blends.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemical Engineering

420. *Thermodynamics and Transport in Microporous Media*
Glandt, E.D. **$99,267**
215-898-6928

The emphasis of this project is on structure and thermodynamics for long linear molecules confined into a disordered solid matrix. The segment–segment and segment–matrix correlation functions are the appropriate measure of the configuration of the confined chains. The thermodynamic properties, i.e., partition coefficients, for linear macromolecules are of great relevance to all chromatographic and related separations. A combination of integral equation theory (polymer RISM in a quenched medium) and molecular simulations are used to compute the intermolecular site-site correlation function, as well as the matrix-site concentration profile. The results show a strong dependence on molecular weight N and polymer concentration, but only a weak dependence on the porosity e of the solid. In the Henry's law regime, the simulation results for the collapse factor (the radius of gyration normalized by the radius of gyration in bulk solution) can be expressed in terms of a single scaling variable, $x = N (1-e)$, where N is the degree of polymerization and e is the porosity of the matrix. It also has been discovered that in the limit of low porosity and for short chains the partition coefficient displays a dramatic dependence on bulk-phase concentration, amounting essentially to an off-on switching of the concentration inside the pore space.

Princeton University
Princeton, NJ 08544

Department of Chemical Engineering

421. *Computational and Theoretical Studies of Homogeneous Nucleation in Supercritical Fluids*
Debenedetti, P.G. **$92,960**
609-258-5480

The thermophysical properties of highly superheated and supercooled liquids, and of supercooled vapors, can be conveniently studied by computer simulation. This is because simulations allow the imposition of constraints that prevent phase separation. Both the restriction of space-averaged density fluctuations, and the localized restriction on the formation of bubbles have been studied so far. The goal of the work is to investigate the dependence of the predicted thermophysical properties on the type of constraint that is imposed. A lattice model of a network-forming liquid with orientation-dependent interactions has been developed to study the thermodynamics of supercooled water. The model can reproduce both types of behavior that have been postulated to explain the anomalous properties of supercooled water a continuous stability limit, and a retracing locus of density maxima with a second, metastable critical point. The continuous stability boundary can also be obtained by making the attractive parameter of generalized van der Waals fluids temperature-dependent. A new simulation technique is being developed to calculate free energies barriers to nucleation. The technique will be applied to study nucleation in supercritical fluids.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

422. *Fundamental Studies of Fluid Mechanics and Stability in Porous Media*
Homsy, G.M. **$105,000**
415-723-2419

This research project treats problems in flow and transport in porous media of interest in energy recovery processes. Both macroscopic Darcy scale and pore scale flows are studied. In the former case, fingering instabilities in homogeneous media are studied for conditions under which the mobility profile is non-monotonic in space due to property variation or the presence of both gravitational and viscous forces. Significant differences in finger propagation relative to that of monotonic mobility profiles were found. New phenomena, termed 'reverse fingering', associated with non-monotonicity have been discovered and explained through large scale simulation. Current work is focused on the interactions between fingering instabilities and flows driven by permeability heterogeneity. Current pore-scale work focuses on the propagation of interfaces of wetting and non-wetting 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, while in the non-wetting case of the viscoelastic moving contact line, normal stresses act to enhance the spatial variation of film thickness, leading to increased instability.

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

Department of Chemistry

423. *Thermophysical Properties of Fluids and Fluid Mixtures*
Stell, G.R. **$116,000**
516-632-7899

Theoretical research continues on the thermophysical properties of fluids based on the use of statistical mechanics 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 a study near completion in which the assumptions of the mean spherical approximation are augmented by a new treatment of ionic association to yield a phase diagram in which the location of phase separation is more accurately predicted. The work on association includes a study of dimerization in a model liquid of reacting atoms in which the core volume of the diatomic product molecule 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.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemical Engineering

424. ***Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems***
Cummings, P.T. **$113,280**
615-974-0227

The objective of this project is to develop fundamentally based predictive theories for the thermodynamic properties and phase equilibria in mixed solvent electrolyte systems. The emphases in the current year are molecular simulation of vapor-liquid phase equilibria in methanol/water and ethanol/water/salt systems using a new water potential, molecular simulation of supercritical aqueous systems, and additional experimental measurements of phase equilibria and densities in alcohol/water/organic salt systems.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemical Engineering

425. ***Interphase Transport and Multistage Separations***
Stewart, W.E. **$85,000**
608-262-0188

This project deals with mathematical modelling and simulation of mass transfer operations. The research includes transport theory, computational methods, and data-based modelling of system performance. This year the integrators, DDASAC and PDASAC, for differential-algebraic initial-value and initial-boundary-value problems were generalized to include jump conditions and automatic stopping at a target value of any state variable or functional of the solution. Initial-step optimization was added to both integrators, and automatic reconciliation of initial and boundary conditions was included in PDASAC as part of the treatment of jump conditions. New Bayesian criteria were developed and demonstrated for statistical discrimination among rival models, using single-response or multiresponse observations. The multiresponse criterion is sharper than that of Young and Stewart [*AIChE J.* **38**, 592, 1302 (1992)] and will be important in further research on fractionation modelling.

Yale University
New Haven, CT 06520

Department of Mechanical Engineering

426. ***Computational and Experimental Study of Laminar Premixed and Diffusion Flames***
Smooke, M.D.; Long, M.B. **$180,806**
203-432-4344

The research centers on an investigation of the effects of complex chemistry and detailed transport on the structure and extinction of hydrocarbon flames in counterflow, cylindrical, and coflowing axisymmetric configurations. Both computational and experimental aspects of the research have been performed in parallel. The computational work has focused on the application of accurate and efficient numerical methods for the solution of the one- and two-dimensional nonlinear boundary value problems describing the various reacting systems. Detailed experimental measurements have been performed on axisymmetric co-flow flames using two-dimensional imaging techniques. In particular, spontaneous Raman scattering and laser induced fluorescence have been used to measure the temperature as well as various major and minor species profiles. Future research investigations will include the development of a flamelet model for turbulent nonpremixed combustion based upon three different flamelet libraries and a computational and experimental study of NO_x formation.

Advanced Batteries

Arizona State University
Tempe, AZ 85287

Department of Chemistry

427. ***Application of New Concepts in Solid Electrolytes, and Pressure-Stabilized Cathode Materials, to Solid State Battery Technology***
Angell, C.A. **$135,213**
602-965-7217

This research continues the investigation and development of the class of ionic rubber electrolytes. The synthesis of low-melting electrochemically stable lithium salts will be pursued. Current focus is on variants of the boron and phosphorus based anions patented by Exxon some years ago. The salt-in-polymer studies will include systems that maximize the weak coupling of the Li ion with the polymer by using sulfide-containing anions. The $Li_4P_2S_7$ + LiSCN + polymer system is expected to have a high decoupling index. Rubberizing polymers that provide additional Li+ ions rather than sequester existing ones will be sought and the optimum charge/mobility polymer structure will be investigated. Adaptions of existing ion dynamics computer simulation programs will be made to research this problem. Synthesis of new structures favorable for holding oxygen at high activity (hence providing a sink for Li) will be sought by using the high pressure synthesis capabilities of the Arizona State University NSF-MRG.

California Institute of Technology
Pasadena, CA 91125

Department of Materials Science

428. *Design of Metal Hydride Alloys for Battery Electrodes with High Cycle Lifetimes*
Fultz, B.; Ratnakumar, B.V. **$175,923**
818-395-4411

This program will design new alloys for service as negative electrodes in nickel-metal hydride battery cells. The two goals are to improve the cycle lifetimes during charge/discharge cycling, and to understand the mechanisms controlling the lifetimes of metal hydride electrodes. The alloy design philosophy is based on controlling the diffusion kinetics of metal ions in intermetallic hydride alloys. Ternary solutes will be added systematically to $LaNi_5$, and in relatively dilute amounts so the good hydrogen storage capacity of binary alloy is not impaired. The effects of ternary solutes on cycle lifetime will be tested systematically for several new alloy compositions, first with alloys based on pure $LaNi_5$, and then with alloys containing misch metal substituted for lanthanum. The Caltech group will prepare the alloys and perform microstructural characterizations, isotherm measurements, and gas-phase thermal cycling experiments. The Battery Systems Group of the Jet Propulsion Laboratory in Pasadena will perform electrochemical characterizations of the electrode alloys and provide facilities for cycle lifetime measurements of a large number of experimental battery cells with different MH electrodes.

Clark University
Worcester, MA 01610

Department of Chemistry

429. *Novel Aluminum and Sulfur Batteries*
Licht, S. **$63,216**
508-793-7112

The work focuses on the development of a high-capacity aluminum sulfur primary battery. Development of this battery will start with the optimization 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 will be used as input to a computer model to predict variations in the anolyte during discharge. This model will be used to improve anodic utilization efficiencies under a variety of discharge rates. Replacement of the mercury in the anode by various additives will be studied and the resultant conversions efficiencies and anodic polarization losses determined. Cells incorporating the most promising modifications will be tested at low discharge rates (membrane separator) and high discharge rates (porous electrocatalyst separated). From these discharge tests, high-energy capacity cells will be designed and tested with a 250-Wh/kg objective.

Hughes Aircraft Company
Torrance, CA 90505

Electron Dynamics Division

430. *Advanced Nickel-Metal Hydride Cell Development*
Lim, H.S. **$113,200**
310-517-7620

This research is directed at developing a new alloy material for use as anodes in nickel-metal hydride cells. Through this collaborative effort of four organizations, three distinctively different alloy preparation techniques are being evaluated. For its part, Hughes is developing a powder preparation technique that will produce the powder with a unique morphology. Hughes already has had some successful results in preparing the powder in the range of 30 to 200-μm in diameter with a preliminary alloy sample. The work is continuing to develop a technique to improve the efficiency of the preparation and controlling the particle size. Powders with various promising alloy compositions will be produced. In an effort to improve the hydride electrode performance, the effects of various surface modifications which includes electrochemical and chemical pre-treatments and surface coatings such as copper and nickel will be investigated. The particle size, particle morphology, and surface modification will be optimized through a cooperative interaction among participating organizations which include Texas A & M University, Brookhaven National Laboratory, and Los Alamos National Laboratory. The alloy powder samples of different particle morphologies will be prepared using three different preparation techniques. Alloy optimization process will be mainly based on pressure-composition isotherm data, specific electrochemical capacity, rate capability, and projected production cost.

University of Minnesota
Minneapolis, MN 55455

Corrosion Research Center

431. *Characterization of Insertion Electrodes in High-Energy Cells*
Smyrl, W.H. **$254,625**
612-625-0717

The research program has three basic thrusts. In the first, the intercalation of Li into carbonaceous is materials is investigated. Researchers have used highly oriented pyrolytic graphites (HOPG) with etched, single atomic layer "pits" as well as defined sites for intercalation of Li which was deposited from the vapor phase. STM measurements were used to characterize the morphology of the surface before and after the exposure of Li vapor. A ring of intercalated Li was formed just inside the pit edge, under the top layer of graphite. The Li moved away from the initial sites in channels that were probably controlled by residual stress in the HOPG. Further work has shown that intercalation from the liquid phase into HOPG can be accompanied by other processes that disrupt the insertion process, and cause degradation of the substrate. Transmission electron microscopy has shown that severe exfoliation and solvent intercalation occurs in $LiC1O_4$/propylene carbonate solutions that are used in lithium battery applications. This is the first direct evidence of exfoliation that has been found, although it had been suspected previously. The exfoliation is completely absent in other electrolytic solutions, namely $LiPF_5$/ethylene carbonate-diethylene carbonate solutions. The reasons for the differences are not understood at present. Additional work is under way to synthesize novel forms of carbon that will have high capacities for Li insertion. Li:C ratios of 1:2 have been obtained (much higher than the 1:6 ratio believed to be the limit previously), but it has not been possible to retain the high capacity on repeated insertion-release cycles. In the second basic thrust, the intercalation host, V_20_5 xerogel, has been studied to establish the physical and chemical properties that may be manipulated by sol-gel processing. Vanadium pentoxide films were spin-coated on nickel/silicon substrates and characterized by XRD, SEM, TEM, and optical and electronic conductivity measurements. A largely amorphous film was obtained by spin coating at high rotation speeds, with the layered microstructure becoming more dominant as the rotation speed is reduced. The electronic conductivity of the films are increased as the amorphous character is increased. Further, the conductivity in the plane of the film is three orders of magnitude larger than the conductivity normal to the surface for highly layered films (consistent with the expectation that transport along the plane of the layers is larger), but the difference is less than two orders of magnitude in amorphous films. The third thrust is to establish the capability of the films to host polyvalent cations in addition to Li. It has been established that a chemical insertion technique can be used to survey different metal cations. The technique consists of reacting a solution of the iodide of the metal of interest with vanadium pentoxide xerogel films. As V_20_5 xerogel films oxidize iodide (the film being reduced at the same time), the metal cation is inserted into the film to maintain electroneutrality. The general technique is being used for Mg, Zn, and Al systems first, with other systems to follow. Those polyvalent cations that are successfully intercalated will be further investigated by electrochemical insertion techniques. Thin film electrodes will be used to fabricate microbatteries to explore the columbic efficiency, energy efficiency, cycle life, and the electrode reactions as a function of relevant parameters such as electrode loading and geometry, insertion degree, rate, potential, cycle number, discharge depth, and temperature.

School of Physics and Astronomy

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

Halley, J.W. **$92,657**
612-624-0395

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 is under development, 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. At the same time, models of relevant anions, including chloride and perchlorate, are being developed to study solvation and ion pairing properties of the electrolytes at a microscopic level. The output from the molecular dynamics studies is used to construct lattice models of the system at larger length and longer time scales appropriate to the transport problem. The lattice models will be used 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
Stony Brook, NY 11794

433. *New Materials Technology For Rechargeable Lithium Batteries*

Skotheim, T. **$100,000**
516-444-8865

Rechargeable batteries with high specific energy are of critical importance for applications where portability is an issue. Recent developments in portable computers and communication devices, such as cellular telephones, have created a need for batteries with ever higher energy storage capacity and longer cycle life. The objective of the proposed 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 technology in both energy storage capacity and cycle life. Moltech's battery will be produced based on a high conductivity polymer electrolyte, a stabilized lithium interface, and high capacity polymeric cathode materials. New polymeric cathode materials with high energy storage capability will be synthesized, characterized and tested during this research period. Multilayer laminates will be fabricated in specially designed thin film production lines.

University of Nevada at Las Vegas
Las Vegas, NV 89154

Department of Physics

434. *Long-Ranged Polymer Dynamic Behavior and Conductivity in Battery Polymer Electrolytes: Poly(ethylene oxide)/Salt Systems*

Selser, J.C. **$20,000**
702-895-3563

The most compelling application driving the intense research into the properties and uses of polymer electrolytes is the development of secondary (rechargeable) lithium batteries. The work proposed here will use light scattering, principally the noninvasive dynamic light scattering technique known as photon correlation spectroscopy, or "PCS", to study long-ranged, slow relaxations in poly(ethylene oxide) (PEO). Polymer hosts are generally acknowledged as among the "top choices" for polymer electrolytes. PEO itself and PEO-based polymer electrolytes are used both for research and for application. The purpose of this work will be to determine, under the same conditions, the relationship between conductivity in PEO electrolytes and long-ranged PEO relaxations in PEO electrolytes, as probed by light scattering. In the first part of the proposed work, unique expertise acquired in this laboratory will be applied to the study of the salt concentration dependence of the slowest, overall, intracoil PEO relaxation in dilute methanol solutions. In this way, the effects of increasing salt concentration on a single, well defined intrapolymer relaxation will be determined. In the second part of the work, pure PEO melts and PEO electrolyte melts containing stoichiometric amounts of selected salts will be investigated. In particular, the salt concentration and temperature dependencies of long-ranged, slow PEO relaxations in PEO electrolytes will be studied. Comparisons of the results from the PEO solution study and the PEO electrolyte study along with a comparison of the PEO electrolyte results with results from studies of the effects of salt concentration and temperature on PEO conductivity will lead to a better understanding of how long-ranged PEO relaxations in PEO electrolytes affect conductivity in these electrolyte systems.

North Carolina State University
Raleigh, NC 27695

Department of Chemical Engineering

435. *Composite Polymer Electrolytes Using Cross-Linked Fumed Silicia Fillers in Low Molecular Weight Polyethylene Oxides: Synthesis, Rheology and Electrochemistry*

Khan, S.A.; Fedkiw, P.S.; **$141,378**
Baker, G.L.
919-515-2324

The objective of this project is the synthesis and evaluation of a composite 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 principle 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 $5x10^{-4}$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. The proposed work includes the following: (a) Surface-modified fumed silicas will be synthesized and characterized. Surface-anchored groups will modulate the aggregation pattern of fumed silicas and their compatibility with polyethylene oxides. Polymerizable monomers such as acrylates and methacrylates will be tethered to the silicas via short alkyl or polyether chains. Chemical cross-linking of the silica network will be induced by radiation, photochemical or thermal methods. (b) The cross-linking reaction will be characteized using molecular and mechanical spectroscopies. Both the chemistry of the cross-linking reaction and the morphology will be characterized using molecular, chemical and rheological tools. (c) Fumed silica polyethylene oxide composites containing lithium salts will be prepared and cross-linked. Key issues are the evolution of the mechanical and electrical properties caused by the curing process. (d) The electrolyte system will be electrochemically characterized: Li^+ transference number, oxidative and reductive stability of the electrolyte, lithium electrode cyclability, and compatibility of the electrolyte with composite cathodes.

Pennsylvania State University, University Park
University Park, PA 16802

Center for Advanced Materials

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

Macdonald, D.D. **$195,940**
814-863-7772

The objective of this research is to define a lithium solid polymer electrolyte intercalation cathode (Li/SPE/IC) battery prototype with improved cycle life through a better understanding of the kinetics and mechanisms of capacity degradation. This will be done by the collaborative interactions of a research group experienced in the design and synthesis of solid polymer electrolytes of polyphosphazenes and a research group experienced in the engineering and electrochemistry of battery systems. The selection and optimization of electrode and polymer electrolyte materials includes developing intercalation cathodes based on V_6O_{13} and solid polymer electrolytes based on polyphosphazenes and optimizing their characteristics. Studies of mechanical degradation caused by battery cycling will be estimated by measuring the expansion and contraction of various cells upon charge and discharge. Electrochemical impedance spectroscopy (EIS) is used to investigate the physico-electrochemical processes such as interface and electrolyte impedance changes and intercalation cathode degradation. Destructive analysis of cell components after cycling due to mechanical (dendrite formation) and thermal (reaction products at localized hot spots) mechanisms will be studied using a variety of diagnostic techniques. Battery system models will be developed to guide new battery development and reduce the effort involved in designing by experiment. Enhancing cycle life in Li/SPE/IC batteries will be pursued by examining the degradation mechanisms elucidated in this research.

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

College of Engineering

437. *Solid Electrolyte–Electrode Interfaces: Atomistic Behavior Analyzed Via UHV-AFM, Surface Spectroscopies, and Computer Simulations*
Garofalini, S.H. **$115,039**
908-932-2216

The proposed research involves using UHV-AFM, XPS, and ISS experimental techniques and molecular dynamics computer simulations to examine structural, dynamical, and chemical properties of solid electrolyte surfaces and the cathode/electrolyte interface. Oxide glasses will be the electrolytes, with lithium phosphate, with and without nitrogen dopant, as the major glass; Li and V2O5 are the electrodes. The UHV-AFM will be used to study localized relaxations within the electrolyte surface induced by cycling the voltage between the tip and the electrolyte (this will be done on clean electrolytes and those with different cathode overlayer thicknesses to determine the thickness at which ionic response to the imposed voltage changes), morphological changes during deposition of the cathode, and nanoheterogeneity in conduction in a nanobattery set-up. Chemical changes due to deposition of submonolayer to multilayer overlayers of cathode-on-electrolyte and the reverse are being studied using XPS and ISS. Molecular dynamics computer simulations are being used to provide an atomistic visualization of this interfacial behavior. XPS analysis of in-situ deposition of Li onto a lithium borate glass shows that absorption of the Li into the glass initially occurs, followed by overlayer formation. The Li penetrates at least into the top 10 nm of the glass, creating a significant compositional change (67% lithia, 33% boria) in the glass surface prior to any imposed voltage or cycling. Lithium phosphate and lithium phosphorus oxynitride have been deposited in situ using RF sputtering and analyzed using XPS. In situ deposition of the electrode onto these electrolyte glasses will be done as mentioned above. A multibody interatomic potential for the electrode V2O5 is being developed for molecular dynamics simulations. This electrode will be brought into contact with a lithium silicate (Li_2O-SiO_2) glass electrolyte in order to study interfacial behavior while a phosphate multibody potential is being developed so that phosphate glasses can be simulated.

SRI International
Menlo Park, CA 94025

438. *Development of Lithium Batteries with Nonflammable Liquid Electrolytes*
Smedley, S. **$232,134**
415-859-6173

The first task in this work addresses the synthesis of siloxane and phosphazene-based solvents properly functionalized to tailor their physical and chemical characteristics. Some candidate electrolytes have been examined to determine dielectric constants, viscosity, and Li ion migrational flux. Electrochemical characterization by DC cycling, cyclic voltammetry, and electrochemical impedance spectroscopy have been carried out.

University of South Carolina
Columbia, SC 29208

Department of Chemical Engineering

439. *Mathematical Modeling of a NiOOH/Metal Hydride Cell*
White, R.E. **$100,171**
803-777-3270

This research focuses on the development of a realistic mathematical model for the performance of a nickel metal-hydride battery (NiOOH/M-H) based on the fundamental physicochemical processes in the battery. The model will be used to predict the behavior of a NiOOH/M-H cell during charge, discharge, and open-circuit for different cell designs and under various operating conditions. The accuracy of the model will be verified by comparing experimental data with its simulations. The model equations were developed using a macrohomogeneous approach for both porous electrodes resulting in a pseudo-two-dimensional representation. The model equations were derived based on mass, charge, and volume balances for both the electrolyte and solid phases and on thermodynamic and kinetic principles. The energy balance equations will be added to account for the effect of temperature on the performance of the cell.

Texas A & M University
College Station, TX 77843

Center for Electrochemical Systems and Hydrogen Research

440. *Cell Components with Emphasis on Hydride Electrolytes for Nickel/Metal Hydride Batteries*
Srinivasan, S. **$96,334**
409-845-8281

The research at Texas A & M (TAMU) involves the physico- chemical characterization of the alloys prepared by collaborators at Brookhaven National Laboratory (BNL), Los Alamos National Laboratory (LANL), and Hughes Aircraft Company (HAC). The objectives of the research are to elucidate the roles of the constituent elements and their composition on the thermodynamics and kinetics of the hydriding and dehydriding reactions, and to optimize the composition and structure of the metal hydride electrodes. For this purpose, electrochemical, microcalorimetric, and SEM/EDAX techniques are being used. Impedance studies show that (1) the discharge step controls the electrochemical hydriding, and not the diffusion of hydrogen into the alloy as in gas-phase hydriding, and (2) the method can be used for optimization of composition and structure of electrodes. The microcalorimetric technique is shown to be useful for determining the thermodynamic parameters for hydrogen absorption and desorption and the results of these measurements are being analyzed to determine the kinetics of these reactions.

A BNL-TAMU collaboration has shown that Ce substitution enhances the cycle-life of the electrodes. Studies are in progress to interpret the reason for Ce improving the performance of the hydride electrodes. In the ongoing TAMU-LANL collaboration, efforts are being made to enhance the performance and stability of alloy electrodes by using the ball-milling technique to coat the alloys. The subsequent electrode material optimization and development will involve an HAC-TAMU collaboration.

Small Business Innovation Research

The following projects were funded by the Small Business Innovation Research (SBIR) Program Office in response to a topic submitted by the Division of Chemical Sciences to the annual SBIR solicitation.

The Phase I projects are funded for 6-1/2 months and are designed to evaluate the merits and feasibility of the ideas proposed. Proposals are considered as the result of a solicitation, and awards are made after a competitive evaluation.

The Phase II projects are funded for two years and constitute the principal research and development effort aimed at proving the feasibility of the concept of carrying the process or product to the point where it can be commercialized. They are continuations of Phase I projects. Again, awards are made on the basis of competitive evaluation. Summaries of new Phase I projects as well as Phase II projects are listed.

ANDCARE, Inc.
Durham, NC 27713

441. *An Advanced Electrochemical Sensor for the Simultaneous Analytical Measurement of Three Chemical Species*

Wojciechowski, M. **$75,000**
919-544-8220

The requirements of complex sample monitoring present a growing need for a new generation of highly specific enzyme electrodes with multianalyte, multisignal capability. This project's objective is to establish the feasibility of novel electrochemical sensors based on the combination of immobilized enzymes and colloidal gold technologies. The specific goal to be pursued in Phase I is to demonstrate the feasibility of an in vitro lipid profile diagnostic device for the simultaneous detection of total cholesterol, high-density lipoproteins, and triglycerides using a disposable biosensor. This lipid profile testing is an important part of current recommendations for reducing cardiac risk and for monitoring therapy for millions of individuals with cardiovascular disease. Deposition of colloidal gold with immobilized enzymes onto separate channels of a multichannel surface to provide spatially resolved, multisignal enzyme electrodes can ultimately lead to a new generation of multianalyte sensors. A new marketable microscale, multianalyte sensor based on novel enzyme immobilization methods will result in a device of improved rapid analytical characterization of multicomponent systems.

Advanced Fuel Research, Inc.
East Hartford, CT 06138

442. *On-Chip Infrared-Spectral Sensors by Superconducting Detector Arrays*

Fenner, D.B. **$123,450**
203-528-9806

Conventional methods of IR spectroscopy for analysis of chemical species are limited to instruments with low-throughput dispersive elements, or moving optics for transform spectroscopy. The application of a new, microoptoelectronic on-chip-transform design for IR spectral measurement is planned. This innovation accomplishes spectral transform of the IR by virtue of a stepped-thickness array of interference filter plates microfabricated onto the detector-array chip assembly. The design allows spectral analysis with both the high-throughput and multiplex advantages. It can be adapted to spectroscopy over a very wide range of wavelengths, limited only by the choice of optical materials for the window and solid-etalon array. The sensor device is small, compact, and rugged, especially if it is fabricated on a 50-mm diameter silicon wafer substrate, as is envisioned. The detectors are photothermal (bolometers) of high-temperature superconducting (HTS) films on silicon. During a previous Phase I project (from The National Science Foundation (NSF)), the central concept of silicon-wafer etalons introducing fringes into IR spectra measured with HTS bolometers was demonstrated. That project, however, made no progress toward demonstrating transform spectroscopy with this design. The new spectrometer invention was filed with the U.S. Patent Office. The present Phase I project with DOE has completed the demonstration of feasibility of the spectrometer by devising, modeling, and testing a design and microfabrication route. This design should considerably enhance the technical likelihood of R & D success and subsequent transfer of such a technology into a manufacturable product. It has been shown that silicon micromachining by lithographic reproduction and wet-etch processing will render large arrays of stepped-thickness plates in relatively few processing steps. This silicon-etalon technology can then be combined with existing HTS-detector technology, which was supported and brought through successful R & D by a previous DOE Phase II project. Realistic model simulations of many device designs have been meticulously explored in the present Phase I project, and have allowed an important engineering focusing of R & D efforts toward designs with greatly improved trade-offs between fabrication and performance. Based on modeling, it is expected that 256-element arrays of stepped etalons and of HTS detectors will be an attainable and effective on-chip spectrometer that can provide excellent resolution, sensitivity, and adaptability to many IR bands, from near-IR to deep far-IR.

BSI Corporation
Eden Prairie, MN 55344

443. Photoaffinity Immobilization of Fusion Proteins on Biosensor Surfaces

Guire, P.E. **$74,280**
612-829-2715

This project is designed to resolve a critical and enduring obstacle to the development of dependable biosensor systems for the timely detection of toxic and infectious agents. A passivated sensor surface will be developed that will associate uniquely with the specific binding protein in its crude source solution and, upon activation by light, covalently bond this protein functionally oriented in a stabilizing, biomolecule-compatible environment. A trifunctional amino acid will be derivatized on one site with a photoactivatable reagent capable upon illumination of forming covalent bonds with essentially any organic target group (including all proteins) under mild reaction conditions. This reagent will then be thermochemically bonded to a ligand for the specific binding protein and to the sensor surface previously passivated with a photoreactive hydrogel, to provide an essentially aqueous environment containing chosen ligand and photoreactive groups adjacent on the sensor surface. This passivated photoaffinity sensor surface will be exposed to aqueous protein mixtures and tested for its efficiency and specificity in photochemical immobilization of the desired binding protein, as well as the storage and use stability of the immobilized sensor protein. In the Phase I effort, a passivating coating for glass surfaces and a photoreactive trifunctional reagent will be prepared, which will be reacted with the passivated surface and with a ligand to provide a photoactivatable affinity surface. This photoaffinity glass is expected to reduce nonspecific protein binding by at least 75% and to immobilize the fusion protein with greater than 50% recovery of DNA-binding activity. Phase II will optimize the reagents and coating process for two or more fusion proteins and demonstrate the feasibility of this chemistry for patterned immobilization on biosensor surfaces. Civilian uses of this biomolecule-compatible photoaffinity sensor surface technology are expected to include the monitoring for hazardous and metabolic (health-relevant) substances in water, air, animal feeds, foods, and physiological fluids. The Department of Defense (DoD) can use the technology in the development of one or more advanced sensor devices for the timely detection of hazardous chemical and biological agents in water, air, and materials.

Bend Research, Inc.
Bend, OR 97701

444. Composite Plasma-Polymer Membranes

Babcock, W.C. **$599,916**
503-382-4100

The goal of this project is to develop an economical process for making composite membranes entirely of plasma polymers and to demonstrate their use in important industrial separations. Such membranes would provide unprecedented selectivity and chemical resistance, enabling their use in many new applications. Membranes are used in a growing number of industrial separations primarily because they are much less energy intensive than are competing technologies. However, currently available membranes are limited in applications in which aggressive chemicals (e.g., petrochemicals or organic solvents) are present, and they often do not exhibit sufficient selectivity to compete with other separation processes. If membranes were available that were resistant to organic chemicals and that exhibited the high selectivities that are possible with plasma polymer, the use of membranes would greatly expand. Plasma-polymer membranes offer a potential solution to both problems due to their crosslinked amorphous structure. They have been shown to exhibit extraordinarily high selectivities, and they are both chemically and thermally stable. The main drawback to the use of plasma-polymer membranes has been that the most selective ones exhibit low permeabilities, and they are brittle in nature (again due to their high degree of crosslinking). Both drawbacks are overcome with very thin membranes, on the order 0.01 to 0.1μm. These thin membranes must be supported by microporous supports in a composite structure. Until now, the only microporous supports useful for supporting plasma-polymer membranes were made of conventional polymers that are not chemically resistant. Thus, it has not been possible to realize the full potential of plasma-polymer membranes for use in aggressive environments. During the Phase I project, it was demonstrated that solvent-resistant microporous support films can be made of plasma polymers. Composite membranes comprising a plasma-polymer selective layer on such a plasma-polymer microporous support were prepared. It was also demonstrated that these composite membranes maintained their flux and selectivity after exposure to methylene chloride, a solvent that will dissolve or soften most conventional polymeric membranes. Furthermore, the composite membrane was flexible enough to be practical. An integrated coating system was designed that will produce composite plasma-polymer membranes directly from suitable monomers. Phase II is directed toward demonstrating economical continuous production of a plasma-polymerized composite membrane, and modularizing this membrane to demonstrate its solvent-resistance and selectivity, as well as its practicability in a commercially acceptable modularized form. This project includes extensive efforts to develop process conditions to make plasma-polymer microporous support films, and to prepare composite membranes cost effectively on a practical scale.

445. High-Performance Membranes for Gas, Vapor, and Liquid Separations

Friesen, D.T. **$75,000**
503-382-4100

Separation processes to recover and purify products account for more than 40% of the energy demand in the Chemical Process Industry (CPI), but membrane processes have gained only a small share of this major market. Conventional membranes have had limitations that have precluded their widespread acceptance in the CPI and other industrial settings. Specifically, membranes either could not withstand exposure to harsh solvents and high temperatures involved in industrial separations or lacked the high permeability and high selectivity to be commercially practical. The goal in this project is to develop a new class of polymers that addresses these limitations. The plan is to apply these high-selectivity, high-permeability polymers to unique solvent- and temperature-resistant hollow-fiber supports to form thin-film-composite membranes suitable for use in the CPI. These membranes will be suitable for applications involving the separation of aromatics from aliphatics (e.g., benzene from gasoline) and olefins from paraffins (e.g., propylene from propane). Phase I should demonstrate the feasibility of using membranes based on this new class of polymers for aromatic–aliphatic and/or olefin–paraffin separations. A series of membranes will be incorporated into small-scale (200 cm^2) solvent- and temperature-resistant hollow-fiber modules, and tested extensively. Phase II will optimize the polymers for separation targets, make larger (1 m^2) modules, and perform pilot-scale tests. The tests will generate the data necessary to set specific technical and marketing targets for commercialization of the technology in Phase III. The polymers to be developed in this project, combined with the solvent- and temperature-resistant hollow-fiber supports developed in previous work, should make possible the use of membrane-based separation systems for a range of applications in CPI. In addition to the separation of aromatics from aliphatics and olefins from paraffins (two of the largest classes of separation in the CPI), other types of separations may be possible, such as the separations of ethyl benzene from styrene or the separation of butylene isomers.

Separations Division

446. Development of Novel Reverse-Osmosis Membrane with High Rejections for Organic Compounds

McCray, S.B. **$204,105**
503-382-4100

Chemical process industry (CPI) separations consume as much as 4.4 quads of energy annually in the United States. Many of these separations involve removing organic compounds from aqueous process streams. Conventional technologies are energy intensive or have environmental drawbacks that make their use less than optimal. Additionally, some processes also destroy the organic compounds, precluding the possibility of recovering or recycling them. Reverse-osmosis (RO) membrane processes offer the potential to significantly improve and simplify treatment of these industrial process streams, but their use has been limited by their inability to remove many industrially important organics. The goal of this program is to develop a new class of RO membranes that can reject high percentages of organic compounds while maintaining high water fluxes. These improved organic-rejecting RO membranes could be used alone or in combination with other technologies in hybrid wastewater-treatment systems that would otherwise be impractical, given the performance of current RO membranes. In Phase I researchers demonstrated the feasibility of the approach by developing membranes with a rejection of 98% for a target organic (phenol) and a water flux of 25 L/m^2h. A technical and economic analysis indicates that this performance will result in wastewater-treatment systems with capital and operating costs that are only 60% of the costs for systems based on conventional technologies. Additionally, systems based on the organic-rejecting RO membranes will use only 20% of the energy required by conventional processes. The objectives of Phase II are (1) to continue the development of these organic rejecting RO membranes, focusing on developing membranes for removal of polar organics, aromatics, and chlorinated hydrocarbons; (2) to incorporate these organic rejecting membranes into solvent-resistant hollow-fiber modules; (3) to scale up modules to a size that will allow for meaningful field tests; and (4) to field-test the technology extensively. This work will pave the way for immediate commercialization of the technology with the Phase III partner.

CeraMem Corporation
Waltham, MA 02154

447. Organic-Inorganic Composite Membranes for Gas Separation and Vapor Permeation

Higgins, R.J. **$75,000**
617-899-0467

The development of specifically engineered polymers and appropriate module designs in the past decade has made possible the commercialization of gas separation membrane technology for several industrial applications. Since currently available membranes and modules are based upon use of organic polymeric materials, they generally are limited to applications involving temperatures of less than about 100 °C. However, there are several potential commercial applications for gas separation membrane technology that involve temperatures in the range of about 100 to 300 °C. For these, commercially viable membranes or modules are currently unavailable. In Phase I, cost-effective gas-permeable membrane modules based on low-cost ceramic supports will be developed. Such modules will be designed for use at temperatures in the range of 100 to 300 °C. An innovative method will be used to apply thin, defect-free membranes, based on thermally resistant polymers, to the ceramic supports. The resulting membrane modules will subsequently be tested at temperatures ranging from 100 to 300 °C for gas separation and vapor permeation properties using two-component gas mixtures. The gas separation–vapor permeation devices to be developed in this project, if successfully scaled up to production-scale ceramic modules in Phase II, will provide a potentially economic membrane-based alternative to competing technologies for many elevated temperature gas separation processes in industrial chemical manufacturing and the petrochemical and refining industries.

Energy and Environmental Research Corporation
Irvine, CA 92718

448. Multiple Air Pollutant Emissions Removal by the Use of a Single Chemical Additive

Zamansky, V. **$600,000**
714-859-8851

Air pollution control technologies for NO_x removal are limited by the relatively inert nature of NO. This difficulty can be overcome by oxidation of NO to much more reactive NO_2. Since flue gas desulfurization systems are required for SO_2 removal after combustion of sulfur containing fuels, and it has been proven that NO_2 can be removed efficiently in SO_2 scrubbers, the conversion of NO into NO_2 becomes a promising strategy for combined NO_x and SO_x removal. A large number of wet and dry scrubbers are already installed in stationary combustion sources or are planned for the near future. Therefore, a process that promotes NO_x removal simply through the injection of chemical additives into combustion gases could have a significant impact on air pollution control strategies. In Phase I, this project demonstrated the feasibility of a novel concept: gas phase multiple air pollutant emissions removal by injection of a single chemical additive into combustion gases within reaction times, temperatures, and other conditions that are in the practical range for its application in stationary combustion sources. Chemical kinetics calculations and experimental data obtained in a laboratory-scale flow reactor and in a pilot-scale Boiler Simulator Facility (BSF) demonstrate that this additive, upon being injected into combustion gases at specific conditions, can efficiently (up to 90–95%) convert to NO_2, SO_2, and CO_2 major gaseous air pollutants: unreactive NO, corrosive SO_3, unburned CH_4, and remove some amount (20%) of CO. Four different chain reactions are involved, and the single reagent can remove multiple air pollutants. In the Phase II project, the principal research on this technology will be performed with injection of the additive alone and in a mixture with methanol. Two types of fuels, natural gas and coal, will be used and two potential applications will be studied and demonstrated: (1) NO_x, SO_2, and hydrocarbons removal from exhaust of coal firing and (2) NO_x and hydrocarbons removal from exhaust of stationary gas engines of water treatment facilities that have potential for inexpensive NO_2 scrubbing. A pilot-scale gas engine and the BSF will be used for natural gas combustion, and the BSF will be used for combustion of a sulfur-containing coal. The objectives of the Phase II project include: optimization of the separate components of the technology for all applications; pilot-scale simultaneous removal of multiple air pollutants; pilot-scale demonstration of an integrated process including reburning, urea injection, additive–methanol injection, and combined SO_2–NO_2 scrubbing; economic and market analysis. This concept should substantially increase competitiveness and commercial potential of the process.

Materials and Electrochemical Research Corp.
Tucson, AZ 85706

449. *Electrode Materials for Rechargeable Lithium Batteries*

Loutfy, R.O. **$75,000**
602-574-1980

Fullerenes are a newly discovered form of carbon (graphite and diamond are the other two forms) with distinctive properties and an unusual molecular structure. Preliminary investigations indicated that fullerene electrode materials exhibit unique electrochemical properties. In this Phase I effort, fullerene nanotube structures will be investigated as novel electrode materials for lithium ion storage and supply for rechargeable lithium batteries. Fullerene electrodes will be fabricated by various techniques and fully characterized. The nature of the electrochemical charging and discharging of fullerene nanotubes as a function of operating conditions will be established. The lithium intercalated fullerene (C_nLi_x) electrodes will also be characterized, including their capacity, stability, charge and discharge characteristics, and efficiency to establish their viability for a high-efficiency secondary battery as a power source for portable electronic equipment. Fullerenes are a newly discovered material with potentially unique properties. Preliminary results indicate that fullerene electrodes could be used to store energy with applications in secondary batteries. The feasibility of this concept could lead to novel electrochemical systems for energy storage and generation.

450. *Development of a Process to Synthesize Tubular Fullerenes*

Withers, J.C. **$141,127**
602-574-1980

The demonstration that fullerenes (buckyballs) can be produced from a carbon arc has opened a complete new field of science that includes producing nanoscale tubes (buckytubes) that are another facet of carbon's synthetic engineering potential. Buckytubes have been reported by two other groups, but the Phase I program developed processing that achieved substantially higher yields (80%) and tube lengths over three times as long (10 μm), as well as a variety of polyhedral structures. The Phase II program plans to optimize the processing to produce further improved buckytubes, optimize the harvesting of the pyrolytic deposit containing the tubes, optimize the fractionating–separating of the tubes from polyhedral shapes and graphite particles, fully characterize the mechanical and electrical properties of the tubes, and produce tubes with preferred mechanical or electrical properties. Activities will be conducted to permit scaleup demonstration and repeatability of optimization processing to synthesize and harvest buckytubes in high-quality clean form for application development, and to provide economic estimates for large-scale production. Concurrently, fundamental investigations will be conducted (1) to demonstrate doping tubes, (2) to establish the mechanism of tube formation, (3) to establish reactive properties compared to buckyballs, and (4) to determine feasibility of producing very long or continuous tubes. The Arizona Fullerenes Consortium of Universities will provide characterization support and consultation on mechanisms. This program will maintain the U.S. lead in fullerene technologies and provide the technology and basis for large-scale production of buckytubes.

Membrane Technology & Research, Inc.
Menlo Park, CA 94025

451. *Novel High Performance Glassy Polymer Composite Membranes for Gas Separation*

Baker, R.W. **$75,000**
415-328-2228

In the last decade, many high-performance glassy polymers, such as polyimides, that combine high gas permeability and high selectivity for one gas over another have been developed. Although these new membrane materials have vastly better intrinsic gas separation properties than the materials in current use, essentially none has been used in commercial membranes. The problem is the lack of adequate, reproducible, large-scale membrane fabrication technology that is applicable to these polymers. In this Phase I project, a new method will be developed for preparing high-performance membranes from glassy polymers. Unlike existing commercial membranes made from glassy materials, the membranes will be multilayer composites in which the glassy selective layer is coated onto a high-flux support. The support itself will have two layers, a microporous substrate and a thin, highly permeable sealing layer. General principles will be derived for making optimized multilayer composite membranes with selective layer thicknesses of less than 0.1 μm from any given glassy polymer, and membranes with potential applications for specific gas separation applications will be identified. A general method of producing ultrathin, defect-free composite membranes with highly selective glassy polymers on a commercial scale would have a significant impact on many gas separation applications such as oxygen–nitrogen separation or removal of carbon dioxide or hydrogen sulfide from natural gas. The use of advanced composite membranes would dramatically improve the overall process economics, and make membrane systems competitive with conventional separation methods in these or other applications.

452. Highly Selective Membranes for the Separation of Organic Vapors Using Super-Glassy Polymers

Pinnau, I. **$75,000**
415-328-2228

The recovery of organic compounds from air and of higher hydrocarbon vapors from methane are related separations of considerable industrial importance. Membranes able to preferentially permeate the minor organic component are being developed for both of these applications. For an efficient process, a high organic vapor–permanent gas selectivity is required. Conventional glassy polymers, which are selective for the permanent gas over the organic vapor, are suitable for this application. Rubbery polymers, which are organic vapor selective, are in commercial use, but have inadequate selectivity for many applications. Recent work showed that multifree-volume, super-glassy polymers such as poly(1-trimethylsilyl-1-propyne) (PTMSP) can exhibit a butane–methane selectivity of 30 with the mixed gases. This selectivity is the highest ever observed for this important mixture and is completely unexpected for a glassy polymer. The reason for this extraordinary result is related to the high free volume and the large intermolecular chain spacing of the super-glassy polymer. In this Phase I project, a detailed study will be conducted of the vapor separation properties of PTMSP, related polyacetylenes, and blends thereof with a number of important organic vapor–gas mixtures. In contrast to results of previous studies of high free volume glassy polymers with permanent gases, these polymers are expected to show stable permeation properties in the presence of organic vapors. Membranes made from high free volume glassy polymers could have a significant impact on many important industrial vapor separations. Possible applications include recovery of high hydrocarbons from natural gas, removal of hydrocarbons from hydrogen in the petrochemical industry, and recovery of hydrocarbon vapors from gasoline storage tanks. The superior selectivity and permeability of super-glassy polymers relative to state-of-the-art rubbery membranes will make membrane systems competitive with conventional separation methods such as cryogenic separation in these or other applications.

REB Research and Consulting
Oak Park, MI 48237

453. Improved Coated-Metal Hydrogen Extraction Membranes

Buxbaum, R.E. **$124,857**
810-547-7942

Palladium-coated refractory-metal membranes are being developed for hydrogen extraction from chemical industry gas mixtures. The need for better hydrogen extraction membranes is particularly severe in refineries for the production of reformulated gasoline and for membrane-reactor use. Palladium-based membranes have been used for decades in hydrogen extraction because of the combination of high permeability and good surface properties, and because palladium, like all metals, is 100% selective for hydrogen transport. Although several stronger, cheaper refractory metals have higher permeabilities than palladium, they are not ordinarily used for hydrogen extraction because their poor surface properties reduce hydrogen transport. It has been shown that coating these metals with palladium removes the surface barriers. The resulting membranes show hydrogen fluxes more than 10 times greater than available with palladium and greater than available with polymers or comparable ceramics. Laboratory-scale tests suggest very economical hydrogen-extraction membranes for use with refinery and technical gas mixtures. Membranes of this sort have run successfully for as long as 10,000 h in a nuclear reactor experiment. Economical fabrication of large, 18-in., thin-walled membranes was attempted during Phase I. The benchmarks sought were 100% selectivity, a minimum permeance of 0.0014 $mol/m^2sPa^{0.5}$, and less than 50% deterioration in one month of operation. These goals were all met, and exceeded significantly in several cases, suggesting highly economical hydrogen extraction if these membranes perform the same in industrial settings. The aim of Phase II research is to take palladium-refractory composite membranes further towards chemical industry commercialization by demonstrating the fabrication and operation of large hydrogen extraction modules and by demonstrating no-fouling operation and longevity in the presence of industrial gas mixtures, and pressure and temperature transients. An economically successful module at this stage must show no leaks, cracks, or loss of selectivity. They must show no significant deterioration, coking, or fouling in six months of operation with commercial gas mixtures. Furthermore, any membrane must demonstrate, on paper, economic feasibility for a specific, large volume industrial need. The plan is to move palladium-coated metal membranes from the laboratory and limited nuclear reactor use towards non-nuclear use in refineries and chemical plants. The first 18-in. membrane modules should be produced. Six-month longevity and nonfouling, nonembrittling operation in the presence of simulated commercial gas mixtures should be demonstrated. Calculations show that these membranes should be very economical for commercial hydrogen recovery for the production of reformulated gasoline, for membrane reactors, and for the production of ultrahigh purity hydrogen, for example, for mobile, solid-state fuel cells.

TDA Research, Inc.
Wheat Ridge, CO 80033

454. Preparation of Low-Density Microcellular Materials from Fullerenes

Bell, W.L. **$211,244**
303-940-2301

Low-density microcellular materials (LDMMs) are carbon- or silica-based porous solids with a range of potential applications. In Phase I, TDA Research, Inc. has prepared novel monolithic fullerene-based LDMMs in two classes: (1) Water-soluble fullerene derivatives were prepared and polymerized to form gels, which were processed by supercritical extraction to yield organic aerogel LDMMs. These fullerene-based organic aerogels have high specific surface area (290–540 m^2/g), high porosity (46%), and small average pore size (6–10 nm). (2) A new fullerene–silicon precursor, soluble in organic solvents, was prepared and polymerized to give silica gels in which fullerene is incorporated molecularly into the silica network. These gels have been prepared in the form of thin films on glass and silicon, free-standing films, powders, and xerogels. The goal of Phase II is to further develop the novel fullerene-based organic and inorganic LDMMs and systematically explore the relationships between the processing conditions and the properties of the resulting materials. Phase II research will first systematically study the fullerene precursor materials and the synthetic chemistry involved in the formation of both the fullerene organic aerogels and the fullerene–silica gels prepared in Phase I. Researchers will also develop fullerene–metal oxide (alumina, titania, silica–alumina, and silica–titania) LDMMs with various forms such as powder, thin films, xerogels, and aerogels. The fullerene derivatives and their resulting organic and inorganic LDMMs will be thoroughly characterized by determining their structure, elemental composition, thermal stability, morphology, apparent density, specific surface area, pore size distribution, and mechanical strength. In addition, the pyrolysis chemistry of these fullerene LDMMs will be studied by pyrolyzing them in an inert atmosphere at various temperatures and characterizing the resulting products in aspects such as microstructure and conductivity. The catalytic properties of the fullerene LDMMs will also be investigated by screening their catalytic activity in typical applications. Finally, market and engineering analyses will be performed to identify the areas in which these novel materials show the best potential application.

455. Continuous Production of Fullerenes from Hydrocarbon Precursors

Wright, J.D. **$211,244**
303-422-7918

Fullerenes, a recently discovered family of closed-shell carbon compounds, have a number of exceptional electronic, optical, and chemical properties. However, they must be available at a reasonable price if they are to find commercial application. Unfortunately, the carbon arc process currently used to produce fullerenes is inherently slow and expensive. Therefore, TDA Research set out to develop a continuous process using hydrocarbon precursors to produce large quantities of low-cost fullerenes. In Phase I researchers built a research quality production apparatus, demonstrated the process, and achieved yields and rates of production that allow production of mixed fullerenes for a small fraction of the current price. The chief advantages of the process are continuous operation, high production rates, and low power consumption. The effects of temperature, pressure, hydrocarbon concentration, and fuel structure on the yield and rate of production will be determined in Phase II. These experiments will be conducted in a reactor with well-defined temperature and flow profiles. Using this information, production reactors will be designed, built, and tested with two different geometries. Using the information from the prototype production reactors, a large-scale (multi-kg/day) production reactor will be designed to be built in Phase III.

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 the Division of Materials Sciences, ER-13, U.S. Department of Energy, Washington, DC 20585.

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	$ 7,071,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	25,414,000
	Radiochemical Engineering Development Center	7,469,000
Sandia National Laboratories, California	Combustion Research Facility	4,171,000
Stanford University	Stanford Synchrotron Radiation Laboratory	10,671,000

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.

Distribution of these samples is guided by policies established with the help of a users advisory committee. More than 795 shipments totaling over 21,000 ampoules have been made thus far. A Users Handbook is updated periodically and available from the Manager.

PERSON TO CONTACT FOR INFORMATION

Dr. Randell E. Winans
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Bldg. 200
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
e-mail: winans@anlchm.bitnet
winans@anlchm.ch.anl.gov

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

#	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	Pittsburgth #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. Designed for chemical research, 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 m*M* can be generated with the 25-ps pulse and concentrations more than 10 m*M* 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, liquid, and gaseous samples. 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.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone: (708) 252-3471
Fax: (708) 252-4993

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 mA (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
	15 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 750 MeV with a critical energy of 486 eV. It has 17 beam ports split into 27 experimental stations, or beamlines, and also supports two insertion devices. The X-Ray Ring operates at 2.5 GeV, 250 mA, with a critical energy of about 5 keV. It has a total of 30 beam ports split into 56 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

Over 3200 scientists from more than 400 institutions were registered as NSLS users during 1993. 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
Upton, NY 11973-5000

Phone: (516) 282-7114
Fax: (516) 282-7206

E-mail: ezr@bnl.gov
ezr@bnl.bitnet

NSLS TECHNICAL DATA*

Storage rings	Key features
VUV	17 ports; $E_c = 25.3$ Å; 0.745 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 to 2480	5 to 35,000	24
Circular dichroism	10.3 to 5904	2.1 to 1200	2
High pressure physics	1 to 10,000 µm	0.124 to 1240 meV	2
	WB; 0.12 to 1.24	WB; 10,000 to 100,000	2
High Q-resolution scattering	WB; 0.12 to 6.20	WB; 2000 to 100,000	15

NSLS TECHNICAL DATA (Continued)

Research area	Wavelength range (Å)	Energy range (eV)	Number of beamlines
Imaging:			
Medical	WB; 0.12 to 124	WB; 10,000 to 1000,000	2
Tomography	WB; 0.12 to 3.10	WB; 4000 to 100,000	3
X-ray microprobe	WB; 0.12 to 3.10	WB; 4000 to 100,000	3
X-ray microscopy/holography	10 to 80	155 to 1240	1
X-ray topography	WB; 0.41 to 3.10	WB; 4000 to 30,000	2
Infrared spectroscopy	1 to 10,000 μm	0.124 to 1240 meV	2
Lithography	124 to 4133	3 to 100	1
Nuclear physics	–	80 to 400 meV	1
Photoemission spectroscopy	2.10 to 6200	2 to 5900	19
Photoionization	2.10 to 4133	3 to 5900	3
Protein crystallography	WB; 0.41 to 3.10	WB; 4000 to 30,000	6
Radiometry	WB; 8.27 to 248	WB; 50 to 1500	1
Small angle scattering:			
Biology	0.66 to 5.90	2100 to 18,800	2
Materials science	0.36 to 6.20	2000 to 34,000	4
Small molecule crystallography:			
Powder	WB; 0.12 to 3.10	WB; 4000 to 100,000	4
Single crystal	0.21 to 6.20	2000 to 59,400	7
Standing waves	WB; 0.62 to 6.89	WB; 1800 to 20,000	2
Surface scattering/X-ray reflectivity	WB; 0.48 to 6.20	WB; 2000 to 26,000	10
Time resolved fluorescence	1393 to 5904	2.1 to 8.9	1
UV reflectometry	WB; 8.27 to 6200	WB; 2 to 1500	2
X-ray emission spectroscopy	2.48 to 50	248 to 5000	2

WB = White Beam
*(from 1993 NSLS User's Manual–48724)

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. 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 they may submit a brief proposal to the Laboratory Director.

PERSON TO CONTACT FOR INFORMATION

Patrick Richard, Director
James R. Macdonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506-2604
E-mail: Richard@phys.ksu.edu

Phone: (913) 532-6783

TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 7 MV
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	Bare ions of C, N, O, F, Ne, Ar, Kr, and Xe
Beam energy	A few to 200 keV/q
Output currents	10^5 to 10^8 part/s

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

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

The Notre Dame pulse radiolysis facility is based on a 5-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 10 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

Experiments may be arranged by proposal to the laboratory director or through collaborations with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

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

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	Workstation (DOS/Intel 486)
Pulse width	5, 10, 20, 50 ns
Time resolution (RC)	2 ns
Pulse current	Up to 1 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

The prime purpose of the High Flux Isotope Reactor (HFIR) is to make research quantities of transuranium isotopes. Californium-252 is also produced as a by-product but is made available for the fabrication of neutron sources. These materials are produced in the flux trap in the center of the HFIR fuel element where a thermal-neutron flux of 3×10^{15} neutrons/(cm$^2 \cdot$ sec) is available to irradiate the curium target material. The HFIR is a beryllium-reflected light-water-cooled and -moderated, flux-trap reactor with a design power level of 85 MW. It burns 93% enriched ^{235}U fuel in aluminum-clad plates. Additional irradiation facilities are provided in the beryllium reflector around the fuel element to increase the production rate of the heavy isotopes.

The HFIR also has, as a secondary purpose, the performance of diverse irradiations, tests, and experiments which benefit from the exceptionally high neutron flux available. In the fuel element flux trap, a hydraulic-rabbit tube provides access to the maximum thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. The beryllium reflector contains numerous experiment facilities with thermal-neutron fluxes up to 1×10^{15} neutrons (cm$^2 \cdot$ sec). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory or other qualified users. Four beam tubes are used for neutron-diffraction experiments, and a small-angle neutron scattering facility sponsored by the National Science Foundation is available for use by researchers from universities, industry, and other national laboratories. Management of this facility has been transferred to the Director of the Office of Nuclear Energy. The funding remains in the Office of Energy Research.

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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 Director of the Office of Nuclear Energy. Base funding is provided by the Office of Energy Research and is supplemented by other agencies when their projects are carried out.

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

Sandia National Laboratories, California
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/Efficiency and Renewable 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, 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 Cray computers.

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.

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TECHNICAL DATA

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
Multipurpose pulsed laser system	High peak power, high resolution doubled YAG and tunable dye lasers: Single mode capability 10 to 500 mJ/pulse 10 to 29 ns/pulse
Low-pressure flames	10 torr to 1 atm Mass spectrometer sampling probe LIF detection of radicals
Atmospheric flames	Diffusion and premixed flames
Vertical turbulent diffusion flame	Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow
Combustion bomb	Simulated constant-volume engine combustion
Internal combustion research devices	Highly repeatable environment for homogeneous charge, diesel combustion, and pulse combustion studies
Experimental diagnostics research facilities	Nonlinear optical spectroscopy Laboratories
Turbulent flame structure laboratory	Rayleigh, Mie, and Raman 2-D imaging

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

Stanford Synchrotron Radiation Laboratory
M.S. 69, P.O. Box 4349
Stanford, CA 94309-0210

SSRL is a national facility for the utilization of synchrotron radiation in materials sciences, chemistry, structural and molecular biology, physics, medical science, and other disciplines. In addition to scientific research, SSRL is committed to the development of advanced insertion devices for enhancing synchrotron radiation and state-of-the-art instrumentation for the utilization of synchrotron radiation. The radiation comes from the 3.5 GeV storage ring, SPEAR, which is dedicated to the production of synchrotron radiation and operates for users 6 to 7 months per year. Presently SSRL has 24 experimental stations on 9 beam lines covering the spectrum from 5 to 45,000 eV. Specialized facilities for protein crystallography and lithography are available. SSRL is a division of the Stanford Linear Accelerator Center.

Specific research performed at SSRL is extremely varied and includes, in the vacuum ultraviolet area: ionization properties of small molecules, structural and electronic properties of microstructures, properties of ultra-thin layers and small clusters, kinetic processes in laser materials, lithography and microscopy, and static properties and dynamic processes of chemisorbed gases.

Research in the chemical and biological sciences includes the following: the structure and function of homogeneous and heterogeneous catalysts, the structure of metal, metal oxide and semiconductor surfaces and their interactions with small molecules, chemical reactivities in the gas phase, the structure of general chemical compounds through EXAFS, multiple wavelength imaging, protein structures and functions, dynamics and fluctuations in biological systems, the nature of membrane structure and membrane protein interactions, the structure and function of metal sites in metalloproteins and metalloenzymes, and medical angiography.

X-ray physics and materials sciences are represented by the following: structure of amorphous materials, coordination of impurities and alloying species, structures of and phase transitions in surfaces and thin surface layers, kinetics of structural changes in materials, phase transitions at high pressure, structure of crystalline materials, electronic structure of materials through edge absorption studies, fundamental X-ray scattering and absorption physics, and atomic physics.

USER MODE

SSRL is currently used by approximately 650 scientists from over 100 U.S. 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, 2284 proposals for research have been received.

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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×wdth, mm	Dedicated instrumentation
				Insertion Devices Stations			
Wiggler Lines–X-ray							
End stations							
4-2 (4 periods)							
Focused	4.6	10.2	Double crystal	2,400 to 10,200	$\sim 5 \times 10^{-4}$	1.0 × 3.0	
Unfocused	1.0		Double crystal	2,400 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
6-2 (27 periods)							
Focused	2.3	22	Double crystal	2,050 to 21,000	$\sim 5 \times 10^{-4}$	1.0 × 4.0	
Unfocused	1.0		Double crystal	2,050 to 32,000	$\sim 10^{-4}$	2.0 × 20.0	
7-2 (4 periods)							Six-circle diffractometer
Focused	4.6	10.2	Double crystal	2,400 to 10,200	$\sim 5 \times 10^{-4}$	1.0 × 5.0	
Unfocused	1.0		Double crystal	2,400 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
10-2 (15 periods)							
Focused	2.3	22	Double crystal	2,400 to 21,000	$\sim 5 \times 10^{-4}$	0.6 × 4.0	
Unfocused	1.0		Double crystal	2,400 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
Side stations							
4-1	1.0		Double crystal	2,400 to 45,000	$\sim 5 \times 10^{-4}$	2.0 × 20.0	
4-3							Two-circle diffractometer vertically focusing mirror
Focused	1.0	Variable	Double crystal	2,400 to 20,000	10^{-4}	0.15 × 20	
Unfocused	1.0		Double crystal	2,400 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
7-1	1.0		Curved crystal	6,000 to 13,000	$\sim 8 \times 10^{-4}$	0.6 × 3.0	Rotation camera
7-3	1.0		Double crystal	2,400 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
VUV/soft X-Ray Stations							
5-1, 5-3 multi-undulator	1.5		4 Gratings	10 to 450	$0.5^{-1} \times 10^{-3}$		
5-2 multi-undulator	1.5		4-Gratings	10 to 1200	$0.5^{-1} \times 10^{-3}$		
10-1	2.0		6m SGM	250 to 1200	$\sim 2 \times 10^{-4}$		
				Bending Magnet Stations			
X-ray							
1-4	2.0		Curved crystal	6,700 to 10,800	4.0×10^{-3}	0.25 × 1.0	Small angle scattering detector
1-5	1.0		Double crystal	2,400 to 30,000	$\sim 10^{-4}$	2 × 17	Area detector/CAD-4
2-1 (focused)	4.8	8.9	Double crystal	2,400 to 8,900	$\sim 5 \times 10^{-4}$	2 × 6	
2-2	1.0		None	3,200 to 40,000		4 × 22	
2-3	1.0		Double crystal	2,400 to 30,000	$\sim 5 \times 10^{-4}$	2 × 20	
VUV/soft X-ray							
1-1	2.0		Grasshopper	64 to 1,000	$\Delta\lambda = 0.1$ to 0.2 Å	1.0 × 1.0	
1-2	4.0		6m TGM	8 to 90	$\sim 1 \times 10^{-3}$	1.0 × 1.0	
3-4	0.6		Multilayer	0 to 3,000	White or $\Delta\lambda/\lambda = 0.6\%$	2 × 8	Vacuum diffractometer/ lithography exposure station
8-1	12		6m TGM	8 to 180	$\sim 1 \times 10^{-3}$	≤1 mm^2	
8-2	5		6m SGM	50 to 1,000	$\sim 1 \times 10^{-4}$	≤1 mm^2	

FY 1994 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 1994 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds
Ames Laboratory	$ 426,000*
Argonne National Laboratory	1,978,000*
Brookhaven National Laboratory	2,026,000
Idaho National Engineering Laboratory	37,000
Lawrence Berkeley Laboratory	2,522,000
Los Alamos National Laboratory	103,000
National Renewable Energy Laboratory	461,000
Notre Dame Radiation Laboratory	402,000
Oak Ridge National Laboratory	1,548,000
Pacific Northwest Laboratories	791,000
Sandia National Laboratories/ New Mexico	45,000
Sandia National Laboratories/ California	1,136,000
Stanford Synchrotron Radiation Laboratory	1,246,000

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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 $2,134,000 for Argonne National Laboratory.

SELECTED TOPICS OF GENERAL INTEREST

INSTITUTION INDEX

This index lists the institutions responsible for the projects cited in this publication. The corporate names are entered in standardized forms found in the authority listing *International Energy: Research Organizations* (ETDE/PUB-3). Each entry includes the project title and citation number.

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. Accent marks are not input because of computer alphabetization. Spelling and transliteration follow standard conventions.