DOE/ER--0144/11
(DE93011855)

Summaries of FY 1993 Research in the Chemical Sciences

AUGUST 1993

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

Prepared by
Office of Scientific and
Technical Information

DOE/ER--0144/11
(DE93011855)
August 1993
Distribution Categories UC-400 and UC-401

Summaries of FY 1993 Research in the Chemical Sciences

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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.

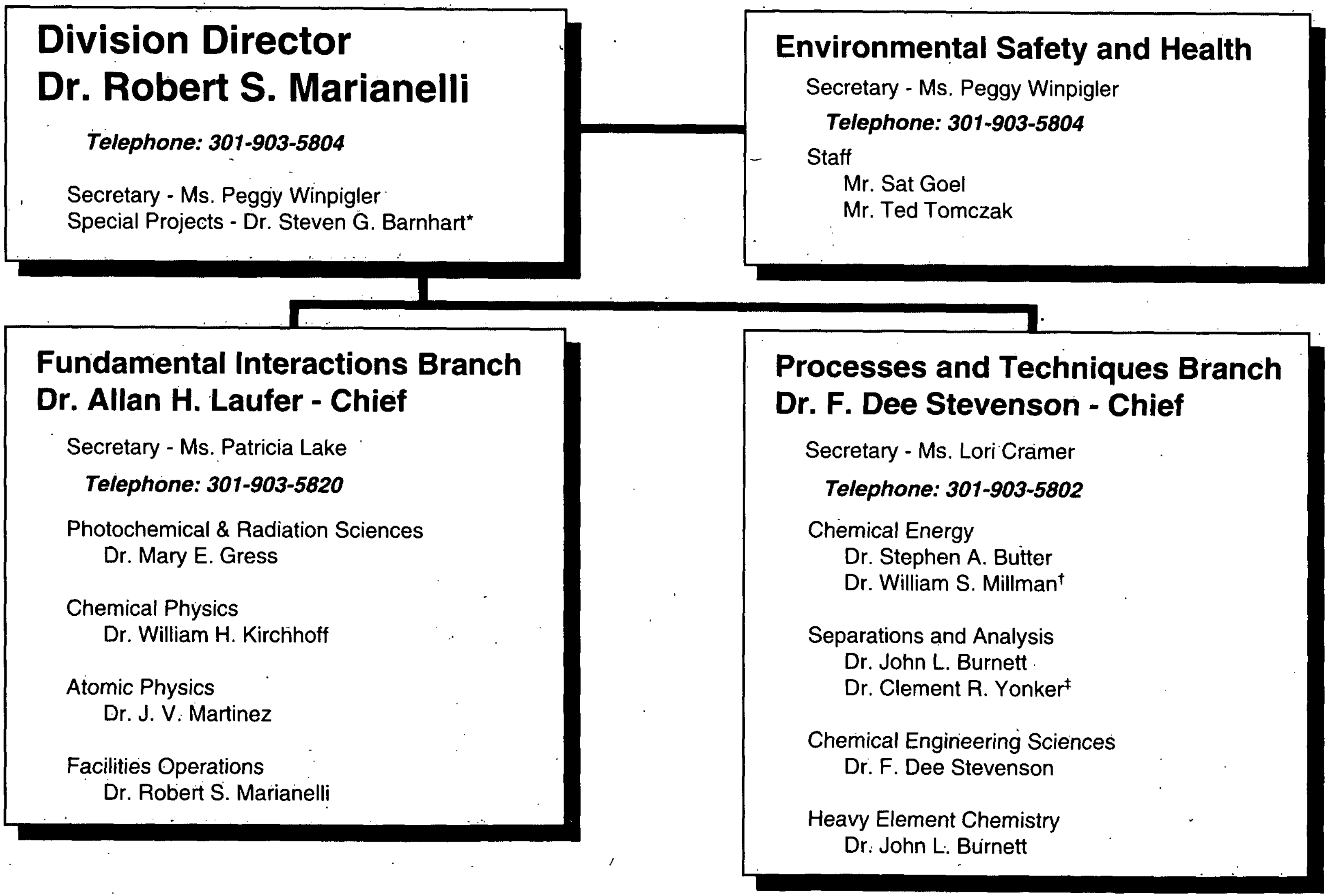
The program takes place in several different kinds of performing organizations. About one-third of the projects are at DOE laboratories and the rest mostly at universities, with a small number of projects at industrial laboratories. In DOE laboratories, much of the research utilizes special unique facilities 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 1993 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.

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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‡ On leave from the Pacific Northwest Laboratory, Richland

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, Livermore, 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 non-automotive 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 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
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Ames, IA 50011

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A. DePristo
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NATIONAL RENEWABLE ENERGY LABORATORY
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Basic Sciences Division
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NOTRE DAME RADIATION LABORATORY
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SANDIA NATIONAL LABORATORIES, ALBUQUERQUE
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Phone: (510) 294-3376

NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **$600,000**

1. ***Electrochemical and Optical Studies of Model Photosynthetic Systems***
   Cotton, T.M.
   515-294-9887

The objective of this project is to prepare and characterize model systems that are functional biomimetic constructions showing fast and efficient photoinduced electron transfer. Such systems are intended to perform the electron transfer functions of the photosynthetic reaction center, having its essential photochemical attributes if not necessarily its chemical structure. The basis for these models is the use of monolayers and multilayer structures, because they allow control over spacings, distances, and orientations. Systems are characterized by spectroelectrochemical methods and the sensitive technique of enhanced Raman spectroscopy, envoked by species on metal surfaces. Recent results, obtained from chlorophyll (electron donor) and viologen (electron acceptor) monolayers have demonstrated long-lived charge separation through the detection of stabilized radicals and other transient species. Vectorial charge separation in vivo depends upon highly ordered structures; therefore the orientational behavior of components of model systems are studied as spread films on water as well as those films formed by spontaneous self-assembly by adsorption onto metal surfaces; these provide much more ordered structures. Orientation by electrostatic fields ("poling") is under study as a more efficient method for orientational control. [2.0 FTE]

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

The primary photoconversion processes of photosynthesis are investigated in order to understand the structure–function relationships that result in the near unit quantum yield and high solar energy conversion efficiency of photosynthetic units. Determination of these relationships is viewed as important to the development of biomimetic solar energy conversion technologies which generate electricity or fuels. The primary photoconversion processes are optical excitation (energy) transfer and electron transport processes in antenna (light harvesting) and reaction center complexes. Laser-based optical frequency domain spectroscopies (e.g., spectral hole burning), developed in this laboratory for biological applications, are used to provide a high resolution window on the primary processes and the electronic structure of the photocatalytic chlorophyll states that drive them. These spectroscopies also yield important information on the interaction between excited chlorophyll states and the protein environment, an interaction that enters into theories of transport dynamics. Photosynthetic units from both purple bacteria and green plants are studied. Data obtained continue to provide fresh insights into energy transfer and electron transport and are used to test existing theoretical models and to develop new models. [2.2 FTE]

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

Ultrafast fluorescence and pump-probe spectroscopies are used to characterize electronic excitation transport in naturally occurring and artificial photosynthetic systems. Recent attention has focused on temperature dependence of energy transfer and annihilation in LCH-II trimers from the photosystem II light-harvesting antenna. Current experiments are examining femtosecond energy transfer and coherent decay in FMO trimers from green photosynthetic bacteria. New studies will investigate energy transfer in monolayer and multilayer template systems on 2-D surfaces, and exciton transport in 1-D aggregates. [2.2 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division **$5,200,000**

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

This program seeks fundamental knowledge of electron transfer (ET) reactions that could be useful in directing and controlling the flow of electrons and energy in photoconversion. Electron transfer rates are studied as a function of distance, thermodynamic driving force, polarity, temperature, and the nature and symmetry of molecules between electron donor and acceptor groups. Control of long-distance ET rates by electronic couplings is a focus of current theoretical calculations and experimental measurements, which use Argonne's 30-ps electron linear accelerator. These pulse radiolysis experiments are also producing remarkable information about ion pairing in solution. Charge transfer across the electrolyte-solid interface in small semiconductor particles is studied with emphasis on the well-defined and surface-modified particles. The dependence of the rate of ET on the energetics and on solvent parameters is studied in freely diffusing as well as in immobilized systems. Electron donor–acceptor groups are bound to the surfaces of the particles at well-defined distances and orientations. The effects of these surface-bound electron donor or acceptor groups on the energy levels in the particle, and on the properties of resultant radicals are investigated using the same pulse radiolysis techniques. [6.2 FTE]

5. *Characterization of Photosynthetic Components*

Norris, J.R.
708-252-3544

The purpose of this project is to prepare and physically characterize the molecular components that are employed in studies of solar energy conversion. One novel and quite important activity of this project is the large-scale production of biological materials highly enriched with nonradioactive isotopes. The isotopic labeling provides a unique means of studying the structure and the dynamic processes involved in efficient solar energy conversion. Currently, Fourier transform–electron paramagnetic resonance electron spin echo envelope modulation, high-field electron paramagnetic resonance, and small-angle neutron scattering are used to examine the protonation, the aggregation, and the microenvironments of components that participate in the solar energy conversion process of natural and artificial photosynthesis. The availability and characterization of these components are prerequisites to the development of practical solar energy processes that are based on natural photosynthesis. [1.0 FTE]

6. *Photosynthesis Research*

Norris, J.R.; Thurnauer, M.; Tiede, D.M.
708-252-3544

The primary goal of this project is to understand the initial events of solar energy utilization in natural photosynthesis such that this knowledge can be used in practical solar conversion processes. Natural photosynthesis achieves its energy conversion and storage by using highly sophisticated chemistry that operates with barriers 10 to 50 times smaller than observed in the best artificial photosynthesis system. Understanding why the natural process exhibits such efficient chemistry will advance considerably the ability to harness solar energy for practical purposes. Because the chemistry of the initial solar energy conversion processes of natural photosynthesis is extremely fast, sophisticated physical and chemical technology is employed in its study. A combination of advanced experimental techniques, including electron paramagnetic resonance (EPR), time domain EPR, optical spectroscopy, time domain optical spectroscopy, and theoretical modeling of natural and genetically modified photosynthetic subunits, is used to probe the structure, the mechanics, and the energetics of the initial events of natural photosynthesis. Already, the project is beginning to suggest plausible new schemes for increasing the efficiency of artificial solar energy devices. [4.4 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

The "high-energy" chemistry that occurs when ionizing and photoionizing radiation interacts with matter is being examined. This research uses specialized techniques and instruments (picosecond electron linac, femtosecond and picosecond lasers, and time-domain magnetic resonance methods) to allow unprecedented and comprehensive studies of short-lived chemical species. The detailed studies of reactive species such as radical cations, solvated electrons, and hydrogen atoms provide the framework for understanding chemical and biological effects of radiation. Chemical reactions of such species are also relevant to fundamental issues in chemical reactivity and technologically important chemical processes. The processes of excited state formation, charge separation and transport, and ion–molecule reactions involve species and reactions that have not been previously examined by real-time methods in the condensed phase. A significant part of this research effort is the elucidation of the role of solvent as it modulates chemical reactivity of electrons and ions. Innovative solvent substitution using low-temperature matrices and "microreactors" such as zeolites allows stabilization and control of reactions of radical ions. [7.5 FTE]

8. *Artificial Photosynthesis*

Wasielewski, M.R.
708-252-3538

The purpose of artificial photosynthesis research is to design, prepare, and study molecules that will convert light energy into useful chemical energy. The primary photochemistry of natural photosynthesis serves as a model for highly efficient conversion of light energy into chemical energy. Artificial photosynthetic charge separation systems are designed to improve upon the performance of the natural protein, and to yield photocatalysts that perform well in typical chemical environments. The initial events of photosynthesis consist of a sequence of picosecond electron-transfer reactions between donors and acceptors that are positioned at critical distances and orientations relative to one another within a large protein. Thus, supramolecular systems that consist of multiple electron donors and acceptors supported by a molecular framework designed to promote efficient, long-lived charge separation are synthesized. These supermolecules maintain well-defined structural, solvation, and electronic relationships between the donors and acceptors. The photophysics and photochemistry of these molecules are examined in detail with primary emphasis on ultrafast light-induced electron-transfer reactions that lead to high-yield energy storage. [3.7 FTE]

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

Department of Applied Science $1,030,000

9. *Porphyrin Chemistry*

Fajer, J.; Barkigia, K.M.; Renner, M.W.
516-282-4521

This program focuses on the multifaceted bioenergetic reactions mediated by porphyrin derivatives, reactions that range from light harvesting and energy conversion in photosynthesis to multielectron catalysis of nitrogen assimilation, regiospecific synthesis, and conversion of carbon dioxide to hydrocarbons. The project uses experimental, structural, and theoretical approaches to identify and characterize the transients and mechanisms of these photochemical and catalytic reactions with the ultimate goal of providing specific guidelines for the development of synthetic photocatalysts. In addition, readily modified synthetic and theoretical models offer useful insights into electron transfer reactions that occur on picosecond timescales. The work utilizes photochemistry, electrochemistry, magnetic resonance, X-ray and neutron diffraction, and synchrotron radiation techniques which are closely supported by theoretical methods. The cumulative thrust of these approaches is to identify the effects of macrocycle, substituents, metal, conformation, and environment on the photophysical, photochemical, and electron-transfer properties of porphyrins in photosynthetic and catalytic reactions. [5.2 FTE]

10. *Electrochemistry and Photoelectrochemistry*

Feldberg, S.W.
516-282-4480

The objective of this program is a fundamental understanding of a variety of electrochemical and photoelectrochemical phenomena. Areas of interest comprise theoretical and experimental investigations. The experimental objective is to understand the role of interfacial structure and organization in a variety of interfacial processes [e.g., double-layer relaxations, charge (ion or electron) transfer between the solution and the electrode, electron transfer between electrode and immobilized or adsorbed redox moieties]. The focus is on heterogeneous electron transfer and, in particular, on the characterization of very fast (submicrosecond) processes. The experimental approach utilizes an indirect laser-induced interfacial temperature-jump (ILIT) technique. At its present level of development ILIT can access interfacial rate processes occurring in the nanosecond time domain arguably exceeding the capabilities of other state-of-the-art electrochemical approaches. With a faster laser and faster amplifiers, the ILIT method will be capable of probing processes occurring in the subnanosecond time domain. Theoretical analyses and computer simulations of a broad range of electrochemical problems comprise a significant, continuing contribution of this program. [2.3 FTE]

Brookhaven National Laboratory
Upton, LI, NY 11973

Chemistry Department **$2,950,000**

11. *Thermal and Photoinduced Reactions in Solution*

Creutz, C.; Newton, M.D.; Seltzer, S.; Sutin, N.; Brunschwig, B.S.; Fujita, E.; Castner, E.
516-282-4359

This program addresses three areas fundamental to the efficient capture and storage of light energy: (1) excited-state formation, chemistry, and photophysics; (2) energy transduction by electron-transfer reactions; and (3) energy storage through chemical transformations. Theoretical and experimental efforts are elucidating the factors controlling electron-transfer rates and excited-state lifetimes; the roles of electronic configuration, separation distance, nuclear-configuration and free-energy changes, as well as the effects of solvent dynamics are being investigated through studies of transition-metal complexes and other donor/acceptor systems. The long-term storage of solar energy as fuels or valuable chemicals requires efficient coupling of light-absorption and chemical transformation processes. Mechanistic studies of the photoinduced and thermal olefin *cis–trans* isomerization address the nature of this coupling in the purple membrane proton pump, a solar energy converter which operates through photocatalyzed and protein-catalyzed *cis–trans* isomerization of its bound retinal. Chemical and mechanistic studies of transition-metal centers in high and low oxidation states are being conducted because such centers can couple photoinduced electron-transfer processes to the bond-forming reactions required in the photodecomposition of water or the photoreduction of carbon dioxide to useful chemicals. [13.4 FTE]

12. *Radiation Chemistry*

Schwarz, H.A.; Bielski, B.H.J.; Holroyd, R.A.; Wishart, J.F.
516-282-4330

This program uses pulse radiolysis, photolysis, and synchrotron X-rays to study the behavior of transient chemical species. Principal areas of investigation are (1) pressure effects on the properties and reactions of electrons in dielectric fluids; (2) X-ray track effects in dielectric fluids; (3) formation and reactions of transition-metal complexes in unusual oxidation states; (4) bimolecular and intramolecular electron-transfer rates; and (5) the nature, thermodynamics, and reactions of radicals produced in aqueous solutions. The studies of electrons in dielectric fluids are of prime importance in understanding the basic processes of radiation chemistry, in the development of new detectors for high-energy physics. The studies of transition-metal complexes are important in developing and understanding certain homogeneous catalysis systems and in schemes for chemical storage of solar energy. Knowledge of the thermodynamics of radicals is essential in understanding their electron-transfer reactions [8.4 FTE]

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

Structural Biology Division **$475,000**

13. *Artificial Photosynthesis*

Calvin, M.; Otvos, J.W.
510-643-5237

The project objective is to devise a synthetic system for storing the energy of visible light. The approach involves basic photochemical research in areas that will improve understanding of the relevant parts of such a storage system. First, there is a photoinduced electron-transfer process across a phase boundary, mimicking the natural photosynthetic process, followed by a stabilization of the initial electron-transfer products. These products are then catalytically converted to hydrogen and oxygen, the results of water photolysis, or to reduced organic compounds and oxygen if carbon dioxide is used as the substrate. For such an energy storage system to succeed, appropriate catalysts must be found for the final step on both the reduction and oxidation sides, the latter of which has proved to be the more difficult and challenging. What is needed is a chemically robust compound that can be transformed easily and reversibly among several oxidation states so that it might, therefore, be able to mediate the multielectron oxidation of water to oxygen. Oligomers of transition metals complexed with macrocyclic ligands appear to be excellent candidates for such a catalyst, and their synthesis and characterization is the main focus of the program. [1.4 FTE]

14. *Chemistry with Near Infrared Photons*

Frei, H.M.
510-486-4325

The objective of this project is to establish useful chemistry that can be driven by the sun's most abundant, long-wavelength photons. Current focus is on reactions that serve as models, or suggest new concepts, in two areas. The first is red and near-IR light-assisted synthesis of organic building blocks and high-value compounds from abundant chemicals. Controlled atom and group transfer reactions are explored by excitation of reactant pairs in inert cryogenic matrices. Laser photochemical and Fourier transform-infrared (FTIR) probing methods are employed to elucidate detailed reaction paths. Most recent examples are highly regio- and stereospecific photooxidations of small alkenes and alkynes by red light-excited nitrogen dioxide. The unique photochemistry of cage reactant pairs is now being explored for new controlled synthesis of high-value compounds in inert zeolite matrices at ambient temperature. In the second area, temporary chemical storage of near-IR photons and conversion into electrical energy, most recent work focuses on the detailed understanding of redox chemistry relevant to the development of regenerative electrochemical cells for near-IR light-to-electricity conversion. An example is the first direct observation of the rise of the one-electron oxidation intermediate upon photooxidation of iodide at dye-sensitized TiO_2. This furnishes new insight into elementary reaction steps of halide oxidation at the semiconductor–solution interface. [2.3 FTE]

National Renewable Energy Laboratory
Golden, CO 80401

Basic Sciences Division **$1,450,000**

15. *Photophysics and Photochemistry of Porphyrin Systems and Photosystem II Reaction Centers*

Connolly, J.S.; Seibert, M.
303-231-1873

Efficient storage of solar energy by electron-transfer (ET) processes depends on both the yield and the lifetime of the redox pair. In homogeneous solutions, rapid reverse ET generally precludes coupling of the initial photoreaction to secondary reactions, which will be necessary in a practical device. Several new molecules have been synthesized that were designed specifically to study the effects of electronic coupling and energetics on the rates of intramolecular ET. Current investigations are concerned with tightly linked molecules in strong electronic coupling between the donor and acceptor moieties that gives rise to emissive charge-transfer states that are highly sensitive to the dielectric environment of the host medium. By appropriate choices of substituent groups these molecules can be "tuned" to function in low-dipolar media. Thus they can be used to probe the dielectric properties of semirigid matrices, including polymers, vesicles, and protein membranes. These results demonstrate that it is possible to assemble multicomponent molecular systems in which the fraction of excited-state energy that can be converted to stored redox is maximized. This will be another significant step in assembling a synthetic photoreaction center. Energy transfer and primary charge separation in isolated antenna and photosystem II reaction-center complexes are also under investigation. [2.5 FTE]

16. *Surface-Modified Semiconductor Electrodes for Solar Photochemical Energy Conversion*

Frank, A.J.
303-231-1962

Fundamental issues are being addressed relating to molecular solids as photosensitizers, ground-state complexes in photochemical systems, chemically modified semiconductor particles, junction modification of semiconductor electrodes, and surface charge recombination at the semiconductor–liquid interface. Extensive work was completed on the photophysical and photocatalytic behavior of a novel molecular semiconductor based on a platinum(II) double salt. The structural, thermodynamic, and photophysical properties of rose bengal and methyl viologen complexes in the presence of SiO_2 were also investigated. Electrostatic interactions of the colloid with rose bengal and methyl viologen were found to have an important and beneficial effect in controlling the photophysical and photosensitizing properties of the dye in the system. A redox functionalized polymer was developed for improving electron-transfer kinetics of TiO_2 colloids by altering the surface environment. Photoinduced electron transfer from TiO_2 particles to electron acceptors appended to the polymer backbone was more favorable than that to solution-solubilized electron acceptors. The photoelectrochemical generation of a shallow p-type region in n-CdTe is being investigated. The photoelectrochemically modified CdTe displays a significant increase in photoconversion efficiency compared with the unmodified material. Surface recombination and charge-transfer processes at the n-Si:liquid interface are also under study. [2.0 FTE]

17. *Photoconversion Processes in Liquid Crystal Porphyrin Films*

Gregg, B.A.
303-231-1285

Energy transfer and electron-transfer processes are being studied in highly ordered thin films of liquid crystal porphyrin. The photoconversion processes in such films are predominantly controlled by the interfacial kinetics of exciton dissociation, rather than by the bulk electric field. The physical processes of energy transfer and asymmetric exciton dissociation occurring in these porphyrin films are similar to those occurring in natural photosynthesis. Interfacial exciton dissociation reactions are being investigated with the use of thin films of materials with discrete electronic states, for example, redox polymers. These films are interposed between the porphyrin and the electrode; the overlap of the energetic states at the interface controls the rate and polarity of the dissociation and electron-transfer processes. The energetic levels of the interfacial films are being tuned throughout the bandgap of the porphyrin to map out the kinetics of these processes. This research will help clarify the mechanisms of photoconversion processes both in molecular semiconductor films and in natural photosynthetic membranes. Measurements of dark currents, photovoltaic effects, impedance properties, and steady-state and time-resolved photoluminescence are currently being performed. A kinetic model describing these systems is being developed. [1.8 FTE]

18. *Quantization Effects in Photoelectrochemistry*

Nozik, A.J.
303-231-1953

Research is being conducted to determine in detail the relaxation dynamics of photogenerated charge carriers at III-V semiconductor–liquid-electrolyte interfaces, and to determine the effects of size quantization in one dimension (quantum films) and in three dimensions (quantum dots) on these dynamics. Of particular interest is the determination of the rates of photoinduced electron transfer to redox acceptors in solution, which can then be compared to the rates at which photogenerated hot electrons cool and transfer their excess energy to the lattice as heat. Quantum well structures containing any combination of Ga, In, As, P, and Al can be grown in the newly constructed, low-pressure metalorganic chemical vapor deposition (MOCVD) in layers as thin as 10 Å. Quantum dots of GaAs as small as about 12 Å are capped with organic groups and can be prepared as stable colloids via low-temperature (< 200 °C) chemical synthesis; quantum dots of InP are now being prepared by similar approaches. [6.0 FTE]

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

Radiation Laboratory **$3,350,000**

19. *Organic Photochemical Processes*

Chateauneuf, J.E.; Hug, G.L.
219-631-5458

Time-resolved spectroscopic techniques are used to directly monitor organic reaction intermediates and measure the kinetics and energetics of photo- and electron-induced processes in order to elucidate detailed mechanisms of these fundamental chemical transformations. The complementary use of laser flash photolysis and pulse radiolysis as initiation sources to selectively generate transient species is instrumental in identification and kinetic analysis of chlorine atoms and in measurement of their solute reactivity. Molecular complexes of chlorine atoms with benzene, pyridine, and carbon disulfide have been characterized. This strategy has also been successful in identifying a variety of intermediates generated by photoinduced electron transfer from sulfur-containing amino acids to aromatic ketone triplets. Absorption and emission techniques are also used to observe quenching of organic triplet states by transition-metal complexes. These results are being analyzed utilizing models of competitive energy–electron transfer. Well-defined photophysical and photochemical probes are also being used to investigate fluid dynamics and chemical interactions in supercritical fluids. Modifications in chemical reactivity due to enhanced diffusivity, solvent and cosolvent interactions, clustering effects, and geminate processes are being investigated. Application of pulse radiolysis to supercritical fluid samples, including supercritical water, is under development. [3.5 FTE]

20. *Quantum Mechanical Studies of Radiation-Produced Intermediates*

Chipman, D.M.; Carmichael, I.C.; Bentley, J.
219-631-5562

Chemical properties of highly reactive species, particularly free radicals and excited-state molecules, are characterized from theory to facilitate interpretation of experimental data on early processes following radiolysis or photolysis. The nature of the ensuing species is elucidated by calculation of various spectroscopic properties using modern methods of ab initio electronic structure theory. In recent work the vibrational and electronic structures of p-phenylenediamine radical cation were computed to analyze time-resolved resonance Raman spectroscopic experiments. The results led to reassignment of several fundamental modes and also provided, for the first time, an explanation of the striking changes in relative intensities observed for different vibrational modes as the excitation wavelength is varied. Accurate determination of one-, two- and three-bond nuclear spin–spin coupling constants was achieved for a variety of hydroxylated alkanes using compact Gaussian basis sets and sophisticated techniques for electron correlation recovery. Scaling procedures were also developed to allow quantitative prediction of these interactions in much larger systems for which only lower level computations are currently feasible. Theoretical methods were employed to disprove an experimental claim of unusual effectiveness of lithium cation as a radical stabilizer in gas-phase reactions. [4.6 FTE]

21. *Inorganic Photochemical Processes*

Ferraudi, G.J.
219-631-7676

Mapping of the electronic excited-state potential surfaces of various families of coordination complexes is being conducted by comparing action spectra of monophotonically and biphotonically induced photoprocesses. Quantum yields for photoreactions induced in biphotonic absorptions and those induced in monophotonic absorptions are determined under conditions corresponding to the same excitation energy. In these studies, the photochemical reactivity of electronic states, not populated directly from the ground state, as well as the photochemical reactivity of short-lived reaction intermediates, is investigated by using time-resolved sequential irradiations. Magnetokinetic effects on the rates of reaction of inorganic radicals with coordination complexes and on inner-sphere electron transfer reactions of coordination complexes are being investigated as a function of the magnetic induction between 0 and 9 tesla. Complementary information concerning the electronic structure of the reactants is being gathered by using time-resolved MCD spectroscopy. Results of these studies are compared with magnetic field effects on the rates of outer sphere electron transfer reactions of coordination complexes. The aim of these investigations is to characterize electronic parameters that determine rates of various photoinduced processes, (e.g., radiationless relaxation, electron transfer, and characteristic excited-state reactions). [3.3 FTE]

22. *Microwave Studies of Radiation-Produced Radicals*
Fessenden, R.W.; Madden, K.P.
219-631-5354

The molecular electronic, structural, and environmental factors controlling reaction rates and pathways for radicals and excited states formed by radiolysis and photolysis are determined by electron paramagnetic resonance (EPR), optical, and microwave absorption methods. Definitive electronic and geometrical structures are determined from EPR spectra for correlation with reactivity patterns. Spin multiplicities in radical formation reactions follow from chemically induced dynamic electron polarization (CIDEP) as do electronic interactions experienced by pairs of radicals or by radicals and excited states during formation and reaction. Kinetic EPR experiments elucidate the variation in nitroso spin trapping rate constants caused by variations in radical structure near the SOMO of carbohydrate model systems. Pilot experiments indicate that steric hindrance and electronic effects also strongly modulate trap-parent radical interactions when cyclic nitrone traps are used. The persistence of hydroxylalkyl radical-nitroso spin adducts has been measured; aminoxyl radical lifetimes varied from tenths of a second to over one year. Microwave dielectric absorption by photochemical intermediates maps their charge distribution to help explain variations in reaction mechanism in solvents of differing polarity. Direct or sensitized yield, mobility, decay kinetics, and chemical availability of photoinduced charge carriers in semiconductor particles and films are also measured by microwave absorption. [4.8 FTE]

23. *Photochemical and Photoelectrochemical Processes for Energy Conversion*
Kamat, P.V.
219-631-5411

Quantized ZnO, TiO_2, and WO_3 colloids are employed to develop optically transparent thin semiconductor films for photoelectrochemical conversion and storage of solar energy. A variety of interesting properties of these thin particulate films (e.g., electrochemical rectification, photoelectrochromic effect, and photosensitization) are studied to improve the efficiency of photoelectrochemical cells. Improvement in photoinduced charge separation is achieved by coupling two semiconductor colloids directly or by bridging them with surface modifiers. Kinetics and mechanistic details of charge transfer processes in coupled semiconductor colloids (e.g., ZnO–CdS) are elucidated with fast kinetic spectroscopy as well as photovoltaic measurements. Methods are being developed to store photoinduced electrons in WO_3 colloids and utilize stored electrons for reduction of oxazine dyes in the dark. Efforts are also being made to extend the photoresponse of large bandgap semiconductors with novel dyes absorbing in the IR (e.g., squaraine dyes). Picosecond and nanosecond laser flash photolysis techniques are being used to probe the mechanisms with which these dyes participate in the charge injection process with semiconductor colloids such as SnO_2, TiO_2, and ZnO. Photochemical reactions on oxide surfaces such as SiO_2 and Al_2O_3 are investigated to improve electron transfer selectivity and efficiency. [5.4 FTE]

24. *Track Effects in Radiation Chemistry*
LaVerne, J.A.; Mozumder, A.; Pimblott, S.M.; Schuler, R.H.
219-631-5563

Experiment and theory are employed to elucidate the effects of particle track structure on radiation chemical kinetics. Heavy ions from the Notre Dame Nuclear Structure Laboratory facility are used to probe the scavenger concentration dependence of the hydrated electron yield in water as a function of particle energy and linear energy transfer. The influences of track structure on the temporal variation of radical and product formation in cyclic hydrocarbons are determined with iodine scavenging techniques. Radiolysis of the Fricke dosimeter with up to 70 MeV/nucleon ions is performed using the superconducting cyclotron at Michigan State University. Diffusion-kinetic techniques for modeling nonhomogeneous radiation chemistry are used to probe the dependences of the observed yields in the radiolysis of aqueous solutions on track geometry and bulk temperature. The kinetics and spatial correlations of the reactions of spur reactants with micromolecules are examined using stochastic simulations. Factors affecting recombination in multiple ion-pair clusters in hydrocarbons are investigated using Monte Carlo and master equation methods. Theoretical models are used to reconcile the initial energy deposition mechanisms in water, hydrocarbons, and liquefied rare gases and their relationship to the observed ionization, luminescence, and product formation. [6.4 FTE]

25. *Influence of Ordered Molecular Assemblies on Photochemical Processes*
Patterson, L.K.
219-631-5403

The kinetics of photochemical- and radiation-induced processes are determined in organized molecular assemblies, such as lipid Langmuir films, to elucidate the mechanisms by which this type of media may be used to exercise kinetic control over reactions relevant to energy storage. Emphasis is placed on modifying the rates and efficiencies of electron or energy transfer to generate and stabilize reactive intermediates. It is shown that interactions of donors, such as lipid functionalized quantized particles or hydrophobic dyes, with appropriate acceptors (e.g., viologens) may be controlled by molecular organization in the assembly. Lipid structure, headgroup charge, surface compression and subphase composition (e.g., pH) are among parameters that are manipulated to alter molecular organization in reaction environments. Steady-state and time-resolved excited-state fluorescence, as well as ground-state absorption and reflectance techniques, are developed to monitor kinetics and characterize the microscopic order of the assembly investigated. Considerable attention is given to the influence of such parameters on both ground-state reactivity and excited-state behavior of chlorophyll and related compounds. Processes involving triplet states or radicals, which pose considerable difficulties for measurement in monolayers, are investigated in micelles by flash photolysis and pulse radiolysis. [4.1 FTE]

26. *Radiation Chemistry Data Center*

Ross, A.B.; Helman, W.P.; Hug, G.L.; Carmichael, I.C.
219-631-6528

Kinetic, spectroscopic, and thermodynamic data for processes in solution involving reactive intermediates, including free radicals and excited states, are being compiled, evaluated, and collected into databases. These compilation efforts are primarily focused on time-resolved photochemical and radiation chemical research. A handbook on photochemistry and photophysics of organic molecules has been completed. Included are quantum yields and rates for various unimolecular and bimolecular excited-state processes, energy levels, and spectral parameters. A critical compilation of quantum yields for photosensitized production of singlet molecular oxygen in solution has been published. Another review in preparation involves rate constants for reactions of transients derived from metal ions and metal complexes in aqueous solution. A database for the chemical kinetics of radical processes in solutions, the NDRL–NIST Solution Kinetics Database, has been released for use on IBM compatible personal computers. The Radiation Chemistry Data Center (RCDC) currently provides online services for searching numeric databases containing rate constants for reactions of inorganic radicals in aqueous solution and a database of triplet–triplet absorption spectral data in condensed phases. A bibliographic database, RCDCbib, is used to produce the current-awareness publication, "The Biweekly List of Papers on Radiation Chemistry and Photochemistry". [4.6 FTE]

27. *Radiation-Induced Chemical Reactions*

Schuler, R.H.; Tripathi, G.N.R.; Patterson, L.K.
219-631-7502

Mechanisms of radiation-induced reactions are being determined by time-resolved absorption and resonance Raman measurements as well as by product analysis. High-pressure liquid chromatographic (HPLC) methods are utilized to examine oxidation processes in the radiolysis of aqueous solutions of organic substrates. In particular, studies of hydroxylation of aromatic systems show that various substituents have pronounced directing effects in determining the position of OH radical attack. Quantitative studies can be conducted at doses ~1000 rads where products are generated at micromole concentrations. These product analysis studies, coupled with time-resolved transient absorption and resonance Raman measurements in pulse radiolysis, give a detailed picture of the mechanisms of attack on organic substrates by initial radiation-produced intermediates. Time-resolved Raman studies also provide structural data concerning intermediates. Of particular note are Raman studies of sulfur containing radicals that give information on electron distribution not available from electron spin resonance studies. Investigation of electron scavenging by halogenated organics is also being conducted utilizing capillary electrophoresis methods that have recently become available. These latter studies are aimed at determining the concentration dependence of electron scavenging to provide information on decay of hydrated electrons in radiation tracks. [9.9 FTE]

Chemical Physics

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program $725,000

28. *Chemical Theory*

DePristo, A.E.
515-294-9924

The focus of this research is the theoretical description of the structure and dynamics of metal clusters in terms of their fundamental atomic and electronic constituents. The goal is to determine the structure and energy of various clusters, and to investigate the relationship between these properties and the reactivity of clusters with different gas-phase molecules. Ab initio and semiempirical quantum mechanical electronic structure techniques are utilized along with classical dynamics and classical Monte Carlo methods. Theoretical developments are directed toward a combination of electronic structure techniques with molecular dynamics (i.e., calculation of forces by solution of the electronic structure problem at each needed geometry in a molecular dynamics simulation). Another effort involves analysis of the kinetics and nonequilibrium structure associated with irreversible or far-from-equilibrium adsorption and catalytic reaction processes on solid surfaces. The goal is to understand the interplay between kinetics and structure. [2.0 FTE]

29. *Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals*

Ng, C.Y.
515-294-4225

The goals of this program are (1) to obtain accurate thermochemical data, such as ionization energies and bond dissociation energies, for neutral polyatomic molecules, radicals, and their ions; (2) to study the photoionization and photodissociation dynamics of molecules and radicals induced by the absorption of UV and VUV photons; and (3) to investigate the reaction dynamics and mechanisms of fast radical–molecule and radical–radical reactions. One current focus is on the studies of organosulfur radicals and transition metal carbonyl compounds and their fragments. Oxidation of organosulfur compounds, which are emitted to the atmosphere due to the incomplete combustion of coal and oil, ultimately leads to the formation of SO_2 and acid rain. Previous studies indicate that the oxidation rate for organosulfur pollutants increases substantially in the presence of UV radiation. The study of the UV and VUV photochemistry of organosulfur species is relevant to the modeling of atmospheric sulfur chemistry cycles. Motivated to obtain a detailed understanding of the catalytic ability of transition metal ions, experiments have been initiated to examine systematically the energetics and reactivities of transition metal carbonyl compounds and their fragments. Recent focuses have also been expanded to include oxygen-containing hydrocarbon radicals. [5.0 FTE]

30. *Molecular Bonding Theory*

Ruedenberg, K.
515-294-5253

Quantitative methods of ab *initio* quantum mechanics are used to determine molecular properties and characteristics of chemical reactions. The efforts are focused on potential energy surfaces, which represent the central conceptual as well as quantitative entities in chemical physics, governing molecular energetics as well as dynamics and kinetics. Global characteristics as well as critical local features (metastable intermediates, transition states, reaction paths, bifurcation, intersections, and so forth) are elucidated through fundamental analyses and examined through large-scale computations in concrete systems. Attention is focused on systems related to hydrogenation, combustion, and atmospheric chemistry, in particular molecules containing carbon, hydrogen, and oxygen. Current investigations determine the potential energy surfaces of the 10 lowest singlet and triplet states of ozone so as to complement the limited experimental information on this important molecule. In other investigations, reaction-path-following methods are developed. Also, quantitative methods are developed for the interpretation of ab initio energy changes along reaction paths in terms of interactions between atoms in molecules that can be fitted into the chemical intuition of nontheorists. The atoms-in-molecules analysis is furthermore used as the basis for identifying methods for a more efficient recovery of electron correlation. [2.5 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $4,050,000

31. *Photoionization–Photoelectron Research*

Berkowitz, J.
708-252-4086

The VUV photoionization of atoms, free radicals, and small molecules is studied at high photon resolution. The transient species are prepared in situ by pyrolysis, sublimation, electrical discharge, or chemical reaction. The ongoing studies of atoms are revealing systematic behavior in the breadth and shape of autoionizing lines, which may be rationalized with a simple theory even though it is inherently a complex, many-body phenomenon. The free-radical studies are currently providing accurate thermochemical information on important intermediates in combustion reactions, and in the plasmas used for thin film technology. In continuing studies of combustion intermediates, the ionization potential of CH_2SH was obtained for the first time, and that of its isomer, CH_3S, was corrected. From these data, heats of formation of CH_2SH, CH_3S, and their cations were derived. These values resolve a discrepancy that had arisen recently between ab initio calculations and other experimental results. Additional studies have been performed on the species CH_2S, HCS, and their cations, thereby completing the understanding of the stepwise decomposition of methanol. In another apparatus, the VUV photoionization spectra of Bi, Bi_2, Bi_3, and Bi_4, as well as Sb_2 and Sb_4, have been obtained. Preliminary data have also been obtained on Sb, SbH, SbH_2, and SbH_3. These results have practical applications in the preparation of semiconductors, provide fundamental information on the behavior of clusters and on the bond energies of Group V hydrides, and will provide a complete, systematic understanding of the autoionization behavior of all Group V atoms. [2.0 FTE]

32. *Metal Cluster Chemistry Research*

Riley, S.J.; Parks, E.K.; Jellinek, J.; Knickelbein, M.B.
708-252-6793

The chemical and physical properties of isolated clusters of transition-metal atoms are studied both experimentally and theoretically. Experimental measurements of chemical reactivity, product compositions, and adsorbate binding energies are made, together with determinations of the nature of adsorption sites and cluster geometrical structure. Another experimental effort studies such physical properties as ionization potentials, the dependence of ionization potential on adsorbate coverage, and the optical absorption spectra of isolated clusters. An interactive theoretical effort studies, via dynamical simulation, such properties as cluster structure, phases and phase changes, stability and fragmentation patterns, and the interactions of clusters with molecules. A goal common to all these studies is to understand how cluster properties depend on structure and how structure depends on cluster size. Ultimately, these studies will provide a better understanding of surface chemistry and heterogeneous catalysis. [7.0 FTE]

33. *Chemical Dynamics in the Gas Phase*

Wagner, A.; Davis, M.; Harding, L.; Shepard, R.; Liu, K.; MacDonald, R.; Michael, J.; Hessler, J.; Gray, S.
708-252-3597

The project mission is to characterize the reactive properties of small molecules and radicals in the gas phase, with an emphasis on those species of importance in combustion chemistry. The mission is conducted by combining theoretical studies in the energetics and dynamics of chemical reactions with experimental studies in chemical dynamics and kinetics. The theoretical effort embraces both large-scale applications of existing theoretical methods and the development of new methods that efficiently exploit advanced computer architectures. The experimental effort encompasses both molecular beam studies of state-to-state processes and shock tube studies of both high- and low-temperature kinetics. A new flow tube apparatus for the measurement of state-resolved product distributions of radical–radical reactions has been recently constructed and the first measurements are being obtained. The close coupling between theory and experiment brings a unique combination of expertise to bear on the study of chemical reactivity. [11.9 FTE]

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

Department of Applied Science **$620,000**

34. Combustion Kinetics and Reaction Pathways

Klemm, R.B.; Sutherland, J.W.
516-282-4022

This project is focused on the fundamental chemistry of combustion. The overall objectives are to determine rate constants for elementary reactions and to elucidate the pathways of multichannel reactions. A multitechnique approach that features three independent experiments provides unique capabilities in performing reliable kinetic measurements over an exceptionally wide range in temperature, 300 to 2500 K. Recent kinetic studies have focused heavily on the methane dissociation system ($CH_4 + Ar \rightarrow CH_3 + H + Ar$ and $H + CH_4 \rightarrow CH_3 + H_2$). Hydrogen atoms were monitored directly in shock tube experiments that employed the extremely sensitive atomic resonance absorption method. Additionally, a discharge flow–photoionization mass spectrometer (DF–PIMS) experiment is used to determine branching fractions for multichannel reactions and to measure ionization thresholds of free radicals. Thus, these photoionization experiments generate data that are relevant to both reaction pathways studies (reaction dynamics) and fundamental thermochemical research. The DF–PIMS apparatus was designed to be operated on the U-11 beam line at the National Synchrotron Light Source. Two distinct advantages of performing PIMS with tunable VUV light are high-detection sensitivity and exceptional selectivity in monitoring radical species. [4.8 FTE]

36. Gas-Phase Molecular Dynamics

Weston, R.E.; Muckerman, J.T.; Sears, T.J.; Preses, J.; Hall, G.E.
516-282-4373

Research in this program explores the energetics and dynamics of molecular collision phenomena and photodissociation, as well as the microscopic factors affecting the structure and dynamics of short-lived intermediates in gas-phase chemical reactions. Both experimental and theoretical techniques are directed toward the study of the spectra of small free radicals, and of state-to-state dynamics of gas-phase collision, energy-transfer, and photodissociation phenomena. The objective is a fundamental understanding of transient species and chemical processes, especially those related to combustion. Experimental tools include diode laser absorption; pulsed excitation using IR, visible, or UV lasers; laser-induced fluorescence and stimulated emission pumping; time-resolved Fourier transform infrared (FTIR) detection of excited species; and time-resolved fluorescence studies. These are augmented by theoretical studies in which quasi-classical, semiclassical, and quantal methods, particularly those combining classical and quantal wavepacket descriptions for different degrees of freedom, are developed and applied to prototypical chemical systems. [11.2 FTE]

Brookhaven National Laboratory
Upton, LI, NY 11973

Chemistry Department **$2,925,000**

35. Energy Transfer Studies in Cluster Impacts

Friedman, L.; Beuhler, R.J.
516-282-4325

This research is concerned with fundamental aspects of the energy transfer that occurs when accelerated cluster ions impact on solid surfaces. The use of nuclear fusion reactions as a diagnostic tool is being explored to study the properties of dense, energetic atomic assemblies produced by the impact of accelerated cluster ions on solid surfaces. Products of fusion reactions have been observed when cluster beams impact on suitable target surfaces. The interpretation of the results of these experiments is clouded by the possibility that accelerated cluster ion beams are contaminated with high-velocity deuterium-containing impurities. An immediate goal is the determination of the extent and nature of collective interactions of projectile cluster ions with target atoms, which lead to fusion reactions and which can be clearly ascribed to cluster impacts. [3.4 FTE]

37. Gas-Phase Photoionization of Molecules and Molecular Complexes

White, M.; Grover, J.R.; DiMauro, L.
516-282-4345

The general aims of this program are the detailed study of molecular photofragmentation dynamics and the characterization of the structure, spectroscopy, and intramolecular dynamics of free radical species and weakly bound molecular complexes. Intense synchrotron and laser radiation sources are used to induce excited neutral or ionic state processes such as dissociation, dissociative rearrangement, chemi-ionization and autoionization, the products of which are probed by a variety of photoionization-based techniques. State-resolved dissociation and photoionization measurements focus on the partitioning of energy and angular momentum in elementary molecular photofragmentation processes. Parallel investigations of weak molecular complexes are aimed at obtaining mechanistic and dynamical information on dissociative rearrangement processes of molecular intermediates produced by photoionization. Time-resolved fluorescence studies are aimed at probing the structure and dynamics of "cold" chemically transient species. Studies of the effects of well characterized laser fields on simple, isolated systems are also under investigation with the ultimate goal of controlling modified collision dynamics for physical and chemical processes. [6.5 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $2,785,000

38. *Energy Transfer and Structural Studies of Molecules on Surfaces*
Harris, C.B.
510-642-2814

The goal of this research is to study the dynamics of excited electronic states on surfaces, at interfaces, and in condensed phases and to develop new laser techniques for studying these dynamics. The research program is both theoretical and experimental in character, and includes nonlinear optical and ultrafast laser techniques in addition to a variety of standard surface science tools for characterizing surfaces and adsorbate–surface interactions. Recent work has centered on the development of new techniques based on two photon photoemission for studying the dynamics of electrons at interfaces on femtosecond time scales and carrier diffusion in semiconductors. The results of this program have a direct bearing on high-speed technological devices and materials, and on other problems of general interest such as the dynamics of electrical transmission in conductors on ultrafast time scales and the optical properties of thin films. [2.5 FTE]

39. *Chemical Dynamics*
Lee, Y.T.; Lester, W.A.; Miller, W.H.; Moore, C.B.; Kung, A.H.; Neumark, D.; Johnston, H.S.
510-486-6154

The objectives of this program are to develop the basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions that have major impact on combustion, advanced energy production, and photochemistry of materials in the stratosphere. These objectives are achieved with a strongly coupled experimental and theoretical–computational approach. Dynamical studies use advanced molecular beams and photofragmentation spectroscopy. Kinetics studies employ photofragment excitation spectroscopy and high-resolution laser spectroscopy. Free-radical photodissociation is probed using fast neutral beams. All experiments employ the latest advances in laser technology, beam source, and detection technologies. New theoretical methods and models are developed both to provide insight into chemical reactivity and the dynamics of reactive processes, and to allow forefront calculations that guide and model various of these experimental studies. Some of the most significant recent results include dissociation mechanism of cyclic and heterocyclic hydrocarbons, essential information on the structure of the transition state of ketene, detailed dynamics of 3- and 4-centered H_2 elimination from ethylene, structure and dynamics of dissociative states of trinitrogen, and detailed theoretical and experimental understanding of dynamical resonances. Progress in theoretical development includes new approaches to quantum scattering and quantum transition state theory, description of molecular interactions on transition metal surfaces, and modeling heterogeneous reactions in the stratosphere. Current studies focus on the energetics and reactivity of free radicals, clusters, and highly excited polyatomic molecules, on the structure and dynamics in the transition state region, on the microscopic mechanisms of primary photodissociation and bimolecular processes, and on the development of a high-power tunable IR laser. [20.0 FTE]

40. *Physical Chemistry with Emphasis on Thermodynamic Properties*
Pitzer, K.S.
510-642-3472

The purpose of this project is the discovery and development of methods of calculation of thermodynamic and related properties of important chemical systems by use of quantum and statistical mechanics together with experimental measurements for key systems. Primary emphasis will be on multicomponent fluids both neutral and ionized, with particular attention to phase equilibria, critical behavior, and the supercritical region. Aqueous solutions of electrolytes which are fully dissociated into ions at temperatures up to 300 °C become largely associated into neutral species at higher temperatures because of the great decrease in the dielectric constant. This aspect requires special theoretical methods now being explored for initial application to NaCl–H_2O in the range from 600 K to at least 1200 K. Recent contributions of this project have included theoretical calculations of the phase relations and critical properties of pure ionic fluids and measurements of these and other properties of binary fluids that model the pure ionic fluid at experimentally accessible temperatures. Investigations often involve collaboration with Lawrence Livermore National Laboratory (LLNL), Oak Ridge National Laboratory (ORNL), or United States Geological Survey (USGS) and concern systems of both geological and industrial importance. [1.0 FTE]

41. *Chemical Physics at High Photon Energies*
Shirley, D.A.
510-486-7633

This project is focused on the future utilization of the Advanced Light Source, now under construction at the Lawrence Berkeley Laboratory, for research in chemical physics. Two major goals are (1) the performance of pathbreaking research based on high-brightness VUV radiation and (2) the training of chemistry Ph.D. students in synchrotron radiation science. Research projects are identified to emphasize those priority research areas that are amenable to study with VUV radiation: chemical reactivity, chemical catalysis, and matter under extreme conditions. Effects are emphasized that can be refined and extended with the advent of third-generation light sources (e.g., angular distribution effects in threshold and near-edge photoexcitation phenomena, very fast processes, and processes requiring very high intensity and energy resolution). Electron correlations in atoms and molecules are studied, especially in the adiabatic (low-energy) limit, where the electronic structure of the continuum is important. Molecular-beam angle-resolved time-of-flight spectroscopy is performed, using supersonic beams. Surface structures are also studied using photoelectron diffraction in the variable energy mode, and observing angle-resolved photoemission extended fine structure (ARPEFS). [7.3 FTE]

Energy and Environment Division — $185,000

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 determine the relationship between dynamic observables and the potential energy surface structure. This provides an understanding of how different regions of the potential influence the dynamics, and thereby the eventual outcome of calculated observables. Functional sensitivity analysis has been applied to classical dynamics studies of energy transfer and to quantum mechanical studies of reactive scattering. Functional sensitivity analysis can be used to identify regions of configuration space of highest sensitivity so that quantum chemists calculate a high density of ab initio points in those regions, and the full sensitivities can be used in guiding the improvement of the potential surface to obtain better agreement between theory and experiment. A second portion of the effort is concerned with modeling combustion chemistry with particular emphasis on the use of sensitivity analysis. [1.0 FTE]

Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

Division of Computational Physics — $40,000

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

This project consists of computer modeling of chemical kinetics of combustion of hydrocarbon and other fuels used for practical combustion systems. The importance of fuel molecular size and structure are of particular interest. Other problems of concern to this project include the kinetics of oxidation of halogenated hydrocarbon species and their relationship to kinetics of analogous hydrocarbon species, thus comparing ethylene oxidation with that of vinyl chloride and carbon tetrachloride with methane. Other related studies have compared methane oxidation with that of silane, structurally the same as methane but with a silicon atom replacing the carbon atom at the center of the molecule. The role of falloff behavior in the unimolecular decomposition of radicals and stable species has also been a central element in this research. As in previous years, the major role has been the identification of those reactions and reaction rates which merit the greatest attention from the theoretical and experimental programs in this larger program, reactions which have the greatest influence on the overall rate of combustion and practical heat release. [0.3 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Molecular Science Research Center — $5,000,000

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

The purpose of this program is to achieve a molecular level understanding of chemical reaction dynamics at condensed phase interfaces. This requires an understanding of the solid substrate and the solvent, and their combined effect upon chemical reaction dynamics. The methods used for these studies will include (1) the synthesis of unique surfaces and interfaces through the 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 be compared quantitatively to ab initio theories, for their validation and development); (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 for physical characterization 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. [8.2 FTE]

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

The molecular theory and modeling project is designed to increase understanding of the fundamental molecular processes important in environmental restoration and waste management. The project integrates ab initio studies of fundamental molecular processes in model molecular systems with modeling of molecular processes in the complex multispecies, multiphase systems found in the environment. Four research areas emphasized are (1) solution chemistry, which is focused on the structure of molecules and the energetics and dynamics of molecular processes in aqueous clusters and solutions; (2) separations chemistry, which is concerned with the structure and energetics of ion-ligand complexes (such as crown ethers) and the dynamics of complex formation in aqueous solutions; (3) chemistry of minerals, which is directed toward understanding the binding of molecules to soil minerals and the dynamics of molecular processes at the interface between minerals and aqueous solutions; and (4) chemistry of amorphous materials, which is focused on molecular processes occurring at the interface between glasses and other amorphous materials and aqueous solutions. This knowledge will further the development of reliable models of contaminant transport and transformation in groundwaters and soils, the assessment of the stability of proposed long-term waste storage forms, and the development of new separation processes for the treatment of high-level wastes. [8.3 FTE]

Sandia National Laboratories, Livermore
Livermore, CA 94551

Combustion Research Facility $2,700,000

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. Simultaneous measurements of NO, OH, major species, temperature, and mixture fraction are obtained in turbulent jet flames. These multiscalar data provide a direct measure of the chemical structure of reaction zones in turbulent flames. These measurements also constitute a unique database for the evaluation and refinement of turbulent combustion models that include complex chemistry and the effects of turbulence–chemistry interactions. The spatial structure of turbulent reacting flow is investigated using quantitative planar imaging techniques. These techniques include simultaneous two-dimensional imaging of CH_4, CH, and OH in turbulent methane flames, simultaneous imaging of NO and temperature, simultaneous imaging of OH and acetone (a fuel marker), and imaging schemes to measure molecular mixing and differential species diffusion. Complementary information on the fundamental processes that couple fluid mechanics and chemistry in turbulent reacting flows is obtained through direct numerical simulations (DNS). Image data and DNS results on the spatial structure of flames provide critical information for the development and evaluation of combustion models for reacting flows with complex geometries. [6.0 FTE]

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

Farrow, R.L.; Rahn, L.A.
510-294-3259

This project develops nonlinear spectroscopic diagnostics in support of the Combustion Research Facility (CRF) programs. Detailed studies are made of processes affecting coherent anti-Stokes Raman spectroscopy (CARS) and resonant wave mixing spectroscopies such as degenerate four-wave mixing (DFWM). CARS is an established technique for time- and space-resolved measurements of temperature and major species concentrations, and DFWM has recently emerged as a more sensitive technique capable of minor species measurements. Processes under study include Doppler effects, collisional broadening and shifts, collisional narrowing, collisional quenching and reorientation, and saturation effects. High-resolution tunable pulsed-laser systems have been developed for CARS, inverse Raman spectroscopy (IRS), DFWM, and nearly degenerate four-wave mixing (NDFWM) experiments. The CARS system is used to measure two-photon saturation effects and to perform pump-probe measurements of inelastic rotational state-to-state rates. Collisional effects such as broadening, shifts, and collapse of Q-branch spectra are measured in gas samples at pressures up to 100 atm and 1200 K with the IRS system. A collisional inhomogeneity, important in describing molecular hydrogen spectra, was recently discovered and is currently under investigation using the CARS and IRS experiments. Measurements are also conducted on water vapor and are being extended to oxygen. The DFWM and NDFWM experiments are being used to study mechanisms and the effects of collisional and saturation processes on resonant wave mixing signal strengths and lineshapes. Current studies on NO and OH molecules have indicated the reduced dependence of the signal on collisional effects near saturation and the importance of mechanisms such as cross-over resonances and thermal gratings. Computer codes for analyzing CARS and DFWM spectra are being developed and transferred to the combustion research community. The CARS code is well-developed and widely used in the United States, with recent versions adapted for use on microcomputer platforms. The DFWM code is under active development, with interest in preliminary versions being shown by several outside groups. This project is supported with facility operations funds. [4.0 FTE]

48. *Flame Chemistry: Modeling and Experiments*

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

The goal of this research is to develop both a qualitative understanding and quantitatively predictive mathematical models of the chemistry of combustion. Emphasis is placed on pollutants, particularly nitrogenous pollutants and soot. Work in nitrogen chemistry largely involves refining the mechanism previously developed to make it more robust and to allow the quantitative prediction of nitrous oxide. Work on soot formation is largely focused on understanding how aromatic compounds are formed in flames of aliphatic fuels. This research embraces (1) low-pressure flame experiments that utilize both laser diagnostics and mass spectrometry, (2) mathematical modeling of flame experiments and other macroscopic experiments in combustion chemistry, and (3) the theoretical prediction of rate coefficients of critical elementary reactions. [4.0 FTE]

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

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

This project supports the development and theoretical investigation of novel techniques and strategies for diagnostic measurements in the Combustion Research Facility (CRF). New laser-induced fluorescence (LIF) strategies and novel stimulated emission, multiphoton, ionization, and ultrafast techniques are included in this work. Developments in planar laser-induced fluorescence (PLIF), one of the most valuable tools available to combustion researchers, have helped overcome low signal strengths in

CH images and have provided flow-tracer images of mixing in turbulent jets. Novel multiphoton techniques for trace species detection, including two-color laser-induced grating spectroscopy (LIGS) and six-wave mixing, are being applied to O, N, H, CO, and H_2 in low-pressure flames. Techniques for the study of ultrafast chemical processes in molecules are being developed in support of ultrafast combustion chemistry research in CRF. This work currently focuses on the important, previously unsolved problem of measuring the time dependence of the intensity and the phase of laser pulses lasting only tens of femtoseconds. Recent development of a novel frequency-resolved optical gating (FROG) technique is being extended to a single-shot measurement capability for two simultaneous pulses. Realization of this effort will result in new and more powerful excite-probe chemical-dynamics techniques and will contribute to a wide range of other diagnostic methods. New methods for generation of femtosecond UV light and high-sensitivity single-shot measurements are also being developed. Theoretical investigations include studies of the fundamental aspects of time- and frequency-domain nonlinear-spectroscopic techniques, perturbation-theory calculations of multiphoton nonlinear techniques, and higher order calculations to investigate high-intensity effects. This project is supported with facility operations funds. [3.0 FTE]

50. *Chemical Kinetics and Dynamics*

Tully, F.P.; Durant, J.L.; Chandler, D.W.; Miller, J.A.; Rohlfing, E.A.; Hayden, C.C.; Gray, J.A.
510-294-2316

The goal of this research is to understand in detail the fundamental chemical processes that occur in combustion. Typical kinetics experiments use the laser-photolysis/laser-induced fluorescence (or long-path IR absorption) technique to follow the course of reactions between, for example, OH and alkenes or Cl-atom and hydrocarbons. A versatile flow-tube kinetics apparatus having both laser- and mass-spectrometric diagnostics has been completed and is being used to study the reactions of NH. Recent theoretical studies have treated reactions such as those between H and O_2, NH and NO, and NH and O_2 using quantum–mechanical and statistical–theoretical methods. Application of GAUSSIAN2 methods to calculation of transition-state energetics has been validated for several chemical systems. Studies of dynamics emphasize collecting quantum-state-resolved data for elementary chemical processes. Ion-imaging studies of the $H + D_2$ reaction have clarified the dynamics of this process and the partitioning of available energy. Recently initiated investigations of internal conversion processes that occur on femtosecond time scales provide information on molecular rearrangements and energy flow. Utilization of laser-induced grating techniques to study SiC_2 spectroscopy and NO_2 photodissociation provides information on molecular structure and dissociation dynamics. [6.0 FTE]

Atomic Physics

Argonne National Laboratory
Argonne, IL 60439

Physics Division $1,500,000

51. *Atomic Physics at ATLAS*

Dunford, R.W.; Berry, H.G.
708-252-4052

In this project, the physics of highly charged ions is studied using the Argonne Tandem/LINAC Accelerator System (ATLAS) heavy-ion accelerator. The electron cyclotron resonance (ECR) ion source, which is part of the uranium upgrade of ATLAS, is also used in these studies. The ECR ion source is on a high-voltage platform which allows the use of ion beams with energies up to 300 keV times the extracted ion charge state. Atomic physics research at ATLAS includes studies of atomic structure and ion–atom collisions. The atomic structure work aims at precision tests of quantum electrodynamics and relativistic quantum theory. The program features UV and X-ray spectroscopy and measurements of the lifetimes for forbidden decays in few-electron systems. 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 program is a high-resolution study of dielectronic recombination (DR) by channeled ions. The uranium upgrade of ATLAS makes possible the study of collisions between two very heavy nuclei at energies near the Coulomb barrier. [4.5 FTE]

52. *Interactions of Fast Atomic and Molecular Ions with Solid and Gaseous Targets*

Kanter, E.P.
708-252-4050

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) atomic and molecular ions with matter. A unique feature of the apparatus is the exceptionally high resolution (~.005° and ~200 psec) in angle and time-of-flight obtained in detecting particles emerging from the target. Unique multiparticle imaging detector systems have been developed which allow detection of multiparticle events consisting of up to 12 particles and yielding three-dimensional views of the particle trajectories. The work includes a general study of the interactions of fast charged particles with matter, emphasizing those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., the feature that each molecular ion forms a tight cluster of atomic ions that remain correlated in space and time as it penetrates the target). These techniques allow the direct determination of the geometrical structures of the individual molecular ions entering the target. These measurements have provided the first direct measurements of not only the spatial probability densities of the nuclei, but also their correlations in several small diatomic and polyatomic molecules. [3.7 FTE]

53. *Fast Ion-Beam/Laser Studies of Atomic Structure*
Young, L.
708-252-8878

This program is directed toward the detailed understanding of atomic structure through high-resolution laser and radio-frequency studies in accelerated beams. The atomic structure measurements provide precision tests of quantum electrodynamics (QED) and relativistic quantum mechanics in few-electron systems, as well as experimental guides to the ab initio understanding of hyperfine structure in multielectron systems. A collaborative effort with a group from Notre Dame has established a program in precision lifetime measurements using the fast-beam laser method at Argonne National Laboratory (ANL). In addition, the lifetime studies are being pursued with a second method, time-correlated single-photon counting using an ultrafast laser pulse for excitation. Collaborative efforts are continuing with the medium energy and weak interaction groups in the Argonne Physics Division to develop laser-driven polarized sources of hydrogen and techniques for trapping and polarizing gas-phase radioactive atoms. [2.5 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division **$800,000**

54. *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]

55. *Atomic Physics*
Prior, M.H.
510-486-7838

This program conducts challenging studies of the structure and interactions of atomic systems in order to 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 upon 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]

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 Heavy Ion Research Facility (HHIRF). Energy spectra of electrons released in collisions of C^{q+} ions ($q = 1,2,3$) with He have shown the charge state dependence of "saddle point" electron production. Energies of electrons ejected in single and double ionizing collisions of He yield information on electron–electron correlation in atomic collisions. 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. Creation of these states in a channel allows the study of electronic collisions with short-lived specific excited states. 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 the European Center for Nuclear Research (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 mounted 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. *EN Tandem Operations*
Dittner, P.F.
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]

58. *Collisions of Low-Energy Multiply Charged Ions*
Meyer, F.W.; Havener, C.C.
615-574-4705

Experimental studies of multicharged ion interactions with neutral atoms are carried out at the lowest attainable kinetic energies, where the electronic potential energy of the reactants becomes an appreciable fraction of the available interaction energy and inelastic collision cross sections depend strongly on the potential-energy curves of the interacting system. Quantitative study of such processes yields important information about quasi-molecular structure and collision dynamics. Emphasis is currently on merged-beam measurements of absolute electron-capture cross sections and direct comparison of results with developing theoretical models at energies in the range from 0.1 to 1000 eV/amu, where the process is poorly characterized. Recent merged-beam results for electron capture by multicharged ions from excited hydrogen atoms are providing further insight into the dynamics of the electron-capture process. Solid surfaces also provide a convenient reservoir of electrons for the study of atomic interactions, and exploratory experimental studies of the neutralization of multiply charged ions in grazing ion-surface interactions are in progress. The current emphasis is on characterizing the energy and angular distributions of ejected electrons in order to better understand neutralization mechanisms. [0.9 FTE]

59. *Theoretical Atomic Physics at Oak Ridge National Laboratory (ORNL)*
Strayer, M.
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 volts 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 Schrödinger 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]

Sandia National Laboratories, Albuquerque
Albuquerque, NM 87185

Department of Plasma Processing Science — *$130,000*

60. *Atomic Processes in Reactive Plasmas*
Greenberg, K.E.; Riley, M.E.
505-844-1243

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, helium discharges. Microwave interferometry and atomic absorption spectroscopy are used to measure spatially resolved electron and helium metastable densities. Measurements of Stark splitting of the helium 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 plasma physics numerical simulations are based on hybrid fluid-Boltzmann codes. The simulations are as ab initio as possible. In particular, the model of He has been carefully chosen to include sufficient levels and transitions as well as surface scattering of ions, electrons, and metastables. All cross sections are taken from published values in the literature. Combined, the results of the experimental and theoretical studies provide insight into the electron and heavy particle kinetics in the plasma. [1.0 FTE]

Chemical Energy

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program $1,189,000

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

A major goal of this project is to understand how organosulfur compounds in petroleum feedstocks are desulfurized upon reaction with hydrogen gas over heterogeneous transition metal catalysts. This large-scale hydrodesulfurization (HDS) process involves initial adsorption of the organosulfur compounds at a metal site on the catalyst surface, followed by reactions that result in cleavage of the carbon–sulfur bonds to give H_2S and hydrocarbons. Since thiophenes are the most difficult compounds to desulfurize, current efforts focus on studies of thiophene binding and reactions that might occur on catalyst active sites. It has been established that thiophene is able to coordinate to metal centers in a remarkable number of ways: (1) via the sulfur, (2) via two or four carbon atoms, or (3) via all five atoms of the ring. Each mode of coordination activates the thiophene to react in different ways. Coordination via either the four carbons or the entire thiophene ring leads upon reaction with hydrogen sources to the cleavage of both carbon–sulfur bonds and the complete desulfurization of thiophene. Two fundamentally different mechanisms for the HDS of thiophene have been proposed based on these studies. Catalytic reactor investigations are being conducted in order to determine which mechanism is actually involved. [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 synthetic fuels, sulfur radicals, and the selective oxidation of organic compounds. The generation of sulfur radicals can be accomplished by the use of laser flash photolysis to generate an alkyl radical from the photohomolysis of an alkyl metal. Following that, the alkyl radical abstracts the hydrogen from an alkane thiol (RSH) to generate the desired RS·. These sulfur radicals react with coordination compounds and organometallics. The kinetics and mechanisms of many such reactions are under investigation. Of particular interest is how the sulfur and metal center interact. This is important to know for coal and petroleum, where sulfur compounds abound. A second area concerns metal radicals. These are 17e organometallic species that can be extremely reactive. Methods to generate them, and then to study their reactions on microsecond time scales, are being developed. These reactions will be developed from the point of view of their being isolobal with the 7e alkyl radicals. In the area of selective oxidations, the use of organometallic metal oxides as catalysts is being explored. One such an example is methyltrioxorhenium (MTO, CH_3ReO_3). Even in aqueous solutions, it is an efficient catalyst for the peroxidation of metal thiolates and thiols, and for a number of interesting organic oxidations. The development of aqueous-based catalysts is important because of environmental restrictions. [4.3 FTE]

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

The main objective of this work is to elucidate fundamental molecular processes occurring on the surface of the small metal particles in supported catalysts and to correlate those molecular processes with surface properties such as composition, morphology, and electronic states. Of special interest is the influence of poisons, promoters, added metals, or other species that can perturb surface properties and subsequently alter catalytic performance. Three topics included in this work are (1) studies of hydrogen chemisorption on various supported metal catalytic systems to probe surface states and to characterize the catalysts; (2) detailed investigations of the adsorption and reaction of small hydrocarbon molecules on highly dispersed metals using a number of techniques including those developed in this laboratory; and (3) use of model reaction kinetic studies to couple the information derived from (1) and (2) above with catalytic performance. This program utilizes a combination of solid-state NMR with various other catalytic experiments. This research naturally divides itself into two broad areas: (1) development of new solid-state NMR techniques/nuclear spin dynamics and (2) applications of these techniques to catalytic science. High-resolution NMR of ^1H, ^{13}C, ^{65}Cu, and the alkali metals as well as other nuclei have been important probes. [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 for 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 and chalcogenide halides 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. 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. *Solid State NMR Studies: Catalytic Chemistry and Materials*

Pruski, M.
515-294-6823

Transient techniques in nuclear magnetic resonance (NMR) of solids are used to probe the physics and chemistry of materials involved in heterogeneous catalysis, fossil fuels, and material science. Examples include (1) use of 2-D NMR and selective excitation NMR experiments to study in situ the dynamics of hydrogen and small hydrocarbon molecules on supported catalysts at various pressures and temperatures of up to 800 K; (2) studies of reactions of hydrocarbons on various supported metal catalysts (e.g., Ru/Sio_2, Cu–Ru/SiO_2, Pt/SiO_2, Ag/SiO_2) using high-resolution, solid-state NMR of ^{13}C (variable temperature MAS and CP/MAS, dipolar oscillation NMR); and (3) ^1H and ^{13}C NMR studies of chemical vapor deposited diamond thin films. Other projects include development of new research capabilities in solid-state NMR (e.g., fast spinning variable temperature magic angle spinning (MAS) probes for evacuated samples), a dynamic angle spinning probe to narrow central transition of quadrupolar nuclei, and application of new nuclear spin dynamics to the studies of surfaces. [1.9 FTE]

66. *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 chemicals 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]

67. *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. A flow nuclear magnetic resonance (NMR) technique has been developed that allowed the ^1H NMR spectra of several fundamentally important reactive molecules, such as *ortho*-xylylene and benzocyclobutadiene, to be obtained for the first time. The work with reactive molecules has resulted in novel and effective ways of producing diradicals, and the reactions of these exceptionally reactive transient intermediates are under study. In addition to studies involving model compounds, some studies involve the pyrolysis of coal itself with the objective of identifying the types of reactive molecules produced in the pyrolysis of coal. [2.0 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemical Technology Division $662,000

68. *Fluid Catalysis*

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

This program uses an array of in situ kinetic and spectroscopic techniques to explore catalytic reaction chemistry at the high pressures and temperatures that are frequently used in industrial processes. In high-pressure nuclear magnetic resonance (NMR) studies of oxo process related chemistry in supercritical fluids, pronounced synergistic effects in mixed-metal catalyst systems that seem to stem from metal-centered radical chemistry have recently been uncovered. The resultant rate increases may ultimately allow use of lower pressures in catalytic hydroformylation. In other research aimed at the selective functionalization of hydrocarbons, a soluble rhodium phthalocyanine complex that activates methane in solution was synthesized and methods of increasing the new catalyst's reactivity are being explored. One approach currently pursued involves combined use of molecular mechanics calculations and experiment to explore structural (and thereby, reactivity) changes that occur in the macrocyclic catalyst when various substituent groups are incorporated. Also investigated are C–H bond activation processes that might lead to catalytic routes for the polymerization of small organometallic precursor molecules to yield preceramic polymers. Organometallic polymers of this type are used in the production of shaped ceramic objects. An electrophilic catalyst for the oligomerization of trimethylaluminum has been identified and efforts are under way to extend this approach to the polymerization of trimethylborane. In a related activity, a new NMR tomographic technique that allows chemical shift measurements while resolving distances on the micron scale has been devised. The new method utilizes the magnetic field gradient present in a toroid cavity resonator and is anticipated to have a wide range of applications in the synthesis and characterization of advanced materials. [4.4 FTE]

Chemistry Division $2,117,000

69. *Premium Coal Sample Program*

Vorres, K.S.
708-252-7374

Eight U.S. coals have been collected, processed, and packaged to preserve the original properties of the pristine coals as much as possible. Over 721 orders have been filled with more than 19,000 ampoules. Inventories of the two most requested samples in ampoules are projected to meet the demand for another 15–20 years at the current rate of shipment, and the reserves in carboys will continue to meet the demand for at least five more decades after repackaging in ampoules. The gas atmosphere is monitored to establish sample stability. Trends in evolution of carbon dioxide for younger coals and methane in higher rank coals have been noted with some interesting exceptions. Microbial growth has been observed from cultures of several of the younger coals. Over 413 scientific papers have been published on work done on these samples. Periodic newsletters keep users up to date on the latest references. The users handbook is being updated with additional analytical information and references as well as a literature summary. [0.5 FTE]

70. *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 $472,000

71. *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. The prime concern of this program is to increase that store of knowledge through the determination of the thermodynamic, kinetic, and structural parameters. A particular goal is to relate all pertinent data and hypotheses in order to develop a predictive capability regarding the behavior of a given system. This capability permits the synthesis of compounds having optimum properties for particular applications. Current topics of interest are reaction kinetics of the formation and decomposition of hydride phases, the preparation and characterization of a new class of hydrogen bronzes prepared from complex oxides, the catalytic properties of metal hydrides and electrochemical characterization of metal–hydrogen systems, and preparation of improved metal hydride electrodes. The major experimental tools and/or techniques are equilibrium pressure–temperature–composition measurements, X-ray diffraction, electrochemical measurements, Fourier transform- infrared (FT-IR) spectrometer measurements, and the use of high-pressure apparatus to study the kinetic behavior of metal hydride suspensions. [2.9 FTE]

Chemistry Department $1,895,000

72. *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. Neutron diffraction studies at the HFBR provide uniquely accurate structural data for these compounds which can then be correlated with their chemical reactivity. The reactivity studies are designed to elucidate the factors that determine the rates and mechanisms of M–H bond cleavage and their concurrent reactions with unsaturated organic substrates. The high selectivity of homogeneous catalysts is also being exploited to develop novel aspects of 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 gas clathrate hydrates. These studies are providing a foundation for understanding the special characteristics of these materials. [14.2 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division **$1,091,000**

73. *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]

74. *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]

75. *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]

76. *Potentially Catalytic and Conducting Polyorganometallics*
Vollhardt, K.P.C.
510-642-0286

Soluble organotransition-metal clusters have 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. This project constitutes an interdisciplinary approach to the designed construction of polymetallic arrays, anchored rigidly on novel π ligands that enforce hitherto unprecedented metallic topologies. Recent advances include (1) the total synthesis of the hexabutadiynyl nucleus, a remarkable potential ligand containing 54 conjugated π electrons; (2) the total synthesis of angular [4]- and [5]-phenylene, novel π systems in which benzene and cyclobutadiene nuclei are fused in an alternating fashion; (3) the unprecedented constructions of multiple metalylcyclopentadienylated cyclopentadienes giving rise to new transition-metal-cluster topologies; and (4) the observation of the first electron-transfer chain catalysis of a ligand-induced intramolecular electron migration in heterodinuclear [WFe(fulvalene)$(CO)_5$]. [2.6 FTE]

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

Isotope and Nuclear Chemistry Division $388,000

77. *Transition Metal Mediated Reactions of SO_2, H_2, and Other Small Molecules*
Kubas, G.J.; Burns, C.J.
505-667-5846

The activation of environmentally/energy-related small molecules, particularly SO_2 and H_2, by transition metal complexes has been the main thrust of the program. Synthesis, structural characterization, and studies of the dynamics–thermodynamics of these systems will be the dominant theme. Of major fundamental importance is delineating the nature of coordination of H_2 and other sigma bonds to metals. Defining the range of H–H internuclear distances and attendant rotational–exchange dynamics, and rationalizing them in terms of chemical bonding is crucial. H_2 complexes will be probed by a variety of state-of-the-art structural and spectroscopic techniques, emphasizing neutron scattering methodology. Thermodynamic and kinetic measurements will be used to correlate the binding strengths of various weak ligands like H_2 to fragments such as $W(CO)_3(PR_3)_2$. Modification of the latter is planned to promote binding of even weaker ligands such as hydrocarbons. A new direction has been initiated relevant to catalysis, that of design of new types of chiral ligands for asymmetric synthesis–hydrogenation. Activation of SO_2 can be disproportionated on metal complexes, transferring its oxygens to other SO_2 molecules to form S, SO_3, S_2O_3, and S_2O_4 fragments. The mechanisms for the various conversions are not well understood, and determination of the systematics and scope of these reactions by expanding to new arenas is under way. Unique SO_2 reactivity with actinide complexes has recently been found (e.g., reaction of $U(OR)_3$ with SO_2 to form the sulfide $[U(OR)_3]_2S$), as the only metal-containing species, and these systems and related metal–sulfur chemistry will be examined further. [1.4 FTE]

National Renewable Energy Laboratory
Golden, CO 80401

Basic Sciences Division $408,000

78. *Basic Research in Synthesis and Catalysis*
DuBois, D.L.; Curtis, C.J.
303-231-7371

The goal of this project is the development of new catalysts for electrochemical reduction of carbon dioxide and carbon monoxide. Previous research on this project has resulted in a new class of carbon dioxide reduction catalysts and the demonstration of three important stoichiometric steps in a proposed electrochemical CO reduction cycle. The carbon dioxide reduction catalysts exhibit current efficiencies greater than 90% for CO production with relatively high catalytic rates and low overpotentials. Current research is focusing on structure–activity relationships to improve catalyst stability and obtain even higher catalytic rates. The conversion of CO to a hydroxymethyl ligand using an electrochemically generated hydride complex has also been demonstrated. This conversion requires three stoichiometric steps, but it is not catalytic. Current studies are attempting to clarify the properties required of both metal hydride and metal carbonyl complexes for catalytic CO reduction. [2.6 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemical Technology Division $551,000

79. *Kinetics of Enzyme-Catalyzed Processes*
Greenbaum, E.; Woodward, J.
615-574-6835

New photoreactions in which a series of structurally and thermodynamically homologous molecular ionic probes communicate with the reducing end of Photosystem I have been discovered. These reactions are based on the in situ photoprecipitation of platinum, osmium, or ruthenium. Significant differences have been observed with each of the probes. A key goal of this work is to understand these differences, especially the way in which specific probes interact with emergent electrons from Photosystem I. For example, not only can $[PtCl_6]^{-2}$ accept electrons from Photosystem I, it was reduced all the way to zero valent platinum. In contrast, $[PtCl_4]^{-2}$ did not accept electrons from Photosystem I at all. The intriguing aspect of this observation is that $[PtCl_6]^{-2}$ formally passes through the $[PtCl_4]^{-2}$ on its way to Pt↓. Also, in each case the overall energetics are highly favorable for reduction to metal. $[IrCl_6]^{-2}$ readily accepts one electron from Photosystem I to form $[IrCl_6]^{-3}$; however, it does not accept subsequent electrons in spite of a highly favorable oxidation potential, +0.77 V. Studies have continued on understanding structure–function relationships in cellulase enzyme components: (1) a simple two-step procedure has been developed for the rapid purification of the catalytic domains of the major cellulase enzymes cellobiohydrolases (CBH) I and II; (2) molecular models have been developed for cellulose I and II, which will aid understanding of the mechanisms involved in enzymatic cellulose hydrolysis; and (3) scanning electron microscopy revealed that CBH I "smooths" the surface of cotton cellulose fibers. Catalytically inactivated CBH I has no effect on cellulose morphology despite its ability to bind. The cellulose-binding domain of CBH I may not function to disrupt the surface of cellulose fibers. [4.0 FTE]

Chemistry Division $2,810,000

80. *Organic Chemistry and the Chemistry of Fossil Fuels*
Buchanan, A.C.; Britt, P.F.; Hagaman, E.W.
615-576-2168

The objective of this program is to conduct fundamental research that advances understanding of the organic chemical structure and reactivity of coal. Reaction mechanisms that underpin thermal and catalyzed reactions of coal are explored through the use of model compounds that represent organic structural features present in the coal macromolecule. Silica-immobilized compounds are being employed to study the impact of restricted mass transport on free-radical reaction pathways. Current investigations focus on retrogressive reaction pathways for silica-immobilized diphenylalkanes and phenethyl phenyl ethers, which are surrogates for aliphatic and ether bridges prevalent in low-rank coals and lignites. Retrogressive reactions are often promoted by restricted diffusion, and this behavior has been found to be exacerbated by cross-linking. The role of solid-state interactions in catalysis of coal conversion is under investigation with silica-immobilized model compounds employed as probes. Current studies focus on solid-state, acid-cracking reactions with 15-nm dispersed aluminosilicate catalysts, and hydrocracking reactions applicable to coal hydropyrolysis employing a dispersed, sulfided molybdenum catalyst. Solid-state nuclear magnetic resonance (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 exploit the ^{13}C-^{19}F dipolar interaction in ^{19}F-labeled organic molecules, polymers, and coals to ellict localized structural information. Fluorination chemistry is being investigated with current emphasis on oxygen replacement chemistry (e.g., alcohols into alkyl fluorides) in low-rank coals using diethylaminosulfur trifluoride and sulfur tetrafluoride. Information derived from these investigations will contribute to the base of scientific knowledge necessary for the development of novel concepts for the conversion of coal to chemicals or fuels in an environmentally acceptable manner. [5.1 FTE]

81. 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 purpose of this program is the experimental study of aqueous chemistry of broad classes of solutes at high temperatures and pressures to establish basic principles governing chemical equilibria and thermodynamic properties of electrolytes. Both the advancement of experimental methods and new models for representation and prediction of behavior over wide extremes of temperature and pressure are important parts of the program. A number of complementary techniques are used up to and beyond the critical temperature of water and its solutions. Current research uses flow calorimetry, densimetry, isopiestic apparatus, electrochemical cells, electrical conductance apparatus, vapor–liquid partitioning cells, and Raman spectroscopy. Chemical equilibria under study are ionization–ion association, metal complexation, metal ion hydrolysis, solubilities, volatilities, and oxidation–reduction reactions. Reaction thermodynamic quantities and excess properties of electrolytes are of interest. New results are bridging the troublesome transition from strong to weak electrolyte behavior, and reaction behavior of new classes of ions and species. Models are being developed for describing variations of both standard-state and excess thermodynamics quantities over wide ranges to temperature and pressure. Results impact strongly the communities in basic solution chemistry and hydrothermal geochemistry, steam generator technology, geothermal technology, environmental chemistry, and nuclear and hazardous waste disposal. [3.2 FTE]

82. Heterogeneous Catalysis Related to Energy Systems

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

A comprehensive program has been developed to examine the structure and reactivity of clean and modified metal surfaces. Analysis of low-energy alkali ion scattering has determined the first and second layer composition and structure of clean and partially oxidized $Mo_{.75}Re_{.25}$ surfaces, an advance that should allow better theoretical descriptions of surface segregation and reconstruction. In addition, ion scattering has recently revealed substrate reconstructions in S/Ni(111) and S/W(100). An increasing focus is to utilize the tunability and intensity of synchrotron radiation to examine both substrate and adsorbate structures. Sulfur core level photoemission indicates that methylthiolate occupies both high and low coordination sites on W(100) surfaces, and the adsorption states exhibit quite different reactivities. Chemical shifts in the W 4f shallow core level photoemmision in the presence of adsorbates including Ni, S, O, and C have been observed and related to substrate structure. Detailed reaction mechanisms have been determined for both aryl and alkyl thiols on Ni(110) surfaces using a combination of techniques that probe both gas-phase and surface species. The control of selectivity by preadsorbed hydrogen and oxygen in ethanethiol reactions has been explored. The preferred reaction pathways in mercaptoethanol are characterized by both thiolate and ethoxide formation. [3.5 FTE]

83. Photolytic Transformations of Hazardous Organics in Multiphase Media

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

This research program constitutes a fundamental investigation of the photochemistry of aromatic hydrocarbons (ArHs) and polynuclear aromatic hydrocarbons (PAHs) both in heterogeneous and aqueous media by product analysis and in situ spectroscopic techniques. The goal of the research is to achieve an enhanced understanding of photochemical processes occurring at industrially and environmentally important interfaces and in aqueous solutions. Work in this laboratory has previously demonstrated that highly polar, nonsemiconducting surfaces can exert large effects in controlling the rates and mechanisms of photoreactions at solid and air interfaces through stabilization of highly polar intermediates such as superoxide and cation radicals. Current research focuses on the photoreactions of PAHs at SiO_2–air interfaces. The photochemistry of ArHs and PAHs in aqueous media, though of notable environmental concern, has not been well studied. Initial studies in this laboratory on the photochemistry of anthracene in water revealed the formation of a novel product that was heretofore unreported. Current investigations center on more highly water soluble PAHs. Among the benefits to be derived from this research is a better understanding of those factors that control the environmental fate and residence times of anthropogenic materials (e.g., PAHs) that are generated through the consumption of fossil fuels. [2.2 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $685,000

84. Free-Radical Chemistry of Coal
Franz, J.A.; Alnajjar, M.S.; Autrey, S.T.; Linehan, J.C.
509-375-2967

The project seeks to develop a predictive model for the evolution of structure and the kinetic behavior of functional groups in coal based on fundamental properties of the appropriate transient intermediates during the thermal or catalyzed degradation of coal under liquefaction conditions. Efforts include determination of the thermochemistry of carbon-centered free radicals substituted with aromatic and heteroaromatic ring systems, ketone, and heteroatom centers. The effects on homolytic C–C and C–H bond strengths of benzylic hydrogen of π-complexation of organometallic groups are under investigation. Hydrogen transfer pathways under coal liquefaction conditions are being investigated using kinetic modeling, semiempirical and ab initio theoretical approaches, high-temperature kinetic studies, and kinetic electron spin resonance methods. The potential surfaces of rearrangements of sulfur-containing free radicals are being investigated using kinetic laserflash spectroscopy and relative rate kinetic methods, and by post-SCF ab initio theoretical calculations. The structure of coal and organic oxygen and sulfur functional groups is being investigated using solid state nuclear magnetic resonance (NMR) methods. [3.7 FTE]

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program $1,145,000

85. 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]

86. Analytical Spectroscopy
Houk, R.S.; D'Silva, A.P.
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) and inert gas afterglows. A comprehensive atlas of spectral lines emitted from the ICP by all common elements is being compiled. 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 directions in ion trapping and time-of-flight mass spectrometry are also investigated. [4.5 FTE]

87. Chemical Analysis at Liquid–Solid Interfaces
Porter, M.D.
515-294-6433

This project examines new approaches for the design, construction, and characterization of monolayer films at liquid–solid interfaces. Efforts focus on (1) developing atomic-scale descriptions of the two-dimensional arrangement of spontaneously adsorbed monolayer films formed from alkanethiols at gold and silver surfaces, (2) probing solvent–monolayer interactions of such monolayers with aqueous and various nonaqueous solvents with in situ Fourier transform infrared (FTIR) reflection spectroscopy, and (3) examining the fabrication for molecular recognition monolayers with organosulfur derivatized cyclodextrin monolayers. The atomic-scale arrangements are probed by both scanning tunneling and atomic force microscopy. The molecular level descriptions are derived primarily from IR reflection and Raman spectroscopies, optical ellipsometry, electrochemistry, and contact angle studies that relate the composition and molecular arrangement (spatial orientation and packing density) of the organic surface structures with the crystallinity and roughness of the substrate. 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-derivitized cyclodextrin monolayers. [2.2 FTE]

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

The central 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 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) spatial and temporal spectroscopic probes to study laser vaporization and laser desorption processes, so that quantitation can become more reliable; (2) electro-rotation and magneto-rotation techniques for selective measurements in solutions; (3) detectors for microcolumn separation schemes that are more sensitive and more reliable; and (4) laser-initiated gas-phase reactions relevant to vapor deposition and etching schemes for material processing. [4.7 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $1,071,000

89. *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 separations science and (2) to elucidate the basic chemistry involved in utilizing these new reagents. The major subdivisions of the program are (1) the study of extractant–diluent interactions with the goal of achieving major alterations in the physical properties of extractant systems; (2) the study of isomer effects on molecular recognition by macrocyclic polyethers with the goal of understanding how conformational changes in the macrocyclic ring affect metal complex stability and macrocycle selectivity; (3) the design, synthesis, and characterization of new classes of macrocylic 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 $419,000

90. *Structure and Function in Electrochemistry*

Adzic, R.
516-282-4480

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 will be the emphasis on in situ determination of the structure of an electrode surface with atomic resolution, during the course of an electrochemical reaction, as well as the identification of adsorbates, intermediates, and products of that reaction, with molecular specificity. X-ray scattering (utilizing the National Synchrotron Light Source), scanning tunneling microscopy (STM), atomic force microscopy, and (nonenhanced) Raman scattering will be the primary in situ probes. Specific studies will focus on (1) establishing the correlation between the structure of single crystal surfaces (with and without foreign metal adatoms) with the rate of electrocatalytic reactions by in situ determination of the surface and adatom structures, geometry of active sites, and identification of adsorbed intermediates during the reaction; (2) examining the reconstruction of electrode surfaces by studying the reconstruction of stepped surfaces of gold and platinum as a function of electrode potential and electrolyte composition; and (3) exploring the possibilities of designing new catalysts for methanol oxidation based on the platinum–metal oxide systems. In situ determination of the overlayer structures of Pb and Bi adatoms on Pt(111) and Pt(100) has been conducted by X-ray diffraction and STM. Atomic-level resolution STM data have been obtained with stepped surfaces of gold and low-index planes of silver. [1.5 FTE]

91. *Microparticle Analysis by Laser Spectroscopy*

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

The objective of this research program is to determine the fundamental properties that are essential in developing laser-based spectroscopic methods for microparticle analysis. Microparticles are present ubiquitously in nature, as well as in many energy-related processes. Because of the minute physical size of these particles, development of ultrasensitive techniques for in situ monitoring of the physical transformation and chemical reaction of these airborne particles is imperative. Laser Raman scattering is currently being investigated as a means for composition analysis of these particles. Quantitative measurements are performed to establish a database on Raman scattering cross sections for common ionic solids such as oxyanions. With an aim to elucidate the chemistry of ionic solution droplets, a unique single-particle suspension technique, combined with the laser Raman scattering probe, is used to levitate and analyze solution droplets of high supersaturation that cannot otherwise be obtained with bulk samples. Resonance Raman scattering is being investigated for sensitivity enhancement of inorganic species such as sulfates and nitrates. The principle of combining laser Raman scattering with mass spectrometric detection is also being developed. The extremely high sensitivity of mass spectrometry makes it particularly suited for ultrafine particles whose chemical characterization cannot be accomplished by any other methods. It is anticipated that the research will lead to increased sensitivity and better selectivity of spectroscopic methods for microparticle analysis. [1.5 FTE]

Idaho National Engineering Laboratory
Idaho Falls, ID 83415

$315,000

92. Negative Ionization Mass Spectrometry
Delmore, J.E.; Appelhans, A.D.; Dahl, D.A.
208-526-2820

The development of techniques for elucidation of gas phase ion formation mechanisms from high-temperature solid-state inorganic matrices is the main emphasis of this program. Two new techniques being developed which are proving to be very useful in this regard are a tube ion source and an ion source imaging instrument. The tube ion source produces ions from large samples which are packed into a refractory metal tube and heated to an appropriate temperature, and the ions emitted from the material analyzed by mass spectrometry. Gases can be diffused through the material in the tube so that high-temperature reactions can be observed. The tube can be transferred into the imaging instrument and the regions in the source which produce ions observed with good depth of focus and resolution of up to three microns. Microstructures on the surface are then analyzed by SAM and SEM and correlated with the ion emitting regions identified by ion source imaging to gain better understandings of the chemical nature of the ion emitting regions. These techniques were recently being used to study a series of refractory oxides which emit intense beams of metal oxide anions at temperatures in the range of 800 to 1100 °C, and understanding of the processes controlling gas phase ion formation were developed. Ion emitting glasses are currently being studied. To develop understanding of these processes it is necessary to model the motion of ions in electric/magnetic fields accurately. In order to meet this need new 3-D mathematical algorithms are under development for computer modeling of ion optic systems. [2.0 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Energy and Environment Division **$214,000**

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

A new powerful technique for chemical separations and analysis is the use of a repetitively pulsed laser material interaction for direct solid sampling. However, the explosive laser material interaction is not fundamentally or experimentally defined for general application. This research program employs several analytical probe techniques, including atomic emission spectroscopy (AES), acoustic sensing, and optical probe laser beam deflection, to resolve the mechanisms of this interaction, and to develop its capabilities for DOE chemical separations and analysis applications. Injecting laser sampled species into an inductively coupled plasma allows simultaneously study of emission intensity due to changes in the laser material interaction and determining of parameters that influence this technique for chemical analysis. The work emphasizes the use of a repetitive pulsed laser material interaction for producing steady-state emission intensity in the inductively coupled plasma. For chemical analysis, steady-state laser sampling can provide improved accuracy and precision (approximately 3%) compared to transient sampling (approximately 50%). Piezoelectric sensors (attached directly to the solid material) are used to study the character and propagation of acoustic waves induced in the material by the incident pulsed radiation. Changes in the acoustic response as a function of laser power and material properties are studied to indicate the existence and time dependence for mechanisms of heating, melting, vaporization, and ablation. Optical probe beam deflection is employed to monitor the region adjacent to the solid surface illuminated by the laser beam to determine heating and cooling, the onset of material removal, and the formation of a laser initiated surface plasma. Fundamental mechanisms describing the explosive laser material interaction will be described by drawing correlations between these acoustic, deflection, and atomic emission data. The laser material interaction has numerous applications to other areas of DOE, including materials, environmental, and health. Fundamental knowledge gained through this work can benefit these applications. [1.7 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Analytical Chemistry Division **$1,962,000**

94. Advanced Spectroscopic Methods for Chemical Analysis
Hulett, L.D., Jr.; Dale, J.M.; Xu, J.
615-574-8955

This work involves the development of new analytical methodology, using sources of spectroscopic particles not commonly available. Unique facilities at Oak Ridge National Laboratory (ORNL), such as the Oak Ridge Electron Linear Accelerator (ORELA) slow positron source, are exploited. Monoenergetic ("slow") positrons are being used to study ionization processes. It has been found that slow positrons effect ionization at lower energy thresholds, and by totally different mechanisms, than those of electrons. This year, a theoretical study of positron induced ionization will complement the experimental work. An ultrahigh vacuum system has been aquired to enable the application of slow positron spectroscopy to surface analysis problems. Positron stimulated desorption and positron stimulated Auger electron emission will be investigated. Positron lifetime spectroscopy, using radioisotope sources, is beinq used to study neutron damage to detector materials that will be used in the Superconducting Super Collider (SSC). The ORELA slow positron source will be used to inject monoenergetic positrons to controlled depths in surfaces. A positron lifetime spectrometer, specially designed for attachment to the ORELA slow positron source, is being built by AT & T Bell Laboratories. They will work with ORNL in lifetime measurements of positrons injected into semiconductor materials and devices. Other collaborators in this work include workers at Vanderbilt University; The University of Texas at Arlington; The University of

Georgia; The University of Tennessee; and State University of New York, Fredonia. [2.8 FTE]

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

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

The purpose of this research program is to develop new techniques for chemical analysis to meet future needs in biotechnology, environmental science, and materials research and processing. Emphasis is on the use of lasers to extend the sensitivity and specificity of the measurements. Ultrasensitive fluorescence detection in microdroplets can now be performed at the single molecule level. Advantages that accrue from counting the analyte molecules rather than integrated measurements on the total volume are being explored. Cavity quantum electrodynamic effects have been observed in the fluorescence lifetime of molecules in microdroplets that may further reduce the minimum detectable concentration of molecules in solution. The use of labeled antibodies to extend these techniques to nonfluorescent molecules is being studied as well. Nonlinear optics effects with tunable pulsed lasers are being used to probe molecular species in gas–solid interfaces. Techniques are being developed to monitor the bulk gas, boundary layer, and surface concentrations of various reagents and reaction products important in chemical vapor deposition. The use of inexpensive single-frequency diode lasers for high-resolution resonance ionization mass spectrometry is also being explored. [1.7 FTE]

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

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

The objective of this work is to expand the frontiers of inorganic mass spectrometry both with regard to instrumentation and sample preparation methodology. Emphasis is currently focused on glow discharge mass spectrometry, where recent advances include development of an rf-powered source that allows ready analysis of nonconducting samples. The goal is to develop methodology to allow application to areas previously closed to this technique. Included among these is isotope ratio measurements, small (1 mg) sample analysis, and direct analysis of samples with no chemical preparation; an example of this last is to analyze rock directly. The combination of a glow discharge source mated to an ion trap mass spectrometer is being investigated. Methodology is being developed to analyze isotopically a wide variety of elements. Isotope dilution is extensively used to obtain quantitative results. [2.3 FTE]

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

Todd, P.J.; Rosseel, T.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 then circumventing it by instrumental or chemical development. For example, secondary ions from lighter rare-earth oxides interfere with analysis of heavier rare-earth ions; mass spectra of doubly charged ions from rare-earth sample show a virtual absence of oxide ions. By basing analysis on doubly charged secondary ions, oxide interferences are thus removed. As another example, 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 to other instrumental configurations, 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, biomedicine, and the Human Genome project. [2.2 FTE]

Chemical Technology Division $1,344,000

98. *Chemical and Physical Principles in Multiphase Separations*

Byers, C.H.; Basaran, O.A.
615-574-4653

Electromagnetic fields can enhance drastically the rates of momentum, heat, and mass transport in fluids. 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 separation processes. The primary focus of the program is to develop a fundamental understanding of the effects of electric fields on liquid drops, with the ultimate goal of using that understanding in devising novel means to dramatically improve transport rates in liquid–liquid systems. Thus, this part of the program addresses such issues as (1) shapes and stability of drops, (2) oscillations of free and supported drops, (3) dynamics of drop formation, (4) drop breakup, and (5) interaction and coalescence of multiple drops. A second thrust entails an exploratory study of the use of electric fields in enhancing liquid–vapor operations. This part of the program addresses such key issues as (1) effects of external electric fields on bubbles, (2) formation of bubbles in an ambient flow field, and (3) free surface flows of pseudo single-phase and multiphase fluids over complicated solid boundaries. Other externally applied force fields (e.g., because of 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. A third focus is examining the use of high-intensity, high-gradient (HIHG) magnetic fields in separations processes. A primary goal of this final thrust is the study of the interactions of charged macromolecular entities in viscous media that are under the influence of HIHG magnetic fields. In addition to multiphase separations, the above three primary thrusts have ramifications in diverse areas of science and technology that range from cloud physics to ferrohydrodynamics to atomization. [2.8 FTE]

99. *Interactions of Solutes, Solvents, and Surfaces: Adsorption and Supercritical Extraction*

Cochran, H.D.; Byers, C.H.
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 other technologies as well. Monte Carlo techniques have been used to study systems of long-chain molecules with supercritical solvents, observing for the first time by molecular simulation (1) varying chain conformation near the solvent's critical point, (2) swelling of a polymer melt by a supercritical solvent, and (3) existence of a lower critical solution point. Neutron scattering experiments have been performed with supercritical fluids using the new cell and cryostat on the small-angle neutron scattering (SANS) instrument at the High Flux Isotope Reactor (HFIR) and the glass and liquid diffractometer (GLAD) instrument at the Intense Pulse Neutron Source (IPNS). By solving the inhomogeneous Ornstein–Zernike equation for solutions in supercritical solvents at equilibrium with a surface, competitive effects have been observed for the first time between adsorption at the surface and solubility in a supercritical solvent. A new generalized quartic equation of state has been demonstrated that offers the advantages of cubic equations of state with improved accuracy because of improved representation of the repulsive contribution in a quartic form. Collateral programs of a more applied nature interact symbiotically with this basic program. [1.0 FTE]

100. *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]

Chemistry Division $939,000

101. *Chemical and Structural Principles in Solvent Extraction*

Moyer, B.A.; Sachleben, R.A.; Burns, J.H.
615-574-6718

Crown ethers, ionizable lariat ethers, and related multidentate compounds are being synthesized and studied to gain insights leading to the selective recognition and separation of metal cations. Principles of thermodynamics and structure pertaining to energy-related separation techniques, especially solvent extraction and ion exchange, receive primary consideration. An important thrust aims at combining neutral and ionizable functionalities in one extractant molecule 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 organophilic sulfonic and carboxylic acid extractants to achieve novel systems for selective separation of alkali, alkaline-earth, and transition metals. Questions being addressed through the synthesis and testing of new substituted crown-ether extractants pertain to the influence of preorganization, metal–ligand complementarity, lipophilicity, inductive effects, and steric factors on extraction selectivity and behavior. Structural aspects are probed extensively by the methods of X-ray structure determination of crystalline model compounds, molecular mechanics, and spectroscopy (e.g., Fourier transform infrared (FTIR), nuclear magnetic resonance (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. [3.9 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $905,000

102. *Fundamentals of Phase Partitioning in Supercritical Fluids*

Fulton, J.L.; Smith, R.D.
509-376-7011

The goal of this project is to obtain fundamental information on kinetic, thermodynamic, and molecular-level structural phenomena in supercritical fluid solutions. Understanding these phenomena will lead to new supercritical fluid separation and reaction processes, and will suggest new approaches for improving existing processes. The scope of these studies spans the range from (1) simple bimolecular solute/solvent interactions to (2) more complex multimolecular clustering and aggregation phenomena, as well as (3) fluid/liquid interfacial phenomena. In the most general sense, this project is exploring supercritical fluid phenomena in order to bridge the gap between the understanding of the gas and liquid states. The approach entails use of spectroscopic techniques such as FT-IR, Raman, and NMR spectroscopy, and small angle X-ray scattering (SAXS). Concurrent are efforts to model the fluid structure (using statistical mechanics and molecular dynamics) and to predict intermolecular and interaggregate attractive potentials (based upon ab initio calculations). A main area of study involves the formation of organized molecular assemblies (e.g., micelles and microemulsions) in supercritical solutions, a potential basis for new separation and reaction processes. Small-angle X-ray- and neutron-scattering are being used to explore the structure of aggregates and the nature of the inter-aggregate attractive interactions in fluids, providing new insights into the forces dictating the phase behavior of these systems. 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]

103. Sources in Analytical Spectrometry

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

This research develops a basic understanding of sources for analytical spectroscopy, and elucidates the fundamental physics and chemistry of new and novel source concepts for mass spectrometry. The work develops information fundamental to direct trace analysis of solid samples. X-ray absorption spectroscopy is used to elucidate analyte-matrix and analyte-substrate interactions. Of particular interest is speciation of trace elements in and on matrices of environmental importance, and the chemical processes that lead to atomization or ionization. The effort includes investigations of work functions of composite surfaces and kinetics of vaporization, and develops understanding of the basic physics and chemistry of new approaches to ionization sources for mass spectrometry. Two new sources are under investigation. The first involves a gentle, specific process for formation of negative molecular ions through electron capture to excited molecular electronic states. The second explores a broadly applicable mass spectrometry based on an electrothermal source that, without complexities introduced by plasmas, permits analysis of microliter samples. [2.5 FTE]

Materials and Chemical Sciences Department

104. Laser-Based Analytical Techniques

Bushaw, B.A.
509-375-2699

Laser ablation methods have been offered as a panacea for remote sampling and analysis of complex solid samples; however, the actual potential of this method has not been realized in practical applications because of a number of problems. These include incomplete sample dissolution and fractionation, limited sensitivity, and poor reproducibility. Direct emission analysis of the plume created by the laser ablation process has appealing simplicity, but at laser intensities suitable for reproducible ablation, the intensity of emission is not sufficient for trace analysis. Attempts to optimize the ablation kinetics and subsequent plasma emission will involve double-pulse laser ablation plasma spark spectroscopy. The emphasis of this program will be directed toward fundamental studies of the laser ablation and secondary laser-induced plasma formation within the ablation plumes. Conventional and coherent laser spectroscopies will be used to analyze the plumes and plasmas in an effort to develop and validate accurate, reliable, and uncomplicated analytical techniques using simpler optical emission spectroscopy. More novel and sensitive laser interrogation methods and instrumentation will be developed naturally in the course of these investigations. [0.8 FTE]

Heavy Element Chemistry

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $1,797,000

105. Heavy Element Chemistry Research

Nash, K.L.; Morss, L.R.; Appelman, E.H.;
Beitz, J.V.; Soderholm, L.
708-252-3581

The actinides and lanthanides represent a unique laboratory for the investigation of the principles of chemical periodicity with their multiple oxidation states, consistent contraction of the trivalent radii across the series, high coordination numbers, distinctive UV-visible spectra, and valence electrons in f-orbitals. The objectives of this program are (1) to exploit the distinctive properties of the f-elements in the development of new reagents and procedures for their processing and use; (2) to compare and contrast the chemical and physical properties of compounds of lanthanides, actinides, and d-transition elements in solid, gas, and solution states; and (3) to understand the role of f-electrons in chemical bonding. Three related but separate program areas address various aspects of actinide–lanthanide chemistry: (1) Heavy element coordination chemistry uses the unique properties of the f-elements to ascertain through thermodynamic, kinetic, and spectroscopic studies the relationship between the structural characteristics of heavy element coordination complexes and their behavior in solutions. (2) Heavy element photophysics and photochemistry considers the chemical and structural consequences of excited state formation of f-element compounds, and the dynamics of relaxation modes in solids, solutions, and gases. (3) F-electron interactions seeks to develop a predictive understanding of the mechanism by which f-ions influence the electronic and cooperative properties of solids that characterize many lanthanide compounds, such as magnetic ordering and superconductivity. Throughout this program, an intimate interface between basic science and its application in solving problems of critical national importance is sought. [9.4 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $1,510,000

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 \$133,000

107. Chemistry of the Heaviest Elements
Hoffman, D.C.; Gregorich, K.E.
510-486-4474

The objectives of this project are (1) to investigate the chemical properties of the heaviest elements to determine the architecture of the periodic table of the elements at its furthest reaches and (2) to assess the influence of relativistic effects in these heaviest elements. The actinide series ends with Lr (element 103), and the change in chemical properties in going to the transactinide elements, Rf(104), Ha(105), and (106), is especially important. Relativistic effects have been predicted to become increasingly prominent for the higher-Z elements; possible observable effects include anomalous trends in ionic radii and stabilization of different oxidation states than are observed in the lighter homologs. These properties can be investigated for the elements from 102 through 106, even though only small numbers of short-lived atoms can be produced. This program includes determining or confirming the most stable oxidation state for each of these elements and exploring their complexes in aqueous solutions. Isothermal gas phase chromatography is used to compare volatilities of the halides of elements 104 and 105 with those of their lighter group 4 and 5 halides. Detailed comparisons of transactinide chemical properties with those of their lighter homologs show that the chemical properties of the transactinides cannot be reliably extrapolated from those of their lighter homologs. Attempts are also 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 \$281,000

108. Actinide Organometallic Chemistry
Burns, C.J.; Sattelberger, A.P.
505-665-1765

The purpose of these investigations is to promote an understanding of the preparation, properties, and reactivity of complexes of the early actinides in comparison with similar compounds of the lanthanides and d-transition metals. From these studies, information can be derived concerning the bonding in these complexes, and the role of the 5f orbitals in their stability and chemical reactivity. This understanding is used to derive insight into the application of new chemistry in the solution of modern technological problems in actinide processing, ceramic preparation, and environmental remediation. During the past year, substantial progress has been made in understanding the oxidation chemistry of both mixed-ring (Cp^*-COT) and homoleptic aryloxide uranium(III) complexes. Investigations have been initiated into the synthesis and reactivity of thorium benzyne complexes. These species have been found to undergo a wide variety of ligand activation reactions. Investigations of uranium organoimido chemistry have produced the complexes $(Me_5C_5)_2U(NPh)_2$ and $(Me_5C_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O)$, the first examples of a new class of molecules: organometallic complexes of uranium(VI). These high-valent complexes are supported by oxo and organoimido ligands, and are therefore isoelectronic with uranyl complexes. They are not isostructural, however, and possess an unprecedented nonlinear N=U=N(O) geometry. [0.6 FTE]

109. Actinide Chemistry in Near-Neutral Solutions
Clark, D.L.; Hobart, D.E.
505-667-4622

The project objective is to provide fundamental physicochemical knowledge pertinent to the behavior of plutonium and other actinides under environmental and physicochemical 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. Significant advances have been made using ^{13}C and ^{17}O nuclear magnetic resonance (NMR) as a speciation tool for study of hydration number, hydrolysis, and complexation of early actinides in near-neutral solution. The project is employing ^{17}O and ^{13}C NMR and single crystal X-ray diffraction to map out the stability fields of monomeric and polymeric actinyl carbonate complexes in near-neutral solution, and to study the kinetics of ligand exchange with carbonate ligands. Solution NMR provides a species-sensitive probe for these complicated and environmentally relevant systems. The study of EDTA and siderophore complexation of Pu(IV) has continued. EDTA is a typical example of common organic co-contaminants in mixed waste contaminated sites and siderophores may be present in groundwaters as a result of microbial biological activity. Researchers have mapped out the stability field of Pu(IV) EDTA employing UV-VIS-NIR spectroscopy as a function of pH and EDTA concentration at room temperature. A study in the synthesis and characterization of technologically important actinophiles based on calixarene ligands has been initiated. Calix[6]arene sulfonate and its substituted derivatives are thought to be potent complexants that are selective enough to extract uranyl ion from seawater. [0.5 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemistry Division $1,311,000

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. [7.0 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $170,000

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 $349,000

112. Turbulent Combustion

Talbot, L.; Cheng, R.K.
415-642-6780

This program involves experimental and numerical investigations of the coupling and interactions 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 of the fluid mechanical processes by investigating flames with simple geometry to facilitate direct comparison between experimental and numerical results. Laboratory flames give free access to interrogation by laser diagnostics and their flow configurations are amenable to numerical simulations. The approach is to study flames with moderate turbulence intensities. Under these conditions, chemical times are significantly shorter than the turbulence times so that the mean burning rate can be derived from the topology of the thin (< 1 mm) wrinkled flame. The current goal is to obtain a physical understanding of the effects of combustion heat release on turbulence, and to quantify the relationship between turbulence intensity and the burning rate. The measurements of turbulence statistics and flamelet topology in several flame configurations have been used to validate theoretical 1-D models by Bray and Libby and the results of direct numerical simulation by Ashurst. A 2-D vortex dynamics simulation of rodstabilized "v" flame that provides a direct comparison of the experimentally measured conditioned velocity statistics has also been developed. The next goal is to investigate flames with high turbulence intensity to provide a closer simulation of the combustion processes in practical systems. [2.2 FTE]

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

Theoretical Division $87,000

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. MC–MD calculations for equimolar, binary, and hardsphere mixtures having mass ratio 0.03 and diameter ratio 0.4 (similar to helium–xenon) have been completed (including rather precise corrections for large-system size and Green–Kubo time) for all but the highest fluid densities. Analytical expressions for the pressure and transport coefficients have been obtained and the results compared with extant theory. The pressure has been compared with both the viral series, for which the 2nd and 3rd viral coefficients are known exactly, and the Mansoori–Carnahan–Starling–Leland theory. The difference between the project values of the pressure and the latter theory are found to increase monotonely with density but reach only 0.4% in the worse case. The transport coefficients are compared with the Enskog theory and modest deviations are found, ranging up to 25% at the highest densities. In addition, a square-well, hard-sphere model for chemical reaction has been studied in the context of the Chapman–Jouguet theory of exothermic reactive fluid flow. Through equilibrium MC, molecular dynamics calculations for this reactive interaction potential, the equation of state and chemical equilibrium in the neighborhood of a detonation Hugoniot curve for this model have been studied. The Hugoniot curve is shown to have the concave upward shape in the p-V plane typical of exothermic materials. [0.5 FTE]

Sandia National Laboratories, Livermore
Livermore, CA 94551

Combustion Research Facility $426,000

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. Numerical simulation of unsteady reacting flow places an emphasis on flame–vortex interactions using the vortex dynamics method and/or direct numerical simulations of the Navier–Stokes equations. Analysis and simulation have shown that flame propagation in weak turbulence has a 4/3 power dependence on turbulence intensity. The previously known quadratic behavior is restricted to periodic flows. Flame propagation in strong turbulence exhibits a maximum speed that is related to the spatial structure of the turbulent eddys. Inclusion of multistep chemistry in curved diffusion flamelets has been initiated in order to compare with planar, strained flamelet results. The linear-eddy mixing model, unique in its representation of the distinct influences of convective stirring and molecular diffusion, has been used to interpret measurements of chemical reactions in spatially homogeneous turbulent flows. This work will contribute to the basic understanding of turbulent reacting flows and aid in interpreting experimental data. [1.7 FTE]

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Akron
Akron, OH 44325

Department of Chemistry

115. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion
Lim, E.C. **$105,000**
216-972-5297

The primary objective of the research program is to gain fundamental understanding of the factors governing the efficiency of charge transfer processes in molecular systems of relevance to photochemical energy conversion. Current emphasis is on the study of intramolecular charge separation and charge neutralization in bichromophoric systems of the general structure M-X-M, where two identical aromatic moieties (M) are joined by a single bridging group X(= CH_2, NH, O, SiH_2, and so forth). Novel biphotonic, as well as more conventional monophotonic, laser excitation schemes are used to create intramolecular charge transfer states in these species. The time- and energy-resolved spectra of these states are then probed by laser kinetic spectroscopy to identify the rate and mode of their decays. The photoisomerization of van der Waals complexes into the corresponding exciplexes are also being investigated in a supersonic free jet for the purpose of probing the factors that influence the efficiency of the conformational isomerization related to the excited-state charge transfer process.

University of Alabama
Tuscaloosa, AL 35487

Department of Chemistry

116. Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids
Kispert, L.D. **$90,000**
205-348-7134

The objectives of this research are to understand 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. Picosecond optical measurements of a highly polarizable polyene as a function of increasing solvent polarity showed a significant decrease in lifetime due to solvent reorientation which stabilized the polar excited state resulting in enhanced charge transfer character and in turm enhanced non-radiative decay. Simultaneous electrochemical and electron paramagnetic resonance (EPR) measurements indicate that upon oxidation of carotenoids with acceptor substituents, 96% carotenoid cation radicals are formed, while 99.7% dications are formed upon the oxidation of β-carotene, or carotenoids with donor substituents, suggesting a reason for the EPR observation of carotenoid radicals in some photosystems and not others. Semiempirical molecular orbital (RHF-INDO/SP) calculations of the canthaxanthin cation radical in solution are in excellent agreement with the electron nuclear double resonance (ENDOR) 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.

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Tempe, AZ 85287

Department of Chemistry

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

The project objective is the synthesis and study of complex four- and five-part molecular devices that mimic natural photosynthetic reaction centers. Results of these investigations will aid in the design of artificial solar energy harvesting systems, increase understanding of natural photosynthesis itself, and provide an entry into the developing field of molecular electronics. For example, a molecular pentad $C–P_{Zn}–P–Q–Q$ has recently been synthesized. It consists of a diporphyrin moiety ($P_{Zn}–P$) linked to a carotenoid polyene (C) and a diquinone species (Q–Q). Absorption of light by the molecule results in photoinitiated electron transfer to produce an initial charge-separated state $C–P_{Zn}–P^{\cdot +}–Q^{\cdot -}–Q$ with a quantum yield of 0.85. A series of subsequent electron-transfer steps leads to a final charge-separated state $C^{\cdot +}–P_{Zn}–P–Q–Q^{\cdot -}$ with an overall quantum yield of ~0.83. This species has a lifetime of 55 μs, and has stored within it about one-half of the energy of the absorbed photon. The knowledge gained from studies of the pentad and simpler molecules is being used to design a new generation of pentad and tetrad molecules in which the quantum yield, lifetime, and amount of stored energy will be further optimized. In addition, these molecular devices are being incorporated into monolayers and other thin films in order to investigate their photoelectrochemical properties.

Boston University
Boston, MA 02215

Department of Chemistry

118. Study of Intermediates from Transition Metal Excited-State Electron-Transfer Reactions

Hoffman, M.Z. **$105,000**
617-353-2494

The electron-transfer quenching of the excited states of transition metal coordination complexes results in their one-electron oxidation or reduction, and the corresponding reduction or oxidation of the quencher. The major objective of this research, which utilizes the techniques of time-resolved spectrofluorimetry, continuous and pulsed photolysis and radiolysis, and electrochemistry, is to gain an understanding of (1) the parameters that govern the efficiency of the formation of energy carriers from the quenching reaction, (2) the dependence of the kinetics and efficiencies of all the mechanistic steps of the overall reaction on temperature and the nature of the solution medium, and (3) the properties and reactivities of the reduced and oxidized species. During the past year, the following projects have been investigated: (1) the determination of the cage escape yields in the oxidative and reductive quenching of the excited states of Ru(II) and Cr(III) as a function of the energy gap between the redox products, the nature of the solution medium, and the temperature; (2) the measurement of the acid-base properties of the excited states of Ru(II)-tris-homo- and heteroleptic complexes that contain 2,2′-bipyridine, 2,2′-bipyrazine, and 2,2′-bipyrimidine; (3) the characterization of one-electron reduced complexes; and (4) the photosensitized initiation of polymerization and oxidation of phenol and its derivatives.

119. Photoinduced Electron Transfer in Ordered Polymers

Jones, G. **$105,000**
617-353-2498

Investigations involve systems capable of photochemical electron transfer between donor and acceptor groups that are bound to polymer or biopolymer (peptide) chains. Objectives of the research include observation of photoinduced electron transfer for groups that are held in proximity through covalent or electrostatic binding associated with polymer or peptide coils. Charge migration among groups on structures such as short peptides and along the axis of an α-helix is of special interest. The factors of medium, separation distance, and the nature of through-space and through-bond pathways for "long-range" electron transfer are under investigation. Systems that have been prepared include (1) di- and tripeptides with pyrene or xanthene dye chromophores attached at one terminus and with modification by addition of an electron donor at the remote terminal amino acid residue; (2) linked aryl systems that incorporate the acridinium ion moiety and various electron donor groups held at fixed distances and structurally enforced into twisted, but variable geometries; and (3) complexes of cationic dyes and polypeptide electrolytes such as glutamate. The latter complexes give rise to large optical activities induced in visible absorption bands that are a signature of long-range order (large helical arrays consisting of dye chromophore stacks). Methods that are employed in these studies include picosecond and nanosecond resolution of phototransients, flourescence probes of polymer (peptide) microdomains, circular dichroism, and molecular modeling. In these studies emphasis is placed on the opportunities provided by synthetic biopolymer systems for design of molecular "scaffolds" and other features in which photoactive groups are held in relatively rigid arrays. The work is important to the understanding of charge separation and transport in both natural and biomimetic systems.

Brandeis University
Waltham, MA 02254

Department of Chemistry

120. Mechanistic Studies of Excited State Chemical Reactions

Linschitz, H. **$101,903**
617-736-2506

This is a broadly based program, designed to clarify the thermodynamic and kinetic factors controlling the efficiency of energy-storing excited state redox reactions. Rates and primary radical yields of triplet–quencher interactions are studied in homogeneous solution using laser flash photolysis with nanosecond resolution. Determination of reaction efficiencies (primary quantum yields) requires evaluation of extinction coefficients of triplets and radicals, using various actinometric techniques. Test systems of interest are ketones, fullerenes, and in particular, new porphyrin derivatives that exhibit charge-transfer (quinoid) excited states, or form ion-paired "dimers" analogous to structures found in plant photosynthesis. Marcus theory is applied to quenching reactions of simple inorganic anions, for which reorganization energies are derived from spectroscopic data. The results are interpreted in terms of the extent of charge transfer (δe^*) in the excited transition state structure. For a large number of triplet–anion systems, $\delta e^* = 1$ (electron) if $\delta G^0{}_{CT}$ of this quenching reaction is $\lesssim 0.2$ V. However, δe^* decreases as $\delta G^0{}_{CT}$ increases further.

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

121. 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

122. *Theoretical Studies of Electron Transfer in Complex Media*
Chandler, D. **$79,998**
510-643-6821

The structures, dynamics, and free energies of the transition states for the prototypical electron-transfer reactions have been determined by computer simulation through application of novel sampling procedures and analytical methods. The research on these systems is concerned with (1) algorithm development for simulating the quantal dynamics for evolution initiated at the transition states; (2) derivation of analytical theories of solvation that will be tested by the simulation results and used to explain measured free energies of activation for electron-transfer reactions; and (3) derivation of simplified dynamical theories for quantum mechanical activated processes. These dynamical theories will be used to interpret and guide current simulation studies, and to suggest new experimental work.

University of California, Irvine
Irvine, CA 92717

Department of Chemistry

123. *Research in Chemical Kinetics*
Rowland, F.S. **$125,000**
714-856-6016

This research is directed toward understanding the rates and mechanisms of various chemical reactions, including some of importance in the atmosphere or in the oceans. Thermal and energetic reactions of radioactive T and ^{38}Cl atoms are studied with gaseous substrates. The addition of thermalized ^{38}Cl atoms to $CF_2{=}CFBr$ is being studied for comparison of the effects on internal energy redistribution with C–F bonds (versus C–H bonds in $CH_2{=}CHBr$). Thermal ^{38}Cl atoms added to the terminal olefinic position in $Sn(CH{=}CH_2)_4$ or $As(CH{=}CH_2)_3$ form $(CH_2{=}CH)_xMCHCH_2{}^{38}Cl^*$ radicals from which the ^{38}Cl atom is able to escape on a time scale much too rapid for consistency with RRKM intramolecular energy equilibration. Additional experiments on ^{38}Cl reactions with a variety of polyvinyl compounds containing central atoms ranging in mass from silicon to lead are being used to characterize these non-RRKM energy transfer processes more precisely. The reactions of thermal ^{38}Cl atoms with hydrogen-substituted chlorofluorocarbon (HCFC) compounds are used to determine the potential importance of an atmospheric sink of stratospheric Cl atoms. The substrate molecules for these reactions are primarily chosen because of their general suitability as substitutes for the CFC molecules in technological applications. Separation procedures are being developed to provide purified 100 microgram quantities of carbonaceous atmospheric molecules (C_2H_6, C_3H_8, OCS) suitable for ^{14}C determination with mass spectrometry. Theoretical calculations are being made of the structures of moelcules such as ClOOCl which are of atmospheric interest.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

124. *Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin*
El-Sayed, M.A. **$135,000**
310-825-1352

The conversion of solar energy into chemical energy in the form of adenosine triphosphate (ATP) by the other photosynthetic system in nature, bacteriorhodopsin (bR), involves five main steps: (1) solar energy deposition, (2) separation of charges accomplished by isomerization, (3) protein relaxation leading to deprotonation of the photosynthetic bacterium (PSB), (4) proton pumping leading to proton gradients, and (5) electric to chemical energy transformation by conversion of ADP into ATP by use of the proton gradients. Studies in this project are concerned with steps 1 through 3. The importance of metal cations (e.g., Ca^{2+}) to the proton pump in bR is well-known, but the mechanism of its involvement is not yet understood. If the four metal cations are removed, observations show that while isomerization and some protein conformation changes take place, the deprotonation step and thus the proton-pumping function of bR, stop. Two possibilities present themselves for the metal cation function: (1) a direct interaction with the positively charged PSB during step 3 above, leading to its deprotonation as a result of electrostatic repulsion or (2) control of the protein conformation changes to change the environment of PSB in step 3 to make it more acidic. To differentiate between these mechanisms, the binding sites of these metal cations need to be located. A program is aimed at determining the binding constants of the Ca^{2+} at different binding sites for native bR and for a number of its mutants in which functionally important residues are genetically substituted by *neutral or nonhydrogen bonding ones. In this manner the* location of the different binding sites is identified.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemistry

125. *Cyclometallated and Cyclometalsilylated Complexes of Transition Elements as Photoredox Sensitizers*

Watts, R.J. **$110,000**
805-893-2032

Conversion of solar energy into chemical potential energy by organometallic photosensitizers and photocatalysts is being studied. The effects of metal–carbon and metal–silicon bonds upon those excited state properties that influence photosensitization and photocatalysis are a focal point of the research. Ortho-metalation of metal centers such as Ir(III), Rh(III) and Re(I) by ligands such as 2-phenylpyridine results in complexes which are often strong photoreducing agents. These absorb visible light and convert a substantial fraction of the absorbed photon energy into chemical potential to drive outer sphere electron transfer substrate reduction reactions. Chemical modifications of these species are presently under study in order to establish what structural features are most influential in facilitating their use as strong photoreductants. Ligands that are capable of chelating metal centers through a combination of N- and Si-coordination sites have been designed and prepared in order to study the use of metal–silicon bonds to promote photochemical reduction of substrates. While the metal–silicon bond, like the metal–carbon bond, serves to enhance electron density at the metal center and to facilitate photoreduction of substrates, it is distinct in its tendency to kinetically labilize under circumstances where the metal–carbon bond is relatively inert. Current research includes the use of laser-induced transient absorption spectroscopy in order to characterize the excited state electron distributions and initial photochemical events subsequent to pulsed excitation of complexes in which N, Si-chelates are bonded to the metal center. The research seeks to establish whether or not metal–silicon bonds are cleaved by visible excitation, and, if so, to determine the subsequent reactivity with substrates and to establish if the metal–silicon bond is once more formed to complete a photochemical reactivity cycle in which the initial complex is regenerated.

Clemson University
Clemson, SC 29634

Department of Chemistry

126. *Intramolecular Energy- and Electron-Transfer Reactions in Polymetallic Complexes*

Petersen, J.D. **$84,329**
803-656-5017

Research has centered around the use of multimetal complexes to effect excited-state, energy- or electron-transfer reactions in these systems. In the energy transfer area, metal dihydride reactive fragments were coupled to azineruthenium(II) or cyanoferrate(II) absorbing fragments. Energetically, only Co(III) hydrido complexes have reactive excited states low enough in energy to be useful. With the Co(III) dihydride complexes [e.g., $(BL)Co(PPhEt_2)_2(H)_2^+$ (where BL is a chelating, aromatic, azine bridging ligand)], synthetic difficulties have prevented multimetal complex generation. A substituted bis(dipyridyl)ethane is used as a bridging ligand because it mimics the only known stable, but nonbridging ligand system, 2,2′-bipyridine. In the area of excited-state, electron transfer, the metal triad systems initially studied are modified. Recent work using $[(NC)_4Fe^{II}(BL)Ru^{II}(tpy)(4,4'\text{-}bpy)Rh^{III}(bpy)_2(MQ^+)]^{4+}$, where BL = 2,2′-bipyrimidine or 2,3-bis(2-pyridyl)pyrazine, tpy = 2,2′:6′,2″-terpyridine, 4,4′-bpy = 4,4′-bipyridine, bpy = 2,2′-bipyridine, and MQ^+ = N-methyl-4,4′-bipyridinium, utilized the Ru(II) center as a light absorber, the Fe(II) center as an electron donor, and the MQ^+ as an electron acceptor. Nanosecond spectroscopy shows quenching within 70 ns of excitation and no transient absorption spectrum characteristic of $MQ^\bullet$. The best conclusion is that the MQ^+ is not of sufficient potential to be reduced by the Ru(II) excited state. Triad systems are being prepared with two modifications. The first involves the modification of the electron acceptor to make it easier to reduce. The second involves the generation of a semiconducting Cu(II) polymer chain to extend the distance between the light absorber and the electron acceptor. Hopefully, these modifications will enable generation of a sustained charge separation.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

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

Elliott, C.M. **$105,000**
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. In other words, 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.

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

Parkinson, B.A. **$102,000**
303-491-0540

The research is directed towards a fundamental understanding of the dye sensitization of semiconductor electrodes. Dye sensitization is an important process in both solar energy conversion and in the photographic industry. Methods of increasing the efficiency of turning incident photons into electrons are sought. One method involves the use of two-dimensional semiconductors that have defect-free surfaces such as SnS_2. These atomically flat surfaces also are ideal for scanning tunneling microscopy (STM). A modified STM method for detecting the position and energy levels of dye molecules adsorbed on these surfaces with molecular resolution is being developed. This is accomplished by modulating a light source at the wavelength of the dye absorption maximum and pulling out the photoinduced contribution to the tunneling current. A simultaneous picture of photocurrent response and topography is then obtained. Questions such as the state of dye aggregation on the surface can then be answered. Recently, methods for increasing the surface area of SnS_2 photoelectrodes have been developed. By chemically etching or photoetching the surface, increases in the quantum yield for electron flow per incident photon have been obtained. New semiconductor substrates for sensitization experiments are also being developed.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

129. Reaction Kinetics and Product Distribution in Photoelectrochemical Cells

Koval, C.A. **$97,000**
303-492-5564

Three processes associated with solar energy conversion are being explored at semiconductor–electrolyte interfaces and in membranes. The first process involves reactions of nonthermalized, photogenerated minority carriers. "Hot" electrons ejected from p-InP photocathodes can be observed via their reduction of 1,2-dibromoethylbenzene (DBEB) to produce styrene and bromide ion. The formation of bromide ion can be monitored amperometrically in a continuous fashion using a p-InP–platinum rotating ring–disk electrode. These experiments demonstrate that at highly doped p-InP electrodes, reduction of DBEB can be very efficient (>30%). Current research involves extension of these experiments to superlattice electrodes and reduction of Fe(II)(cyclopentadienyl)(arene) complexes as another redox system capable of observing hot carriers. The second process under investigation is the kinetics of electron transfer (ET) for thermalized majority carriers. An electrochemical cell that uses only a drop of solution has been developed for measuring rates of electron transfer at interfaces between redox electrolytes and 2-D semiconductors such as $n\text{-}WSe_2$. Despite the good diode performance of these interfaces, the ET mechanism did not conform to the bimolecular rate law suggested by the standard theoretical models. The exchange current density was found to be independent of solution acceptors even with a concentration range spanning six orders of magnitude. The third process is photofacilitated membrane transport, which explores the use of solar energy for selective separation processes. Preliminary experiments have shown that spiropyran dyes can be used to pump metal ions uphill against their concentration gradients.

Columbia University
New York, NY 10027

Department of Chemistry

130. Charge Generation and Separation at Liquid Interfaces

Eisenthal, K.B. **$115,000**
212-854-3175

The current research activities are directed towards setting up a femtosecond second harmonic capability and a picosecond sum frequency capability to study charged molecules, neutral molecules, and charge exchange at liquid interfaces. The femtosecond second harmonic system at 625 nm will be operational shortly. In the sum frequency experiments a visible picosecond pulse is mixed with an IR picosecond pulse through their nonlinear interaction with interface molecules. By varying the IR frequency, the vibrational spectra of the interfacial molecules is obtained. The generation of sum frequency light using 532 nm and an IR pulse has been applied to C–D vibrations in alkyl compounds and $-C{\equiv}N$ vibrations of nitriles at the air/water interface. For acetonitrile, the peak at the air/water interface is at the same frequency as in the bulk solution whereas the benzonitrile is blue shifted with respect to both bulk neat benzonitrile and gas phase benzonitrile. The origin of this presumed hydrogen bonding induced blue shift is being investigated. The orientational structure capability of sum frequency generation was demonstrated by polarization measurements of the sum-frequency signal, which yielded a tilt angle of 34° for the orientation of the benzonitrile long axis with respect to the interface normal.

131. *Theoretical Studies of Photoactive Molecular Systems: Electron Transfer, Energy Transport, and Optical Spectroscopy*

Friesner, R.A. **$109,544**
212-854-2202

Three projects are currently being pursued. First, an empirical pseudopotential method has been developed for calculating bandgaps of semiconductor particles, which yields results accurate to a 0.1 eV when compared to experiment for CdS particles. Predictions have been made for GaAs and GaP particles, which include a turnaround of the bandgap to the red at very small particle sizes. Attempts are made to calculate the absorption lineshape by coupling the pseudopotential model to molecular dynamics simulations. The second project involves the use of Redfield relaxation theory to calculate electron-transfer rates in bridged donor–acceptor systems. An efficient algorithm has been developed so that large systems with hundreds or thousands of quantum levels can be treated via the Redfield equations. This is applied to generally study the effects of intermediate levels and to understand long-range electron transfer through DNA. Finally, development continues on the electronic structure code that will be used to calculate electron-transfer matrix elements.

Department of Electrical Engineering

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

Osgood, R.M., Jr. **$50,000**
212-854-4462

Photodissociation of Cl_2, CCl_4, and CH_3Br 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. Photodissociation of CL_2 at UV wavelengths causes desorption of Cl atoms and formation of $AsCl_3$. TOF at 351 nm shows direct absorption leads to photofragmentation: at 193 and 248 nm, charge transfer between adjacent molecules initiates fragmentation. For CCl_4, postirradiation TPD shows a threshold coincident with the GaAs band gap. Thus, substrate electron-hole pairs promote adsorbate dissociation. This mechanism applies to CH_3Br. TOF shows site-specific CH_3Br bond cleavage in the first layer, induced by electrons at the conduction band minimum (CBM) or hot electrons. 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 states. This is confirmed by PL yield, which decreases upon irradiation. Above one monolayer, CH_3Br dissociates by hot electrons or direct absorption. The direct absorption TOF signal depends on coverage for thick adlayers because of optical interference between the incident laser beam and its reflection.

Dartmouth College
Hanover, NH 03755

Department of Chemistry

133. *Photoinduced Dipoles and Charge Pairs in Condensed Phase*

Braun, C.L. **$100,000**
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). Exploration of charge carrier separation at the interface between donor and acceptor layers is under way. The fast photocurrent measurements revealed that the dipole moments of excited molecules in solution could be measured with the same techniques. The 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

134. *Charge Separation in Photoredox Reactions*

Kevan, L. **$130,000**
713-743-3250

This research is directed toward an improved molecular understanding of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies such as micelles and vesicles. Photoionization of alkylporphyrins, alkylphenothiazines and derivatives, and alkyltrimethylbenzidines in frozen solutions of vesicles, micelles, and reverse micelles to produce net charge separation are being studied by electron spin resonance and electron spin echo modulation spectroscopy. These instrumental techniques make possible the detection of the local environment of the photoproduced radical cation with respect to the vesicular structure. Current emphasis is on location control of electron donors and electron acceptors relative to the assembly interface by attachment of variable length alkyl chains and modification of the interface with cosurfactants. In the last year a newly synthesized series of alkyltrimethylbenzidines has been initially studied and compared with comprehensive studies of alkylphenothiazines. Changes in location are monitored by electron spin echo modulation spectroscopy.

The photoionization efficiency is being assessed by electron spin resonance intensities. This work is leading to better molecular structural control of photoinduced charge separation efficiency.

Marquette University
Milwaukee, WI 53233

Department of Chemistry

135. *Photophysical and Photoredox Studies of Transition Metal Complexes and Zeolite-Entrapped Assemblies*
Kincaid, J.R. **$102,000**
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 phtalocyanines 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. Most recent results indicate that entrapment of tris-ligated ruthenium(II) complexes within the supercages of Y-zeolite not only eliminates photodecomposition processes that proceed through population of ligand-field excited states, but also may destabilize ^{3}metal-to-ligand charge transfer (^{3}MLCT) states thereby increasing their lifetimes. Thus, current attention is being focused on synthetic elaboration of such zeolite-entrapped species and detailed elucidation of their photophysical and photoredox behavior. In addition, several fundamental issues involving the inherent photophysical properties of members of these classes of compounds are being addressed. Thus, a series of complexes are being studied by systematic synthetic manipulation of various factors that dictate the relative importance of alternate decay pathways. Finally, previously documented position-dependent deuteration effects on ^{3}MLCT state lifetimes of $Ru(bpy)_3^{2+}$ are being extended to a series of methylated bipyridines wherein an inverse-deuterium effect has been observed (ie., the lifetime of the deuteriated complex is shorter than that of the natural abundance analogue).

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

136. *Photochemical Approaches to Conversion of Light to Electricity or Fuel*
Wrighton, M.S. **$240,000**
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 at Boston
Boston, MA 02125

Department of Chemistry

137. *Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions in Homogeneous and Heterogeneous Media*
van Willigen, H. **$100,000**
617-287-6147

The project is concerned with the study of the factors that affect the kinetics and efficiency of photoinduced electron transfer reactions. The formation and decay of electron transfer products is monitored with time-resolved electron paramagnetic resonance (TREPR) techniques. The time evolution of the TREPR spectra not only reflects the kinetics of free radical formation and decay, but also of spin state dynamics because of chemically induced electron polarization (CIDEP) mechanisms. Spin polarization effects are a valuable source of information on the mechanism of the electron transfer process. For this reason, a major focus of the work during the past year has been the development of data analysis methodologies with which the rates of photochemical processes and spin state evolution can be extracted from the spectroscopic data. The photoinduced hydrogen abstraction reactions involving acetone and 2-propanol or acetone and t-butylperoxide have been used as model systems for tests of these methods. The data analysis techniques have been applied in the study of solvent and concentration effects on the photoinduced electron transfer from (tetrasulfonated) Zn tetraphenylporphyrin (ZnTPPS) to benzoquinone. Studies are being performed of photoinduced electron transfer reactions in heterogeneous media such as micelles and involving reactants adsorbed in the pores of silica gels. In such systems the unique spatial distribution of reactants and products may promote forward electron transfer while inhibiting the energy wasting back electron transfer process. Ongoing work is concerned as well with the photoreduction of C_{60} by electron donors such as triarylamines and hydroquinone.

University of Minnesota
Minneapolis, MN 55455

Department of Chemistry

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

Barbara, P.F. **$115,000**
612-625-0064

This research involves 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. The transient optical spectroscopy of the contact charge transfer (CCT) bands is studied to measure relaxation dynamics and electron transfer kinetics. The approach is to prepare a nonequilibrium system by exciting the CCT band with an ultrashort light pulse and then to measure the subsequent dynamical evolution by an ultrashort probe pulse. By monitoring the ultrafast photodynamics that are induced by excitation of the CCT band, the dynamical evolution of the solvent and spatial coordinates are studied as the system relaxes and undergoes thermal electron transfer. During the first year of support the basic approach of this grant was applied to study of the bromine benzene charge transfer complex.

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

Lipsky, S. **$102,980**
612-624-9581

Studies are conducted on photophysical properties of organic molecules that have relevance in determining their behavior when subjected to high-energy radiation. Recent work includes the following: (1) The fluorescence quantum yields from neat saturated hydrocarbon liquids are measured at excitation energies below and above their ionization thresholds. Analysis of the energy dependence of these yields provides a new technique for determining photoionization efficiencies that is much less perturbative than previous techniques. Additionally these studies have provided a somewhat more detailed picture of the nature of the ionizing transition in liquids and of the subsequent electron plus positive ion recombination. (2) The effect of a magnetic field on the geminate recombination of ion pairs in neat liquid hydrocarbons at low temperature is measured. This study examines the kinetics of loss of spin coherence in a well-defined single pair system. Such measurements are useful in unraveling the behavior of more complex, multiple-pair systems generated by high-energy radiation. (3) An anomalously efficient energy transport process involving a neat liquid hydrocarbon as donor and an aromatic impurity as acceptor is measured. Although the mechanism of the transport remains unknown, involvement of an ion-pair state of the hydrocarbon appears to be implicated.

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

Chemical Kinetics and Thermodynamics Division

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

Neta, P. **$200,000**
301-975-5635

The pulse radiolysis technique is applied to the study of electron transfer processes in a variety of chemical systems. Reactive intermediates are produced in solution by electron pulse irradiation and the kinetics of their reactions are followed by time-resolved absorption spectrophotometry. These studies are concerned with mechanisms, kinetics, and thermodynamics of reactions of organic and inorganic radicals and unstable oxidation states, in aqueous and nonaqueous solutions. The emphasis is 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. Current measurements focus on solvent effects on the rate constants for reactions of these radicals, which are found to be very substantial. These effects provide insight into the mechanism and permit prediction of medium effects on similar reactions. A special concern of this work is the study of electron transfer reactions of metalloporphyrins, which permit 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 whose behavior is also investigated.

University of New Orleans
New Orleans, LA 70148

Department of Chemistry

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

Piotrowiak, P. **$98,000**
504-286-6840 **(15 months)**

These investigations focus primarily on the influence of two factors on the efficiency of the photoexcited charge separation and/or excitation transfer processes: 1, the effect of the relative symmetry of the molecular orbitals of the donor, the bridging unit, and the acceptor and 2, the importance of the medium reorganization, with a particular emphasis on ionic association. In area 1, during the first project year a large number of rigid model systems with very well controlled dihedral angles between the donor and acceptor units was prepared. Currently, a variety of spectroscopic measurements on these molecules is being performed, both at this laboratory, as well as in collaboration. The electronic interactions in excited singlet state, triplet state, radical cations, and radical anions of the parent molecules are being investigated. Of particular interest are at this stage the results of the high-resolution fluorescence and double-photon ionization molecular beam studies on bifluorenes. In addition to geometry effects, the influence of weak degeneracy breaking (e.g., as a result of selective isotope substitution or cluster formation with "solvent" moieties) is being studied in a systematic manner. In area 2, the synthetic work towards donor–bridge–acceptor systems with tethered permanent counter ions is in progress. Also, the nanosecond time-resolved microwave conductivity apparatus, which will be used in charge separation studies, has been assembled. The donor–acceptor compounds necessary for the measurements of time-resolved depolarization of microwave conductivity have been prepared.

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

Department of Chemistry

142. *Excited State Processes in Transition Metal Complexes. Redox Splitting in Soluble Polymers*
Meyer, T.J. **$145,000**
919-962-6319

In conjunction with the derivatization of soluble polymers, polypyridyl complexes of Ru(II), Os(II), and Re(I) are being investigated for applications in energy conversion processes at the molecular level. Based on the photochemical and photophysical properties of these complexes, patterns of behavior are emerging that allow excited state stabilities and lifetimes to be predicted and controlled by making synthetic changes. By utilizing transient laser techniques and emission and resonance Raman spectroscopies, the roles of electronic structure, molecular vibrations, and the medium on properties and lifetimes are also being investigated systematically. The results of these studies are leading to new classes of chromophores which absorb light broadly throughout the near-UV/visible and have excited states that are stable and relatively long-lived. Synthetic methods have been developed for attaching derivatives of these complexes to soluble polymers along with organic units that can act as electron or energy transfer donors or acceptors. Photophysical studies on the resulting complex molecular assemblies show that polymers can be designed in which photoinduced electron or energy transfer events can be initiated and controlled on single polymeric strands. New derivatized polymers are being designed and synthesized that will mimic the light-harvesting, electron transfer abilities of the reaction center of photosynthesis. When combined with fast transient measurements following laser excitation, these materials are providing a basis for exploring long-range electron and energy transfer on individual polymeric strands.

University of North Carolina at Charlotte
Charlotte, NC 28223

Department of Chemistry

143. *Mixed-Metal, Multielectron Photocatalysts for Solar Energy Conversion*
Rillema, D.P. **$114,000**
704-547-4445

The design and synthesis of potential solar energy photocatalysts is the focus of the investigation. Two rhenium(I) tricarbonyl systems have been studied in detail. One study consisted of examining the photophysical properties of complexes of the type $[Re(L\text{-}L)(CO)_3py]^+$, where L-L is 1,10-phenanthroline and phenanthroline derivatives containing methyl or phenyl groups, and py is pyridine. All the complexes were highly emissive at room temperature in solution or at 77 K in a glass. The emission maxima ranged from 510 to 548 nm, emission lifetimes were on the order of microseconds at room temperature (3–12 μs), and emission quantum yields were high (0.17 to 0.29). Results from the photophysical measurements performed at low temperature indicated the presence of two unequilibrated emitting states, a ^{3}MLCT and ^{3}LC state. The second study consisted of examining the photophysical properties of charge separation in $[Re(bpm)(CO)_3(MeQ^+)]^{2+}$ and $[Re(bpm)(CO)_3(py\text{-}PTZ)]^+$, where bpm is 2,2′-bipyrimidine, MeQ$^+$ is N-methyl-4,4′-bipyridinium ion, and py-PTZ is 10-(4-picolyl)phenothiazine, and comparing them to similar properties found in $[Re(bpm)(CO)_3py]^+$. The emission intensity was similar in the MeQ$^+$ and py derivatives, but was quenched in the py-PTZ complex. This quenching was probed by transient absorption spectroscopy and resulted in observing the growth and decay of the charge separated transient, $[Re(bpm^-)(CO)_3(py\text{-}PTZ^+)]^+$. The growth occurred within 900 ps, and its decay, attributed to back electron transfer occurred with a rate constant of $5.5 \times 10^7\ s^{-1}$.

Northwestern University
Evanston, IL 60208

Department of Chemistry

144. *Dynamic Structural Effects and Ultrafast Bimolecular Kinetics in Photoinduced Charge Transfer Reactions*
Hupp, J.T. **$130,000**
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 (ET) reaction rate. Current experiments at the rate extremes (i.e., ultrafast and moderately slow) are yielding important new information concerning the role of solvent, including (1) decoupling of ultrafast, adiabatic ET from the conventional dynamics of solvent motion, conversely and (2) tremendous attenuation of slower ET kinetics by an unprecedented solvent gating mechanism. New results from area 4 have led to experimental confirmation of the so-called 3-state model of valence delocalization developed by several theoretical groups over the past 11 years.

145. *Vibrational Dynamics in Photoinduced Electron Transfer*

Spears, K.G. **$97,284**
708-491-3095

Both theory and experiment suggest that molecular vibrations and distortions are important controlling elements for electron transfer. The objective of this project is to make direct measurements of vibrational motions immediately after the electron transfer. The experimental results will be important for theoretical tests of electron transfer models where, previously, estimated effects due to vibrational motion were inferred indirectly. A new method of picosecond IR absorption spectroscopy will be used to monitor electron transfer kinetics. Intramolecular electron transfers will be studied with porphyrins rigidly linked to electron acceptors, where electron transfer is initiated by optical excitation of the porphyrin. Direct charge transfer excitation of solvent caged, contact ion pairs, will also be investigated. A transient IR spectroscopy system will be modified to give 2-3 ps pulse durations. Compounds are being synthesized for study of electron transfer in inorganic charge transfer complexes.

Ohio State University
Columbus, OH 43210

Department of Chemistry

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

Dutta, P.K. **$100,000**
614-292-4532

Photochemistry in constrained heterogeneous medium offers opportunities for stabilizing photodriven redox products that cannot be readily stabilized in homogeneous solution. Toward that goal, the interior cages of zeolites and the lipid-like interior of a layered double metal hydroxide are being explored as possible sites for photochemical reactions. Intrazeolitic photoelectron transfer reactions between $Ru(bpy)_3^{2+}$ and methylviologen in neighboring cages are being examined. The interesting aspect of these reactions has been the discovery of a pathway that leads to long-term stabilization of the redox products. The photochemical efficiency of this process is greatly enhanced by assembling a trimolecular redox system in which the electron transfer is observed from the photoexcited zeolite entrapped $Ru(bpy)_3^{2+}$ to a neutral viologen in solution via an intrazeolite viologen electron relay. Optimum charge separation is observed if the reduction potentials of the trimolecular system have correspondingly higher values. Influence of zeolite particle size on the efficiency as well as access to the hole ($Ru(bpy)_3^{3+}$) is being actively pursued. Layered metal hydroxides have been used as a host to construct membranes, which exhibit novel structural and dynamic features. Incorporation of porphyrin and pyrene photosensitizer molecules in the membrane and their photoredox properties are being explored.

Pennsylvania State University, University Park
University Park, PA 16802

Department of Chemistry

147. *Electron Transfer Reactions in Microporous Solids*

Mallouk, T.E. **$165,107**
814-865-6553

This project uses zeolitic materials (aluminosilicate zeolites and clays, and layered and tunnel structure oxide semiconductors) as organizing media for artificial photosynthetic systems. The solid host lattice allows one to assemble multicomponent electron transfer systems through a combination of ion-exchange and size-exclusion effects. By selectively depositing catalyst particles, such as elemental platinum, inside the host solid, it is possible to achieve permanent light-induced charge separation in the form of hydrogen and an oxidized electron donor molecule. Using this strategy, visible light-driven photolysis of hydrogen iodide has been demonstrated with the sensitized layered semiconductor $K_4Nb_6O_{17}$ and related materials. At present the efficiency of this process is low because charge recombination at the semiconductor-solution interface competes effectively with tunneling of electrons perpendicular to the layers, which is required for hydrogen evolution at the internally sited catalyst particles. Electron transfer systems in which the host solid is a nonelectroactive aluminosilicate (zeolites and clays) are also being studied. In this case a photosensitizer (typically a $Ru(bpy)_3^{2+}$ derivative) is present at the solid–solution interface, and other electroactive components (molecular electron donors and acceptors, and oxide semiconductor clusters), are sited inside and/or outside of the host. Using this strategy three- and four-component systems can be prepared, and charge-separated-state lifetimes on the order of hundreds of microseconds are readily achieved. The factors that control self-assembly, charge separation, and recombination in these systems are currently being studied.

148. *Polar Solvation and Electron Transfer*

Maroncelli, M. **$105,000**
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 Pittsburgh
Pittsburgh, PA 15260

Department of Chemistry

149. *Time-Resolved Optical Studies of Charge Relaxation and Charge Transfer at Electrode Interfaces*
Waldeck, D.H. **$120,000**
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

150. *Asymmetric Polymeric Porphyrin Films for Solar Energy Conversion*
Wamser, C.C. **$110,000**
503-725-4261

This project involves the synthesis and characterization of novel thin-film polymer membranes made from porphyrins. The polymer films are prepared by interfacial polymerization of a pair of reactive monomers, for example from tetra(p-hydroxyphenyl)porphyrin (THPP) in aqueous base with tetra(p-chlorocarbonylphenyl)porphyrin (TCCPP) in chloroform. Typical film thicknesses are in the range of 0.01 to 10 micrometers depending on the particular monomers and reaction conditions. The films display a unique chemical asymmetry, in the sense that opposite surfaces of the films show distinctive differences in the concentration and type of functional groups that are present. When placed between semitransparent electrodes and irradiated with either steady-state broad-band light or a pulsed laser, these films develop directional photopotentials of up to 250 mV. The directional photopotentials are considered to be a manifestation of the chemical asymmetry of these interfacial films, that is, photoinduced charge separation involves electron transfer in the direction that corresponds to the predicted trends of oxidation and reduction potentials of the various porphyrins within the polymer film. The major goals of the current research are (1) characterization of the structural asymmetry of the films and its correlation with the photoactivity and (2) optimization and control of the asymmetric photoactivity.

University of Rochester
Rochester, NY 14627

Department of Chemistry

151. *Photochemistry of Dithiolate Complexes of the Platinum Group Elements*
Eisenberg, R. **$120,000**
716-275-5573

Emissive complexes of the platinum group elements are under investigation in the context of light to chemical energy conversion. The specific systems being studied are four-coordinate dithiolate complexes of PT(II) containing either a chelating diimine, diolefin, or diphosphine ligand or bis(tertiary phosphine) ligands. All of the complexes emit in rigid media at 77 K while the diimine derivatives show the unusual property of solution luminescence. The diimine dithiolate systems also exhibit an intense solvatochromic band that has been assigned through spectroscopic studies to be a metal modified interligand charge transfer. Photophysical measurements on one set of diimine dithiolate complexes including emission quantum yield and lifetime determinations as a function of temperature have established the presence of multiple emitting states in those systems. However, other diimine derivatives in which the dithiolate is maleonitriledithiolate have been found to have only a single emitting state although the emission is highly structured. For all of the dithiolate complexes that do not contain a diimine ligand, the 77-K emission is assigned to a metal-to-ligand charge transfer state involving the dithiolate ligand. During the past year, electron transfer quenching studies of the emission from Pt(diimine)(ecda) systems (ecda = ethyl-2-cyano-3,3-dithiolatoacrylate) have been performed and have led to an estimate of the excited state reduction potential of ~1.0 v for these complexes. New dianionic bis(dithiolate) complexes have been prepared and are found to emit brightly in rigid media at 77 K. The complex $Pt(ecda)_2^{2-}$ also undergoes photooxidation in the presence of halocarbons while $Pt(qdt)_2^{2-}$ (qdt = quinoxalinedithiolate) exhibits considerable sensitivity to pH in both absorption and emission bands. Other d^8 square planar complexes have also been synthesized and their optical properties and photochemistry are under examination.

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

Miller, R.J.D. **$95,000**
716-275-4079

The rectifying properties of semiconductor liquid junctions make these systems among the simplest and most efficient systems for converting and storing optical energy in the form of interfacial charge separation. However, the primary events of interfacial electron or hole carrier transfer and competing nonradiative (energy loss) channels are not well understood at surfaces. This research has explored the use of three novel optical techniques, surface space charge electro-optic sampling, surface-restricted transient grating spectroscopy, and femtosecond optical Kerr spectroscopy (OKE) to obtain the time evolution of the surface spatial distribution of photogenerated charge carriers, the photocarrier population dynamics at semiconductor interfaces, and the solvent modes responsible for charge localization and separation, respectively. These studies have shown that carriers arrive at GaAs(100) surfaces on the 100-femtosecond (fs) time scale. Improvements in time resolution, using surface grating spectroscopy, have shown interfacial hole transfer is occurring on the picosecond time scale. The OKE approach to solvent dynamics has determined the response of water to a field is multiexponential with a major relaxation component of 100 fs. The observed interfacial hole transfer to Se^{-2} acceptors is occurring on this same time scale. This observation illustrates charge transfer processes can occur in the strong electronic coupling limit and can be competitive with carrier thermalization. These results demonstrate that it is possible to specifically engineer interfaces to maximize energy conversion efficiencies by minimizing energy loss through carrier thermalization. The carrier thermalization dynamics at specific interfaces remain to be conducted to determine the overall potential gains in efficiency.

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

Whitten, D.G. **$132,000**
716-275-1858

These investigations are focused on light-induced redox reactions in solution that can lead to efficient and potentially useful net chemical reactions. Most of these processes are initiated by single-electron-transfer quenching of an excited state followed by subsequent steps often involving cooperative reactions between ion radicals formed in the quenching step. The studies have used visible and near UV light-absorbing donors and acceptors; in most cases the fragmentable electron donors and acceptors, which react with these excited molecules, do not absorb light in the near UV or visible, and thus have no long wavelength photochemistry in the absence of the excited partner molecule. The fragmentable donors used are molecules that typically have at least one heteroatom functionality (amine, alcohol or thiol), which is the site of the single-electron transfer oxidation by the excited acceptor. The fragmentable acceptors used are benzylic halides or ethers that have strongly electron-drawing groups on the aromatic ring. Very rapid fragmentation reactions were observed in a number of cases following single-electron transfer quenching of the excited state. Studies of the rate and mechanisms of these reactions are providing a paradigm for understanding ion–radical fragmentation reactions. A number of cases are being examined where single-electron transfer quenching of an excited state can culminate in net two-electron redox reactions to give metastable and potentially recyclable products. Altogether these studies are focusing on both reversible and irreversible two-electron redox reactions that occur as a consequence of single-electron-transfer quenching of an excited state.

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

Department of Chemistry

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

Isied, S.S. **$90,000**
908-932-3764

This research involves the study of long-range intramolecular electron transfer reactions across constrained polypeptides and those that possess secondary structures. Examples of such peptides are oligoproline derivatives, alpha helices, and cyclic peptides. Donor acceptor metal ions are attached at the N and C terminals and the side chains of these polypeptides and the intramolecular electron transfer reactions are studied using pulse radiolysis and flash photolysis techniques. Some of the most recent results to date from this research indicate that intramolecular electron transfer across 40Å occurs with a time constant of 100 microseconds across nine proline residues. This distance is equivalent to the diameter of a small protein. The studies with these model compounds are expected to lead to a better understanding of the pathways employed by electron transfer proteins.

Stanford University
Stanford, CA 94305

Department of Chemistry

155. *Energy Transfer Processes in Solar Energy Conversion*

Fayer, M.D.
415-723-4446

The main objectives of this research program are (1) the understanding of electronic excitation energy transport and (2) electron transfer in artificial systems. The experimental and theoretical research in this project is focusing on complex systems of chromophores, such as chromophores in micelles and chromophores attached to polymer back bones, or chromophores in systems with energy disorder. By clustering chromophores in micelle or polymer systems, the efficiency of energy transport can be greatly increased. However, in complex systems the dynamics become intricate. New detailed experiments along with sophisticated theory are being utilized to understand such systems. Following photoinduced electron transfer from a donor to an acceptor, highly reactive radical ions are generated. However, electron back transfer (geminate recombination) can destroy the ions before they can go on to do useful chemistry. In liquid solutions, there is a competition between geminate recombination and separation of the ions by diffusion. In this project a combination of experiments and statistical mechanical theory is being used to understand and influence forward and back electron transfer processes. In the two areas, excitation energy transfer and electron transfer, the time scales for the important events are very short. Therefore, psec experiments have been developed and continue to be developed to provide direct probes of the important dynamics.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

156. *Studies of Radiation-Produced Radicals and Radical Ions*
Williams, T.F. **$125,000**
615-974-3468

The objective is to characterize the structure and reactivity of organic free-radical and radical-ion intermediates generated by irradiation of molecular systems. A particular focus is the study of the radical ions that are generated in the primary chemical processes resulting from the absorption of high-energy radiation, since these charged species play an important role in the mechanisms of both radiation and photochemical effects. Radical cations are formed radiolytically under matrix-isolation conditions by γ-irradiation of solid solutions of the parent compounds in Freon matrices at low temperatures. Conversely, radiolytic reduction can be accomplished in hydrocarbon and other organic matrices where the positive hole is trapped and the electron can migrate to a solute molecule. Electron spin resonance and electronic absorption spectroscopy are used to characterize these paramagnetic species; measurements of g factors and hyperfine coupling constants on isotopically labeled and diastereomeric radicals reveal information about molecular geometry and spin density distribution. Specific projects include (1) structural aspects of novel species, (2) ion-molecule reactions and rearrangements, (3) photochemistry of radical ions, and (4) structure-reactivity relations.

University of Texas at Austin
Austin, TX 78712

Department of Chemistry and Biochemistry

157. *Vectorial Electron Transfer in Spatially Ordered Arrays*
Fox, M.A. **$160,000**
512-471-1811

Mechanisms of photocatalytic oxidation and reduction reactions of organic adsorbates on native and chemically modified semiconductor surfaces can be altered by modifying the chemical bonds on the surfaces. Organometallic coordination polymers and organic dyes are being tested as relays for multiple electron transfer. Electrodes modified for electrocatalytic studies are being prepared by anchoring the specifically designed electrocatalysts by covalent binding, electrosorption, and chemisorption of redox active polymer layers. Spatially controlled monolayer and bilayer coatings can attain electrical rectification in those photoelectrochemical cells. Polymers (homopolymers and block copolymers) are being synthesized as vehicles for efficient light collection and vectorial energy migration.

158. *Photoredox Processes at Polymer–Water Interfaces*
Webber, S.E. **$115,000**
512-471-3633

The overall motivation of this research project is to examine polymer-bound or polymer-associated chromophores for transduction of photon energy via photoredox reactions. Earlier work examined these reactions for chromophores bound to polyelectrolytes or polyacids in aqueous solution. For the singlet state it is essential for the polymer to partially protect the excited state chromophore from the quenching species to a degree that quenching does occur but that no "ion-pair complex" forms. These polyacids can adsorb onto the hydrophobic surface of commercial polystyrene microspheres (polysciences) in such a way that the anthryl groups appear to be partially protected from the aqueous phase. Both the singlet and triplet state of the anthracene can be quenched by a zwitterionic viologen (SPV) with the efficient production of ion pairs at any pH. This result is especially noteworthy for the singlet state because it contrasts sharply with the results obtained with the same polymer in homogeneous solution. The yield of ion pairs per quenching event is very good (> 0.3, depending on spin state and pH) and the lifetimes are longer than milliseconds (no decay is observed in 1 ms). Block polymers and grafted alternating polymers containing chromophores have been studied at polymer film interfaces using photophysical methods. The latter polymer type has been found to act as a emulsifier for an emulsion polymerization, which produces microspheres similar to those described above except that the microsphere is intrinsically photoactive.

Tulane University
New Orleans, LA 70118

Department of Chemistry

159. *Photoinduced Energy Transfer in Transition Metal Complex Oligomers*
Schmehl, R.H. **$165,000**
504-865-5573 **(15 months)**

This research involves the synthesis and spectroscopic examination of polymeric transition metal complex sensitizers that exhibit vectorial energy transfer to one terminus of the polymer. 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 that serves to tune the electronic properties of the metal (the repeating unit for a homopolymer is $[(\text{bpy-R-bpy})\text{ML}(\text{bpy-R-bpy})\text{ML}]_x$). Synthetic methods were developed for the preparation of bis-bipyridines having a variety of R moieties, and recent efforts have focused on preparing a ligand with a phenyl bridge (bpy-ph-bpy). In addition, complexes have been prepared in which two metal centers with different tuning ligands are linked together: $[L_2M_1(\text{bpy-ph-bpy})M_2L'_2]$ where M = Os, Re, Ru, and L = bpy, 4,4′-dicarboxyester-2,2′-bipyridine, 2,2′-biquinoline, and so forth. In most complexes of the series excitation of metal-to-ligand charge transfer (MLCT) transitions on the metal center with the higher energy MLCT state results in rapid energy transfer to charge transfer states on the other metal center. The influence of the excited-state energy gap and donor excited-state localization on energy migration between the metal centers can be examined with this series. Transient absorption spectra of complexes having bpy-ph-bpy as bridging ligand indicate that the lowest energy excited state of the complex is MLCT in nature and does not involve bridging ligand localized states; complexes of other closely related bridging ligands clearly exhibit excitation energy trapping on the bridging ligand.

Washington State University
Pullman, WA 99164

Department of Chemistry

160. *Investigations of Charge-Separation Processes in Metal Complexes*

Crosby, G.A. **$94,992**
509-335-5605

The research is focused on the nature of the interactions between near-degenerate excited states of disparate orbital origins in metal complexes. The intent is to identify the molecular determinants of the barriers and their relationship to the electronic states coupled through the barriers. Types of near-degenerate excited states under investigation are metal-to-ligand charge transfer (MLCT) states, n–π^* excited states, ligand-field (LF) states and ligand-to-ligand charge transfer (LLCT) excited states. Concommitant investigations are under way to measure the zero-field splittings of the triplet manifolds by means of Optically Detected Magnetic Resonance and to relate the parameters of the sublevels to the nature of the interacting states. Species under investigation are of the generic formulas $[Rh(NN)_3]^{3+}$, $Re(I)(NN)(CO)_3Cl$, and Pt(NN)(SS), where NN = nitrogen heterocycle, SS = coordinated thiol. The ultimate goal of the research is to arrive at a degree of understanding of these systems such that new complexes containing excited states with extensive charge separation can be designed and synthesized for use in solar energy harvesters.

Wayne State University
Detroit, MI 48202

Department of Chemistry

161. *Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates*

Endicott, J.F. **$120,000**
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 intermolecular energy transfer of 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) $Ru(bpy)_2^{2+}$ and the acceptor is a covalently linked metal complex, the donor and acceptor centers usually behave reasonably independently, and comparable electronic coupling parameters are obtained from the different experimental studies. An exception seems to occur in complexes containing the Ru^{II}-CN-Ru^{III} moiety. Electrochemical and kinetic data imply that electronic coupling is so strong in these systems that they cannot be described by simple perturbational models. Ru–CN–Co systems seem to be much better behaved. Systems with electron transfer, Co(II) or Ru(III) acceptors, and the same linker vary in their back-electron-transfer rates by several orders of magnitude. Back electron transfer involving quartet cobalt(II) centers appears to be electronically forbidden, with an electronic retardation factor of about 10^{-3}.

Chemical Physics

Aerospace Corporation
Los Angeles, CA 90009

Space and Environment Technology Center

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

Cohen, N.; Koffend, J.B. **$83,079**
310-336-7427

The project objective is to measure the rate coefficients for reactions of OH radicals necessary for understanding and predicting hydrocarbon combustion. The experiments are being performed in a shock tube at combustion temperatures near 1200 K and near atmospheric pressure. Transition state theory (TST) calculations have been 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 data are not available. Experimental measurements of rate coefficients for reactions of OH radicals with hydrogen, methane, ethane, propane, 2,3-dimethylbutane, neopentane, isobutane, isooctane, cyclopentane, ethylene, acetylene, acetone, formaldehyde, methanol, and ethanol have been completed. For most of these, TST calculations have been made. The reaction of OH with methyl radicals has also been measured and compared to other studies to assess the relative importance of different possible reaction channels.

University of Akron
Akron, OH 44325

Department of Chemistry

163. *Molecular Eigenstate Spectroscopy: Application to the Intramolecular Dynamics of Some Polyatomic Molecules in the 3000 to 7000 cm^{-1} Region*
Perry, D.S. **$125,175**
216-375-6825

An IR double resonance spectroscopic technique is being developed that can be applied at high resolution in a free jet. The precision offered by two frequency dimensions, each with sub-Doppler resolution, combines with spectral simplification at low temperatures to make it possible to study very complex IR spectra in unprecedented detail. This methodology, together with companion single resonance studies, provides an incisive probe of the mechanisms responsible for the redistribution of vibrational and rotational energy within individual molecules. The molecules, propyne, 1-butyne, and ethanol, show qualitatively different behavior, with different roles and strengths for the anharmonic, Coriolis x,y and Coriolis z-type couplings. Random matrix calculations are in progress to elucidate further the mechanisms that are being revealed by the experiments. These kinds of coupling mechanisms are responsible for the crucial energy randomization step of unimolecular reactions and may strongly influence bimolecular relaxation rates and condensed phase relaxation processes.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

164. *Electronic Structure and Reactivities of Transition Metal Clusters*
Balasubramanian, K. **$99,200**
602-965-3054

The electronic and geometric structural properties of clusters containing heavy atoms serve as models for regions of surfaces. Thus, investigation of the nature and reactivities of small cluster particles provides important clues to the understanding of catalysis and chemisorption. Electronic properties, such as ionization potentials, electron affinities, energy separations of low-lying states, and binding energies of these clusters and their reactivities vary dramatically with size. Many transition metal clusters are under investigation. In particular, theoretical investigations of Ir_3, W_4, Zr_3, Rh_4, Pt_3, Au_2, Ni_4, Pt_3Au, Pd_3Au, and Pt_4 are being conducted. The properties investigated are geometries, ionization energies, electron affinities, and the separations of the low-lying electronic states. The electronic properties and excited states of metal dimers, such as Ag_2, Os_2, Ir_2, and so forth, are also being studied from which the spectroscopic properties of these metal dimers are obtained. The reactivities of small cluster particles are also investigated with model reactions such as $M_3 + H_2$ and $M_2 + H_2$. The potential energy surfaces of all third row transition metal dihydrides and their ions are being determined with the objective of understanding the reactivities of these atoms and ions with H_2. The $Pt + CO$, $Pt_2 + CO$, $Pd_2 + CO$, $Cu + CO$, $Ag + CO$, $Au + CO$, $Cu_2 + CO$, $Pt_3 + H$, $Pd_3 + H_2$, $Pd_3 + H$, and $Ni_3 + H$ systems are also being studied. These investigations are conducted using a complete active space MCSCF (CASSCF) followed by higher order configuration interaction calculations. Relativistic effective potentials are used for the heavy atoms in the molecule, and spin-orbit and correlation effects are introduced simultaneously through a relativistic configuration interaction (CI) scheme.

165. *Generation Detection and Characterization of Gas-Phase Transition-Metal Aggregates and Compounds*
Steimle, T.C. **$76,418**
602-965-2636

Purely theoretical approaches to model transition metal reactions are rapidly developing. However, there is a paucity of experimentally derived information that serves both as a test of the quality of these models and provides guidance for their modification. Accordingly, obtaining experimental information relevant to the development of reaction models involving transition metals is important. Measuring molecular properties that are easily related to the bonding character and that are routinely predicted by theoretical means is of particular interest. To this end, the bound portions of the potential energy surface associated with the metal containing systems are studied utilizing high-resolution molecular beam optical and microwave spectroscopy. These studies employ a laser ablation–reaction source that is skimmed to produce a well collimated molecular beam sample. Optical spectra are recorded at a resolution dictated by the natural linewidth (~30 MHz), which is sufficient to resolve Stark shifts and hyperfine structure. Molecular beam pump–probe microwave-optical double resonance (PPMODR) studies are also performed. The PPMODR studies provide information on a single electronic state, thus circumventing many of the problems associated with perturbations in the optical spectrum. Permanent electric dipole moments, magnetic hyperfine, and electric quadrupole interactions are a direct probe of the bonding and have been determined for MoN, NbN, TiO and TiN. A wide variety of transition metal containing compounds can be generated via the laser ablation–reaction scheme and studies of more complex compounds have been initiated.

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Department of Chemistry

166. *Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding*
Lichtenberger, D.L. **$106,000**
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 has been (1) to directly probe the electronic interactions between metals and molecules through a wide variety of ionization spectroscopies and other techniques and (2) to investigate the relationships with bonding modes, structures, and chemical behavior. During this period of the project (1) the electronic features of diphosphines and monophosphines in their coordination to metals were characterized, (2) theoretical and experimental investigations of the bonding capabilities of C_{60} to transition metals were conducted, (3) techniques for the imaging of single molecules on gold substrates that emphasizes the electronic backbonding from the metal to the molecule were developed, (4) the high-resolution photoelectron spectrum of pure C_{70} in the gas phase were obtained, (5) the bonding of acetylide ligands to the bonding of other small organic molecules with metals were compared, and (6) the photoelectron spectra and bonding of η^3-cyclopropenyl groups to metals were reported. In each case, these are the first studies of their type.

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Los Angeles, CA 90024

Department of Chemistry and Biochemistry

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

Felker, P.M. **$98,000**
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 supersonic molecular beams. In the past year progress has been made in several areas. The first pertains to the application of mass-selective, ionization-detected stimulated Raman spectroscopies (IDSRS) to the size-specific vibrational spectroscopy of solute–solvent$_n$ clusters. The vibrational spectra of benzene-$(N_2)_n$ benzene-Ar_n, and carbazole-Ar_n clusters have been measured in this area. The second area involves the application of IDSRS methods to studies of jet-cooled benzene clusters. Spectra for clusters as large as benzene$_{13}$ have been obtained. The third pertains to the use of IDSRS methods in the study of intermolecular vibrational transitions in van der Waals complexes. In this area benzene-Ar, -Kr, -N_2, and -benzene have been studied. It is likely that studies such as this will be a rich source of information in the future on intermolecular potential energy surfaces.

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Washington, DC 20064

Department of Chemistry

168. *Studies of Combustion Kinetics and Mechanisms*

Gutman, D. **$153,000**
202-319-5385

The purpose of this research is to gain new quantitative knowledge of the kinetics and mechanisms of the reactions of polyatomic free radicals that are important in hydrocarbon combustion processes. The free radicals are generated in a heated tubular reactor by the decomposition of molecules using pulsed UV-laser photolysis. The ensuing reactions are monitored in time-resolved experiments using photoionization mass spectrometry. Reaction rate constants are measured as a function of temperature (to 1000 K) and pressure (1 to 20 torr), and the primary reaction products are determined to obtain basic information regarding the fundamental kinetics and dynamics of the reaction under study. This information also provides a rational basis for extrapolating observed kinetic behavior of free-radical reactions to the harsher conditions of actual combustion processes. Reactions under study include recombination of free radicals (e.g., $CH_3 + CH_3$), unimolecular decomposition of free radicals (e.g., n-C_3H_7, t-C_4H_9, and CH_3CHCl), and reactions of these free radicals with molecular oxygen (e.g., $C_4H_5 + O_2$) and atomic oxygen (e.g., $CH_3 + O$). In most instances, results obtained are the first quantitative determinations of the kinetic behavior of the reaction under study. When this information is incorporated into global models of combustion chemistry, it provides significant improvements in the reliability of these models to predict major chemical properties of burning processes.

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Chicago, IL 60637

James Franck Institute

169. *Bond Selective Chemistry Beyond the Adiabatic Approximation*

Butler, L.J. **$98,000**
312-702-7206

The series of experiments pursued for this project develop a unified understanding of bond-selective molecular dissociation processes important in combustion. They elucidate how the coupling between electronic states in polyatomic molecules plays a central role in both promoting and inhibiting bond-selective chemistry, perhaps even more so than the more thoroughly understood process of intramolecular vibrational energy redistribution. 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. This year the study of three systems was initiated in which the breakdown of the Born–Oppenheimer approximation alters the expected branching between chemical bond fission pathways. Experimental and theoretical studies on CH_3SH, one of the major gaseous organosulfur pollutants produced in the combustion of oils and coals, investigates the preferential fission of the S–H bond over the weaker C–S bond upon photoexcitation in the UV. Other studies investigate the competition between C–Br and C–I fission in 1,3-iodobromopropane and the competition between bond fission channels and H_2 elimination in methyl amine.

170. Quantum Dynamics of Fast Chemical Reactions

Light, J.C. **$98,000**
312-702-7197

This research is focused on 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 using the quantum thermal averaged flux–flux correlation function evaluated by diagonalizing the Hamiltonian in a three-body discrete variable representation. Applications to the thermal rate constants of the hydrogen isotopic exchange reactions show good agreement with experiments over a wide temperature range. 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. A comparison of time-dependent and time-independent approaches to the evaluation of state-to-state reaction probabilities has shown that the time-independent approach is preferable, even for evaluation at many scattering energies, providing the Green's function is represented in a diagonal basis. The dynamics of electronically nonadiabatic collisions are now being treated using the two diabatic surfaces, together with an appropriate interaction team. 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 "frictional" nonadiabatic approach simplifies the treatment of reactant and product coordinates, thus simplifying the calculation of state-to-state probabilities and rate constants.

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Department of Chemistry and Biochemistry

171. Laser Photoelectron Spectroscopy of Ions

Ellison, G.B. **$141,641**
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, $\hbar\omega_o$. The resultant detached photoelectrons with kinetic energy, KE, are energy analyzed by means of a set of electrostatic hemispherical analyzers. $M^- + \hbar\omega_o \rightarrow M + e(KE)^-$. Analysis of the photoelectron spectra enables the extraction of 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). During the last year a review article that critically contrasts three methods to measure R–H bond energies was completed, a spectroscopic study of the phenylnitrene anion was finished, and an overhaul of the light source of the photodetachment spectrometer was successfully completed. An ArIII laser that provides ~100 W of 3.531 eV photons has been fabricated and installed. Three approaches that are commonly used to determine the R–H bond energies of gas phase polyatomic molecules have been discussed: (1) the study of radical kinetics, (2) the use of negative ion thermochemical cycles, and (3) photoionization mass spectroscopic techniques. These three methods can be used on a large number of species (hundreds) and have an accuracy between ±3 kcal/mol and ±0.2 kcal/mol. The purpose of the article was to compare these three experiments with each other and to demonstrate by direct comparison that they achieve consistent results. Aromatic ions are being studied and the first of the systems is the most famous organic nitrene, phenylnitrene. The approach to the study of C_6H_5N is to scrutinize the photoelectron spectrum of the radical anion, $C_6H_5N^-$. The negative ion photoelectron spectra furnish a measure of the electron affinity of phenylnitrene; $EA(C_6H_5N)$ is 1.45 (± 0.02) eV and $EA(C_6D_5N)$ is 1.44 (± 0.02) eV. The photoelectron spectrum of $C_6H_5N^-$ is composed of an extensive Franck–Condon envelope that suggests that the electric charge is strongly delocalized over the radical anion. Besides detachment of the $C_6H_5N^-$ ion to the ground state of phenylnitrene, $\tilde{X}\ ^3A_2$, the spectra also contain bands that belong to the singlet state of C_6H_5N, $\tilde{a}\ ^1A_2$. The ΔE_{ST} is 18.0 (± 0.5) kcal/mol in excellent agreement with recent ab initio computations. In the previous laser system, the photoelectron spectrometer was placed in the extended cavity of an ArII ion laser (Spectra-Physics model 171-08). Using the multimode intracavity radiation working on a single line in the visible region (488 nm or 514.5 nm) achieved a circulating power of roughly 100 W with a beam waist of 0.2 mm. The most energetic line accessed with the standard ArII laser was the line at λ_o = 488.0 nm that generates 2.540 eV photons, thus limiting the study to molecular ionic systems that are bound by 2.540 eV or less. In order to address these problems, a laser build-up system that will generate over 100 W of UV laser light with a polarization that can be easily varied has been fabricated.

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

Leone, S.R. **$100,000**
303-492-5128

A time-resolved Fourier transform infrared (FTIR) emission technique is used for the study of molecular photofragmentation processes, energy transfer, and reaction dynamics. The apparatus unites a commercial FTIR spectrometer with a high repetition rate excimer laser. Through the use of time synchronization methods, high performance infrared detectors, and multipass light collection optics, spectra are obtained from a number of molecules and polyatomic radical species following these laser induced processes. In new experiments, single collision energy transfer events and radical–radical reactions are studied for the first time with high resolution and time-resolved capability. Results are obtained on the radical–radical reactions CH_3 with O atoms, C_2H_5 with Cl and CF_3 with H. A new product channel is detected for the CH_3 + O reaction, which produces H_2 + CO + H. Collisions of fast H atoms (2.2 eV) with H_2O and HF are studied to obtain complete vibrational and rotational state distributions. A strong alignment is observed in the H_2O antisymmetric stretch, indicating that a constrained, in-plane collision must occur.

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Department of Chemistry

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

Bersohn, R. **$95,000**
212-854-2192

Elementary gas-phase reactions, both bimolecular and unimolecular, are being studied by laser generation of reactants and detection of the reaction products by laser-induced fluorescence (LIF) and multiphoton ionization (MPI). Special emphasis has been placed on the generation of vacuum ultraviolet light to detect atoms. An intense source of 121.6-nm light has been developed and used to dissociate hydrides and probe the resulting hydrogen atoms. When O atoms react with acetylene, two possible reactions occur: O + HCCH → CH_2 + CO and O + HCCH → HCCO + H. The hydrogen atom kinetic energy, the CO rovibrational state distribution, and the absolute yield of each channel are being measured as a function of hydrogen isotope and vibrational excitation of the acetylene in the C–C stretch and the symmetric C–H stretch.

174. *Laser-Enhanced Chemical Reaction Studies*

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

This project employs extremely high-resolution IR 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 probed by measuring the time-dependent Doppler profile of the molecular IR transitions. The quenching of molecules with chemically significant amounts of vibrational energy has been investigated using this approach. The mechanism for this quenching process has been found to proceed via two distinct physical processes. In the first process, which occurs via soft, long-range collisions, the hot donor molecules exchange energy resonantly with the vibrational modes of the bath molecules, without any significant excitation of the bath rotational or translational motion. In the second process, hard, short-range repulsive collisions transfer roughly a few kT of internal vibrational energy from the hot donors to the translational and rotational motions of the bath molecules, without exciting the vibrational modes of the bath. Photodissociation dynamics which produce hot Cl atoms are also being monitored with quantum-state resolution using a new multiphoton ionization technique to investigate product Cl atom fragment recoil direction and velocity. These experiments are designed to probe the dynamics of such photodissociation reactions and to compare them with predictions based on known potential energy curves for the parent molecule.

175. *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 and energy transfer collisions involving reactive species important in combustion. Current emphasis in the project is on the reactions of the free radicals H, OH, and CH_3 with hydrocarbons. The research is part experimental and part computational. In the experiments, laser excitation methods are used to prepare initial quantum states of the molecular reactants, laser photodissociation of appropriate precursors generates the reactant free radicals and controls the collision energy, and laser spectroscopic methods are used to determine the quantum state distributions of the products. The experiments yield state-to-state absolute cross sections for the investigated reactions, and the dependence of these cross sections on the identity of the initial energy states of the reactants. The experimental measurements are complemented by theoretical calculations of the measured quantities as a way of developing detailed molecular-level understanding of the dynamics. The theoretical calculations are classical and semiclassical. Some of the work on the project involves the development of laser spectroscopic techniques for reactant state preparation and product state analysis, and the development of computational techniques for the theoretical calculations.

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Department of Applied and Engineering Physics

176. *Resonance Ionization Spectroscopy of Combustion Radicals*

Cool, T.A. **$92,920**
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 hydrocarbon flames. A new ultrasensitive detection technique, made possible with the advent of tunable VUV laser sources, enables the selective near-threshold photoionization of all radical intermediates in premixed hydrocarbon and chlorinated hydrocarbon flames. Three project objectives may be briefly summarized: (1) to measure concentration profiles of radical species in premixed hydrocarbon and chlorinated hydrocarbon flames for the development, refinement, and verification of chemical kinetic flame modeling calculations; (2) to develop resonance ionization detection schemes for in situ monitoring of flame radical concentration profiles; and (3) to perform resonance ionization spectroscopic studies of electronic states of combustion radicals to promote an improved understanding of the electronic structures of these species.

Department of Chemistry

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

Houston, P.L. **$98,007**
607-255-4303

State-resolved differential reaction cross sections provide perhaps the most detailed information about the mechanism of a chemical reaction, but heretofore they have been extremely difficult to measure. This project explores a new technique for obtaining differential cross sections with product state resolution. The three-dimensional velocity distribution of state-selected reaction products is determined by ionizing the appropriate product, waiting for a delay while it recoils along the trajectory imparted by the reaction, and finally projecting the spatial distribution of ions onto a two-dimensional screen using a pulsed electric field. Knowledge of the arrival time allows the ion position to be converted to a velocity, and the density of velocity projections can be inverted mathematically to provide the three-dimensional velocity distribution for the selected product. The main apparatus has been constructed and tested using photodissociations. The research will both develop the new technique and employ it to investigate methyl radical, formyl radical, and hydrogen atom reactions which are important in combustion processes. Specifically, the reactions of CH_3 with H_2 and H_2CO; of HCO with O_2; and of H with CH_4, CO_2, and O_2 will be characterized.

Laboratory of Atomic and Solid State Physics

178. Photochemical Dynamics of Surface-Oriented Molecules

Ho, W. **$110,000**
607-255-3555

The main objective of the project is to understand the dynamics of elementary chemical reactions by studying photochemical dynamics of surface-oriented molecules. In addition, the mechanisms of photon-surface interactions need to be elucidated. Experiments are being carried out to measure the translational energy distribution of the photoproducts by the time-of-flight (TOF) technique as a function of the photon wavelength, intensity, polarization, and pulse duration. The TOF mass spectrometry using the pulse counting technique has been assembled. Initial experiments have been carried out to study the photodesorption of O_2 and photoproduction of CO_2 from coadsorbed O_2 and CO on Pt(III) at 85 K using 620 nm and 310 nm pulsed light of about 100 fs duration. The photoyields have a very nonlinear dependence on the laser intensity. A mechanism involving photogenerated hot carriers is consistent with these initial results. These results are significantly using 355 nm pulsed light of about 7 ns duration. Two-pulse correlation mass spectrometry and second harmonic generation spectroscopy have been used to probe the time scale of photodesorption of O_2 from Pt(III).

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Atlanta, GA 30322

Department of Chemistry

179. Theoretical Studies of Combustion Dynamics

Bowman, J.M. **$92,313**
404-727-6592

The objectives of this research project are (1) to provide a detailed understanding of dynamical processes in gas-phase reactivity and energy transfer and (2) to examine reactions of relevance to combustion. The two major projects currently under way are (1) reduced dimensionality theory of diatom–diatom reactions and (2) resonances in recombination reactions. The reduced dimensionality quantum approach has been applied to a study of mode specific effects in the reactions $H + HOD \rightarrow OH + HD$ or $OD + H_2$ and $H + H_2O \rightarrow OH + H_2$. Both reactions have been studied experimentally, and strong mode specific effects were seen. Using a realistic potential surface, the branching ratios to form OH vs. OD were calculated and found to depend sensitively on whether the OD or OH stretch in HOD was initially excited. The calculated ratios are generally in very good agreement with experiment. Vibrational energies and wavefunctions have been calculated up to and above the dissociation energy of HO_2. Adiabatic energies have also been calculated along reaction paths for the dissociation products $H + O_2$ and $OH + O$, and these will be used to obtain rigorous variational transition theory unimolecular rate constants. The same approach is being taken in a study of the recombination reaction $C + H_2 \rightarrow CH_2$, using a new ab initio potential.

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

Lin, M.-C. **$94,000**
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 utilized to monitor these radicals using 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.

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Center for Computational Quantum Chemistry

181. *Theoretical Studies of Hydrocarbon Combustion Chemistry*

Schaefer, H.F., III **$100,000**
404-542-2067

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 unimolecular rearrangements of cyclobutyne to butatriene, of methylcarbyne to the vinyl radical, and of triplet vinylidene to acetylene. Other problems of current interest are the singlet-triplet energy separation in methylcarbene, the infrared spectra of benzyne and cyclopentadienylideneketene, the structure and fundamental vibrational frequencies of tetraethynylethylene, a joint theoretical-experimental effort directed toward the characterization of the *cis* $\tilde{a}\ {}^3B_2$ electronic state of acetylene, the ring opening conformational potential energy hypersurfaces of trimethylene and oxirane, the protonation of ethane, the very floppy structure of [7] circulene, and the highly strained [4] paracyclophane molecule. Research continues on structural and mechanistic aspects of the important $C_2H_5 + O_2$ reaction.

Department of Chemistry

182. *Photodissociation and Spectroscopy of Gas Phase Bimetallic Clusters*

Duncan, M. **$94,936**
706-542-1998

Metal cluster molecules composed of a variety of two component mixtures are produced in a molecular beam using laser vaporization methods. Electronic spectroscopy of bimetallic clusters such as Ag–Al, Ag–K and Ag–Li provides the opportunity to study heteronuclear metal bonding interactions. Photodissociation studies of larger (10–30 atoms) Bi–Cr, Pb–Sb, and so forth systems investigate the possibility of segregated bonding in metal mixtures. Additional photodissociation studies focus on metal–carbon mixed clusters known as metallocarbohedrenes ("met–cars"). Other electronic spectroscopy experiments probe metal dimers (e.g., Ag_2) with "physisorbed" rare gas atoms (Ar, Kr, Xe). These experiments provide vibrational frequencies and binding energies at cluster "surfaces". Overall, these various measurements of fundamental bonding interactions exemplified by metal clusters are used to evaluate their potential as models for bulk surface chemistry and catalysis.

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Division of Applied Sciences

183. *Fundamental Spectroscopic Studies of Carbenes and Hydrocarbon Radicals*

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

The project employs millimeter-wave rotational spectroscopy to obtain full definitive spectroscopic identification, accurate spectroscopic constants in the lowest vibrational states, and structures of highly reactive carbenes and carbon-chain radicals that are key intermediates in combustion processes. The HCCS radical, previously seen with low resolution in the optical region, was detected and, for the first time, the fine-structure and lambda-doubling constants in the ${}^2\Pi$ ground state were determined. An equilibrium structure of the cumulene carbene, H_2CCC, was determined to an accuracy comparable to which the stable molecule ketene, H_2CCO, is known by converting the measured ground state rotational constants of five isotopic species to equilibrium constants using vibration-rotation constants calculated ab initio. The structure derived from four isotopic species of the HCCCO radical and the large carbon-13 hyperfine structure observed in one isotopic species suggests that the HCCCO geometry differs significantly from the allenic structure predicted by theory. An entirely new spectrometer with a cell specially designed for the production of hydrocarbon radicals and carbenes by H atom abstraction from stable precursor molecules has been constructed. Detection of the known carbene molecules, c-C_3H_2 and H_2CCC, by H atom abstraction from allene and methyl acetylene demonstrates that carbenes are produced in detectable concentrations in reactions of either fluorine or chlorine atoms with hydrocarbon molecules containing multiple C–C bonds, implying that new carbenes may be detectable by this technique.

Department of Chemistry

184. *Laser Spectroscopy of Hydrocarbon Radicals*

Chen, P. **$155,000**
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. Tunable VUV laser photoionization of the methyl radical, CH_3, was coupled to ZEKE pulsed-field ionization (PFI) detection for that result.

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Department of Chemical Engineering

185. *Kinetics of Combustion-Related Processes at High Temperatures*

Kiefer, J.H. **$98,000**
708-996-3469

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 has defined much of the pyrolysis kinetics of ethylbenzene, pyridine, cyclohexene, toluene, benzene, 1,3-butadiene, and formaldehyde. A study of the dissociation of vinylacetylene led to the proposal of a new mechanism for acetylene polymerization, and this mechanism has now been employed in a successful modeling of both previous and new shock tube data on this reaction over a wide range of conditions. Current work involves the study of allene/propyne and methane pyrolysis, further investigation of falloff effects in large-molecule dissociation, and new measurements of vibrational relaxation and dissociation induction times in large molecules: norbornene, norbornadiene, and several others. Studies of halocarbon pyrolysis, carbontetrachloride, and the trifluorohalomethanes are in progress or completed.

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Department of Chemistry

186. *Theoretical Studies of Nonadiabatic and Spin-Forbidden Processes: Reactions and Spectroscopy of Radical Species*

Yarkony, D.R. **$90,000**
410-516-4663

This research program focuses on studies of spin-forbidden and electronically nonadiabatic processes involving radical species relevant to combustion reactions and combustion diagnostics. To study the electronic structure aspects of these processes, a unique and powerful system of electronic structure programs developed over the past nine years, the BROOKLYN codes, is employed. These programs address questions basic to the understanding of elementary combustion reactions not tractable using more standard quantum chemistry codes. Particularly relevant to this research program are the capabilities (1) to treat the spin-orbit interaction within the context of the full microscopic Breit–Pauli approximation, (2) to determine the interstate derivative couplings that result in the breakdown of the single surface Born–Oppenheimer approximation, (3) to locate surfaces of (actual–avoided) intersection of potential energy surfaces of the same symmetry, and (4) to locate the minimum energy point on the surface of intersection of two potential energy surfaces of different spin multiplicity. During the current performance period the capability to locate additional points on this crossing surface, for which an arbitrary number of internal coordinates are held fixed and the remaining coordinates are optimized to reduce the energy of the point on the surface of intersection, has been added. This algorithm will have significant impact on the ability to characterize spin-forbidden electronically nonadiabatic processes. These methods have been used to treat spin-forbidden processes relevant to combustion reactions and diagnostics. This work complements experimental efforts at Department of Energy funded laboratories. Motivated by concerns of the spin-forbidden predissociation $N_2O(X^1\Sigma^+) \rightarrow N_2(X^1\Sigma_g^+) + O(^3P)$, and longstanding interest in the atmospheric quenching reaction, $N_2(X^1\Sigma_g^+) + O(^1D) \rightarrow N_2(X^1\Sigma_g^+) + O(^3P)$ a study in which the crossing surfaces corresponding to the intersection of the lowest singlet surface of N_2O and the three triplet surfaces correlating with $N_2 + O(^3P)$ has been largely completed. In situ detection of nascent OH is an important problem in studies of combustion processes. To address the question, a study of the spin-forbidden photodissociation process $OH(X^2\Pi) + h\nu \rightarrow OH(A^2\Sigma^+) \rightarrow O(^3Pj) + H(^2S)$ was performed. This combined electronic structure–quantum dynamics study is unique in that all the relevant intersurface (nonadiabatic) interactions are determined using large-scale multiconfiguration self-consistent field–configuration interaction (MCSCF–CI) wavefunctions.

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Applied Physics Laboratory

187. *Q-Branch Raman Scattering and Modern Kinetic Theory*

Monchick, L. **$92,000**
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 proposes generalizing the quantum kinetic equations to include off-energy-shell scattering (incomplete collisions), mixtures with finite radiator–scatterer concentrations, and open shell molecules. The rarefied gas dynamics methods will then be applied to their solution. These will be more complex than methods devised for the Waldmann–Snider generalization because of the occurrence of the Fano collision operator rather than the on-energy-shell counterpart. It is further proposed to investigate 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

188. *Laser Spectroscopy and Dynamics of Transient Species*

Clouthier, D.J. **$69,367**
606-257-1790

Experiments are in progress to study the vibrational and electronic spectra and excited state dynamics of a number of transient sulfur- and oxygen-containing species. Supersonic jet techniques, including pyrolysis jet spectroscopy, reactive jet spectroscopy, and discharge methods are being used to generate and expansion cool the reactive species for studies of the electronic spectra. A time-of-flight mass spectrometer is under construction for resonance-enhanced multiphoton ionization studies of nonfluorescent states. High-resolution Fourier transform infrared (FTIR) spectroscopy has been used to obtain the first detailed information on the ground state vibrational energy levels of formyl chloride (HCOCl). Sub-Doppler intracavity dye laser spectroscopic studies of S_1 thioformaldehyde (H_2CS) have shown that there is extensive rotation-induced vibrational mixing in the high vibrational levels of the ground state. A variety of excited state S_1–T_1 and S_1–S_0 interactions have been characterized. Reactive jet spectroscopy, in which exothermic chemical reactions in the throat of a supersonic jet are used to create new reactive species, has been used to detect the FS_2 free radical for the first time. A rotational analysis of the spectrum is in progress. Other work is continuing on thiozone (S_3), tetrasulfur (S_4), sulfine (H_2CSO), and formic acid (HCOOH).

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemical Engineering

189. *Aromatics Oxidation and Soot Formation in Flames*

Howard, J.B. **$119,000**
617-253-4574 **(15 months)**

The oxidation of aromatics and the formation of soot in flames are being studied with emphasis on mechanisms and kinetics of the dominant reactions. The research includes experimental measurement of profiles of stable and radical gas species concentrations through the reaction zone of low-pressure one-dimensional flames. The oxidation of benzene by hydroxyl radicals and oxygen atoms is studied by introducing benzene as a fuel additive in hydrogen–oxygen flames whose OH and O concentrations profiles are experimentally known. A molecular-beam-sampling instrument, with online mass spectrometry and quartz probe sampling followed by GC, GC/MS, FTIR, and NMR analyses, is being used to study species including fullerenes and other high molecular weight compounds. Soot particles are being studied by solvent extraction techniques. Net reaction rates calculated from the data are used to test hypothesized reaction mechanisms. Probe samples from the soot-particle inception zone of a flame have been found to include high molecular weight compounds of up to 1000 amu and larger, containing alkyne, alkene, and alkane structures. Substantial quantities of fullerenes C_{60} and C_{70} can be produced in flames, and their relative amounts can be varied over a wide range by use of different flame conditions. Some of the fullerenes produced have not been observed previously.

Department of Chemistry

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

Field, R.W.; Silbey, R. **$145,000**
617-253-1489

Stimulated Emission Pumping (SEP) and Dispersed Fluorescence (DF) spectra of acetylene (C_2H_2) contain information about the rates, mechanisms, and specific energy flow pathways that govern short-time intramolecular vibrational redistribution (IVR), the evolution from regular to chaotic dynamics, and bond-breaking isomerization processes (such as acetylene↔vinylidene) on the electronic ground state potential surface. The combination of low resolution DF and high resolution SEP spectroscopy has proven to be unexpectedly powerful in revealing unambiguously interpretable short-time dynamics, now that all factors controlling the relative intensities of SEP transitions (especially Fermi and Coriolis perturbations and "axis-switching" effects) are fundamentally understood. Detailed analysis of relatively simple vibrational perturbations at low energy has been shown to account accurately and comprehensively for the complex, multistate interactions (and rapid IVR) that occur at high energy. SEP spectra of the formyl radical (HCO) sample the rotation-vibration structure and dissociation lifetimes of vibrational resonances on the electronic ground state potential surface that lie up to 10,000 cm^{-1} above the HCO $\rightarrow$ H + CO dissociation limit. These resonance lifetimes, which exhibit extreme vibrational mode specificity, are relevant to the efficiency of collisional stabilization of HCO.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

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

Westmoreland, P.R. **$81,000**
413-545-1750

Elementary reactions in combustion are studied using molecular-beam mass spectrometry (MBMS) of free-radical and stable species in flames, predicted reaction kinetics using quantum reaction theories, and tests of mechanisms using whole-flame modeling. Measuring and modeling oxidation and molecular-weight growth of C_3 hydrocarbon flames are the present emphases. Work in the second year has focused on mapping low-pressure propene flat flames: (1) a fuel-lean $C_3H_6/O_2/Ar$ flame at a fuel-equivalence ratio of 0.229, pressure of 30 Torr, and burner velocity of 57 cm/s (298 K) and (2) a fuel-rich $C_3H_6/O_2/Ar$ flame having equivalence ratio of 1.64, 35 Torr pressure, and 27.3 cm/s velocity. Profiles or single data points have been measured for 51 species from H-atom to naphthalene. The theoretical and modeling research predicts most profiles quite well. Further work aims to improve the relatively poor prediction for allyl and C_4^+ species as well as the absence of C_3H_xO species observed in the flame.

Department of Chemistry

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

Jackson, B.E. **$81,000**
413-545-2583

The goal of this study is to better understand metal-catalyzed reactions by examining the dynamics of several molecule–surface reactions. These systems are studied theoretically using recently developed time-dependent techniques. Much effort has been devoted towards treating the molecule quantum mechanically when necessary, and including the effects of finite surface temperature. The dissociative sticking of H_2, HD, and D_2 on Cu and Ni surfaces has been examined in detail. This is an important step in several reactions, and all molecular degrees of freedom can now be included either quantum mechanically or classically. The variation in reactivity with translational and internal molecular energy, the angle and site of surface impact, and the details of the molecule–metal interaction potential has been examined. Similar techniques are being used to study the Eley–Rideal mechanism for the recombinative desorption of adsorbed H, D, and Cl atoms with gas phase H and D atoms. Reaction cross sections and time-of-flight and final-state distributions can now be computed. The trapping of H_2 and other diatomics in weakly bound molecular precursors to dissociative adsorption is being examined.

University of Michigan
Ann Arbor, MI 48109

Department of Atmospheric, Oceanic, and Space Sciences

193. Energy-Transfer Properties and Mechanisms

Barker, J.R. **$117,649**
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, resonance-enhanced multiphoton ionization, and photothermal methods. "Half-collision" experiments involving dissociation of van der Waals molecules are also planned, in which final state distributions are monitored. The aim is to develop a workable theoretical model for predicting 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

194. Variational Transition State Theory

Truhlar, D.G. **$105,000**
612-624-7555

This project involves the development and applications of generalized transition state theory and multidimensional semiclassical tunneling approximations to chemical reaction rates. Several practical versions of variational transition state theory (VTST) and multidimensional semiclassical tunneling approximations have been developed, improved, and implemented. The methods have been applied to thermal rate constants, using transmission coefficients based on ground-state tunneling. Reliable methods have been developed for calculating chemical reaction rate constants and kinetic isotope effects that remain practical even for large molecules; they are being applied to reactions of polyatomic organic molecules. Another important aspect of this work is the development of algorithms for calculating reaction rates on the basis of electronic structure information. Both interpolation procedures and direct dynamics methods are under development. New methods for including anharmonicity and for modeling force fields have been developed as well. A general, portable computer program, POLYRATE, has been developed and is available from Quantum Chemistry Program Exchange and Computer Physics Communications Program Library, and a new version of this computer code, version 5.0, has recently been finished. The new version is improved in terms of its capabilities and its ease of use.

Departments of Chemistry and Physics

195. State-to-State Dynamics of Molecular Energy Transfer

Gentry, W.R.; Giese, C.F. **$106,000**
612-625-2894

The transfer of energy between molecules is an intimate part of virtually every dynamical process in chemistry. It is a particularly important aspect of combustion dynamics in the gas phase because the energy released in combustion reactions is large, and because the redistribution of that energy among the reacting molecules can profoundly influence their rates of reaction in subsequent steps. In this research project, molecular energy transfer phenomena are being studied at the most fundamental level possible by the observation of discrete changes of quantum states in single bimolecular collisions at precisely controlled kinetic energies. Current effort is directed toward the study of rotationally and electronically inelastic collisions of molecular free radicals, with NO serving as the prototype for such species. Rotationally resolved differential cross section measurements have now been carried out for both multiplet-conserving and multiplet-changing collisions of NO ($^2\Pi_{1/2}$) with Ar, yielding the first such detailed insight into the coupling of nuclear and rotational angular momentum in such systems. Concurrent theoretical analysis is also under way.

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

Chemical Science and Technology Laboratory

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

Cavanagh, R.R.; King, D.S. **$88,000**
301-975-2368

This research uses lasers and state-resolved, laser diagnostics 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 allows 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(111)] and of surface-state-driven chemistry on a semiconductor [NO/Si(111) 7 x 7]. Current work is directed at resolving competing reaction and relaxation mechanisms for the photoinduced chemistry of metal carbonyls on semiconductor and metal surfaces, comparing reaction mechanisms for $Mo(CO)_6$ following adsorbate- and substrate-localized excitations proceeding on Si(111) versus Pt(111).

197. *Kinetics Database for Combustion Modeling*

Herron, J.T.; Tsang, W. **$101,000**
301-975-2569

Measured and theoretically derived data on the rate constants for elementary reactions associated with combustion of fossil fuels are the basis for modeling and designing complex practical systems. The goal of this project is to provide a chemical kinetics database for combustion chemistry, and to make this database available to the user community through archival publications, reports, and databases for use on personal computers. Data evaluation is the core of the program. The strategy has been to start with methane and then add increasingly more complex fuel type molecules to the database, which now includes data for hydrocarbon molecules through C_4, oxygen containing species, unsaturated compounds, and related free radicals. Over 1300 elementary reactions are now included in the database. Current activities involve the further expansion of the work on unsaturated compounds with the evaluation of data on the reactions of phenyl. Expansion of the database to include alkynes, aromatic, and heterocyclic species will continue. Eventually the database will also need to provide data for nitrogen- and sulfur-containing species related to pollutant formation.

Physics Laboratory

198. *Spectroscopic Investigation of the Vibrational Quasi-Continuum Arising from Internal Rotation of a Methyl Group*

Hougen, J.T. **$75,000**
301-975-2379 **(14 months)**

This project studies the vibrational quasi-continuum in acetaldehyde because methyl groups are known promotors of intramolecular vibrational relaxation (IVR). It aims to understand (1) torsional motion below and above the barrier, (2) traditional vibrational states, and (3) interactions in levels with excitation of both kinds of motion. All torsion-rotation levels below the barrier are now essentially completely understood experimentally and theoretically. Levels above the barrier are qualitatively different and theoretical work on these using rotational energy surfaces has begun. Concerning traditional vibrational states, a CO_2 side-band laser jet-cooled spectrum showed that the "methyl rocking fundamental" near 920 cm^{-1} is in fact a combination band involving one quantum of the torsion. The presumed Fermi resonance partner band (C–C stretch at 867 cm^{-1}) has been recorded (laser diode, jet cooling) because Fermi resonance interactions are often invoked in explanations of IVR. Analysis of the room-temperature Fourier transform spectrum (764 cm^{-1} fundamental) is proceeding well, with some evidence of vibration–torsion interaction even at this low energy. The carbonyl stretch (diode) and its first overtone (CO_2 side-band) have been recorded under supersonic cooling conditions. Preliminary assignments for the overtone band indicate moderate interaction with the bath states.

University of New Orleans
New Orleans, LA 70148

Department of Chemistry

199. *Identification and Temporal Behavior of Radical Intermediates Formed during the Combustion and Pyrolysis of Gaseous Fuels*

Kern, R.D., Jr. **$83,000**
504-286-6847

Toluene serves as an important fuel additive and is known to produce large quantities of soot in fuel-rich combustion and in pyrolysis. Although the thermal dissociation has been investigated by a variety of shock tube techniques over a wide range of temperatures, total reaction pressures, and initial reactant concentrations, there remain several unresolved questions about the mechanism and disagreements in the experimental data. In order to formulate a comprehensive reaction mechanism to model the experimental data over a wide range of temperatures and pressures, it was necessary to perform falloff calculations to assess the relative importance of the two channels in the initial step (dissociation of toluene into phenyl and methyl radicals versus benzyl radical and hydrogen atom). Other key questions involve the decomposition rates of benzyl and phenyl radicals. A 28-step mechanism is successful in modeling reaction profiles reported in studies using time-of-flight mass spectrometry, laser schlieren densitometry, and atomic resonance absorption spectroscopy. It was concluded that the two initiation channels have equivalent rates in the temperature range of 1400–1600 K. However, the channel producing phenyl and methyl radicals is dominant at higher temperatures primarily because of the irreversibility of the phenyl radical decomposition channel.

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

Department of Chemistry

200. *The Energetics and Dynamics of Free Radicals, Ions, and Clusters*
Baer, T. **$92,000**
919-962-1580

The structure and energetics of free radicals, ions, and clusters are investigated by photoelectron photoion coincidence (PEPICO) and analyzed with ab initio molecular orbital and statistical theory RRKM calculations. Molecules are prepared in a molecular beam so that their internal as well as translational energies are cooled to near 0 K. The primary experimental information includes ionization and fragment ion appearance energies, and the ion time-of-flight (TOF) distributions. This study has led to a new method for determining whether a cluster ion, $(AB)_2^+$ has come from the corresponding neutral dimer $(AB)_2$, or whether it came from a dissociative ionization event of some higher order cluster. The results to date show that most cluster ions have been formed by dissociative ionization of higher order clusters, which indicates that most cluster ionization energies reported in the literature are only upper limits. This approach has also aided the study of free radicals which invariably are produced in the presence of pyrolysis contaminants. Dissociative ionization products (broad TOF peaks) can be clearly distinguished from direct ionization of the free radical itself (narrow TOF peaks).

University of Oregon
Eugene, OR 97403

Department of Chemistry

201. *Dynamical Analysis of Highly Excited Molecular Spectra*
Kellman, M.E. **$89,095**
503-346-4196

A dynamically based theoretical framework for analysis of highly excited vibrational states of polyatomic molecules is investigated. The goal is classification of molecular dynamics from experimental spectra. Three research areas are explored with application to species and/or methods of interest in combustion processes. The first is bifurcation analysis applied to spectra of molecules with classically chaotic dynamics involving many 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. The second area is semiclassical analysis of quantum spectra corresponding to the bifurcation analysis of many coupled oscillator systems. The third area 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

202. *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. **$99,000**
814-865-7242

Research is being conducted to elucidate the basic mechanisms by which metal alloys, metals on oxide supports, and metal oxides serve as catalysts, and to ascertain the role that degree of aggregation, structure–physical geometry, electronic states, and charge of these materials play in governing their catalytic reactivity. This includes (1) investigation of the reactivity of metal alloys and a determination of the influence of their charged state; (2) determination of the kinetics of association (adsorption) of various reactants and unraveling the mechanisms of certain oxidation reactions known to be catalyzed on metal cluster alloys, and a study of the role of coclustered oxides and also of the oxides alone; and (3) thermochemical measurement of the adsorption of gaseous species onto alloy and metal oxide cluster systems. In particular, research is being conducted with metal–metal oxide clusters involving their interactions with ammonia, benzene, methanol and ethanol, CO, H_2, and NO_x. Additionally, in terms of sorting out the charge-reactivity relationships for metal alloys, reactions of various aluminum clusters containing substituted atoms such as Cu, Mg, Fe, Ni, Zn, Mg, Mn, Co, and Ti are being pursued. Finally, as a follow-up to the recent discovery of metallo–carbohedrenes (Met–Cars), their potential catalytic role in many of the above-mentioned reactions will be investigated.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemistry

203. *Spectroscopy and Reactions of Vibrationally Excited Transient Molecules*
Dai, H.-L. **$110,000**
215-898-5077

Radicals, due to their short lifetimes and low concentrations, present great challenges for kinetic studies and spectroscopic characterization of structures. This is particularly true for studies related to vibrational levels, since vibrational transitions are usually weak and require a high concentration of species for detection. By dispersing fluorescence from an electronic excited state induced by laser excitation, the rotation–vibration levels in the electronic ground state can be detected. Since electronic transitions are usually much stronger than vibrational transitions, the sensitivity is much improved. The use of a step-scan FT spectrometer to disperse the laser-induced fluorescence allows sensitive detection of the fluorescence with high resolution over a wide energy range. Furthermore, the dispersed fluorescence spectra can be recorded with fast time resolution. The advantages of the step-scan FT spectrometer have been clearly demonstrated in a study of methylene (CH_2). A spectrum over 4000 cm^{-1} wide, covering the vibrational levels of the lowest singlet state between 4000 and 8000 cm^{-1}, at 0.5 cm^{-1} resolution, can be taken from a sample containing only 10 mTorr CH_2 in just several hours of laser operation. The CH_2 lifetime under the experimental condition is only a few hundred nanoseconds. The spectrum can be taken with a 50-ns resolution. Time-resolved dispersed fluorescence spectra following the excitation of a single rovibronic level allow energy transfer and reaction pathways and rates to be deduced and a much better understanding of the kinetics of this important transient species in combustion.

204. Spectroscopy and Reaction Dynamics of Collision Complexes Containing Hydroxyl Radicals

Lester, M.I. **$123,900**
215-898-4640

The aim of this program is to rigorously characterize the intermolecular potential energy surface between the hydroxyl radical and various collision partners. Most recently, several additional intermolecular vibrational levels of the excited electronic state correlating with OH A $^2\Sigma^+$ (v = 0) + Ar have been identified in fluorescence excitation spectra and confirmed by hole-burning experiments. The OH–AR levels identified include the lowest level, an excited bend with a lower degree of stretching excitation than previously reported, as well as levels with two quanta of bending excitation. This data has been used to refine a semiempirical potential for OH A $^2\Sigma^+$ (v = 0) + Ar. The vibrational energies of the bound states computed for the adjusted potential agree to within 1% of the experimental values. Predissociative levels of electronically excited OH–AR that lie as much as 350 cm^{-1} above the first dissociation limit have also been observed by laser-induced fluorescence. Complexes prepared in these levels undergo rotational predissociation by converting excess OH rotational excitation into relative translational energy of the fragments. The metastable level energies, lifetimes, and product rotational distributions have been evaluated. These measurements will enable the short-range anisotropy of the OH A $^2\Sigma^+$ + Ar potential to be determined with unprecedented detail.

Princeton University
Princeton, NJ 08544

Department of Chemistry

205. Analysis of Forward and Inverse Problems in Chemical Dynamics and Spectroscopy

Rabitz, H.A. **$102,000**
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 interrelationships 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 indirectly 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 iterative 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. Both forward as well as inverse simulations are being performed.

Department of Mechanical and Aerospace Engineering

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

Dryer, F.L. **$89,000**
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}–5 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.

207. *Aromatic-Radical Oxidation Kinetics*

Glassman, I.; Brezinsky, K. **$90,197**
609-258-5199

The research effort during the past year has focused on developing an explanation for the very important discovery that there are anomalously high CO_2 concentrations observed early in the reaction sequence of the oxidation of cyclopentadiene. To explain this observation, a number of plausible mechanisms have been developed that now await experimental verification. One experimental technique for verifying mechanisms, used successfully in previous DOE-supported research, is to probe the reacting system by perturbing the radical concentrations. Two forms of chemical perturbation of the oxidation of cyclopentadiene begun during this past year are (1) the addition of NO_2 and (2) the addition of CO to the reacting mixture. Some experimental difficulties associated with the perturbation technique are currently being resolved.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemical Engineering

208. *Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges*

Fontijn, A.
518-276-6508

The goal of this project is to provide accurate data on the temperature dependence of the kinetics of elementary combustion reactions in order to gain a better fundamental understanding and predictive ability of the chemistry involved, and to serve combustion modelers. Experimental measurements are made in high-temperature photochemistry (HTP) reactors, which allow observations on single reactions in isolation in the 300 to 1800 K range. Studies of a series of reactions of ground-state oxygen atoms with H_2, D_2, the C_2-hydrocarbon molecules, chlorine-substituted ethylenes, propylene, the four isomeric butenes, 1,3-butadiene, benzene, and hydrogen chloride have been completed as has that of the reaction between ground state hydrogen atoms with hydrogen chloride. A technique for studying chlorine atoms at high temperatures has been established and is being applied to reactions with H_2 and hydrocarbons. A method for predicting rate coefficients over wide temperature ranges for oxygen-atom reactions with olefins has been developed. In addition to conventional transition state theory, it uses estimated data for H abstraction. Good agreement with experiment has been obtained.

Rice University
Houston, TX 77251

Department of Chemistry

209. *Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals*

Curl, R.F., Jr.; Glass, G.P. **$89,000**
713-527-4816

This research is directed at the detection, monitoring, and study of the chemical kinetic behavior by IR absorption spectroscopy of small free-radical species thought to be important intermediates in combustion. 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.

210. *Supersonic Bare Metal Cluster Beams*

Smalley, R.E. **$110,000**
713-527-4845

Transition metal clusters of size from one through several hundred remain the prime focus of this work because of their importance in catalysis. Studies of the bare metal clusters in supersonic beams and levitated in magnetic traps continues. Photoelectron spectral measurements of the mass-selected negative cluster ions were found to correlate well with the measured reactivity of the clusters toward dissociative chemisorption with molecular hydrogen and nitrogen. The magnetic levitation apparatus of this project was upgraded with a much larger magnet that will soon provide more extensive measures of clusters to much larger sizes. Extensive research is also in progress to produce such metal clusters trapped in fullerene cages and in fullerene tubes. When partially opened, these fullerene-encased metal clusters may be useful as a new class of catalysts.

University of Rochester
Rochester, NY 14627

Department of Chemistry

211. *Low-Energy Ion–Molecule Reactions and Chemi-Ionization Kinetics*

Farrar, J.M. **$91,000**
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 transfer reactions of O^- with small molecules including NH_3, H_2O, and HF. F^- product kinetic energy distributions in the O^- + HF system show structure attributable to the formation of OH in vibrational states $v' = 0, 1$, and 2. The energy dependence of the product vibrational state distribution shows that at the highest collision energies, reactive trajectories are influenced by the attractive well, but also by the effect of the short-range repulsion. The data also provide the first evidence that the reaction takes place through an intermediate $[OHF]^-$ complex. Rotationally inelastic collisions show evidence for a rotational rainbow in the HF product distribution. The measurement of cross sections for reactive as well as nonreactive collisions has allowed the application of inversion models that determine opacity functions for chemical reaction. A series of experiments in which vibrationally excited molecules are prepared by laser excitation is planned.

212. *Spectroscopic Probes of Vibrationally Excited Molecules at Chemically Significant Energies*

Rizzo, T.R. **$79,000**
716-275-2304

This project involves the application of multiple-resonance photofragment spectroscopy for investigating energy transfer and dissociation of the dynamics of highly vibrationally excited molecules. Two major goals of this work are (1) to provide information on potential energy surfaces of combustion-related molecules at chemically significant energies and (2) to test theoretical modes of unimolecular dissociation rates critically via quantum-state resolved measurements. Traditional spectroscopic techniques provide information about the low-energy regions of the surface near a molecule's equilibrium geometry; however, during chemical reaction, molecules sample highly excited regions of the surface. Several new multiple-laser techniques have been developed that allow access to the potential surface at chemically significant energies and at the same time eliminate thermal spectral congestion. One such technique, IR-optical double resonance spectroscopy, has been applied to interrogate the dissociation dynamics of H_2O_2 and HN_3 at the level of individual quantum states, providing stringent tests of statistical theories of unimolecular reactions as well as the accuracy of ab initio potential energy surfaces. Current efforts are under way to extend this approach to investigate the potential energy surfaces of small free radicals.

University of Southern California
Los Angeles, CA 90089

Department of Chemistry

213. *Reactions of Carbon Atoms Using Pulsed Molecular Beams*

Reisler, H. **$95,000**
213-740-7071

The reaction dynamics of carbon atoms in their ground and first excited states 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 the second reactant. Products are monitored by LIF, and E,V,R,T product distributions are determined. An example of an elementary reaction that is currently under investigation is the reaction of carbon with nitrous oxide. The CN products, which are observed under nearly single-collision conditions, are produced with an inverted vibrational distribution and "hot" rotational distribution. The NO products, on the other hand, are produced mainly in v=0, but they are rotationally hot. The results suggest that the reaction exhibits predominantly direct character while influenced by the attractive force towards a CNNO intermediate. Current efforts are concentrated in studying the role of translational energy in this and other carbon atom reactions. In addition, endothermic reactions of atomic carbon with vibrationally excited hydrocarbons are being investigated.

214. *Reactions of Small Molecular Systems*

Wittig, C. **$140,000**
213-740-7368

This research is concerned with detailed aspects of reactions involving small polyatomic systems. Reaction cross sections are obtained from near-threshold to collision energies as high as 21,000 cm^{-1} for reactions of H atoms with N_2O, NO_2, and O_2. In addition, product V,R,T excitations are thoroughly mapped throughout the accessible energy ranges. In the past (i.e., $H + CO_2 \rightarrow OH + CO$), these measurements have shown marked variations of reaction cross-section vs. collision energy at energies where statistical theories fail and product excitations are known to be nonstatistical. Experiments using Rydberg time-of-flight spectroscopy will exploit the VUV/TOF method. In addition to photodissociation studies (C_2H_2 and HCN), bimolecular reactions are amenable to this technique, and are stressed. Several reactions will be examined that give H atoms: (1) $O(^1D) + H_2 \rightarrow OH + H$ and $F + H_2 \rightarrow HF + H$ will be used to test the machine, (2) $OH + CO \rightarrow CO_2 + H$ where a high-resolution H-atom kinetic energy distribution can yield a complete mapping of CO_2 internal excitation, and (3) $NH(a^1\Delta) + NO \rightarrow N_2O + H$. Further experiments involve overtone species which are then photodissociated to yield monochromatic hydrogen atoms at lower energies than are available by direct photodissociation. This can bridge the gap between hot-atom experiments at high center-of-mass kinetic energies and the lower energy collisions that correspond to thermal systems.

Stanford University
Stanford, CA 94305

Department of Mechanical Engineering

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

Hanson, R.K.; Bowman, C.T. **$145,000**
415-723-1745

This program involves two complementary activities: (1) development and application of continuous wave (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 radical–molecule and radical–radical reactions relevant to combustion. Species under current investigation in the spectroscopic portion of the research include NO and CH_3; this has necessitated the development of a unique intracavity frequency-doubling system for the CW laser which operates at wavelengths in the range of 210–230 nm. Reactions under study include unimolecular decomposition of ethane ($C_2H_6 \rightarrow 2CH_3$), and the bimolecular methyl reactions $CH_3 + CH_3 \rightarrow C_2H_4 + H_2$ and $CH_3 + CH_3 \rightarrow C_2H_5 + H$.

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

Department of Chemistry

216. *Ionization Probes of Molecular Structure and Chemistry*
Johnson, P.M. **$87,000**
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 photoelectron spectroscopy, and multiphoton fluorescence spectroscopy provide sensitive tools for examining the excited state structure of molecules and how they undergo various processes such as dissociation and autoionization. These methods also provide means of the detection of minute quantities of molecular species in difficult environments. One of the primary objects of study is carbon dioxide. The selectivity of multiphoton ionization techniques for photochemically stable states enables the discrimination of detailed spectral structure from a continuous background and a better understanding of the molecule's electronic structure and photodissociation. Multiphoton photoelectron spectroscopy explores the mechanisms of ionization and autoionization in intense laser fields, and multiphoton fluorescence experiments reveal the end products of dissociative processes. Experiments on the photochemistry of homogeneous and heterogeneous clusters of aromatic molecules such as benzene use ionization techniques to elucidate the nature of the photoproducts. A primary tool in these studies is threshold ionization spectroscopy, which provides high resolution ion vibrational spectra. A version of this method which incorporates mass resolution is being developed and applied to the photochemical reactions of mixed clusters such as benzene-O_2.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

217. *Thermochemistry of Transition-Metal Clusters*
Armentrout, P.B. **$82,845**
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. Thermodynamic information on bare metal clusters (cations and neutrals) will be obtained by collision-induced dissociation (CID) and photodissociation experiments. Progress to date includes complete CID measurements of the binding energies of the cluster ions of titanium, iron, cobalt, nickel, and chromium and preliminary work on vanadium. Construction of the cluster ion photodissociation spectrometer is completed. Photodissociation of Co_2^+, Co_3^+, Ti_2^+, V_2^+, and Fe_2^+ has been studied and dissociation thresholds determined. Future work planned includes the examination of the unimolecular decay kinetics of energized clusters and studies of the reactions of cluster ions with species such as H_2, O_2, N_2, CO, CO_2, NH_3, and hydrocarbons.

University of Washington
Seattle, WA 98195

Department of Chemistry

218. *Atomic Probes of Surface Structure and Dynamics*
Jonsson, H.; Heller, E. **$109,000**
206-685-1804

Recent experiments have demonstrated that atomic beam scattering is a very powerful tool for in situ studies of kinetic processes at surfaces, such as diffusion, annealing, and growth. Calculations are being performed of He atom scattering to relate the results of atomistic computer simulations of these processes to the experimentally measured intensities. The scattering calculations enable close comparison of simulation and experiment, and strengthen the microscopic interpretation of the measurements. Atomic beam scattering (in particular He atom scattering) is, furthermore, a unique and powerful tool for the study of "fragile" surfaces such as rare gas overlayers and Langmuir films. Calculations of He atom scattering from overlayers (Xe and CO) on metal surfaces (Pt, Ag, Cu) are being performed to characterize, by comparison with experimental data, the electron density at the surface and to study superlattice structure. Methods are also being developed that will allow faster and more accurate atom scattering calculations, both elastic and inelastic. The goal is to describe the scattering semiclassically, not only the diffractive scattering, but also the selective adsorption resonances. The method, "Cellular Dynamics", has been shown to give excellent results even for chaotic motion over long times.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemistry

219. *The Photodissociation and Reaction Dynamics of Vibrationally Excited Molecules*
Crim, F.F. **$114,000**
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.

220. *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 can help in the development of absorption diagnostics in research in combustion kinetics. A variation of resonant two-photon ionization (R2PI) will be explored in which tunable ω_{IR} excites the radical vibrationally and ω_{UV} selectively ionizes only the vibrationally excited molecules. Development of the IR + UV R2PI experiment is under way. In the meantime, optical R2PI and pulsed field ionization (PFI) detection has been used to obtain new vibrational spectra of unstable species such as the benzyl and phenylsilane cations. In benzyl, a great deal has been learned about the vibronic coupling mechanism in the mixed 1^2A_2-2^2B_2 system near 450 nm by projecting the mixed states onto the manifold of cation vibrational states. In phenylsilane$^+$, the sixfold barrier to internal rotation of the silyl group is small ($V_6 = +19\ \mathrm{cm}^{-1}$). The mechanisms of coupling of torsional states with vibration, overall rotation, and other electronic states is beginning to be understood. In addition, a new model of internal rotation in aromatic compounds based on natural resonance theory is being developed.

Atomic Physics

California State University, Fullerton
Fullerton, CA 92634

Department of Physics

221. *Few-Body Coulomb Systems*
Feagin, J.M. **$61,500**
714-773-3366

Wannier theory has been developed for the four-particle threshold breakup of H^- by positron impact. The escape of two electrons and a positron introduces a new feature into the Wannier formalism: multiple threshold configurations each with a characteristic energy dependence for excitation. Because the center of charge and center of mass are displaced from one another, the system requires a distinction to be drawn between configurations with identical potential energies but different excitation energies (i.e., between Coulomb correlations and Coulomb dynamics). In a related project, schemes for propagating two-electron wavepackets in helium and H^- directly in time are being investigated. Particular attention is paid to the proper representation of the Coulomb singularities within a finite lattice approximation. A time-dependent lattice wavepacket permits the computation of correlation functions and, for example, system energy spectrums including resonance widths. Finally, a model of resonant transfer and excitation in a crystal channel is being improved to better represent the symmetries and the temperature of the channel and compare with new measurements.

Clark Atlanta University
Atlanta, GA 30314

Department of Physics

222. *Studies of Photon and Electron Interactions with Atoms and Ions*
Msezane, A.Z. **$84,000**
404-880-8798

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, and the possible use of Padé approximations to recompute the elastic and inelastic cross sections have been studied.

University of Colorado
Boulder, CO 80309

Joint Institute for Laboratory Astrophysics

223. *Near-Resonant Absorption by Atoms in Intense Fluctuating Fields*
Smith, S.J. **$27,000**
616-347-8815

Experimental investigations are conducted of the behavior of atoms coherently excited by a near-resonant, intense laser field on which statistically well-characterized and well-controlled phase/frequency fluctuations have been imposed. In current studies of non-Markovian processes, a two-level system (the $3S_{1/2}$–$3P_{3/2}$ transition in optically pumped atomic sodium) is driven with a strong pump field(s) and by a weak probe field that is a time-delayed replica of the pump(s), these fields being derived from the same noise-modulated primary laser beam. One now completed study involves measurement of the transmitted intensity of the probe (using one pump) as a function of delay time. Amplification of the probe is observed for time delays comparable to the lifetime of the upper level, in contrast to absorption at other moderate delays. A study in progress utilizes two counter-propagating pump beams and a weak probe in a four-wave-mixing (FWM) configuration. A phase conjugate (signal) is generated, propagating counter to the probe. The signal intensity is measured as a function of probe delay and pump power. Use of an atomic beam minimizes the problem of averaging over velocity groups in comparing measurements with recent theories of non-Markovian processes.

Department of Physics

224. *Physics of Correlated Systems*
Greene, C.H. **$105,000**
303-492-4770

A variety of atomic systems displaying correlations or nonseparable quantum behavior will be investigated theoretically. A major effort is being undertaken to find the most efficient theoretical description of open-shell atomic systems, emphasizing atoms heavier than argon, and including the transition metals and their negative ions. The possibility of a nearly ab initio multichannel quantum defect description of these complex systems will be investigated, making use of recent rapid progress in understanding electron correlations in atoms with a few valence electrons. New general methods will be investigated and detailed calculations will be performed for selected prototype systems including the halogen atoms. A second part of this work is the investigation of particle–particle correlations in comparatively simple few-body atomic systems, such as H^{--}, Ps_2, and high doubly excited states of He and H^- approaching the Wannier threshold region. For these systems adiabatic hyperspherical coordinate methods will be used primarily. These should help to sort out the qualitative dynamical features such as the major decay and excitation pathways, as well as to identify quantitative resonance energies in these systems.

University of Connecticut
Storrs, CT 06269

Department of Physics

225. *Experiments in Ultracold Collisions*
Gould, P.L. **$87,781**
203-486-2950

The goal of this project is to investigate atomic collisions at extremely low energies (i.e., temperatures below 10^{-3} K). The interest in these ultracold collisions is two-fold. On the one hand, collisions at such low energies are qualitatively different from those at higher energies. Unique features include the large deBroglie wavelength of the colliding atoms, the importance of long-range attractive potentials, and the possibility of spontaneous decay during a collision. On the other hand, most applications of laser-cooled atoms will require high density where collisions play a limiting role. Understanding collisions is therefore crucial for further progress. Ultracold atoms are prepared using laser cooling techniques. Rubidium atoms are cooled, compressed, and confined in a magnetooptical trap using diode lasers. Measurements of properties (e.g., temperature) of the trapped atom sample are being performed as these are necessary for interpretation of collision experiments. Because a variety of collisions can occur in the trap (some of which lead to ejection from the trap), experiments are under way to directly detect the products of specific collisions such as those that change hyperfine state or fine-structure state. Detection will be by state-selective laser ionization. Experiments involving collisions of atoms in highly excited Rydberg states are also planned. Reactions to be studied include associative ionization, Penning ionization, and excitation transfer.

226. *Plasma Density and Field Effects on Atomic Reactions*
Hahn, Y. **$83,523**
203-486-4469

Theoretical study of the effects of plasma environment on atomic collision processes in fusion plasma is being continued. A crictical review of the previous work in this field was completed, specifically on the pressure broadening of spectral lines. A general theory of the plasma effects on atomic processes is formulated that includes both the effects of ionic and electronic microfields, in terms of the effective time-dependent plasma potentials (EPP). The detailed structure of EPP that depend on the plasma density and temperature was examined, and an exact solution of the atomic states in this EPP is obtained in limited basis functions covering a few low-lying states. Reliable approximation procedures are being developed to simplify the method of solution, so that the theory may be applied to high Rydberg states of interest. The plasma-distorted (dressed) wave functions are then used to evaluate the radiative recombination cross sections in hydrogen plasma. Eventually, the theory will be extended to the direct as well as resonant processes involving muliply charged ions of the carbon plasma. Along with the EPP theory, the conventional rate equation approach to plasma modeling is being examined in terms of the Fokker–Planck equations, again for the hydrogen plasma. The relevance of the EPP approach to multimode variable polarization laser–atom interaction is pointed out. Study of doubly excited resonance states of ions and atoms with two valence electrons is being conducted, adopting the pseudopotential and HF procedure.

Cornell University
Ithaca, NY 14853

Nuclear Science and Engineering Program

227. *Interactions of Highly Charged Ions with Atoms at keV Energies*
Kostroun, V.O. **$180,000**
607-255-4991

The goal of this experimental project is to investigate fundamental processes in low-energy, very highly charged ion-atom (ion) collisions at kinetic energies typical for controlled thermonuclear fusion plasmas. Processes studied include single, double, and multiple electron capture by the projectile, target ionization, and different decay modes of the projectile excited states formed in collisions. The data obtained are useful in modeling plasma behavior and contribute to a general understanding of atomic collisions. Of particular interest are Ar^{q+} on H_2, He, Ar, etc. collisions at 30–100 qeV ($8 \leq q \leq 16$) incident energy. The Ar^{q+} were produced by the Cornell superconducting solenoid, cryogenic Electron Beam Ion Source (CEBIS). Extracted ions were charge state analyzed, decelerated, and crossed with a gas target. In different experiments, the absolute total cross sections for one- and two-electron transfer, high-resolution projectile energy gain spectra, and angular distributions were obtained for different collision systems. Measured Ar^{8+} on Ar energy gain spectra and angular distributions for the 7+ projectile final charge state are not consistent with the common interpretation of the sharp peaks observed in the energy gain spectrum as due to single electron capture into definite final states of the projectile.

Georgia Institute of Technology
Atlanta, GA 30332

School of Physics

228. *Statistical Fluctuations in Lasers*
Roy, R. **$90,139**
404-894-5265

The mutual coherence and phase dynamics of spatially coupled solid-state lasers has been investigated theoretically and experimentally in the laboratory. The measurement of mutual coherence is made using a video camera to observe the visibility of the fringes formed when the light from the two lasers is superposed. Phase locking between the two lasers is observed when their electric fields overlap by as little as one part in a million. The effect of phase fluctuations due to spontaneous emission is included in the theoretical model. The effect of four-wave mixing between two strong pump fields at distinct frequencies propagating in an optical fiber has been studied both theoretically and experimentally. The optical energy of the pump waves is redistributed into sidebands generated within the fiber due to four-wave mixing. The exchange of energy between pump waves and sidebands has been shown to be periodic or chaotic, depending on the strength and detuning of the waves. A new conservation law for the power of the waves at the pump and sideband frequencies was analytically derived and experimentally verified. The spatial evolution of the sideband amplitudes will also be investigated.

Harvard University
Cambridge, MA 02138

Harvard-Smithsonian Center for Astrophysics

229. *Theoretical Investigations of Atomic Collisions*
Dalgarno, A. **$146,000**
617-495-4403

Cross sections for multiphoton Raman and Rayleigh scattering and multiphoton ionizaton of hydrogen and cesium have been calculated using a formulation expressed in terms of solutions of inhomogeneous differential equations. Collisions at ultralow temperatures are under study. The extreme sensitivity to the interaction potentials at large distances has been demonstrated. Methods for the accurate prediction of long-range interactions are under development. The ejection of two electrons by a single high-energy photon has been investigated and an apparent contradiction in the literature has been resolved. Calculations are in progress for H_2. Calculations of cross sections for charge transfer of N^{++} in He have been completed.

Kansas State University
Manhattan, KS 66506

Department of Physics

230. *Atomic Physics of Strongly Correlated Systems*
Lin, C.D. **$146,000**
913-532-6786

This project is directed at the understanding of the three-body systems in atoms and molecules, including the calculations of excitation and rearrangement collision cross sections. Mass-weighted hyperspherical coordinates are used to solve the Schrodinger equation in the adiabatic approximation where the angular equations are solved by higher-order finite-element methods. The photoabsorption spectra of two-electron atoms and ions are calculated using the hyperspherical close-coupling method, and the resonance positions, widths, and other parameters are evaluated. The close-coupling method based on the two-center atomic orbitals is applied to obtain electron transfer cross sections from laser-excited target atoms and examine the dependence of probabilities on the magnetic quantum numbers of the target atom. Two-electron transition processes in ion–atom collisions are also being investigated.

231. Atomic Physics with Highly Charged Ions
Richard, P. **$1,970,000**
913-532-6783

The project will (1) study inelastic collision phenomena involving highly charged projectile ions and (2) interpret spectral features resulting from these collisions. Highly charged beams are provided at low velocities by the cryogenic electron beam ion source (CRYEBIS) and at high velocities by the 6-MV tandem Van de Graaff accelerator and recently installed superconducting linac. At low velocities, electron capture by multiply charged projectiles, up to O + 8, Ar + 17, and Xe + 44, on rare gas targets are being studied. Quantities measured include (1) capture cross sections, differential in transverse momentum transfer and in the final charge states of projectile and recoil; (2) the electronic energy release in the reaction, deduced from the recoil longitidunal momentum after the collision; and (3) characteristic X radiation emitted at the end of the cascading chain, following capture into excited states. Capture from the ground state 3s and laser excited 3p state of sodium has been measured, and a Rydberg electron sodium target is under construction for extension of these studies. All capture data are used in a joint theoretical–experimental collaboration to formulate models for and test calculations of single- and multiple-electron transfer. At high velocities, processes in which quasi-free electrons act as independent ionizing and exciting agents are being studied. The role of the electron–electron interaction in the mutual excitation of projectile inner-shell and target outer-shell electrons is studied using high-resolution, zero-degree electron spectroscopy, and is being extended through longitudinal momentum transfer spectroscopy, using a cooled gas jet. The elastic scattering of quasi-free target electrons in the potentials of highly charged projectile ions is being measured and reveals marked diffraction structures that are amenable to a theoretical description using a partial wave analysis and the impulse approximation. Additional projects include study of fragmentation patterns of molecules struck by fast, highly charged ions, and of the interactions of slow and fast, highly charged ions with surfaces and fullerenes. Theoretical work on all of the above projects is being conducted.

University of Kansas
Lawrence, KS 66045

Department of Chemistry

232. Atomic Physics in Strong Fields
Chu, S.-I. **$88,000**
913-864-4094

New nonperturbative theoretical formalisms and practical computational techniques are being developed for ab initio comprehensive investigation of several intense-field atomic and molecular multiphoton and nonlinear dynamical processes of current significance. Included are: (1) Development of the complex-scaling Fourier grid Hamiltonian method for accurate and efficient treatment of many-body resonance states (energies and widths) without the need of using the conventional basis set expansion technique. The method is being applied to the exploration of laser-induced chemical bond "hardening" and stabilization and trapping of small molecules (H_2^+) in intense laser fields (a novel high-intensity phenomenon recently uncovered). (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 and superintense laser fields. (3) Nonperturbative study of multiple high-order harmonic generation of atoms in intense laser fields via acceleration framework.

University of Kentucky
Lexington, KY 40506

Department of Physics and Astronomy

233. The Coherent Evolution of Weakly Bound States in Collisions and Fields
Cavagnero, M.J.; **$165,000**
Harmin, D.A. **(18 months)**
606-257-6733

Physical processes governed by the dynamics of weakly bound atomic electrons are investigated. The first of these involves the response of a Rydberg atom to a time-dependent electric field, as utilized in the experimental technique of selective field ionization. This study involves interference effects associated with the coupling of overlapping Stark manifolds in a novel version of the multilevel Landau–Zener effect. A second investigation centers on the time evolution of Rydberg states in distant collisions with singly charged ions. Analyzed from a frame that rotates with the internuclear axis, this problem is equivalent to studying the response of an atom to perpendicular electric and magnetic fields that vary with time. Both of the above investigations focus on the role of the quantum defects of alkali atoms in moderating population transfer among Rydberg states. Finally, the properties of weakly bound electrons in a dynamic dipole field are being studied for eventual application to a theory of muon and antiproton capture in atoms.

234. Coherent Excitation of Autoionizing Resonances
Martin, N.L.S. **$86,000**
606-257-5840

Coherent excitation, by electron-impact, of autoionizing levels of the Group II B transition-metal atoms is being studied. An electron–electron coincidence technique is used to observe interference effects caused by the coherent excitation of overlapping known $J = 1$ odd parity levels and previously undetected $J = 0,2$ even parity levels. The effects vary rapidly with ejected-electron energy due to the resonant nature of the autoionization process. Experiments are at present being carried out in Cd at small scattering angles, in the plane wave Born approximation regime, in order to investigate the spectroscopy of the optically forbidden $J = 0,2$ even parity levels. High-quality (e,2e) spectra have been obtained for ejected-electron directions parallel to, and at the magic angle away from, the momentum transfer axis. The former experiments yield the $J = 1,0$ plus $J = 1,2$ interference cross terms, while the latter experiments isolate the $J = 1,0$ terms. The data agrees well with theoretical calculations provided that a significant extra phase is incorporated in the scattering amplitudes. The source of this extra phase is not understood and is currently being investigated. Once the small scattering experiments in Cd, and their analysis, have been completed, spectra measured at larger scattering angles will be obtained to determine the relative phases and magnitudes of the complex excitation amplitudes of J = 0,1,2 levels. The experiments will then be repeated in Zn and Hg; these have similar atomic structure to Cd, but the alignment of the even and odd parity levels is thought to be different in all three elements.

University of Louisville
Louisville, KY 40292

Department of Physics

235. *Hydrogen Atom and Molecule Collisions*
Kielkopf, J. **$84,000**
502-588-5990

The work concentrates on investigating the interaction between atomic hydrogen and other atoms when the emission or absorption of a photon is part of a collision process. A focused YAG laser pulse produces breakdown in high-pressure molecular hydrogen. The spectrum of the laser-generated plasma reveals transient states of the excited hydrogen atom interacting with protons. Microseconds later, the cooler atomic gas is a target for tunable VUV laser spectroscopy of neutral atomic collisions. For gas densities of several atmospheres these techniques are sensitive to the simultaneous interaction of an excited atom with many other neutral perturbers. In another experiment, an ArF 193-nm laser photodissociates H_2O to produce free H and OH. Excited states of OH are selectively created by the absorption of one or two photons of tunable laser light. Lineshapes are measured to determine lifetimes for excited OH to predissociate, and the continuum emitted in radiative dissociation is observed to record the transient O + H half collision on a picosecond time scale. Other work is also planned on Al + H collisions in the presence of a 193-nm laser light, and online broadening in alkali-H spectra.

Michigan Technological University
Houghton, MI 49931

Department of Physics

236. *Theoretical Hyperfine Structure Constants for Transition-Metal Atoms and Ions*
Beck, D.R. **$65,532**
906-487-2019 **(14 months)**

Knowledge of hyperfine structure of transition-metal atoms is useful for diagnostic purposes in plasma fusion devices. A series of recent measurements on the ions when compared with ab initio Dirac–Fock calculations, have shown large, systematic differences for many of the levels, which went unexplained prior to this work. Similar discrepancies have been found for fine structure, which is of concern in catalysis and other areas. In recent work on small transition metals (Sc II and Y II), the discrepancies have been reduced to only 8% by using moderate size relativistic configuration interaction calculations. Accurate results for the (d + s)^n energy differences are essential for accurate hyperfine results. The present work is for a more complicated species, Zr II (d + S)^3. For this, more powerful algorithms are introduced, which should suffice for the remainder of the transition metals. The average fine structure error is only 0.075 eV, and hfs constants are accurate to 17%. There is a strong indication that the data sets used for Zr II can be transported, more or less en mass, to isoelectronic and isogroup ions, yielding similar accuracies. Because very little is known of properties of double and higher ionization stages, the work [on (d + s)^n levels] will be valuable in filling in this part of the periodic table.

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

Physics Laboratory

237. *Electron–Atom Collisions Studies*
McClelland, J.J. **$97,660**
301-975-3721

Two types of experiments are conducted utilizing the interaction of a frequency-stabilized CW laser beam with an atomic chromium beam. In one class of experiments the laser beam serves to optically prepare the chromium atoms in a well-defined quantum state, providing a state-selected, spin-polarized atomic target for electron collision studies. Spin-polarized electrons collide with the prepared chromium atoms and scatter either elastically or superelastically. The scattered signal is detected as a function of scattering angle, and individual state-to-state cross sections are determined, permitting extremely detailed comparisons with theory. In the other type of experiment, the chromium atoms are manipulated with the laser beam. Transverse laser cooling is performed using "optical molasses", resulting in collimation and concentration of the atomic beam. After this, the atoms are focused by passing through a standing wave laser field. The focused atoms are incident upon a substrate, where they deposit in the form of lines with width about 40 nm or less and spacing of 212 nm. These nanofabricated lines represent an entirely new way to make nanometer-scale structures on a surface. Future work will include extension of the techniques to two dimensions, to make dots, and eventually to the creation of arbitrary patterns.

University of Nebraska at Lincoln
Lincoln, NE 68588

Department of Physics and Astronomy

238. *Dynamics of Collision Processes*
Starace, A.F. **$72,000**
402-472-2795

Investigations of collision processes important for energy-related technologies and governed by the dynamics of three interacting charged particles are the focus of this project. The systems of three interacting charged particles are described using either hyperspherical coordinate methods or a combination of variational R-matrix and quantum defect theory methods. Recent investigations include (1) two- and three-photon detachment of the negative hydrogen ion (H^-) with particular attention to the role of electron correlation effects; (2) two-color detachment of H^- with excitation of H(n = 2), with particular attention to the role of long-range dipole field effects; and (3) variational R-matrix calculations of photodetachment of the negative lithium ion, with particular attention to excitation of excited lithium atom states n having $2 \leq n \leq 6$.

University of Nevada at Reno
Reno, NV 89557

Department of Physics

239. *Screening Resonances in Plasmas*
Winkler, P. **$43,966**
702-784-6792

In the investigation of plasmas consisting of positive atomic ions and electrons, a good understanding of the interaction potential between these two species is essential. Compared to the vacuum case, the force between the charges is modified because of short-range order and dynamical screening effects introduced by neighboring ions and fast electrons, respectively. These modifications determine one-electron properties (e.g., spectral lines that serve as key quantities in plasma diagnostics) as well as more-electron properties (e.g., dielectronic recombination rates that account for plasma losses). As a first step beyond the usual Debye–Hueckel treatment of screening, realistic electron–ion potentials were derived from pair distribution function calculations and examined for the occurrence of low-lying scattering resonances in the s-wave channel. In all cases studied, such resonances were found. The required computational techniques have been developed further and tested using analytic model potentials. Plasma screening affects also the interaction potential between the electrons. The incorporation of this modification requires sophisticated many-body techniques and is not yet completed. It is likely that earlier predictions of the stability of negative hydrogen ions in plasmas must be revised because of the screened electron interaction. This will impact the interpretation of astrophysical plasmas as well as of cool laboratory plasmas.

University of New Mexico
Albuquerque, NM 87131

Department of Physics and Astronomy

240. *H^- Spectroscopy*
Bryant, H.C. **$120,000**
505-277-3044

The spectroscopy of H^-, important to fusion research, astrophysics, and accelerator physics is studied at Los Alamos Meson Physics Facility (LAMPF). The techniques developed for relativistic beams are currently being applied to study multiphoton processes in this negative ion. Using a high-power carbon dioxide laser, photons in the 10.6 micron line are Doppler-shifted to energies in the ion's rest frame ranging from 34 to 400 MeV allowing study of multiphoton electron detachment involving 2 to 22 photons at an H^- beam energy of 800 MeV. The simplicity of the system under study, combined with the effective tunability of a high-intensity laser, makes these measurements unique. Another study using a powerful YAG laser concerns how the high-lying, doubly excited states in the negative hydrogen ion undergo double detachment. Current results indicate that so-called "ridge-states", which may be related to the Wannier double detachment mechanism, are being observed. An extensive survey of the systematics of these states is under way. Further studies of electric field effects and passage through foils on the stability of H^- are also in progress.

University of Notre Dame
Notre Dame, IN 46556

Department of Physics

241. *Rydberg States in Multiply Charged Ions*
Livingston, A.E. **$80,973**
219-239-7554 **(15 months)**

The excitation, structure, and decay characteristics of Rydberg states in highly charged ions 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 sodium-like ions to improve the determinations of the associated ionization energies in high-Z alkali systems. Implementation of position sensitive photon detection is also under way for the spectroscopic measurements in this program of atomic structure studies in multiply charged ions.

Pennsylvania State University, Lehman
Lehman, PA 18627

Department of Physics

242. *Electron Transfer, Ionization, and Excitation in Atomic Collisions*
Winter, T.G.; Alston, S.G. **$70,000**
717-675-9278

The theory of electron transfer, ionization, and excitation in ion-atom collisions is being studied for intermediate and higher collision energies (for example, proton energies of at least 100 keV). At intermediate energies, many electronic states are strongly coupled, and a Sturmian-pseudostate approach is taken to account for this interaction. At higher energies, the collision may be treated perturbatively; for these energies, a distorted strong-potential Born approximation is appropriate. Both electron transfer and ionization from the K shell have recently been treated for collisions between protons and carbon atoms using the coupled–state approach, and this work is now being extended to neon targets. The distorted strong-potential Born approximation for electron transfer has recently been conducted for collisions between protons and these two targets as well as argon targets. When applied to the same systems, the two approaches agree very well at higher intermediate energies, an excellent confirmation of their consistency. In addition, the differential cross section for electron transfer in collisions between 295-keV protons and helium atoms has been determined using a second-order Faddeev approximation. Agreement of this higher-order perturbative result and experimental results is generally quite good.

University of Pittsburgh
Pittsburgh, PA 15260

Department of Physics and Astronomy

243. *New IR Photon Absorption Processes*
Bayfield, J.E.
412-624-9280

The fast ionization of atoms by very short pulses, and its possible suppression at extreme pulse intensities, is an active field of investigation at present. A number of theoretical and numerical studies have been made by others, often based on the atom being either the simplest (hydrogen) or one-dimensional. Experiments that directly test the results of such studies have been very few, because of the special and trying techniques presently required. This program has investigated whether past studies of laser multiphoton ionization of excited hydrogen atoms and of 1-D microwave ionization of highly excited hydrogen atoms can be combined and extended to address the new issues. A laser multiphoton ionization apparatus has been rebuilt, and experiments to observe strong-field IR laser ionization of 1-D excited hydrogen atoms have been conducted. Laser ionization signals have been observed that are 4% of the total background signal. An improvement of the signal-to-background ratio to a value around three appears possible.

Rice University
Houston, TX 77005

Department of Physics

244. *Theoretical Atomic Collision Physics*
Lane, N.F. **$86,000**
713-527-4026

Theoretical calculations are being conducted to determine cross sections, rates, and other measurable quantities, such as orientation and alignment parameters, for collision processes of possible importance in advanced energy research. Present emphasis is being placed on charge transfer and state changing in collisions of ground and excited (including low Rydberg) alkali atoms, with other atoms, molecules, and ions. Intracollisional interference effects arising from localized electron "scattering" during the collision are observed and analyzed. The dependence of cross sections on the orbital alignment of the initial excited atom (for nonspherical states) also is investigated.

Department of Space Physics and Astronomy

245. *Radiative Properties of Strongly Magnetized Plasmas*
Weisheit, J.C. **$102,000**
713-527-4939

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 radiative opacities and other quantum transport coefficients. Strong fields ($B > 10^7$ Gauss) arise in a variety of transient laboratory environments—Z-pinches, some 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 $n(r)$. (This is in lieu of Kadomtsev's nonlinear, second-order ordinary differential equation for a spherically symmetric electrostatic potential.) Analytical solutions have been obtained for two simplified cases and some numerical results, for the general case. Computed charge densities exhibit features consistent with heuristic predictions and with published hydrogenic distributions. Such calculations reveal field-strength regimes where (1) departures from spherical symmetry are important, but (2) complete factorization of $n(r)$ in cylindrical geometry is inadequate.

University of Rochester
Rochester, NY 14627

Department of Physics and Astronomy

246. *Study of Atoms Exposed to Intense Laser Pulses*
Eberly, J.H.; Meyerhofer, D.D. **$120,000**
716-275-3288

High-intensity laser–atom interactions are studied both experimentally and theoretically. 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 1-μm. 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. 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 the way in which highly excited atomic level populations can be established in the course of multiphoton ionization. The calculations will focus on short-pulse laser fields similarly strong as those employed in the experimental program.

University of Southern California
Los Angeles, CA 90089

Department of Physics and Astronomy

247. *Amplitude Modulation of Atomic Wavefunctions*
Cooke, W.E. **$90,000**
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.

Department of Physics

248. *Behavior of Atoms in a Strong Radiation Field*
Shakeshaft, R. **$140,000**
213-740-7888 **(17 months)**

The behavior of two-electron systems, helium and the negative hydrogen ion, in a strong linearly polarized field is studied by numerically solving the time-dependent Schrödinger equation on a complex basis. The extent to which electron–electron correlation prevents multielectron atoms from becoming stable in strong high-frequency fields is to be determined. The work will shed further insight on the phenomena of stabilization, and also on the dynamics of multiphoton–multielectron processes in general.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Physics and Astronomy

249. *The Production and Destruction of Metastable Negative Ions*
Pegg, D.J. **$94,000**
615-974-7831

This project involves an experimental study of photon–negative ion interactions using a crossed laser-ion beam apparatus. Forward-directed photoelectrons from the interaction region are energy analyzed using a spherical-sector electron spectrometer. The resulting spectra provide information on the kinetic energies and yields of the ejected photoelectrons. Their angular distributions can be measured by rotating the linear polarization vector of the laser beam. Recently, cross sections for the photodetachment of Li^-, Be^-, and B^- have been determined. The first measurement of the angular distribution of electrons detached in the photodetachment of Be^- has been reported. A precise measurement of the electron affinity of Li has been made by investigating the near-threshold behavior of the partial cross section for the process that leaves the Li atom in its first excited state. The electron affinity of a metastable Be atom has been measured using a hybrid technique employing photodetached and autodetached electron spectroscopy.

Texas A & M University
College Station, TX 77843

Cyclotron Institute

250. *Excitation of Atoms and Molecules in Collisions with Highly Charged Ions*
Watson, R.L. **$89,500**
409-845-1411

The Texas A & M K500 superconducting cyclotron and its associated electron-cyclotron-resonance ion source provide unique capabilities that are being used to explore collision processes of high-Z ions at high energies. The primary emphasis of this work is directed toward the investigation of electron capture and loss processes in single collisions with atoms and simple molecules. Recent experiments have been performed to examine the total kinetic energy (TKE) release accompanying dissociation reactions resulting from one- and two-electron capture collisions of 97 MeV Ar^{14+} with CO molecules. Three parameters were recorded for each event: (1) projectile post-collision charge, (2) time-of-flight of the first-arrival C or O ion; and (3) difference in flight time, δt, between the C and O ions. Analyzable δt distributions were obtained for 17 ion pairs ranging from C^{1+} $+O^{1+}$ to C^{4+} $+O^{4+}$ and C^{3+} $+O^{6+}$. The average TKEs obtained by transforming the δt distributions into kinetic energy distributions showed that the molecular states populated in electron capture collisions lead to the release of considerably more kinetic energy than those populated by pure ionization. It was also found that reactions producing ion pairs in which the O-charge was greater than the C-charge were much more prevalent for electron capture collisions and they were characterized by significantly higher TKEs.

University of Texas at Austin
Austin, TX 78712

Department of Physics

251. *State-to-State Energy Transfer in Atomic Collisions*
Keto, J.W. **$118,000**
512-471-5029

Studies of state-to-state energy transfer cross sections and radiative lifetimes for $Xe^*(6p,6p',7p)$ and $Kr^*(5p)$ states in xenon and krypton buffer gases were recently completed. These results are relevant to kinetic models of both excimer lasers and the IR xenon laser. The state-to-state rates were determined for all product states that could be observed in the spectral range from 120–1100 nm by their fluorescent intensity and from the time dependence of fluorescence from the product channel. Excitation transfer from Xe^* to Kr^* and reverse was found to be important for all Xe^* excited states above the $Kr^*(5s)$ threshold. Energy transfer back from Kr*(5s) prefers Xe*(5d) that form the lasing transitions in the IR. Since the detectors for observing these transitions are too slow for studies of their dynamics, experiments are being attempted to observe the dynamics of states of Xe*(5d) using two-color, pulse-probe laser induced fluorescence. Experiments have also been initiated to measure termolecular harpooning reactions between Xe* and Cl_2 in krypton buffers. Previously, a large termolecular rate was observed in xenon buffers but not in argon buffers. A model has been developed that assumes that a collision between the excited state and a buffer atom transiently lowers the ionization potential of the excited state, thereby increasing the harpoon reaction rate. The model predicts a rate for krypton buffers intermediate to that of xenon and argon.

University of Toledo
Toledo, OH 43606

Department of Physics and Astronomy

252. ***Semiempirical Studies of Atomic Structure***
Curtis, L.J. **$61,000**
419-537-2341

The atomic structure and properties of highly ionized many-electron systems are studied through the combined use of sensitive semiempirical data systematizations, precision experimental measurements, and specialized theoretical computations. 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 sources, and conventional light sources. Large blocks of data are systematized and parametrized along isoelectronic, homologous, isoionic, Rydberg, and yrast series, with the aim of providing a comprehensive and reliable database. Examples of investigations conducted during the past year include (1) precision measurements of lifetimes in S VII and Cl VIII, and the use of these results to obtain reliable extrapolative predictions for higher members of the Ne isoelectronic sequence; (2) experimental lifetime measurements and spectroscopic databased parametrizations in the Zn and Be isoelectronic sequences, which have revealed predictive relationships between spin-allowed and spin-forbidden transitions; (3) precision measurements of lifetimes of resonance transitions in Si IV; and (4) the extension of the use of simultaneous multiplexed measurement of decay curves utilizing position-sensitive detectors to the determination of lifetimes of intercombination transitions in the Mg, Al, and Si isoelectronic sequences.

253. ***Negative Ion–Atom Collisions***
Kvale, T.J. **$63,833**
419-537-2980

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 completed this year on the UT-Negative Ion Energy-Loss Spectrometer at The University of Toledo. The scattered ions were charge-state analyzed and all three charge-state components (H^-, H^0, H^+) were simultaneously detected in these measurements. In addition to the electron detachment total cross section measurements, this experimental technique allowed measurements of the secondary emission coefficient γ for energetic H^0 atoms striking a copper surface. The goals for the present year are (1) to commence the H^- ion energy-loss measurements for the target excitation–ionization processes in which H^- survives the collision; (2) to implement the energy upgrade of the accelerator to 100 keV, which brings the collisions further into the impulsive energy region; and (3) to complete the modifications to the accelerator to allow measurements of angular differential cross sections (ADCS) for the above processes.

Tulane University
New Orleans, LA 70118

Department of Physics

254. ***Few Electron Transitions in Atomic Collisions***
McGuire, J.H. **$60,000**
504-865-5520 **(16 months)**

The dynamics of atomic interactions with electrons, protons, ions, photons, and antimatter are studied by evaluating and analyzing cross sections for scattering of atoms. The emphasis is on basic understanding of how few- and many-electron systems interact, with particular interest on the role of the electron–electron correlation interaction in reactions of atoms with charged particles. Researchers are developing methods to evaluate interaction rates for processes in which two or more electrons are active. This year a technique was published which enables evaluation of double excitation and excitation-ionization of atoms. Such multielectron processes play a role in the energy transfer of multiple excited and ionized systems, which include effects of radiation on atoms, solids and biological materials in the environment. Development of practical techniques for predicting and analyzing rates for multielectron transitions in large molecules is now in progress. These methods are being used to analyze experimental data at laboratories in Oak Ridge, Tennessee; Aarhus (Denmark); the Hahn Meitner Institute in Berlin; Kansas State University; Stanford University; RIKEN in Japan; and at other laboratories in this country and abroad. These studies enable detailed understanding of the dynamics of atoms and molecules in the environment.

Vanderbilt University
Nashville, TN 37235

Department of Computer Science

255. ***Theoretical Studies of Atomic Transitions***
Fischer, C.F. **$220,000**
615-322-2926

Atomic structure calculations are being performed to predict properties such as energy levels, binding energies, photoionization cross sections, and lifetimes of excited states. Accurate computational procedures are being devised (1) to predict properties even when they cannot be obtained from experiment and (2) to assist in the identification of observed data. The multiconfiguration Hartree–Fock (MCHF) method, optionally corrected for relativistic effects in the Breit–Pauli approximation, is used for these computations. Recent calculations have emphasized the electron affinities of the alkaline earths and the $3d4s^24p^{1,3}D$ states of Sc^-. Spline algorithms are used to obtain continuum wave functions and Rydberg series. These methods are being tested in the study of photoionization in He and H^- and are now applied to the identification of levels observed in a two-photon spectrum of Ca. Large scale, systematic methods have been applied to the study of oscillator strengths in nitrogen. Of special interest are spin-forbidden transitions. Breit–Pauli results will be compared with fully relativistic calculations.

University of Virginia
Charlottesville, VA 22901

Department of Physics

256. *Studies of Autoionizing States Relevant to Dielectronic Recombination*
Gallagher, T.F. **$119,987**
804-924-6817

The objective of this research program is to understand dielectronic recombination, the recombination of ions and electrons through autoionizing states, an important energy loss process in fusion plasmas. The reverse process, the decay of the autoionizing states is being examined in detail by laser spectroscopy. The autoionization rates and angular distributions of electrons from Mg 3pns and 3pnd states have been measured and found to be in good agreement with theoretical calculations. Preparations to measure the autoionization rates of the 3pnf states, as a final test of the theory in zero field, are under way. Presently the autoionization rates of Mg states in electric fields are being measured. Some aspects of the results, those obtained in microwave fields, agree with the simplest model of electric field effects, one based on an isolated resonance picture. However, many of the gross features observed in static fields are only in qualitative agreement with the simplest model, suggesting the need for refinements in the theory. In a static field the Ba autoionization rates do agree with the simplest model, and Ba in static fields will be reexamined in detail to see how the isolated resonance picture evolves to a channel description analogous to quantum defect theory.

Western Michigan University
Kalamazoo, MI 49008

Department of Physics

257. *Near Threshold Excitation and Ionization of Open-Shell Atoms*
Berrah-Mansour, N. **$125,000**
616-387-4955 **(24 months)**

The objective of this research is to probe fundamental processes of atomic structure and the dynamics of 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–antiphotoionization experiments will be performed to study shake processes and postcollision interaction, focusing initially on vacancy cascade phenomena, and emphasizing the use of coincident detection of ions and electrons. Quantitative studies of such processes 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 between 280 and 1210 eV have been performed at the BESSY synchrotron facility. Measurements compared with the most recent calculations show the importance of initial-state correlations and final-state correlations.

258. *Correlated Charge-Changing Ion–Atom Collisions*
Tanis, J.A. **$98,000**
616-387-4941

Experimental investigations of atomic interactions involving excitation, ionization, and charge transfer in collisions of few-electron ions with various targets are conducted. The major emphasis of this work is the study of those collision interactions involving two active electrons, and particularly those in which the electron–electron interaction plays a significant role. Processes studied are of interest from both fundamental and applied points of view. The studies involve few-electron ions with $1 \leq Z \leq 36$ and energies ranging from < 5 keV/u to > 40 keV/u. Accelerators at Indiana University; Lawrence Berkeley Laboratory; Michigan State University; Western Michigan University; and the Institute of Nuclear Research, Debrecen, Hungary are utilized. In the past, the central focus of this work has been the study of resonant recombination, namely, resonant transfer excitation (RTE) and dielectronic recombination (DR). More recently, however, the emphasis has been shifting toward studies of multiple ionization and continuum-electron emission, and, specifically, the importance of electron-correlation effects in these processes. This latter area (i.e., continuum-electron emission) is expected to constitute the major focus of future work. To this end, a sophisticated electron spectrometer system, which will greatly enhance capabilities, is currently under construction.

The College of William and Mary
Williamsburg, VA 23185

Department of Physics

259. *Negative Ion Detachment Cross Sections*
Champion, R.L.; Doverspike, L.D. **$106,000**
804-221-3510

The long-term goal of this research project is to develop a thorough understanding of the collisional dynamics of systems in which negative ions collide with atoms and gas-covered surfaces. The current experimental studies are designed to investigate gas-phase, two-body collisions and to examine 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 alkali and halogen anions with atomic hydrogen and deuterium. Future studies of this type will include collisions of negative ions with ozone. In the field of negative ion sputtering from surfaces, the experiments are devised to investigate the detailed dynamics of such sputtering and the related secondary electron emission resulting from the impact of atomic species with collision energies below 500 eV. The role of sputtered negative ions, which subsequently autodetach, is currently being examined.

Chemical Energy

University of Arizona
Tucson, AZ 85721

Department of Chemistry

260. *A Model Approach to Hydrodenitrogenation Catalysis*
Wigley, D.E. **$109,107**
602-621-4118

Efforts are under way to develop homogeneous models for hydrodenitrogenation catalysis that will allow an examination of possible mechanistic pathways by which HDN substrates are reduced and their C–N bonds cleaved. Since the preferred HDN substrate binding mode is expected to dictate the extent and selectivity of ring hydrogenation, the coordination and reactivity of pyridines, quinolines, and other HDN substrates to highly electrophilic transition metal centers has been examined. The study makes extensive use of alkoxide ligands, which provide relevant models for supported catalysts: they support high-oxidation metal centers and afford metal–oxygen ligation. These studies have uncovered the following: (1) An η^1(N)-quinoline → η^2(N,C)-quinoline bonding mode conversion in a model compound of tantalum (viz. (η^1(N)-quin)Ta(O-2,6-C_6H_3-i-$Pr_2)_3Cl_2$) has been observed upon reducing this complex by 2 electrons. (2) The studies have demonstrated that η^2(N,C)-quinoline coordination selectively activates the bound heterocyclic ring (only) to hydrogenation. (3) Finally, a regioselective C–N bond scission has been effected by nucleophilic attack of an η^2(N,C) pyridine complex when (η^2(N,C)-2,4,6-NC_5H_2-t-Bu_3)Ta(O-2,6-C_6H_3-i-$Pr_2)_2Cl$ is reacted with $LiBEt_3H$. This final result is significant in providing precedent for a long-standing, unresolved mechanistic problem in HDN catalysis, viz. how the strong C–N bonds in heterocyclic compounds are cleaved. These studies have afforded a number of likely catalyst precursors for homogeneous catalytic studies to be undertaken and have suggested a means to develop model HDN substrate → catalyst complexes in which a saturated heterocycle is bound η^2(N,C) to tantalum. Exploratory efforts are under way to determine if η^2(N,C) heterocycle coordination can be demonstrated in complexes of molybdenum and tungsten and to what extent such compounds are valid reactivity models for HDN.

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

261. *Carbon Deposition and Deactivation of Metallic Catalysts*
Baker, T.K.
205-844-2007

A combination of experimental techniques including controlled atmosphere electron microscopy, thermogravimetry and flow-reactor studies have been used to study the formation of carbon deposits resulting from the interaction of platinum with ethylene and acetylene. It was found that in order to produce significant amounts of carbon on the metal it was necessary to perform the reaction in the presence of added hydrogen. Attention has been focused on all of the steps involved in the reaction including those which occur at the metal–gas interface, diffusion of carbon through the metal particles and eventual precipitation at the metal–carbon interface to form a carbon filament. In both cases, as the amount of hydrogen in the reactant gas was increased, there was a corresponding increase in the degree of crystalline perfection of the carbon filaments which were produced on the platinum particles. This effect was more pronounced for acetylene than ethylene, and if the metal was treated in a mixture of acetylene containing excess hydrogen, it was possible to produce filaments which had identical oxidation characteristics to those of graphite. This behavior can be correlated with the interfacial phenomena associated with the metal–carbon interaction.

Boston College
Chestnut Hill, MA 02167

Department of Chemistry

262. *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) under conditions of thermal activation. PAH ring systems figure prominently in the molecular architecture of coal, but prior to this systematic program of study, little was known about the chemical transformations that PAHs undergo at high temperatures, such as those employed in the uncatalyzed gasification and liquefaction of coal. This year has brought to light several new examples of carbon atom scrambling reactions in PAHs at high temperatures, and a systematic pattern of reactivity has begun to emerge: it now appears that the ease with which two adjacent carbon atoms can switch places in a PAH correlates with the pi-bond order between those two carbon atoms. In parallel work, a new high-temperature synthesis was developed for pyracylene, a key 14-carbon tetracyclic subunit of spheroidal C_{60} and the higher fullerenes. A ^{13}C-labeled version of pyracylene is being prepared to assess whether or not this ring system is capable of 1,2-bond switching, as 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

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

Bercaw, J.E. **$143,972**
818-356-6577

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 α olefin polymerization catalysts. Synthetic strategies for more active and enantiomerically pure metal complexes have been devised. These compounds will be evaluated with respect to their potential as olefin polymerization catalysts. Investigations continue on the structure of the transition state for chain propagation utilizing stereochemical and isotopic labels. A transition state analog recently synthesized will be examined for evidence of an α agostic interaction.

University of California, Davis
Davis, CA 95616

Department of Chemical Engineering

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

Gates, B.C. **$95,000**
916-752-3953

The goals of this research are to characterize the structure and bonding of "molecular" metal complexes and clusters of metals including Re, Ir, and Pt on the surfaces of MgO, γ–Al_2O_3, and La_2O_3; zeolites are also used. Some of the metal oxide supports are high-surface-area powders and some are single crystals. 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 extended X-ray absorption fine structure (EXAFS), temperature-programmed desorption, IR, Raman, and NMR spectroscopies; some of the 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 surfaces and also for the supported metal clusters; it is a bonding distance and suggests the presence of metal atoms bearing a small positive charge at the metal cluster–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 of the surface or the presence of metal atoms interacting with surface oxygen ions with intervening hydrogen in the interface. Similar iridium clusters have been prepared from salt precursors in zeolite L; 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

265. Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes

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

The chemistry of alkoxide-ligated complexes of yttrium and the lanthanide metals is being investigated to determine how the special properties of these relatively abundant metals, which are readily available in the United States, can be utilized in compounds that can withstand a variety of reaction conditions. Trimetallic tertbutoxide complexes have been selected from the wide variety of polymetallic species recently discovered and structurally characterized for the reactivity studies on these alkoxide compounds. Reactions with alkylaluminum reagents and cyclopentadienyl reagents have provided new mono- and bimetallic alkoxides that appear to have unusual patterns of reactivity compared to previous results on organometallic complexes of these metals. The alkylaluminum and cyclopentadienyl derivatives react with alkyllithium reagents to make new products whose isolation has been hindered by their apparently high reactivity. Products derived from C–O and C–H activation reactions have been isolated; although, the mechanisms of these reactions are undefined at present. These results suggest that the alkoxide ligands will provide new opportunities to utilize the special chemistry available from these elements.

University of California, San Diego
La Jolla, CA 92093

Department of Chemistry

266. *New Molecular Precursors for Low-Temperature Routes to Oxide Materials*
Tilley, T.D. **$97,918**
619-534-6159

This project addresses basic research directed toward new approaches to advanced materials that could impact the efficient use and conversion of energy. Specifically, the purpose of this work is to develop low-temperature routes to stoichiometric oxide materials containing more than one metallic component. Currently the method of choice is a sol–gel synthesis in which mixtures of metal alkoxides are hydrolyzed. However, this method is plagued by the fact that metal alkoxides invariably exhibit different rates of hydrolysis, which normally result in formation of inhomogeneous mixed-metal oxides. The focus is on development of general syntheses to homogeneous mixed-metal systems that allow useful processing methods (to thin films, porous ceramics, fibers, and so forth) and on discovery of routes to new materials with tailored properties. This research is based on initial findings that metal complexes of the siloxide ligand $OSi(O^tBu)_3$ eliminate isobutylene and water cleanly at remarkably low temperatures (100 to 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 140 °C to MO_24SiO_2 materials. Extremely homogeneous oxide networks are obtained in this way. The low temperatures at which such conversions take place allow for the thermolysis to be carried out in refluxing hydrocarbons, thereby offering an alternative to the sol–gel approach. Materials produced in solution this way have high surface areas (ca. 500 m^2g^{-1}). Initial experiments indicate that thermolyses in the solid state can provide surprisingly ordered microstructures for the resulting oxide materials. This technique is being investigated for other Lewis acidic metals such as aluminum and yttrium, and also for late transition metal complexes. It is hoped that this method for the generation of oxide networks can be used to obtain materials with new structural, electronic, optical, and/or catalytic properties.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemical and Nuclear Engineering

267. *The Activation and Decomposition of Alkanes on Group VIII Transition Metal Surfaces: Dynamics, Kinetics, and Spectroscopy*
Weinberg, W.H. **$88,300**
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)–(l x 2), Ir(111), Pt(110)–(l 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.

Department of Chemistry

268. *Studies Relevant to the Catalytic Activation of Carbon Monoxide*
Ford, P.C. **$132,000**
805-893-2443

This research is concerned with quantitative investigations of fundamental metal complex reactions that have relevance to the homogeneous catalytic activation of carbon monoxide and other C_1 compounds. Among these are mechanistic studies of the activation of metal carbonyl cluster compounds by halide ions (commonly used cofactors in CO catalysis) and continuous-flow reactor studies of water–gas shift catalysts heterogenized on polystyrene-based polymers. 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 to establish guidelines for the design and engineering of new chemical systems for more efficient (therefore, environmentally friendly) applications of energy and chemical feedstocks.

Carnegie-Mellon University
Pittsburgh, PA 15213

Department of Chemical Engineering

269. *H_2SO_4-Modified ZrO_2 and ZrO_2/SiO_2 Aerogels as Solid Superacids*
Ko, E. **$88,216**
412-268-3857

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

270. *Polyoxoanion-Mediated Methane Activation and Functionalization: Molecular*

Design of New Homogeneous and New Solid-State/Heterogeneous Catalysts

Finke, R.G. **$115,512**
503-346-4622

A primary goal of this research is to develop a chemical paradigm for polyoxoanion–supported transition-metal catalysis (e.g., from the novel catalyst precursor $[(Bu_4N)_5Na_3][(1,5\text{-}COD)Ir^{\bullet}P_2W_{15}Nb_3O_{62}]$, with an emphasis on small molecule (H_2, O_2, H_2O_2, CH_4) catalytic activation and functionalization (CH_4, RH). Several avenues of investigation were successful this past year, as detailed below. During the past year, a patent was filed on the oxidation of cyclohexene using the $[(1,5\text{-}COD)Ir^{\bullet}P_2W_{15}Nb_3O_{62}]^{8-}$ catalyst precursor and the preferred oxidant cyclohexene. Mechanistic studies of this reaction demonstrate that it is the first bona fide polyoxoanion-supported catalyst system, and a full paper detailing the evidence supporting this statement is under construction. A review of the polyoxoanion research at Oregon will also appear shortly as part of an international workshop on polyoxoanion chemistry held in Bielefeld, Germany July 15–17, 1992. A second exciting area of current polyoxoanion research is in so-called "inorganic porphyrin analog catalysts". Such catalysts mimic the important oxidation chemistry of biological metalloporphyrin catalysts, but have the distinct advantage that they are all inorganic and thus robust and oxidation resistant. A new structural type, the complex $(P_2W_{17}O_{61}Ru)_2\text{–}O^{16-}$ a bimetallic inorganic porphyrin-like precatalyst system, was discovered and crystallographically characterized this past year. This unprecedented polyoxoanion structure contains a $Ru^{IV}\text{–}O\text{–}Ru^{IV}$ bridge and is a candidate for multielectron redox catalysis studies, work currently in progress.

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

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

The stereochemistry and mechanism of the formation of diosmacyclobutanes from olefins are being investigated. In this reaction, which models the chemisorption of olefins onto metal surfaces, stereochemistry is retained about the double bond. The mechanism involves slippage of the outgoing olefin onto a single olefin, and associative exchange of the olefin from that site. Assignment of the vibrational modes of the diosmacyclobutane $Os_2(CO)_8(\mu\text{-}C_2H_4)$ and the osmacyclopropane $Os(CO)_4(C_2H_4)$ has given fingerprint vibrational spectra for ethylene chemisorbed on metal catalyst surfaces in either a di-σ or a metallacyclopropane fashion. The vibrational frequencies of an ethylidene-bridged diosmium complex have also been assigned, so that ethylidene species can also be recognized on catalyst surfaces. Reaction of an osmacyclobutane with 1,3- or 1,2-dienes (allenes) gives initial 1,2 (rather than 1,4) addition to the Os_2 unit.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

272. *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. New p-cymene ruthenium complexes containing the tetramethylpyrrolyl ligand or the pentamethylpyrrole ligand have been synthesized. The new complexes have been characterized by spectroscopic techniques and in one case by an X-ray diffraction study. The reactivities of the new ruthenium pyrrole complexes are being studied. For example, methoxide ion in methanol appears to reduce the ruthenium (II) complex $[(p\text{-}cymene)Ru(NC_4Me_4)]$ OTF to a ruthenium (0) derivative $[(p\text{-}cymene)Ru(HNC_4Me_4)]$. Spectroscopic data for the latter complex suggest that the aromatic p-cymene ligand has been distorted from an η^6 to an η^4 coordination mode. In contrast, the reaction of methoxide ion with $[(p\text{-}cymene)Ru(MeNC_4Me_4)](OTF)_2$ appears to result in nucleophilic addition to the pyrrole ligand. Further reactivity of the resulting modified pyrrole ligand is being investigated. The effect of coordination by high-valent metal ions on the reactivity of the pyrrole ligand is also being studied with a series of tantalum (V) pyrrole complexes that contain amide and/or chloride coligands.

Columbia University
New York, NY 10027

Department of Chemistry

273. *Model Studies in Hydrocarbon Oxidation*

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

University of Connecticut
Storrs, CT 06269

Department of Chemistry

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

Suib, S.L. **$95,000**
203-486-2797 **(15 months)**

The goals of this research program are to prepare, characterize, and find applications for synthetic todorokite materials. Todorokites are octahedral molecular sieves (OMS) consisting of mixed valent manganese oxide tunnel structures. These one-dimensional tunnel structure materials have a pore size of about 6.9 Å. Several divalent ions such as Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} have been substituted for Mn^{2+} in these systems, yielding a variety of transition-metal OMS materials. Framework substitutions for manganese have been done by adding dopant concentrations to the sol precursors. Substitution for cations either in the tunnels or in the framework of these materials leads to differences in acidic and thermal properties. These materials are weak acid catalysts that primarily contain Lewis acid sites. Another major application of these systems involves total oxidation of hydrocarbons and carbon oxides such as C_4H_{10} and CO. Such materials can be more active than commercial oxidation catalysts. Adsorption studies show that molecules having pore sizes less than about 6.9 Å such as c-C_6H_{12} and CCl_4 are sorbed. The use of such materials as getters or catalysts to react with small toxic molecules like NH_3 and NF_3 is also being explored. Current synthetic efforts involve preparation of large single crystals and generation of other OMS materials having different pore sizes.

University of Delaware
Newark, DE 19716

Center for Catalytic Science and Technology

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

Barteau, M.A. **$83,200**
302-831-8905

The last decade has seen increasing use of oxygenates, including alcohol blends and methyl tertiary butyl ether (MTBE), as octane enhancers in gasoline. Current trends include the introduction of "environmental gasolines", reduction of some high-octane hydrocarbons including butanes and aromatics, and legislative requirements for increased oxygen content as a means of improving air quality. This research focuses on the structural requirements of both surface and reactant for the activation of C–H, C–C, and C–O bonds of oxygen-containing molecules on transition metal surfaces of importance in oxygenate synthesis. It applies surface science techniques to determine the kinetics, pathways, and intermediates in the reactions of oxygenates. By varying in a systematic fashion the identity and structure of the surface, and the structure of the probe reactants, the influences of these may be elucidated. Recent experiments have established diverging reaction pathways for decarbonylation of higher alcohols and aldehydes on the Rh(111) surface. Aldehydes form surface acyls, while results for alcohol decarbonylation implicate a surface oxametallacycle intermediate. Other routes to these key intermediates have been demonstrated using $\alpha\beta$-unsaturated reactants, epoxides, and halohydrins. The last of these have demonstrated new surface chemistry: the pinacol rearrangement of halohydrins on a zero-valent metal. The results of these studies are of potential importance in the development of new chemical processes (e.g., epoxide synthesis), as well as for the development of heterogeneous catalysts for synthesis and utilization of oxygen-containing feedstocks and fuels.

Department of Chemistry and Biochemistry

276. *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

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

Friend, C.M. **$90,000**
617-495-4052

Desulfurization reactions induced by mixed phases of cobalt, molybdenum, and sulfur have been investigated in an effort to understand how cobalt functions as a promoter for this class of reactions. Sulfur induces a restructuring of the cobalt overlayers on Mo(110) by forcing segregation of the cobalt into 3-D crystallites. Cobalt generally increases the rate of hydrogenation and consequently increases the selectivity for hydrogen-addition reactions. The kinetics for desulfurization depend strongly on the precise structure of the cobalt overlayers. In addition, restructuring of the Co structures occurs during the course of reaction because sulfur is deposited on the surface during desulfurization. A methodology has been developed for deriving bonding and structural information from vibrational spectra as part of the mechanistic work. A combination of several different surface spectroscopies and theory have been employed in this effort. The current goals are to better characterize the structures of the cobalt overlayers and to define the reaction mechanism for desulfurization on the mixed Co–S–Mo phases.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Chemical Engineering

278. *Selective Carbon Oxygen Bond Scission during Reactions of Oxygenates on Single Crystal Catalysts*

Masel, R.I. **$98,000**
217-333-6841

All of the previous studies of the decomposition of alcohols, aldehydes, and ketones on single crystals of group VIII metals have shown that the majority of the carbon–oxygen bonds stay intact during the decomposition process. However, recently it was discovered that the carbon–oxygen bond in methanol can be selectively broken if the surface structure of the platinum catalyst is appropriately tailored. The objective of this project is to determine whether this is general chemistry. The decomposition of a wide range of oxygenates on several carefully chosen faces of group VIII metals will be examined to see when C–O bond scission occurs. The surface chemistry of the resultant fragments will be studied and work directed toward the synthesis of higher hydrocarbons. The research will use a variety of surface spectroscopic techniques including temperature programmed desorption (TPD), X-ray-photoelectron spectroscopy (XPS), IR, electron energy loss spectroscopy (EELS), atmospheric pressure reactors, and molecular beams.

School of Chemical Sciences

279. *Electron Transfer Activation of Coordinated Thiophene*

Rauchfuss, T.B. **$108,000**
217-333-7355

The project objective is the development of new pathways for the desulfurization of fossil fuels by metal ions. Metals of interest are ruthenium, rhodium, and molybdenum, all of which are known to be active catalysts for hydrodesulfurization. The model substrates are thiophenes. The redox state of the metal–thiophene ensemble strongly influences the structure, reactivity, and dynamics of coordinated thiophene. Base hydrolysis of cationic thiophene complexes involves nucleophilic attack at sulfur followed by C–S bond cleavage. The protonation of reduced thiophene complexes also results in C–S bond cleavage.

Indiana University
Bloomington, IN 47405

Department of Chemistry

280. *The Molecular Precursor Strategy for the Production of Superconducting Oxides*

Caulton, K.C. **$115,000**
812-855-4798

A molecular prerequisite for chemical vapor deposition (CVD) or sol–gel conversion from molecular precursors $M_8M'_bOR_n$ to ceramic materials $M_8M'_bO_{n/2}$ is the synthesis of the binary metal alkoxides $M(OR)_m$ and also rational methods for linking these together at a controlled stoichiometry. The last annual report described $ClCu^{II}Zr_2(OR)_9$ and $Cu_4Zr_4O_3(OR)_{18}$. A monovalent copper analog was made of the first of these two compounds, and it was found that $Zr_2(OR)_9^-$ unit incorporates two Cu^I centers, yielding $Cu_2Zr_2(OR)_{10}$. This compound is central to demonstrating the oxidative aggregation central to the "molecular precursor thesis": $Cu_2Zr_2(OR)_{10}$ was reacted with O_2 and H_2O to form $Cu_4Zr_4O_3(OR)_{18}$. It has also been established that bulk thermolysis of both $Cl(CuZr_2(OR)_9)$ and $Cu_2Zr_2(OR)_{10}$ shows two sharp weight losses at moderate (<400 °C) temperatures to give Cu^0 and ZrO_2. Studies of highly volatile fluorinated precursors have continued. Synthesis and characterization of $Na_2(THF)_4Cu(OCH(CF_3)_2)_4$, $Na_3(THF)_3Y(OCH(CF_3)_2)_6$, and $Na(THF)_2Cu(OC(CH_3)(CF_3)_2)_3$ are now reported. CVD studies of the first compound reveal the segregated deposition of NaF and Cu^0 in distinct thermal zones. The chemical origin of this unusual behavior is currently being sought in dissociation of the heterometallic precursor into binary metal alkoxides.

281. *Metal Alkoxides: Models for Metal Oxides*

Chisholm, M.H. **$123,000**
812-855-6606

The central M_xO_y skeletons of alkoxide-supported clusters of molybdenum and tungsten represent models for the subunits of reduced oxides of these elements, and their hydrocarbon coatings make them soluble in hydrocarbon solvents and thus amenable to study by solution techniques. Alkoxide/siloxide ligands are electronically and sterically tunable, and cluster units provide templates for the development of a diverse field of organometallic chemistry. Specific attention is devoted to the homogeneous activation of carbon monoxide and dinitrogen and the subsequent chemistry of carbido and nitrido metal alkoxide clusters. Reactions of alkynes, alkenes, dienes, and eneynes are also under investigation in the light of recent developments in the chemistry of $W_2(OR)_6$ compounds. During the past 12 months a significant new initiative has been made into the field of polynuclear polyhydrides supported by alkoxide ligands. Examples include the octahedral W_6 cluster $W_6(\mu\text{-}H)_4(H)(\mu\text{-}OPr^i)_8(OPr^i)_5$ and the butterfly cluster $Mo_4(\mu\text{-}H)_2(\mu_3\text{-}H)(OBu^t)_7(HNMe_2)$. The disposition of hydride ligands in these clusters reveals that they prefer to cluster on faces leading to a segregation of metal–oxygen rich and metal–hydrogen rich regions within the cluster. These hydrido clusters are catalytically active toward the hydrogenation of olefins, and an investigation of their reactivity toward carbide and nitride ligands is planned. The attachment of thiophenes to the M_2–M_x centers by metallation has been found to facilitate ring opening and addition reactions. This work provides insight into plausible reaction steps in hydrodesulfurization (HDS) processes.

282. *A Model Approach to Vanadium Involvement in Crude Oil Refining*

Christou, G. **$108,500**
812-855-2399

The project is directed toward (1) identifying the fate of crude oil vanadyl impurities under the reducing and sulfur-rich conditions during hydrodemetallation (HDM) and hydrodesulfurization processes and (2) determining possible mechanistic pathways for the buildup of nuclearity in V/S aggregates. The latter study is intended to provide insights into the intermediate stages of the formation of polymeric vanadium sulfides during crude oil hydroprocessing. Some recent effort has been concentrated on the preparation of a number of monoatomically bridged vanadyl units, and their spectroscopic and magnetic properties. Most effort, however, has been on the formation and study of V/S aggregates. The mononuclear anion $[VS_4(SPh)]^{2-}$ cleanly reacts with CS_2 to form $[V_2(S_2)_2(CS_3)_4]^{4-}$, and the latter then undergoes a number of reactions at the $CS_3{}^{2-}$ ligand, with small organic molecules. Parallel reactions with COS proceed analogously. A particularly interesting product has resulted from the reaction of $[VS(edt)_2]^{2-}$ salts (edt^2 = ethane-1,2-dithiolate) with H^+ sources; the product is $(NEt_4)_3[V_6O_2S_4(edt)_6]$ and possesses a planar $[V_4(\mu_3\text{-}S)_4]$ core related to the two-dimensional sheet structure of VS_2. Two vanadyl groups are attached to the V_4 core via sulfide and edt sulfur atoms. The V_6 complex thus provides a structural insight into the adsorption of vanadyl groups onto the surface of growing vanadium sulfide crystallites during industrial HDM processes.

283. *Free-Radical and Concerted Reactions in Coal Liquefaction*
Gajewski, J.J. **$105,000**
812-855-1192

This project is continuing efforts to understand the high-temperature cleavage reactions of alkyl-aromatic coal liquefaction model compounds. Examination of the tetralin pyrolysis has revealed first-order kinetics for the reaction at all pressures and temperatures with a small rate acceleration in the liquid phase. The product distribution changes from unimolecular cleavage to dehydrogenation to ring contraction as the concentration increases. Because the latter two reactions are accelerated by radical initiators, the mechanism is a free radical chain. However, the kinetics and the initiators are not as yet understood. Other work has revealed that the pyrolysis of chroman (1-oxatetralin) gives ring contraction and ortho-cresol as major products. Trapping experiments with 2-butene reveal stereospecific 4 + 2 cycloaddition of a reasonable intermediate, orthobenzoquinone. Work continues on developing a force field for organometallic compounds.

University of Iowa
Iowa City, IA 52242

Department of Chemistry

284. *Synthesis and Chemistry of Cationic d^0 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 focused on cationic $Cp_2Zr(R)(L)^+$ and related systems that are now accepted to be the active species in Cp_2MX_2-based olefin polymerization catalysts. This work identified the key features required for high insertion reactivity in early metal systems: an electrophilic metal center, a d^0 metal electron configuration, and one or more vacant (or virtual) coordination sites cis to the M–R ligand. Current work is directed to the development of new classes of cationic early metal alkyls that incorporate these features in non-Cp_2M ligand environments. A series of Zr and Hf alkyl complexes $(N_4\text{-macrocycle})M(R)_2$ (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. By design, the pockets of these macrocycles are too small to accommodate the large group 4 metal ions, so the metal sits out of the N_4-plane and cis structures are imposed. Base-stabilized cations [*cis*-(N_4-macrocycle)M(R)(L)][BPh_4] (L = TBF, RCN, PMe_2Ph) and base-free cationic systems [(N_4-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. These results establish that cationic, d^0 (N_4-macrocycle)$M(R)^+$ complexes support electrophilic metal alkyl reactivity. Current work is focused on the development of more highly electron-withdrawing macrocycles that should maximize the electrophilicity of the metal center in these systems and thus increase reactivity.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

285. *Homogeneous Models of Ammoxidation Catalysis*
Maatta, E. **$104,000**
913-532-6687

The project is concerned with the preparation and study of transition-metal complexes incorporating nitrogenous ligands of relevance to commercial ammoxidation processes. Prominent examples of such systems include allylimido ($L_nM{\equiv}N\text{-}CH_2\text{-}CH{=}CH_2$) and alkylideneamido ($L_nM{=}N{=}CH\text{-}CH{=}CH_2$) complexes. A new allylimido complex of tungsten(V), $[(Ph_3PO)_2Cl_3W{\equiv}N\text{-}CH_2\text{-}CH{=}CH_2]$, has been prepared which incorporates oxidatively inert triphenylphosphine oxide ligands. This species has been characterized by a single-crystal X-ray diffraction study and displays the rather uncommon cis, mer-geometry. Further studies of this species will elaborate its reactivity. Synthesis and study of imido derivatives of various polyoxometalate anions also continues. The hexamolybdate system, $[Mo_6O_{19}]^{2-}$, has been successfully functionalized to produce a tolylimido analogue, $[Mo_6O_{18}(Ntol)]^{2-}$, and it appears that two isomeric forms of this material can be isolated: the two forms presumably are differentiated by the presence of either a terminal or a μ_2-imido ligand. The possibility of interconversion between these isomers is being studied, as is the preparation of multiply substituted imido-hexamolybdates.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

286. *Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane*
Klier, K.; Simmons, G.W.; Herman, R.G. **$120,000**
215-758-3577

The objective of this research is to develop an understanding of the fundamental processes involved in the catalytic conversion of methane to oxygenates and C_2 hydrocarbons over Pd surfaces. Catalytic, structural, and spectroscopic methodologies are being utilized to probe the pressure gap and structure sensitivity of the activation of methane and oxygen on several different Pd surfaces. Methane decomposition was shown to take place on the stepped–kinked Pd(679) surface at pressures ≥ 1 torr and temperatures ≥ 400 K by a mechanism that is best explained by the Luntz–Harris model involving thermally-assisted tunneling. The amount of monomeric carbon found at 400 K is equivalent to the step area, indicating a significant role of surface defects in methane decomposition. At 600 K, however, the surface carbon form methane oligomerizes into clusters, leaving 75% of the Pd surface free for further reactions. Based on this picture, monomeric carbon can be "frozen" because of the existence of an energy barrier for oligomerization. New results for Pd(311) show essentially the same behavior as that of Pd(679). Pd(111), Pd(679), and Pd(311) bind oxygen quite strongly, and diffusion into the metal occurs at 900 K before desorption. However, the subsurface oxygen causes the subsequent surface bonding Pd–O to be weak, and a new reactive state of surface oxygen is generated on Pd(111) and Pd(679) in this way. The Pd(100) face binds oxygen weakly via well-known structures, and new surface phase transformations have been discovered that may have bearing on catalysis. For example, the c(2 x 2) structure disproportionates around 500 K into a rare, mobile phase and the dense phase before any oxygen desorbs. The equilibration kinetics have been successfully modeled and lateral dipole interactions accounted for a strong dependence of energy of desorption from the rare phase on coverage. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) data have been obtained and interpreted with clean Pd(100) and c(2 x 2)O–Pd(100). With the former, forward focused diffraction dominates and the Pd(100) plane is unrelaxed to 3-4 layers, to within 0.02Å. With the latter system, a complete geometric–electronic picture is emerging and indicates that any adsorbate-Pd surface structure could be determined by these methods. Using a UV source, detailed studies of electronic structure of valence bands (VB) in chemisorbed layers of reactants are being conducted. This type of experiment provides for testing theory and identifying electron orbitals that participate in chemisorption by determining energy dispersion E(k) by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). Solid state theoretical calculations performed in this laboratory have identified the observed VB effects as bonding interaction of O 2p$\|$ orbitals with Pd $4d_{zx,yz}$ orbitals that dominate the surface states of Pd near the M-point of the Brillouin Zone.

Louisiana State University
Baton Rouge, LA 70803

Department of Chemical Engineering

287. *Gallium Zeolites for Light Paraffin Aromatization*
Price, G.L. **$79,900**
504-388-3068

Research is being conducted to determine the relationship between structural details of gallium ZSM-5 zeolites and their catalytic function for aromatization of light paraffins. Emphasis is placed on understanding the role played by gallium, how it is incorporated into the zeolite, whether it goes into exchange sites, into lattice tetrahedral sites, or simply becomes occluded into or on the lattice. The determination of what changes occur to both the gallium and the zeolite during the activation process is being studied as is the reaction mechanism. Zeolite characterization studies include X-ray diffraction, IR, NMR, and microbalance studies. Reaction mechanism studies include the use of isotopic tracers, traditional kinetic studies, and transient response kinetics.

Department of Chemistry

288. *Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Models and Precursors for Fullerenes*
Rabideau, P.W. **$100,000**
504-388-8859

This research program deals with the chemistry of large polynuclear aromatics with curved surfaces. Of particular interest are corannulene, C_{20}, and two C_{30} hydrocarbons that are called hemifullerenes. These compounds are models for fullerenes, the recently discovered, large carbon clusters. Fullerenes are produced by laser vaporization of graphite or coal, and their metal derivatives show great promise as superconductors. This research program has three objectives (1) Alkali metal addition to convex aromatics will be studied. Polyanion structure will be investigated theoretically by semiempirical and ab initio calculations, and experimentally by nuclear magnetic resonance (NMR) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Interest lies with the amount/location of metal(s) added, ion pairing, and electron density distribution. (2) The regio- and stereochemistry of the reduction (alkylation) of these macrocyclic rings with alkali metals in ammonia and other solvents will be investigated. The Birch reduction of buckminsterfullerene leads all the way to $C_{60}H_{36}$, and reductive methylation with lithium/tetrahydrofolate (THF) incorporates from 1 to 24 methyl groups. Hence the detailed pathway of buckminsterfullerene reduction is not fully understood and this program will provide insight. (3) Finally, the synthesis of C_{30} compounds may permit a new synthesis of C_{60} by dimerization that could accommodate selective ^{13}C substitution.

University of Louisville
Louisville, KY 40292

Department of Chemistry

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

The organometallic chemistry of bimetallic compounds that have CO_2 or CO_2-containing bridging ligands is being studied to provide a basis for understanding proposed intermediates in catalytic conversions of CO_2. Some of the bimetallic compounds are being prepared via reactions between metallocarboxylate anions and a second metal complex having a readily displaceable anion. A number of iron–rhenium and iron–tin complexes have been prepared and some have been structurally characterized. Three types of CO_2-bridged complexes are now known: μ_2-η^2 complexes in which one carboxyl oxygen remains free and two types of μ_2-η^3 complexes. The latter compounds differ according to their carboxyl C–O bond distances and according to the extent of carbene character in the metal to carboxyl carbon bond. The μ_2-η^2 complexes are converted to μ_2-η^3 complexes of the carbene type upon heating, but this reaction has been shown to be reversible in some cases. Two new metallocarboxylate anions, $(\eta^5{-}C_5Me_5)Re(CO)(NO)CO_2{}^-K^+$ and $(\eta^5{-}C_9H_7)Fe(CO)(PPh_3)CO_2{}^-K^+$, have been generated recently and new bimetallic compounds derived from them are being characterized which should provide additional assistance in defining the steric and electronic effects that control binding and reactivity of the bridging CO_2 ligand. Researchers have completed the structural characterization of $(\eta^5{-}C_9H_7)Fe(CO)(PPh_3)CO_2SnPh_3$, a compound of the μ_2-η^3 type, which exhibits the largest difference in carboxyl C–O bond distances yet observed for any system type. Large distortions of the carboxyl C–O and O–Sn bond lengths in this compound are the result of steric interactions involving the indenyl ligand. Reactions of the CO_2-bridged compounds with electrophiles are currently under investigation. Reactions of the metallocarboxylate anions with alkene and alkyne-coordinated metal cation complexes yield carboxyalkene and carboxyalkyne-bridged bimetallic complexes. The chemistry of these is being studied also.

University of Maryland at College Park
College Park, MD 20742

Department of Chemistry and Biochemistry

290. *Odd-Electron Organometallic Chemistry of Relevance to Hydrocarbon Functionalization*
Poli, R. **$70,508**
301-405-1809

The general objective of this project is to test the feasibility of C–H functionalization by organometallic radicals. General routes are being investigated to generate low-valent, reactive odd-electron systems. One class of target compounds consists of dihydride complexes with a 17-electron configuration, and one strategy currently being investigated is oxidation, followed by deprotonation, of saturated trihydride complexes. The previously unreported $[Cp_2NbH_3]^+$ that has the unpaired electron localized on the Cp rings was generated and identified by *electron paramagnetic resonance* (EPR) *spectroelectrochemistry* at 193 K. Synthetic work of precursors to trihydride complexes of molybdenum and tungsten led to the preparation of Cp^*MoX_3 (X = Cl, Br) and Cp^*WCl_3 which show complex rearrangement reactions. For example, Cp^*MoBr_3 exists in at least three different forms: $[CpMoBr_3]_2$, $[Cp^*{}_2Mo_2Br_4]Br_2$, and $[Cp^*{}_2Mo_2Br_4][Cp^*MoBr_4]_2$. The new trihydride complexes $CpMoH_3(dppe)$ and $Cp^*MoH_3(dppe)$ have been synthesized and their electrochemical oxidation is currently being investigated. Another class of target compounds consists of 17-electron complexes with bulky phosphine ligands whose dissociation may establish an equilibrium with 15-electron species. CoL_4 species (L = tertiary phosphine) are an example. The PMe_3 compound was previously reported in the literature but incompletely characterized. Other similar complexes with bulkier L are being investigated.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

291. *High-Pressure Heterogeneous Catalysis in a Low-Pressure, Ultrahigh Vacuum Environment*
Ceyer, S.T. **$105,000**
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. The results of these investigations on steam reforming, hydrogenation, and hydrogenolysis reactions on Ni(111) will provide critical tests of the mechanisms for these heterogeneous catalytic reactions proposed from high-pressure kinetic measurements.

292. *Controlled Synthesis of Polyenes by Catalytic Methods*
Schrock, R.R. **$130,000**
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.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

293. *Kinetics and Dynamics of Oxidation Reactions Involving an Adsorbed CO Species*
Harold, M.P. **$71,500**
413-545-6143

This research addresses the complex steady-state and dynamic phenomena that are encountered during catalytic oxidation reactions on both supported metal and metal oxide catalysts. Reaction systems of interest include methanol oxidation on $Pt/CeO_2/Al_2O_3$, ethylene oxidation on vanadium oxide (VO: V_2O_5, oxidized; V_2O_3, reduced), and NH_3 oxidation by NO on VO. Each of these reaction systems can exhibit intriguing phenomena, including long transients, oxidation-reduction cycling, thermokinetic oscillations, and steady-state multiplicity. A combination of kinetics and emission Fourier transform infrared (FTIR) studies are being conducted to provide the data necessary to formulate elementary step kinetic models. In particular, rival kinetic models of methanol oxidation on Pt are being discriminated based on their abilities to predict the apparent activation energy and reaction orders in the different rate-controlling regimes. The kinetic models are formulated from adsorbed intermediate (CO, methoxy species) data obtained using in situ FTIR. Of particular importance is the impact of the CeO_2 additive on the overall activity and selectivity (formation of CO versus CO_2). The capability of emission FTIR spectroscopy to monitor metal–oxygen vibrations in metal oxides is being exploited in the VO-catalyzed reaction systems. The intensities of selected IR peaks infer the metal oxidation state during reaction. Unsteady-state oxidation and reduction experiments using the emission IR spectra provide information about the time scales of these processes as well as the oxidation state pathways involved.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

294. *Hydrogen Induced C–C, C–N, and C–S Bond Activation on Pt and Ni Surfaces*
Gland, J.L. **$149,952**
313-764-7354

Hydrogenolysis of well-characterized adsorbed organic monolayers by coadsorbed atomic hydrogen on single crystal surfaces of Ni and Pt is the primary focus of this research. The structure and coordination modes of adsorbed reactants will be varied in a systematic way in an effort to characterize hydrogen addition selectivity and the kinetics of elementary hydrogen addition processes on well-characterized metal single-crystal surfaces. Nickel and platinum have been chosen as representative surfaces with high and low hydrogenolysis activity. The addition of adsorbed atomic hydrogen to C–C, C–N, and C–S bonds in adsorbed species of the type $-CH_2R$, $-NH_2R$, and $-SR$ will be characterized where R represents attached methyl, cyclohexyl, and phenyl groups. Ex situ interrupted reaction studies will be used to characterize monolayer hydrogen addition reactions for hydrogen pressures up to 10^{-4} torr by focusing on the adsorbed species remaining on the surface after reaction. In situ kinetic experiments will be performed for promising hydrogen addition reactions using fluorescence yield near edge spectroscopy (FYNES) to characterize the structure and reactivity of adsorbed carbon containing monolayers in pressures up to 10 torr of hydrogen. Basic understanding of the primary factors that control hydrogen addition selectivity and reactivity on metal surfaces will be increased by focusing on the issue of hydrogen induced bond activation on metal surfaces.

University of Minnesota
Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

295. *Homogeneous–Heterogeneous Combustion: Chemical and Thermal Coupling*
Schmidt, L.D. **$94,200**
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_2 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

296. Late Transition Metal Oxo and Imido Complexes

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

The synthesis and reactions of oxo, imido, hydrazido, dioxygen, and nitrosoarene complexes of the late transition metals are being studied. The interest in these complexes is primarily as models for species on late transition metal surfaces. The goal is to develop the chemistry of these model complexes as an aid to understanding the many important catalytic reactions that occur on late transition metal surfaces. Initial efforts at developing synthetic procedures for the oxo and imido complexes have been successful and have produced complexes that do mimic many of the properties of the analogous surface species. These properties include high basicity and oxo and nitrene transfer activity. Studies to explore the versatility of the synthetic procedures and the reaction chemistry of the complexes are continuing. Also being developed are model reactions for the dissociation and recombination of molecular oxygen on the metal surface. It was found that dioxo complexes can be oxidatively induced to eliminate molecular oxygen and that gold hydrazido complexes will decompose to gold clusters with elimination of tetrazenes, modeling recombination of atomic oxygen on metal surfaces. The latter reaction represents a novel and efficient method for the preparation of gold clusters, previously unavailable or available only in low yields.

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

Department of Chemistry

297. Reductive Coupling of Carbon Monoxide to C_2 Products

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

Both stoichiometric and catalytic coupling reactions have been realized during studies of the chemistry of carbyne and nitrene complexes. In the early transition-metal arena protonation of aryloxycarbyne ligands in the presence of free alkyne forms a vinylcarbene unit from insertion of the alkyne into the metal carbene bond. Intramolecular coupling of a phosphonium carbyne with a cis carbonyl ligand has been promoted with added nucleophile. Monomers with both carbene and alkyne ligands in the coordination sphere of d^4 tungsten centers resist coupling as the geometry of both ligands is inappropriate for metallocyclobutene formation. Ammonia addition to $[Tp'(CO)(PhC_2H)W(NCMe)]^+$ results in linking of the alkyne and nitrile ligands via a nitgrogen atom to form a six-membered aromatic metallocycle ring. Access to simple amido, imido and nitride ligands in the $Tp'(CO)_2W{\equiv}N$ system is encouraging for developing low-oxidation-state chemistry with multiple metal–nitrogen bonds. A low-temperature mechanistic study revealed that hydride addition to $Tp'(CO)_2W(NPh)^+$ occurs at a carbonyl ligand first and then hydride migration to the nitrene unit forms the amido product. In late transition-metal studies the copper(1) complex $Tp'Cu(C_2H_4)$ has been found to catalyze carbene transfer from ethyl diazoacetate to both olefins and alkynes. The same metal reagent also catalyzes nitrene transfer reactions from PhI=NTs to olefins.

Northwestern University
Evanston, IL 60208

Department of Chemical Engineering

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

Kung, H.H. **$135,000**
708-491-7492

The selective conversion of low-priced saturated hydrocarbons to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher value can be of great technological importance. For practical purposes, the ability to produce only one desired product among many possibilities, some of which are extremely thermodynamically favorable, is important. The emphasis of this project is to elucidate the properties of oxidic catalysts that could achieve these conversions efficiently by selective oxidation. 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. This explanation also explained the higher activation energy of the reaction observed on the higher laoding samples. Interestingly, when these catalysts were used to study the oxidation of pentane, it was found that maleic anhydride was produced as one of the major products on the higher loading sample, whereas dehydrogenation to pentenes was the dominant reaction on the low loading sample. The difference in the types of reactions between butane and pentane is being further investigated.

Department of Chemistry

299. 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 pathways 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 in situ 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 catalytic centers by in situ 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 $B(C_6F_5)_3$ as an alkide abstraction reagent. Finally, these results encouraged study of the adsorption of $Th(\eta^3\text{-allyl})_4$ on Al_2O_3. This yields heterogeneous arene hydrogenation catalysts which rival or surpass conventional platinum metal catalysts in activity, and which effect the very rapid exchange of saturated hydrocarbon C–H groups with D_2.

300. Chemical Interactions in Multimetal–Zeolite Catalysts

Sachtler, W.M.H.	**$109,000**
708-491-5263	

This research focuses on zeolite-based catalysts containing two transition elements of different reducibility. Conditions have been identified under which Rh, Pt, or Pd is completely reduced; the second metal (Fe, Ni, Co, or Mn) remains largely ionic, but induces dramatic changes in catalytic performance of the Pt group metal. Causes for this catalyst promotion include (1) enhanced reducibility, leading to bimetal clusters; (2) chemical anchoring, leading to enhanced metal dispersion; and (3) “SMSI effect” (i.e., interaction of TM ions with adsorbed molecules). Formation of alloy clusters in (Pd + Co)/NaY is induced by enforced migration of Co ions to large cages. Hydrogenation of CO over neutralized Rh/NaY leads exclusively to hydrocarbons, but oxygenates are formed over (Rh + Mn)/NaY. In (Pd + Fe)/NaY and (Pd + Fe)/NaHY most Fe ions are reduced to Fe^{2+}, but some to Fe^0. Surprisingly, bimetallic clusters containing only one or two Fe atom(s) exhibit ferromagnetic resonance signals; FTIR and Mössbauer data testify strong interaction of Fe and Pd. NO_x reduction over Cu/ZSM-5 catalysts is enhanced by traces of Pt, but Pt-rich catalysts are inferior to Cu/ZSM-5. PtGa/ZSM-5 is less selective for aromatization of C_3 than Ga/ZSM-5.

301. 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 the oxo, sulfido, carbido, and hydrido ligands and their derivatives. Extensive cluster chemistry is observed for the carbido ligand, which for example, can be converted to the CCO ligand and from there to acetylide and acetylene ligands using methods developed in this laboratory. Clusters were prepared containing the C_2 through C_4 units using a CCO ligand as the carbon source. The chemistry of cluster bound oxygen is somewhat more limited than that of carbon, but a recently found example demonstrates that the oxo ligand can be an effective nucleophile. In related recent research, researchers observed the transformation of coordinated S ligand.

University of Oklahoma
Norman, OK 73019

Department of Chemistry and Biochemistry

302. 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 $(MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (1) have revealed that a variety of Lewis acids react with 1 to promote rapid decarbonylation with production of various novel adducts–derivatives of the Lewis acid with $Cp'_2Nb(O)R$. 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 $Cp'_2Nb(CO)R$ (2) complexes in the thermolyses of $Cp'_2Nb(CO_2)R$, it was discovered that 2 [and $(C_5H_5)_2Mo(CO)$ (3)] react rapidly with molecular oxygen to produce the corresponding CO_2 complexes $(\eta^5\text{-}C_5H_4CH_3)_2Nb(\eta^2\text{-}CO_2)R$ (1) and $(C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (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 $CP'_2NbCO(H)$ produces $Cp'_2Nb(O)(\eta^1\text{-}OCOH)$, 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, $Cp'_2Nb(\eta^2\text{-}COS)$. In the catalytic area, solutions of $[(PhMe_2P)_3Rh(NBD)]BF_4$ (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 $[H_2Rh(PMe_2Ph)_3(S)]BF_4$ (6; S = H_2O, THF) that insert CO_2 to give formato species $[HRh(S)(PMe_2Ph)_3(\eta^1\text{-}OCHO)]BF_4$ and $[HRh(S)(PMe_2Ph)_2(\eta^2\text{-}OCHO)]BF_4$, 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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Department of Chemical Engineering

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

Vannice, M.A. **$132,000**
814-863-4803

The project objectives are (1) to elucidate the chemistry involved in the creation of metal-support interactions that have a pronounced influence on adsorption and catalytic behavior, (2) to use these effects to alter favorably 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 and the chemical and physical state of the metal and support. Early studies produced over 100-fold rate enhancements for CO and acetone hydrogenation and increased selectivity from zero to over 35% for crotyl alcohol formation from crotonaldehyde, rather than butyraldehyde, when Pt was dispersed on titania. Special active sites at the metal-support interface have been proposed to explain this behavior. Recent results for acetophenone hydrogenation over Pt show enhanced selectivity to phenylethanol (from 60% to 90%) using TiO_2 as a support. Au/TiO_2 catalysts were initially found to be excellent CO oxidation catalysts at room temperature. Recent studies have confirmed this and have shown they retain activity below 273 K. The influence of Cl and H_2O is now being examined. 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 is being used to investigate CO and acetone adsorbed on a Pt foil, a TiO_x-covered Pt foil, a TiO_2 single crystal, and a Pt-covered TiO_2 single crystal. Present results indicate the acetone carbonyl bond interacts more strongly with a foil than a Pt(III) surface. Studies of benzene, toluene, and xylene hydrogenation have shown that turnover frequencies (TOFs) on Pd can be increased using acidic supports. The addition of methyl groups to the ring decreases TOF values on both Pd and Pt. The presence of acidic adsorption sites on the support supplied by spilled-over hydrogen from the Pd or Pt crystallites has been proposed to explain this behavior. The behavior of polyaromatic hydrocarbons is now being investigated by studying the vapor-phase hydrogenation of l-methylnapthalene.

Department of Chemistry

304. *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 $[Cp(CO)(PPh_3)Mn{-}C{\equiv}CR]^-$ 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.

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

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

The catalysis of organic 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 two principal areas of transition metal catalyzed transformations of small molecules. The first involves investigations of homogeneous metal catalyzed processes for the synthesis of several different carbon monoxide containing polymers and the study of the reactivity of the resultant materials. The principal goals in this area are (1) 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; (2) the synthesis of regiospecific, stereospecific and, ultimately, chiral alternating olefin-carbon monoxide copolymers using appropriate catalysts; and (3) the synthesis of alternating copolymers of functionalized olefins with carbon monoxide. The second principal research area encompasses new catalytic systems involving both heterogeneous and homogeneous metal components for the specific oxidation of hydrocarbons. Specifically, the scope and the mechanism of the palladium and platinum-catalyzed oxidation of olefins, alkanes, and arenes by dioxygen in aqueous medium in the presence of coreductants will be investigated.

Department of Materials Science and Engineering

306. *Determination of the Distribution of Hydrogen in Coal by Fourier Transform Infrared (FTIR) Spectroscopy*

Painter, P.C. **$103,000**
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 c^* and blob model of DeGennes to obtain an expression for the free energy. Previous work has allowed researchers to account for hydrogen bonding and they are now calculating the phase behavior of various coal–solvent mixtures. A particularly intriguing result of this work is that this new model predicts a clustering effect, or compositional heterogeneities, in swollen coal gels.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemical Engineering

307. *Support Effects Studied on Model Supported Catalysts*

Gorte, R.J. **$93,000**
215-898-4439

The effect of oxide composition and structure on the properties of supported metal catalysts is being examined. The model catalysts are prepared by depositing catalytic metals onto flat, oxide substrates and can be characterized by Auger electron and X-ray photoelectron spectroscopies. Transmission electron microscopy is being used to examine the structure of the metal particles and overlayers. On these samples, desorption rates for simple reactants can be measured using temperature-programmed desorption (TPD) without interference from diffusion and readsorption. TPD is being used to examine the effect of particle size and substrate composition on the desorption kinetics of simple reactant molecules, and steady-state reaction measurements at near atmospheric pressures are being used on the same sample to determine how the changes in desorption rates affect catalytic rates.

Department of Chemistry

308. *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. This project has resulted in the discovery of well-characterized ruthenium complexes $(Me_3P)_3Ru(H)_3(SiR'_3)$ that catalyze the dehydrogenation of tertiary silanes at 150 °C to produce a distribution of linear and branched carbosilanes. In the presence of hydrogen acceptors such as *t*-butyl ethylene, catalytic dehydrocoupling is rapid at 80–100 °C. Mechanistic studies indicate that the key C–H activation is achieved by β-hydrogen elimination from silyl ligands to generate transient metal silaolefin complexes of the type $L_nRu(\eta^2\text{-}R_2Si{=}CR'_2)$, and that competing α-elimination leads to catalytic silane redistribution reactions. Secondary silanes such as Me_2SiH_2 undergo 1,1-dehydrogenative coupling in the presence of hydrogen acceptors to yield oligomeric polysilanes of composition $(Me_2Si)_n(MeHSi)_m$ $(n + m \sim 10)$. Formation of Si–Si bonds rather than Si–C bonds results from facile α-H elimination in $Ru\text{-}SiMe_2\text{-}H$ species. Current studies are aimed at increasing the selectivity of Si–C and Si–Si bond forming processes relative to redistribution, and understanding reactions leading to catalyst degradation so that more robust catalysts can be developed.

309. *Synthesis and Properties of New Preceramic Materials*

Sneddon, L.G. **$108,000**
215-898-8632

Because of their high strengths, low densities, high temperature and chemical stabilities, and controllable electronic properties, ceramics and ceramic-composite materials are in the forefront of advanced materials technologies. Most ceramic materials can already be produced in large quantities via conventional powder techniques; however, these materials, because of their brittle and refractory properties, are not easily formed into complex shapes. Therefore, applications of advanced ceramics as films, fibers, coatings, or other complex shaped materials will require new ceramic processing methods. This work is focused on the development of new polymeric-precursor synthetic routes that would 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 borazine-based polymers, including polyvinylborazine, polyborazylene, and borazine-modified polysilazanes. 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 methodolgy needed to produce new inorganic monomers and polymers is also a key component of this project.

310. *Catalytic Hydrogenation of Carbon Monoxide*

Wayland, B.B. **$124,000**
215-898-8633

Observations of metalloformyl complexes produced by reactions of CO, and reductive coupling of CO to form metallo α-diketone species have suggested a multiplicity of routes to organic oxygenates that utilize these species as intermediates. Thermodynamic and kinetic-mechanistic studies are used in guiding the design of new metallospecies to improve the thermodynamic and kinetic factors for individual steps in the coupling and hydrogenation of CO. Variation of the electronic and steric effects associated with the ligand arrays along with the influences of the reaction medium provides the chemical tools for tuning these factors. Recent studies have focused on the use of rhodium(II) metalloradicals for activating both CO and hydrogen. Variation of the ligand steric requirements for a series of rhodium(II) porphyrin complexes has resulted in obtaining selective reductive coupling of carbon monoxide and metal carbonyl species that accomplish one-electron reactions at the carbonyl carbon. Potential utilization of this new range of CO reactivity in forming organic oxygenates is being explored through the use of bifunctional catalyst systems designed to couple the unique ability of rhodium complexes to produce formyl and diketone intermediates with a second catalyst that hydrogenates these intermediates.

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Department of Chemistry

311. *Studies of Supported Hydrodesulfurization Catalysts*

Hercules, D.M. **$104,000**
412-624-8300

The aim of the research is to investigate the Mo(W) oxidation states and catalytic activity relationship in reduced Mo(W)/Al_2O_3, Mo(W)/TiO_2 and Mo(W)/SiO_2 catalysts. The ultimate objective of the study is to identify required Mo(W) oxidation states for various catalytic functions. X-ray photoelectron spectroscopy (XPS) and electron spectroscopy for chemical analysis (ESCA) were used to determine the distribution of W oxidation states in a 5-wt % WO_3/TiO_2 catalyst reduced in hydrogen in the temperature range 400–700 °C. Because the region of interest, W 4f, overlaps with the Ti 3p energy level, a multiple analysis procedure, which included deconvolution, nonlinear least squares curve fitting (NLLSCF) and factor analysis (FA) were used to analyze the data. Deconvolution was better able to resolve the peaks in this region and thus elucidate the position of the W components for each reduction temperature. It was shown that there are a maximum of 3 W 4f doublets. The W $4f_{7/2}$ peaks of these components were located at 35.5 eV, 33.3 eV, and 31.1 eV, and they were assigned to W^{+6}, W^{+4}, and W^0, respectively. FA verified the presence of 3 spectral W components. X-ray diffraction (XRD) verified the presence of W^0 at the reduction temperature of 675 °C. NLLSCF, using the positions from deconvolution, was able to determine the distribution of W oxidation states as a function of reduction temperature. W^{+6} steadily decreased with increasing reduction temperature, W^{+4} initially appears at 408 °C and goes through a maximum around 550 °C; W^0 was detected following reduction at 550 °C and was the only species present for reduction temperatures higher than 665 °C. From the distribution, it could be said that a 5 wt % WO_3/TiO_2 catalyst most likely undergoes two different reduction pathways: (1) $W^{+6} \rightarrow W^{+4} \rightarrow W^0$ and (2) $W^{+6} \rightarrow W^0$.

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

Yates, J.T., Jr. **$161,000**
412-624-8320

This research is concerned with the use of vibrational spectroscopy 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) spectroscopic FT-IRAS studies on C–H bond softening in hydrocarbons interacting with single crystal metal surfaces, (3) studies of electron stimulated migration of adsorbates on stepped single crystals, and (4) fundamental studies of the metal–support interaction on both real and model metal catalysts supported on Al_2O_3 and SiO_2. Both HREELS and transmission IR spectroscopy are employed in project (4).

Purdue University
West Lafayette, IN 47907

Department of Chemistry

313. *Anchoring Strategies for Bimetallic Species in Zeolites*

Bein, T. **$92,000**
317-494-5495

This research program is aimed at the development of new immobilization concepts for organometallic fragments in the crystalline pore structure of zeolites and other microporous materials. A new approach is explored by introducing heterobinuclear organometallic compounds as candidates for linking catalytic functions to zeolite frameworks. Furthermore, it is planned that intrazeolite bimetallic clusters will be prepared through controlled decomposition of zeolite-anchored heterobimetallic compounds. The chemistry and reactivity of $Me_3SnMn(CO)_5$ in zeolite NaY and HY was studied with extended X-ray absorption fine structure (EXAFS) spectroscopy and in situ Fourier transform infrared/temperature programmed desorption–mass spectroscopy (FTIR/TPD–MS) techniques. Subsequently, the tin–cobalt complex, $Me_3SnCo(CO)_4$, has been a focus of detailed studies. The reactivity of tricarbonyl(cyclopentadienyl)(trimethylstannyl)molybdenum in new mesoporous hosts has also been explored. A recent development is the design of vanadium oxo species in different micro- and mesoporous hosts. Researchers use a comprehensive combination of analytical techniques that allow probing of local structural changes at the molecular level. These techniques include EXAFS spectroscopy utilizing synchrotron radiation, in situ FTIR coupled to thermodesorption/MS, UV–near-IR, and charge-coupled device (CCD) Raman. Diagnostic catalytic studies of hydrocarbon conversions will address issues such as the location of catalytically active sites, stability against migration, and shape selectivity introduced by the molecular sieve pore structure.

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

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

The project continues to explore the utility of high-valent, early transition metal compounds for conducting the catalytic hydrogenation of arene rings. Recent developments have involved the isolation and study of organometallic compounds that are reasonable intermediates in the catalytic hydrogenation of arenes by Group 5 metal hydride compounds. The kinetics and stereochemistry of the catalytic hydrogenation of benzene, 1,3-cyclohexadiene and cyclohexene by the cyclohexadiene complexes $[(ArO)_3M(\eta^4\text{-}C_6H_8)]$ (ArO = 2,6-diisopropylphenoxide) have been investigated. A new series of heterogeneous catalysts for conducting arene hydrogenation have been developed by depositing Group 5 metal organometallic precursors on oxide supports. High activity for hydrogenation of even hindered arenes has been achieved. The activity and regio- and stereochemistry of the catalytic hydrogenation by these homogeneous and heterogeneous catalysts have been compared. The exact nature of the surface supported catalysts is being investigated.

315. *Fundamental Studies of Reactive Intermediates in Homogeneous Catalysis*

Squires, R.R. **$75,000**
317-494-7322 **(24 months)**

A flowing afterglow triple quadrupole instrument is being used to study the gas-phase reaction dynamics and thermochemistry of organometallic species relevant to catalysis. A nearly complete set of first-row metal carbonyl anion bond strengths has been measured. Most of the metal–ligand bond strengths in $M(CO)_n^-$ ions (M = V–Ni; n = 3–6) are 38–46 kcal/mol, which can be taken as the intrinsic bond strength. In some cases, the first few ligands bonded to a bare metal anion have significantly weaker bond strengths. These bond strengths correlate with the promotion energy necessary to reach a state of the metal anion suitable for bonding. The anion bond energies have been combined with literature data to derive neutral metal–ligand bond strengths for M = Cr, Fe, and Ni. Studies of the intermediate $Fe(CO)_4COOH^-$ have been used to complete the thermodynamic profile of the $Fe(CO)_5$-catalyzed water-gas shift reaction in the absence of solvent. Although decarboxylation of $Fe(CO)_4COOH^-$ is exothermic by 4 ± 7 kcal/mol, there is a barrier of 19 ± 3 kcal/mol. Construction of a selected-ion flow tube triple quadrupole apparatus has been completed, and initial studies of the CH_2Cl^+ ion have been conducted. An electrospray ionization source for the analysis of organometallic species in solution has been built and is currently being tested.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemistry

316. *Selective Transformations of Carbonyl Ligands to Organic Molecules*

Cutler, A.R. **$129,000**
518-276-8447

Carbonylation of α-alkoxyethyl ruthenium complexes $(\eta^5\text{-indenyl})(L)(CO)Ru\text{–}CH(OR)CH_3$ [L = PPh_3, PEt_3, $P(OMe)_3$; R = Me, Et] gave isomerized α-alkoxypropionyl derivatives, $(\eta^5\text{-Ind})(L)(CO)Ru\text{–}C(O)CH_2CH_2OR$. Treatment of $(\eta^5\text{-Ind})(CO)_2Ru\text{–}CH(OR)CH_3$ with PEt_3 (room temperature) provided the same products. These CO insertion–isomerization studies have been extended to $(\eta^5\text{-Ind})(CO)_2Ru$-*n*-/*i*-propyl complexes. Obtaining the necessary alkyl complexes entailed synthesizing and characterizing η^2-alkene complexes, $(\eta^5\text{-Ind})(L)(CO)Ru(\eta^2\text{-}CH_2{=}CHR)^+$. Diastereoselective, $Mn(CO)_5C(O)Ph$-catalyzed hydrosilation of $Cp(L)(CO)Fe\text{–}C(O)CH_3$ [L = PPh_3, PEt_3, $P(OMe)_3$, $P(OPh)_3$] has been established. Examples of RR, SS and RS, SR diastereomers of $Cp(L)(CO)Fe\text{–}CH(OY)CH_3$ [Y = $SiHPh_2$, $SiHEt_2$, Me, Et] were prepared; the alkoxyethyl complexes were obtained through alcoholysis of the siloxyethyl systems. With a variety of Rh catalysts, $Cp(L)(CO)Fe\text{–}C(O)CH_3$ and dihydrosilanes transform directly to their vinyl derivatives, $Cp(L)(CO)Fe\text{–}CH{=}CH_2$. Rh-catalyzed $PhSiH_3$ reduction of Fe acyl complexes efficiently affords alkyl derivatives, $Cp(L)(CO)FeCH_2R$ [R = Me, Et, t-Bu, Ph, and so forth]. This silane with Mn-catalysis (e.g., $Mn(CO)_5C(O)Ph$) quantitatively convert esters $RC(O)OR'$ to ethers RCH_2OR', an unprecedented reaction. These reactions, often exothermic, can be conducted on a preparative scale with a wide range of ester substrates, including unsaturated and lactones. A kinetics and mechanistic study on the $Mn(CO)_5$(p-toluoyl)-catalyzed SiH–SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ (room temperature in C_6D_6) has been completed. Preequilibrium kinetics were consistent with second-order isotope exchange reaction. Plots of initial velocities v_0 against $(HSiMe_2Et)_i$ are consistent with saturation kinetics. Graphical analysis of double reciprocal or Lineweaver–Burk plots (linear) is in accord with a ping-pong Bi Bi mechanism that operates under rapid equilibrium conditions and involves coordinatively unsaturated manganese silyls, $(CO)_4Mn\text{–}SiR_3$, as active catalysts. These manganese silyls interconvert by sequentially adding one substrate silane and then releasing a product silane. A related mechanism apparently operates during $[Mn(CO)_4Br]_2$-catalyzed alcoholysis of $HSiMe_2Ph$, N_t = 11,200 h^{-1} for 2-butanol. Tertiary and unsaturated alcohols (1:1 with silane) work with 0.08% precatalyst.

University of Rochester
Rochester, NY 14627

Department of Chemistry

317. 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 fused polycyclic hydrocarbons to give eta-2 complexes and/or C–H bond activation products. The relative energetics of these two processes is dependent upon the loss of resonance energy in the aromatic fragment. The effects of electron withdrawing groups on the stability of the eta-2 complexes have also been examined. Reactions on a series of trispyrazolylborate complexes of rhodium have been examined. The complexes [HB(3,5-dimethylpyrazolyl)$_3$]Rh(CNR)$_2$ where R = neopentyl or 2,6-xylyl have been prepared and found to undergo photochemical oxidative addition or arenes. Reaction with phenylazide gives the extremely photolabile carbodiimide complex [HB(3,5-dimethylpyrazolyl)$_3$]Rh(CNR)(PhN=C=NR), which lose the carbodiimide ligand with unit quantum efficiency. The reactive fragment that is produced reacts with arenes and alkanes to give stable oxidative addition products. The mechanism of reverse reaction (reductive elimination of benzene) has been examined in detail and is found to occur by way of reversible formation of a fluxional η^2-benzene complex that then reacts with isocyanide in a rate-determining bimolecular step. Competitive activation of alkanes has been examined, showing that this fragment is more selective than either Cp*Rh(PMe$_3$) or Cp*Ir(PMe$_3$). The rates provided by reductive elimination studies have been used to establish relative metal–carbon bond strengths for a series of hydrocarbons, and indicate that differences in D(M-R) are greater than differences in D(R-H). Methane has been activated thermally at 2000 psi. Further studies of functionalization reactions are under way.

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

Department of Chemistry

318. 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 (nonphotochemical) alkane transfer–dehydrogenation under high pressures of dihydrogen. 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^{i}Pr$_3$)Cl and [Rh(PMe$_3$)$_2$Cl]$_2$. The latter systems require only moderate pressures of dihydrogen. Apparently, the role of hydrogen in all cases is to add to the complexes that then dissociate to afford the species H$_2$Rh(PMe$_3$)$_2$Cl. The dihydride then reacts with hydrogen-acceptor to give the fragment Rh(PMe$_3$)$_2$Cl that 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. The highly unsaturated monomeric complex, Rh(P^{i}Pr$_3$)$_2$Cl, is found to react in cyclooctane solution to give H$_2$Rh(P^{i}Pr$_3$)$_2$Cl (ca. 60% yield) and cyclooctene. The reaction efficiency is limited by ligand dehydrogenation reactions. In the presence of a good hydrogen acceptor, norbornene, transfer–dehydrogenation is observed. The efficiency of this reaction, however, is also severely limited by ligand dehydrogenation; only 4.1 turnovers cyclooctene have been obtained. Future work will focus in part on the development of complexes RhL$_2$Cl where L has properties similar to that of P^{i}Pr$_3$ but is more resistant to dehydrogenation.

Department of Physics and Astronomy

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

Madey, T.E. **$105,000**
908-932-5185

Model bimetallic catalysts (i.e., ultrathin films of metals on metals) are being studied with the goal of probing the relationship between microscopic surface structure and chemical reactivity. The focus of these studies is on planar but atomically rough single crystal surfaces, such as bcc(111) and fcc(210). These are morphologically unstable surfaces that can undergo massive surface reconstruction and faceting when covered with ultrathin metal films (ca. 1 monolayer thick) upon annealing to elevated temperatures. For ultrathin films of certain metals (Rh, Pd, Ir, Pt, Au) on W(111) and Mo(111) the film-covered surfaces reconstruct to form microscopic pyramidal facets having predominantly (211) orientations upon annealing above ca. 800 K. Fractional monolayers of O and S also cause faceting. In contrast, ultrathin films of Ti, Co, Ni, Cu, and Ag do not induce faceting. Both LEED and ultrahigh vacuum scanning tunneling microscopy (UHV-STM) are used to characterize surface morphology and to measure facet size distributions. The faceting occurs for overlayer elements having Pauling electronegativities greater than 2.0, suggesting that electronic effects are playing a role in structure changes. The reactivity of faceted surfaces is being probed using a structure-sensitive catalytic reaction, the hydrogenolysis of n-butane.

University of South Carolina
Columbia, SC 29208

Department of Chemistry

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

The current objective is to study the nature of the chemical transformations of unsaturated hydrocarbons that have amine containing substituents by metal cluster complexes. The principal objectives are to determine (1) the nature of C–H and C–N bond cleavage and bond formation processes at multinuclear metal sites and (2) the nature of the coordination and reactivity of activated amines in metal cluster complexes and the relationship of these to the bond transformation processes. Additional studies are focused on reactions of cluster complexes containing activated amine ligands with hydrogen for the purpose of characterizing important hydrogenation and hydrogenolysis reactions. The reactions of strained ring carbocycles and heterocycles containing one nitrogen or sulfur atom are being studied to try to ascertain factors that may promote the opening of the rings.

University of Southern California
Los Angeles, CA 90089

Department of Chemistry

321. *Chemistry of Bimetallic and Alloy Surfaces*
Koel, B.E. **$100,000**
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

322. *Studies of the Stabilities and Reactions of Solution-Phase Organic Radicals*
Bausch, M.J. **$94,000**
618-453-6461

Research in this project aims to develop a more complete understanding of the stabilities and reactions of delocalized (molar mass > 100 g) organic radicals, radical ions, and their precursors. Microelectrode-based fast scanning cyclic voltammetric (FSCV) techniques have proven useful in examination of the redox properties of selected species as well as the reactions of the electrochemically generated products. For example, the use of FSCV enables evaluations of the solution-phase kinetics of carbon-centered radical dimerizations. These experiments are yielding new facts that quantify both steric and electronic factors that affect the velocity at which delocalized solution-phase carbon-centered radicals react. Ongoing research is designed to enable evaluation and comparison of heterolytic and homolytic bond strengths for bonds present in organic radicals, radical cations, and radical anions. The redox properties of aromatic species such as phenalene, benzanthrene, and corannulene are also being investigated. Analyses of the data that result from these experiments enable formulation of new hypotheses that should more accurately rationalize the formation and subsequent reactions of organic radicals and add new insights into the understanding of chemical reactions associated with the combustion and conversion of fossil fuels.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

323. *The Dynamics of Adsorption on Clean and Adsorbate-Modified Transition Metal Surfaces*
Madix, R.J. **$144,000**
415-723-2402

Dissociative adsorption is often believed to be the first step in catalytic processes involving alkanes. Two pathways to dissociation have been identified; namely, precursor-mediated and direct collisional activation. Precursor-mediated dissociation involves first the molecular adsorption of the alkane and may dominate the process at low incident kinetic energies, whereas at higher energies, dissociation may occur during the collisional encounter with the surface. Both the dynamics of the molecular adsorption of propane and the dissociative adsorption of ethane were studied on Pt(110) using supersonic molecular beam techniques combined with methods of surface science to further the understanding of alkane activation by metals. All experiments were performed with a Pt(110) crystal that showed the low-energy electron diffraction pattern characteristic of the (2 x 1) reconstruction. Molecular beams of differing velocities were formed by seeding propane into helium. Adsorption probabilities were measured as a function of angle of incidence and kinetic energy. The adsorption probability of propane at normal incidence onto the clean Pt(110) surface decreases as the incident kinetic energy is increased. The adsorption probability scales as $E_T\cos^{0.4}\theta$, provided the beam in incident along the azimuth parallel to the close-packed direction on the surface. For molecules incident along the azimuth normal to the close-packed direction, the adsorption probability decreases with increasing angle of incidence, a clear consequence of the microroughness of this surface. To complement the extensive studies of ethane adsorption on Pt(111), a careful study was made of the dissociative adsorption of ethane on Pt(110). For beams incident along the azimuth parallel to the close-packed direction, the dissociative adsorption probability increased with the normal component of the incident translational energy over the entire range of energies studied, as was observed for Pt(111) . The reaction probabilities can be predicted from the values on Pt(111), indicating that the reaction dynamics on Pt(111) and the (111) microfacets of the (110) surface are identical.

State University of New York at Binghamton
Binghamton, NY 13902

Department of Chemistry

324. Photochemistry of Intermolecular C–H Bond Activation
Lees, A.J. **$79,560**
607-777-4478 **(24 months)**

This research is focused on determining the photophysical and photochemical mechanisms of several transition-metal organometallic complexes known to undergo light-induced intermolecular C–H bond activation reactions with hydrocarbon substrates. In a detailed study of the photochemistry of $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ ($Cp = \eta^5\text{–}C_5H_5$; $Cp^* = \eta^5\text{–}C_5Me_5$) it was unexpectedly found that photosubstitution processes with entering phosphine and phosphite ligands took place via an associate mechanism, while the intermolecular C–H/Si–H bond activation occurred by a dissociative process. These reactions have now been characterized by UV-visible and FTIR spectroscopy and photochemical quantum efficiencies have been determined for these processes; a complete mechanistic picture has been described that accounts for photophysical deactivation and the ligand substitution and C–H/Si–H bond activation steps of $CpRh(CO)_2$ and $Cp^*Rh(CO)_2$ in hydrocarbon solutions. In addition, the C–H bond activation photochemistry of the $(HBPz^*_3)Rh(CO)_2$ (Pz^* = 3,5-dimethylpyrazolyl) complex in room-temperature alkane (RH) solution has been investigated. This C–H bond activation reaction is unusual because the photochemistry is so clean and the reactant can be completely converted to the corresponding $(HBPz^*_3)Rh(CO)(R)H$ product. Absolute photochemical quantum efficiencies have been obtained for intermolecular C–H bond activation following excitation at various wavelengths in the near-UV and visible regions. These results reveal that two different electronically excited states are implicated in the photochemistry of this molecule and a mechanism for intermolecular C–H bond activation in this system is currently being formulated. Ongoing work involves study of analogous pyrazoyl complexes and their photochemical mechanisms.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

325. Mechanistic Examination of Organometallic Electron-Transfer Reactions
Atwood, J.D. **$112,133**
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 such as H^+, CH_3^+, Br^+, and CO^{2+} 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 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. The group transfer reactions provide a new mode of reactivity that may have applications to CO reduction chemistry (CO^{2+} transfer) and to selectivities in the various catalytic reactions of hydrocarbon fragments (R^+ and H^+ transfer). Halogen transfer, formally as X^+, is also observed. Transfer of X^- does not occur from Group 6 anionic halides, $M(CO)_5X^-$ to $Mn(CO)_6^+$. Transfer of hydride as H^- does occur. 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

326. The Relationship between Hydroxyl Groups on Oxide Surfaces and the Properties of Supported Metals
Schwarz, J.A. **$83,000**
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 the 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

327. ***Correlations between Surface Structure and Catalytic Activity/Selectivity***
Goodman, D.W. **$203,500**
409-845-0214

This project involves an investigation of the issues that are keys to understanding the relationship between surface structure and catalytic activity/selectivity. A strong emphasis is placed on the origins of the special properties of mixed-metal catalysts. 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), temperature programmed desorption (TPD), low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), Fourier-transform infrared absorption spectroscopy (FT-IRAS), and atomic force (AFM) and scanning tunneling microscopies (STM). The project objectives are (1) the investigation of the unique catalytic properties of ultrathin metal films with emphasis on methanol synthesis and carbon monoxide oxidation; (2) the understanding of the nature of the electronic modification found in metal overlayer systems compared to their bulk analogs and the relationship of the perturbations to the special chemistry exhibited by these systems; and (3) the simulation of supported metal catalysts using metal deposits on thin oxide films (e.g., Ni, Cu) onto a well-characterized thin oxide film of the support material (e.g., Al, Si, Mg).

328. ***Catalysts and Mechanisms in Synthesis Reactions***
Lunsford, J.H. **$105,000**
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 hot metal and metal oxide surfaces during a catalytic reaction. The detection of methyl radicals using the MIESR system has been particularly effective in establishing the mechanism for the oxidative coupling reaction, in which methane is converted to ethane and ethylene. Recently it has been demonstrated that methane and molecular oxygen react over lanthanum oxide and neodymium oxide in the temperature range 1200 to 1350 K to form hydroxyl radicals that emanate into the gas phase. The less basic cerium oxide and ytterbium oxide form 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. The rotational temperature of the hydroxyl radicals is essentially the same as the temperature of the catalyst. Hydroxyl radicals are believed to be formed by the abstraction of hydrogen atoms from water, probably at surface peroxide ions. These hydroxyl radicals may play an important role in catalytic combustion.

University of Texas at Austin
Austin, TX 78712

Department of Chemical Engineering

329. ***Catalytic Hydrocarbon Reactions over Supported Metal Oxides***
Ekerdt, J.G. **$90,000**
512-471-4689

This research program is directed toward developing a fundamental understanding of how catalyst composition, redox ability, and structure control the catalytic properties of metal oxides. Oxide systems that permit the examination of the role of metal oxide cations separately and in pairwise combinations are being developed. Organometallic complexes containing allyl, cyclopentadienyl, or carbonyl ligands are exchanged with the hydroxide ligands of silica, alumina, titania, and zirconia. The exchange technique is used to achieve high metal oxide loadings without the formation of supported crystallites. The supported complex is subsequently oxidized to generate a supported oxide. Isolated anions, such as MoO_4^{2-}, and polyanions, such as $Mo_7O_{24}^{6-}$, form from these precursors when the oxides are maintained in an ambient environment, and isolated structures, such as MoO_6, are formed under anhydrous conditions. Monometallic complexes of Mo, W, and Cr, and heterobimetallic complexes of MoW are being used to prepare supported metal oxides. The research involves characterization of the organometallic deposition process, characterization of the resulting oxides using spectroscopic techniques, studies of the photoreduction of the oxides to lower oxidation states, and studies of the catalytic properties in oxidation, metathesis, and reductive aldehyde/ketone coupling reactions.

Department of Chemistry

330. Morphological Aspects of Surface Reactions

White, J.M. **$135,000**
512-471-3704

This work focuses on substrate morphology and on fragments synthesized by thermal, electron, and photon activation. (1) Low energy electron diffraction, Auger electron spectroscopy, and scanning tunneling microscopy were used to determine the local morphology of a low temperature thermally faceted $TiO_2(001)$ rutile surface in ultrahigh vacuum (UHV). The observed step structure on (011) planes and the structure of (114) facets suggest facet growth by surface migration. (2) Temperature programmed desorption (TPD) indicated that C_2H_3I, n-C_3H_7I, i-C_3H_7I, $ClCH_2I$, and $Cl(CH_2)_3I$ dissociate thermally during TPD after adsorption at 100 K. The resulting hydrocarbon fragments recombine, without further C–H or C–C bond breaking, and desorb as higher hydrocarbons by forming C–C bonds. A new tool was developed for diagnosing surface reactions that involve C–H bond cleavage–predosed oxygen TPD (POTPD), a technique based on scavenging surface H(a) by small amounts of preadsorbed O(a) to form water. (3) For π-bonded benzene on Ag(111), exposure to low-energy electrons results in selective decomposition of C_6D_6(a) to surface D atoms and phenyl fragments, which recombine and desorb as phenyl at 275–390 K. (4) For ethyl chloride, methyl bromide, and methyl iodide on Ag(111), irradiation with UV photons leads to bond breaking; while some of the resulting hydrocarbon fragments desorb, fractions are retained and recombine to form saturated hydrocarbons in postirradiation TPD.

Tulane University
New Orleans, LA 70118

Department of Chemical Engineering

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

Gonzalez, R.D. **$89,997**
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, separations, 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 based bimetallic catalysts with superacid properties for use in octane enhancement. 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. 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

332. 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, CO_2, etc.) intermediate in C_1–C_2 catalytic reactions. The second goal entails the characterization of ligand intermediates in other important feedstock conversions, and the identification of new types of binding modes and bond activation processes. Mechanistic understanding of key steps and insight for the design of new catalysts are sought. The following topics are under active investigation: (1) the determination of relative ligand-binding affinities towards a representative Lewis acidic metal center, including divergent kinetic and thermodynamic O=C–C=C selectivities; (2) the characterization of unusual metal C–H “sigma bond” complexes as reaction intermediates; (3) new base-induced vinylic C–H bond activation reactions of alkene ligands; (4) the synthesis, structure, and reactivity of complexes that contain unsupported and supported C_2 and C_3 linkages spanning two metals; (5) C–H 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 linked redox states.

333. 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. These techniques may be 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 ^{13}C chemical shielding tensors in single crystals; (2) improving theoretical methods for the calculation of shielding tensors; (3) developing the off-angle spinning technique to obtain principal values of shielding tensors; and (4) applying ^{13}C shielding tensor methods in the characterization of high-rank coals. The geometry of a mechanism that orients a single-crystal sample to characterize its chemical shift tensor was derived. This mechanism combined with two-dimensional correlation spectroscopy forms a powerful method for measuring chemical shift anisotropy in complex single crystals. Using two variable angle spinning techniques along with a variety of other NMR spectroscopic methods, carbon-13 NMR shielding tensors have been determined for a variety of polycyclic aromatic systems and hydroaromatics such as acenapthalene, perylene, triphenylene, and several naphthalene derivatives. Emphasis on details in hydroaromatics, because of their importance as hydrogen sources, will be stressed in future years. Theoretical calculations have been extended to these model compounds to explain and support the experimental conclusions. Spectroscopic analyses of nonprotonated to protonated aromatic carbons agree with elemental analyses and dipolar dephasing NMR techniques. These new methods are useful for analyzing the structure of high-rank coals; the fraction of condensed carbons obtained may be used to estimate average cluster size in condensed polyaromatic hydrocarbons, and these data are key parameters in coal devolatilization theories being developed in concert with personnel at the Sandia Combustion Research Facility in Livermore, California.

Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

Department of Chemical Engineering

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

Cox, D.F. **$66,000**
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 $SnO_2(110)$ surface is being investigated because of the flexibility allowed in controlling surface cation coordination numbers, oxidation states, and the selective introduction of two different types of surface oxygen vacancies. The effects of these surface properties on the catalytic reaction pathways of C_1 to C_3 oxygenates are being examined. Previous results for methanol and formic acid oxidation have shown that the dissociation of Bronsted acids 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 gives near zero conversions of both acids because of a decrease in the basic character of the surface associated with the loss of in-plane surface oxygen anions. The relative acidity and basicity of the two specific surface defects are currently being tested with probe reactions.

University of Washington
Seattle, WA 98195

Department of Chemistry

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

Campbell, C.T. **$103,000**
206-543-3287

Catalysts resulting from mixtures of Cu and ZnO are used for several chemical reactions that strongly impact energy technologies. This catalytic system also offers a unique prototype for basic study because it is a case where the support material clearly makes a very critical difference in determining catalytic activity. Whether the critical role of this ZnO support is to stabilize an active Cu + 1 site at the surface, or to maintain ultrathin films of metallic Cu in an active morphological form, still has not been unambiguously demonstrated. The experiments performed here are designed to clearly identify the active form of surface Cu in the methanol synthesis reaction over these catalysts and to elucidate the influence of ZnO on the morphological and chemical properties of supported thin Cu films. The kinetics of methanol synthesis over a clean Cu(110) surface are being compared to those over industrial Cu–ZnO catalysts and vapor-deposited Cu thin films on ZnO single-crystal faces. 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 and scanning tunneling microscopy. 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. These results should have general significance to catalyst systems where the interaction between metal particles and their oxide support play a critical role either in controlling particle morphology or in controlling the electronic character of the metal particles.

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

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

New synthetic methods for the preparation of persistent transition metal centered radicals of the general form $\cdot Re(CO)_3(PR_3)_2$ (R = bulky alkyl) have been developed. Preliminary study of the reactivity of selected examples indicates that they will react under mild conditions with substrates such as hydrogen and possibly with methane. Extension of this chemistry to biradicals is currently being studied. The research program is primarily directed to understanding the mechanism and selectivity of these novel reactions. The radical species have been characterized by electron paramagnetic resonance (EPR) spectroscopy and X-ray crystallography. Extensions and modification of the synthetic method to provide additional examples of persistent radicals and biradicals are under way.

Wayne State University
Detroit, MI 48202

Department of Chemistry

337. ***Novel Selective Heterogeneous Catalysts***
Brenner, A. **$80,000**
313-577-2503 **(24 months)**

The primary goal of this research is to create a new type of selective heterogeneous catalyst. The new catalysts will mainly consist of supported metals that have been carefully poisoned by molecular compounds, thereby inducing site isolation between the active metal centers. Essentially, a homogeneous-like heterogeneous catalyst will be synthesized that can combine the engineering advantages of a heterogeneous catalyst and the better selectivity of a homogeneous catalyst. During the past year some of these catalysts have been synthesized, their unusual selectivity assessed by a model reaction, and some of the parameters that are important in creating high selectivity determined. In particular, whereas some conventional metal catalysts show substantial scrambling during olefin hydrogenation, appropriately poisoned forms show very high (homogeneous-like) selectivity. A new research direction was also initiated during the past year in response to the increasing need for cost-efficient catalysts for pollution control. Mixed-metal catalysts of supported Mo and Pd were synthesized, characterized, and their activity and selectivity measured for the reduction of nitric oxide to nitrogen under a variety of conditions. These catalysts can rival the performance of much more expensive rhodium-containing catalysts that are currently used for automotive pollution control. The detailed results have been published in a series of papers.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemical Engineering

338. ***Experimental and Kinetic Modeling of Acid/Base and Redox Reactions over Oxide Catalysts***
Dumesic, J.A. **$121,400**
608-262-1092

This research project involves the characterization of catalyst acidity, ^{2}D nuclear magnetic resonance (NMR) studies of Bronsted acid sites, and kinetic, calorimetric, and spectroscopic studies of methylamine synthesis and related reactions over acid catalysts. The approach of this work is to explore quantitative correlations between the factors that control the generation, type, strength, and catalytic properties of acid sites on zeolite catalysts. These systematic studies involving microcalorimetry, thermogravimetric analysis, IR spectroscopy, and NMR spectroscopy provide information about the nature and strength of acid sites in zeolites. This information is vital in understanding the catalytic cycles involved in methylamine synthesis and related reactions over zeolite catalysts. In particular, the following acid-catalyzed reactions are under investigation: methylamine syntheses from ammonia and methanol, dimethyl ether formation from methanol, dimethyl ether hydration to methanol, methylamine disproportionation reactions, and methylamine syntheses from lower methylamines and methanol. This research will be extended to include other solid acid catalyst systems, such as AlPOs, SAPOs, and solid superacids. Other acid-catalyzed reactions under investigation include the alkylation of toluene with methanol and the alkylation of isobutane with light olefins. These reactions are of interest because of the need for new generations of solid acid alkylation catalysts to replace liquid acids for environmental reasons.

Department of Chemistry

339. ***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 a 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, Mn–Pt compounds will be explored since Mn–alkene complexes are labile. (2) The recent discovery of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$, the second example of a dimer of d^6-16e fragments 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 basic reactions of Re=Re are being studied. An effort will be made to use reversible H_2 addition to M=M compounds in the development of new bimetallic catalysts. (3) Reinvestigation of a spurious report of Cp^* $Co{\equiv}CoCp^*$ led to the discovery of the paramagnetic cobalt cluster $Cp^*{}_3$ Co_3 $(\mu\text{-}H)_4$. The reactions of this cluster with CO, CNR, and alkynes are under investigation. (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

340. ***Aluminum Coordination and Active Catalytic Sites in Aluminas, Y Zeolites, and Pillared Clays***
Fripiat, J. **$85,000**
414-229-5852

Four major accomplishments are reported: (1) Different species of aluminum were detected in the surface layers of a transition alumina and of the nonframework alumina in ultrastable Y by cross-polarization from the protons of chemisorbed ammonia. These findings seem to eliminate trigonal aluminum as a surface species, but they suggest that upon dehydration pentacoordinated aluminum is transformed into an active distorted tetrahedral Al appearing at 50 ppm. (2) Nano-sized aluminas in which the main component is Al^{v} were produced by a new sol–gel route. (3) Through measurements of ^{31}P longitudinal relaxation rates from 100 to −80 °C, it was shown that the proton adduct $TMPH^{+}$ of trimethylphosphine (TMP) is not mobile on the surface of acid catalysts while the Lewis adduct TMP:L is mobile. (4) Carbenium ions have been considered as essential intermediates in the cracking of hydrocarbons. It has been shown that the adsorption of *tert*-hydrogen containing molecules on H mordenite containing strong acid Lewis sites leads to the formation of free radicals at $\leq$ 100 °C. The radical is stable up to $\sim$160 °C where it can be transformed into a carbenium ion. This result may provide an important step toward the understanding of the mechanistic aspect of cracking.

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

Tysoe, W.T. **$95,126**
414-229-5222

The long range goal of this research project is to develop sufficient understanding of the reactions and surface interactions responsible for coupling of CO hydrogenation intermediates with alkene homologation reactions to allow prediction of both the most desired catalysts and the most favorable conditions. Previous studies have shown Mo to be an effective catalyst for both hydrogenating CO to a CH_2 intermediate and intercepting that intermediate with ethylene to produce propylene in a homologation reaction. This research program will aim at understanding and exploiting this unique chemistry over Mo-derived catalysts to develop strategies for synthesizing hydrocarbons. Efforts will concentrate on clarifying the nature of the active surface for these reactions starting with a Mo(100) surface and varying its oxygen coverage in conjunction with determining the high pressure reaction kinetics. The kinetic studies will be complemented by careful surface characterization before and after reaction to ensure that any changes to the surface that may occur during the course of the reaction are understood. The project will attempt to identify active intermediates spectroscopically and also through independent synthesis of potential surface species. The particular intermediates being initially concentrated on are carbenes and metallocycles.

Yale University
New Haven, CT 06520

Department of Chemical Engineering

342. A Spectroscopic and Catalytic Investigation of Active Phase: Support Interactions

Haller, G.L. **$114,200**
203-432-4378

The active site of a catalyst (metal, mixed metals, oxide, or mixed oxides) may be influenced by the immediate environment, promoters, the support, etc. The project objective is to characterize active sites by a combination of catalytic/chemisorptive probes and spectroscopic methods with the goal of correlating site structure and support interaction with catalytic function. The principal spectroscopies are extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) and solid-state NMR. X-ray absorption is used to investigate the metal–metal and metal–zeolite interaction of Pt–Ni, Pt–Re, and Pt–Sn in L-zeolite in an effort to understand the unique *n*-hexane to benzene selectivity of Pt/L-zeolite catalyst and to develop sulfur-tolerant catalysts by interaction of Pt with a second metal. *n*-Hexane aromatization is the primary catalytic probe, and electron microscopy is used to complement X-ray absorption. Solid-state NMR of ^{1}H, ^{27}Al, and ^{29}Si are used to investigate acidity in amorphous and crystalline silica aluminas, which are used as supports for metals and metal oxides. The acidity of the support may play a direct bifunctional role in the reaction or act as an anchor for the active phase. Cumene cracking and 2-methyl-2-pentene isomerization are the primary catalytic probes for acidity.

Department of Chemistry

343. Catalytic Oxidation of Hydrocarbons by Binuclear Fe Complexes

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

This project is investigating the ability of metalloenzyme reactivity models to catalyze the oxidation of alkane–arene molecules. Of particular interest is the conversion of methane to methanol. The objective of this project is to characterize the reactivity properties of nonheme dinuclear iron complexes, characterize any intermediates formed during oxygen atom transfer chemistry, and elucidate the mechanisms and specificity of the reactions. Additionally, comparisons and contrasts with heme systems will be studied. Diferrous, ferrous–ferric, and diferric complexes were synthesized from simple multidentate polyamide ligands and spectroscopically characterized. The ferrous-containing complexes are capable of acting as oxygen atom transfer catalysts, giving rise to both epoxidation and allyl oxidation products when reacted with simple olefins. An isostructural cobalt(II) dimer yields only epoxidation products. Intermediates observed during catalytic turnover are currently being examined.

344. Alkane Photoreactions with Mercury Vapor

Crabtree, R.H. **$95,000**
203-432-3925

The research is designed to understand alkane conversion and find new methods to synthesize useful derivatives. Mercury photosensitized reactions with hydrogen and ammonia to generate hydrogen atoms that undergo addition reactions with alkanes or functionalized hydrocarbons are being investigated. Also being examined are alkane conversions to hydroperoxides, amines, alcohols, sulfonic acids, and ketones, for example. Hg^{*} reacts with NH_3 to give H atoms and NH_2 radicals. These, in turn, react with a variety of organic compounds to give amines and imines. For example, reaction with methane gives methylene imine. In a static reactor this gives a polymer, but in a special recirculating reactor, it gives $CH_2{=}NH$ at a fast recirculation rate and methylene imine and higher imines, such as acetaldehyde imine, at a slower recirculation rate. Attack by alkyl radicals on methylene imine is implicated as the mechanism of homologation.

Separations and Analysis

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

345. *Interfacial Chemistry in Solvent Extraction Systems*
Neuman, R.D. **$106,000**
205-844-2017

A comprehensive investigation of the interfacial chemistry of solvent extraction systems is being undertaken to provide a fundamental understanding of liquid–liquid extraction of metal ions in hydrometallurgical and nuclear waste processing technologies. Present research emphasizes characterization of the physicochemical nature of the microscopic interfaces (i.e., reversed micelles, microemulsions, and other association microstructures), which form in both practical and simplified acidic organophosphorus extraction systems associated with nickel, cobalt, and sodium. In order to improve upon the model recently proposed by this group for the aggregation of metal-extractant complexes, further study of a series of novel findings which are contrary to current literature views on reversed micellar structure is in progress. In addition, the macroscopic liquid–liquid interfacial behavior of extractant molecules and their interactions with metal ions continue to be investigated with advanced laser techniques. For example, laser-induced fluorescence is providing information on the dynamic properties and structural organization of model extractant molecules in the interfacial region. Optical reflectivity measurements are being extended to solvent extraction systems to determine whether "thin" or "thick" interfaces occur in practical liquid–liquid extraction processes. This unique research program augurs for significant enhancement of the science and technology of solvent extraction processes.

Brigham Young University
Provo, UT 84602

Department of Chemistry

346. *Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport*
Lamb, J.D. **$99,000**
801-378-3145

The macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems is being investigated. Potential macrocyclic carriers are synthesized, then screened by measuring pKa values, extraction equilibrium constants, partition coefficients for various metal cations, NMR, and X-ray crystal structures. Macrocycles of particular interest are then studied in the potentially practical emulsion, hollow fiber, and dual module supported liquid membrane systems. Research involves design, synthesis, and characterization of new proton-ionizable macrocycles that permit coupling of cation transport to the reverse flux of protons. Macrocycles containing single and multiple pyridone, triazole, phosphono, and sulfonamide functional groups are under study where the ionizable proton is part of the macrocycle ring. Current focus is given to the effect of temperature on these separations systems. A novel high temperature calorimeter has been constructed and is being used to determine the utility of temperature changes in making macrocycle-based separations.

Brown University
Providence, RI 02912

Department of Chemistry

347. *Photochemical Generation of the Optoacoustic Effect*
Diebold, G.J. **$84,000**
401-863-3586

The properties of the photoacoustic effect generated by laser irradiation of solid bodies are being investigated. The response of an isotropic solid body to the absorption of optical radiation is described by an inhomogeneous wave equation for a displacement potential. Through use of the wave equation, mathematical expressions have been obtained for the response of optically thin bodies to sinusoidally modulated radiation, as well as to pulsed radiation. Experiments are being carried out to investigate in detail the predictions of theory. In particular, two limiting cases of the response of solid bodies where the duration of the exciting light pulse is either long or short compared with the transit time of sound across the solid are being investigated. The goal of this research is to obtain a fundamental understanding of the properties of the photoacoustic effect. At the same time the possibility of an analytical technique where acoustic parameters characteristic of a body can be determined by recording photoacoustic waveforms is being investigated.

Colorado School of Mines
Golden, CO 80401

Department of Chemical Engineering

348. *A Mechanistic Study of Molecular Sieving Inorganic Membranes for Gas Separation*
Way, J.D. **$86,000**
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 microstructure of the membrane, the membrane surface chemistry, and the separation performance of the membrane. An example of the membrane materials under investigation is the silica hollow fiber membrane manufactured by PPG Industries. A further objective is to use molecular dynamics to simulate the transport of penetrants in pores of molecular dimensions. The ceramic membranes will be characterized by measurement of pore size distribution using physical adsorption and small-angle X-ray scattering and by measurement of pure gas adsorption isotherms for gases of industrial and environmental interest including He, H_2, CO_2, NO, SO_2, O_2, N_2, CH_4, CO, and CCl_2F_2 at pressures up to 35 atm and temperatures up to 300 °C. The effect of surface chemistry, specifically surface hydroxyl groups, on the transport of gases will be independently studied. FT-IR spectroscopy will be used to quantify the concentration of surface hydroxyl groups. To investigate the separation of gas mixtures, fluxes and separation factors will be measured for pure gases, binary and multicomponent mixtures including O_2/N_2, NO/N_2, CO_2/CH_4, and N_2/CCl_2F_2.

Columbia University
New York, NY 10027

Department of Chemistry

349. Utilization of Magnetic Effects as a Means of Isotope Enrichment

Turro, N.J. **$90,000**
212-854-2175

The project objective is to provide a theoretical and experimental understanding of the factors leading to separation of isotopes based on their magnetic properties. The research performed has been driven by the radical pair theory which connects the reactivity of a geminate radical pair with magnetic interactions between the odd electrons and the nuclei. The optimization of these interactions requires that the radical fragments move in a restricted reaction space so that the separation of the fragments can occur and reduce important electron–electron interactions, yet return of the fragments into a zone in which self reaction is possible. These ideas have led to investigations of radical pair chemistry in nanoscopic restricted reaction spaces (e.g., micelles, porous silica, zeolites, cyclodextrins) and have demonstrated the correspondence of the restricted space with the constraints imposed on a pair of radical centers by a connection of atoms as found in long chain biradicals. The efficient separation of 13-C (spin 1/2) from 12-C (spin 0) and 17-O (spin 5/2) from O-16,18 (spin 0) has been demonstrated. Current investigations are focused on the separation of heavy isotopes of atoms such as silicon and sulfur. In addition to the investigations of isotopic separations, the dynamics of the reactivity of the radical pair have been investigated by time resolved laser spectroscopy with analysis by optical and magnetic resonance methods.

University of Delaware
Newark, DE 19716

Department of Chemistry and Biochemistry

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

Wirth, M.J. **$79,211**
302-831-6771

Laser spectroscopic methods are used to investigate experimentally the structure and dynamics of monolayer stationary phases used in liquid chromatography. These studies address the molecular details of the chromatographic retention process to guide the design of more selective stationary phases. The spectroscopic experiments sense the configurations of the alkyl chains in bonded C_{18} stationary phases and the orientations of solutes interacting with these chains during chromatographic retention. Orientation and orientational distributions of chains and solutes are characterized by the polarization dependences of linear and nonlinear spectroscopic excitation. The dynamics of chains and solutes are characterized by their picosecond reorientation behavior. These studies examine the effects of such important factors as chain density and mobile phase composition on the chain and solute orientations. These same experimental tools are being applied to the newly emerging self-assembled monolayer stationary phases, developed in this laboratory, to understand the fundamental basis of their retention properties.

Duke University
Durham, NC 27708

Department of Chemistry

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

McGown, L.B. **$72,000**
919-660-1545

This project approaches the analysis of complex samples, including humic substances, coat liquids, and human serum, from two directions. In one, the uniqueness of the sample matrix is preserved and exploited for purposes of sample characterization, classification, and fingerprinting. Phase-resolved fluorescence spectroscopy (PRFS), a frequency-domain fluorescence lifetime technique, is the key to these studies of the significance of dynamic, physicochemical processes in the spectral characterization of complex samples. Such information is not available from separation-based techniques that employ chromatography or extraction to remove the components from the sample matrix. Malta chemometric techniques, also under development, are essential to the analysis and interpretation of multidimensional PRFS data. 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 dynamic systems under investigation. The second direction addresses the inaccuracies that may occur in quantitation of an analyte due to the same uniqueness of the sample. Accurate calibration is often not possible if the fluorescence characteristics of the analyte are highly sample dependent. One solution is to perform a physical separation of the analyte through extraction and/or chromatography. A different approach to this problem is being explored in which organized bile salt media is used to provide a uniform microenvironment for the analyte within the sample, thereby accomplishing an in situ extraction of the analyte to minimize matrix effects without a physical separation or extraction of the bulk sample. Current studies are directed towards fundamental studies of bile salt aggregation, reversed micellization, and applications to analysis of fossil fuel-derived materials.

University of Florida
Gainesville, FL 32611

Department of Chemistry

352. The Glow Discharge as an Atomization and Ionization Source

Harrison, W. **$91,000**
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. One major research emphasis involves investigating the effect of impurity species on the fundamental processes occurring in dc and rf glow discharge plasmas. Impurities commonly present in the glow discharge include water vapor, oxygen, nitrogen, hydrocarbons, and their dissociation products. 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. By varying the discharge gas, and consequently the metastable energies available for Penning ionization, the profile of the transient ion signals are altered depending on the gas-cathode combination. A continuum source xenon arc lamp has been coupled with the glow discharge to study the fluorescence emission. This method results in a simpler spectra and has the potential of providing multielemental analysis with lower detection limits than previously used spectroscopic methods.

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

Winefordner, J.D. **$104,370**
904-392-0556

Laser-excited atomic spectrometric methods are being investigated in order to achieve high spectral selectivity and detection power. The techniques being studied involve laser-enhanced ionization in flames, atmospheric furnaces, and low-pressure environments; laser-enhanced fluorescence in flames, inductively coupled plasmas (ICPs), and furnaces; and double resonance fluorescence in flames and ICPs for nonmetals. The techniques are used for both diagnostic measurements of spectral characteristics of atomic and ionic species in flames, plasmas, and furnaces as well as for analytical measurements. The emphasis is to achieve extremely high detection powers (subpart per trillion concentrations or femtogram amounts of elements) with extremely high spectral selectivities and very high freedom from matrix interferences. The diagnostic studies are directed toward (1) a more thorough understanding of the mechanisms of atomization, ionization, and dissociation of analyte species in plasmas and furnaces; (2) the optimization of experimental conditions to obtain the best analytical results by means of laser fluorescence dip spectroscopy; and (3) the development of resonance ionization detectors for ultrahigh photon detection sensitivity.

The George Washington University
Washington, DC 20052

Department of Chemistry

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

Montaser, A. **$77,500**
202-994-6480

New high-temperature plasmas, new sample introduction systems and diagnostic techniques, and a new plasma source mass spectrometer are being developed for rapid elemental analysis of gases, solutions, and solids. These devices 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. Emphasis is placed on (1) generation and fundamental investigation of helium inductively coupled plasmas (He ICP) that are suitable for the excitation of high-energy spectral lines, to enhance the detecting power of a number of elements; (2) investigation of RF-powered glow discharges for direct analysis of nonconductive solid samples; (3) development and characterization of low-cost sample introduction systems that consume microliter or microgram quantities of samples; (4) investigation of dual-beam, light-scattering interferometry for simultaneous measurements of droplet-size and velocity distributions of aerosols from various nebulizers, and for time-resolved studies of desolvated aerosol; (5) examination of the utility of electrical mobility techniques for measuring particle size distribution in the range of 10 to 1000 nm; and (6) simulation and computer modeling of He ICPs and mixed-gas discharges to predict the behavior of plasmas on a fundamental basis. This investigation addresses fundamental principles behind the measurements, evaluation of the analytical potentials of the devices developed, and demonstration of the analytical methods in representative samples.

Georgia Institute of Technology
Atlanta, GA 30332

Department of Chemistry and Biochemistry

355. *Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)*

Browner, R.F. **$86,000**
404-894-4020 **(24 months)**

The particle beam interface has been studied from two perspectives: (1) the physical nature of the crystalline form and size of the particles generated by the interface and (2) the use of the interface for laser desorption (LD) and matrix-assisted laser desorption (MALD) mass spectrometry. The particles generated by the interface have been trapped at low pressure and measured by scanning electron microscopy. Also, the actual mass transport of material through the interface to the detector has been determined for a variety of conditions, including the use of volatile and involatile buffers. These may act as carriers and increase mass transport at low analyte concentrations or, if they are very volatile, they may explosively reduce the particle size of the analyte and effectively reduce analyte mass transport. The rational design of optimum "transport buffers" may now be attempted. A 3-W Ar ion laser has been shown to be highly effective in generating largely intact $(M + K)^+$ ions from thermally labile molecules of both low and intermediate molecular weight (250–750 Da). The particle beam system acts to desolvate the liquid chromatography effluent, which then impacts on a ceramic probe in the ion source area of the mass spectrometer and interacts with the laser beam. The LD and MALD mass spectra show essentially no evidence of thermal degradation, even for very thermally labile species such as aidicarb and cholesterol. Additionally, useful structural information may also be obtained by electron ionization of the laser-desorbed molecules.

Hampton University
Hampton, VA 23668

Department of Chemistry

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

Urasa, I.T. **$56,000**
804-727-5398

The program involves the use of dc plasma atomic emission spectrometry in combination with ion chromatography to study the chemistry of and develop analytical methods for element speciation in aqueous solutions. Emphasis has been placed on transition metals. The proposed new thrust will incorporate this method with naturally occurring chelating ligands, synthetic chelating resins, and post column derivatization to improve detection sensitivity and to facilitate simultaneous multielement speciation. Further investigation will also be directed toward elucidating the effect of sample condition and/or sample processing on element speciation. Of particular interest in this regard is the transformation that some of the elements may undergo during sample treatment.

University of Houston
Houston, TX 77204

Department of Chemical Engineering

357. *Mechanisms of Thickening, Cake Filtration, Centrifugation, Expression, and Ceramic Processing*

Tiller, F.M. **$98,600**
713-743-4322

Fluid/particle separation operations are fundamental to such diverse fields as wastewater, clean rooms, mining, ceramics, clogging of oil wells, pulp and paper, membranes, food, and pharmaceuticals. Processing of particles (colloids, pigments, emulsions, drops, bubbles, aerosols, and so forth) and their separation from the associated fluids (gas, liquid) is the link which brings together these and many other areas. Basic operations include filtration, centrifugation, thickening, cycloning, deliquoring, washing, flotation, coalescence, screening, and membrane separations. A few general principles involving relative motion of fluids and particles, Brownian diffusion, stress/deformation relations in particulate beds, flocculation and coagulation, colloidal phenomena, and flow through compactible media represent the scientific foundation on which engineering systems are built. This program aims at incorporating the fundamental principles into mathematical models, testing the formulations, and applying the results to industrial processes. Typical of topics being developed are (1) unification of the theory of filtration, centrifugation, and thickening; (2) new theoretical formulas for centrifugal sedimentation and filtration; (3) relating sedimentation characteristics to cake behavior; (4) optimization of tubular filter design; (5) optimization and minimization of the use of filter aids; (6) new generalized methods for thickener design; and (7) laboratory testing methodology for prediction and control of solid/liquid separations.

University of Idaho
Moscow, ID 83843

Department of Chemical Engineering

358. *Drop Oscillation and Mass Transfer in Alternating Electric Fields*

Carleson, T.E.; Budwig, R. **$39,470**
208-885-7652

The current work is being conducted as a follow up to previous work on a theoretical and experimental study of drop oscillation and flow induced by an alternating electric field in a charged and uncharged drop. Preliminary experimental and theoretical studies of droplet mass transfer under an alternating field are under way. An acoustically levitated drop will be subjected to an alternating field to produce drop oscillation. The effect of drop oscillation on mass transfer of a laser induced fluorescent dye will be monitored by digitizing images of the drop and determining the concentration of the dye in the drop from the color intensities. An experimental apparatus has been constructed and images of mass transfer in the absence of an alternating field have been taken and analyzed. A numerical model using the FIDAP software is being developed to compare with the mass transfer measurements.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Chemistry

359. *Molecular Aspects of Transport in Thin Films of Controlled Architecture*
Bohn, P.W. **$84,000**
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 ($\leq$100 Å) 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. Application to the system of poly(styrene) being swollen in n-hexane reveals large changes in the intensity of C–C backbone stretch as the solvent front moves through the probe region. Fitting to kinetic models reveals that the polymer relaxation is ca. a factor of 3 slower than the solvent motion.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

360. *Hadamard Transform Spectrometry: A New Analytical Technique*
Fateley, W.G.; Hammaker, R.M. **$82,000**
913-532-6298

A Hadamard transform spectrometer (HTS) has been developed for the visible and near-infrared (IR) spectral regions. A second generation of stationary Hadamard encoding masks has been developed for the no-moving-part near-IR Hadamard transform (HT) Raman spectrometer. Demonstrations of spectral subtractions, the theoretical multiplex advantage, and a new selective multiplex technique have all been accomplished. An HTS has been developed for photoacoustic spectrometry (PAS) in the visible spectral region. Depth profiling has been accomplished by varying the modulation frequency or by phase sensitive detection at the appropriate modulation frequency. A two-dimensional stationary Hadamard encoding mask has been used to develop an HT imager. Images have been obtained using laser-induced fluorescence (LIF), Raman scattering, and surface-enhanced Raman scattering (SERS). A second HT imager has been developed using photoacoustic detection to generate images at different depths in the sample to provide a three-dimensional mapping capability. The next efforts will include addition of the spectral dimension to both imagers as well as upgrading the HT Raman spectrometer with new detection system electronics and decreasing data acquisition time for the one-dimensional stationary Hadamard encoding mask by operation above room temperature using on-board heaters.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

361. *Perforated Monolayers*
Regen, S.L. **$74,000**
215-758-4842

This research is aimed at creating a fundamentally new class of synthetic membranes based on two-dimensional assemblies of "molecular pores" (i.e., perforated monolayers). The ultimate goal of this program is to fabricate membranes that can be used to separate small molecules on the basis of their size, shape, and polarity. The feasibility of constructing a perforated Langmuir–Blodgett (LB) film that exhibits molecular sieving behavior has recently been demonstrated. Specifically, composite membranes derived from LB multilayers of a calix[6]arene-based surfactant and a cast film of poly[1-(trimethylsilyl)1-propyne] show significant permeation selectivity (permselectivity) toward He, N_2, and SF_6. Current efforts are focusing on fine tuning the permselectivity of such composites by adjusting the effective diameter of the individual molecular pores.

Louisiana State University
Baton Rouge, LA 70803

362. *Sensitized Luminescence in Organized Media*
Warner, I.M. **$93,000**
504-388-2829

This research involves three fundamental areas of study (1) the use of micelles with specific counterions for development of select sensitized luminescence probes, (2) the use of tailor-made cyclodextrin derivatives for sensitized luminescence measurements, and (3) an examination of calixarenes as host molecules for analytical measurements through selective guest–host chemistry. An example of research area (1) is the exploration of the analytical utility of novel surfactants for sensitized luminescence measurements. These surfactants have been synthesized and use lanthanide ions as counterions. Preliminary studies indicate that these surfactants, when used in reverse micelles, show enhanced selectivity for sensitized luminescence measurement of aromatic molecules with polar substituents. Such molecules are believed to be more carcinogenic and mutagenic than their more hydrophobic parent compounds. Research area (2) involves a synthesis of novel cyclodextrin derivatives for additional selectivity in sensitized luminescence measurements. These molecules will add the additional constraint of size conclusion to this already very selective analytical technique. Research area (3) involves the synthesis and study of calixarenes for improved analytical measurements through new guest–host chemistry. The 4-, 6-, and 8-member calixarenes have been synthesized in the laboratory and are currently being studied.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemical Engineering

363. *Solubilization of Trace Organics in Block Copolymer Micelles for Environmental Separations Using Membrane Extraction Principles*
Hatton, T.A. **$89,900**
617-253-4588

The strong solubilizing powers of block copolymer micellar solutions are exploited for the removal and/or recovery of halogenated and nonhalogenated, aromatic and polyaromatic hydrocarbons from aqueous solutions. The work consists of the following tasks: (1) experimental determination of the thermodynamic and dynamic properties of a representative range of solutes and block copolymer micelle systems; (2) characterization of the structure of the loaded micelles as a function of temperature and polymer concentration and composition using light and neutron scattering techniques; (3) comparison of the self-consistent mean field theory calculations with the results of a new molecular Monte Carlo simulation algorithm, which can elucidate to geometric properties and polydispersity of loaded block copolymer micellar solutions; and (4) exploration of the engineering aspects of the proposed separations scheme through the design and construction of an experimental rig to allow for quantitative determination of extraction efficiency under a variety of operating conditions. Different approaches for the regeneration of the micellar solutions are to be explored. The results are to be used in an economic evaluation of the proposed membrane extraction scheme.

Michigan State University
East Lansing, MI 48824

Department of Chemistry

364. *Direct Probing of Chromatography Columns by Laser-Induced Fluorescence*
McGuffin, V.L. **$61,875**
517-355-9715 **(9 months)**

The objective of this research program is to improve the understanding of fundamental hydrodynamic and physicochemical phenomena in chromatography and related separation methods. A unique and powerful approach has been developed to study such phenomena by direct examination of the chromatographic column using laser-based detection techniques. These techniques have enabled, for the first time, the direct observation and measurement of solute zone migration along the column and have facilitated the development of theoretical models to describe these phenomena. Specific studies have included the following: (1) thermodynamic characterization of solute retention on monomeric and polymeric octadecylsilica materials near their first-order phase transition; (2) hydrodynamic characterization of solute zone dispersion in packed beds as a function of linear velocity, temperature, and pressure; and (3) examination of nonequilibrium processes that arise in regions of spatial discontinuity, such as solute injection and elution. In each of these studies, substantial knowledge has been gained of the fundamental phenomena that are responsible for chromatographic separations.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

365. *High Definition Raman Imaging*
Morris, M.D. **$100,000**
313-764-7360

High-definition Raman imaging is performed with a microscope and a microprobe, using a tunable dual birefringent Fabry–Perot filter in the imaging mode and a spectrograph in the microprobe mode. The system provides complete 3-D and multispectral capability at 512 x 512 pixels per image, as well as confocal Raman microscpectroscopic capability. Failure mechanisms in composite materials used in automobile weight reduction are studied by imaging distributions of components. The target material is reinforced fiber glass, where sizing and binder distribution near failure points are assessed. Raman imaging is used as a high-definition imaging thermometry for mapping small temperature changes in agarose gels used in nucleic acid separations. The microprobe mode is used to measure heat transport in electrophoresis capillaries.

University of Minnesota
Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

366. *Continuous Reaction Chromatography*
Carr, R.W. **$86,700**
612-625-2551

Chromatographic separation in a continuous flow chemical reactor can be used to separate the products of a reaction at the same time that the reaction that is forming them takes place. This separation permits equilibria to be shifted and the thermodynamic limitations of the reversible reaction in a fixed bed to be overcome. Thus, high-purity product streams, and conversions far beyond those of static equilibrium, can be obtained in continuous operation rather than with pulsed injection of feed. The relative motion of the feedstream and the chromatographic bed is required for this to be achieved. A configuration meeting this criterion is the countercurrent moving bed, which was the subject of earlier theoretical and experimental research. The practical difficulties of moving a bed of granular solid against a gas stream have led to the consideration of simulated countercurrency, which is accomplished by switching the feedstream along a series of entrances to a fixed bed. Switches are made at predetermined time intervals, and the feed is cycled back to the beginning after completing a pass along the fixed bed. An equilibrium stage model of this arrangement predicts excellent performance (product purity and reactant conversion), and a differential model of a segmented section variant has been similarly successful. Laboratory-scale apparatus with computer-controlled switching has been constructed to a design based upon the segmented section approach. An experimental investigation of the catalytic hydrogenation of 1,3,5-trimethylbenzene has been completed. Results corroborate the expectation of high product purity and high conversion. A comparison of the countercurrent moving bed reactor with simulated countercurrency has also been done. The application of simulated countercurrency to reactions of methane (natural gas) to form useful feedstocks and fuels is under investigation. For methane oxidative coupling, up to 90% selectivity for the reaction products ethane and ethylene, and approximately 60% conversion of methane has been achieved thus far.

University of Missouri at Rolla
Rolla, MO 65401

Department of Chemistry

367. *Molecular Recognition of Enantiomeric Hydrocarbons by Liquid Functionalized Cyclodextrins: A New Approach for Geochemical Research*

Armstrong, D.W. **$74,000**
314-341-4429

Chiral isoprenoid and hydroaromatic compounds occur in all crude oils, coals, shales, and most sediments. Many of these compounds are referred to as biological markers because they are thought to be derived from biological sources, and their presence, relative concentrations, or stereochemistry can provide information as to a geological deposit's age, maturity, diagenetic history, and so forth. Because of the previous lack of effective and efficient analytical methodologies for resolving hydrocarbon enantiomers, the stereochemical information encoded in these molecules is largely untouched. A series of derivatized α-, β-, and γ-cyclodextrin chiral stationary phases (CSPs) were used for the gas chromatographic resolution of several racemic tetralins, indans, and octahydrophenanthrenes, as well as cyclic and acyclic isoprenoids. 2,6-Di-O-pentyl-3-O-(trifluoroacetyl) (DP-TFA) derivatized β- and γ-cyclodextrins are able to resolve a wide variety of volatile racemic compounds. The enantiomeric recognition mechanism of cyclodextrin-based gas chromatography (GC) stationary phases was investigated. The retention behavior of homologous series showed that lengthening the side alkyl chain increases the retention time but does not affect enantioselectivity. The thermodynamic parameters, free energy, enthalpy, and the difference in free energy, enthalpy, and entropy between enantiomers were evaluated for 24 enantiomeric pairs. From this data, it appears that the compounds can be arranged in two groups. One group has high values for enthalpy, entropy, free energy, and the corresponding difference parameters between enantiomers. The second group has significantly lower values for all parameters. Compounds belonging to the second group follow an enthalpy–entropy compensation regression (ln k′ vs. ΔH) while the group I compounds do not. Also on a given column the mass capacity for group II compounds is significantly higher than that for group I compounds. A small difference was found in the mass-transfer behavior of the two groups of compounds. There may be at least two different chiral recognition mechanisms with the derivatized cyclodextrin gas chromatographic stationary phases. It is postulated that one mechanism involves cyclodextrin (CD) inclusion complex formation and the other does not. Cyclodextrin, bonded to silica gel and used as a gas–solid chromatographic stationary phase provides a practical and efficient means for separating a wide variety of volatile C_1–C_7 hydrocarbons and inorganic gases at ambient to elevated temperatures. Conditioning the columns at high temperature (300 °C) for several hours increased efficiency and resolution. The separation of these gases involves multiple retention mechanisms. For unsaturated hydrocarbons and inorganic gases containing double bonds, the cyclodextrin GSC column can act as a polar stationary phase analogous to silica gel. However, for saturated hydrocarbons and nonpolar gases it acts as a nonpolar phase. The columns and an analogous silica gel column with several standards were thoroughly evaluated.

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

Chemical Kinetics and Thermodynamics Division

368. *Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation*

Sieck, L.W. **$155,000**
301-975-2563 **(13 months)**

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 association 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

369. *Solid-State Voltammetry and Sensors in Gases and Other Nonionic Media*

Murray, R.W. **$77,500**
919-962-6296

Miniaturized electrochemical cells based on the use of microdisk, microband, and interdigitated array electrodes have been employed in a program aimed at developing a range of electrochemical methodologies suitable for quantitative voltammetry of electroactive solutes dissolved in solid and semisolid polymeric solvents. Potential sweep, step, and ac microelectrode voltammetries have been evaluated and adapted to measurement of exceedingly slow transport of electroactive solutes, with particular application to transport phenomena in poly(ether) "polymer electrolyte" solvents. Transport rates of dissolved electron transfer donors and acceptors are studied as a function of polymer MW, phase-state, small molecule plasticization, temperature, electrolyte concentration, and of the equivalent charge transport by electron self exchanges between dissolved donor–acceptor pairs. Methods are also being developed for measurement of electron transfer dynamics in polymer solvents with attention to slow solvent dipole/solvent dynamics control of electron transfer rates and to diffusion-rate dependent distances-of-electron transfer as would occur when diffusion is very slow. These first quantitative voltammetric measurements in solid and semisolid state phases are aimed at developing a capacity for fundamental, quantitative studies of solid-state charge and mass transport phenomena and at their exploitation for solid-state analysis.

Purdue University
West Lafayette, IN 47907

Department of Chemistry

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

Freiser, B.S. **$100,000**
317-494-5270

A major focus of this past year has been on uncovering new bimolecular photochemistry in the gas phase involving metal-containing ions. The study of gas-phase ion photochemistry at the low pressures used in Fourier transform mass spectrometry (FTMS) has, thus far, been largely limited to unimolecular photodissociation and, for negative ions, photodetachment processes. Compared to the wealth of information on condensed-phase systems, reports of bimolecular photochemistry in the gas phase are rare. This is caused in part by the long times between collisions in the gas phase, permitting unimolecular dissociation and radiative relaxation to dominate. The current work more than doubled the number of reported examples in the literature, further demonstrating the potential of this new type of photochemistry. Using multiphoton IR absorption to create long-lived vibrationally excited ground state intermediates, five general reaction types were demonstrated: (1) photoinduced deceleration of exothermic reactions; (2) photoinduced secondary fragmentation whereby an internally excited product ion is generated that can undergo fragmentation; (3) photoactivated ligand switching; (4) photoinduced isomerization; and (5) photoenhanced hydrogen–deuterium exchange. Ultimately, this new photochemistry will permit absorption information on ions to be obtained in IR.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemical Engineering

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

Belfort, G. **$88,000**
518-276-6948

To obtain an understanding of synthetic membrane fouling by proteins, the molecular interactions between cellulose acetate (CA) films and various proteins were measured with the Surface Force Apparatus. These interactions were highly dependent on pH. This was not the case for protein–protein or CA film-mica interactions. Some proteins appear to be partially unfolded at low pH. This could be exacerbated in the presence of fluid shear near the membrane surface or in the membrane pores. Intermolecular forces between these same proteins and a hydrophobic surface have also been measured. Strong attraction at the pI was observed

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

372. *Determination of Solvation Kinetics in Supercritical Fluids*

Bright, F.V. **$93,000**
716-829-3615

The research centers on improving the understanding of solvation processes in supercritical fluids. Specific topics include (1) determination of the kinetics of solute–fluid interaction; (2) quantifying the effect(s) of entrainers on solute–fluid dynamics; (3) documenting the influence of solute–fluid clustering on the rates of chemical reactions; (4) investigating the effects of fluid parameters on classic solute–solute interactions; (5) probing the dynamical aspects of reverse micelles formed in near and supercritical continuous phases; and (6) determining the structure of enzymes incubating in supercritical fluids. Picosecond, time-resolved fluorescence spectroscopy is used to probe the system dynamics. To date results from this project have provided key insights into the (1) time scale for solvation; (2) rate at which fluid–entrainer exchange can occur; (3) solute–fluid clustering process; (4) size and composition of the clustering domain; (5) homogeneity of the solute–fluid domain; (6) effects of fluid density and temperature on solute–solute interactions; and (7) ability to control the internal dynamics of reverse micelles formed in near- and supercritical alkanes. This information is leading to a more detailed molecular understanding of the chemistry of supercritical fluid solvation.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering and Materials Science

373. *Mechanisms of Gas Permeation through Polymer Membranes*

Stern, S.A. **$67,500**
315-443-4469 **(9 months)**

The development of new, energy-efficient membrane processes for the separation of gas mixtures requires a better understanding of the mechanisms of gas solution and diffusion in polymer membranes. Glassy polymers are particularly attractive membrane materials because of their high gas selectivity. Solubility and diffusion coefficients of gases in glassy polymers can be strongly nonlinear functions of the penetrant gas pressure (or concentration in polymers). This behavior has been attributed to "excess" (nonequilibrium) free volume of glassy polymers and can be described satisfactorily by a "dual-mode sorption" model. The higher poly(alkyl methacrylates) could have an uncommonly small "excess" free volume, because of the small difference in the thermal expansion coefficients above and below their glass-transition temperature (Tg). Consequently, it was of interest to determine whether the solubility behavior of light gases in poly(alkyl methacrylates) is affected by the magnitude of their excess free volume. Accordingly, the solubility of CH_4, C_2H_6, and CO_2 in poly(n-butyl methacrylate)(PnBMA) was remeasured in detail over a range of temperatures below its Tg (20–23 °C) and at pressures up to 35 atm. An analysis of the data in the framework of the dual-mode sorption model has shown that the dependence of the solubility coefficients for CH_4 and CO_2 on the gas pressure is not different from that observed with many other glassy polymers. Hence, the "excess" free volume of the PnBMA is larger than anticipated, probably because this polymer exhibits sub-Tg transitions that create additional free volume. The solubility of CO_2 at higher pressures and of C_2H_6 at all pressures studied deviates from dual-mode sorption behavior because PnBMA is plasticized (swelled) by these gases.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

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

Alexandratos, S.D. **$87,000**
615-974-3399

A new method of preparing substrate-selective bifunctional ion exchange/coordination resins has been proposed based on interpenetrating polymer networks. It has been found that the microenvironment around each ligand within the polymer matrix may be probed with binding constants calculated through Langmuir adsorption isotherms. For example, the strength of the imidazole–substrate interaction is seen to be a function of the imidazole's microenvironment (varied by copolymerizing N-vinylimidazole with ethyl acrylate). The microenvironment thus provides an additional variable for increasing a given ligand's selectivity within a series of metal ions. In the imidazole–acrylate polymer, Cu(II) is held 10 times more strongly than Co(II) by the imidazole ligand when no acrylate is present and almost 100 times more strongly when the imidazole–acrylate ligands are present in an equimolar ratio. (The acrylate has no affinity for either metal.) Ligand–substrate molecular selectivities are being quantified with various probe molecules, including phenylphosphinic acid and benzenesulfonic acid. The sensitivity of the ligand–substrate interaction to differences in the polymer matrix to which the ligand is bound has been quantified through a Hammett-type linear free energy relationship study using a polymer-bound amine and a series of substituted benzoic acids.

375. *Study of the Surface Properties of Ceramic Materials by Chromatography*

Guiochon, G. **$86,000**
615-974-0733

The aim of this work is a better understanding of the surface properties of solid powders, in order to characterize powder lots and predict some of their properties during processing. A correlation between the adsorption energy distribution and the quality of a series of lots of alumina powders has been established. Current work involves powders of silica, porous silica, and chemically bonded silica. The procedure developed involves the measurement of the adsorption isotherms of selected probes on the surface under study, and the determination of the distribution of the adsorption energy of these probes. The adsorption isotherms of the selected probes are measured by Elution of a Characteristic Point (ECP), using a porous layer open tubular (PLOT) column. The adsorption energy distribution is derived by solving numerically the integral equation relating the adsorption energy distribution, the adsorption isotherm on each type of sites (assumed to be homogeneous), and the measured isotherm. The adsorption energy distribution of a surface depends on the nature of the probe used, so a series of probes is needed to characterize a surface.

376. *Capillary Electrokinetic Separations with Optical Detection*

Sepaniak, M.J. **$79,000**
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)) 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. In addition, the feasibility of performing separations using a nonaqueous solvent–fullerene electrochromatographic system is being explored. 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 interculation 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

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

Russell, D.H. **$86,000**
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 on N_2 lasers. 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 ion 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

378. *Metal Ion Complexation by Ionizable Crown Ethers*

Bartsch, R.A. **$93,000**
806-742-3069

Goals of this research are the synthesis of new metal ion complexing agents and their applications in metal ion separation processes. 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 on metal ion complexation behavior. Thermodynamic parameters for alkali metal cation complexation by crown ethers with ionized pendent groups are being determined by titration calorimetry. The novel ligands are being evaluated in competitive solvent extraction and in liquid membrane transport of alkali metal and alkaline earth cations. Novel ion exchange resins are being prepared from dibenzocrown ethers with pendent acidic functions. In addition to ion exchange sites, these resins also possess crown ether units for metal ion complexation. Sorption behavior of these resins for alkali metal, alkaline earth, and heavy metal cations is being assessed. For selected resins, applications in concentrator columns for these metal ions are being explored.

379. Novel Approaches to Ionic Chromatography

Dasgupta, P.K. **$77,000**
806-742-3064

The project objectives are (1) to achieve high-sensitivity, high-resolution chromatographic techniques for the analysis of ionic species and (2) to explore new strategies for the identification of ions and the reduction of consumables. Novel uses of the ion exchange process and properties of ion exchangers are explored. Recent accomplishments include the following work: (1) The development of a rapid and precise technique for the conductometric measurement of the disassociation constant of a weak acid. The determination does not require the measurement of pH and can be made in minutes. (2) An amperometric micro sensor for water vapor based on electrolytic current conduction in a perfluorosulfonate ionomer thin film either by itself or as a composite with P_2O_5 has been developed. The sensor can measure water from 2 ppm to saturation levels. (3) Several types of membrane-based generators that can electrodialytically generate ultrapure ionomer NaOH solutions have been developed. These solutions have been used for gradient ion chromatography to obtain unprecedented baseline stability, calibration stability, and response linearity. The eluent concentration gradient is controlled by electrical programming of the source rather than by mechanical proportioning of two or more liquids. The generation procedure can be applicable to most electrochemically stable ionic chemicals which can be produced in solution in ultrapure form.

University of Texas at Austin
Austin, TX 78712

Department of Chemical Engineering

380. Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications

Koros, W.; Paul, D. **$86,999**
512-471-5866

This project focuses on synthesis and characterization of polymeric materials for advanced gas separation membrane applications. The fundamental sorption and diffusion coefficients governing the permeability and permselectivity of such materials are being measured with both pure and mixed gas feeds. Polymers in the polycarbonate, polyester, and polyimide families with high permeabilities for important commercial gases such as hydrogen, carbon dioxide, and oxygen have been identified by systematic variation in the structures. In addition to high permeabilities, several of these materials have shown very attractive permselectivities for gas pairs such as H_2/CH_4, CO_2/CH_4, and O_2/N_2. Applications at elevated temperatures are receiving extra attention. Measurements at temperatures over 200 °C have been made to characterize the influence of molecular structure on thermal stability of transport and separation properties for a large number of polymers synthesized under DOE support. Structural changes that produce favorable trade-offs in the permeability and selectivity within a given family have in common a tendency to produce simultaneous inhibition of intrachain mobility and interchain packing. A fortunate coincidence appears to exist in the fact that the molecularly rigid materials being developed also have better thermal stabilities than more flexible chain analogs in the same polymer families. Some of the better candidate materials have been tested in a related project involving hydrogen removal in a membrane-assisted reactor to favorably bias the equilibrium in favor of the forward reaction for dehydrogenation processes.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

381. Laser Flash Photolysis, EPR and Raman Studies of Liquids at Elevated Pressures

Eyring, E.M. **$100,000**
801-581-8658

Elucidation of rates and mechanisms of chemical reactions in liquids and at liquid–solid interfaces using high-pressure experimental techniques is the main focus of this research. A high-pressure stopped-flow spectrophotometer has been constructed to study the mechanisms of formation and dissociation of metal ion complexes in solution. This equipment is being used to investigate the kinetic properties of polyaminocarboxylate complexes of gadolinium(III) ion in aqueous solutions. An elevated pressure electron paramagnetic resonance (EPR) experiment is being developed to study the environment of gadolinium(III) and other paramagnetic ions adsorbed on molecular sieves. The feasibility of making simultaneous Raman spectral and electrochemical measurements at elevated pressures that would permit a correlation of Raman structural information on adsorbed species with the electrode potential is being explored. Previous laser flash photolysis kinetic studies of metal carbonyl complexes in toluene at elevated pressures are being extended into supercritical carbon dioxide solutions.

382. Time-Resolved Analytical Methods for Liquid/Solid Interfaces

Harris, J.M. **$95,000**
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 development and understanding of chromatographic methods, solid-phase extraction techniques, immobilized analytical reagents, and optical sensors. Chemical interactions that govern in these processes cannot generally be identified solely by equilibrium concentration measurements, since the steady-state behavior of the system does not reveal the mechanisms or dispersion in surface interactions, nor is structural information determined. The goal of this research 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. In addition, several methods are being adapted to perturb interfacial chemistry, including stopped-flow, temperature-jump, and photoexcitation techniques. Depending on the speed of the kinetics and spectral features available for detection, the rates of relaxation of the surface chemistry to these perturbations are measured with time-resolved fluorescence, phosphorescence, and Raman spectroscopies. The experiments are applied to a variety of interfacial chemical phenomena including: transport of molecules at the interface and through porous matrices; monolayer adsorption, desorption, and reorganization kinetics; rates of binding and irreversible adsorption of molecules to silica and other insulating surfaces; measurements of stability of bound monolayers; and kinetic studies of interfacial charge-transfer and metal ion complexation.

Department of Metallurgical Engineering

383. Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species

Miller, J.D. **$100,000**
801-581-5160

This research program is designed to develop a detailed understanding of adsorption phenomena at solid–liquid interfaces, especially those important to flotation chemistry. Froth flotation is one of the most outstanding examples of applied surface chemistry and is used in the food, petroleum, pulp–paper, and mineral industries. The use of this technology is perhaps most significant in the mineral industry. Several novel experimental techniques are being developed to analyze surfactant adsorption at mineral–water interfaces and to describe the impact of adsorption phenomena on the hydrophobic character of the surface. Among the new experimental techniques are in situ Fourier transform infrared (FTIR) internal-reflection spectroscopy (IRS) with reactive internal-reflection elements, laser Raman spectroscopy, and nonequilibrium electrophoresis. These techniques are being used in concert with transferred Langmuir–Blodgett (LB) monolayers to answer fundamental questions about the adsorption density, adsorption state, and order/conformation of surfactants adsorbed at mineral interfaces. In addition, study of the oxidation/polymerization of adsorbed unsaturated surfactants has created a new dimension to flotation chemistry. The results obtained will provide the basis for new reagent schedules to improve separation efficiency and to promote energy conservation. The importance of surface charge in soluble-salt flotation systems has been established through a novel nonequilibrium electrophoretic mobility technique and the results were found to support the lattice ion hydration theory for surface charge generation. In this case, collector colloid adsorption seems to account for the hydrophobic state that leads to selective flotation. For semisoluble salt minerals, the fluorite–oleate system has been examined in great detail by in situ FTIR IRS, especially in terms of identifying the nature of the carboxylate bonding with surface calcium ions in three distinct regions of the adsorption isotherm. The conformational features of the adsorbed oleate have been examined as a function of adsorption density and as a function of temperature. Finally, oxygen and temperature excursions are being used to determine the reactivity of the double bond for adsorbed unsaturated collector species. Laser Raman spectroscopy and near-IR FTIR IRS, have been used to examine both fluorite and calcite surfaces in oleate solutions. Several insoluble oxide mineral systems are being examined, including the sapphire–sodium dodecylsulfate (SDS) and quartz–dodecylamine systems. Collector adsorption phenomena in these systems are being studied with respect to the conformational order of adsorbed surfactant species.

Virginia Commonwealth University
Richmond, VA 23284

Department of Chemistry

384. Enhancement of Fluorescence Detection in Chromatographic Methods by Computer Analysis of Second Order Data

Rutan, S.C. **$82,000**
804-367-1298

The fluorescence responses observed for polyaromatic hydrocarbon compounds are susceptible to changes in the chemical surroundings of the molecules. The purpose of these studies is the development of mathematical methods that allow quantification of fluorescent species, despite errors caused by these perturbations to the spectra. A fluorescence detector for liquid chromatography has been developed based on an intensified diode array detector. Data for polyaromatic hydrocarbons have been obtained, and analyzed using several methods, such as factor analysis and generalized rank annihilation, which take into account both the spectroscopic and chromatographic information provided by the chromatography system. Current studies are focused on the development of approaches to be used with gradient liquid chromatography. An additional area of research is the development of kinetic methods of detection for planar separation methods, such as electrophoresis or thin-layer chromatography. These experiments provide data as a function of two parameters; in this case, the fluorescence intensity is measured as a function of reaction time and elution (or migration) distance. The data are then analyzed by using regression methods to fit the intensity vs. time data at each position along the elution profile, using models based on zero-order or first-order kinetics. Quantitative detection has been achieved for alkaline phosphatase isozymes that have been separated using electrophoretic methods.

Washington State University
Pullman, WA 99164

Department of Physics

385. *UV Laser–Surface Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials*
Dickinson, J.T. **$109,620**
509-335-4914

A better understanding of the mechanisms involved in the laser desorption/ablation of neutral atoms, molecules, radicals, and ions from solid surfaces can benefit the analysis of materials using laser mass spectroscopy and allow more control in the acquisition of the desired information, optimization of conditions for sensitivity, and improved interpretation of the acquired spectra. Several concurrent approaches are being used to determine in more detail the mechanisms and consequences of UV laser beam exposure of surfaces, in particular on wide band gap inorganic materials. This work includes careful measurements of the ablation threshold and near-threshold response of the irradiated substrate in terms of electronic, thermal, and chemical effects using well-defined laser beams (e.g., beam profiles and fluences). Carefully prepared substrates are characterized before and after laser irradiation in terms of surface and near-surface chemical composition, topography, and microstructure. The role of defects in the substrate is carefully examined, particularly in terms of photon energy conversion to thermal and photochemical processes. The influence of applying two simultaneous stimuli, such as UV laser bombardment with either electron, ion beams, or a second laser beam, to produce excitations or defects in the surface/near-surface region is also being probed.

University of Wyoming
Laramie, WY 82071

Department of Chemistry

386. *Solid-Matrix Luminescence Analysis*
Hurtubise, R.J. **$90,000**
307-766-6241

The major goal of this project is to obtain a fundamental understanding of the physicochemical interactions that are important for the fluorescence and phosphorescence of aromatic compounds adsorbed on solid matrices. Several spectral techniques are used in the research. Filter paper, sodium acetate, and cyclodextrin/salt mixtures are used as solid matrices. The modulus values of filter paper as a function of adsorbed moisture are obtained over a wide range of moisture contents. Theories on the modulus of paper relate the water content of paper to the number of effective hydrogen bonds in paper. Equations are derived that correlate the modulus of filter paper to the phosphorescence quenching phenomena of organic phosphors adsorbed on filter paper. Also, photophysical data are obtained for model compounds adsorbed on deuterated sodium acetate and compared to similar photophysical data for model compounds adsorbed on sodium acetate. These data reveal what physicochemical interactions are responsible for the nonradiative transitions from the triplet state to the ground state for model phosphors. Also, a substantial amount of photophysical data are acquired for lumiphors adsorbed on α-cyclodextrin/NaCl mixtures to establish the kinetics of the radiative and nonradiative transitions from the adsorbed phosphors.

Heavy Element Chemistry

Florida State University
Tallahassee, FL 32306

Department of Chemistry

387. *Research in Actinide Chemistry*
Choppin, G.R. **$117,000**
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

388. *Development of Immobilized Ligands for Actinide Separations*
Paine, R.T. **$99,871**
505-277-1661

The primary goals of this project are (1) to design new families of organic extractants suitable for the separation of d-element and f-element ions from complex liquid and solid waste matrices and (2) to develop methods for covalently attaching these agents to solid supports. In particular, synthetic schemes for ligands containing two or more functional groups in 1,2-, 1,3- and 1,4-positions on a carbon backbone with high orientational flexibility are favored. Functional groups most commonly employed are organo-phosphoryl, nitrosyl, sulfinyl, sulfonyl, and carbonyl. Ligand coordination chemistry is studied in an effort to determine key factors that result in selective ion binding. 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

389. The Electronic Structure of Heavy-Element Complexes
Bursten, B.E. **$66,000**
614-292-1866

The electronic structure of a variety of actinide-containing complexes is being investigated, primarily by using local density functional (LDF) methods. The principal LDF formalism used is the fully relativistic discrete-variational Xα (DV-Xα) method. Application of the DV-Xα method to the calculation of the optical excitation energies of the f^1 actinide hexafluorides PaF_6^{2-}, UF_6^-, and NpF_6 has led to very satisfactory agreement between the calculated transition energies and those observed experimentally. These studies are being extended to more complex f^1 systems, such as $(\eta^8\text{-}C_8H_8)_2Pa$ and $Pa(\eta^3\text{-}BH_4)_4$. The organothorium complex Cp_3Th ($Cp = \eta^5\text{-}C_5H_5$), which has a d^1 ground electron configuration is also being reinvestigated as part of this project. The electronic structure of new and unusual organoactinide molecules, such as derivatized versions of $Cp_2U(NR)_2$ are also being investigated as a continuation of the ongoing investigation into the bonding in cyclopentadienyl actinide organometallics. Finally, studies have begun into the electronic structure of actinide–fullerene complexes in order to determine the important orbital interactions between the actinide center and the fullerene cage.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

390. Physical–Chemical Studies of Transuranium Elements
Peterson, J.R. **$155,000**
615-974-3434

This project provides training for pre- and postdoctoral students in chemical research with the transuranium 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. New knowledge is being accumulated in the following areas: (1) the role of the 5f electrons in the bonding in actinide elements and compounds; (2) the spectroscopic, crystallographic, and thermodynamic properties of these materials as related to general theories; (3) the chemical and physical consequences of radioactive decay in the bulk-phase solid state; and (4) the range of validity of the actinide hypothesis. Current research emphasis is on: (1) characterization of lanthanide and actinide compounds via phonon Raman spectroscopy; (2) use of luminescence spectroscopy to probe the structure of lanthanide and actinide compounds; (3) absorption, luminescence, and Raman spectrophotometry of lanthanide and actinide materials under pressure; (4) measurement of the enthalpies of solution of selected lanthanide and actinide compounds; (5) direct or indirect (via radioactive decay) synthesis of actinide compounds containing unusual oxidation states; (6) broader applications of studies to determine the physical and chemical consequences of radioactive decay in the bulk-phase solid state; and (7) growth of single crystals of lanthanide and actinide compounds on the milligram scale.

Chemical Engineering Sciences

University of California, San Diego
La Jolla, CA 92093

Department of Applied Mechanics and Engineering Sciences

391. Premixed Turbulent Combustion
Libby, P.A. **$60,000**
619-534-3168 **(24 months)**

In the past this project involved several areas of research concerned with premixed turbulent combustion, the characteristics of laminar flamelets, the surfaces within a turbulent flame where chemical reactions occur at the molecular level, and premixed flames in stagnating turbulence. During the past year the research focused primarily on the second area. Because flames in stagnating turbulence are rich in problems of fundamental interest (e.g., the problem of the extinction of turbulent flames), there are five or six laboratories in Western Europe and one in the United States conducting experimental investigations on their properties. The first two theoretical studies of these flames utilizing the k-ϵ theory of turbulence to characterize the fluid mechanics of the flow were completed and published in *Combustion and Flame*. These concerned opposed and impinging jets of turbulent reactants. Interest in these flames has led researchers to analyze the corresponding nonreactive turbulent flows; several journal articles on this work have been published and several manuscripts are in preparation or under review. Research continues on application of the Bray–Moss–Libby theory for the aerothermochemistry of premixed turbulent combustion to these flames. Close coordination is maintained with ongoing experiments conducted elsewhere. A study of highly idealized premixed combustion in a channel is progressing.

Clarkson University
Potsdam, NY 13699

Department of Chemical Engineering

392. *Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures*

Lucia, A. **$54,805**
315-268-6674

The analysis framework for multistage binary separators has been expanded. Global solution uniqueness has been rigorously established for all sets of product composition specifications, while multiplicity has been rigorously established for internal flow and standard specifications of reflux ratio and bottom flow. These and previous analyses have been reclassified through the development of a general concept known as constrained separations. Analytical results have also been established for multicomponent, multistage separators with fixed heat duty and pressure profiles. Practical aspects of all analyses have been related to process design, simulation, operation, and control considerations. Complicated periodic and chaotic behavior for Newton's method has been observed on several common separation process models. A multivariable extension of the dogleg strategy to the complex domain has been developed and Cauchy–Riemann differentiability has been used to establish various theoretical properties that have practical use with regard to global convergence. Global convergence to a solution has been illustrated for a variety of separation process examples and initial values.

Colorado School of Mines
Golden, CO 80401

Department of Chemical Engineering and Petroleum Refining

393. *Composition of Dependence of Fluid Thermophysical Properties: Theory and Modeling*

Ely, J.F. **$116,241**
303-273-3885

The goal of this research is to develop predictive models for the thermophysical properties of fluid mixtures, in the form of computer codes, which can be easily incorporated into industrial design and control packages. The principal focus of the research is on equilibrium and nonequilibrium properties of asymmetric fluid mixtures and on predictive theories for equilibrium properties pertaining to liquid–liquid and liquid–solid phase transitions in asymmetric systems; that is, mixtures with large polarity and/or size differences.

Colorado State University
Fort Collins, CO 80523

Department of Chemical Engineering

394. *Study of Improved Methods for Predicting Chemical Equilibria*

Lenz, T.G.; Vaughan, J.D. **$101,000**
303-491-7871

In today's competitive international economic environment, it is important that U.S. industry be capable of rapidly bringing to market a wide variety of new products. This project involves developing molecular-level computational models that are very valuable in accelerating product and process development efforts. In particular, recent publications resulting from this work have demonstrated the effectiveness of force-field techniques for accurate prediction of the thermodynamic properties of isolated molecules. These models, when coupled with appropriate thermophysical property information such as sublimation/vapor pressure data, afford the capability of predicting a wide range of chemical equilibria for complex molecules. Such an approach is much more cost effective than, and a natural complement to, detailed laboratory experimentation. Software developed in this project recently became available through Quantum Chemistry Program Exchange as Program 593. Current project efforts involve building and generalizing this force-field-based software for accurate prediction of thermochemical properties. Further developments will center on important heteroatom parameterization (initially for oxygen and nitrogen) and will employ state-of-the-art charge equilibration techniques not available to date in other thermochemical force fields. Development of this predictive thermochemical model will also involve carefully chosen supporting bomb calorimetry, X-ray crystallography, and vapor/sublimation pressure studies.

Cornell University
Ithaca, NY 14853

School of Chemical Engineering

395. *Theory and Simulation of Fluids of Associating Chain Molecules*

Gubbins, K.E. **$227,217**
607-255-4385

This work will develop new and rigorous theoretical and molecular simulation methods for the study of the adsorption behavior of fluids in well-characterized porous materials. In particular, fluids in porous carbons, aluminophosphates, and pillared clays are studied. The work may later be extended to other well-characterized porous materials. Studies in the first stage of the project are on adsorption, heat of adsorption, phase changes, hysteresis, and diffusion for simple fluids (inert gases, methane, nitrogen) and their mixtures. As a second stage of the work, studies will concern the behavior of water in carbons and aluminophosphates, which is quite different from that of the simple gases. The project includes an experimental program in adsorption and micro Fourier transform infrared (FTIR) spectroscopy to support the modeling effort.

396. *Molecular Simulation of Phase Equilibria for Complex Fluids*

Panagiotopoulos, A.Z. **$125,000**
607-255-8243

The objective of this project is to investigate phase equilibria for complex fluids using molecular simulation techniques. Current research focuses on three main types of systems. The first area is polymeric systems, including polymer–solvent and polymer–polymer immiscibility studies. The first reported calculation of phase coexistence for a truly macromolecular continuous system is complete. The scaling of critical temperature and density with degree of polymerization has also been determined. 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. The third area studies ionic systems for which earlier work identified a number of obstacles in determining the phase behavior by simulation because of the extremely strong forces present. The main simulations techniques used are the Gibbs ensemble and Chain Increment Monte Carlo methods developed earlier.

Department of Mechanical and Aerospace Engineering

397. *Reaction and Diffusion in Turbulent Combustion*

Pope, S.B. **$95,000**
607-255-4314

The overall objective of the project is to provide a better understanding of the coupled processes of mixing and reaction in turbulent combustion. This is to be achieved through three approaches. First, direct numerical simulations (DNS) are being performed of reaction in isotropic turbulence. The reaction scheme is constructed to be as simple as possible while retaining the essential features of non-premixed combustion chemistry. Second, stochastic Lagrangian models of molecular mixing will be constructed, based on the DNS results. Third, turbulent mixing will be studied in terms of molecular motion. The focus of the work has been on the first topic. The simulated combustion is characterized by three parameters: the Reynolds number, the Damkohler number, and the normalized r.m.s. mixture fraction. For a mixed value of Reynolds number the stability diagram has been determined as a function of the other two parameters. For conditions close to extinction, detailed statistics are being extracted from the simulations and compared to existing theories and models.

University of Delaware
Newark, DE 19716

Department of Chemical Engineering

398. *New Generation of Group Contribution and Equation-of-State Models*

Sandler, S.I. **$95,669**
302-831-2945

To make intelligent, cost-effective decisions for the design of processes for new chemicals; for developing technologies such as synthetic fuels processing; for ways of reducing industrial polluting emissions; for pollution remediation; and for estimating the environmental fate, transport, and bioaccumulation of chemicals, accurate methods of predicting and correlating thermodynamic properties and phase equilibrium are needed. The research under this grant is centered on two related areas. The first is the development of the next generation of thermodynamic prediction methods for the phase equilibria of complex, multifunctional chemicals. This effort is based on group contribution methods, but unlike previous approaches, has used computational quantum mechanics to identify groups in a nonambiguous way. The computational quantum mechanical supermolecule methods are being used to include hydrogen-bonding and other strong association effects in group contribution methods. The second research area deals with the proper modeling of long chain molecules. This activity is proceeding along two paths. One is to use molecular dynamics computer simulation and statistical mechanical theory to develop a correct description of chain molecules ranging from small hydrocarbons to long chain polymers. The second path is to use already existing equations of state with new mixing rules developed to account for free volume effects in polymer solutions.

University of Illinois at Chicago
Chicago, IL 60680

Department of Chemical Engineering

399. *Transport Properties of Dense Fluid Mixtures Using Nonequilibrium Molecular Dynamics*

Murad, S. **$70,000**
312-996-5593

A novel technique has been developed to examine the dynamic behavior of fluids in confined geometries. Both equilibrium and nonequilibrium molecular dynamics have been used to examine the anisotropy in the diffusion coefficients, and thermal conductivity, as a function of wall permeability. A unique feature of the technique is that it allows for the permeability of the wall to be varied from almost the permeable limit to the impermeable. Results have clearly indicated that at low wall permeabilities, transport coefficients exhibit strong anisotropy in systems such as slit, tubular, and cubic micropores. The behavior of fluids under external electric fields and heat fields has also been examined using nonequilibrium molecular dynamics. Results have confirmed the occurrence of heat-induced polarization in fluids, as well as the reciprocal effect, a change in thermal conductivity in the presence of an external electric field.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemical Engineering

400. *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 measurements of macroscopic phase behavior, spectroscopic measurements of specific molecular interactions, as well as spectroscopic measurements of local effects due to nonspecific interactions (i.e., 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 model coal compounds and for polymer–solvent mixtures.

University of Maryland at College Park
College Park, MD 20742

Institute for Physical Science and Technology

401. *Thermophysical Properties of Supercritical Fluids and Fluid Mixtures*
Sengers, J.V. **$133,400**
301-405-4805

The project is concerned with the effects of critical fluctuations on the thermodynamic and transport properties of fluids and fluid mixtures. It has become evident that these fluctuations affect the thermophysical properties of fluids in a large range of temperatures and densities. An improved model has been developed for the thermodynamic properties of fluids that includes the crossover from singular behavior at the critical point to classical behavior far away from the critical point and applied to such fluids as carbon dioxide and ethane up to temperatures as high as twice the critical temperature. This theoretical model is being generalized to binary mixtures with application to mixtures of carbon dioxide + ethane and of ethane + methane. Applications to alternative refrigeration fluids are also included. Furthermore, an attempt is being made to incorporate the effects of critical fluctuations into simple equations of state commonly used in chemical engineering. The present research on transport properties focuses on the effects of critical fluctuations on the thermal conductivity of fluids and fluid mixtures.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

402. *Theoretical Studies of Solid–Fluid Phase Equilibria*
Monson, P.A. **$92,000**
413-545-0661

This project is concerned with research into the theory of solid–fluid phase equilibria, especially for systems with anisotropic intermolecular forces and for mixtures. The main goal of the work is to develop tractable theories that can be applied to a variety of problems in solid–fluid equilibria. The project has two components. In the first, the cell theory of solids is being extended to the cases of nonspherical molecules and mixtures. This provides free energies and chemical potentials for the solid phase, which can then be combined with results from liquid state theories to determine phase equilibria. In the second component, Monte Carlo computer simulations are being used to determine stable crystal structures, free energies, and chemical potentials for various model systems. Information about the solid phase thermodynamics and solid–fluid equilibria of hard dumbbell systems has been obtained and used to formulate a generalized van der Waals theory for the freezing of molecular liquids. A generalization of the cell theory has been used to develop a theory for the properties of hard sphere mixtures in the solid state. This theory has been used to make accurate predictions of solid–fluid equilbria for hard sphere mixtures. The extension of the theory to systems with attractive forces is under way.

National Institute for Petroleum and Energy Research
Bartlesville, OK 74005

Department of Fuels Research

403. *Thermodynamic Properties for Polycyclic Systems by Noncalorimetric Methods*
Steele, W.V. **$200,000**
918-337-4210

The main objective of this research project is to develop 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 after six months include the following: (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. (2) Gas-phase vibrational spectra were obtained for 2-methylfuran and 2- and 3-methylthiophene. Agreement between calorimetrically derived and values-derived entropies statistically was obtained for a narrow temperature range. (3) Complete gas-phase frequency assignments were made for 2,3-dihydrofuran and 2,5-dihydrofuran. (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 completed.

National Institute of Standards and Technology, Boulder
Boulder, CO 80303

Thermophysics Divison

404. 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 the development and refinement of 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) 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) study of the critical loci in mixtures using scaling theory for equilibrium processes and mode coupling approaches for dynamical phenomena. The neutron scattering studies make use of the National Institute of Standards & Technology (NIST) neutron facility and emphasize colloidal systems of polystyrene mixtures in a partially deuterated solvent; this approach optimizes contrast matching capabilities. The resulting data complement computer simulations in a study of heterogeneous phases using ideas from density functional theory. These efforts, including analysis of both phase equilibria and transport properties in the critical region, will allow the refinement of computerized predictive models of primary importance to the energy and chemical industries.

North Carolina State University
Raleigh, NC 27695

Department of Chemical Engineering

405. 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 an equation of state that is capable of predicting the experimentally observed thermodynamic 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 extension of the Generalized Flory theory to binary mixtures of hard chain molecules that differ in segment size, (2) the evaluation of second virial coefficients for square-well chain fluids using Monte Carlo simulations, and (3) the determination of transport coefficients for hard chain molecules using molecular dynamics simulation. Work has begun on extending the Generalized Flory-Dimer theory to heteronuclear fluids. The aim here is to use this as a basis for the development of a new group contribution approach for estimating the properties of fluids when no experimental data is available. 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

406. Thermodynamics and Transport in Microporous Media

Glandt, E.D. **$99,000**
215-898-6928

The project objective is to determine the effects of micropore confinement on the macroscopic properties of simple and complex molecular species. The focus of the work in earlier years was on transport phenomena, more specifically on how the diffusivity of small, nearly spherical molecules depends on the structure of the disordered medium through which they are permeating. The current emphasis is on structure and thermodynamics for long linear molecules. The correlation functions and partition coefficients for linear macromolecules are properties of relevance to all chromatographic and related separations. A combination of molecular simulations and integral equation theory ("polymer RISM in a quenched medium") have been used to compute the intermolecular site–site correlation function, as well as the matrix-site concentration profile. The theoretical 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, $x = N(1 - e)$.

Princeton University
Princeton, NJ 08544

Department of Chemical Engineering

407. *Molecular Interactions in Dilute Supercritical Mixtures: Molecular Dynamics Investigation*
Debenedetti, P.G. **$67,000**
609-258-5480

An automated neighbor list algorithm with multiple time step for the simulation of large systems via molecular dynamics has been developed. For simulations involving between 1,000 and 20,000 atoms, the computational time requirement grows linearly with the system size. The algorithm is three times faster than standard nonautomated neighbor list codes. Molecular dynamics simulations and integral equation calculations of model supercritical mixtures have been performed to investigate solute–solute interactions at high dilution. Significant enhancements in the first peaks of the solute–solute distribution function were found for attractive mixtures, the effect being more pronounced at subcritical densities. Repulsive mixtures show much milder enhancements. These short-ranged features are not related to critical anomalies. For model systems interacting via dispersive forces, first peak enhancements in the solute–solute distribution functions do not translate into the formation of stable solute aggregates. The simulations and integral equation calculations agree with recently derived equations that show that the solute–solute correlation function in an infinitely dilute near-critical mixture always decays to unity from above, regardless of whether the mixture is attractive or repulsive.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

408. *Fundamental Studies of Fluid Mechanics and Stability in Porous Media*
Homsy, G.M. **$105,000**
415-723-2419

This research treats various problems in flow and transport in porous media of interest in energy recovery processes. A major focus is the study of fingering instabilities that occur during displacements caused by differences in viscosity, density, or both. The fluids may be miscible or immiscible and a combined program of experiments, analytical theories, and large scale simulations are used in the project. Current research is focused on 1, miscible displacements in two and three dimensions, 2, fingering with non-monotonic mobility profiles, and 3, dynamics of contact line displacement in flow of immiscible nonwetting fluid pairs. Research on 1 is focused on the similarities and differences in fingering with isotropic and anisotropic (velocity-dependent) dispersion in two and three dimensions. Very recent work shows that the macroscopic behavior is the same in two and three dimensions because of the similarity in vorticity production mechanisms. Research on 2 shows a large difference in nonlinear fingering when propagating fingers encounter regions of locally stable mobility differences. Research on 3 is focused on understanding the hydrodynamic forces responsible for spatial instability of the motion of contact lines for both Newtonian and non-Newtonian fluids.

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

Department of Chemistry

409. *Thermophysical Properties of Fluids and Fluid Mixtures*
Stell, G.R. **$116,000**
516-632-7899

A new exact statistical mechanical off-lattice formalism for describing fluids equilibrated in porous media has been developed. Quantitative results from this approach are being obtained for appropriate reference models and compared to simulation results for the same models that are being generated in parallel. Work on models that exhibit chemical association continues, with increased focus on associating chains of monomers and related models. Results for the thermodynamics of the fully associated limit of such models (in particular, the pearl-necklace limit) have been obtained and prove to be highly accurate. Work also continues on phase separation and critical phenomena in ionic fluids. It has been established that one can expect Ising-like behavior in the restricted primitive model (RPM) but that a variety of other behaviors can be expected in ionic fluids for which Hamiltonian terms not found in that model are present. Supplementing this exact analysis, a study was made of the behavior of certain popular approximations (such as the hypernetted chain approximation) with an eye toward understanding which features of their predictions are artifacts of approximation.

University of Virginia
Charlottesville, VA 22903

Chemical Engineering Department

410. *Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems*
Cummings, P.T.; **$167,000**
O'Connell, J.P.
804-924-6248

The objective of this project is to develop fundamentally based predictive theories for the thermodynamic properties and phase equilibria in mixed solvent and mixed salt electrolyte systems. The emphases in the current year are (1) molecular simulation of vapor–liquid phase equilibria in ethanol/water, water/salt, and ethanol/water/salt systems; (2) molecular simulation of supercritical aqueous systems; (3) development of correlations for thermodynamic properties mixed solvent and mixed salt electrolyte solutions; and (4) 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

411. ***Interphase Transport and Multistage Separations***
Stewart, W.E. **$85,000**
608-262-0188

This project deals with mathematical modeling of mass transfer processes. Objects of research include transport theory, computational methods, and data-based models of system performance. In the current year the correlation of sieve-tray heat and mass transfer was improved, achieving the same goodness of fit with a smaller set of dimensionless groups and eliminating one scaling variable. The scaling analysis of heat and mass transfer in wall turbulence was generalized to include the region of leveled-off transfer coefficients in tubes and ducts. A nonmonotone line search strategy was added to the parameter estimation package, GREG, and a more general Jeffreys prior, valid for multiresponse data sets with gaps in the observations.

Yale University
New Haven, CT 06520

Department of Mechanical Engineering

412. ***Computational and Experimental Study of Laminar Premixed and Diffusion Flames***
Smooke, M.D.; Long, M.B. **$186,393**
203-432-4344

The objective of this work is to understand the effects of detailed chemistry and mass transport on the structure and extinction of premixed and nonpremixed hydrocarbon flames. The work considers both a computational and an experimental approach. Computationally, the coupled nonlinear elliptic equations are solved for the conservation of mass, momentum, species balance, and energy in two-dimensional axisymmetric geometries with adaptive finite difference methods. The model employs both detailed transport coefficients and finite rate chemistry. The computational work focuses on the effects of boundary conditions, reaction mechanisms, and burner configurations on the structure of methane–air flames. The experimental portion of the work applies nonintrusive spontaneous Raman spectroscopy to image simultaneously the major species in the flame. Laser induced fluorescence is used to measure trace radical species. The research goals include the refining of the experimental techniques and the accuracy with which such measurements are made along with the development of a more fundamental understanding of the important fluid dynamic and chemical interactions that occur in such systems.

Advanced Battery Technology-National Laboratories

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

Department of Applied Science

413. ***Synthesis and Characterization of Metal Hydride Electrodes***
McBreen, J. **$250,000**
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 hydride materials for rechargeable batteries. This project is a coordinated team effort between Brookhaven National Laboratory (BNL), Texas A & M University, Hughes Aircraft Corp., and Los Alamos National Laboratory (LANL). The proposed work at BNL focuses on alloy development and the application of in situ methods at the National Synchrotron Light Source (NSLS) such as X-ray absorption (XAS), X-ray diffraction (XRD), X-ray tomography, magnetic susceptibility, and scanning tunneling microscopy (STM) to elucidate the hydride phases and the role of the alloying elements in hydrogen storage and corrosion inhibition. In situ studies will be complemented by ex situ studies such as neutron diffraction and thermodynamic studies. This information will be used in the development of new stable lightweight hydride materials.

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

414. ***Application of Pulsed Laser Deposition to the Study of Rechargeable Battery Materials***
Cairns, E.J. **$200,000**
510-486-5028

A wide range of rechargeable batteries contain complex metal oxide powders as key active ingredients. For example, transition-metal oxides in the form of spinels, pyrochlores, and perovskites are under consideration for the electrocatalyst in the bifunctional air electrodes in Zn/air cells. Many of these same oxides are being considered as intercalation materials for lithium battery cathodes. Performance studies of these high-surface-area powders are limited by uncertainties in the solid–electrolyte interfacial area. Techniques for the production of thin, dense layers of complex metal oxides are required. The pulsed laser deposition process has recently been applied at Lawrence Berkeley Laboratory (LBL) for the production of high Tc superconductor films for use in practical devices. This technique will be used to produce smooth electrochemically active metal oxide films on conductive supports. Electrocatalyst films will be extensively characterized and then fabricated into rotating-disk electrodes for mechanistic studies of the oxygen reduction and evolution reactions. Comparison of true kinetic currents on different electrocatalysts will lead to an optimal oxide composition for the bifunctional air electrode. Intercalation oxide films will be used for studies of Li transport and electrolyte stability as a function of oxide structure and orientation.

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

Kinoshita, K. **$200,000**
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) proposes a fundamental research program on the synthesis, characterization, and modification of carbon-based materials to improve their properties for use in electrochemical systems. The wetting by aqueous electrolytes, polymer–plastic and carbon interactions, double-layer capacity, electronic conduction, and electrocatalyst–support interactions, and changes to these properties by modifying the physicochemical properties of carbon-based materials, will be investigated.

416. *Characterization of the Li–Electrolyte Interface*

Ross, P.N., Jr. **$225,000**
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 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 in 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.

Los Alamos National Laboratory
Los Alamos, NM 87545

Center for Materials Science

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

Schwarz, R.B. **$125,000**
505-667-8454

This research is focused on materials for a rechargeable nickel–metal hydride (Ni–MHx) cell 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. Alloy powders will be prepared by mechanical alloying (MA), a high-energy ball milling technique. Investigations will concentrate on alloys of the type AB_2 (e.g., TiV_2 and $NiTi_2$) and AB_5 (based on $LaNi_5$). These binary alloys will be alloyed with several other elements to improve the kinetics of hydrogen absorption–desorption and the hydrogen storage capabilities, especially during cyclic loading. Preparation and investigation of alloy powders with layered morphologies will be conducted. The powder structure will be studied by scanning and transmission electron microscopy to identify the structural changes that occur when the material degrades after many hydrogen loading cycles.

Oak Ridge National Laboratory
Oak Ridge, TN 37831

418. *Rechargeable Thin-Film Batteries*

Bates, J.B. **$200,000**
615-574-6280

The purpose of this program is to conduct the research needed for the development and commercialization of rechargeable thin-film lithium batteries for consumer electronics and medical devices. Research carried out at Oak Ridge National Laboratory over the past several years has led to the discovery of a new electrolyte that has enabled the successful demonstration of rechargeable thin-film lithium batteries. When compared to commercial rechargeable lithium batteries, the thin-film batteries have several unique features, including unsurpassed energy density, specific energy, cycle life, performance, and safety. These batteries could be used in many consumer products such as on-chip micropower sources and power sources for laptop computers, transdermal drug delivery systems, touch memories, and cellular telephones. However, there are significant issues remaining to be addressed before these batteries are ready for commercialization. These include developing a reliable packaging method, conducting long-term cycle life experiments, measuring cell performance as a function of temperature, and developing bipolar multicell batteries. Exploring new thin-film batteries and fabrication schemes is an important aspect of this research. This reverse cell fabrication study could lead not only to a free-standing battery, but could also result in a solution to the problems of cycle life and safety of conventional rechargeable lithium batteries.

Sandia National Laboratories, Albuquerque
Albuquerque, NM 87185

419. Doping of Lithium Manganese Oxide for Improved Battery Performance
Doughty, D.H.; Levy, S.C. **$260,000**
505-845-8105

Cathode performance is critical to overall lithium ion rechargeable battery performance and impacts some of the most important challenges in the development of commercial lithium ion rechargeable batteries, namely energy density, cycle life, and rate capability. This investigation focuses on the influence of doping lithium manganese oxide cathode materials on the fundamental properties that control cathode performance. The goal of these studies is to develop improved understanding of the chemical and physical properties that determine the performance of manganese oxide cathodes as well as to produce improved materials and preparation techniques for cathodes. While the effects of surface area, pore volume, and grain 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 is no basic understanding of the optimum doping levels nor of the relative importance of different variables. Published literature is preliminary in nature and is conflicting. This study provides a detailed and systematic investigation into the synthesis and doping effects in this class of compounds and is likely to elucidate the underlying chemistry, enabling the preparation of materials with improved properties.

Advanced Battery Technology-Offsite Institutions

Arizona State University
Tempe, AZ 85287

Department of Chemistry

420. Application of New Concepts in Solid Electrolytes, and Pressure-Stabilized Cathode Materials, to Solid State Battery Technology
Angell, C.A. **$133,018**
602-965-7217

This research to further develop ionic rubber solid electrolytes proceeds along several lines. The synthesis of low-melting electrochemically stable lithium salts will be pursued. Salts containing asymmetric anions such as chlorofluoromethane sulfonates will be prepared. The salt-in-polymer studies will include systems that maximize the weak coupling of the Li ion with the polymer. The $Li_4P_2S_7$ + LiSCN + polymer system is expected to have a high decoupling index. Rubberizing polymers that contribute to the conductivity rather than sit there as neutral participants will be sought, developed, and evaluated. High-pressure syntheses of glassy and crystalline cathode materials will use the glass-forming properties of V_2O_5 with Li manganate and Li permanganate modifications. The synthesis of crystalline cathode materials that contain tetravalent transition elements like manganese or nickel in the Si^{4+} position will be attempted using high oxygen potential starting components.

Case Western Reserve University
Cleveland, OH 44106

Chemistry Department

421. Application of In Situ and Ex Situ Spectroscopic Techniques for the Study of Electrode Materials with Relevance to Energy Generation and Energy Storage
Scherson, D.A. **$200,000**
216-368-5186

This work includes research on three different electrochemical systems. The research on nickel oxide electrodes will seek to identify the structural and electronic properties of nickel hydrous oxides induced by incorporation of other metals into the lattice. An array of in situ structural and spectroscopic techniques including X-ray absorption fine structure (XAFS), attenuated total reflection Fourier transform infrared (FTIR), substrate-induced stimulated electronic Raman scattering (SERS), and UV-visible RAS will be used. Quark cluster model (QCM) gravimetry will be used to quantify the migration of metal cations in and out of the lattice. The rates of self discharge will be monitored using ring-disk electrode techniques. The research on nickel hydride electrodes will use some of these same techniques to examine the roles of selected elements such as Al or Ti on the properties of nickel-based compounds like $LaNi_5$. Research on Li intercalated carbon electrodes will focus on elucidating the structure–electrochemical performance relationships of Li_xC_6 electrode systems, and full characterization of the nature of the passive film on Li in nonaqueous electrolytes. An array of in situ and ex situ electronic and structural probes will be used. These include, in addition to those proposed for the Ni systems, X-ray diffraction and nuclear magnetic resonance (NMR) methods. QCM and electrochemical methods will also be employed. Work on air cathodes for Zn–air cells will involve modification of the electrolyte within the air electrode, separator, and Zn anode. The objective is to reduce the gain or loss of water through the use of nonionic and ionic polymers, inorganic gelling agents, and anion conducting polymers as electrolyte replacements.

Clark University
Worcester, MA 01610

Department of Chemistry

422. *Novel Aluminum and Sulfur Batteries*
Licht, S. **$66,733**
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.

Electro Energy, Inc.
Brookfield, CT 06804

423. *BiPolar Nickel-Metal Hydride Battery*
Klein, M. **$194,378**
203-740-7369

This work focuses on developing a multicell nickel metal hydride battery suitable for use in consumer portable products. Life-limiting problems associated with oxygen evolution during sealed cell operation will be addressed using starved electrolyte, open pore separator cells and cells incorporating a back side anode recombination approach. A 3 x 3 in. electrode test cell configuration will be used to conduct development activities on cell components such as the hydride electrode, nickel electrode, and separator material. Integration of the results from this work is expected to result in a multicell battery for testing and evaluation.

Giner, Inc.
Waltham, MA 02154

424. *Bifunctional Air Electrodes for Metal–Air Batteries*
Swette, L.L. **$90,749**
617-899-7270

Specific objectives of this program are (1) to prepare catalysts, $LaNiO_3$ and/or $La_{1-x}Ca_xCoO_3$, in high surface area form using modified metal oxide preparation methods; (2) to physically–chemically characterize them for crystalline structure, phase purity, stoichiometry, surface area and electrical conductivity; (3) to test for electrochemical stability over a bifunctional potential range; (4) to develop bifunctional electrode structures based on the Giner, Inc. integrated-dual-electrode approach using floating electrode performance tests as an initial measure of electrode optimization; and (5) to conduct extended performance testing of the electrodes in a bifunctional O_2/O_2 cell with posttest verification of catalyst stability.

Hughes Aircraft Company
Torrance, CA 90505

425. *Advanced Nickel–Metal Hydride Cell Development*
Lim, H.S. **$81,483**
310-517-7620

This research is directed at developing new alloy materials for use as anodes in nickel metal hydride cells. Through this four-part collaborative effort, three distinctly different alloy preparation techniques will be evaluated. For its part, Hughes is developing a powder preparation technique that will produce the powder with a unique morphology. The initial operating parameters of the preparation technique will be optimized using a metal such as iron, and then expanded to the alloy studies. Promising compositions of various alloy types will be produced and evaluated with this system. It is expected that particles from 50 to 200 μm in diameter can be produced by this technique. In an effort to improve the hydride electrode performance, the effects of surface modifications through anodic oxidation, chemical treatment, or coating of the alloy materials with metals such as copper and nickel will also be investigated. The particle size and surface treatment effects will be optimized through an iterative process involving characterization of the samples by the Texas A & M University and Brookhaven National Laboratory (BNL) collaborators. The effects of particle morphology will be studied by varying the alloy preparation techniques through the collaborative efforts at Los Alamos and Brookhaven National Laboratories. Alloys will be selected based on various performance criteria including specific capacity of the alloy, rate capability, isotherm pressure (self discharge is expected to be related to this criterion), and projected powder production costs.

University of Minnesota
Minneapolis, MN 55455

Corrosion Research Center

426. *Characterization of Insertion Electrodes in High-Energy Cells*
Smyrl, W.H. **$250,000**
612-625-0717

One purpose of the research program is to verify that xerogel films of V_2O_5 will act as hosts for the same cations in nonaqueous solvents as they do in aqueous solutions. Mg, Zn, and Al will be used initially because of their high energy combined with availability, low cost, and increased safety compared to Li systems. The stoichiometry and thermodynamics of cation insertion will be investigated by electrochemical coulometry and concurrent quartz crystal microbalance gravimetry. In addition, changes in surface morphology will be studied using phase detection interferometric microscopy. The rate and cation diffusion coefficient for the bulk and interfacial region will be studied using impedance measurement techniques. Characterization of the surface and bulk structure and cation environment will be investigated using scanning tunneling microscopy and X-ray scattering and reflection studies. The extent and influence of surface films on Li ion intercalation into well-defined highly oriented pyrolitic graphite surface structures will be studied. Samples will be prepared by vapor phase deposition of Li on structured graphite surfaces. The surface and bulk characterization of the samples will be carried out by the same methods that will be employed for the V_2O_5 xerogel electrodes. The incorporation and characterization in microbatteries will be conducted in collaboration with staff at Oak Ridge National Laboratory (ORNL). Thin film electrodes will be supplied and used to fabricate microbatteries and then determine the coulombic 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

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

Halley, J.W. **$90,975**
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 theoretical and, through collaboration, experimental techniques that have not previously been applied to these materials. In this theoretical study, molecular dynamics are used to investigate local structure and dynamics. The results of the molecular dynamics simulations are then utilized to construct models studied in Monte Carlo simulations to provide information on transport properties. Development of linked simulation models on at least two time and length scales is also included. Local ion and polymer structure, including solvation of cations and anions, is probed through molecular dynamics simulations using the best available interatomic interaction potentials. To address issues of transport and other physical phenomena occurring at longer length and time scales in these systems, the insights and quantitative information provided by the molecular dynamics studies will be used to construct a lattice model for study by Monte Carlo (or other) numerical techniques. Both simulation models will also later be applied to a study of the interface between the electrolyte and electrodes.

Pennsylvania State University, University Park
University Park, PA 16802

Center for Advanced Materials

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

Macdonald, D.D. **$202,000**
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 expansions 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

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

Garofalini, S.H. **$123,045**
908-932-2216

This research focuses on using ultrahigh vacuum atomic force microscopy (UHV-AFM), X-ray photoelectron spectroscopy (XPS), and ion scattering spectroscopy (ISS), to examine structural, dynamical, and chemical properties of solid electrolyte surfaces and the cathode–electrolyte interfaces. This includes a study of (1) localized relaxations within the electrolyte surface induced by the voltage on the AFM tip (the AFM voltage probing will be done on clean electrolytes and those with different cathode overlayer thicknesses to determine parameters of Li ion mobility, the thickness at which the ionic response of the Li to the imposed voltage changes); (2) morphological changes during deposition of the cathode; (3) thin film nanoheterogeneity in conduction in a nanobattery setup in which the tip will act as a source of electrons to the cathode; and (4) chemical and structural changes due to deposition of submonolayer to multilayer overlayers of cathode-onto-electrolyte and electrolyte-onto-cathode using XPS and ISS. Molecular dynamics computer simulations are used to provide an atomistic visualization of the interfacial behavior, the structure of the cathode–electrolyte interface, and the effect of nitrogen on the structure of the bulk phosphate glass and on the above thin films and interfaces. It has recently been shown that additions of nitrogen to the phosphate glasses significantly increase both conductivity and charge–recharge stability of the cell device.

SRI International
Menlo Park, CA 94025

430. Development of Lithium Batteries with Nonflammable Liquid Electrolytes

Smedley, S. **$230,837**
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. These are chosen because their chemical modifications are tractable. Si/C and P/C ratios will be adjusted to minimize flammability and optimize self-extinguishing properties. These electrolytes will be examined to determine dielectric constants, viscosity, boiling point, flammability, conductivity, and identification of the ones that provide the maximum Li ion migrational flux. Electrochemical characterization by DC cycling, cyclic voltammetry, and electrochemical impedance spectroscopy will examine their electrochemical behavior with Li metal and MnO_2 electrodes. The best electrolytes will be transferred to Duracell laboratories for testing in the laboratory equivalent of a real Li cell. This includes cell performance and cyclability at ambient temperature and at -20 °C. Shelf life will be approximated by storage at 60 °C for a predetermined period. Underwriter Laboratories will test the cells to the point of rupture for flammability, percussive force, and explosion dangers.

University of South Carolina
Columbia, SC 29208

Department of Chemical Engineering

431. Mathematical Modeling of a NiOOH/Metal Hydride Cell

White, R.E. **$99,532**
803-777-3270

This research focuses on the development of a realistic mathematical model for the performance of a NiOOH/M-H battery based on the fundamental physicochemical processes in the battery and the external applications circuit. There will be experimental verification. The model will then be used to predict the electrical and thermal behavior of a cell during charge, discharge, and open-circuit for different cell designs and operating conditions. This work extends previous mathematical models to include the metal hydride electrode instead of a gas-fed hydrogen electrode. A porous NiOOH electrode on a sintered Ni metal substrate is chosen as the modeling positive electrode and NiOOH/$Ni(OH)_2$ active deposited material in a KOH electrolyte. The changes in the values of five polarizations will be studied with the operation of the cell and the design parameters: the concentration polarization due to a variation in KOH concentration; the potential drop in the electrolyte phase; activation polarization of the electrochemical reaction; polarization due to slow proton diffusion in the solid phase; and ohmic drop across the solid active material phase in the electrode. The model will be developed from first principles using a macrohomogeneous and pseudo-two-dimensional approach to describe the porous media in the cell. The governing equations will be derived based on mass, charge, and volume balances for both electrolyte and solid phase and on thermodynamic and kinetic principles. The transport properties of diffusion, migration, and electrical conduction in the electrolyte phase and the solid phase will be included in the governing equations. An energy balance equation 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

432. Cell Components with Emphasis on Hydride Electrolytes for Nickel/Metal Hydride Batteries

Srinivasan, S. **$141,047**
409-845-8281

The research at Texas A & M involves the physical-chemical characterization of the alloys prepared by collaborators at Hughes, Brookhaven National Laboratory (BNL), and Los Alamos National Laboratory (LANL). This includes scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) for examining the morphology and elemental composition of the alloys. The gas phase characterization of the alloys includes determination of the pressure–composition isotherm and calorimetric characteristics for hydrogen absorption–desorption as a function of temperature. The thermodynamic data so derived will be used to select the best alloys for electrode fabrication and performance evaluation. Electrochemical characterization includes determination of the charge–discharge and cycle life characteristics of the electrodes. They will also be examined using SEM–EDAX and X-ray photoelectron spectroscopy to gain information on electrode morphology and microstructure. The electrolyte will be analyzed to monitor for dissolution of alloying constituents. The self-discharge and capacity retention behavior of the electrodes will be determined and the chemical stability will be established.

The subsequent electrode material optimization and development will be done at Hughes with assistance from Texas A & M.

Tufts University
Medford, MA 02155

Electro-Optics Technology Center

433. *Collaborative Research on Advanced Microbatteries*
Goldner, R. **$135,535**
617-627-3136

The goal of the research on $LiCoO_2$ thin film cathodes is to provide material having properties close to those of bulk material, namely, a maximum open circuit voltage of about 4.7 volts, a room-temperature Li ion diffusion constant close to 5×10^{-8} cm^2/sec, and a capacity of nearly one equivalent. The research on thin film Li insertion anodes focuses on Li_xC and $Li_{1+x}TiS_2$ and seeks to deposit thin films with properties as good as or better than those reported for bulk samples with the same compositions. The goal of the research on amorphous $LiNbO_3$ as a solid electrolyte is to obtain room-temperature lithium ion conductivity in thin films comparable to that obtained for roller-quenched glassy lithium niobate, together with effective electronic resistivities. The properties of aluminum nitride protected from moisture by a coating of aluminum oxide are being examined as a sealing layer to isolate the microbattery structure from the environment.

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.

Advanced Fuel Research, Inc.
East Hartford, CT 06108

434. *On-Chip IR-Spectral Sensors by Superconducting Detector Arrays*
Fenner, D.B. **$74,717**
203-528-9806

Conventional methods of IR spectroscopy for analysis of chemical species are limited to offline instruments. The project will examine the application of a new, smart-detector design for IR-spectral resolution. This innovation accomplishes spectral resolution of IR directly on the detector chip assembly, and allows spectral analysis over a very wide wavelength range, limited only by the choice of optical window materials. This new spectral sensor is very small, compact, and rugged, especially if it is fabricated on a silicon wafer substrate. During a previous Phase I (NSF), the central concept was demonstrated, a spectrometer application was pursued, and a U.S. patent filed. The sensor uses a monolithic-detector array fabricated with an interference-filter array. The detectors are photothermal (bolometers) of high-temperature superconducting films on silicon. Testing in an FTIR spectrometer verified that the device functioned as expected in model simulations. The present Phase I program will adapt this design innovation into a spectral sensor for chemical species analysis and monitoring in a form suited to portable field installations and flexible programmability. Numerous specific expressions of this type of device can be envisioned and will be the basis for much of the Phase II activity.

Bend Research, Inc.
Bend, OR 97701

435. *Composite Plasma-Polymer Membranes*
Babcock, W.C. **$74,969**
503-382-4100

The potential advantages of membrane processes for separations are well known; however, current membrane systems have captured only a small fraction of the potential market, primarily because they are made from polymers that are not durable enough for many applications and they do not have sufficient selectivity for clean separations. Plasma-polymer membranes offer a solution to both problems. These membranes exhibit extraordinarily high selectivity, and they are so highly crosslinked that they are both chemically and thermally stable. The goal of this program is to develop a composite membrane consisting of a microporous support on which a thin, highly selective layer is deposited: all from plasma polymers. Such a membrane would overcome current selectivity and durability shortcomings of membranes. Additionally, the process for making such membranes will prepare the way for making membranes directly from any of a wide range of organic or inorganic monomers and mixtures thereof, thereby extending the useful range of separation properties and overcoming the ever-increasing costs and the limitations on membrane-separation properties associated with using specialty polymers for membrane materials.

Separations Division

436. *Development of Novel Reverse-Osmosis Membranes with High Rejections for Organic Compounds*

McCray, S.B. **$499,911**
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.

Ciencia, Inc.
West Hartford, CT 06108

437. *Online Microsensors for Analytical Chemical Measurements*

Fernandez, S.M. **$74,949**
203-528-9737

The present program offers an innovative approach to microsensing that is expected to result in compact, rugged, versatile, highly sensitive sensor systems capable of sophisticated online spectral analysis for analytical chemical measurement in a broad class of chemical processes. These sensors are to be designed to operate in real world factory environments and to be capable of sensing micron-scale phenomena. They are true online sensors, not automated "grab sample" techniques. The key innovations include (1) the use of laser-induced fluorescence to provide high sensitivity and high specificity in complex mixtures of similar compounds; (2) the use of acoustooptically tuned filters to replace the conventional scanning grating monochromators in current use in the laboratory to make rugged factory-compatible devices; (3) optical access that allows application to optically dense media; (4) imaging, fiber optic, and microscopic techniques to address very small sample sizes and to quantify inhomogeneity within a sample; and (5) high-speed analysis techniques to permit real time operation. The sensors will be used in on-line, real-time analytical chemical measurement for industrial process control. Cost savings achieved from reduced energy utilization and increased quality control make this approach practical to implement.

Energy and Environmental Research Corporation
Irvine, CA 92718

438. *Multiple Air Pollutant Emissions Removal by the Use of a Single Chemical Additive*

Zamansky, V. **$75,000**
908-534-5833

Air pollution control technologies for NOx reduction 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 NOx and SOx removal. A large number of wet scrubbers are already installed in stationary combustion sources or are planned for the near future. Therefore, a process that promotes NO 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 develops a novel concept: gas phase multiple air pollutant emissions removal by injection of a single chemical additive into combustion gases at high temperatures. Chemical kinetics calculations and experimental data available from the literature predict that an additive exists that upon being injected into combustion gases at specific conditions can efficiently convert to NO_2, SO_2, and CO_2 all major gaseous air pollutants: unreactive NO, unburned CO, corrosive SO_3, unburned hydrocarbons, and dangerous organic byproducts. NO_2 and SO_2 can be efficiently scrubbed in a slightly modified calcium-based SO_2 scrubber. The Phase I effort will provide a laboratory-scale feasibility demonstration of the critical steps of the process, the conversion of NO to NO_2, SO_3 to SO_2, and CO to CO_2 in the gas phase within reaction times, temperatures, and other conditions that are in the practical range for its application in boilers and furnaces.

Materials and Electrochemical Research Corp.
Tucson, AZ 85706

439. Development of a Process to Synthesize Tubular Fullerenes

Withers, J.C. **$500,000**
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

440. Solid Polymer Electrolyte Membranes for Olefin Separation

Pinnau, I. **$75,000**
415-328-2228

Separation of olefins from saturated hydrocarbons is an industrially important gas separation that is highly energy intensive using current technology. Membrane separation processes generally use much less energy than conventional processes such as distillation. Polymeric membranes have been applied successfully to a number of gas separations, including nitrogen production from air and hydrogen removal from refinery streams. However, the selectivities and gas fluxes of polymeric membranes for olefin separation from saturated hydrocarbons are insufficient. Facilitated transport membranes often have higher selectivities than polymeric membranes. Facilitated transport membranes use reactions with a complexing agent incorporated into the membrane to selectively enhance the permeability of one of the components of a gas mixture. Two problems limit the application of facilitated transport membranes to industrial gas separation applications: (1) membrane instability and (2) low gas fluxes. The goal of this program is to produce chemically and mechanically stable facilitated transport membranes with high gas fluxes and high selectivities for the separation of olefins from saturated hydrocarbons. The selective membranes will consist of a polymer material that can dissolve the metal ion to be used as the gas complexing agent. This solid polymer electrolyte will be formed into a thin-film composite membrane. Phase I will demonstrate the feasibility of developing these polymer electrolyte composite membranes for the separation of olefins from saturated hydrocarbons. In contrast to previous facilitated transport membranes, the polymer electrolyte composite membranes are expected to be stable under high-pressure operation and to exhibit substantially higher gas fluxes than conventional facilitated transport membranes.

Moltech Corporation
Stony Brook, NY 11794

441. Advanced Biosensors for Analytical Chemical Measurements

Skotheim, T. **$250,000**
516-444-8866

The main focus of this project is the development of biosensors based on immobilized toluidine blue-O as the electron transfer mediator, nicotinamide adenine dinucleotide (NAD), and dehydrogenase enzyme. The immobilization matrix is a hydrophilic polymer material with an electrochemical window optimized for electrochemical measurement. The biosensor developed has high current densities for the substrate within the physiological concentration range. Several polymers containing covalently or electrostatically attached TBO molecules were synthesized and tested as electron transfer mediators for glucose dehydrogenase (GDH) and NAD. It has been shown that immobilized TBO molecules can be used in NADH biosensors. The glucose sensors constructed from immobilized TBO, NAD, and GDH on a graphite surface, protected by a hydrophilic ionic polymer film formed by ionic crosslinking, showed significantly higher sensitivity than carbon paste electrodes. The magnitude of the currents achieved, ~100μA/cm2, is sufficient for the development of practical biosensors. Preliminary investigation showed that the sensitivity and linearity are controlled by the enzyme/glucose electron transfer reaction. It is also observed that the electron transfer rate between TBO and NADH is dependent on interactions with the electrode surface.

Physical Sciences, Inc.
Andover, MA 01810

442. Time Resolved Nitric Oxide Measurements in Combustion Exhausts

Parker, T.E.; Caledonia, G.E. **$75,000**
508-689-0003

This research and development program will produce an instrument capable of providing real-time measurements of NO concentrations in power-plant or internal-combustion engine exhausts. This instrument will be capable of monitoring transients in emission with a resolution of 10 ms or less. This approach utilizes an inexpensive, high-resolution instrument concept that is easily extendable to species other than NO. The motivation for this new capability is clear. Federal clean-air initiatives are pushing future emissions standards for NO_x to ever-lower levels. A real-time, nonextractive NO monitor can be used as the sensor in a feedback control loop; information derived from the measurement system will allow diesel engine manufacturers to critically assess their engines' pollutant performance over their entire operating envelope. The key to the technical approach is to measure concentrations of NO with absorption diagnostics in the IR and package the instrument in a fashion that facilitates its application to severe environments. Concentrations of NO are derived from single-line absorption measurements near 5.2 μm. This wavelength is chosen specifically (1) to avoid spectroscopic features from other gases typical of combustion exhausts and (2) to be insensitive to typical loadings of particulate in these flows.

REB Research and Consulting
East Lansing, MI 48823

443. *Improved Coated-Metal Hydrogen Extraction Membranes*

Buxbaum, R.E. **$72,912**
517-353-5383

Coated-metal membranes are suggested for hydrogen extraction from gas mixtures (e.g., in petrochemical plants) in the production of reformulated gasoline and for membrane-reactor use. Palladium-based membranes have been used for decades for 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. Several refractory metals are higher in permeability, and are stronger and cheaper than palladium: they are not ordinarily used for hydrogen extraction because poor surface properties reduce hydrogen transport. When these metals are coated with palladium, however, the surface barriers are removed. The resulting membranes show permeabilities more than 10 times greater than available with palladium. Further, membranes made from these metals can be thinner than with palladium because these metals are stronger. This combination should allow very economical hydrogen-extraction membranes for use with petrochemical and technical gas mixtures. The current membranes are still too thick and too small for practical application. The first larger, thin-walled tubular membranes will be coated, and the hydrogen transport in these membranes will be measured. These steps will aid commercialization by providing practical membranes for use in bench-scale industrial tests, and by providing important benchmark transport data.

TDA Research, Inc.
Wheat Ridge, CO 80033

444. *Preparation of Low-Density Microcellular Materials from Fullerenes*

Bell, W.L. **$500,000**
303-420-4329

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.

445. *Zeolite Membranes for Gas Separations*

Jiang, Z. **$75,000**
303-422-7819

Porous inorganic membranes can be used at high temperatures, and have high fluxes, mechanical strength, and chemical stability. However, commercially available inorganic membranes have large pores (>40 Å), and a wide pore-size distribution. While such membranes are ideally suited for removing high-molecular weight components from a liquid stream (ultrafiltration), their ability to separate gases is limited. Because these membranes operate on Knudsen diffusion, their separation coefficients are far too low for use in gas separations. On the other hand, zeolite membranes have much smaller pores, and a well defined pore size distribution. Since they separate molecules by molecular sieving, they offer very high selectivity. Unfortunately, while the potential of zeolite membranes has long been recognized, there is still no suitable processing method by which either self-supported zeolite membranes or composite membranes (a zeolite-film on a porous support) can be made. In Phase I, ZSM-5 zeolite films will be prepared on Al or Si substrates using a novel synthetic method, and then the chemical composition, morphology, thermal stability and ion exchange ability of the resulting films will be characterized. Phase II will further refine the preparation process, optimize the film characteristics, and measure the permeability and separation factor of supported zeolite gas-separation membranes.

446. Continuous Production of Fullerenes from Hydrocarbon Precursors

Wright, J.D. **$500,000**
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.

ADDENDUM

Information on the following grants was received too late for their inclusion in the body of this book.

Separations and Analysis

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Analytical Chemistry Division

447. ***Mass Spectrometry R&D for Organic Analysis***
McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E.; Ramsey, R. S.

The objective of this research program is to improve understanding of the chemical and physical processes that take place in the mass spectrometry of organic molecules. Particular emphasis is placed on reactions that take place in the course of a mass spectrometric experiment. These include unimolecular reactions, biomolecular reactions, termolecular reactions, and the many types of reactions that may take place in the ionization process. In the area of ionization, heavy emphasis is currently placed on electrospray, glow discharge, positron capture, and laser desorption. Unimolecular, bimolecular, and termolecular reaction studies are currently focused on multiply charged ions derived from electrospray as well as high mass singly charged ions. Research in ion activation is also heavily emphasized. In particular, collisional activation in the quadrupole ion trap is modeled and is being developed for threshold dissociation measurements. Electron- and photo-induced dissociation of high-mass ions is also of interest. The knowledge gained from these studies often leads directly to improved methods for mass spectrometric analysis as well as new means for characterizing ion chemistry. Both advance the state-of-the-art in analytical organic mass spectrometry.

Photochemical and Radiation Sciences

Oregon Graduate Institute of Science and Technology
Beaverton, OR 97006

Department of Chemical and Biological Sciences

448. ***Membrane-Based Photochemical Systems as Models for Photosynthetic Cells***
Hurst, J. K. **$50,000**
(6 months)

This project aims to improve the conceptual understanding of the influence of microphase separation and compartmentation upon oxidation-reduction processes. Three goals are (1) to use interfaces to promote charge separation and increase lifetimes of the initial redox products, (2) to identify mechanisms of transmembrane redox across bilayer membranes, and (3) to develop regenerative cycles for water photolysis. Concerning goal 1, photoinduced charge separation in totally artificial self-assembling photoredox systems has been achieved, the quantum efficiencies of which approach that of natural photosynthesis; lifetimes of the immediate products, which are phase-separated, exceed 10 ms. With respect to goal 2, viologen transmembrane redox mechanisms have been unambiguously identified, which involve either "flip-flop" diffusion or long-range electron tunneling between reactants bound at the opposite membrane interfaces. Either of the pathways can be selected by appropriate derivatization of the redox dopant ion. Goal 3 entails determination of water oxidation mechanisms by a series of dimeric ruthenium μ-oxo ions. These studies have involved the use of ^{18}O isotopic tracers, as well as various structural and kinetic methods. Current efforts are directed at incorporating these components into integrated systems for water photolysis and developing photogated switchable conducting membranes exhibiting rectification. The latter may be useful as prototype devices for other forms of energy conversion.

Princeton University
Princeton, NJ 08544

Department of Chemistry

449. Resonance Raman Spectroscopy of Photoreaction Centers

Spiro, T. G. **$110,000**

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 pheophytin molecules, 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 are 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.

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 is a process based on the need for collaboration by the off-site scientist with one or more in-house staff members.

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 Dr. Iran Thomas, Director 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	$ 7,125,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	26,259,000
	Radiochemical Engineering Development Center	7,636,000
Sandia National Laboratories, Livermore	Combustion Research Facility	4,379,000
Stanford University	Stanford Synchrotron Radiation Laboratory	11,196,000

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 research community with long-term supplies of a small number of premium coal samples that can be used as standards for comparison. The premium coal samples produced from each coal and 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. Coals were mined, transported, processed into the desired particle and sample sizes, and packaged in environments as free of oxygen as possible while maintaining the natural moisture content in order to ensure that the coals will be in as pristine and stable a condition as possible.

AVAILABILITY

The first samples became available in mid-1985, and the set of eight samples was completed in early 1987. These samples are available to research personnel at a nominal replacement cost. A very limited quantity of lump coal, stored under similar inert conditions, is available on special request for special physical property measurements. Distribution of these samples is guided by policies established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples. More than 727 shipments totaling over 19,000 ampoules have been made. A Users Handbook is updated periodically and available from the Manager.

PERSON TO CONTACT FOR INFORMATION

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USDOE-CH ARGN

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

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne linear electron accelerator was designed for chemical research. The moderate energy of the electron accelerator (maximum energies of 21 MeV transient mode, 14 MeV steady state) allows the use of the electron beam for the generation of transient species without nuclear activation. The pulse width can be varied from 25 ps to 10 μs. 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 μM can be generated with the 25-ps pulse, and concentrations in excess of 10 mM can be generated with the longest pulse. Instrumentation for 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 use the short pulse capability of the LINAC can also be made, both in absorption and emission. 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.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

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TECHNICAL DATA

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

NATIONAL SYNCHROTRON LIGHT SOURCE (KC-03-01-04)

Brookhaven National Laboratory
Upton, NY 11973

The National Synchrotron Light Source (NSLS) is the nation's largest facility dedicated to the production of synchrotron radiation. The facility has two electron storage rings: a vacuum ultraviolet (VUV) ring which operates at an electron energy of 750 MeV designed for optimum radiation at energies between 10 eV and 1 keV, and an X-ray ring which operates at 2.5 GeV to optimize radiation between 1 keV and 20 keV. The X-ray ring accommodates 32 experimental ports and the VUV ring accommodates 20. Each of these ports can be split into two to four beam lines. By the end of 1993, the Light Source had 83 operational experimental beam lines. Of these, four lines are dedicated to beam diagnostics.

From their conception, the designs of the storage rings included long, field free straight sections for special radiation sources (wigglers and undulators). The two straight sections on the VUV ring and the five available on the X-ray ring now have a variety of wigglers and undulators providing radiation that is anywhere from one to several orders of magnitude brighter than that from the comparable bending magnets. These devices are the sources for a wide variety of experiments in the biological, chemical, and materials sciences. Active General User programs are under way on most of the insertion device lines at the Light Source.

Photons, as a probe, provide information about the electronic and atomic structures of interest to the chemical, biological, and materials sciences. The techniques fall broadly into two areas: spectroscopy and scattering. At the NSLS, they are applied to forefront research: imaging in both real space (e.g., X-ray microscopy, tomography, angiography) and reciprocal space (e.g., protein crystallography, X-ray topography), surface science (e.g., photoemission, surface diffraction, infrared spectroscopy), and recently magnetism (e.g., magnetic X-ray scattering, spin polarized photoemission). These are but a few of the exciting research opportunities at the NSLS. As of April 1, 1993, over 2572 scientists from 405 universities, laboratories, corporations, and foreign institutions are registered users of the research tools available at the NSLS.

Proprietary research can be performed at the NSLS. The DOE has granted the NSLS a Class Waiver under whose terms the Proprietary User is obligated to pay the full cost recovery rate for NSLS usage. In return, the user has the option to take title to any inventions made during the proprietary research program and to treat as proprietary all technical data generated during the proprietary research program. During FY 1992, eight corporations utilized 378 shifts of NSLS operations to conduct proprietary research.

USER MODES

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in establishment of comprehensive long-range experimental programs. Beam lines are either constructed by Participating Research Teams (PRTs), Insertion Device Teams (IDTs), or by Brookhaven staff members. The institutional representation on the PRTs and IDTs totals 83. Each PRT and IDT is entitled to up to 75% of their beam line's operational time for a three-year term. The remaining beam time is made available to scientists categorized as "General Users."

General Users are scientists interested in using existing NSLS facilities for experimental programs. The NSLS runs three scheduling cycles per year. Access to the facility is through a proposal system. Proposals are reviewed by NSLS staff for technical feasibility, safety, and personnel resources, and checked by the cognizant beam line personnel for conformance to the beam line's capabilities. General User proposals are subject to review by a Proposal Study Panel. All beam line/time allocations are assigned by the NSLS General User Oversight Committee. Liaison and utilization support is provided to the General User by the cognizant beam line personnel. One hundred and seventy-three new General User proposals along with 256 beam time requests against existing proposals were submitted during FY 1992. A total of 2286 days of beam time were allocated to General Users on the X-ray and UV rings during FY 1992.

A program is available to support faculty/student research groups performing experiments at the NSLS. The program is designed to encourage new users to the facility and defray expenses incurred during exploratory visits to BNL, and while conducting initial experiments at the Light Source. It is aimed at university users having only limited grant support for their research. Sixty scientists, 28 faculty and 32 students representing 20 universities, participated in this program in FY 1992. One hundred and twenty institutions have now participated in this program since its inception in 1984.

PERSON TO CONTACT FOR INFORMATION

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bnl::pinkston

TECHNICAL DATA*

Storage rings	Key features	Operating characteristics
VUV electron	High brightness; continuous wavelength range (E_c 25 Å); 17 ports	0.75 GeV electron energy
X-ray electron	High brightness; continuous wavelength range (E_c 2.5 Å); 30 beam ports	2.5 GeV electron energy

Research area	Wavelength range (Å)	Energy range (eV)	Number of instruments
Circular dichroism	1400 to 6000	2.1 to 8.9	1
Energy dispersive diffraction	WB; 0.1 to 103	WB; 120 to 100,000	3
EXAFS, NEXAFS, SEXAFS	WB; 0.4 to 2480	WB; 5 to 35,000	19
Gas phase spectroscopy/ atomic physics	WB; 0.6 to 6.2	WB; 2000 to 20,000	3
High pressure physics	0.1 (Å) to 10,000 (μm)	0.12 (meV) to 100,000 (eV)	3
Infrared spectroscopy	2.5 (μm) to 10,000 (μm)	0.12 (meV) to 490 (meV)	1
Lithography/microscopy/ tomography/radiography/	WB; 0.1 to 124	WB; 3 to 100,000	10
Medical research	WB; 03 to 3.1	WB; 4000 to 36,000	3
Nuclear physics	–	80 to 400 (meV)	1

TECHNICAL DATA (Continued)

Research area	Wavelength range (Å)	Energy range (eV)	Number of instruments
Photoionization	0.6 to 4000	3 to 20,000	2
Radiometry	WB; 8.3 to 248	WB; 50 to 1,500	1
Reflectometry	20 (Å) to 10,000 (μm)	0.12 (meV) to 620 (eV)	2
Research & development/ diagnostics	WB	WB	12
Time resolved fluorescence	350 to 6000	2.1 to 3.5	2
Topography	WB; 0.1 to 3.1	WB; 4000 to 100,000	3
VUV & X-ray photoemission spectroscopy	0.3 to 6199	2.0 to 40,000	27
X-ray crystallography	0.1 to 6.2	2000 to 100,000	10
X-ray fluorescence	WB; 0.1 to 620	WB; 20 to 100,000	4
X-ray scattering/ diffraction	WB; 0.1 to 6.2	WB; 2000 to 100,000	28
X-ray standing wave	WB; 0.4 to 4.1	WB; 300 to 34,000	2

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
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 < 100μ 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. Detectors having response times of ~2 ns are available. For typical optical absorption studies, where one produces $10^{-5}M$ of intermediates, spectral and kinetic information can be obtained on species having extinction coefficients in excess of 100 M^{-1} cm^{-1}. Conductometric methods in aqueous solution cover the pH range of 3 to 11. Data are recorded digitally and stored in magnetically readable form for rapid off-line examination of spectral and kinetic details.

COLLABORATIVE USE

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

PERSON TO CONTACT FOR INFORMATION

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

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	MicroVAX II
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

EN-TANDEM (KC-03-01-03)

Physics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 7.2 MV. A wide variety of ion species is available. Two 90° magnets with a stripper foil between them follow the accelerator so that a range of charge states is available for any ion at a given energy. Available facilities include (1) an ~14-meter flight tube with the capability of doing very small angle scattering and detecting individual charge states; (2) high-resolution Auger-electron spectrometer; (3) an Elbek magnetic spectrgraph with position sensitive detectors; (4) Si(Li) detectors and a curved crystal spectrometer; (5) data acquisition and analysis is performed using a CAMAC-based VAX-11/750 computer system.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a research proposal to the EN-Tandem manager.

PERSON TO CONTACT FOR INFORMATION

P. F. Dittner
Bldg. 5500, MS 6377
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6377

Phone: (615) 574-4789

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 7.2 MV
Source beam currents	Several hundred nA to several μA
Output currents	Up to 2 μA, depending on the ion species and charge state
Repetition rate	DC only
Magnet limitations	$ME/q^2 \leq 80$

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 · 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 · 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 Assistant Secretary for Nuclear Energy. The funding remains in the Office of Energy Research.

PERSON TO CONTACT FOR INFORMATION

J. E. Lee — Phone: (615) 574-8288
Research Reactors Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831

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

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

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

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

PERSON TO CONTACT FOR INFORMATION

R. M. Wham — Phone: (615) 574-7071
Chemical Technology Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6384

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

Sandia National Laboratories, Livermore
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 or 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/Conservation 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/ER Office of Scientific Computing supports nonlinear analysis of combustion systems, and DOE/BES Materials Sciences supports 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.

PERSON TO CONTACT FOR INFORMATION

William J. McLean, Phone: (510) 294-2687
Director
Combustion and Materials
Science and Technology Center
Sandia National
Laboratories
Livermore, CA 94551-0969

or

George A. Fisk, Phone: (510) 294-3376
Manager
Combustion Sciences
Programs
Sandia National
Laboratories
Livermore, CA 94551-0969

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 20 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, biology, physics, medical science, and other disciplines. In addition to scientific research utilizing synchrotron radiation, the laboratory program includes the development of advanced sources of synchrotron radiation (e.g., insertion devices for the enhancement of synchrotron radiation, new ring designs) and the development of 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 25 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 Sanford 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 site 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 130 institutions in 32 states and 10 foreign countries. Access to the facility is through a refereed proposal system. Proposals are due September 1 and March 1 each year. The booklet "User Guide" available from SSRL contains information pertinent to proposal submittal. To date, 2211 proposals for research have been received.

PERSON TO CONTACT FOR INFORMATION

Katherine Cantwell — Phone: (415) 926-3191
Manager, User
Research
Administration
SSRL
M.S. 69, P.O. Box 4349
Stanford, CA 94309-0210

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 (8 pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim5\times10^{-4}$	1.0 × 3.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim10^{-4}$	2.0 × 20.0	
6-2 (54 pole)							
Focused	2.3	22	Double crystal	2,400 to 21,000	$\sim5\times10^{-4}$	1.0 × 3.0	
Unfocused	1.0		Double crystal	2,400 to 45,000	$\sim10^{-4}$	2.0 × 20.0	
7-2 (8 pole)							Six-circle diffractometer
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim5\times10^{-4}$	1.0 × 3.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim10^{-4}$	2.0 × 20.0	
10-2 (31 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim5\times10^{-4}$	1.0 × 3.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim10^{-4}$	2.0 × 20.0	
Side stations							
4-1	1.0		Double crystal	2,800 to 45,000	$\sim5\times10^{-4}$	2.0 × 20.0	
4-3							Two-circle diffractometer vertically focusing mirror
Focused	1.0	Variable	Double crystal	2,800 to 45,000	$\sim5\times10^{-4}$	.3 × 20	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim10^{-4}$	2.0 × 20.0	
7-1	1.0		Curved crystal	6,000 to 13,000	$\sim8\times10^{-4}$	0.6 × 3.0	Rotation camera
7-3	1.0		Double crystal	2,800 to 45,000	$\sim10^{-4}$	2.0 × 20.0	
VUV/soft X-Ray Stations							
5-1, 5-3 multi-undulator	1.5		4 Gratings	10 to 450	$0.5^{-1}\times10^{-3}$		
5-2 multi-undulator	1.5		4-Gratings	10 to 1200	$0.5^{-1}\times10^{-3}$		
10-1	2.0		6m SGM	200 to 1000	$\sim2\times10^{-4}$		
				Bending Magnet Stations			
X-ray							
1-4	2.0		Curved crystal	6,700 to 10,800	0.3×10^{-3}	0.25 × 1.0	Small angle scattering detector
1-5	1.0		Double crystal	2,800 to 30,000	$\sim10^{-4}$	3 × 20	Area detector/CAD-4
2-1 (focused)	4.8	8.9	Double crystal	2,800 to 8,900	$\sim5\times10^{-4}$	1 × 4	
2-2	1.0 to 6.1		None	3,200 to 40,000		4 × 22 to 4 × 134	
2-3	1.0		Double crystal	2,800 to 30,000	$\sim5\times10^{-4}$	3 × 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	$\sim1\times10^{-3}$	1.0 × 2.0	
3-1	2.0		Grasshopper	25 to 1,000	$\Delta\lambda = 0.05$ to 2 Å	1.0 × 1.0	
3-2	4.0		Seya-Namioka	5 to 40	$\Delta\lambda = 0.2$ to 6 Å	2 × 7	
3-3	8 to 10	4.5	UHV double crystal (jumbo)	800 to 4,500	$\sim5\times10^{-4}$	1.5 × 2.5	
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	$\sim1\times10^{-3}$	≤1 mm^2	
8-2	5		6m SGM	50 to 1,000	$\sim1\times10^{-4}$	≤1 mm^2	

FY 1993 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 1993 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds
Ames Laboratory	$ 425,000*
Argonne National Laboratory	1,800,000*
Brookhaven National Laboratory	2,080,000
Idaho National Engineering Laboratory	20,000
Lawrence Berkeley Laboratory	2,260,000
Los Alamos National Laboratory	50,000
National Renewable Energy Laboratory	200,000
Notre Dame Radiation Laboratory	265,000
Oak Ridge National Laboratory	1,590,000
Pacific Northwest Laboratories	1,000,000
Sandia National Laboratories/ New Mexico	15,000
Sandia National Laboratories/ California	980,000
Stanford Synchrotron Radiation Laboratory	1,194,000

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*In addition to the amounts shown, funds for General Purpose Equipment are provided to these laboratories. The amounts are $155,000 for Ames Laboratory and $2,200,000 for Argonne National Laboratory.

SELECTED TOPICS OF GENERAL INTEREST

Microheterogeneous Systems
2, 3, 14, 15, 16, 17, 23, 25, 119, 130, 131, 132, 134, 135, 137, 140, 142, 146, 147, 150, 153, 155, 157, 158, 448

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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.