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Summaries of FY 1992 Research in the Chemical Sciences

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U.S. Department of Energy
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Division of Chemical Sciences

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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 1992 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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- Mr. Ted Tomczak

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Chemical Physics
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Atomic Physics
- Dr. J. V. Martinez

Facilities Operations
- Dr. Robert S. Marianelli

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Dr. F. Dee Stevenson - Chief

Secretary - Ms. Lori Wiles

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- Dr. William S. Millman**

Separations and Analysis
- Dr. John L. Burnett
- Dr. Clement R. Yonker***

Chemical Engineering Sciences
- Dr. F. Dee Stevenson

Heavy Element Chemistry
- Dr. John L. Burnett

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

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* On leave from the National Institute of Standards and Technology
** On leave from the University of Wisconsin - Milwaukee
*** On leave from the Pacific Northwest Laboratory

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 fundamental research in solar photochemical energy conversion, whereby fuels or energy may be produced by visible light excitation of small molecules or solids. The photochemistry research includes organic and inorganic photocatalysis in homogeneous and heterogeneous media, electron transfer rates and mechanisms, photosynthesis, and photoelectrochemistry. The radiation chemistry research is concerned with the chemical effects produced by absorption of energy from ionizing radiation. A small part of the program is devoted to research in hot atom chemistry, i.e., the study of the effects of nuclear decay and the consequent release of energy on chemical reactions.

Chemical Physics (KC-03-01-02)

The Chemical Physics program supports research in a diverse set of disciplines with a goal of providing basic knowledge in areas related to the nation's energy needs. A significant portion of the program is in the many-faceted area of chemical kinetics, including energy transfer, chemical dynamics involving state-selected chemistry, unimolecular and bimolecular reaction kinetics, as well as the reactions of clusters. Research efforts in molecular structure, spectroscopy, and theoretical chemistry are also well represented in this program. In addition, there is a growing effort in surface dynamics.

Special emphasis is placed on basic research related to combustion; spectroscopy, theory, and the kinetics of elementary combustion reactions are of special interest. A major user-oriented facility, the Combustion Research Facility (CRF) at Sandia Laboratories/Livermore is supported by this program. This laboratory offers the use of advanced instrumentation to interested combustion scientists from universities, industry, and national laboratories.

Atomic Physics (KC-03-01-03)

The Atomic Physics program supports experimental and theoretical efforts associated with the study of atom and atomic ion structures, energy levels and lifetimes of quantum states, and of transport and exchange processes characterizing transfer of energy and momentum. These studies strive to obtain the most accurate and complete fundamental knowledge of the properties and interactions of photons, electrons, atoms, and ions. Continued emphasis of this research is on the understanding of relatively high energy atomic physics that involves atoms stripped of all or almost all electrons and of atoms and ions in which electrons are promoted to upper energy levels. The study of processes that lead to the production of coherent radiation and of how its statistical properties are manifest in atomic physics also constitutes part of this program. Limited support is also provided for optical and plasma physics research.

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.

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
Iowa State University
Ames, IA 50011

Chemical Sciences—Fundamental Interactions
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Phone: (515) 294-9924

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Chemistry Division
L. M. Stock
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BROOKHAVEN NATIONAL LABORATORY
Upton, Long Island, NY 11973

Department of Applied Science
L. Petrakis
Phone: (516) 282-3037

Chemistry Department
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Phone: (516) 282-4301

National Synchrotron Light Source
D. McWhan
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IDAHO NATIONAL ENGINEERING LABORATORY
EG&G Idaho, Inc., P.O. Box 1625
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LAWRENCE BERKELEY LABORATORY
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LOS ALAMOS NATIONAL LABORATORY

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NATIONAL RENEWABLE ENERGY LABORATORY

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Richland, WA 99352

Chemical Sciences Department
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Phone: (509) 375-2272

SANDIA NATIONAL LABORATORIES, ALBUQUERQUE

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Albuquerque, NM 87185

F. L. Vook
Phone: (505) 844-9304

SANDIA NATIONAL LABORATORIES, LIVERMORE

Livermore, CA 94551

Combustion Research Facility
J. S. Binkley
Phone: (510) 294-2174

NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **$615,000**

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

The objective of this research is the preparation of model systems that have the photoinduced electron-transfer characteristics of the photosynthetic reaction center. A wide spectrum of systems is being investigated, ranging from model systems based completely on synthetic molecules or analogs of natural molecules, to systems in which most, or all, of the elements have been derived from natural sources. Excluded are those constructions that are solely reconstitutions of functional in vivo parts produced by biochemical separations. The fundamental mode of attack is the use of monolayers and multilayers to produce the systems of interest. Three approaches are being followed: preparation of spread monolayers at the air/water interface, self-assembly adsorption techniques, and formation of multilayer systems by the Langmuir–Blodgett film transfer method. The principal instrumental techniques used for characterization include electrochemistry, laser Raman spectroscopy, and scanning tunneling microscopy. Additional information is obtained by optical absorption and linear dichroic spectroscopy of the monolayer systems. [2.0 FTE]

2. ***Photoinduced Electron-Transfer Reactions in Protein Matrices***
Kostic, N.M.
515-294-7715

This research focuses on two rate-determining factors in photoinduced electron-transfer reactions: the pathway for the transfer from the electron donor to the acceptor, and the thermodynamic driving force. The donors are ferrocytochrome *c* (in the ground electronic state) and zinc cytochrome *c* (in the triplet excited state), while the acceptor is cuprisplastocyanin. These proteins are studied because the redox-active metal ions in them are fully characterized, fixed in three dimensions, and replaceable with various nonbiological metals. The proteins are associated flexibly by electrostatic forces, and both rigidly and flexibly by covalent crosslinks. The rates of electron transfer within the complexes have been determined by laser flash kinetic spectroscopy. The experiments are designed to show whether ground-state electron-transfer reactions require rearrangement of the donor and the acceptor into an optimal configuration. Comparisons of kinetics of the excited-state reactions in precursor and encounter donor–acceptor complexes with those of the corresponding ground-state reactions have elucidated the role of transfer pathway and the thermodynamic driving force on the electron-transfer rate. The rate has been shown to depend on the transfer pathway more when the driving force is low than when it is high. Even though the donor and the acceptor are highly charged, their association has been found to depend on hydrophobic as well as electrostatic interactions. [2.0 FTE]

3. ***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]

4. ***Ultrafast Spectroscopy and Reaction Dynamics***
Struve, W.S.
515-294-4276

Ultrafast fluorescence and pump-probe spectroscopies are used to characterize electron excitation transport in naturally occurring and artificial photosynthetic systems. Recent attention has focused on (1) pump-probe studies of energy transfer in LCH-II trimers from the photosystem II light-harvesting antenna and (2) pump-probe studies of the P700- and F_x-containing core protein from photosystem I. A future study will investigate energy transfer in monolayer and multilayer template systems on two-dimensional surfaces. The first two of these projects have shown that energy transfer steps span a wide range of timescales (subpicosecond to picosecond) in these photosystem I and II antennae, which comprise over 50% of all the chlorophyll in the world. They have also reconciled conflicting views of these antenna energy transfers proposed by two other groups using more limited techniques. [2.2 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $5,200,000

5. *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 for directing and controlling the flow of electrons and energy in photoconversion. ET rates are studied as functions 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 for current theoretical calculations and experimental measurements. Pulse radiolysis with Argonne's 30-ps electron linear accelerator is especially useful for obtaining electronic couplings without interference from other interesting variables. Charge transfer across the electrolyte–solid interface in small semiconductor particles is studied with particular attention to the well-defined, 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. The effects of surface-bound electron donor or acceptor groups on the energy levels in the particle, on selective electron/hole scavenging, and on the properties of resultant radicals are investigated using the same pulse radiolysis techniques. [5.8 FTE]

6. *Characterization of Photosynthetic Components*
Norris, J.R.
708-252-3544

The project objective is to develop systems for use in studies of solar energy conversion. In order to understand and to develop highly efficient forms of artificial solar energy conversion, the basic physical and chemical features of the individual compounds, solvents, matrices, and light-harvesting antennae are required. Normal and isotopically altered chemicals or special assemblies are provided to enhance the utility of the spectroscopies used in the study of photoinduced charge separation. A unique facility is operated for large-scale culture and isotopic labeling of algae and photosynthetic bacteria. [1.1 FTE]

7. *Photosynthesis Research*
Norris, J.R.; Thurnauer, M.; Bowman, M.K.; Tiede, D.M.
708-252-3544

This project has two main objectives. The first objective is to uncover the basic principles of the chemistry and physics involved in the primary photoinduced charge separation that occurs in photosynthetic bacteria and green organisms. Three areas are emphasized. (1) The mechanism of charge separation as produced by photoinduced electron transfer in natural photosynthesis is probed at the molecular level. (2) Theoretical models for electron transfer are proposed to explain and complement the experimental work. (3) Advanced instrumentation and computer techniques are employed to help establish the mechanisms involved in natural and artificial photosynthesis. Charge separation parameters deduced from these studies of natural photosynthesis are then used to design and prepare molecules and molecular assemblages that will convert light energy into useful chemical energy in the laboratory. The systems being studied, mainly by optical and magnetic resonance spectroscopies, include natural, isotopically substituted and chemically manipulated photoactive assemblies, solutions, and compounds. [4.5 FTE]

8. *Reactive Intermediates in the Condensed Phase: Radiation and Photochemistry*
Trifunac, A.D.; Sauer, M.C., Jr.; Bartels, D.M.; Werst, D.W.
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 and electrons provide the framework for understanding chemical and biological effects of radiation. Chemical reactions of such species are also relevant to both fundamental issues in chemical reactivity and technologically important chemical processes. The processes of charge separation and transport, excited states, 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. [7.7 FTE]

9. *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. [3.8 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $1,030,000

10. *Porphyrin Chemistry*
Fajer, J.; Barkigia, K.M.; Renner, M.W.
516-282-4521

This program focuses on the multifaceted bioenergetic reactions driven 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 encompasses experimental, structural, and theoretical approaches that seek 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 bioreactions 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 and partition 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]

11. *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 measurement 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 directly related to this program and of interest to colleagues comprise a significant, continuing contribution of this program. [2.3 FTE]

Chemistry Department $2,990,000

12. *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. [12.3 FTE]

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

This program uses pulse radiolysis and photolysis to study the behavior of transient chemical species. Principal areas of investigation are (1) properties and reactions of electrons in dielectric fluids; (2) photoionization 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, and in controlling dielectric breakdown in transformers. 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. [8.3 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Biodynamics Division $455,000

14. *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]

15. *Chemistry with Near Infrared Photons*
Frei, H.M.
510-486-4325

Extension of the wavelength response of photochemical reactions of interest in solar photochemistry into the near-infrared spectral range is very important for substantial improvement of the use of the sun's energy for chemical purposes. The search for chemical reactions that can be initiated with these long wavelength quanta is the main goal of this work. Focus is on reactions that may serve as models, or suggest new concepts for chemical storage of near infrared photons, their conversion into electrical energy, and use in photocatalysis and chemical synthesis. Controlled atom transfer reactions are explored in inert, cryogenic matrices by excitation of reactant pairs with red and near infrared light. Reaction paths are mapped by trapping of short-lived transients and elucidation of their structure by FT-infrared spectroscopy. Most recent examples are regio and stereocontrolled photooxidation of alkenes and alkynes by red light excited nitrogen dioxide. These studies form the basis of controlled chemical synthesis of organic building blocks with long wavelength solar light in a room-temperature matrix. Sensitive, time-resolved emission and absorption spectroscopy is used for the study of redox chemistry in aqueous solution. A most recent example is 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 $1,420,000

16. *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. Some new molecules have been synthesized that contain anthraquinone (AQ) attached directly to the periphery of a porphyrin (P) macrocycle. Strong electronic coupling between the P and AQ moieties is highly sensitive to small changes in the dielectric environment of the host medium. Fluorescence quenching in low-dipolar media involves intramolecular ET from the photoexcited porphyrin donor to the AQ acceptor, yielding an emissive charge-transfer (CT) state. These results show that it is possible to design more complex systems in which the fraction of long-lived, excited-state energy that can be converted to stored redox energy is maximized. Based on these dyad structures, a triad molecule carrying two different quinones linked by a rigid hydrocarbon bridge has been assembled. Evidence for two-step ET in this molecule in a low-dielectric solvent (benzene) has been obtained by time-resolved microwave conductivity and picosecond fluorescence spectroscopy. This is 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. [2.8 FTE]

17. *Surface-Modified Semiconductor Electrodes for Solar Photochemical Energy Conversion*
Frank, A.J.
303-231-1962

Research is being conducted on the light-induced charge-generation mechanism in conductive polymers and across the polymer:semiconductor junction, a molecular water-reduction catalyst for derivatizing semiconducting particles, and molecular particles for photosensitization. The charge carriers that evolve during the photoexcitation of semiconductorlike films of poly(3-methylthiophene) (PMeT) were characterized by light-induced electron spin resonance and photoinduced absorption. Extensive work was completed on a novel molecular water-reduction catalyst for chemically derivatizing TiO_2 particles. Optical and X-ray photoelectron spectroscopy (XPS) measurements provided detailed information on the nature of this platinum bipyridine complex and its attachment to the surface of TiO_2. Both the photophysics and photosensitizing behavior of a new molecular semiconductor, a platinum(II) double salt, are being investigated. Current-voltage, capacitance-voltage, and optical measurements are being utilized to characterize the temperature dependence of the charge-transfer mechanism across the PMeT:CdTe junction. [2.0 FTE]

18. Photoconversion Processes in Liquid Crystal Porphyrin Films

Gregg, B.A.
303-231-1285

Liquid crystal porphyrins (LCPs) tend to self-assemble into ordered arrays spontaneously. Thus, large area, highly ordered thin films of these organic semiconductors can be easily prepared. Energy and electron transfer processes are being investigated in these films as a function of both the film order and the nature of the electrical contacts. Theory predicts that adiabatic electron transfer between species possessing discrete electronic energy levels will be governed by the Franck–Condon overlap between the donor and acceptor. This overlap may, in principle, be employed to kinetically select for a desired reaction (forward electron transfer) while inhibiting undesired reactions (recombination). Thus, electrodes in LCP cells possessing discrete electronic levels at the appropriate potential should promote (e.g., facile photoelectron injection while inhibiting both hole injection and recombination). Redox polymers have been chosen as electrode materials possessing approximately discrete electronic levels that can be tuned, by varying the redox center, over the potential range of the LCP bandgap. Evidence of kinetic selectivity has been observed. Efficient photoelectron injection or photohole injection can be achieved with the appropriate redox polymer. These systems are being characterized by measurements of dark currents, photovoltaic effects, impedance properties, and steady state and time-resolved photoluminescence. [1.0 FTE]

19. Quantization Effects in Photoelectrochemistry

Nozik, A.J.
303-231-1953

Quantization effects in photoelectrochemistry are being intensively investigated in quantum films (two-dimensional systems) and in quantum dots (zero-dimensional systems). Hot carrier cooling in quantum film and bulk GaAs photoelectrodes has been quantitatively characterized by determining the time constant (τ_{avg}) for the hot electron loss rate; quantum films have been shown to have values of τ_{avg} that are almost two orders of magnitude longer than bulk GaAs when the photocarrier density is $> 5 \times 10^{18}$ cm^{-3}. Systems to measure electron transfer rates to compare with τ_{avg} have been developed. Systems to produce slowed hot carrier cooling in quantized semiconductors at low light intensity have also been synthesized. GaAs quantum dots that exhibit clean optical spectra have been characterized in detail. A model has been developed to calculate the absorption spectrum of a colloid containing quantum dots; the particle size distribution can be estimated from this model. Future work will measure the electron transfer rates and hot electron cooling rates as a function of critical parameters for various quantum film and quantum dot configurations and compositions. Resonant tunneling quantum film structures will be used to test theories of heterogeneous electron transfer. [6.0 FTE]

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

Radiation Laboratory **$3,250,000**

20. Organic Photochemical Processes

Chateauneuf, J.E.; Hug, G.L.
219-239-5458

Time-resolved absorption and emission techniques are used to characterize detailed aspects of the photophysics and photochemistry of reaction intermediates. This information yields a more complete mechanistic understanding of photoinduced processes and provides modification and control of chemical systems. Considerable mechanistic insight is being obtained by application of pico/nanosecond laser flash photolysis (LFP) to such systems. The kinetics and energetics of 1,2-atom migration, atom abstraction, insertion, cyclopropanation, and protonation of divalent carbon intermediates are being elucidated. Luminescence decay of synthesized polyelectrolytes is being simulated by model theories of incoherent electron and energy transfer to moving acceptors in reduced dimensions. As a complement to photolytic techniques, pulse radiolysis is being used to investigate halogen atom kinetics, fragmentations of thermal and photolytically unstable radical ions, and formation of three-electron bond disulfides from amino acids. Additionally, investigations of molecular dynamics in supercritical fluids reveal unique and dramatic pressure effects on absolute rate constants. For example, enhancement in the photoreduction of benzophenone triplet occurs in the critical region of supercritical CO_2 and is attributed to local augmentation of substrate concentrations. Factors that control a variety of reactivities in supercritical fluids are currently under investigation. [3.5 FTE]

21. Quantum Mechanical Studies of Radiation-Produced Intermediates

Chipman, D.M.; Carmichael, I.C.; Bentley, J.
219-239-5562

Chemical properties of transient free radicals and excited state molecules are characterized by modern methods of ab initio electronic structure theory to facilitate the interpretation of experimental data from early processes following radiolysis or photolysis. The nature of the ensuing free radicals is elucidated by theoretical determination of spin density distributions for comparison with electron spin resonance experiments. Recent work explains the unexpectedly large effect of hydroxyl substitution on spin densities in cyclohexadienyl and H_2CN radicals. In addition, the origin of conflicts in experimental analyses of spin solitons in transpolyacetylene has been identified. Competitive pathways for consumption of reactant species in spin trapping experiments are characterized by computation of the energies of reduced forms of nitrosoalkanes. An electron correlation technique has been developed which accurately determines one-bond nuclear spin–spin coupling constants in saturated organic systems, allowing reliable prediction of substituent effects and conformational dependence. Theoretical calculation of force fields assists experimental interpretation by resonance Raman spectroscopy of the vibrational structure of free radicals. An explanation has recently been found for the striking differences between the vibrational force constants of the CS bond in thiophenoxyl and the analogous CO bond in phenoxyl radical. [3.1 FTE]

22. *Inorganic Photochemical Processes*
Ferraudi, G.J.
219-239-7676

The dynamics of excited- and ground-state redox reactions in coordination complexes are being investigated under magnetic fields between 0 and 9 Tesla. Such Zeeman perturbation is used to probe electronic parameters that determine rates of various photoinduced processes (e.g., radiationless relaxation of excited states, inner and outer sphere electron transfer, and characteristic excited state reactions). Magnetodynamic effects on rates of redox reactions between inorganic radicals (e.g., Cl_2^-, Br_2^-, CO_3H) and coordination complexes are being characterized and compared with similar effects on rates of inner-sphere and outer-sphere electron transfers between coordination complexes. Variables in these studies are the electronic structure of the radical, electronic configuration of the metal ion in the coordination complex, and various nuclear spin contributions. The photochemical reactivity of coordination complexes in electronic states, not populated directly from the ground state, is investigated by using time-resolved sequential biphotonic excitations. Quantum yields for photoreactions induced with sequential biphotonic excitations of coordination complexes and for photoprocesses induced with monophotonic excitations are determined at the same photonic energies. Mapping of some electronic excited state potential surfaces using comparisons of the action spectra for various monophotonically and biphotonically induced photoprocesses follows from these studies. [4.4 FTE]

23. *Microwave Studies of Radiation-Produced Radicals*
Fessenden, R.W.; Madden, K.P.
219-239-5354

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. EPR spectra give definitive electronic and geometrical structures for correlation with the reactivity patterns. Electron spin polarization (CIDEP) is used to define electronic interactions experienced by pairs of radicals or by radicals and excited states during formation and reaction. Current studies of spin trapping focus on rate constants for spin adduct formation and decay in aqueous media, using a variety of hydroxyalkyl radicals and spin traps. These studies are used to clarify mechanisms of rearrangement reactions involving hydroxyalkyl radical spin adducts. Such information facilitates proper identification of the parent radicals involved. The strength of microwave dielectric absorption by photochemical intermediates maps their charge distribution to help explain variations in reaction mechanism in solvents of varying polarity. Rapid internal charge rearrangements in excited states are identified and their rates measured using the dispersive component of the microwave signal. Microwave absorption is further used to determine yields, mobility, decay kinetics, and chemical availability of photoinduced charge carriers in semiconductor particles as well as in films. [4.4 FTE]

24. *Photochemical and Photoelectrochemical Processes for Energy Conversion*
Kamat, P.V.
219-239-5411

The kinetics and mechanistic details of the charge transfer processes in metal oxide–metal chalcogenide coupled semiconductor colloids (e.g., ZnO–CdS) and dye coated semiconductor colloids are being elucidated with fast kinetic spectroscopy as well as photovoltaic measurements. Methods are being developed to modify electrode surfaces with ultrasmall semiconductor particles by chemical and electrochemical deposition. Increased surface area and the improved energetics of these modified electrodes enhance the photon to photocurrent efficiency of sensitization processes involving dyes such as the squaraines. Improvement in photoinduced charge separation is also being achieved by bridging a semiconductor (CdS) and a metal colloid (Au) with bifunctional surface modifiers such as mercaptoethylamine. Picosecond and nanosecond laser flash photolysis techniques are being used to probe the mechanism by which the singlet and triplet excited dyes participate in the charge injection process involving large bandgap semiconductor colloids such as TiO_2 and ZnO. Front face emission measurements and diffuse reflectance laser flash photolysis of opaque or semitransparent systems (e.g., dye loaded semiconductor particles or polymers) are being conducted to elucidate the role of support material in controlling the selectivity and charge transfer efficiency of surface photochemical processes. [5.4 FTE]

25. *Track Effects in Radiation Chemistry*
LaVerne, J.A.; Mozumder, A.; Pimblott, S.M.; Schuler, R.H.
219-239-5563

Variations in radiation chemical kinetics caused by track structure are examined experimentally. The processes following radiolysis and photoionization are modeled by theoretical techniques. In heavy ion radiolysis, luminescence decay and product yield dependence on scavenger concentration are used to determine the dependence of temporal variations in radicals and excited states on particle energy and linear energy transfer (LET). Other measurements concentrate on the production of O_2/HO_2 generated by particles with energies up to 70 MeV/nucleon. Such studies utilize the accelerators of the Notre Dame Nuclear Structure Laboratory, the Argonne Tandem/LINAC Accelerator System (ATLAS) facility of Argonne National Laboratory, and the Michigan State superconducting cyclotron. Stochastic and deterministic kinetic methods are employed to determine the dependences of aqueous radiation chemistry on track geometry and density of primary species. These same methods are utilized to probe the very early chemistry associated with photoionization. They are further used to determine the consequences of scavenging one type of radiation-induced reactant on the chemistry of its sibling reactants. Theory is employed to elucidate electron transport mechanisms in dielectric liquids. The influences of field strength, scavenger concentration, and track structure on time-dependent yields in liquid hydrocarbons and liquefied rare gases are predicted by kinetic models. [6.9 FTE]

26. *Influence of Ordered Molecular Assemblies on Photochemical Processes*

Patterson, L.K.
219-239-5403

Effects of molecular organization on reaction mechanisms are characterized for photochemical, radiation-induced, and thermal processes. Steady state and time resolved excited state spectroscopies as well as ground state absorption and reflectance measurements are used to define alterations in processes already well characterized in isotropic media. These studies are directed toward determining mechanisms by which the anisotropy of organized systems may be utilized to exercise kinetic control over reactions of interest, especially those related to solar energy storage. Spread monolayers at the air–water interface are extensively utilized because these provide means by which organization may be controlled and the thermodynamic state of the system may be monitored. Lipid structure, surface packing, subphase composition, and gas phase content are among parameters which are manipulated to alter molecular organization in reaction environments and probe subsequent kinetic response. Considerable attention is given to the influence of such parameters on ground and excited state behavior of chlorophyll. Aggregation behavior of aromatic dyes and subsequent effects on their excited state behavior are determined spectroscopically. Processes involving triplet excited states and lipid radicals, which pose difficulties for measurement in monolayers, are investigated by flash photolysis and pulse radiolysis in micellar systems. [4.1 FTE]

27. *Radiation Chemistry Data Center*

Ross, A.B.; Helman, W.P.; Hug, G.L.; Carmichael, I.C.
219-239-6528

Information on excited states and free radicals in solution is collected and evaluated. The scope of these compilation efforts is mainly encompassed by research on time-resolved photochemistry and radiation chemistry. Yields and kinetic data for the intermediates, and auxiliary information, are being entered into computer readable databases. A handbook on photochemistry and photophysics of organic molecules is being completed. Among the information to be included are quantum yields and rates for various unimolecular and bimolecular excited-state processes, energy levels, and spectral parameters. A current data compilation project covers quantum yields for photosensitized production of singlet molecular oxygen in solution. Another review in preparation involves rate constants for reactions of transients derived from metal ions and metal complexes in aqueous solution. An IBM-PC-compatible database for the chemical kinetics of radical processes in fluid solutions, is being implemented. The RCDC currently provides an online service for searching a database 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) may soon be added. RCDCbib is used to produce the current awareness publication, "The Biweekly List of Papers on Radiation Chemistry and Photochemistry." [5.1 FTE]

28. *Radiation-Induced Chemical Reactions*

Schuler, R.H.; Tripathi, G.N.R.; Patterson, L.K.
219-239-7502

Time-resolved absorption and resonance Raman methods are being used to examine the structure and reaction kinetics of short lived reaction intermediates. The unique application of Raman methods to examine pulse radiolytically produced intermediates provides information on free radicals that cannot be obtained by more conventional spectroscopic methods. Recent emphasis has been placed on sulfur containing radicals whose structure cannot be examined by electron spin resonance (ESR) because of rapid spin relaxation. Raman studies show that the unpaired spin in these radicals is largely localized on the sulfur atoms, in contrast to the delocalization manifest in studies of related oxygen containing radicals. It has been shown that pulse radiolysis-absorption spectroscopic methods can be used very effectively to examine the kinetics of protonation and deprotonation of phenolic compounds and thus provide background information on rates of acid-base equilibration for this important class of compounds. More conventional radiation chemical experiments apply chromatographic methods to determine product distribution in studies of the concerted effects of substitution on the relative rates of OH attack at the different positions of aromatic systems. Chromatographic and pulse radiolytic methods are also being used to examine the sites of electron attack on polyhalogenated hydrocarbons. [8.8 FTE]

Chemical Physics

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **$725,000**

29. *Chemical Theory*

DePristo, A.E.
515-294-9924

The focus of this research is the theoretical description of the structure and dynamics of metal and semiconductor 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. 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]

30. Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals
Ng, C.Y.
515-294-4225

The project objectives are (1) to provide accurate thermochemical data for molecules, clusters, radicals, and molecular ions and (2) to study the mechanisms and dynamics of elementary chemical processes relevant to combustion chemistry. A new photoion–photoelectron coincidence (PIPECO) technique has been developed that makes possible the measurement of the photoelectron spectrum (PES) of minor species with concentrations less than 1% of a gaseous mixture. The PIPECO method is ideal for measuring the PES of radicals because radicals are usually generated by discharge, reaction, or pyrolysis in mixtures with their precursors. A project to systematically measure the PIPECO spectra of radicals related to combustion is currently under way. A supersonically cooled laser photodissociation radical beam source has been developed. This source will allow accurate ionization energy measurements of polyatomic radicals. Another area of interest involves the study of the excimer laser photofragmentation dynamics and energetics of a series of sulfur-containing compounds and their clusters. In addition to information about the internal energy distributions of photofragments, these experiments will provide reliable estimates of the C–S and S–S bond energies of these compounds. Recently, a laser photodissociation–photoionization method has been developed which allows the measurements of absolute state-to-state photodissociation cross sections of radicals. [5.0 FTE]

31. Molecular Bonding Theory
Ruedenberg, K.
515-294-5253

Properties of molecules and characteristics of chemical reactions are predicted using quantitative methods of ab initio quantum theory. Current efforts are focused on reactions involving molecules essential for hydrogenation, combustion, and atmospheric chemistry, in particular containing carbon, oxygen, and hydrogen. Since molecular energetics, dynamics, and kinetics fundamentally derive from the potential energy surfaces of reacting molecular systems, these energy functions are globally determined by electronic computations for all atomic geometries pertinent to the reactions under study. Closely examined are the critical regions (metastable intermediates, transition states, reaction paths, bifurcations, intersections, and so forth) which provide insights appreciated by experimentalists yet difficult to access by experiment. Presently in progress is a comprehensive study of the ten lowest states of ozone for which spectroscopic information is limited and inconclusive. In order to provide a conceptual understanding of the significant energy differences, ab initio methods are developed that identify electronic rearrangements during chemical reactions and quantitatively explain energy changes in terms meaningful to the nontheorist's chemical intuition. In order to enhance quantitative accuracy and extend reliable applicability to larger systems, methods are developed for the more efficient recovery of electronic correlation energy changes occurring in the course of chemical reactions. [2.5 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $4,025,000

32. Photoionization–Photoelectron Research
Berkowitz, J.
708-252-4086

The vacuum ultraviolet photoionization of atoms, free radicals, and small molecules is studied at high photon resolution. The transient species are prepared in situ by pyrolysis, electrical discharge, or chemical reaction. The ongoing studies of atoms are revealing systematic behavior in the breadth and shape of autoionizing lines, which can 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 silane plasmas used for thin film technology. Recently completed work on Si_2H_n species has provided strong evidence that Si_2H_2 and $Si_2H_2^+$ are cyclic $Si(H_2)Si$, unlike the triply bonded C_2H_2. The heats of formation of nearly all the Si_2H_n and $Si_2H_n^+$ have been determined, as have the various Si–Si and Si–H bond energies. In continuing studies of combustion intermediates, the ionization potential of CD_3O was observed for the first time, and that of its isomer, CD_2OH, was verified. From these data, heats of formation of CH_3O and CH_2OH and their cations were derived. Preliminary data have also been obtained on the sulfur analogs, CH_3S and CH_2SH. In another apparatus, the VUV photoionization spectrum of C_{60} has been obtained for the first time. Ongoing studies with this same apparatus include As_n, Sb_n, and Bi_n, the results of which have practical applications in the preparation of semiconductors. [2.2 FTE]

33. 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 change in ionization potentials induced by adsorption, 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, 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. [6.6 FTE]

34. *Chemical Dynamics in the Gas Phase*

Wagner, A.; Davis, M.; Harding, L.; Harrison, R.; 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 is about to come on-line. The close coupling between theory and experiment brings a unique combination of expertise to bear on the study of chemical reactivity. [13.1 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $620,000

35. *Combustion Kinetics and Reaction Pathways*

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

The scientific objectives of this project are (1) the measurement of absolute rate constants for combustion-related reactions of fuel compounds and intermediate species and (2) the determination of pathways for multichannel reactions. This project is focused, in both cases, on the fundamental aspects of combustion chemistry. 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. Some recent kinetic studies include: O + H_2O (1050 to 2030 K), H + CH_4 (900 to 1700 K), and CH_4 + Ar (thermal decomposition of methane, 1730 to 2130 K). A discharge flow-photoionization mass spectrometer (DF-PIMS) experiment is used to identify primary products from multichannel reactions, to determine photoionization spectra for reactants and products, and to measure ionization energies of free radicals. The DF-PIMS apparatus was designed to be operated on the U-11 beamline at the National Synchrotron Light Source (NSLS) and thus take advantage of tunable vacuum ultraviolet light to improve detection sensitivity and selectivity in monitoring free radicals. Recent results from the DF-PIMS studies include (1) semiquantitative measurements of branching for the reaction of N atoms with C_2H_5 radical and (2) photoionization studies of H_2CN, H_2COH, C_2H_5, and C_2H_3 radicals. [4.6 FTE]

Chemistry Department $2,915,000

36. *Energy Transfer Studies in Cluster Impacts*

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

This research is concerned with fundamental aspects of energy transfer when accelerated cluster ions impact on solid surfaces. Large polyatomic ions accelerated to velocities between 10^6 and 10^8 cm/s deposit energy primarily in translational degrees of freedom in target atoms with production of compressed atomic assemblies with very-high translational energy density. The use of nuclear fusion reactions as a diagnostic tool to investigate the properties of these atomic assemblies is being explored. A focus of this work is to determine whether a small fraction of target atoms may acquire sufficient translational energy to drive nuclear fusion reactions. Products of fusion reactions have indeed been observed when cluster beams impact on suitable target surfaces. The major effort so far has been directed toward establishing whether these reactions are indeed a result of cluster impact. The current lack of a theoretical model demands exhaustive investigation to establish definitively whether clusters or artifacts are responsible for the fusion products observed in the cluster impact studies. [2.6 FTE]

37. *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 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 infrared, visible, or ultraviolet lasers or ultraviolet synchrotron radiation; laser-induced fluorescence and stimulated emission pumping; time-resolved Fourier transform infrared 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. This program also provides assistance to some of the outside users of beam line U11 at the National Synchrotron Light Source (NSLS). [9.3 FTE]

38. *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, 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 high-intensity laser fields on simple, isolated systems are also under investigation with the ultimate goal of controlling modified collision dynamics for physical and chemical processes. [5.4 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $2,935,000

39. *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]

40. *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 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 infrared laser. [20.0 FTE]

41. *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]

42. *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 path-breaking research based on high-brightness vacuum ultraviolet 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 vacuum ultraviolet 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

43. *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

44. *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

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

The Chemical Structure and Dynamics program responds to the need for a fundamental molecular level understanding of chemistry at environmental interfaces. The research is built around the established relationship between structure and function (reaction dynamics) that is the underpinning of molecular science. The structural studies are key to the direct comparison with theory. Real time dynamics measurements of atomic/molecular motions during chemical reactions provide for a molecular level description of reaction dynamics. One program element relies upon the synthesis and characterization of microscopic models of condensed phase chemistry. Atomic and molecular clusters are a form of matter whose properties lie outside the realm of general chemical experimental science. They not only provide a quantitative basis for comparison with theory but are the source of a microscopic understanding of the condensed phase. Another initiative brings a combination of state-of-the-art lasers and atomic resolution surface mapping tools (i.e., scanning tunneling microscopy (STM)) to the study of interfacial chemistry. The combination of lasers and surface mapping tools allows direct observation of reactions on realistic chemical surfaces. The cluster and surface science initiatives illustrate two elements of a broad program including structure and dynamics studies of molecules in isolation, condensed in microstructures, in solution, and on extended surfaces. [10.5 FTE]

46. *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 pretreatment of high level wastes. [8.5 FTE]

Sandia National Laboratories, Livermore
Livermore, CA 94551

Combustion Research Facility $2,700,000

47. *Combustion Research Facility (CRF) Diagnostics Research: Coherent Raman Processes*

Lucht, R.P.; Farrow, R.L.; Rahn, L.A.
510-294-3089

This project develops coherent Raman diagnostic techniques in support of Combustion Research Facility (CRF) programs. Detailed studies are made of processes affecting coherent anti-Stokes Raman scattering (CARS), a leading technique for time-resolved measurements of temperature and major species concentrations. Processes studied recently include collisional broadening, Doppler broadening and narrowing, collisional reorientation of rotational alignment, saturation, and elastic vibrational dephasing. In particular, a new theory has been developed to account for the asymmetric nature of observed hydrogen lineshapes as a result of this work. A high-resolution CARS system is used to examine the saturation behavior of CARS resonance and to perform pump-probe measurements of inelastic rotational state-to-state transfer rates. The modification of CARS spectra at high pressure due to collisional narrowing has been extensively investigated for nitrogen and carbon monoxide. This work will be extended to other gases such as oxygen. Inverse Raman spectroscopy has also been used to develop a database of spectral parameters for important combustion species such as nitrogen, carbon monoxide, hydrogen, and water vapor. This work is being extended to include oxygen, and new emphasis will be put on the effects of foreign gas broadening of oxygen and previously studied species. A computer code for analyzing CARS spectra and for determining temperatures and concentrations is maintained and upgraded to incorporate advancements in spectral models. This code is used widely in the United States by other groups using CARS for combustion measurements. This project is supported with facility operations funds. [5.0 FTE]

48. *Combustion Research Facility (CRF) Diagnostics Research: Advanced Methods*

Lucht, R.P.; Gray, J.A.; Koszykowski, M.L.; Trebino, F.P.
510-294-3089

This project supports the development and theoretical investigation of new, nonlinear, laser-based techniques in support of Combustion Research Facility (CRF) programs. Resonant wave-mixing techniques are developed for detecting and measuring trace species in combustion environments. Temperature measurements and imaging of OH and temperature measurements of NH have been achieved using degenerate four-wave mixing (DFWM). High resolution DFWM studies of collisional and Doppler broadening in NO and OH, laser intensity effects in NO, and flame measurements of NO and OH are currently under way. Six-wave mixing has been used to detect the hydrogen atom in a flame environment. A significant theoretical effort involving both perturbative and nonperturbative approaches to solving the fundamental density matrix equations for resonant wave-mixing processes is conducted in parallel with the experimental efforts. New techniques are also being developed for the study of ultrafast chemical dynamic processes in molecules of importance in combustion chemistry. A technique based on induced thermal gratings has been developed to measure ultrafast laser pulse widths, self-phase modulation, and chirp. Another recently developed pulse measurement technique, frequency-resolved optical gating (FROG), is being developed for the simultaneous determination of intensity and phase of the electric field during a femtosecond laser pulse. The antiresonant ring transient spectroscopy (ARTS) technique has been developed for sensitive excite-probe measurements of ultrafast processes. This project is supported with facility operations funds. [4.0 FTE]

49. *Flame Chemistry: Modeling and Experiments*

Miller, J.A.; Kee, R.J.; Durant, J.L.; Fisk, G.A.
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 nitrogeneous 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]

50. *Turbulent Reacting Flow Research*

Sweeney, D.W.; Schefer, R.W.; Barlow, R.S.; Paul, P.H.; Chen, J.H.
510-294-3138

This experimental and computational research project is directed toward an increased understanding of the coupling and competition between chemical kinetics and mixing in turbulent reacting flows. Simultaneous point measurements of spontaneous Raman scattering, Rayleigh scattering, and laser-induced fluorescence of OH and NO are obtained in turbulent nonpremixed jet flames. These multispecies data allow direct evaluation of the effects of turbulent mixing on chemical states in flames. Departures from chemical equilibrium occur when mixing rates are fast relative to characteristic chemical kinetic rates. Measurements are compared with equilibrium states, with calculated thermochemical states in strained laminar flames, and with turbulent flame simulations based upon Monte Carlo pdf models and reduced chemical mechanisms. 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, large-field imaging of OH in high-Reynolds-number flames, 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 evaluation of combustion models for reacting flows with complex geometries. [5.0 FTE]

51. *Chemical Kinetics and Dynamics*

Tully, F.P.; Durant, J.L.; Chandler, D.W.; Miller, J.A.; Rohlfing, E.A.; Hayden, C.C.; Fisk, G.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 technique to follow the course of reactions between, for example, OH and alcohols or between CH and hydrogen. Recent experiments have discovered a catalytic mechanism for the dehydration of alcohols. A versatile flow-tube kinetics apparatus having both laser and mass-spectrometric diagnostics has been completed and is being used to study reactions of NH. Recent theoretical studies have treated reactions such as those between H and NH_3, H and HNCO, and F with CH_3OH using quantum-chemical and statistical-theoretical methods. Studies of dynamics emphasize collecting quantum-state-resolved data for elementary chemical processes. Photofragment-imaging studies of methyl-halide photodissociation and H + HI reaction have clarified the dynamics of these processes and the partitioning of excess energy. Recently initiated investigations of processes that occur on femtosecond time scales are providing insight about how energy moves through molecules. Research on the reactions of carbonaceous clusters produced by laser vaporization is aimed at determining how soot precursors form during combustion. Theoretical and experimental investigations of C_3 clusters show that this species exhibits complicated dynamics on a potential-energy surface that has an unusually flat bend and strong stretch/bend interaction. [5.0 FTE]

Atomic Physics

Argonne National Laboratory
Argonne, IL 60439

Physics Division $1,530,000

52. *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 ultraviolet (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]

53. *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]

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

This program is directed toward the detailed understanding of atomic and molecular ion 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. The molecular structure measurements provide tests of ab initio computation of wave functions and molecular parameters of simple diatomic molecules for the first row of the periodic table, in addition to radio-frequency data of use to astronomers. Collaborative efforts are continuing with the medium-energy physics and weak interactions 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]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $225,000

55. *Atomic Physics Research*
Johnson, B.M.
516-345-4552

Photoionization and related processes are studied using synchrotron radiation, gas-phase targets, ion beams, and ion traps. Most of the work utilizes the X-26 beamline at the National Synchrotron Light Source (NSLS). Noble-gas targets allow for the study of isolated, closed-shell atoms. Ion-sources are used to extend measurements to open-shell systems. Very cold, multiply ionized atoms are produced at energies of less than 100 meV through inner-shell photoionization in ion traps. Rate coefficients for charge exchange in symmetric and asymmetric interactions are measured at collision energies much lower than attainable by any other technique. Fluorescence radiation and electron emission following the primary photoionization event are monitored, and the final charge-state distributions, after accounting for charge exchange in subsequent ion–atom interactions, are measured. The new emphasis is on photon-scattering from bound electrons. [1.5 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $700,000

56. *High-Energy Atomic Physics*
Gould, H.A.
510-486-7777

The goals of this program are to search for a permanent electron electric dipole moment (EDM), to understand atomic collisions of highly relativistic heavy ions, and to test quantum electrodynamics in a strong static Coulomb field. Recent results include a new technique for determining electron impact ionization cross sections of highly ionized atoms as well as achieving the best upper limit to the electron EDM. Finding an electron EDM would be proof of new physics, not contained in the standard model, and would be as significant a discovery as the results expected from the Superconducting Super Collider. Present activities include (1) an attempt to observe, measure, and calculate accurately the differential cross sections for capture from pair production, a new relativistic atomic collision process in which 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 and (2) developing a more sensitive EDM experiment. [2.5 FTE]

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

Studies of the structure and interactions of atomic systems are made to provide the most detailed description of their behavior, and to stimulate theoretical understanding of the observed phenomena. The program exploits the ability of state-of-the-art electron cyclotron resonance (ECR) ion sources at Lawrence Berkeley Laboratory (LBL) to produce intense, highly charged beams for the conduct of low-energy ion–atom collision studies. Detailed study of multiple electron capture collisions at low velocities, where quasi-molecular behavior prevails, forms a major part of the research program. Current emphasis is on developing a complete experimental description of double capture from He targets, including specification of the final quantum state, impact parameter, and energy dependences. Auger spectroscopy is a major tool used for insight into highly excited structures and the charge transfer mechanisms. The program benefits substantially from collaborative efforts with colleagues outside LBL. [1.5 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Physics Division $1,650,000

58. Theoretical Atomic Physics at Oak Ridge National Laboratory (ORNL)

Bottcher, C.
615-574-4580

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]

59. 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). 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. Radiative electron capture in crystal channels is being studied as a function of the ion energy loss and use of crystal models to determine impact parameter dependent cross sections. 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. In collaboration with Swedish scientists, experiments are being mounted at the Stockholm Heavy Ion Storage Ring (CRYSIS) to measure dissociative recombination between electrons and molecular ions (e.g., HeH^+, HD^+). [4.6 FTE]

60. 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 6.5 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, the 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 electron–electron interactions in transfer and excitation, angular distribution of Auger electrons following the collision of highly charged ions with an He target gas, the channeling of oxygen ions through thin crystals, angular coincidence of electron-target recoil ion, and the use of a 30-MeV Cl^{5+} "hammer beam" to produce highly charged recoil ions in order to study charge exchange. [1.3 FTE]

61. Collisions of Low-Energy Multiply Charged Ions

Meyer, F.W.; Havener, C.C.; Phaneuf, R.A.
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 quasimolecular 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. [1.0 FTE]

Sandia National Laboratories, Albuquerque
Albuquerque, NM 87185

Department of Plasma Processing Science $155,000

62. *Atomic Processes in Reactive Plasmas*
Greenberg, K.E.; Riley, M.; Gerardo, J.B.
505-844-1243

The goal of this project is to gain an understanding of the fundamental electron/molecule and chemical mechanisms occurring in low-temperature glow discharges. These types of plasmas are commonly used to process materials (e.g., chemical vapor deposition of thin films and reactive ion etching). Various experimental methods including Raman spectroscopy, laser-induced fluorescence, optogalvanic spectroscopy, infrared absorption spectroscopy, and microwave interferometry are used to determine neutral and charged particle densities throughout the plasma. Optical and optical-microwave techniques are used to measure Stark shifts of atomic and/or molecular energy levels to determine electric field strengths in the sheath regions (and the bulk) of the plasma. Numerical simulations are also an important element of the research. These simulations, based on Boltzmann and hybrid Boltzmann-fluid codes, will be used to determine the electron-energy distribution function and to help understand the complex chemical mechanisms in these systems. Comparisons between experiment and simulation are the key to unraveling the physics and chemistry of these plasmas. [1.0 FTE]

Chemical Energy

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program $1,301,000

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

The 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. [2.1 FTE]

64. *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 formation. Efforts are directed at reactions in homogeneous solution in which metal–carbon bonds are made and broken. One reaction of fundamental interest is the bond homolysis process $L_nM{-}R \rightarrow L_nM + R\cdot$, and its reverse, radical capture or colligation. The kinetics of thermally induced homolysis reactions are being examined for complexes of chromium, nickel, and cobalt; metal–carbon dissociation energies can be derived from such determinations. Very rapid colligation rates are being determined by means of laser flash photolysis experiments. Other reactions of metal alkyl complexes in which the metal–carbon bond is cleaved are also being studied, including hydrolysis and electrophilic reactions. Another aspect of this work concerns the kinetics and mechanisms of reactions in which alkyl radicals react with transition metal complexes. These include other colligation reactions, as well as reactions in which the free radical is oxidized or reduced by a transition metal. Reactions of $R\cdot$ with O_2 are also being studied, as are reactions of alkane thiyl radicals, $RS\cdot$, with metal complexes. Electron transfer reactions of excited-state complexes are also under investigation for $Cr(polypyridyl)_3^{3+}$, $Cr(cyclam)(NH_3)_2^{3+}$, and Eu_{aq}^{3+}. [4.3 FTE]

65. *Multiple Pulse NMR Studies: Catalysis and the Chemical Constitution of Coal*
Gerstein, B.C.
515-294-3375

Transient techniques in NMR of solids are used to probe the physics and chemistry of materials involved in heterogeneous catalysis, fossil fuels, and materials science. Examples include (1) the use of multiple quantum spin counting of strongly dipolar coupled clusters of protons to determine stoichiometries of hydrocarbon fragments adsorbed on supported bimetallic catalysts used for reforming; (2) the use of NMR of quadrupolar nuclei such as ^{133}Cs and ^{63}Cu to characterize the chemical states of catalysts such as zeolites and alkali metal-doped copper oxides, and the use of NMR of ^{51}V and ^{17}O to characterize possible active sites for C_4 hydrocarbon oxidation in vanadium–phosphorus–oxide catalysts; (3) the use of dipolar oscillation NMR to determine internuclear distances in unstable organic molecules trapped in frozen matrices at 80 K; and (4) the use of dynamic angle spinning (DAS) to narrow the central transition of quadrupolar nuclei such as ^{17}O in active catalysts. [2.9 FTE]

66. *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, additive metals, or other species that can perturb those 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 ^{1}H, ^{13}C, ^{65}Cu, and the alkali metals as well as other nuclei have been important probes. [1.9 FTE]

67. *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]

68. *Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts*

Schrader, G.L.
515-294-0519

This research is providing new fundamental information about catalysis by metal oxides and sulfides, including the mechanisms of catalytic reactions, the structure and composition of catalysts, and the properties of surfaces. The metal oxides and sulfides being investigated are used extensively by industry for selective oxidation and hydrodesulfurization. Specific applications include oxidation of paraffins and hydroprocessing of petroleum or coal-derived liquids. A complement of experimental approaches is being used to perform kinetic measurements and comprehensive catalyst characterization. In situ spectroscopic techniques, such as laser Raman, Fourier transform infrared, and NMR spectroscopies 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]

69. *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 ^{1}H 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

70. *Fluid Catalysis*

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

The aim of this research is to explore new catalytic chemistry and catalytic reaction mechanisms to activate small molecules (e.g., CO, CO_2, CH_4, N_2) that often require extreme conditions of temperature and pressure to produce useful products. Maximal concentrations of reactant gases are achieved by making use of their complete miscibilities with supercritical fluids, which also have the potential to alleviate gas–liquid mixing and catalyst recovery problems typical of many homogeneous catalytic processes. Current research uses high-pressure NMR measurements to investigate the reactions of dicobalt octacarbonyl, the oxo catalyst, under hydroformylation process conditions. The catalytic process had not previously been explored by in situ NMR methods at the high pressures and temperatures required for the reaction, and considerable unsuspected chemistry has now been uncovered by this approach. Most noteworthy is the predominance of radical chemistry which results in ^{13}C NMR contact shifts for CO, and a variety of dynamic NMR effects in the ^{59}Co and ^{1}H NMR spectra. These observations, combined with the high-pressure NMR magnetic susceptibility measurements, indicate that the Co–Co bond in $Co_2(CO)_8$ is weaker than previously suspected and support the hypothesis that the $17e^-$ radical, $\cdot Co(CO)_4$, could be operative in hydroformylation catalysis. In other research directed toward the activation of methane, catalytic complexes containing rhodium centers bound to solubilized phthalocyanine ligands are being synthesized. In this approach, methane is activated by means of the rhodium center's ability to form reasonably strong, but still reactive, metal–carbon and metal–hydrogen bonds. 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 useful in the production of shaped ceramic objects. [4.5 FTE]

Chemistry Division $1,907,000

71. *Chemical Constitution of a Low-Volatile Bituminous Coal*

Stock, L.M.
708-252-3570

Chemical and spectroscopic methods are being used to establish the constitution of Pocahontas No. 3 coal (Argonne Premium Coal Sample Program 5). This higher ranking coal was selected for study to investigate the general proposal that such highly aromatic coals have a lower degree of polymerization and, generally speaking, a simpler structure than low ranking subbituminous coals or lignites. The quantitative work on the magnetic resonance spectrum of the samarium(II)-treated coal is complete. The aromatic carbon atom distribution has been established by this technique. The aliphatic carbon atom distribution had been elaborated through Ru(VIII) oxidation. These results have been coupled with other information, for example, mass spectroscopic data, new solubilization chemistry, XANES spectroscopy, to provide a prototypical structure for this coal that accounts for its chemical and spectroscopic properties. [1.0 FTE]

72. *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 636 orders have been filled with more than 19,000 ampoules. Inventories of the two most-requested samples were increased during the summer of 1991. The materials in the ampoules are projected to meet the demand for another 15–20 years for these samples, and the reserves will continue to meet the current demand level for several decades. The gas atmosphere is monitored to establish sample stability. Over 320 scientific papers have been published on work done with these samples. A Users Handbook has been updated to include the most current bibliographic information, and a literature summary is being prepared by a group of experts. A symposium on "Research with Argonne Premium Coal Samples" was organized in conjunction with the fall 1991 American Chemical Society meeting. [0.4 FTE]

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

Winans, R.E.; Hayatsu, R.; Dyrkacz, G.R.; Botto, R.E.; Carrado, K.A.; McBeth, R.L.; Melnicoff, P.E.; Bloomquist, C.A.A.
708-252-7479

The objective of this project is to obtain fundamental information on the chemical and physical structures of the Argonne premium coals and their maceral constituents to facilitate prediction of their thermal, chemical, and biological reactivity. Novel methods for the separation of coal macerals are being developed to provide ultrahigh-resolution partitioning of submaceral groups and to advance large-scale separation techniques. Argonne Premium Coal Samples and their separated macerals are subjected to selective modification and solubilization, and to liquefaction (with Amoco Oil) to provide samples for a large array of characterization studies. Featured analytical approaches include true solid-state NMR imaging, laser desorption mass spectrometry, tandem mass spectrometry, and synchrotron X-ray absorption spectroscopy. Synthetic layered molecules with catalytic potential for large, coal-derived molecules are being designed, prepared, and characterized. Data derived from the premium coals are being assimilated into statistically accurate pictures of coal structures. This information is vital in the development of advanced processes for the utilization of fossil fuels in accordance with the National Energy Strategy. [8.6 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $613,000

74. *Structure and Function in Electrochemistry*
Adzic, R.
516-282-4480

The objective of this program will be the enhancement of the understanding of the relationship between interfacial structure and function in electrochemical processes. The experimental effort will utilize several recently developed in situ methods for atomic level characterization of the morphology of active surfaces under actual reaction conditions: X-ray scattering (utilizing Brookhaven National Laboratory's (BNL's) National Synchrotron Light Source) and scanning tunneling and atomic force microscopy techniques can now be used as in situ probes of the atomic structure of electrochemical interfaces while retaining chemical and/or electrochemical control of the interface. Initial efforts will address questions about electrochemically induced restructuring of gold and platinum surfaces; the roles of adatoms (on gold) and concomitantly adsorbed anions in a variety of electrochemical processes. A long-range objective will be to learn how to design and produce surfaces with predictable properties which could enhance the rate of a heterogeneous electron transfer, direct electrosynthesis, or heighten electrode sensitivity and selectivity. One can envision myriad applications (e.g., energy conversion (solar to electrical energy, fuel cells), electrical energy storage (batteries), electrosynthesis and electroanalysis (sensors), and corrosion control). [0.2 FTE]

75. *High-Temperature Chemistry*
Egan, J.J.
516-282-4488

This project addresses the thermodynamic, transport, and electronic properties of alloy and metal–molten-salt systems at high temperatures. Alloys are studied in both the liquid and solid state with emphasis on systems which form liquid and solid compound semiconductors. Both electrochemical and calorimetric measurements are being used to explore and characterize these systems. Galvanic cells using solid CaF_2 electrolytes are employed to examine alloy systems and molten salts. Results yield metal activities, diffusion coefficients, ranges of homogeneity, as well as concentration and mobility of electrons and holes in alloy systems. In molten salts, the thermodynamic properties and conductivities are obtained. A high-temperature twin Calvet-type calorimeter is also operated to study ionic alloys. The electronic component of conductivity of molten salts is being examined by special polarization techniques, because this property is so important in determining the efficiency of electrolysis in the production of metals and the self-discharge of molten-salt batteries. Results of this work are explained in terms of atomic models. [1.3 FTE]

76. *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, and the catalytic properties of metal hydrides and electrochemical behavior of metal hydride electrodes. The major experimental tools and/or techniques are equilibrium pressure/temperature/composition measurements, X-ray diffraction, Fourier transform infrared (FT-IR) spectrometer measurements, and the use of a high-pressure apparatus to study the kinetic behavior of metal hydride suspensions. [2.9 FTE]

Chemistry Department $1,840,000

77. *Structure and Reactivity in Catalysis and Advanced Materials*
Koetzle, T.F.; McMullan, R.K.; Andrews, M.; Bullock, R.M.; Hrbek, J.; Rodriquez, J.A.
516-282-4384

This program probes fundamental aspects of chemical catalysis from a multi-faceted perspective that 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 biomass conversion. 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 fast-ion conductors and gas clathrate hydrates. These studies are providing a foundation for understanding the special characteristics of these materials. [12.4 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $1,091,000

78. *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 two-dimensional 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, since batteries based on lithium and fluorine would be unsurpassed in their energy-density features. In addition, novel oxidation-state fluorides are being synthesized and structurally characterized to provide a comprehensive basis for better theoretical models, which should bring an improved capability to predict physical and chemical behavior. Previously unknown or little studied high-oxidation-state species constitute a large part of this effort. Such species are also investigated for their efficiency and specificity as chemical reagents. [2.1 FTE]

79. *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 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. To meet these objectives, a variety of surface diagnostic techniques are used to characterize supported and unsupported catalysts before, during, and after reaction. The information thus obtained is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation. [2.5 FTE]

80. *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). Two of the most significant recent discoveries in the project are that liquified xenon and krypton can be used as inert solvents for C–H activation, and that weak metal-alkane and metal-xenon (krypton) complexes intervene as intermediates in these reactions. Current work is directed toward utilizing these results (1) to activate a range of new substrates, such as solids and gases that are difficult to liquefy (e.g., methane); (2) to develop methods for determining the structure and investigating the reactivity of the transient alkane and noble gas complex intermediates involved in C–H insertion processes; (3) to understand the thermodynamics and kinetics of C–H activation; (4) to extend the process to O–H, N–H, and C–F activation; and (5) to develop better methods for using C–H activation to convert alkanes into functionalized organic compounds. [5.0 FTE]

81. *Formation of Oxyacids of Sulfur from SO_2*
Connick, R.E.
510-642-4981

The work is directed towards a fundamental understanding of the chemical processes involved in acid rain. Of immediate interest is the oxidation of bisulfite ion by oxygen and peroxides, reactions which occur in most flue-gas desulfurization processes and in atmospheric water droplets containing absorbed sulfur dioxide. The approach is to determine rate laws and mechanisms of reaction. For peroxide oxidation this is reasonably straightforward. Oxygen oxidation, however, is much more difficult to treat because the reaction proceeds by a chain, with consequent extreme sensitivity to impurities acting as catalysts or inhibitors. A secondary and not closely related goal is to determine the factors controlling the rate of substitution reactions in the first coordination sphere of metal ions in solution. Computer modeling has been extended to three dimensions with 500 particles. The simulation reveals structures of activated complexes for this important reaction. [.75 FTE]

82. *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. For this purpose, new synthetic organic methodology has been developed that allows the stepwise chemo-, regio-, and loco- (i.e., identity of the metal sequence in heterometallic systems) specific building-up of cluster-chains. Many of their physical and chemical properties are unparalleled and include (1) extreme ligand deformations, (2) highly strained metal–metal bonds, (3) intramolecular organic fragment migrations, (4) intrachain electron transfers, and (5) thermally reversible photochemical storage processes. [2.6 FTE]

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

Isotope and Nuclear Chemistry Division $388,000

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

This research has focused on the basic chemistry of environmentally and energy-related small molecules, primarily SO_2 and H_2, mediated by transition metal complexes. A fundamental understanding of the cleavage of S=O and H–H bonds will allow development of and mechanistic insights into new methods of chemical conversion. Disproportionation of SO_2 occurs on reaction with polysulfido complexes $Cp'_2M_2S_n$ (M = Mo, Cr; n = 4,5) to give sulfur and SO_3 (bound to sulfide as SSO_3). The structure of an intermediate, $Cp'_2Cr_2S_5{\cdot}SO_2{\cdot}SO_2$, indicates the mechanism of disproportionation involves initial association of SO_2 molecules by Lewis acid-base binding, followed by oxygen transfer. The scope of this type of reactivity, which may be widespread and lead to improved methods for SO_2 conversion, is being examined. The discovery of side-on bonding of H_2 molecules to metals represents the first stable sigma-bond complex and serves as a prototype for other such activations (e.g., C–H in hydrocarbons). Structural and inelastic neutron scattering studies of $Cr(CO)_3(H_2)P_2$ and $Mo(CO)(H_2)P_4$ systems (P = phosphine) are in progress to further define the reaction coordinate for H–H bond rupture and the dynamics and vibrational modes of bound H_2. The extremely low rotational barrier of H_2 (0.5–2.5 kcal/mol) is being measured and correlated with its effects on H–H bond length determinations and degree of $M \rightarrow H_2\ \sigma^*$ backbonding. Binding of H_2O, ethylene, and thiophene on the same complexes that coordinate H_2 is also being investigated, and the strength of water and H_2 binding appears to be surprisingly comparable, which may be relevant to biological activation of H_2. Isotopic exchange between D_2 and H_2O catalyzed by these complexes is also under study. [1.4 FTE]

National Renewable Energy Laboratory
Golden, CO 80401

Basic Sciences Division $408,000

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

The major objectives of this project are the synthesis of new catalysts for the electrochemical reduction of carbon dioxide and carbon monoxide, and the study of mechanistic features and structure-reactivity relationships for these catalysts. Previous research on this project resulted in the development of a new class of carbon dioxide reduction catalysts. Mechanistic studies of these complexes are being used to develop better catalysts. For example, the original catalysts had rate constants of 13 M^{-1} sec^{-1} and current efficiencies for CO production of approximately 55%. These have been improved to 160 M^{-1} sec^{-1} with current efficiencies greater than 90%. Current research is focusing on improving catalytic rates and catalyst stability. Similar studies are in progress to develop homogeneous catalysts for electrochemical reduction of CO. Three important steps in one possible cycle have been demonstrated. Electrochemical generation of reactive metal hydride complexes of nickel and platinum has been achieved. A number of these complexes undergo an intermolecular hydride transfer to carbonyl ligands of cationic carbonyl complexes to generate metal formyl complexes. Protonation of one formyl complex followed by a second hydride transfer to generate a hydroxymethyl complex has also been demonstrated. Cleavage of the latter complex by protonation would result in methanol formation. Current efforts are directed at developing a catalytic cycle based on this chemistry and understanding these fundamental reactions. [2.6 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemical Technology Division $546,000

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

Novel photophysical phenomena were observed in isolated spinach chloroplasts that were metallized by precipitating colloidal platinum onto the surfaces of the thylakoid membranes. A photobioelectrochemical cell was constructed using platinized chloroplasts entrapped on a fiberglass filter pad as the photosensitive material. In this two-electrode device, a platinum gauze electrode made pressure contact with the chloroplasts, and a silver/silver-chloride electrode made pressure contact with the electrolyte-impregnated filter paper pad. Upon illumination, an oriented photocurrent was observed that is consistent with the vectorial photochemical model of the reaction centers in photosynthetic membranes. The kinetics of interfacial photoelectron transfer in this cell were studied using the technique of repetitive flash illumination. By driving the photocurrent response into steady state, using multiple flash frequencies, and normalizing the photoresponse to the rate of flashing, the frequency response of the photocurrent was determined. As expected, in the low-frequency, linear region, the normalized photocurrent response was constant. However, as the rate of flashing increased (above 100 Hz), the yield of photocurrent per frequency interval decreased. This decrease in yield was interpreted as the inability of the thermally activated electron transport chain of photosynthesis to keep pace with the higher rates of reaction center excitation. The reciprocal of the frequency at which the normalized photocurrent has fallen to one half is called the turnover time. In this experiment, this occurred at ~200 Hz, corresponding to a turnover time of 4 ms. A cellobiohydrolase II core protein from *Trichoderma reesei* was found to physically disrupt or disperse cotton macrofibrils without any hydrolysis taking place. An immobilized and stabilized β-glucosidase has been developed that can be used for the continuous hydrolysis of cellobiose for weeks without any loss in activity. [4.0 FTE]

Chemistry Division $2,849,000

86. Organic Chemistry and the Chemistry of Fossil Fuels

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

Fundamental research on the chemical structure and reactivity of coal aims to develop insights that 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 economically viable, environmentally acceptable manner. Solid-state NMR methods are being developed for studies of the local structure of chemically modified coals. Current research is focusing on the use of NMR techniques that exploit the ^{13}C–^{19}F dipolar interaction in ^{19}F-labeled organic molecules, polymers, and coals to derive structure/reactivity information. An example of fluorination chemistry under investigation is the conversion of carboxylic acids to acyl fluorides in low rank coals using sulfur tetrafluoride. Model systems are being developed to explore the impact of mass transport limitations on reaction mechanisms relevant to the thermal and catalyzed reactivity of coal. Current research focuses on (1) retrogressive reaction channels for fluid-phase and surface-attached ether compounds representative of ether bridges prevalent in low rank coals and lignites, (2) hydrogen transfer pathways in diffusionally restricted environments as explored through thermolysis of two-component surfaces, and (3) role of solid-state interactions in catalysis of coal conversion employing surface-immobilized model compounds as solid-state molecular probes. [4.6 FTE]

87. 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 aim of this program is to establish basic principles governing chemical and thermodynamic behavior of aqueous solutions of broad classes of solutes at high temperatures and pressures. Advancement in experimental methods and the development of new models for exploring and representing behavior over wide extremes of conditions are important parts of this program. A range of diverse but complementary techniques are employed to obtain precise data to and beyond the critical conditions of water and its solutions. Chemical processes under present study are ionization-ion association, complexation, hydrolysis, solubilities, volatilities, and oxidation reduction. Thermodynamic quantities of interest are excess properties and ion-interaction parameters, molar volumes, and reaction thermodynamics. Principal methods in use are: flow calorimetry, isopiestic methods, electrochemical cells, electrical conductivity, densimetry, liquid–vapor partitioning, and Raman spectroscopy. New results are leading to models for describing variations with temperature, pressure, and composition for both standard state and excess thermodynamic quantities. A new initiative is being explored to represent solution properties using molecular dynamics simulations. Results for this program have major impact in basic solution chemistry, basic hydrothermal geochemistry, steam generation technology, utilization of geothermal resources, nuclear waste disposal, and environmental transport of metals. The approaches and techniques developed here for species identification and the study of reaction equilibria have broad applicability in the waste management and environmental restoration activities of the Department of Energy. [3.8 FTE]

88. Heterogeneous Catalysis Related to Energy Systems

Overbury, S.H.; Huntley, D.R.; Mullins, D.R.; Krause, M.O.
615-574-5040

Surface analytical techniques are used to study reactions and structure on single crystal substrates. Problems of primary interest have been the reaction of sulfur containing molecules on metal substrates and structure of bimetallic and sulfided surfaces. The temperature programmed reactions of hydrogen sulfide, methanethiol, ethanethiol, benzenethiol, mercaptoethanol, ethanedithiol, and benzene have been studied on Ni(110) by high resolution electron energy loss spectroscopy, X-ray photoemission, deuterium exchange, and desorption spectroscopy. Fundamental information about mechanisms and kinetics for desulfurization and decomposition has been obtained. The chemisorption and reaction of selected organosulfur molecules on W and Ru substrates have been studied by substrate core level photoemission and S 2p photoemission utilizing soft X rays from synchrotrons. The thermal stability and stages of decomposition of surface intermediates and surface sulfidation have been studied. Reactions on metal surfaces have been modeled using semiempirical molecular orbital theory and bond order conservation methods. Low-energy ion scattering has been applied to study the structure of sulfided Ni(111) and sulfur induced reconstruction of this surface. Bimetallic surfaces such as thin films of Sn on Cu(111), Ni(111), and Pt(111); Cu and Ni on W(100); and surfaces of Pt_3Sn, NiAl, and Mo–Re alloys have been studied to answer questions about structure and component distribution at these surfaces. [3.6 FTE]

89. *Photolytic Transformations of Hazardous Organics in Multiphase Media*
Sigman, M.E.; Zingg, S.P.
615-576-2173

This program investigates 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. Silica gel surfaces have been shown to produce dramatic effects on the kinetics of PAH photodecomposition and on the subsequent fate of the primary photoproducts. These effects are manifest at the solid/gas or solid/liquid interface. Enhanced reactivities in SiO_2/solvent slurries are attributed to the polarity of the surface. Adsorption isotherm and spectroscopic studies have also been undertaken to better elucidate the nature of the solid/liquid interface. Direct photolysis of PAHs at SiO_2/air interfaces has been found to give rise, in certain cases, to oxidation products analogous to those obtained from TiO_2 mediated photo-oxidation. The photochemistry of ArHs and PAHs in aqueous media, though of significant environmental importance, has not been well studied. Initial studies of PAH photochemistry in water revealed products arising from a cation radical pathway. These studies are being extended to ascertain the generality of electron ejection pathways in the aqueous photochemistry of PAHs. These studies will be of value in enhancing the basic understanding of photochemical processes occurring at interfaces and under environmentally relevant conditions. [2.2 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $685,000

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

The objective of this project is to determine kinetics, thermochemistry, and mechanisms of key radical and radical ionic pathways important to thermal degradation of coal. Efforts include the determination of bond strength in aromatic heteroatom-containing organic structures; absolute rates of organic free-radical rearrangements; rate expressions for atom transfer reactions involving radicals and radical ions; and activation of strong carbon–carbon bonds via π-complexed organometallic groups. Methods include nanosecond kinetic laser flash photolysis, kinetic electron paramagnetic resonance spectroscopy, cyclic voltammetry, and laser photoacoustic calorimetry. Ab initio quantum chemical calculations at various levels of electron correlation are being applied to study free radical and excited state reactions of organosulfur structures. Solid-state NMR methods for the characterization of carbon, organooxygen, and organosulfur structure in coal using multinuclear solid-state NMR methods are under development. [3.7 FTE]

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program $1,145,000

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

The project objective is to devise practical, innovative methods for separation and chemical analysis. Chromatographic separation and speciation of anions and metal cations are accomplished by ion chromatography and by complexation (of metal ions), followed by liquid chromatographic separation. New resins and complexing reagents are synthesized as part of this research. Resins with hydrophilic chemical substituents are highly effective for use in solid-phase extraction. Chelating reagents and resins are prepared and used for isolation of selected metal ions from aqueous samples. These new materials will be useful in attacking the waste cleanup problems of the 1990s. New liquid-chromatographic and gas-chromatographic methods are being developed for the important problem of determining small amounts of water in chemicals and other materials. [2.1 FTE]

92. *Analytical Spectroscopy*
Houk, R.S.; D'Silva, A.P.
515-294-9317

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]

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

This project examines new approaches for the construction and characterization of monomolecular 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 n-alkanethiols at gold and silver surfaces, (2) probing solvent–monolayer interactions of n-alkanethiol monolayers with aqueous and various nonaqueous solvents with in situ Fourier transform infrared 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 infrared reflection spectroscopy, 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]

94. *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 $1,331,000

95. *Separations Science Related to Nuclear and Hydrometallurgical Technology*

Horwitz, E.P.; Nash, K.L.; Diamond, H.;
Dietz, M.L.; Gatrone, R.C.
708-252-3653

The primary objectives of this project are threefold. The first is to study extractant isomer–diluent interactions with the goals of improving the solubility of highly polar extractants in hydrocarbons, of gaining further insight into how conformational changes in the dicyclohexano 18-crown-6 moiety influence the extraction of Sr^{2+} and K^+, of developing new biphasic systems involving polyoxyethylene functional groups, and, of understanding the basic similarities and differences in bulk phase extraction and extraction chromatography. The second objective is to design, synthesize, and characterize new classes of aqueous-soluble nonphosphorus complexing agents for metal ion separation. These new complexants are designed to form water-soluble, stable complexes with tri-, tetra-, and hexavalent metal ions in highly acidic media and to decompose under mild thermal and/or oxidizing conditions to form environmentally acceptable species. The third objective is to develop improved methods for synthesizing organophosphorus extractants and particularly extractants containing steric hindrance, by studying the pathways for converting one or more phosphorus–oxygen bonds into phosphorus–carbon or phosphorus–hydrogen bonds. All three objectives are directed toward applications in (1) nuclear technology, such as actinide separations, waste processing, and by-product recovery from nuclear waste and (2) hydrometallurgical processing and groundwater decontamination. [3.5 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $618,000

96. *Analytical Techniques with Synchrotron Radiation and Ion Beams*

Jones, K.W.; Spanne, P.
516-282-4588

The project uses X-ray and ion-beam microscopy methods for study of catalysts, characterization of coal, and other chemical systems. Experiments to improve the performance of the synchrotron-based X-ray microscope are aimed at achieving a spatial resolution of 1 μm with a photon flux integrated over all energies of 10^{10} photons/(s-μm^2) or more. A number of different catalyst systems are being investigated with the X-ray microscope including polyolefins, fluid catalytic cracking (FCC) catalysts, and hydrotreating catalysts. Applications to studies of porosity and fluid flow in different systems, including catalysts, are being initiated. These experiments demand the highest possible values of X-ray microscope resolution and beam intensity. Ion beams are being used in complementary experiments to profile hydrogen and other light elements in several types of catalysts. [1.9 FTE]

97. *Microparticle Analysis by Laser Spectroscopy*

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

Aerosol particles are present ubiquitously in nature and in many energy-related processes as well. In order to elucidate the formation mechanisms and understand the subsequent chemical transformation under a variety of reaction conditions, it is imperative to develop ultrasensitive analytical techniques for in situ monitoring of these suspended microparticles. This project focuses on elucidation and determination of the fundamental properties that are essential in developing laser-based spectroscopic methods for microparticle analysis. Current research activities include (1) systematic investigation of the Raman scattering cross-sections for ionic solids composed of oxyanions, using the single particle levitation technique; (2) elucidation of the chemical states of the solute molecules in highly concentrated solution droplets at the onset of phase transformation; and (3) establishing the selectivity and sensitivity of the resonance Raman scattering process, using a stream of droplets generated by a vibrating orifice. Combined with state-of-the-art instrumentation, 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

98. 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 are currently 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 to develop understanding of the process controlling gas phase ion formation. 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 the ongoing development of mathematical algorithms for computer modeling of ion optic systems is conducted. [1.0 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Energy and Environment Division — $214,000

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

A comprehensive program is under way to study the mechanisms that describe the explosive removal of material induced by high-power pulsed-laser irradiation (laser sampling). For chemical separations and analysis, laser sampling can provide direct solid analysis, simultaneous multielement analysis, microanalysis, and spatial characterization. Acoustic monitoring, optical probe beam deflection, and atomic emission spectroscopy are studied to indicate distinct mechanisms occurring during the interaction. A new 125-MHz piezoelectric sensor is being investigated to study the propagation of acoustic waves induced in the material by the pulsed laser irradiation. Changes in the acoustic frequency 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 to determine heat transfer into the sample, the onset of phase change, and the formation of a laser initiated surface plasma (density gradient). Atomic emission spectroscopy is used to monitor the stoichiometry of the laser-sampled material and the existence of preferential vaporization. This material is transported to an inductively coupled plasma (ICP) for excitation to emission. By drawing correlations between these acoustic, deflection, and atomic emission data, fundamental mechanisms describing the interaction of pulsed laser radiation with solid material can be elucidated. [1.7 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Analytical Chemistry Division — $1,962,000

100. Mass Spectrometry R & D for Organic Analyses
Glish, G.L.; Van Berkel, G.J.; Goeringer, D.E.; Ramsey, R.S.
615-574-2456

The objective of this work is the development of new and improved methods for the analysis of organic molecules via mass spectrometry. One aspect of this involves the study of gas-phase ion chemistry and physics. By better understanding the fundamental processes involved in the various aspects of mass spectrometry experiments, analytical methods can be developed based on a solid framework of knowledge. Some of the processes of interest are ionization, unimolecular and bimolecular reactions, and ion activation. Several areas within the realm of ionization are being studied. These include electrospray ionization, glow discharge ionization, positron ionization, and ionization by controlled ion/molecule reactions. In the area of ion activation the fundamentals of collisional activation at various energies and under different instrumental conditions, along with surface-induced dissociation and photodissociation are of interest. The knowledge gained from this work is used to improve the analytical methods and techniques used in mass spectrometry. This will help improve the methods for analyzing organic molecules and the methods for studying the gas-phase ion chemistry and physics of molecules. [2.6 FTE]

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

The general goal of this work is to determine how new and uncommon physical phenomena can be utilized as spectroscopic methods of analysis. Present work is concentrated in the applications of slow and fast positrons. The mass spectrometry of large organic molecules ionized by positrons and desorption products from surfaces bombarded with positrons is under study. New works to be initiated are the analysis of plastic films and heavy metal alloys, and studies of positron scattering from alkali metal vapors. Instrumentation developed for the study of positron attachment spectroscopy will be evaluated for its practicality in electron attachment and MS–MS spectrometry. This work involves collaboration with Vanderbilt University, University of Texas, Arlington, the University of Georgia, the University of Tennessee, and State University of New York, Fredonia. The Tennessee Center for Research and Development serves as an avenue for technology transfer. [2.8 FTE]

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

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

This research program involves the development of new laser-based chemical analysis concepts that can improve specificity and/or sensitivity beyond that of techniques presently available. Current experimental activities include gas and condensed phase ultrasensitive luminescence detection, nonlinear optics, and resonance enhanced multiphoton ionization spectroscopy. The techniques being developed address measurement problems in biotechnology, materials science, and environmental monitoring. Ultrasensitive luminescence experiments in the condensed phase involve measurements of microdroplets that allow the detection of one fluorescent molecule with near unity efficiency. Approaches to couple this promising detection capability to microbore separation techniques such as open tubular liquid chromatography and capillary electrophoresis in its various forms of implementation are being explored. Nonlinear optical studies of surfaces are being considered as a probe of molecular species present at gas/solid interfaces. Such information will be extremely valuable for understanding a number of phenomena such as the growth of materials by chemical vapor deposition. Work continues on the use of diode lasers for resonance ionization mass spectroscopy (RIMS). Emphasis is placed upon the use of multiple diode lasers to achieve ionization of atomic species. [3.0 FTE]

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

Smith, D.H.; Barshick, C.M.; Duckworth, D.C.; Van Berkel, G.J.
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]

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

Todd, P.J.; Christie, W.H.; Rosseel, T.M.; Short, R.T.
615-574-6824

The objective of this research is to gain a better understanding of sputtering and secondary ionization as it applies to secondary ionization mass spectrometry (SIMS). Both inorganic and organic SIMS and application to surface, depth, bulk, isotopic ratio, and imaging problems are of interest. The yield and chemistry of secondary ions and sputtered neutrals are dominated by matrix effects, often in a complementary way. In the inorganic work, changes in the behavior of secondary ions and sputtered neutrals are studied as source conditions are changed. A current application area is the site-specific chemical behavior and mass transport of inorganic pollutants in soil, rock, and other environmental matrices. A new Cameca IMS-4f ion microscope/microprobe is used to study variations in metal and isotope content in mineral grains of environmental importance. In organic SIMS, compounds are fragmented or modified chemically upon ion bombardment. Tandem mass spectrometry (MS/MS) is used for organic imaging and surface analysis. This approach mitigates matrix effects in organic SIMS by its ability to characterize ions by both m/z ratio and structure. This research is applicable to many current technical problems in materials science, health science, and environmental and waste technology. [2.2 FTE]

Chemical Technology Division $1,344,000

105. *Chemical and Physical Principles in Multiphase Separations*

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

The main goals of this program are (1) to conduct fundamental studies on the use of electromagnetic fields to enhance the effectiveness of multiphase separations and (2) to probe by experimental and theoretical means transport fundamentals associated with enhanced separations. Currently, there are major thrusts in field-enhanced liquid–liquid, liquid–vapor, and fluid–solid separations. From the mathematical standpoint, the majority of physical situations under investigation are free boundary problems. These include the statics and dynamics of drops and multiphase viscous free surface flows. In liquid–liquid separations, the primary focus is on analysis of effects of electric fields on droplets and emphasizes (1) equilibrium shapes, stability, and bifurcations of drops; (2) hydrodynamics of drop formation; (3) oscillations of free and pendant/sessile drops; and (4) physics of break-up and coalescence. In liquid–vapor separations, key issues are to develop a better understanding of (1) effects of external fields on polarizable media (e.g., bubbles) and (2) fluid dynamics of bubbly liquids. In the fluid–solid arena, the focus is on examining the use of high-intensity, high-gradient (HIHG) magnetic fields. This investigation addresses interactions of charged particles or macromolecular entities in viscous media which are under the influence of HIHG magnetic fields. [2.8 FTE]

106. *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. Basic research is focused on relating macroscopic properties of mixtures to intermolecular interactions and molecular correlation functions for the highly asymmetric systems characteristic of extraction by supercritical fluids and adsorption from supercritical fluids. Neutron scattering experiments of solutions of argon in supercritical neon are under way to provide data to test theories and simulations of dilute, near-critical solutions. In such solutions long-range density fluctuations, characteristic of closeness to the vapor–liquid critical point of the pure solvent, strongly influence the local microstructures around dilute solute molecules and also the bulk properties important in separations. Previous work is being extended to include challenging systems that are important in technological applications. Supercritical aqueous solutions and polymers in supercritical solution are being simulated using molecular dynamics and Monte Carlo techniques. Studies of adsorption from supercritical solutions are being performed based on the inhomogeneous Ornstein–Zernike equation. Theoretical studies of multicomponent supercritical solutions are continuing with both integral equation theory and conformal solution/fluctuation theory approaches. [1.0 FTE]

107. *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

108. *Chemical and Structural Principles in Solvent Extraction*

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

Principles of thermodynamics and structure pertaining to solvent-extraction and other energy-related separation techniques are the foci of this task. With emphasis on crown ethers and related multidentate compounds, experimental efforts address questions concerning the cooperativity of extractant functionalities in providing for the selective recognition and extraction of metal cations. 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, potential extractants for small alkali metal cations. Alternatively, neutral macrocycles are being combined with organophilic sulfonic and carboxylic acid extractants to achieve novel synergistic systems capable of selective separation of transition and alkaline earth metals. Efforts to design and synthesize new crown-ether extractants are also addressing the effect of hydrocarbon substituents on lipophilicity, structure, and extraction properties. To provide basic insight into systems of interest, model extractants are studied by an array of techniques. Structural aspects are probed extensively by the methods of X-ray structure determination of crystalline model compounds, molecular mechanics, and spectroscopy (e.g., FTIR, NMR, UV/vis, and Raman). Thermodynamic aspects are probed by distribution measurements, titration calorimetry, potentiometry, and other physical measurements; results are interpreted with the aid of advanced multiequilibrium modeling techniques. [3.7 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $1,305,000

109. *Analytical Mass Spectrometry Research*

Gordon, R.L.; Hubbard, C.W.; Styris, D.L.;
Baer, D.R.
509-376-1907

This project generates new knowledge important to the field of mass spectrometry and develops techniques to improve and expand the applications in this field. The project presently consists of two parts: (1) research to elucidate and predict the properties of new surface ionization source materials and (2) research directed toward the fundamental understanding and development of new mass spectrometric techniques. Research into the properties of new surface ionization materials explores the effects of surface impurities on work functions in order to model the surface ionization efficiencies of new materials. The electronic behavior of binary refractory systems based on rhenium is being investigated by surface work function measurements, Auger electron spectroscopy, and ultraviolet photoelectron spectroscopy. Models developed from these data will be used to predict the work function behavior of composite surfaces. The research to provide understanding and development of new mass spectrometric techniques addresses a broadly applicable mass spectrometry which uses a single source for both thermal atomization and electron impact ionization. Laser-assisted negative ionization is also being investigated as a means for gentle, specific ionization of large molecules. [2.1 FTE]

110. Laser-Based Analytical Techniques

Miller, R.J.; Cannon, B.D.
509-375-2968

The objective of this research project is to provide basic knowledge of molecular properties necessary for development of improved laser analytical technologies that are sufficiently selective and sensitive to be applicable to real environmental samples. This requires a quantitative understanding of the structural and dynamical properties of molecules. High resolution, resonantly enhanced multiphoton ionization (REMPI) methods will be used to measure molecular energy level patterns and to examine spontaneous decay mechanisms such as predissociation and autoionization that compete with the stimulated absorption process. This information is needed to identify optimum excitation schemes for laser based analyses of organic and inorganic molecules. Laser ablation will be combined with REMPI detection for determinations of chemical speciation of solid wastes and of environmental contaminants absorbed within soils and other geochemical materials. Electron attachment from Rydberg atoms is proposed as an efficient, fragmentation-free source for negative ion mass spectroscopic analyses of complex organic molecules. Studies will characterize Rydberg states of alkali metals and their decay dynamics. Electron attachment cross sections will be measured for prototype molecules as functions of collision and electron binding energies. This knowledge will enable efficient preparation of molecular negative ions for analytical applications. [0.9 FTE]

111. Fundamental Phase Partitioning in Supercritical Fluid Chromatography

Smith, R.D.; Fulton, J.L.
509-376-0723

The goal of this project is to obtain fundamental information on the kinetic, thermodynamic, and molecular level phenomena related to structure 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 processing methods. The pressure-dependent effects on the fluid structure are being measured spectroscopically and predicted theoretically. X-ray- and neutron-scattering studies are exploring 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 expanded understanding of solvation and structure in both the supercritical and liquid phases. [1.6 FTE]

112. Mechanisms of High-Temperature Atomization in Chemical Analysis

Styris, D.L.
509-376-1907

This project uses real-time mass spectrometry and atomic absorption spectrometry techniques to elucidate high-temperature surface chemistry and mechanisms that control high-temperature surface induced atomization used in analytical chemistry; unique applications of these surfaces are developed and refined. Knowledge obtained from this project is providing the basis needed to broaden and improve applications of spectrometries that rely on electrothermal vaporization sources. The gas-phase species created by these high-temperature surfaces during their rapid thermal ramping in vacuo and at atmospheric pressure are monitored in real time. Condensed-phase species that form on these surfaces during heating are being investigated by EXAFS spectroscopy. Surface state theory and available thermodynamic data are applied and kinetics are determined in order to help identify and characterize the controlling chemical and physical processes. Mechanisms associated with the unique hollow-anode plasma furnace atomization nonthermal excitation spectroscopy source, developed on this project, are also being investigated through emission spectrometry. The research primarily involves pyrolytic graphite surfaces because o the extensive use of this material for electrothermal atomization sources. However, high-temperature tantalum surfaces have been investigated and atomization mechanisms on high-temperature quartz surfaces, such as those used in hydride generation spectroscopy, have been studied. A unique two-step furnace vaporization system is providing controlled vaporization and atomization in order to quantify preatomization losses that have been identified by the real-time mass spectroscopy. Mechanisms controlling the electrothermal atomization of meta halides is currently under investigation. Data on molecular, near surface, bulk diffusion in high-temperature pyrolytic graphite are also being obtained. [1.1 FTE]

Heavy Element Chemistry

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $1,797,000

113. Heavy Element Chemistry Research

Nash, K.L.; Morss, L.R.; Appelman, E.H.; Beitz, J.V.; Soderholm, L.
708-252-3667

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 ultimate objectives of this program are to exploit the distinctive properties of the f-elements in the development of new chelating agents, to develop a predictive understanding of the properties of f-elements, to compare and contrast the chemistry of these elements in solid and solution states (with d-transition elements), and 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 elucidate the basic chemistry (thermodynamics and kinetics) of coordination complexes in aqueous solutions to better design more effective and selective chelating agents, and to address their decomposition. (2) Heavy element spectroscopy considers the electronic structure, photophysics, and photochemistry of f-elements to provide insight into the chemical consequences of excited state formation, and the dynamics of relaxation modes in solids, solutions, and gases. (3) The f-electron interactions program explores the relationships between the electronic structure of f-elements in solids, and properties such as crystal structure and magnetic susceptibility. Cooperative properties like magnetic ordering and superconductivity are modeled using insights gained from these studies. [7.0 FTE]

Lawrence Berkeley Laboratory
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Berkeley, CA 94720

Chemical Sciences Division $1,510,000

114. Actinide Chemistry

Edelstein, N.M.
510-486-5624

Development of new technological processes for the use, safe handling, storage, and disposal of actinide materials relies on the further understanding of basic actinide chemistry and the availability of a cadre of trained personnel. This research program is a comprehensive, multifaceted approach to the exploration of actinide chemistry and to the training of students. Research efforts include synthetic organic and inorganic chemistry for the development of new chemical agents and materials; their chemical and physical elucidation through various characterization techniques; and thermodynamic and kinetic studies for the evaluation of complex formation. One aspect is the development and understanding of complexing agents that specifically and effectively sequester actinide ions. Such agents are intended for the decorporation of actinides in humans and in the environment. Extensive studies are under way to prepare organometallic and coordination compounds of the f-block elements that show the differences and similarities among the f-elements, and between the f- and d-transition elements. Optical and magnetic studies on actinides provide information about electronic properties as a function of atomic number. The construction of an actinide branch line and endstations at the Advanced Light Source to measure directly the electronic structure of actinide materials has been proposed. [11.0 FTE]

Nuclear Science Division $153,000

115. Chemistry of the Heaviest Elements

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

The objective of this project is the determination of the chemical properties of the heaviest elements to determine the architecture of the periodic table of the elements at its furthest reaches and to assess the influence of relativistic effects in these heaviest elements, and throughout the periodic table. A program to investigate some of the most fundamental chemical properties of elements 102 through 106 is being undertaken. 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 the range and stability of other oxidation states in aqueous solutions. Detailed comparisons of transactinide chemical properties with those of their homologs are being made by studying the formation and stability of anionic complexes in aqueous solution. Attempts are continuing to try to produce and identify new, longer-lived isotopes of the heaviest elements which 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 $365,000

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

The primary goals of the program are the investigations of the solution chemistry, spectroscopy, and theory of the early actinide elements as a function of oxidation state and coordination environment. From these studies, insight is gained into the role of 5f-orbitals in chemical reactivity and structural properties. During the past year, investigations of the preparation of actinide complexes in novel carbocyclic coordination environments have continued with the extension of mixed-ring (cyclopentadienyl/cyclooctatetraenyl) chemistry to include the trivalent oxidation state. Reaction of the uranium(III) complex, $(C_5Me_5)(C_8H_8)U(THF)$, with trimethylsilyl iodide results in the formation of the unusual bridging iodide species, $[(C_5Me_5)(C_8H_8)U(\mu\text{-}I)]_x$, which has been structurally characterized. Halogen abstraction reactions of trivalent uranium halide and alkoxide complexes have also been studied, leading to an interesting series of mixed halide and alkoxide–halide complexes. The investigation of high-valent uranium chemistry has brought to light interesting counterion effects in metathesis reactions of the uranyl ion with the bis(trimethylsilyl)amide ligand. Finally, an interesting dichotomy in the chemistry of uranium(IV) and thorium(IV) has been elucidated in alcoholysis reactions to produce the tetrahedral aryloxide complexes $An(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$. [0.6 FTE]

117. Actinide Chemistry in Near-Neutral Solutions
Hobart, D.E.; Clark, D.L.
505-667-9313

The project objective is to provide fundamental physicochemical knowledge pertinent to the behavior of plutonium and other actinides under environmental near-neutral pH conditions. Thorium through plutonium silicates have been prepared by a hydrothermal method, and characterization of naturally occurring actinide silicate minerals is progressing. Silicates are major anions in the host rock for the proposed Yucca Mountain nuclear waste repository site. The dynamic behavior of ligand exchange between free and coordinated carbonate ions on plutonium(VI) and americium(VI) carbonate complexes has been examined by ^{13}C nuclear magnetic resonance (NMR) line-broadening techniques. Solution NMR provides a species-sensitive probe for these complicated and environmentally relevant systems. This work constitutes the first direct observation of any americium species by NMR. X-ray absorption spectroscopy (XAS) studies of neptunium(V) sorption on the iron hydroxy-oxide mineral, *goethite*, have been published. The study of ethylenediaminetetraacetic acid (EDTA) and siderophore complexation of Pu(IV) has progressed. 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. Solution spectra have been analyzed and attempts have been made to produce single crystals of Pu-EDTA complexes for solid-state structural determinations. [0.6 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemistry Division $1,293,000

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

An understanding of the chemistry and physics of the actinides and transactinides is being developed systematically by determining their thermochemical, structural, and electronic properties as a function of electronic configuration. Experimental studies are focused primarily on the Cm through Fm elements that are produced in the High Flux Isotope Reactor. The high-pressure behavior of actinide elements, alloys, and compounds yields unique information concerning 5f-electron delocalization, bonding systematics, and critical atom–atom separations. Thermodynamic information is obtained utilizing solution calorimetry, high-temperature mass spectrometry, differential thermal analysis/scanning calorimetry experimental techniques, as well as theoretical calculations. Mass spectrometry studies search for and characterize new gas-phase species of the actinides that exist in unusual oxidation states. Relativistic quantum mechanical calculations provide electronic structures and properties (ionization potentials, radii, and so forth) and bridge the actinides and transactinides. Solid-state spectroscopy (Raman, luminescence, fluorescence, absorption) is used to define structural environments and electronic levels and transitions in actinide materials. Future research thrusts include (1) examining the electronic structure and dynamics of transplutonium free atoms and molecules by electron spectroscopy and (2) photoionization studies of actinide materials through the use of time-of-flight mass spectrometry coupled with a tunable laser. [6.2 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Sciences Division $170,000

119. 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

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

The interaction between fluid mechanical turbulence and chemical reactions in laboratory-scale premixed and nonpremixed turbulent flames is studied experimentally using laser diagnostic techniques. A theoretical/numerical study of premixed turbulent flames using the two-dimensional vortex dynamics method is also being conducted. The objective is to obtain a better understanding of the fundamental physical processes controlling turbulence–combustion interactions. Such knowledge is basic to the development of theories that can address a variety of practical combustion problems that are relevant to combustion efficiency and pollutant emissions. At present, experiments are focused on studying flame conditions with fluid mechanical time scales much larger than those of chemical reactions. Simplified theoretical treatment of these flames is possible and several models have been developed that need experimental validation and verification. The experiments are focused on obtaining space and time resolved statistical data of scalar and velocity fluctuations to study the effects of large heat release on the turbulent flow fields of four flame configurations, and using planar laser imaging techniques such as high speed cine tomography to determine the scales of the flame structures. The statistical data are compared with model predictions in addition to determining the effects of turbulence intensity on the burning rates. The tomographic data are analyzed by the fractal technique to investigate the spatial scales of the flame. These scalar scales are directly related to the burning rate of premixed turbulent flame under these experimental conditions and are the source terms in many theoretical models. [3.0 FTE]

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

Theoretical Division $87,000

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

The thermophysical properties of mixtures of particles interacting through simple interaction potentials are evaluated, using both equilibrium Monte Carlo (MC) and molecular dynamics (MD), as well as nonequilibrium molecular dynamics. The properties under investigation include the equation of state and transport properties, including mutual and self diffusion, shear and bulk viscosity, thermal conductivity, and thermal diffusion. Fundamental questions arising in the theory of fluids and fluid mixtures are addressed where numerical "experiments" are appropriate. MCMD calculations for equimolar, binary, hard-sphere mixtures having mass ratio 0.03 and diameter ratio 0.4 (similar to helium–xenon) have been completed (including corrections for large system size and Green–Kubo time) for low-to-moderate fluid densities, to obtain the first density corrections to the mean free time and the transport coefficients predicted by the Boltzmann and Enskog theories respectively. The linear (in density) corrections for the transport coefficients are small (0.1 to 0.2 of V_0/V, for V the volume and V_0 the close-packed volume of an equivalent pure hard-sphere fluid), positive for the shear viscosity and negative for the others. By virtue of the smallness of these corrections, the Enskog theory provides a rather accurate account of the transport properties even in a mixture of spheres of such discrepant diameters. In addition to extending these calculations to higher density, effort has begun on the study of chemical reaction at fluid densities. A hard-sphere, square-well model has been devised as a simple but realistic alternative to the artificial "predissociative" potential and the rather elaborate Tersoff potentials. The implications of the model are under consideration. [0.5 FTE]

Sandia National Laboratories, Livermore
Livermore, CA 94551

Combustion Research Facility $371,000

122. 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. Calculations of three-dimensional Navier–Stokes flow combined with a field equation for constant density premixed flame propagation reveal that two-dimensional images do provide a statistical measure of flame curvature. The probability of surface geometry and the relationship with strain rate will guide future flame calculations with realistic chemistry. Vortex dynamics simulations of a pulse combustor have shown, by comparison with experiment, that strain rate quenching of a premixed flame is a key in the energy release rate, which governs the successful operation of these combustors. 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. Results from this work will contribute to the basic understanding of turbulent reacting flows, assist in planning experiments, and aid in interpreting experimental data at the Sandia Combustion Research Facility (and elsewhere), and improve capabilities for predictive modeling of reacting flows in practical geometries. [1.7 FTE]

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Akron
Akron, OH 44325

Department of Chemistry

123. *Dynamics of Charge Transfer Excited States Relevant to Photochemical Energy Conversion*
Lim, E.C. **$120,000**
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

124. *Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids*
Kispert, L.D. **$88,790**
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. Studies of carotenoids have shown that the first excited singlet state lifetime of β-carotene equals 10 picoseconds and lengthens as the conjugated chain length decreases. The short lifetime is a result of nonradiative decay mechanisms within the carotenoids. Simultaneous electrochemical and electron paramagnetic resonance (EPR) measurements indicate that upon oxidation of canthaxanthin, 96% carotenoid cation radicals are formed, while 99.7% dications are formed upon the oxidation of β-carotene, 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 carotenoid cation radicals are in excellent agreement with the electron nuclear double resonance (ENDOR) measured methyl proton couplings and the planar configuration of the polyene chain. Attempts are under way to manipulate the host matrix in such a manner as to understand the carotenoid function (i.e., protection, quenching, energy transfer, and antenna) and to ultimately develop predictive mechanisms for directing the outcome of photochemical events.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

125. *Photoinitiated Electron Transfer in Multichromophoric Species–Synthetic Tetrads and Pentads Featuring Diquinone Moieties*
Gust, J.D., Jr.; Moore, T.A.; **$166,000**
Moore, A.L.
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.

University of Arizona
Tucson, AZ 85721

Department of Biochemistry

126. *Photochemical Energy Conversion by Membrane-Bound Photoredox Systems*
Tollin, G.
602-621-3447

Mechanisms of photochemical electron transfer in chlorophyll-containing lipid bilayer vesicles are being investigated using laser flash photolysis and electrochemical techniques. Current effort is being spent on developing strategies for use of redox proteins as electron donors and acceptors for photochemical energy storage, and on studies of the mode of interaction of such proteins with lipid bilayers using nuclear magnetic resonance (NMR), cyclic voltammetric, and photoelectrochemical methods. Kinetic measurements and time-resolved difference spectra are used to elucidate the sequence of electron transfer and the reaction mechanisms. Both peripherally bound redox proteins (e.g., plastocyanin, cytochrome *c*, and ferredoxin) as well as integral membrane proteins (e.g., cytochrome oxidase) are being investigated. Present studies use systems that carry out vectorial electron transport across the bilayer between redox protein donors and acceptors and those carrying out multistep electron transfers involving quinone or viologen mediators and several redox proteins in a linear or cyclic sequence. Lipid molecules covalently modified by attachment of redox mediators and protein binding sites are being used to facilitate transbilayer electron flow. The primary goal is to achieve conditions in which light energy is efficiently stored in redox products that can be coupled to such potentially useful systems as hydrogen generation, nitrogen fixation, and proton translocation, or used in direct conversion to electricity.

Boston University
Boston, MA 02215

Department of Chemistry

127. *Study of Intermediates from Transition Metal Excited-State Electron-Transfer Reactions*
Hoffman, M.Z. **$118,000**
617-353-2494

Transition metal coordination complexes, especially those of Ru(II), serve as photosensitizers in model photochemical systems for the conversion and storage of light energy. The electron-transfer quenching of the excited state of the photosensitizer results in its 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 preparation and characterization of Ru(II)-tris-homo- and heteroleptic complexes containing di-, tri-, and tetraazine ligands; (2) the determination of cage escape yields in the oxidative and reductive quenching of the excited states of Ru(II) and Cr(III) complexes as a function of the energy gap between the redox products, the nature of the solution medium, and the temperature; (3) the properties of one-electron reduced Ru(II) complexes; (4) the reductive quenching of the excited state of $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine); and (5) the photosensitized initiation of polymerization and oxidation of phenol and its derivatives.

128. *Photoinduced Electron Transfer in Ordered Polymers*
Jones, G. **$110,000**
617-353-2498

Investigations concern the photochemistry of biopolymer systems that have been modified with covalently or electrostatically bound dye molecules. An objective of the research is the demonstration that electron transfer between bound dye and pendant groups that are native to the biopolymer can be observed and that charge migration along the polymer surface among electroactive groups is important. The efficiency of electron or hole migration along the polymer chain is expected to depend on the helicity of the biopolymers selected for study and the characteristic interaction of neighboring organic functional groups. Three dye/polymer systems have been most recently investigated. (1) Poly-L-tryptophan modified by attachment of the organic dye, eosin, at the N-terminal residue of the peptide has been studied by laser flash photolysis in terms of electron or hole transfer between the dye moiety and biopolymer side chains. (2) Several peptides have been prepared that contain electroactive (tryptophan and tyrosine) and nonelectroactive residues (alanine) which permit the spacing of electron donor and acceptor groups (including a dye conjugate) at intervals of varying distance for study of photoinduced electron transfer rates. (3) Polyelectrolytes related to polyacrylic acid have been used to electrostatically bind (heavily load) aggregates of dye molecules such as crystal violet and pseudoisocyanine; electron transfer between dye aggregates and co-bound groups on the polymer chain has been investigated. In these studies emphasis is placed on the opportunities provided with synthetic biopolymers for design of proximal groups for electron transport and the potential role of secondary structure of modified biopolymers in controlling charge separation.

Brandeis University
Waltham, MA 02254

Department of Chemistry

129. *Mechanistic Studies of Excited State Chemical Reactions*
Linschitz, H.
617-736-2506

This program is designed to clarify the mechanisms of photochemical redox reactions in homogeneous solution, in order to understand better the factors controlling efficiencies of energy conversion (primary quantum yields) in these processes. These factors include thermodynamic parameters and kinetic variables such as temperature, viscosity, and solvent polarity. For triplet excited states, which favor efficient radical separation, mechanisms for spin relaxation within the primary reaction complex play a key role. Of particular interest are the photophysics and photochemistry of porphyrins. Two large classes of these compounds being studied are (1) new derivatives which exhibit charge-transfer (quinoid) excited states and (2) ion-paired "dimers" which are analogs of structures found in natural photosynthesis. Molecular "reorganization" effects, which strongly influence rates of all redox processes, are being studied in quenching reactions of aquoanions and cations, and in photoprocesses involving competitive electron and H-atom transfer. Photochemical processes in fullerenes are being identified and characterized.

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

130. Picosecond Dynamic Studies of Electron Transfer Rates at III–V Semiconductor/Liquid Interfaces

Lewis, N.S. **$125,000**
818-356-6335

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 of light emission and photocurrent transients 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 solution. Excess holes and electrons are created by a picosecond light pulse, and then recombine via various pathways, including the one of primary interest—interfacial charge transfer. This 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. Chemical modification of the interface is then performed, and light emission decays are then monitored, in order to determine the kinetic changes induced by surface modification. Transition metal ions have been found to enhance the rates of charge transfer, which is in agreement with earlier measurements on related systems in this laboratory. While it might be expected that interfacial charge transfer rates could also be obtained from measurements of light-induced current decays, the effects of RC shaping on these electrical signals must be investigated. Studies of photocurrent transients in the n-Si/CH_3OH/dimethylferrocene and n-TiO_2/H_2O/NaOH systems have produced strong evidence for the insensitivity of these measurements to charge transfer kinetics. Instead, an equivalent circuit consisting of a series arrangement of semiconductor space-charge and solution double-layer elements has been found to explain the experimental results adequately. The photocurrent responses have been found to be dominated by the external circuit resistance and space-charge capacitance, and the form of the decays has been altered by deliberate manipulation of each variable. This project will be extended in the future to cover other semiconductor and liquid combinations of importance in solar energy conversion schemes.

University of California, Berkeley
Berkeley, CA 94720

Department of Chemistry

131. Theoretical Studies of Electron Transfer in Complex Media

Chandler, D. **$80,000**
415-643-6821

The structures, dynamics, and free energies of the transition states for the prototypical aqueous ferrous–ferric electron-transfer reaction have been determined by computer simulation through application of a novel sampling procedure. The research on this system 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

132. Research in Chemical Kinetics

Rowland, F.S. **$175,000**
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. Thermalized ^{38}Cl atoms added to the terminal olefinic position in $Sn(CH{=}CH_2)_4$ or $As(CH{=}CH_2)_3$ form $(CH_2{=}CH)_xMCH{-}CH_2{}^{38}Cl^*$ 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 (CFC) 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.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

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

El-Sayed, M.A. **$132,000**
310-825-1352

The conversion of solar energy into chemical energy in the form of 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 PSB, (4) proton pumping leading to proton gradients, and (5) electric to chemical energy transformation by conversion of ADP into ATP. These studies deal with steps one through three. The function of the protein during the photocycle has been examined in a systematic (but indirect) manner. The effect of temperature and pH changes on the photocycle kinetics revealed the changes of the mechanism of the deprotonation process at pH = 10–11. The protein structure near the active site seems to open up in this pH range leading to a diffusion controlled deprotonation process rather than one that is determined by the rate of the protein conformation changes that occur under physiological conditions. The effects of different amino acids on the kinetics of the cycle have been examined by studying different mutants. The important of metal cations (e.g., Ca^{2+}) on the proton pump is well known in bR. The reason is not yet understood. A program aimed at determining the binding constants of the Ca^{2+} at different binding sites was started. Two high affinity and four weak affinity sites are observed. The binding of Ca^{2+} to the high affinity sites displaces two protons each, suggesting the binding involves two conjugate acids (e.g., aspartates or glutamates). The efficiency of the proton pumping process is found to be related to the fraction of Ca^{2+} ions bound to the site, next to the one with the highest affinity. It is hoped that energy transfer and single site mutation studies can assist in determining the distance of the metal cations from retinals and the amino acids involved in their binding.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemistry

134. Cyclometallated and Cyclometalsilylated Complexes of Transition Elements as Photoredox Sensitizers

Watts, R.J. **$105,000**
805-893-2032

This program researches the effects of visible irradiation of metal complexes in condensed media. The range of physical phenomena resulting from interaction of these complexes with visible light includes absorption and emission, intramolecular radiationless transitions, bimolecular energy transfer, bimolecular electron transfer, photoisomerization, photochemical degradation, solvent rearrangement, photovoltaic effects, and photoelectrolytic effects. This range of phenomena is under study with a variety of spectroscopic, photochemical, structural, and electrochemical methods that emphasize the use of pulsed lasers to probe fast kinetic events subsequent to light absorption. The metal complexes at the focal point of this program are characterized by the presence of metal–carbon and/or metal–silicon bonds, and include d^6 metal ions such as Ir(III), Rh(III), and Ru(II) as well as d^8 metal ions such as Pt(II) and Pd(II). Common themes that unite studies of these types of metal–ligand combinations are the relatively electron-rich nature of the metal centers and the presence of low-energy charge-transfer excited states with long lifetimes. These fundamental properties contribute to the potential use of many of these complexes as strong photoreducing agents and as molecular probes to study rearrangement of the solvent cage subsequent to excited state formation. A recent adaptation of this research has been in preparation of metal complexes in which two coordination sites are occupied by easily displaced solvent ligands. These complexes are being deposited on platinum electrode surfaces as a preliminary step toward studying their possible participation as electrocatalysts and/or photoelectrocatalysts for reduction of carbon dioxide.

Clemson University
Clemson, SC 29634

Department of Chemistry

135. Intramolecular Energy- and Electron-Transfer Reactions in Polymetallic Complexes

Petersen, J.D. **$82,424**
803-656-5017

Research has utilized the preparation of multimetal systems to couple covalently a highly absorbing metal center (antenna fragment) to a second metal center capable of carrying out a useful chemical reaction (reactive fragment). This molecular design has been used in both excited-state energy- and electron-transfer processes. On the basis of previous studies, with Rh(III)-based reactive fragments, the reactive, excited state was lowered by using Co(III) homologs. The photochemistry of $[(NC)_3Fe^{II}(tpp)Co^{III}(PPh_3)H_2]$

and $[(tpy)Ru^{II}(tpp)Co^{III}(PPh_3)H_2](PF_6)_3$, where tpp = 2,3,5,6-tetrakis(2-pyridyl)pyrazine and tpy = 2,2′:6′,2″-terpyridine, display photoproduction of H_2 at an irradiation threshold of $1.8 \mu m^{-1}$. These latter systems are not as thermally stable as the Ru/Rh systems, since the mono phosphine systems do not stabilize the dihydride. In the area of optically induced charge separation, three component systems have been prepared. The central portion of the system is an antenna fragment whose function is to absorb light. An additional requirement is that the excited-state, antenna fragment undergo facile redox processes. Coupled to this fragment are two metal centers, one containing an electron donor and one containing an electron acceptor. One of the initial systems, $(NC)_4Fe^{II}(bpm)Ru^{II}(tpy)(4,4'\text{-}bpy)Rh^{III}(bpy)_2(MQ^+)^{4+}$, where bpy = 2,2′-bipyridine, bpm = 2,2′-bipyrimidine, 4,4′-bpy = 4,4′-bipyridine, and MQ^+ = N-methyl-4,4′-bipyridinium (monoquat), shows that irradiation at the Ru(II) shows emission quenching presumably caused by excited-state, electron transfer to MQ^+. Another system involves a metal polymer spacer, based on Cu(II) between the Ru(II) absorber and a quinone acceptor.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

136. Reaction Kinetics and Product Distribution in Photoelectrochemical Cells

Koval, C.A. **$98,985**
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. A new system has been developed for the detection of "hot" electrons ejected from p-InP photocathodes at energies above the conduction band edge. The reaction involves the reduction of 1,2-dibromoethylbenzene 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. Extension of this system to other p-type materials and for use in collaborative picosecond kinetic studies is anticipated. The second process under investigation is kinetics of electron transfer 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 two-dimensional semiconductors such as n-WSe_2. For couples located in the bandgap, concentration studies indicate that the rate determining step is not a "bimolecular" reaction of majority carriers at the surface of the semiconductor with molecules in solution as predicted by theory. The third process is photo-facilitated membrane transport. This is a new project to explore the use of solar energy for selective separation processes. One component in a mixture is extracted into a membrane by reaction with a membrane-bound carrier. The reaction is reversed photochemically at the opposite side of the interface allowing the selected component to be driven uphill against a concentration gradient.

Columbia University
New York, NY 10027

Department of Chemistry

137. Charge Generation and Separation at Liquid Interfaces

Eisenthal, K.B. **$130,000**
212-854-3175 **(15 months)**

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≡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.

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

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

This project describes the development and application of novel theoretical methods to the microscopic calculation of electron transfer, energy transport, and optical spectra of molecular systems of importance in solar photochemistry. The theoretical methods include a new algorithm for ab initio electronic structure calculations, a semiclassical surface hopping approach to hot electron dynamics, efficient techniques for diffusive energy and charge transport simulations, numerical methods for determining the optical spectra of large tight binding and one-electron pseudopotential Hamiltonians, and a strategy for solving the Redfield equations for a large number of system levels. These methods will be applied to the following specific problems: (1) calculation of electron-transfer matrix elements of rigid, bridged donor–acceptor molecules; (2) simulation of the optical spectra of semiconductor particles; (3) determination of the survival probability of excitation diffusing on a polymer with traps, and the relationship of this process to the polymer geometry; (4) electrochemical simulations in complicated geometries; (5) simulation of hot electron dynamics at the semiconductor/liquid interface; and (6) fundamental investigation of the effects of strong electronic coupling on energy and electron transfer, in the context of recent experimental studies of energy transfer in the photosynthetic reaction center and electron transfer mediated by DNA.

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

Valentini, J.J. **$90,000**
212-854-7590

This research project addresses the dynamics of chemical reactions and energy transfer collisions of reactive species having excited internal energy states or hyperthermal translational energies. Current emphasis in the project is on the reactions of free radicals such as H, OH, and CH_3 with H_2, CH_4, and other hydrogen containing polyatomic molecules, reactions which are important in combustion. The research is primarily experimental. It uses laser excitation methods to prepare initial quantum states of the molecular reactants, laser photodissociation of appropriate precursors to generate the reactant free radicals and control the collision energy, and laser spectroscopic measurement of 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. These experimental measurements are complemented by theoretical calculations of the measured quantities as a way of developing detailed molecular-level understanding of the dynamics. Of necessity some of the work on the project involves the development of laser spectroscopic techniques for reactant state preparation and product state analysis, and also the development of computational techniques for the theoretical calculations.

Department of Electrical Engineering

140. *Photogenerated Carrier-Induced Reactions on 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) and temperature programmed desorption (TPD) under ultrahigh vacuum (UHV) conditions has revealed several new fundamental mechanisms for photochemistry on semiconductor surfaces. Photodissociation of Cl_2 by UV wavelengths causes the desorption of Cl atoms and formation of $AsCl_3$. At 351 nm, TOF studies reveal direct absorption to a dissociative state resulting in photofragmentation; at 193 and 248 nm, charge transfer between adjacent molecules initiates fragmentation. For CCl_4, postirradiation TPD of GaCl shows a clear threshold that coincides with the GaAs band-gap, the wavelength dependence shows that adsorbate dissociation is promoted by substrate electron-hole pairs. This mechanism is also operable for CH_3Br, at less than monolayer coverage, as determined by the wavelength independent kinetic energy of the CH_3 radicals at UV and visible wavelengths. Above one monolayer, dissociation proceeds by two independent channels, dissociative electron attachment and direct absorption, as shown by a 1 eV CH_3 TOF feature at 248 and 193 nm and a 2.5 eV feature at 193 nm. Furthermore, the direct absorption TOF signal oscillates as a function of coverage for thick layers, because of optical interference between the incident laser beam and its reflection. The effect provides a new method for measuring molecular orientation in adsorbed layers.

Dartmouth College
Hanover, NH 03755

Department of Chemistry

141. *Photoexcited Charge Pair Escape and Recombination*

Braun, C.L. **$75,000**
603-646-2500

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is studied in solids and liquids. Measurement of transient absorption by electrons is used to resolve the picosecond time scale recombination of the geminate charge pairs formed by laser photoionization of solute molecules in liquid hexane. The observed decay kinetics are studied as a function of temperature and photon energy and are found to be consistent with a detailed theory of Coulomb-field-dominated, diffusive recombination of geminate electron-cation pairs. The kinetic measurements give direct information about the initial distribution of electron-cation radii in the thermalized charge pairs. In solid-state electron donor-acceptor materials comprised of organic molecules, the escape and recombination mechanism is apparently quite different. Photocurrent that arises from single-photon excitation in the charge-transfer absorption band of the 1:1 mixed crystal, phenanthrene:pyromelliticdianhydride rises in less than a few nanoseconds. Thus, the observed photocurrent does not originate from dissociation of the relaxed charge-transfer (CT) excited state that is observed by fluorescence to have a lifetime of 12 nanoseconds. It is possible that the fast-rising photocurrent originates from reorientation of the CT exciton in an applied electric field. Attempts to assess that possibility led to the discovery that the reorientation of dipolar excited states (in solution) can be followed by time-resolved conductivity measurements. That technique may be generally useful for quantifying the subnanometer motion of charge pairs. In order to understand factors that limit efficient charge-pair separation in such charge-transfer solids, various donor-acceptor geometries are being explored.

University of Houston
Houston, TX 77204

Department of Chemistry

142. *Charge Separation in Photoredox Reactions*

Kevan, L. **$125,000**
713-749-3732

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 photoreduction of alkylmethylviologens 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 alkylphenothiazine negatively and positively charged derivatives has been studied. 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

143. *Resonance Raman and Photophysical Studies of Transition Metal Complexes in Solution and Entrapped in Zeolites*
Kincaid, J.R. **$83,000**
414-288-3539

The long term goal of the project involves the study of the photochemical and photophysical properties of transition metal complexes of nitrogen heterocycles (especially polypyridines and related ligands). Current interest is focused on the effect of ligand asymmetry; either inherent or environmentally induced. Specifically, resonance Raman (RR), time-resolved resonance Raman (TR^3), and lifetime measurements are used to investigate the structure and dynamics of the ground and ^{3}MLCT excited states of asymmetric bipyridine complexes of ruthenium(II) under various conditions (i.e., dissolved in various solvents or trapped in the supercages of Y-zeolite). Studies have been completed on complexes comprised of the inherently asymmetric ligands pyridyl-pyrazine and 4-methyl-2,2′-bipyridine. In addition, a relatively large number of zeolite-entrapped heteroleptic complexes involving the ligands bipyridine, bipyrazine, bipyrimidine, 4,4′-dimethyl bipyridine and 4-methyl-2,2′-bipyridine have been prepared and characterized by absorption, emission, RR, and TR^3 spectroscopies. The results indicate that the zeolite cavity in some cases induces shifts in emission maxima and also affects the lifetime of the ^{3}MLCT state.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

144. *Photochemical Approaches to Conversion of Light to Electricity or Fuel*
Wrighton, M.S. **$325,000**
617-253-1597 **(16 months)**

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

145. *Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions*
van Willigen, H. **$118,000**
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. Measurements have been performed also on donor–acceptor systems solubilized in micelles or adsorbed in the pores of silica gel.

University of Minnesota
Minneapolis, MN 55455

Department of Chemistry

146. *Ultrafast Studies on Intermolecular Electron Transfer in Contact and Solvent-Separated Ion Pairs*
Barbara, P.F. **$150,000**
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. The proposed experiments and analyses will clarify and test several of the conventional assumptions and theoretical conclusions of contemporary electron transfer theory.

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

Lipsky, S. **$99,999**
612-624-9581

Photophysical properties of organic molecules are being studied that have relevance in determining their behavior when subjected to high-energy radiation. Because ion pairs are important precursors of chemical damage in irradiated liquids, recent studies have concentrated on their properties. The ion pairs are generated by photoionization, and their decay is observed by (1) recombination (to give fluorescence) and (2) "escape" (to give photocurrent). Observations are made as functions of photon energy, nature of the liquid, and strength of externally applied electric and magnetic fields. Current work includes (1) measurements of fluorescence spectra and fluorescence quantum yields from recombining geminate positive ions and electrons in neat hydrocarbon liquids as a function of excitation energy (this study gives information on the nature of the intermediate electronic states that are generated during the annihilation process); (2) measurement of the effect of a magnetic field on geminate ion recombination fluorescence induced by pulsed vacuum ultraviolet excitation of neat hydrocarbon glasses (the magnitude of this effect provides information on loss of spin coherence during the time interval of recombination); and (3) measurement of the electric field dependence of the photocurrent spectra of anthracene in hydrocarbon solutions. From these data are developed theoretical models of the nature of the ionizing transition in liquids.

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

Chemical Kinetics and Thermodynamics Division

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

Neta, P.
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 of metal ions. Reactions are studied in both aqueous and nonaqueous solutions. The studies focus on the unique ability of pulse radiolysis to provide absolute rate constants for reactions of many inorganic radicals and organic peroxyl radicals, species that are key intermediates in many chemical processes. A special emphasis of this work is the study of electron transfer reactions of metalloporphyrins that may be applicable to solar energy conversion systems. These include the one-electron reduction and oxidation of metalloporphyrins, either the ligand, to produce π-radical anions and cations, or the metal center, to form unstable oxidation states. Subsequent reactions of the resultant species with colloidal catalysts may lead to solar energy storage (e.g., to decomposition of water to hydrogen and oxygen). For these studies, pulse radiolysis is utilized to characterize specific reactions, and photochemical experiments are carried out to measure the yields of products.

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

Department of Chemistry

149. *Excited State Processes in Transition Metal Complexes. Applications to Redox Splitting in Soluble Polymers*

Meyer, T.J. **$130,000**
919-962-6319

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 stabilities and lifetimes to be predicted. 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 being investigated systematically. Synthetic methods have been developed for attaching derivatives of these complexes to soluble polymers along with organic fragments which can act as electron or energy transfer donors or acceptors. Studies on these complex arrays show that polymers can be designed in which photoinduced electron or energy transfer events can be initiated and controlled on single polymeric strands. Polymeric systems are currently being designed that will mimic the light-harvesting, electron transfer capabilities of the reaction center of photosynthesis, and provide a basis for exploring long-range electron or energy transfer.

University of North Carolina at Charlotte
Charlotte, NC 28223

Department of Chemistry

150. Oligomer and Mixed-Metal Compounds: Potential Multielectron Transfer Agents

Rillema, D.P. **$98,000**
704-547-4445

The design and synthesis of potential solar energy photocatalysts is the focus of the investigation. Details regarding the photophysical properties of copper(I), platinum(II), rhenium(I), and a bimetallic rhenium(I)/ruthenium(II) complex were examined. The copper(I) complex contained the 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane ligand and underwent featureless emission at 692 nm (λ_{ex} = 450 nm) in a 4:1 EtOH:MeOH glass at 77 K. The platinum(II) complex contained biphenyl dianion as a bidentate ligand along with pyridine or acetonitrile occupying the other two coordination sites. Excitation at 355 nm in solution at room temperature resulted in ligand centered emission which could be theoretically matched by computer simulation allowing for deduction of E_{oo}, $\hbar w$, S and $\Delta\bar{\upsilon}_{1/2}$-values. Temperature dependent emission lifetimes allowed for determination of the energy of activation for populating a ligand field state from the emitting state. The rhenium(I) complexes contained four carbonyl ligands and a heterocycle such as 2,2′-bipyridine. These tetracarbonyl complexes emitted in fluid solution at room temperature at approximately 490 nm when excited at 355 nm and underwent photochemical loss of carbon monoxide upon steady state irradiation. The rhenium/ruthenium complex containing rhenium(I) and ruthenium(II) bridged by 1,2-bis(4-methyl-2,2′-bipyridyl-4-yl)ethane luminesced at 602 nm in fluid solution at room temperature. Excitation at 355 nm into the rhenium(I) chromophore resulted in energy transfer to the ruthenium(II) site enhancing the emission intensity at 620 nm.

Northwestern University
Evanston, IL 60208

Department of Chemistry

151. Dynamic Structural Effects and Ultrafast Bimolecular Kinetics in Photoinduced Charge Transfer Reactions

Hupp, J.T. **$125,000**
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) studies of ultrafast bimolecular redox quenching of very short-lived excited states, based on greatly accelerated diffusional transport in a supercritical medium. A significant accomplishment during the current year has been the induction of redox isomerization (intramolecular ET) in polypyridyl bridged metal systems by selective solvation and by selective polyether ligand (second sphere) binding. Time resolution of the former has been achieved for a prototypical system, $(bpy)_2ClOs$-trimethylenebipyridine-$Ru(NH_3)_5^{4+}$, via an unusual method: pulsed accelerated-flow spectroscopy. Under mildly exothermic final conditions (ca. 2 kcal/mole) electron transfer (ET) is fairly slow ($k = 2 \times 10^4 s^{-1}$). This may be contrasted with the observation of much faster ET kinetics ($k = 3 - 50 \times 10^{12} s^{-1}$) for a family of highly exothermic, cyanide-bridged metal–metal systems.

152. Vibrational Dynamics in Photoinduced Electron Transfer

Spears, K.G. **$128,241**
708-491-3095 **(14 months)**

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

153. Photoinduced Electron Transfer Reactions in Zeolite Cages

Dutta, P.K. **$85,000**
614-292-4532

Photochemistry in constrained heterogeneous medium offers opportunities for stabilizing photodriven redox products that cannot be readily done in homogeneous solution. Towards 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. The novelty of the zeolite architecture allows for synthesis of $Ru(bpy)_3^{2+}$ molecules within its cages as a function of controlled contact with neighboring $Ru(bpy)_3^{2+}$ molecules. At the highest possible loading, the $Ru(bpy)_3^{2+}$ molecules are arranged in a tetrahedral packing. Major spectral perturbations, including a red-shift of the metal-to-ligand charge transfer (MLCT) band, shifts in bipyridine ring breathing modes, emission, and lifetime quenching are observed. The highly polar nature of the intracrystalline space and the dense packing of $Ru(bpy)_3^{2+}$ molecules resembles the effects of elevated pressures. Intrazeolitic photoelectron transfer reactions between $Ru(bpy)_3^{2+}$ and methylviologen in neighboring cages were observed. The interesting aspect of this reaction was the discovery of a pathway that led to long-term stabilization of the redox products. It is proposed that a particular arrangement of stacked methylviologen molecules leads to electron hopping and longer range electron transfer. Efforts are under way to understand this mechanism and improve the efficiency of this process. Layered metal hydroxides have been used as a host to construct membranes, which exhibit novel structural and dynamic features. Incorporation of photosensitizer molecules in the membrane and their photoredox properties are being explored.

Oregon Graduate Institute of Science and Technology
Beaverton, OR 97006

Department of Chemical and Biological Sciences

154. Fundamental Studies in Oxidation-Reduction in Relation to Water Photolysis

Hurst, J.K. **$115,000**
503-690-1073

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, photo-induced 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.

Pennsylvania State University, University Park
University Park, PA 16802

Department of Chemistry

155. The Gaseous Free-Radical and Ion Chemistry of Silanes, Germanes, and Phosphines

Lampe, F.W. **$65,000**
814-865-3029

During the current year emphasis of these studies in gaseous ion chemistry is concentrated on the reactions of GeH_3^+ ions with C_2H_4 and on the formation and properties of SnH_5^+. It was the analogous system of SiH_3^+ ions and C_2H_4 that demonstrated in previous work the unexpected existence of long-lived, energy-rich collision complexes. The previous work in this project had demonstrated the existence of SiH_5^+ and GeH_5^+ and provided the first experimental measurements of the proton affinities of SiH_4 and GeH_4 so it is only a natural extension to attempt to answer the same questions about SnH_5^+ and SnH_4. In the vacuum-ultraviolet photochemistry work, efforts this year are concentrated on the photochemically induced reactions of GeH_2 with HI, and C_2H_4 and on the details of the photodecomposition of SnH_4. None of these systems has been subjected to experimental investigation.

156. Polar Solvation and Electron Transfer

Maroncelli, M. **$135,000**
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

157. *Time-Resolved Studies of Carrier Recombination at the Semiconductor-Electrolyte Interface*

Waldeck, D.H. **$85,000**
412-624-8430

The main emphasis of this project is to develop a quantitative understanding of the kinetics of photogenerated carriers in a semiconductor electrode. The commonly used diffusion model has been shown to neglect important aspects of the semiconductor's electronic properties and of the carrier dynamics. The phenomena which need to be included in a comprehensive, quantitative model are (1) for doped material the bimolecular nature of radiative carrier recombination is important under high excitation conditions and evolves to quasi-unimolecular recombination as the carrier population relaxes; (2) the space charge field influences the recombination, even under pulsed laser excitation, and should be included in a quantitative model; and (3) the influence of surface properties on the recombination has been studied by chemically derivatizing the interface, and the fluorescence decay is shown to be much more sensitive to the recombination than steady-state electrical parameters. Simulations show that the surface recombination velocity of the material can appear dispersive as a result of trap filling at the interface. This phenomenon is a many-body effect and difficult to treat quantitatively. Presently, the modeling of these processes and their influence on the recombination is being developed.

Portland State University
Portland, OR 97207

Department of Chemistry

158. *Asymmetric, Interfacially-Polymerized Porphyrin Films for Artificial Photosynthesis*

Wamser, C.C. **$95,000**
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. 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.

Princeton University
Princeton, NJ 08544

Department of Chemistry

159. *Photoinduced Charge Separation in Solid State and Molecular Systems*

Bocarsly, A.B. **$85,000**
609-258-3888

This study involves the deliberate chemical modification of II-VI semiconductor-based photoelectrochemical cell interfaces in order to arrest photodecomposition processes while enhancing the efficiency of light to electricity conversion. Illumination of a II-VI interface in a $Fe(CN)_6^{4-/3-}$ containing electrolyte is found to produce a layer of cadmium metallocyanide on the electrode surface. This overlayer has alkali cation exchange properties. It is found that the redox properties (energetic and kinetic) of the overlayer can be controlled by intercalation of appropriate cations. Thus, the semiconductor/overlayer interfacial properties can be maximized with respect to both the band structure of the semiconductor and the thermodynamics of the electrolyte. Consideration of this type of interfacial microstructure has led to the development of an n–CdSe based cell (ferrocyanide electrolyte) with good stability and monochromatic light energy to electricity conversion efficiencies (488 nm) of 30 to 40%. Further improvement in the observed photovoltage can be obtained by substitution of $Mo(CN)_8^{4-}$ for $Fe(CN)_6^{4-}$ in the interfacial layer. Once the cyanometalate overlayer has been formed and stabilized, substitution of an optically transparent electrolyte, such as CN^- or ascorbate for the cyanometalate electrolyte, produces an electrolyte suitable for conversion of white light to electricity. To date, electricity conversion efficiencies of 6% have been observed for solar irradiation using an ascorbate electrolyte, while a CN^- electrolyte produces a current doubling effect yielding a limiting quantum yield of 1.8. Improvement in the electrocatalytic behavior of the cyanometalate interface can be accomplished by "doping" small platinum particles into the cadmium ferrocyanide lattice. This is accomplished by reacting the simple salt $PtCl_4$ with ferricyanide in solution and using the product of this reaction as the semiconductor derivatizing reagent. This interfacial system allows for the efficient photooxidation of transparent electrolytes such as methanol and iodide.

University of Rochester
Rochester, NY 14627

Department of Chemistry

160. Photochemistry and Charge Transfer Chemistry of Dithiolate Complexes of the Platinum Group Elements

Eisenberg, R. **$110,000**
716-275-5573

Aspects of light to chemical energy conversion are under investigation in the context of new emissive complexes of platinum. The specific systems being studied are four-coordinate dithiolate complexes of Pt(II) containing either a chelating diimine or diphosphine ligand or bis(phosphine) ligands. The diimine dithiolate complexes exhibit luminescence in fluid solution at 298 K while all of the other complexes emit in rigid media at 77 K. The diimine dithiolate systems also show an intense solvatochromic band that has been probed by systematic ligand substitution. Based on these results, it is concluded that the solvatochromic absorption in these planar four-coordinate complexes corresponds to a Pt(d)/S(p)-π^*(diimine) transition, and this assignment is supported by extended Hueckel molecular orbital (EHMO) calculations and electrochemistry. The emission spectra of several complexes have been examined extensively to determine the nature of the excited state(s) in these complexes. Evidence is found for multiple emitting states in the diimine complexes having a 1,1-dithiolate ligand while only a single emitting state is observed in related systems having a 1,2-dithiolate ligand. For the former the major emissive state at temperatures above 140 K is from a ^{3}(Pt(d)/S(p)-π^*(diimine)) state, whereas for the latter the emission is assigned as ^{3}(Pt(d)/S(p)-π^*(mnt)). Selected diimine complexes are found to undergo both oxidative and reductive quenching of the emission, leading to the possibility that these systems may be viable as photoredox catalysts. For some systems which show interesting properties, poor solubility has limited spectroscopic and photochemical studies. Therefore, new dithiolate ligands and related complexes having greater solubilities are being prepared in order to characterize these systems more fully.

161. Ultrafast Optical Studies of Surface Reaction Processes at Semiconductor Interfaces

Miller, R.J.D. **$90,000**
716-275-4079

Electron transfer processes at interfaces constitute a large and important class of surface reactions. In addition, the rectifying properties of semiconductor interfaces make these systems among the simplest and most efficient systems for converting and storing optical energy. 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 two novel optical techniques (1) surface space charge electro-optic sampling and (2) surface restricted transient grating spectroscopy, to obtain the time evolution of the surface spatial distribution of photogenerated charge carriers and the photocarrier population dynamics at semiconductor interfaces, respectively. These studies have shown that carriers arrive at GaAs(100) surfaces on the hundred femtosecond time scale and subsequently undergo interfacial charge transfer in less than 30 psec to appropriate acceptors. These dynamics are competitive with carrier thermalization processes and support the concept that it may be possible to significantly improve energy conversion efficiencies by minimizing energy loss through carrier thermalization. The exact dynamics still need to be resolved. A new laser system has been developed in the first year of funding that is capable of <50 femtosecond time resolution. This system will have sufficient time resolution to resolve completely both the electron and hole carrier nonradiative relaxation processes as well as the interfacial carrier charge transfer dynamics.

162. Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Solutions

Whitten, D.G. **$130,000**
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. Recent efforts have used chiefly visible light-absorbing acceptors; in most cases the electron donors studied do not absorb light in the near ultraviolet or visible and would thus have no long wavelength photochemistry in the absence of the acceptor. The donors typically have at least one heteroatom functionality (amine, alcohol, thiol, thioether, ether) which is the site of the single-electron transfer oxidation by the excited acceptor. Suitable location of a second heteroatom can result in the selective labilization of a specific C–C bond in the molecule so that the net reaction is a two-electron oxidative carbon–carbon bond cleavage process in the donor concurrent with a net two-electron reduction of the acceptor. Frequently the sites of initial single-electron transfer oxidation of the donor and of permanent two-electron redox are quite different. These studies are furnishing a paradigm for understanding this reactivity. These investigations are leading to an understanding of solvent effects, stereochemical requirements, the role of acceptor and donor structure, and reaction energetics. It has been found that relatively low energy light can promote the clean and efficient cleavage of strong carbon–carbon bonds and that initial single-electron transfer at one site in an organic donor can culminate in clean two-electron oxidation at another site several atoms removed from the initial point of attack.

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

Department of Chemistry

163. Long-Range Intramolecular Electron Transfer Across Synthetic Polypeptides
Isied, S.S. **$110,000**
201-932-3764

This research involves the study of long-range intramolecular electron transfer reactions across polypeptides that possess secondary structures. Examples of such peptides are oligoprolines and alpha helices. Donor acceptor metal ions are attached at the N and C terminals 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. The observation of such unexpectedly rapid intramolecular electron transfer rates over long peptide distances suggests that the electron transfer studies across other peptides with defined secondary structure are important and may lead to a better understanding of the pathways employed by electron transfer proteins.

University of South Florida
Tampa, FL 33620

Department of Chemistry

164. Fluorescence Spectrophotometry as a Probe of Inter- and Intramolecular Electron Transfer in Liquids
Stevens, B. **$75,000**
813-974-2896

Electron transfer quenching of 9,10-dicyanoanthracene fluorescence by electron donors in polar solvents over the temperature range 273 to 323 K is analyzed in terms of the finite sink model which provides well-defined criteria for reaction-limited, diffusion-limited, and diffusion-influenced systems. Reaction-limited quenching by donors of higher oxidation potential in solvents of low viscosity provides intrinsic quenching rate constants k which exhibit Arrhenius behavior with a common pre-exponential factor of $9 \pm 1 \times 10^{11}$ l/mole sec. In the diffusion limit exhibited by donors of low oxidation potential in viscous media, the recovered effective quenching (electron-transfer) distance R is found to increase with reduction in quencher oxidation potential interpreted as long-range quenching in the solvent-separated pair which masks inefficient encounter quenching in the inverted region. The same donors in low viscosity media exhibit diffusion-influenced quenching characterized by a static quenching limit indicative of temperature-independent long-range electron transfer; this is being examined in terms of electron tunneling. It is planned to examine quenching dynamics in solvent mixtures with variable viscosity and uniform dielectric constant (and vice versa) with a view to recovering effective transfer distances and their dependence on these parameters. The quenching of electron acceptors by rubrene endoperoxide leads to endoperoxide cycloreversion (> C–O–bond fission) whereas electron donors sensitize rupture of the peroxy bond, demonstrating for the first time that the direction of electron transfer can influence the nature of (solar energy storage) products. Studies of dual fluorescence exhibited by electron-donor–acceptor systems linked by conjugated bridges have been extended to include transient absorption measurements with picosecond time resolution both in the presence and absence of polar quenchers. These, together with recordings of the fluorescence response functions, are currently undergoing analysis.

Stanford University
Stanford, CA 94305

Department of Chemistry

165. Energy Transfer Processes in Solar Energy Conversion
Fayer, M.D. **$155,000**
415-723-4446

Light from the sun or artificial sources is absorbed readily by molecules. In green plants, absorbed sunlight is used to drive photosynthesis. Two types of dynamical transport processes are important in green plants, electronic excitation transport, and electron transfer. These processes will also be important in methods to convert sunlight to artificial fuels. Theoretical and experimental studies of excitation and electron transfer are being pursued. Of particular interest are molecular systems that can self-assemble into structures that facilitate excitation transport. For the first time detailed theoretical and experimental studies of excitation transport on a micelle surface and between micelles in concentrated micelle solutions have been undertaken. Experiments show enhanced transport as the micelle concentration is raised. The companion theory can quantitatively account for picosecond experimental measurements of excitation transport. The theory and experiments are also being applied to microphase separated domains in polymeric solids. Photoinduced electron transfer is being studied in liquids. Theory and picosecond experiments are examining the influence of molecular diffusion on electron transfer and radical ion quenching by electron back transfer. Previous studies have assumed that electron transfer only occurs upon contact of the molecules involved or that diffusion is either infinitely fast or infinitely slow. The new theory describes transfer as distance dependent for any rate of molecular diffusion and includes electrostatic interactions among ions. Picosecond experiments are being used to test the theory.

Syracuse University
Syracuse, NY 13244

Department of Chemistry

166. *Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane-Mimetic Systems*
Fendler, J.H. **$120,000**
315-443-4146

Size-quantized semiconductor particles, generated at bilayer lipid membrane and monolayer interfaces, are used in artificial photoconverting systems. Cadmium sulfide, zinc sulfide, and their mixtures (with grain sizes between 50 Å and 200 Å) are characterized by absorption spectroscopy, transmission electron microscopy, scanning tunneling microscopy, and scanning electrochemical microscopy. Investigation of size-dependent photoelectron transfer allows the optimization of these systems for photochemical solar energy conversion.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

167. *Studies of Radiation-Produced Radicals and Radical Ions*
Williams, T.F. **$120,000**
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

168. *Vectorial Electron Transfer in Spatially Ordered Arrays*
Fox, M.A. **$160,00**
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.

169. *Electron Transfer Reactions in Microporous Solids*
Mallouk, T.E. **$108,000**
512-471-5903

This project uses microporous solids as organizing media for artificial photosynthetic systems. The solid (zeolite, clay, or layered oxide semiconductor) is analogous to the membrane proteins found in natural photosynthesis, in that it fixes the relative positions of photoactive and electroactive components, which are $Ru(bpy)_3^{2+}$ derivatives, semiconductor clusters, and electron relay molecules. The purpose of the microporous solid is twofold. First, it allows one to assemble a multicomponent, vectorial electron transport chain by a combination of size-exclusion and ion exchange effects. In favorable cases, this results in visible light-driven transport of electrons from one end of the chain to the other with reasonable quantum efficiency (10–20% in zeolites L, Y, and mordenite). Since the ultimate donor and acceptor are separated spatially, the lifetime of the charge separation (hundreds of microseconds) is much longer than that attained with the same components in homogeneous solution. Second, since the microcrystalline solid admits only molecules of a certain charge and size, it is possible to achieve permanent charge separation by putting a hydrogen evolution catalyst inside the structure. Using this strategy, visible light-driven photolysis of hydrogen iodide has been demonstrated with the sensitized layered semiconductors $K_4Nb_6O_{17}$ and $KTiNbO_5$. The quantum efficiency for hydrogen evolution is much lower than that of initial charge separation. The factors which control geminate charge recombination are being studied, as are zeolite-based systems which contain internally sited platinum and sensitized semiconductor clusters. This project also involves studies of long distance electron transfer between molecules coadsorbed on semiconductor particles. The role that superexchange via delocalized semiconductor orbitals plays in accelerating intermolecular electron transfer rates is being investigated.

170. Polymers at Liquid–Liquid Interfaces: Photophysics and Photoredox Chemistry

Webber, S.E. **$95,000**
512-471-3633

The project objective is to effect charge separation from excited states of chromophores bound to amphiphilic polymers which are adsorbed at the interface between water and a hydrophobic polymer surface or an organic solvent. In general, amphiphilic polymers exhibit stable adsorption because of multiple site interactions at the interface. Ionic groups on the polymer chain provide a driving force for separation of charged radicals via electrostatic repulsion. The hydrophobic–hydrophilic interface can further partition the radical products and increase the overall quantum yield, in addition to protecting the aromatic cation from attack by water. Two polymer systems are being studied: (1) alternating polymers such as poly(vinylnaphthalene-*alt*-maleic acid) and (2) block polymers such as poly(styrene-*co*-vinylnapthalene-*blk*-methacrylic acid). The first category of polymer can be modified by grafting alkyl chains (e.g., $C_{18}H_{37}NH_2$) or NH_2 terminated polystyrene chains by an imidization reaction. There are several different aspects to these studies. The adsorption properties of these polymers on polystyrene or polyethylene surfaces must be determined. Both classes of polymers have been shown to be surface active. Contact angles with respect to water demonstrate that the surface treated by these polymers becomes much more hydrophilic, which is expected if the aromatic chromophores are the points of adsorption. The efficiency of excited state quenching and charge separation upon excited state quenching (usually by means of viologens) must be assessed in these heterogeneous systems.

Washington State University
Pullman, WA 99164

Department of Chemistry

171. Investigations of Charge-Separation Processes in Metal Complexes

Crosby, G.A. **$95,008**
509-335-5605

A systematic program to elucidate the orbital natures, spin signatures, and fine structures of the low-lying (emitting) excited states of metal complexes is under way. The studies focus on d^6 (Re I), d^8 (Rh I, Pt II), and d^{10} (Zn II, Cu I, and Au I) complexes. Types of excited states under investigation are metal-to-ligand charge transfer (MLCT) states, n-pi* states, ligand-field (LF) states, and ligand-to-ligand charge transfer (LLCT) states. Special attention is being directed to the measurement of thermally accessible Franck–Condon barriers that separate near-degenerate excited states of disparate orbital parentages. The experimental results are being related to theoretical computations in order to ascertain the degree of metal orbital participation in the excited states. Concomitant experimental investigations of the splittings of LLCT triplet spin levels of optically detected magnetic resonance are under way, and these splittings are being related theoretically to the charge distributions in the excited molecules as revealed by various molecular orbital approximations.

Wayne State University
Detroit, MI 48202

Department of Chemistry

172. Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates

Endicott, J.F. **$115,000**
313-577-2607

The major goals of this research project involve the systematic investigation of models that will describe various aspects of the photoinduced transfer of charge or 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 relaxation 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, with the effects of this coupling being manifested largely in photophysical behavior, and, to a lesser degree even in ground state spectroscopic and electrochemical behavior. In complexes for which the donor excited state is $(^3CT)Ru(bpy)_2^{2+}$ and the acceptor is a covalently linked metal complex, the donor and acceptor centers usually behave reasonably independently. The behavior of these complexes is adequately described by a simple sequence of steps, mostly localized at these centers: (1) light absorption by the donor to produce an FC excited state, (2) vibrational and electronic relaxation within the donor to generate the lowest energy CT excited state, (3) equilibration between the donor and acceptor, and (4) relaxation of the electronically excited system. Systems with electron transfer, Co(III) 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 appear 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

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

Cohen, N. **$85,000**
310-336-7427 **(15 months)**

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

174. Molecular Eigenstate Spectroscopy: Application to the Intramolecular Dynamics of Some Polyatomic Molecules in the 3000 to 7000 cm^{-1} Region

Perry, D.S. **$76,550**
216-375-6825

An infrared 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 infrared 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

175. Electronic Structure and Reactivities of Transition Metal Clusters

Balasubramanian, K. **$120,000**
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 Au_6, Ag_6, Cu_6, Pd_4, Ir_3, W_4, Zr_4, Zr_3, Rh_4, 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 $Pt_3 + H_2$, $Pt_3 + H$, $Pd_3 + H_2$, $Pd_3 + H$, 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.

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

Steimle, T.C. **$76,026**
602-965-2636

This project concerns an experimental study of transition-metal aggregates and transition-metal-containing compounds in the gas phase. The goals of the project are (1) to generate new transition-metal-containing compounds, (2) to develop a sensitive nondestructive method for the detection of these compounds, (3) to characterize the electronic and geometrical properties of these compounds, and (4) to relate these properties to their chemical behavior. Particular emphasis will be placed on metals that are known to activate hydrogen, oxygen, or simple alkanes. These metals include nickel, silver, copper, gold, platinum, and palladium. The technique to be employed is based on coupling high-resolution laser and microwave spectroscopy with novel molecular beam sample preparation schemes.

University of Arizona
Tucson, AZ 85721

Department of Chemistry

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

Lichtenberger, D.L. **$108,000**
602-621-4749

The formal relationship between measured molecular ionization energies and thermodynamic bond dissociation energies has been developed into a single equation that unifies the treatment of covalent bonds, ionic bonds, and partially ionic bonds. This relationship has been used to clarify the fundamental thermodynamic information relating to metal–hydrogen, metal–alkyl, and metal–metal bond energies. A direct observation and measurement of the stabilization energy provided by the agostic interaction of the C–H bond with the metal has been obtained. The ionization energies have also been used to explain the rates of carbonyl substitution reactions of $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ complexes. Further developments in the instrumentation and methods of gas phase and surface photoelectron spectroscopy are under way. Especially interesting has been the recent application of these techniques to the characterization of the soccer-ball shaped C_{60} molecule, buckminsterfullerene, and its interaction with a metal surface. The high-resolution valence ionizations in the gas phase reveal the high symmetry of the molecule, and studies of thin films of C_{60} reveal weak intermolecular interactions. Scanning tunneling and atomic force microscopy reveal the arrangement of spherical molecules on gold substrates, with significant delocalization of charge from the metal surface.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

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

Felker, P.M. **$118,000**
310-206-6924

This project has two facets. The first is the development of methods of nonlinear Raman spectroscopy for application in studies of sparse samples. The second is the application of such methods to structural and dynamical studies of molecules, complexes, and clusters in supersonic molecular beams. Progress has been made in several areas. The first pertains to theoretical and experimental developments in Fourier transform stimulated emission spectroscopy (FT-SES) and Fourier transform hole-burning spectroscopy (FT-HBS). The second involves the development of ionization-detected stimulated Raman spectroscopies (IDSRS) for the size-selective vibrational spectroscopy of species in molecular beams. The third involves the application of IDSRS methods to studies of jet-cooled benzene clusters. In this area the geometries of the benzene dimer and trimer have been of particular concern. The fourth pertains to extensive IDSRS studies of hydrogen-bonded complexes containing phenols where the focus has been on vibrational modes sensitive to hydrogen bonding. The fifth relates to IDSRS studies of carbazole-$(Ar)_n$ and benzene-$(Ar)_n$ clusters where size-selective vibrational spectra at subwavenumber resolution have been obtained for n as large as 22 (for the benzene system).

Catholic University of America
Washington, DC 20064

Department of Chemistry

179. Studies of Combustion Kinetics and Mechanisms

Gutman, D. **$150,000**
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 ultraviolet-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., C_2H_5, CH_3CO, and $M\text{–}C_5H_{11}$), and reactions of these same free radicals with molecular oxygen (e.g., $C_2H_5 + O_2$). 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.

University of Chicago
Chicago, IL 60637

James Franck Institute

180. Quantum Dynamics of Fast Chemical Reactions

Light, J.C. **$92,000**
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. The rate constants can be expressed as the trace of the thermally averaged flux-flux correlation function. For three atom systems, the Hamiltonian is expressed in a square integrable basis in hyperspherical coordinates, evaluated in the discrete variable representation, and diagonalized to obtain the eigenvalues and eigenvectors. The projections of the thermal flux operator on these permit evaluation of the thermal rate constant for each total angular momentum, J, and each temperature. Evaluation of the rate constants for the isotopic hydrogen exchange reactions on the SLTH potential energy surface agree well with experiment from 300 to 1500 K. The use of optical potential to make the method more robust and more efficient is under development. The branching ratios and final state distributions from the dissociation of H_3 Rydberg states using a full three-dimensional wave packet propagation period in a discrete variable representation have been examined. Good agreement is found with the experimentally observed final translational energy distribution.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

181. Laser Photoelectron Spectroscopy of Ions

Ellison, G.B. **$106,314**
303-492-8603

Photoelectron spectra of negative ions are analyzed to determine molecular electron affinities, vibrational frequencies, and electronic splittings of the product radicals. In the photodetachment experiment, a 0.6 keV, mass-selected ion beam is intersected with radiation from a CW laser. The kinetic energy of the detached photoelectron is determined by means of a set of electrostatic hemispherical analyzers. From the radiation wavelength and the kinetic energy of the product electron, the electron affinities and vibronic levels of the product radicals can be determined. Most recently, the methylnitrene (CH_3N) and phenylnitrine (C_6H_5N) radicals have been studied by photodetachment studies of the corresponding anions CH_3N^- and $C_6H_5N^-$. Singlet methylnitrene is interesting because it is formally a transition state that relaxes to CH_2NH. The chemistry and spectroscopy of the phenylnitrine radical have been extensively studied and are very confusing. The electron affinity of CH_3N has been obtained as has the energy separation between the ground and the first excited electronic state. The electron affinities of C_6H_5N and C_6D_5N have been measured. Studies on these species are continuing.

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

Leone, S.R. **$97,000**
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 reaction of CH_3 with O atoms. A new product channel is detected, 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, inplane collision must occur.

Columbia University
New York, NY 10027

Department of Chemistry

183. Energy Partitioning in Elementary Gas-Phase Reactions

Bersohn, R. **$93,000**
212-854-2192

Elementary gas-phase reactions, both bimolecular and unimolecular, are being studied by laser generation of reactants and laser-induced fluorescence of the reaction products. 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 which has been used to dissociate hydrides and probe the resulting hydrogen atoms. Light near 135 nm has been used to detect chlorine atoms in both fine structure states. Experiments are planned on mode specific chemistry. The reaction of oxygen atoms with acetylene will be studied by comparing the reaction products resulting from acetylene excited in the C–C stretch, the symmetric C–H stretch, and cold acetylene.

184. 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. Chemical reactions between hot Cl atoms and stable hydrocarbon molecules are being monitored with quantum state resolution using a new multiphoton ionization technique to investigate product HCl molecules. These experiments are designed to probe the dynamics of such reactions and to compare them with results obtained in a study of the reaction between deuterated cyclohexane and Cl atoms which produces a DCl product with cold rotational but hot translational degrees of freedom. The quenching of highly energetic and reactive $O(^1D)$ atoms by CO_2 through a variety of physical and chemical mechanisms can be studied by the IR laser probe technique. The vibrational levels of CO_2 produced by this quenching process can be characterized by rather high vibrational temperatures. The bending state manifold has a temperature of approximately 1500 K while states with one quantum of asymmetric stretching excitation can be described by temperatures of over 2000 K. These observations are consistent with the breakup of a tightly bound CO_3 complex in which significant amounts of the 1.97 eV energy of the $O(^1D)$ are channeled into vibrations of the CO_2. Indirect evidence for very high rotational excitation in the first asymmetric stretch vibrational level of CO_2 has also been found for this quenching process.

Cornell University
Ithaca, NY 14853

Department of Applied and Engineering Physics

185. Resonance Ionization Spectroscopy of Combustion Radicals

Cool, T.A. **$70,000**
607-255-4191

Resonance two-photon ionization spectroscopy has been used for medium resolution studies of the formyl radical (HCO and DCO), an important reaction intermediate in hydrocarbon combustion. A low temperature (5 K) jet-cooled molecular beam and laser photolysis apparatus was employed. Rotationally resolved transitions to the $3p\ {}^2\Pi$ Rydberg state and to the $\tilde{B}\ {}^2A'$ state yield new spectroscopic constants. Vibronic analysis of subband positions originating from both A' and A'' symmetry components of the $3p\ {}^2\Pi$ Rydberg states of HCO and DCO yields values for the Renner–Teller parameter ε, dipolar coupling constant g_k, quartic anharmonicity parameter g_{22}, harmonic bending vibrational frequency ω_2, anharmonicity constant x_{22}, and spin-orbit splitting constant A. Values of the harmonic frequencies ω_2 and anharmonicity constants x_{22} for the bending vibrations of the HCO and DCO $\tilde{X}\ {}^2A'$ ground states are also determined. Term values, the three harmonic vibrational frequencies and six anharmonicity constants are measured for the $\tilde{B}\ {}^2A'$ states of both molecules. $\tilde{B}$ state bending vibration fundamental frequencies of 1382 cm^{-1} and 1213 cm^{-1} are measured for HCO and DCO, respectively. The highest fundamental frequencies of 2597 cm^{-1} for HCO and 1944 cm^{-1} for DCO correspond to CH(CD) stretching, while the lowest fundamental frequencies of 1066 cm^{-1} for HCO and 922 cm^{-1} for DCO correspond to the vibration of a one-electron C–O bond.

Department of Chemistry

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

Houston, P.L. **$92,718**
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

187. Photochemical Dynamics of Surface-Oriented Molecules

Ho, W. **$105,000**
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(111) at 85 K using 620 nm and 310 nm pulsed light of about 100 fs duration. Both O_2 and CO_2 desorb with translational energies which do not fit well to a Boltzmann distribution but are consistent with a high-temperature (about 750 K) distribution. The photoyields have a very nonlinear dependence on the laser intensity. A mechanism involving photogenerated hot carriers is consistent with these initial results.

Emory University
Atlanta, GA 30322

Department of Chemistry

188. Theoretical Studies of Combustion Dynamics

Bowman, J.M. **$87,196**
404-727-6592

The objectives of this research project are to provide a detailed understanding of dynamical processes in gas-phase reactivity and energy transfer, and to examine reactions of relevance to combustion. Currently two major projects are under way, reduced dimensionality theory of diatom–diatom reactions and resonances in bimolecular scattering. The reduced dimensionality quantum theory of atom–diatom reaction has been extended to describe diatom–diatom reactions in which one bond is nonreactive. This is quite a general situation for metathesis reactions, such as $OH + H_2 \rightarrow H_2O + H$ and $H_2 + CN \rightarrow HCN + H$. The new theory is based on hyperspherical coordinates for the two degrees of freedom involved in the bond breaking and bond making. The nonreactive degrees of freedom are described using "cylindrical" coordinates that are perpendicular to the plane containing the polar coordinates. Code development is finished, and results on the $H_2 + CN$ have been obtained. New results have also been obtained on mode selectivity in $H + H_2O$ and $H + HO\Delta$. Detailed quantum studies of direct and resonant scattering are continuing for the H + CO system, which is serving as a prototype recombination reaction. In addition to the coupled channel scattering calculations that are continuing and focusing on nonzero total angular momentum, L^2 stabilization calculations of resonances have been completed. The L^2 calculations of all bound states and numerous quasi-bound states of nonrotating HO_2 have also been completed.

189. *Kinetics and Mechanisms of Reactions Involving Small Aromatic Reactive Intermediates*

Lin, M.-C. **$90,500**
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 will be 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. The kinetics and mechanisms of the reactions important to combustion chemistry will be emphasized in these studies.

University of Georgia
Athens, GA 30602

Center for Computational Quantum Chemistry

190. *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

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

Duncan, M. **$72,427**
404-542-1998

Metal cluster molecules composed of a variety of two component mixtures are produced in a molecular beam using laser vaporization–pulsed nozzle techniques. Bimetallic clusters provide the opportunity to study bonding patterns and fundamental interactions that are not present in pure component systems. This project focuses on bimetallics containing silver, aluminum, or bismuth in mixtures with the transition metals chromium and iron. These systems are studied with mass selected photodissociation spectroscopy and laser photoionization spectroscopy using a reflectron time-of-flight mass spectrometer system. Additional experiments probe the spectroscopy of these clusters with rare gas atoms or small molecules "adsorbed" on their "surfaces." These measurements on bare clusters and cluster complexes provide rotational, vibrational, and electronic energy levels, dissociation energies, and potential energy surfaces for these systems to evaluate their relevance as models for bulk surface chemistry and catalysis.

Harvard University
Cambridge, MA 02138

Division of Applied Sciences

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

Thaddeus, P.; Gottlieb, C. **$75,000**
617-495-7340

This project emphasizes millimeter-wave spectroscopy of new, highly reactive carbenes and carbon-chain radicals produced in low-pressure discharges through flowing mixtures of combustion gases. The purpose is to provide definitive spectroscopic identification, accurate spectroscopic constants in the lowest vibrational states, and accurate structures of the key intermediates in reactions leading to aromatic hydrocarbons and soot particles in combustion. During the past year the rotational spectra of the propynonyl radicals HCCCO and DCCCO have been analyzed and a partial structure has been determined. This work constitutes the first spectroscopic identification of propynonyl, which recently has been shown to be a product in the three-body addition reaction of CCH with CO; it provides a foundation for further spectroscopic investigation at other wavelengths. Several thousand lines from sulfur bearing molecules, including a few hundred magnetic lines from new radicals, were also observed in a wide frequency survey in a discharge through CS_2 and C_2H_2. Remarkably little is known about small sulfur bearing radicals, several of which should be identified in this experiment. Rotational transitions in previously unobserved low-lying excited vibrational states of the CCH radical and the carbene ring cyclopropenylidene (C_3H_2) have been measured, yielding spectroscopic constants that should aid future IR investigations of these important combustion intermediates. New millimeter-wave/far IR instrumentation is being developed to increase the sensitivity for detection of new reactive molecules by an order of magnitude.

Department of Chemistry

193. Laser Spectroscopy of Hydrocarbon Radicals

Chen, P. **$91,053**
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 supersonic jet expansion. The species chosen for study are important intermediates in hydrocarbon combustion processes. Resonant multiphoton ionization and one-photon vacuum ultraviolet photoionization with mass and photoelectron detection are used to obtain structural and thermochemical data on the species in the jet. A detailed thermochemical study of three isomeric C_3H_2 carbenes verifies a valence-bond model that predicts the homolytic bond dissociation energy in radicals. In each case, the carbene singlet–triplet gap was found to be the numerical correction to a bond additivity estimate of $\Delta H_f[C_3H_2]$. The first rotationally resolved electronic spectra for allyl radical, C_3H_5, and deuterated isotopomers was recorded by mass-resolved resonant multi-photon ionization (MPI) spectroscopy. The origin band of the $C^2B_1 \leftarrow X^2A_2$ is found at 248.15 nm. An adiabatic ionization potential for vinyl radical, C_2H_3, was determined from the vacuum ultraviolet photoelectron spectrum of the radical. The measured ionization potential is significantly lower than earlier estimates, and leads to a revision of the heat of formation of vinyl cation.

University of Illinois at Chicago
Chicago, IL 60680

Department of Chemical Engineering

194. Kinetics of Combustion-Related Processes at High Temperatures

Kiefer, J.H. **$96,000**
708-996-3469

The purpose of this project is to determine rates and mechanisms for fuel hydrocarbon pyrolysis 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 ultraviolet 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 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 methane.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemistry

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

Yarkony, D.R. **$85,000**
410-516-4663

This research program focuses on studies of spin-forbidden and electronically nonadiabatic processes involving radical species which are relevant to combustion reactions and combustion diagnostics. To study the electronic structure aspects of these processes a system of electronic structure programs, developed over the past six years, is employed to address questions basic to the understanding of elementary combustion chemistry processes which are not tractable using more standard quantum chemistry codes: (1) treatment of the spin-orbit interaction within the context of the full microscopic Breit–Pauli approximation; (2) determination of the interstate derivative couplings which result in the breakdown of the single-surface Born–Oppenheimer approximation; and (3) location of seams of actual/avoided crossings and minimum energy crossings of potential energy surfaces. These methods have been used to treat three spin-forbidden processes that are relevant to combustion chemistry and diagnostics. The feasibility of the spin-forbidden process $CH_3O^+(^3A_2) \rightarrow CH_3O^+(^1A') \rightarrow HCO^+(X^1\Sigma^+) + H_2(X^1\Sigma_g{}^+)$ has been demonstrated. This radiationless decay process limits the ability to detect CH_3O by photoionization methods. In situ detection of nascent OH is an important problem in studies of combustion processes. Reliable theoretical modeling of the influence of predissociation on laser induced fluorescence detection of OH requires accurate $A^2\Sigma^+ \sim 1^4\Sigma^-$ spin-orbit couplings, which are not available. The requisite couplings and modeling of this radiationless decay process is currently in progress. The spin-forbidden radical–molecule reaction $CH(X^2\Pi) + N_2(X^1\Sigma_g{}^+) \rightarrow HCN(X^1\Sigma^+) + N(^4S)$ is important in the production of NO in flame fronts. The rate constant for this reaction is difficult to measure. Potential energy surfaces for this reaction are being developed based on high quality ab initio electronic structure calculations from which the rate constant may be deduced.

University of Kentucky Lexington, KY 40506

Department of Chemistry

196. *Laser Spectroscopy and Dynamics of Transient Species Formed by Pyrolysis Reactions*

Clouthier, D.J. **$70,901**
606-257-1790

The spectroscopy and excited-state dynamics of transient species formed by pyrolysis reactions are currently under investigation. The experimental techniques of pyrolysis jet spectroscopy, high resolution intracavity dye laser spectroscopy, and Fourier transform infrared (FTIR) spectroscopy are used to identify and characterize transient molecules and free radicals. In recent work, the sub-Doppler spectra of CoO, VO, and H_2CS were studied using intracavity techniques. Analysis of the hyperfine structure in the spectra of the transition metal oxides provides information on the ground and excited state electronic configurations. The thioformaldehyde work shows extra levels associated with mixing of the excited state with the ground state. This spectroscopic evidence is in direct accord with previous studies of fluorescence lifetimes and quantum yields reported earlier. In other work gas phase infrared spectra of formyl chloride and deuteroformyl chloride were obtained and are being analyzed. The UV spectrum of formic acid and various deuterated isotopomers were studied under supersonic jet conditions.

Massachusetts Institute of Technology Cambridge, MA 02139

Department of Chemical Engineering

197. *Aromatics Oxidation and Soot Formation in Flames*

Howard, J.B. **$150,000**
617-253-4574

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

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

Field, R.W.; Silbey, R. **$143,000**
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 for the complex, multistate interactions (and rapid IVR) that occur at high energy accurately and comprehensively. 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 4000 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

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

Westmoreland, P.R. **$78,000**
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. Work in the first year has focused on oxidation and molecular-weight growth in low-pressure propene flat flames. Temperature and concentration profiles of 19 species have been mapped in 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). Point measurements of eight other species were also made. In a fuel-rich $C_3H_6/O_2/Ar$ flame,. profiles of temperature and of 21 species have mapped. Flame conditions were an equivalence ratio of 1.64, 35 torr pressure, and 27.3 cm/s velocity. In parallel to the experimental work, the theoretical and modeling research has examined chemically activated reactions important in the propene flame.

Department of Chemistry

200. *Theory of the Dissociation Dynamics of Small Molecules on Metal Surfaces: Finite Temperature Studies*
Jackson, B.E. **$70,876**
413-545-2583

The goal of this study is to gain a better understanding of metal-catalyzed reactions via a detailed examination of the dynamics of molecule–metal interactions. Much effort has focused on treating the molecule as quantum mechanically as possible, and including the effects of finite surface temperature. Recently developed time-dependent quantum techniques have been used to compute the dissociative sticking probability of H_2 on various metal surfaces. All molecular degrees of freedom are included either quantum mechanically or classically. The dependence upon translational and internal molecular energy, the angle and site of surface impact, and the details of the molecule–metal interaction potential were examined. Similar techniques have been used to study the Eley–Rideal mechanism for the recombinative desorption of adsorbed H atoms with gas-phase H atoms. Extremely accurate methods for coupling the molecule to the thermal vibrations of the solid have been developed. They are being used in a general study of sticking, as well as to examine the trapping of H_2 and other diatomics in weakly bound molecular precursors to dissociative adsorption.

University of Michigan
Ann Arbor, MI 48109

Department of Atmospheric, Oceanic, and Space Sciences

201. *Energy-Transfer Properties and Mechanisms*
Barker, J.R. **$112,882**
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 energies 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. Chemical species are chosen for study on the basis of their physical properties, including symmetries, dipole moments, isotopic composition, vibration frequencies, internal rotors, and so forth. The aim here 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

202. *Variational Transition State Theory*
Truhlar, D. **$105,000**
612-624-7555

This project is concerned with 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 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 that remain practical even for reasonably complicated molecules; they are being applied to reactions of polyatomic molecules and clusters and to secondary deuterium kinetic isotope effects. 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 are being developed as well. A general, portable computer program, POLYRATE, has been developed and has been submitted to Quantum Chemistry Program Exchange, and a new version of this computer code, version 4.0, has recently been finished. The new version is greatly improved in terms of ease of use.

Departments of Chemistry and Physics

203. *State-to-State Dynamics of Molecular Energy Transfer*
Gentry, W.R.; Giese, C.F. **$130,000**
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 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. Focus is on the vibrational and rotational energy transfer in collisions of polyatomic molecules with atoms. So far three different polyatomics have been examined, each of which exhibits different dynamical phenomena. Excitation of ground-state molecules can be highly mode-selective, with coupling between vibrational and rotational degrees of freedom which is indicative of the specific collision geometries which lead to excitation of a selected mode. Recent work extends these studies by incorporating into the experiments the additional capability of studying transfer of energy from selectively prepared excited states of molecules. The latter experiments employ lasers both to prepare the initial state and to probe the final state after the collision. Concurrently, theoretical investigations of the vibrational and rotational dynamics in each system are also being pursued.

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

Chemical Science and Technology Laboratory

204. *Laser Studies of Chemical Dynamics at the Gas–Solid Interface*

Cavanagh, R.R.; King, D.S. **$86,000**
301-975-2368

The focus of the present research is on laser diagnostics of molecular desorption from surfaces. Both optically and thermally driven processes are examined, using quantum state specific detection to characterize the details of the energy transfer process. Recent experiments have probed laser-induced desorption of NO from Pt(111) and Si(111). A range of desorption laser wavelengths (from 1907 to 355 nm) can be used to stimulate desorption processes, providing insight into the nature of the excited states involved. Population distributions of the desorbed NO molecules (translational, vibrational, rotational, and spin-orbit) are then probed to clarify the details of the energy transfer mechanism. On metal substrates, hot electron mediated desorption has been demonstrated. On Si(111), a coverage dependence in the desorption process has been observed that involves surface states of the (7 x 7) reconstructed surface at low coverage and bulk carriers at high coverage. These state-resolved measurements are providing the basis for understanding optically excited, carrier-driven processes at surfaces, leading to new insights into fruitful strategies for laser-driven surface reactions. Current work is directed at establishing the importance of excited carriers for other simple adsorbates (such as CO) and the role of direct absorbate photodissociation of more complex molecules such as $Mo(CO)_6$ on semiconductors and metals.

205. *Kinetics Database for Combustion Modeling*

Herron, J.T.; Tsang, W. **$99,000**
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 1200 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 propyne and benzene. 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

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

Hougen, J.T. **$75,000**
301-975-2379

This project focuses on phenomena related to the vibrational quasi-continuum in acetaldehyde, which was chosen for study because methyl groups are promoters of intramolecular vibrational relaxation. The investigation has three parts: (1) understanding internal-rotation motion below, at, and above the barrier; (2) understanding traditional vibrational states; and (3) understanding interactions in levels with excitation of both kinds of motion. Remeasurements and theory development have led to a complete understanding of infrared and microwave data available for the ground and first excited torsional states. The group in Nizhnii Novgorod has provided a submillimeter spectrum from 164 to 417 GHz, where a search is beginning for transitions in the second torsional state (just below the top of the barrier) and the third torsional state (just above the barrier). The Brussels group has recorded a Bruker Fourier transform infrared (FTIR) spectrum of two low-lying vibrational modes. Analysis is progressing well, but a jet-cooled diode spectrum will be recorded to better understand the bandcenters. A CO_2 side-band laser spectrum of a higher vibrational fundamental near 900 cm^{-1} has already been recorded. That spectrum is much richer in lines than expected, indicating that methyl top interactions related to intramolecular vibrational redistribution (IVR) may set in at much lower energies than previously thought.

University of New Orleans
New Orleans, LA 70148

Department of Chemistry

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

Kern, R.D., Jr. **$80,000**
504-286-6847

One of the important questions pertinent to the soot formation process is the formation of the first aromatic ring from acyclic fuels. It is generally accepted that the reactions of propargyl radicals provide an efficient pathway(s) to form benzene in both flames and nonoxidative reaction systems. The study of the thermal decompositions of several precursor compounds to propargyl radical, allene, propyne, and propargyl chloride, have yielded valuable information with regard to their respective decomposition rate constants and the kinetic steps leading to benzene formation. The database has been amplified by the use of two complementary shock tube techniques employed over a wide range of temperature and pressure: time-of-flight mass spectrometry and laser schlieren densitometry. The major route to benzene appears to be 2 $C_3H_3 \rightarrow C_6H_6$. Another investigation is related to the question of incineration of chlorinated aromatic compounds. The pyrolysis of chlorobenzene was undertaken to elucidate the various reactions involved. Of particular interest is the observation of the accelerating effect of chlorine atoms upon the formation of polyaromatic compounds relative to their production rate in the absence of chlorine atoms.

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

Department of Chemistry

208. The Energetics and Dynamics of Free Radicals, Ions, and Clusters
Baer, T. **$88,000**
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. The cold samples also make possible the study of rotational effects in dissociation reactions. The dissociation onset for a reaction is shifted to higher energies when the molecule is cooled to 0 K. The participation of the rotations is thus evident in the measured shift in the dissociation onset. Loose and tight transition states are thought to differ in this respect. However, quantitative data for this effect are lacking.

University of Oregon
Eugene, OR 97403

Department of Chemistry

209. Dynamical Analysis of Highly Excited Molecular Spectra
Kellman, M.E. **$84,980**
503-346-4196

A dynamical framework for theoretical analysis of highly excited rotation-vibration spectra of polyatomic molecules is investigated. Three areas of research are pursued with application to species and/or methods of interest in combustion processes. The first area is classification of molecular dynamics from experimental spectra. Catastrophe and bifurcation analysis are applied to spectra of chaotic systems and, in particular, to many coupled oscillators and coupled rotation-vibration spectra with the objective of analysis and prediction of spectral patterns and characterization of bimolecular reactivity. The second area concerns the development of techniques for identifying and determining dynamical constants of motion and quantum number assignments for observed spectra. The third is the development of bootstrap fitting methods for the determination of molecular potential surfaces from highly excited spectra.

Pennsylvania State University, University Park
University Park, PA 16802

Department of Chemistry

210. 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. **$140,000**
814-865-7242

The influence of electronic structure and charge state on the reactivity of metal alloy, oxide, and mixed metal oxide clusters is investigated by preparing distributions of ionized clusters, allowing them to react with molecular species, and analyzing the final distribution of molecule–metal clusters by mass spectroscopy. Reactions of such species as O_2, NO, and NO_2, simple hydrocarbons, CO, and H_2O are studied on aluminum anion clusters doped with various metals as functions of composition and cluster size. Preliminary experiments have shown marked changes in "magic numbers" (clusters consisting of specific numbers of atoms that show markedly different chemistry) brought about by insertion of one heteroatom into a metallic cluster. For the metal alloy clusters, the experiments will be used to evaluate the relative importance of the spherical Jellium model of electronic structure (which should be relatively size independent) against a model in which the electronic structure is dominated more by the underlying atomic structure of the metal cluster.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemistry

211. Spectroscopy and Reactions of Vibrationally Excited Transient Molecules
Dai, H.-L. **$108,000**
215-898-5077

A new time-resolved Fourier transform spectroscopic technique that is capable of 50 nsec temporal resolution and 0.25 cm^{-1} spectral resolution in the visible has been developed for the study of transient species. The time-resolved capability of the spectrometer is achieved by running the interferometer in a step-scan mode and recording the signal with real-time resolution at each mirror position. The temporal and spectral resolution has been demonstrated by detecting the scattered light from a dye laser pulse and by dispersing the laser induced fluorescence from an I_2 gas cell in the 16,000 to 19,000 cm^{-1} region. This technique can be used to obtain vibrational spectra of a molecule over a wide energy range with single rotational level selectivity by dispersing the laser induced fluorescence in the visible or UV region. The fast time resolution ensures that transient species with lifetimes on the order of 10^{-8} sec can be detected. Furthermore, energy transfer kinetics of the transient molecule in the electronically excited state can be monitored straightforwardly. Rotationally resolved spectra of the bending overtones and combination levels of CH_2 in the lowest singlet state have been obtained this way. Rotational relaxation rates and selection rules for the CH_2 first excited singlet state have been characterized. The time-resolved capability can be extended to the IR region. The spectrometer can be operated in both the emission and absorption modes. Time-resolved emission and absorption spectra from IR to UV can be obtained for transient molecules with low concentration using this technique.

212. *Spectroscopy and Reaction Dynamics of Collision Complexes Containing Hydroxyl Radicals*

Lester, M.I. **$95,000**
215-898-4640

The goal of this program is to obtain a detailed picture of the intermolecular potential between the open-shell hydroxyl radical and various collision partners. Most recently, the attractive well regions of the intermolecular potentials correlating with OH ($X\ ^2\Pi$) + Ar ($^1S_0$) have been probed by stimulated emission spectroscopy of the weakly bound OH–Ar complex. Virtually all of the bound states supported by the intermolecular potentials have been accessed, from the zero-point level to the dissociation limit. The excited intermolecular bending and stretching vibrations sample a wide range of orientations and distances, thereby characterizing a significant portion of the intermolecular potential surface. A global potential energy surface for the OH ($X\ ^2\Pi$) + Ar ($^1S_0$) system is currently being derived based on this experimental data. Stimulated emission pumping has also been used to examine the repulsive wall of the potential as much as 200 cm^{-1} above the first dissociation limit via many predissociative resonances and bound-free transitions. OH–Ar complexes prepared in metastable levels which lie above the dissociation limit undergo predissociation by using OH rotational or spin-orbit excitation to break the weak OH–Ar intermolecular bond. Perturbation theory calculations have been carried out to understand the physical origin of these dynamical processes.

Princeton University
Princeton, NJ 08544

Department of Chemistry

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

Rabitz, H.A. **$137,000**
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. In analysis of dynamics and spectroscopy, a well-defined set of hierarchical (forward) steps are known to lead from the most basic electronic interaction level up to observable spectroscopic and dynamical processes. In recent years, new computational methods have made possible practical calculations along this hierarchy, and this aspect of the research is concerned with analyzing the interrelationships between information along the flow through the use of advanced sensitivity analysis techniques. The ultimate aim is an understanding of how macroscopic observables are influenced by detailed structure in the underlying fundamental molecular potentials as well as orbital structure at the electronic level. The research described above aims to provide a means for maximally extracting the physical information content from theoretical studies, but it also indirectly provides a basis to establish practical and numerically stable algorithms for inverting laboratory data back to more fundamental information. In particular, the forward sensitivities generated for analysis may be used to form the kernel of an iterative inversion process. The techniques are specifically designed to be stable and capable of yielding potential information free of imposed model forms. These new tools have been applied to study several systems, including elastic He scattering from solid surfaces, inelastic He–H_2 collisions, and reactive F + H_2 and H + H_2 collisions. Both forward analysis as well as inverse simulations were performed.

Department of Mechanical and Aerospace Engineering

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

Dryer, F.L. **$85,000**
609-258-5206

Using an atmospheric pressure flow reactor (APFR) and a new variable pressure flow reactor (VPFR) facility, homogeneous combustion chemistry is studied over a wide range of conditions: pressure, 1 to 15 atm; temperature, 650 to 1200 K; and reaction time, 10 to 20,000 ms. Gas sampling of stable reactant, intermediate, and product species concentrations provides substantial definition of the phenomenology of reaction mechanisms as well as a very constrained set of pure kinetic information to be compared with numerical models. Analytical techniques used for detecting hydrocarbons and carbon oxides presently include gas chromatography, gas chromatography/mass spectrometry, nondispersive IR, and Fourier transform infrared spectrometry (FTIRS). The VPFR is presently being adapted for resonance absorption measurements of OH. The modeling aspects of the program emphasize the use of a hierarchical mechanistic construction along with path and elemental gradient sensitivity analyses in developing detailed kinetic mechanisms and determining elementary rate parameters through perturbation studies of the CO/H_2/oxidant systems by small amounts of additives. Chemical issues of particular interest include perturbations of the $CO/H_2/O_2$ system to study the chemistry of HO_2 reactions and the pyrolysis and oxidation mechanisms of simple aldehydes, alcohols, and olefins.

215. Aromatic-Radical Oxidation Kinetics
Glassman, I.; Brezinsky, K.
609-258-5199

The long range goal of this research program is to develop a sufficient understanding of the details of the oxidation chemistry of aromatics so that comprehensive, predictive, chemical kinetics models can be developed. Significant progress in understanding the required details has been made in both experimental and modeling areas. The experimental research on the oxidation of cyclopentadiene has focused on identifying the key elementary reaction steps necessary to explain the transformation of a C6 to a C4 species through the intervention of C5 species. The motivation for the experimental examination has come out of efforts to develop models of the oxidation of toluene and benzene applicable to predicting species profiles at flow reactor conditions and to predicting laminar flame speeds.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemical Engineering

216. Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges
Fontijn, A. **$75,000**
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 by the high-temperature photochemistry (HTP) technique, which allows 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, propylene, the four isomeric butenes, benzene, and hydrogen chloride have been completed as has that of the reaction between ground state hydrogen atoms with hydrogen chloride. The apparatus dedicated to this project uses flash lamp photolysis. A number of short wavelength cutoff filters and photolytes are used in different experiments to check against undesirable photolysis effects, which were detected in some reactions. Computerized mathematical procedures to verify objectively that the atom decrease with time does not deviate from exponentiality have been introduced. Studies using an excimer laser photolysis source for O atom production are under investigation.

Rice University
Houston, TX 77251

Department of Chemistry

217. Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals
Curl, R.F., Jr.; Glass, G.P. **$86,000**
713-527-4816

This research is directed at the detection, monitoring, and study (by infrared absorption spectroscopy) of the chemical kinetic behavior of small free-radical species thought to be important intermediates in combustion. Ketenyl radical, HCCO, is a major product when atomic O reacts with acetylene in combustion systems. The rate constant for the reaction of ketenyl with O_2 was measured as 6.5(6) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} by means of infrared kinetic spectroscopy. An upper bound for the rate constant for the reaction between HCCO and C_2H_2 was determined as 1 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. HCCO was produced by 193 nm excimer laser photolysis of ketene and probed with a tunable infrared diode laser operating at 2014 cm^{-1}. The acetylenic CH stretch of propargyl radical ($HCCCH_2$) near 3322 cm^{-1} has been observed by infrared laser kinetic spectroscopy at Doppler limited resolution. Propargyl is prepared by flash photolysis of propargyl bromide (or propargyl chloride) at 193 nm (ArF excimer) and its transient infrared absorption probed by a cw color center laser.

218. Supersonic Bare Metal Cluster Beams
Smalley, R.E. **$184,292**
713-527-4845

Experiments are performed using two key techniques for studying gas phase clusters—Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and UV photoelectron spectroscopy (UPS) to gain insight as to how chemisorption processes occur on transition metals. Systematic studies are performed to measure the H_2 chemisorption rate on both positive and negative clusters of Fe, Co, and Ni using FT-ICR. Some very interesting and informative correlations are revealed between the H_2 chemisorption rates and the electron structure data obtained by UPS. The rate of H_2 chemisorption on clusters of each of these elements appears to correlate very closely to the difference between the ionization potential (IP) and the electron affinity (EA). This indicates that the variation in reactivity is due mainly to an electronic rather than geometric effect. In fact, these variations in reactivity with cluster size may be explained by a modification of the metallic shell model which works well for alkali metal and coinage clusters. Additional experiments will be performed to verify that this hypothesis applies to a broad range of transition metals.

University of Rochester
Rochester, NY 14627

Department of Chemistry

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

Farrar, J.M. **$88,500**
716-275-5834

Crossed ion beam–neutral beam reactive scattering experiments are being performed on several systems with the goal of using energy disposal measurements and angular distributions to extract dynamical information on collision mechanics as well as potential surface topology. Recent studies have focused on the O^- + H_2O system, endothermic by 0.36 eV, and driven by translational energy in excess of the threshold. A very rapid change in dynamics from rebound to complex to stripping over a narrow energy range provides details on the nature of impact parameters leading to reaction, as well as lifetimes of intermediate complexes. Kinetic energy distributions for reactive OH^- products and nonreactive O^- assess the validity of statistical energy partitioning models for this system. Similar measurements have been conducted on the exothermic O^- + NH_3 system. Measurements of reactive and nonreactive collisions in the systems OD^- + NH_3 and OD^- + CH_4 are currently under way and will probe the heights of isomerization barriers for proton transfer and isotope exchange by using branching ratios as a function of incident translational energy. A series of experiments on these same systems is planned that employs reagent vibrational excitation to probe the competitive roles of internal excitation and translation in driving these processes.

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

Rizzo, T.R. **$75,000**
716-275-2304

The goal of this work is to develop new spectroscopic techniques to interrogate molecules at high vibrational energies on their ground potential energy surface. 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. Infrared-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. The most recently developed technique permits the measurement of high vibrational overtone spectra in a supersonic molecular beam. This approach is based upon selective dissociation of molecules from high vibrational overtone levels via CO_2 laser multiphoton excitation. Application of this scheme to CH_3OH has greatly simplified the $\Delta v_{OH}=4$ and $\Delta v_{OH}=5$ overtone spectra, revealing features of the potential energy surface related to the dynamics of the highly excited molecule.

University of Southern California
Los Angeles, CA 90089

Department of Chemistry

221. *Combustion-Related Studies Using Weakly Bonded Complexes*

Beaudet, R.A. **$90,000**
213-740-4125

Binary van der Waals complexes relevant to combustion are being prepared and studied using tunable infrared radiation diode laser spectroscopy. The complexes are prepared in supersonic expansions using pulsed slit nozzles. In the first phase, geometries and other molecular properties are being determined from vibration-rotation spectra. In the second phase, these complexes will be used as precursors in photoinitiated reactions. Two classes of binary complexes are being investigated. The first involves molecular oxygen (e.g., O_2–HCN, O_2–HF, O_2–HCl, O_2–HBr, and O_2–hydrocarbons) and corresponding photoinitiated reactions. These complexes are interesting because upon photodissociating the hydride portion, the reaction of H and O_2 via the vibrationally excited $HO_2^\dagger$ intermediate can be studied [e.g., BrH–O_2 + hv(193 nm) → Br–H–O_2 → Br + $HO_2^\dagger$ → Br + OH + O]. The spectrum of O_2–N_2O has now been obtained and is being analyzed. This will be the first triplet spectrum ever analyzed. The second thrust area is the study of a unique set of species involving oxygen atoms and small molecules such as HF, HCl, HBr, HCN, and hydrocarbons. Since the reactions of $O(^3P)$ and small molecules have significant activation energies, the complexes survive in supercooled jets, and the oxygen atom will lie in a shallow well just outside the barrier. $O(^3P)$ has been prepared by the photolysis of SO_2 at 193 nm in the expansion slit. An apparatus with crossed slit nozzles is being designed in order to react two species and to detect the state product distributions by infrared absorption spectroscopy.

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

Reisler, H. **$115,000**
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 with a maximum for v=0 at J = 49.5. The highest rotational level populated is lower than the maximum allowed by the energetics. 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.

223. Reactions of Small Molecular Systems

Wittig, C. **$100,000**
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

224. Spectroscopy and Kinetics of Combustion Gases at High Temperatures

Hanson, R.K.; Bowman, C.T. **$140,000**
415-723-1745

This research 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 currently under 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. Shock tube studies of reaction kinetics currently are focused on reactions of CH_3 radicals.

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

Department of Chemistry

225. Ionization Probes of Molecular Structure and Chemistry

Johnson, P.M. **$92,000**
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

226. Thermochemistry of Transition-Metal Clusters

Armentrout, P.B. **$82,251**
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, and nickel, and preliminary work on vanadium and chromium. Construction of the cluster ion photodissociation spectrometer is nearing completion. 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. Contrasts in the decomposition kinetics for collisionally and photoexcited clusters will enable studies of the energy transfer dynamics.

University of Washington
Seattle, WA 98195

Department of Chemistry

227. Atomic Probes of Surface Structure and Dynamics

Jonsson, H.; Heller, E. **$103,000**
206-543-1767

Atomic beam scattering (in particular He atom scattering) is 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 Xe overlayers on Pt(111) are being performed to characterize, by comparison with experimental data, the electron density at the surface and to study superlattice structure of the Xe layers. Methods are being developed that will allow much faster and more accurate atom surface scattering calculations, both elastic and inelastic. The goal is to describe the scattering semiclassically, not only the diffractive scattering, which previously could be handled by Gaussian wavepacket techniques, but also the selective adsorption resonances, which could not be handled. This will be made possible by a new "cellular dynamics" approach which is more accurate. It has been shown to give excellent results even for chaotic motion over long times. The semiclassical techniques are being applied to atom-surface inelastic scattering, starting with a simpler but interesting test problem: the scattering of helium atoms from buckyballs. The inelastic scattering cross section will be evaluated by correlation function techniques that will then be applied to the surface scattering.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemistry

228. Unimolecular Reaction Dynamics and Vibrational Overtone Spectroscopy of Highly Vibrationally Excited Molecules

Crim, F.F. **$165,000**
608-263-7364

This research is designed to determine the nature of highly vibrationally excited molecules, to probe unimolecular reactions at the level of individual quantum states, and to study the dynamics of electronic photodissociation from vibrationally excited states. In these experiments, pulsed laser excitation of a vibrational overtone transition prepares a highly vibrationally excited molecule and with time-resolved spectroscopic detection of products, monitors their subsequent decomposition. This approach (1) provides data on unimolecular reactions of large and small molecules in room-temperature gases and supersonic expansions and (2) probes the role that vibrational excitation plays in electronic photodissociation dynamics. These latter experiments potentially determine the nature of the initial state prepared by vibrational overtone excitation and reveal unique electronic photodissociation dynamics for vibrationally excited molecules. Measurements of the populations of the product quantum states and the rates of decomposition in vibrational overtone-initiated unimolecular reactions permit detailed comparison with different theoretical models. These studies test statistical theories of unimolecular reactions and provide data on the dynamics of isolated molecules that are useful for understanding combustion processes, atmospheric chemistry, and laser-initiated reactions. Two recent examples of exploiting highly vibrationally excited molecules to achieve unique chemistry are the bond-selected photodissociation and bimolecular reaction of HOD. In these experiments, vibrational excitation of the O–H bond leads to its preferential cleavage.

Atomic Physics

California State University, Fullerton
Fullerton, CA 92634

Department of Physics

229. Few-Body Coulomb Systems

Feagin, J.M. **$60,000**
714-773-3366

A set of collective coordinates especially appropriate for describing few-body threshold breakup are used to reformulate the Wannier theory in terms of a familiar theory of small oscillations. The coordinates have many novel and interesting features, including, for example, reduced masses which depend on a parameter determined by the Coulomb interaction associated with the "Wannier saddle". Because the Wannier saddle is known to characterize many kinds of Coulomb correlations, these coordinates will be used to study collective motions of few-body systems. State-of-the-art two-electron probability densities have been computed in hyperspherical coordinates and have been found to follow, in shape and number, predicted molecular nodal patterns. A model of resonant transfer and excitation (RTE) in a crystal channel has been developed to study electron-pair correlations in heavy-ion collisions. The model was used to explain channeling of titanium ions through thin gold crystals. In addition, a new method for extending quantum diffusion calculations of two-electron atoms is being developed. It involves computing two-electron states with fast Fourier transforms to propagate the time-dependent Schrödinger equation in real and in complex time.

Clark Atlanta University
Atlanta, GA 30314

Department of Physics

230. *Theoretical Investigation of Electron–Ion Interaction*
Msezane, A.Z. **$80,000**
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 which take into account correlation and core-polarization effects are used to calculate integral and differential cross sections. Detailed multistate photoionization calculations performed are (1) ground and excited atomic states to investigate the recently predicted strong satellite enhancement of the single-channel cross sections in sodium and potassium and to delineate the accompanying resonance structure and (2) excited states from innershell to investigate and understand the recent predictions and experimental measurement of strong enhancement of shake-up satellites and many-electron effects in sodium and potassium. Electron impact excitation is studied near threshold of core-excited atomic quartet and doublet states, particularly those quartet states that are metastable against autoionization (e.g., Na I), of atoms. Excitation of singly and multiply charged positive ions is also studied to determine target wave function effects and effects of scattering approximations.

University of Colorado
Boulder, CO 80309

Department of Physics

231. *Physics of Correlated Systems*
Greene, C.H. **$100,000**
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

232. *Experiments in Ultracold Collisions*
Gould, P.L. **$83,901**
203-486-2950

The goal of this project is to investigate atomic collisions at extremely low energies. These low energies are achieved by laser cooling techniques and correspond to temperatures below 10^{-3} K. Rubidium atoms are cooled with light from diode lasers and held in a magneto-optical laser trap at densities up to 10^{10} cm^{-3}. Collisions that convert internal energy into kinetic energy are observed by monitoring the ejection of atoms from the trap following such an exoergic collision. 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. The interest in ultracold collisions is twofold. On the one hand, collisions at these extremely 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.

233. *Plasma Density and Field Effects on Atomic Reactions*
Hahn, Y. **$93,193**
203-486-4469 **(16 months)**

Theory is used to study effects of plasma environments on atomic collision processes. The study is directed to determine how atomic collision reaction rates used in modeling are influenced by the presence of external fields as well as plasma microfields and plasma particles. Current emphasis is to determine how the electric field mixes the states involved in the atomic reactions and how the plasma particles induce collisional transitions of the atomic states. Both the direct and resonant modes of the reactions will be analyzed, properly incorporating the plasma density effects. The collisional transition and field mixing effects will be treated simultaneously. A simple theoretical procedure for modifying the existing rates is being formulated to correct for density effects. An efficient way of estimating the resonant reaction rates is being developed and will be applied to study complex M-shell ions, where the level density becomes too dense to be treated by the conventional theory. These studies should help meet the need of quality data for plasma modeling.

Cornell University
Ithaca, NY 14853

Nuclear Science and Engineering Program

234. *Interactions of Highly Charged Ions*
Kostroun, V.O. **$305,000**
607-255-4991

The goal of this experimental project is to investigate fundamental processes that occur in low-energy, very highly charged ion–atom (ion) interactions at kinetic energies typical of controlled thermonuclear fusion plasmas. Processes being studied include single, double, and multiple electron capture by the projectile, target ionization, and the mode of decay of projectile excited states formed in the collision. Understanding these processes will assist modeling plasma behavior and interpretation of diagnostics. Of particular interest are how and why argon ions at 2.3 qkeV ($8 \leq q \leq 16$) incident kinetic energy, gain only one or two electrons in collisions with argon atoms while the atoms themselves can lose up to eight. The argon ions were produced by the Cornell Electron Beam Ion Source (CEBIS) by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam. The extracted ions were charge-state analyzed and crossed with a gas target cell. The absolute total cross sections for one and two electron transfer, the charge state distribution of recoil targets, and the energy spectra of electrons emitted in the argon ion–atom collisions were obtained from three different experiments. These data should allow elucidation of the mechanism involved in such collisions.

Georgia Institute of Technology
Atlanta, GA 30332

School of Physics

235. *Statistical Fluctuations in Lasers*
Roy, R. **$77,788**
404-894-5265

Four-wave mixing between the pump and probe fields with fluctuations on arbitrary time scales have been studied. The effect of four-wave mixing between two strong pump fields at distinct frequencies propagating in an optical fiber has also been studied both theoretically and experimentally. The optical energy of the pump waves is redistributed into sidebands generated within the fiber because of 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 novel source of broadband incoherent radiation is under preparation in the laboratory. A tunable titanium-doped sapphire laser with an intracavity acoustooptic frequency shifter will be used to generate tunable radiation with gigaHertz bandwidths. Such a source may find applications in laser cooling of atomic and molecular beams.

Harvard University
Cambridge, MA 02138

Harvard-Smithsonian Center for Astrophysics

236. *Theoretical Studies of Highly Ionized Species*
Dalgarno, A. **$143,000**
617-495-4403

Cross sections for the charge transfer of protons in collisions of neutral chlorine atoms and of chlorine ions in collisions with neutral hydrogen atoms have been determined. The rate coefficient for the exothermic channel at 1000 K is 10^{-12} cm^3s^{-1}. Resonances in the photodetachment spectrum of the negative hydrogen have been analyzed using the hyperspherical coordinate method. Multiphoton Raman and Rayleigh scattering and multiphoton ionization of hydrogen and cesium are under study using a formulation expressed in terms of solutions of inhomogeneous differential equations. Collisions at ultralow temperatures are being studied.

Kansas State University
Manhattan, KS 66506

Department of Physics

237. *Atomic Physics of Strongly Correlated Systems*
Lin, C.D. **$140,000**
913-532-6786

This project is directed at the understanding of the formation and the decay properties of multiply excited states of atoms and ions. The shape of Coulombic three-body systems in hyperspherical coordinates is examined by studying the density functions with the mass ratio of the particles. The radiative and the electron emission rates are calculated and the systematic trends are analyzed. The coherence of atomic excited states after atomic collisions are examined using both the classical models as well as quantum mechanical models to assess the limitation of the classical theories. Electron spectra of doubly excited states following double electron capture are calculated and compared to experimental results. Procedures have been established where diabatic states in the avoided crossing region can be constructed and a single channel quantum defect theory where the electron is in the combined fields of a Coulomb potential and a dipole potential is derived.

238. *Atomic Physics with Highly Charged Ions*
Richard, P. **$1,638,000**
913-532-6783

The study of inelastic collision phenomena with highly charged projectile ions and the interpretation of spectral features resulting from these collisions remain as the major focal points in the atomic physics research at the J.R. Macdonald Laboratory at Kansas State University. Recent experimental work is divided into collisions at high velocity using the primary beams from the accelerator and collisions at low velocity using the cryogenic electron bombardment ion source (CRYEBIS) facility and secondary beams (recoil ions produced in a high-velocity collision) in a so-called secondary ion recoil source (SIRS) geometry. Theoretical calculations have been performed to describe accurately inelastic scattering processes of one-electron and many-electron type, and to predict accurately atomic transition energies and intensities for X-rays and Auger electrons. The study of one-electron outer shell processes in fast ion–atom collisions includes the systematic measurement and calculation of binary encounter collisions with target electrons studied by electron emission spectroscopy and the measurement of single electron capture by high-velocity bare ions on atomic and molecular hydrogen. The role of electron–electron interaction in two-electron processes has been investigated in projectile K-shell to L-shell excitation, in projectile K-shell ionization, and resonant transfer excitation. Multielectron processes at low energy have been investigated by studying dielectronic recombination and electron impact excitation of helium-like argon, by studying K X-ray emission from Ar^{17+} projectiles interacting with a Ge surface, and by studying Ar^{q+} + Ar recoil-projectile coincidence, using the EBIS source, and Ar^{6+} + He recoil-projectile coincidence using SIRS. Multielectron processes at high velocity have been investigated by studying projectile q - recoil q coincidences in ion–He collisions leading to single ionization, double ionization, transfer ionization, and single electron capture, by studying differential cross sections for multiple ionization of Ne and Ar by fast protons, by studying total cross sections and molecular orientation in O^{8+} - D_2 collisions, by studying the recoil ion momentum spectroscopy, and by studying multielectron ionization in charge transfer dominated ion–atom collisions. Inner shell processes and molecular fragementation in high-velocity heavy ion–atom collisions have also been investigated.

University of Kansas
Lawrence, KS 66045

Department of Chemistry

239. *Atomic Physics in Strong Fields*
Chu, S.-I. **$63,000**
913-864-4094

Several new nonperturbative theoretical formalisms and practical numerical techniques are being developed for ab initio comprehensive investigation of several intense-field multiphoton and nonlinear dynamical processes of current interest. Included are (1) development of the complex-scaling Fourier-grid Hamiltonian method for accurate and efficient determination of atomic and molecular resonance states without the need of using the conventional basis set expansions, which is being applied to the study of multiphoton and above-threshold dissociation of H_2^+ in intense laser fields; (2) development of the generalized Floquet theory and fast Fourier transformation technique for probing multiphoton excitation and ionization dynamics, as well as quantum localization and diffusion phenomena in microwave-driven Rydberg atoms: classical vs. quantum chaos; and (3) development of the L^2 non-Hermitian Floquet matrix method with extended Sturmian basis for the nonperturbative treatment of intensity-dependent ac Stark shifts and ionization widths of excited states of atomic hydrogen, as well as multiphoton ionization/above-threshold ionization of more complex atoms such as H^-.

University of Kentucky
Lexington, KY 40506

Department of Physics and Astronomy

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

Investigations of physical processes governed by the dynamics of weakly bound atomic electrons are investigated. The first of these involves a study of the response of prepared Rydberg atoms to time-dependent electric fields. The second, a study of collisions of ions with Rydberg-atom targets, is designed to address a fundamental three-body process of importance in plasma environments. The capture of slow muons in atomic hydrogen, a process that has applications to the physics of energy-loss spectra, muon-catalyzed fusion, and nuclear spectroscopy, will also be studied.

241. *Coherent Excitation of Autoionizing Resonances*
Martin, N.L.S. **$98,000**
606-257-5840 **(16 months)**

Investigations of collision processes which are important for energy-related technologies are conducted. Studies are being made of coherent excitation, by electron-impact, of autoionizing levels of the Group II B transition-metal atoms. 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. Coincidence spectra taken at small scattering angles, in the plane wave Born approximation regime, are used to determine the spectroscopy of the optically forbidden $J = 0,2$ even parity levels. Spectra measured at larger scattering angles are interpreted to determine the relative phases and magnitudes of the complex excitation amplitudes of $J = 0,1,2$ levels. These experiments are being conducted using Cd, where the effects of coherent excitation have already been observed. The measurements 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

242. *Spectroscopic Studies of Hydrogen Collisions*
Kielkopf, J. **$81,000**
502-588-5990

Studies are being made of atomic collisions in the cooling gas that results when a plasma is generated by focusing light from an ArF (1930 Å) excimer laser onto molecular hydrogen and other targets. Time-resolved vacuum ultraviolet emission from a dissociated and highly ionized plasma reveals information about collisions between excited atoms and ions just a few nanoseconds after the excitation pulse stops. Many microseconds later, when the atomic gas has cooled and is no longer radiating, laser spectroscopy with state selective excitation probes neutral collisions. For example, four-wave mixing in Hg vapor produces tunable light near Lyman-α that is used to observe direct absorption and fluorescence from neutral H-atoms undergoing low energy collisions. Such spectroscopic effects are detected in the far wing of the spectral line, which for atomic H is throughout the vacuum UV. Other related work includes the observation and analysis of O + H interactions in the radiative dissociation of OH, population inversion and lasing in Al + H_2 plasmas, and excited alkali-H radiative collisions.

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

Physics Laboratory

243. *Electron-Atom Collision Studies*
Kelley, M.H.; McClelland, J.J. **$93,500**
301-975-3722

Crossed-beam scattering experiments are carried out using low-energy spin-polarized incident electrons and optically pumped atoms. Laser-optical pumping of the target atoms prepares either spin-polarized ground state atoms, or spin-polarized, aligned, and/or oriented excited-state atoms. Electrons scattered from the optically pumped atoms are detected as a function of scattering angle, incident energy, and relative spin orientation. These experiments are designed for fundamental tests of the reliability of theoretical electron scattering calculations, with particular emphasis on the role played by exchange. Sodium has been the major focus of this work to date, since with its single valence electron, it provides a good model system for investigation of exchange in electron–atom scattering. Currently, the apparatus is being modified to study optically pumped chromium. The incident spin-polarized electron has the opportunity to exchange with each of the six target valence electrons in the chromium atom. As a result, a wide and complex range of exchange phenomena should be observed.

University of Nebraska
Lincoln, NE 68588

Department of Physics and Astronomy

244. *Dynamics of Collision Processes*
Starace, A.F. **$69,000**
402-472-2795

Investigations of collision processes important for energy-related technologies and governed by the dynamics of three interacting charged particles are being carried out. The systems of three interacting charged particles are described using either hyperspherical coordinate methods or a combination of R-matrix and quantum defect theory methods. Among the collision process being investigated are high-energy detachment collisions of negative ions with various target atoms, single and multiphoton detachment of H^- and negative alkali ions, and low-energy electron scattering from alkali atoms. Recently, the inclusion of H(n = 2) final states in the description of H^- detachment collisions has been shown to give marked improvement in the agreement of theory with experimental data. For 2-photon detachment of H^- with excitation of H(n = 2), a half-cycle of long-range dipole-field-induced oscillation of the cross section above threshold has been identified. Such oscillations have never been observed experimentally.

University of Nevada at Reno
Reno, NV 89557

Department of Physics

245. *Screening Resonances in Plasmas*
Winkler, P. **$43,970**
702-784-6792

In the investigation of plasmas consisting of positive atomic ions and electrons a good understanding of the interaction potential between those 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–Hückel 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. Enhanced recombination rates are being calculated. The required computational techniques have been developed and tested using analytic model potentials. The incorporation of the realistic electron–ion potentials into the calculation of various ionic pair functions has been completed. Stimulated by very recent fusion research in the UK, the recombination probability of helium ions immediately after a fusion event has been studied.

University of New Mexico
Albuquerque, NM 87131

Department of Physics and Astronomy

246. *Relativistic Atomic Beam Spectroscopy*
Bryant, H.C. **$115,000**
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.

Pennsylvania State University, Lehman
Lehman, PA 18627

Department of Physics

247. *Electron Transfer, Ionization, and Excitation in Atomic Collisions*
Winter, T.G.; Alston, S.G. **$68,000**
717-675-9278

Theory is used to study electron transfer, ionization, and excitation in ion–atom collisions at intermediate and higher collision energies. At intermediate energies (e.g., proton energies on the order of 100 keV) many states have time to interact strongly during the collision; a coupled-Sturmian-pseudostate approach is taken to account for this interaction. At higher energies (e.g., proton energies on the order of 1 MeV) the interaction may be treated perturbatively, for example, using the strong-potential-Born approximation. Coupled-state and perturbative approaches to electron transfer, as well as ionization, in prototypical (one-electron) p–He^+ collisions have been smoothly joined. Attention is now focused on more complex collisional systems: (1) electron transfer and ionization from the K shell of neutral targets, such as carbon atoms, by proton impact is studied, in which the interaction between the active electron and the C^+ ion can be modeled by a one-electron potential and (2) transfer-excitation (simultaneous projectile excitation and electron transfer) in collisions between hydrogenic ions (e.g., O^{7+}) and helium atoms is studied using the impulse version of the distorted, strong-potential-Born approximation.

University of Pittsburgh
Pittsburgh, PA 15260

Department of Physics and Astronomy

248. *New Infrared Photon Absorption Processes*
Bayfield, J.E. **$120,000**
412-624-9280 **(18 months)**

The simultaneous application of resonant UV and nonresonant mid-IR laser radiation is a possible approach for the spatially localized subpicosecond noncollisional breakdown of gases. Fast atomic beam experiments are being carried out on the carbon dioxide IR laser multiphoton ionization of optically excited hydrogen atoms in selected stark states, with principal quantum numbers selected between n = 5 to 10. At present, IR laser intensities of 1 gigawatt per square centimeter and subnanosecond laser pulse lengths are being used. At n = 10 the peak laser pulse strength is seven times the static field strength needed for rapid ionization. At n = 5 the initial Rabi frequency is one quarter the laser frequency which in turn is one half the initial electron orbit frequency; then the laser field strength is equal to the threshold value for classically chaotic ionization. Both of these strong-field regimes are previously unstudied at IR wavelengths and may feature IR laser ionization rates enhanced over perturbative values. The study of hydrogen atoms in extremal Stark states makes it possible to estimate accurate quantum and classical ionization rates. A further experiment has been designed to study the dependence of strong field ionization on atom orbital angular momentum.

Rice University
Houston, TX 77005

Department of Physics

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

Theoretical methods are being applied in the calculation of cross sections, collision rates, and other observables, such as orientation and alignment parameters, that describe collision processes that are of fundamental interest and important to advanced energy research. Projects of current interest include studies of ionization and state-changing in collisions between low-Rydberg atoms and atoms, ions, and molecules; dependence of cross sections for various state-changing collisions involving excited atoms on the initial angular momentum and orbital alignment of the atom; and excitation and electron transfer in ion–atom and ion–molecule collisions. Quantum mechanical, semiclassical, and classical methods are used where appropriate.

Department of Space Physics and Astronomy

250. *Radiative Properties of Strongly Magnetized Plasmas*
Weisheit, J.C. **$120,000**
713-527-4939 **(18 months)**

Atomic properties in strong magnetic fields ($B > 10^7$ Gauss) are studied. The goal of this research project is to establish the effects of intense magnetic fields on radiative opacities. A novel computational scheme is being developed to describe multielectron atoms/ions in intense magnetic fields. The approach involves an ansatz which separates electronic motion in the z (i.e., B-field) direction and in the ρ–ϕ plane. The former is described by a one-dimensional equation of the Thomas–Fermi type that depends parametrically on ρ, and the latter, by an ordinary, two-dimensional Landau wavefunction. Unlike methods suggested previously, the Thomas–Fermi charge density is being calculated numerically, using the explicit forms of the Landau wavefunctions. Solutions of a nonlinear differential equation are sought to obtain the electron density. This approach is expected to be self-consistent, and to apply to a wide range of ions and magnetic field strengths. It will be used to compute a Slater-type exchange term in subsequent self-consistent field calculations that include an approximate treatment of the ion's diamagnetic interaction. The results will provide a check of published claims that the Thomas–Fermi charge distribution for atoms in strong fields is spherical.

University of Rochester
Rochester, NY 14627

Department of Physics and Astronomy

251. *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 theoretically and experimentally. The principal experimental tool will be the Table Top Terawatt (T^3) laser. The relationship between the tunneling or barrier suppression regime and the multiphoton regime will be studied by varying laser pulse width and bandwidth independently. The characteristics of photoionization will be studied. Theoretical investigations will continue using ab initio wave functions calculated for one-dimensional and three-dimensional model atoms. The principal areas for new work will be the improvement of numerical methodology and the study of atom stabilization under strong radiation fields. The theoretical effort will lead naturally to support of experimental work as well.

University of Southern California
Los Angeles, CA 90089

Department of Physics

252. *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 of frequency, ω, sufficiently high that $h\omega$ is substantially larger than the energy required to remove one electron is studied. 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

253. *Production and Destruction of Metastable Negative Ions*
Pegg, D.J. **$86,000**
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. Cross sections for the photodetachment of Li^- have been determined and found to agree with theory at a comparable level of accuracy. 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. Measurement of the photodetachment of B^- is currently under way.

Texas A & M University
College Station, TX 77843

Cyclotron Institute

254. *Excitation of Atoms and Molecules by Collisions with Ions*
Watson, R.L. **$89,500**
409-845-1411

Transient molecular ions of CO^{Q+} (where Q = 1 to 7) have been produced in single collisions of 97 MeV Ar^{14+} projectiles with neutral CO molecules. The resulting dissociation products were identified by coincidence time-of-flight spectroscopy in which the time-of-flight of the first ion to reach the detector and the time difference between the first ion and its partner were recorded event-by-event. An iterative matrix transformation procedure was employed to convert the time-difference spectra for the prominent dissociation channels into total kinetic energy distributions. Analysis of the total kinetic energy distributions and comparisons with the data available for CO^{2+} and CO^{3+} from synchrotron radiation experiments led to the conclusion that ionization by Ar-ion impact populates states having considerably higher excitation energies than those accessed by photoionization. Production yields, dissociation fractions, and branching ratios also were determined. The results indicated a preference for dissociation channels leading to symmetric or nearly symmetric charge division. An enhancement of the total ionization yields for high Q was observed, and it suggests that electron transfer followed by LMM Auger decay plays an important role in determining the final charges of the dissociation products.

University of Texas at Austin
Austin, TX 78712

Department of Physics

255. Kinetic Studies Following State-Selective Laser Excitation

Keto, J.W. **$195,000**
512-471-5029

During the past year, measurements 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 completed. These results are relevant to kinetic models of both excimer lasers and the infrared xenon laser. The state-to-state rates to specific product channels are determined both from their fluorescent intensity and from the time dependence of fluorescence from the product channel. All product states are studied that can be observed in the spectral range from 120 to 1100 nm. Excitation transfer from Xe* to Kr* and reverse are observed in the energy pathways. This process is important for all Xe* excited states above the Kr*(5s) threshold. Energy transfer back from Kr*(5s) is preferentially to Xe*(5d). The completion of these studies enables the study of 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. Experiments to study this reaction are just beginning.

University of Toledo
Toledo, OH 43606

Department of Physics and Astronomy

256. Semiempirical Studies of Atomic Structure

Curtis, L.J. **$58,000**
419-537-2341

The energy level structure, transition probabilities, and general spectroscopic properties of highly ionized many-electron systems are studied through the combined use of sensitive semiempirical data systematizations, selected 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 observations, and conventional light sources. Large blocks of data are predictively systematized and parameterized along isoelectronic, homologous, isoionic, Rydberg, and yrast series, to provide a comprehensive and reliable database. Examples of investigations carried out during the past year include (1) isoelectronic systematizations of two and three valence electron systems which combine new and existing lifetime measurements with intermediate coupling information deduced from observed energy level data; (2) accurate semiempirical extrapolation and interpolation of energy levels, ionization potentials, and core polarizabilities for all ions in the Li sequence, and the use of these data to deduce transition probabilities by the semiempirical CAHS method; (3) high precision relative lifetime measurements in the Li sequence by a new technique utilizing a position sensitive detector; and (4) studies of cancellation effects in transition probabilities which explain recently measured anomalies in the Au isoelectronic sequence.

257. Measurements of Scattering Processes in Negative Ion–Atom Collisions

Kvale, T.J.
419-537-2980

Measurements of various scattering processes occurring in intermediate energy collisions between H$^-$ ions and target atoms of He, Ne, Ar, and atomic hydrogen are in progress. The existing fast ions and/or atoms are charge-state analyzed to allow measurements of absolute total cross sections for single- and double-electron detachment, as well as measurements of processes in which H$^-$ remains intact during the collision. The latter processes will necessitate completion of the instruments necessary for the implementation of the ion energy-loss spectroscopy technique. The goals for the current year are (1) to complete the single- and double-detachment measurements in 3–50 keV, H$^-$ + He collisions; (2) to proceed to the ion energy-loss measurements; (3) to implement the energy upgrade of the accelerator to 100 keV; and, finally, (4) to proceed with the construction of the devices necessary for angular differential cross section measurements. These measurements will provide stringent tests of ion–atom collision theory at intermediate energies.

Vanderbilt University
Nashville, TN 37235

Department of Computer Science

258. Theoretical Studies of Atomic Transitions

Fischer, C.F. **$135,000**
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. These methods are being tested in the study of photoionization in He and H$^-$. A four-node Intel iPSC/860 hypercube is used to conduct large wavefunction studies. A partial wave expansion for Li ^2S state is being obtained and convergence of the hyperfine parameter and mass polarization correction will be investigated. Some large-scale relativistic calculations have been performed for Pr^{+3} using a modified version of the General Relativistic Atomic Structure Program

(GRASP). This code will now be used to investigate configuration mixing in Gd with a half-filled *f*-shell.

University of Virginia
Charlottesville, VA 22901

Department of Physics

259. ***Autoionizing States Relevant to Dielectronic Recombination***
Gallagher, T.F. **$110,584**
804-924-6817

This research program is focused on the properties of autoionizing states of Mg. These states are the intermediate states in the dielectronic recombination of Mg^+ and electrons to produce neutral Mg atoms. The experiments under way, using laser excitation, are precisely the inverse of dielectronic recombination, an important cause of radiative power loss in fusion plasmas. An analysis of measurements of the angular distributions of the electrons ejected from autoionizing Mg 3pnd states and a comparison of the results to the angular distributions calculated from semiempirical K matrices are under way. It appears that the K matrix approach gives a good description of the atomic physics and thus should form the basis of the most realistic calculations of dielectronic recombination rates to date. Measurements of the autoionization rates of the Mg autoionizing states in electric fields have begun. These measurements will mimic the effects of plasma microfields on dielectronic recombination.

Western Michigan University
Kalamazoo, MI 49008

Department of Physics

260. ***Correlated Charge-Changing Ion–Atom Collisions***
Tanis, J.A. **$95,000**
616-387-4941

Experimental studies of fundamental atomic interactions involving excitation, ionization, and charge transfer are conducted for collisions of few-electron ions with neutral gas targets or electrons. A major emphasis of this research is the study of two-electron interactions, and particularly those in which the electron–electron interaction and electron correlation play a role. Specific interaction mechanisms are isolated and identified using coincidence techniques in which charge-changed projectile ions emerging from the collision region are associated with X rays, recoiling target ions, or electrons produced in the interaction. The studies typically involve ions with $2 \leq Z \leq 92$ in charge states $q \geq Z/2$ and energies ranging from less than 5 keV/u to more than 100 MeV/u. Accelerator facilities at Lawrence Berkeley Laboratory, Argonne National Laboratory, Michigan State University, Western Michigan University, and Indiana University are used in this work. Principal areas of investigation are (1) resonant recombination in ion–electron collisions, (2) double ionization mechanisms in helium at intermediate to high velocities, and (3) continuum electron capture associated with bound state capture. A new electron spectrometer system that will greatly enhance investigation in this latter area is being constructed.

The College of William and Mary
Williamsburg, VA 23185

Department of Physics

261. ***Negative Ion Cross Sections Detachment***
Champion, R.L.; Doverspike, L.D. **$104,000**
804-221-3510

The long-term goal of this research project is to develop a thorough understanding of the collisional dynamics of systems which include negative ions. 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 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 oxygen and sulfur anions with atomic hydrogen, deuterium, and ozone. Future studies of this type will include alkali anions. In the field of negative ion sputtering from surfaces, the experiments are devised to investigate the 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

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

262. ***Carbon Deposition and Deactivation of Metallic Catalysts***
Baker, T.K. **$125,000**
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.

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. **$138,435**
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. Organoscandium and organoyttrium derivatives have been prepared and found to function as one-component Ziegler/Natta olefin polymerization catalysts. Most recently, a chiral linked yttrocene derivative *rac*-$[Me_2Si(\eta^5\text{-}2\text{-}SiMe_3\text{-}4\text{-}C_5H_2CMe_3)_2Y(\mu\text{-}H)]_2$ capable of the isospecific polymerization of α olefins was designed and synthesized. The transition state for chain propagation is also being examined. An α "agostic" C–H interaction in the olefin insertion step has been implicated using "deuterium isotopic perturbation of stereochemistry", indicating a quite different geometry for the transition state for olefin insertion than had been widely assumed.

University of California, Irvine
Irvine, CA 92717

Department of Chemistry

264. Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes

Evans, W.J. **$108,100**
714-856-5174

The chemistry of yttrium and the lanthanide metals, a unique group of relatively abundant metallic elements readily available in the United States, is being studied to learn how to exploit the special chemical, physical, and catalytic properties available from compounds of these elements. Complexes of these metals containing alkoxide and aryloxide ligands have been synthesized to determine their utility as soluble, robust precursors upon which to build reactive organometallic functionality. A variety of mono-, bi-, and trimetallic complexes can be obtained by varying the nature of the alkoxide ligand, and the multimetallic structure provides additional opportunities for developing the chemistry. Reactions of trimetallic *tert*-butoxide complexes with organometallic aluminum and alkali metal reagents have revealed surprising new classes of mixed-metal and mixed-ligand complexes as well as unexpected new synthetic pathways. Routes to YAl_2 and YAl_3 complexes, a solubilized form of YCl_3, and an unusually stable alkoxide-bridged bimetallic unit have been discovered. As the details of these reactions are established, a range of new opportunities to better exploit the special chemistry available from these metals should be revealed.

University of California, San Diego
La Jolla, CA 92093

Department of Chemistry

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

Tilley, T.D. **$136,273**
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 alkoxide 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. The low temperatures at which such conversions take place allow for the thermolysis to take place 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

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

Weinberg, W.H. **$88,300**
805-893-8528

The project objective is to combine molecular beam techniques, mass spectrometric measurements in a bulb environment, and high-resolution electron energy loss spectroscopy (EELS) to provide as complete an understanding as possible concerning alkane activation and reactions on Group VIII transition metal surfaces. The hydrocarbon reactants studied are methane, ethane, propane, n-butane, i-butane, and cyclopropane; the surfaces employed, which display remarkably different reactivities, are Ir(110)–(1 x 2), Ir(111), Pt(110)–(1 x 2), and Ru(001). The beam experiments clarify the dynamics of both direct and trapping-mediated alkane activation. The bulb experiments involve mechanistic studies with isotopically labeled molecules, and the high-resolution EELS is employed to determine the rate of reaction and the pathway of subsequent dehydrogenation, hydrogenation, and decomposition reactions on the surface. Dynamic Monte Carlo simulations are planned to gain additional quantitative insight into the rates of a number of elementary surface reactions that occur during the alkane adsorption and activation.

Department of Chemistry

267. *Studies Relevant to the Catalytic Activation of Carbon Monoxide*

Ford, P.C. **$128,500**
805-893-2443

This research is concerned with quantitative investigations of fundamental metal complex reactions which have relevance to the homogeneous catalytic activation of carbon monoxide and other C_1 compounds. Work includes mechanistic studies of the formation and reactivities of nucleophile–carbonyl complexes, which are intermediates in a number of different catalytic processes, as well as continuous flow reactor studies of the water gas shift and related reactions as activated by solution phase or polymer supported metal carbonyl catalysts. Related investigations in progress are applications of fast reaction methodologies, principally laser flash photolysis with infrared or optical detection, to prepare and to study the reaction dynamics of reactive intermediates proposed as key species in the catalytic activation of CO, other C_1 compounds, hydrocarbons, and various small molecule substrates. For example, recent studies have addressed the quantitative reactivities of intermediates in the migratory insertion of CO into carbon metal bonds. The goals are to delineate the fundamental principles of such catalytic processes, thus to establish and extend molecular engineering guidelines for the design of new chemical systems for efficient use and applications of energy and chemical feedstock resources.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

268. *Chemically Modified Electrodes and Related Solution Chemistry*

Elliott, C.M. **$101,98**
303-491-5204

The primary goal of this research is the development of polymer-coated electrodes containing electroactive materials that alter the chemical and/or physical properties of the electrode–solution interface in useful ways. Several such electrodes have been prepared. The fundamental processes of electron and ion transport in such modifying polymers are being studied. In the course of these studies a new type of electronically conducting "organic" polymer has been developed, and this material is under study. There are two aspects to the studies of chemically modified electrodes. On one hand, schemes for incorporating electroactive systems of interest into polymers are being developed; on the other hand, molecules that are of potential interest (e.g., catalysts) for incorporation into polymer films are being studied. Different synthetic procedures appropriate for each material under study are investigated in order to chemically incorporate the molecules of interest into polymers. For example, a number of novel metalloporphyrins have been prepared, and their redox chemistry is under investigation both in solution and polymer-bound. Polymer films formed from these porphyrins on electrode surfaces catalyze the oxidation of certain olefins in solution. Other polymers under study form a new class of electronic conductors which may have applications to problems of catalysis by greatly increasing the effective surface area of electrodes. Several of these materials also have novel electrochromic and redox-adjustable ion exchange properties. The primary methods of investigation of these surfaces are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry, and rotated disk voltammetry.

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

Norton, J.R. **$108,600**
303-491-5609

The stereochemistry of the formation of diosmacyclobutanes from olefins is under investigation. This reaction models the chemisorption of olefins onto metal surfaces and it is believed that both reactions retain stereochemistry about the double bond. Diosmacyclobutanes are also excellent vibrational models for olefins chemisorbed on metal surfaces, and it was found that the vibrational frequencies of an unsubstituted diosmacyclobutane agree very well with those of ethylene on Pt(III). The vibrational frequencies of an ethylidene-bridged diosmium complex are also being assigned, so that ethylidene species can be recognized on catalyst surfaces. Methods were also developed to use NMR in liquid crystal solvents to determine the structure of mononuclear and dinuclear ethylene complexes in solution. For the dinuclear ethylene complex and unsubstituted diosmacyclobutane, the results agree well with those determined in the solid state by neutron diffraction.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

270. Lewis Acid Modified Molybdenum Sulfide Complexes

DuBois, M.R. **$83,277**
303-492-5039

The objective is to characterize the reactivity of molybdenum (Mo) sulfide sites in discrete dinuclear complexes. The project may provide a basis for identifying possible mechanisms in the reactions of supported metal–sulfide catalysts. A kinetic and mechanistic study of the reactions of hydrogen with cationic complexes of the formula $[(C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$, I, has been completed. In the presence of a nitrogen base, the reactions proceed to form a neutral hydrosulfido complex $[(C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SR)]$, II, and an equivalent of protonated base. Kinetic data, which indicate a second order rate law, Rate = $K[H_2][I]$, are consistent with direct activation of hydrogen by the cation. Activation enthalpies for the reactions of H_2 with cations where R = thienyl and CH_2CO_2Me are in the range of 75–85 kJ/mol. On the basis of previously reported activation enthalpies for reactions of metal complexes with H_2, the data seem most consistent with a heterolytic cleavage of hydrogen. Investigations of the most likely sites of proton and hydride addition to the dimers have therefore been conducted. Hydride addition to the sulfide ligand of I to form II has been characterized. Spectroscopic data suggest that proton addition to neutral complexes similar to II may occur at either sulfur or metal ion sites. The studies suggest new mechanisms for hydrogen activation by metal sulfide complexes.

University of Connecticut
Storrs, CT 06269

Department of Chemistry

271. Structure Sensitivity of Cobalt/Iron Alloys and Clusters in Zeolites

Suib, S.L.
203-486-2797

The goals of this research program include research in three related areas. Transient and steady state kinetic studies of structure sensitive reactions of cyclopropane (c–C_3H_6) and hydrogen over zeolites is the first. Transient kinetic studies have been done with a high resolution mass spectrometer detector to show that molecular H_2 is trapped in the sodalite cages of X and A zeolites at 1 atm and 37 °C. Cyclopropane on the other hand, chemisorbs to different extents in various ion-exchanged and metal-loaded zeolites. Low-level impurity Fe^{3+} ions in zeolites complicate interpretation of spectroscopic and catalytic studies of these systems in a second related area of research. Efforts were focused on selectively substituting Fe^{3+} ions in the frameworks of various zeolites to understand their role in catalytic reactions such as with c–C_3H_6 and H_2. Experimental and theoretical simulations of electron paramagnetic resonance, Mössbauer, and other spectroscopic data have led to observation of framework tetrahedral, defect hydroxyl, and octahedral dispersed iron oxide clusters in these systems. These studies led to isomorphous substitution of other ions like B^{3+} in zeolites. The third area of research involves the synthesis, characterization, and catalysis of a new class of molecular sieve manganese oxide tunnel structure materials. Both hollandite and todorokite synthetic derivatives have been produced and characterized. These materials are cation exchangers, have Lewis and Brönsted acid sites, are thermally stable to temperatures of 500 °C, and are crystalline.

University of Delaware
Newark, DE 19716

Center for Catalytic Science and Technology

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

Barteau, M.A. **$81,500**
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. These observations suggest that the identities of the primary products of CO insertion on metal catalysts may depend on the identities of surface hydrocarbon ligands. Results for alcohol decarbonylation implicate a surface oxametallacycle intermediate, and other routes to this species are currently under investigation. Quantitative correlations for the activity of transition metals for conversion of C_1 oxygenates have also been developed. The systematization of this chemistry will provide opportunities for understanding and development of heterogeneous catalysts for synthesis and utilization of oxygen-containing feedstocks and fuels.

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

Gates, B.C. **$93,600**
302-831-2347

The goal of this research is to characterize the structure and bonding of "molecular" metal complexes of tungsten, rhenium, osmium, iridium, and platinum, bonded to the surfaces of metal oxides (MgO, γ–Al_2O_3, and SiO_2). The surface complexes are synthesized by reaction of organometallic precursors such as metal carbonyls and allyls with the support surfaces, and characterized by EXAFS used in combination with temperature-programmed decomposition and infrared, Raman, and NMR spectroscopies. These "molecular" precursors are treated to give highly dispersed metals that are characterized by the same techniques. Thorough results have been obtained for rhenium carbonyls on alumina and magnesia. $HRe(CO)_5$ forms a surface complex formulated as $Re(CO)_3(HOMg)_n(OMg)_{3-n}$. The surface has been treated to vary the ratio of O to OH groups, and n has been varied from 0 to 3. The structures have distinctive infrared spectra, and the Re–O, Re–C, and Re–C–O bond distances determined by EXAFS spectroscopy characterize the electron donor properties of the surface ligands. Supported iridium carbonyls have been formed on MgO from $Ir_4(CO)_{12}$. The carbonyl ligands have been removed to give Ir_4 and Ir_6 clusters, and the metal–support interface has been characterized by EXAFS and Raman spectroscopies. For each, Ir–Mg and Ir–O distances have been determined and used to construct models of the metal–support interface and infer the role of hydrogen at the metal–support interface. There are two Ir–O distances, the shorter one (2.2 Å) being nearly the same as the Re–O distance in the Re subcarbonyl on magnesia and suggesting a polarization of the Ir at the interface. The longer distance (2.6 Å) may indicate an interaction between a zerovalent Ir atom and O at the interface or an Ir–O interaction with intervening H.

Department of Chemistry and Biochemistry

274. *Oxidation Catalysis with Tris(pyrazolyl)borate Metal Complexes*
Theopold, K.H. **$80,000**
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

275. *Mo-Catalyzed Heteroatom Removal Reactions: Effects of Promoters on Mechanism*
Friend, C.M. **$88,400**
617-495-4052

Molybdenum-induced sulfur and oxygen removal reactions have been investigated because of their importance in catalytic deoxygenation of fuels and desulfurization of fuel feedstocks. There has been emphasis on the effect of surface modification by sulfur and oxygen since they are present during catalytic processing. Both sulfur and oxygen inhibit C–H bond breaking, leading to higher selectivity and slower kinetics for hydrocarbon production. Sulfur blocks the adsorption of reactive intermediates, resulting in lower yields of hydrocarbon. In contrast, oxygen does not inhibit adsorption, suggesting that it resides below the surface plane. Recent work suggests that the strength of the C–S and C–O bonds dictates the selectivity and kinetics for heteroatom removal by Mo. All experiments were performed under ultrahigh vacuum conditions on well-characterized single-crystal Mo using several surface spectroscopies. Current studies are concentrated on understanding the structure and HDS promotion effect of Co overlayers on Mo(110) with a p-(2 x 2) sulfur overlayer.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Chemical Engineering

276. *Selective Carbon Oxygen Bond Scission during Reactions of Oxygenates on Single Crystal Catalysts*
Masel, R.I. **$96,000**
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

277. *Electron Transfer Activation of Coordinated Thiophene*

Rauchfuss, T.B. **$176,300**
217-333-7355 **(24 months)**

The project objective is to elucidate the pathways involved in the desulfurization of thiophenes by metal ions. Metals of interest are ruthenium, rhodium, and molybdenum, all of which are known to be active catalysts for hydrodesulfurization. The redox state of the metal–thiophene ensemble strongly influences the structure, reactivity, and dynamics of coordinated thiophene. Reduced thiophene complexes are highly reactive towards protons, metal ions, and dioxygen. Cationic thiophene complexes on the other hand are attacked by hydroxide, a process that involves nucleophilic attack at sulfur and C–S bond cleavage. The mechanism and scope of these processes is being explored with attention to their relevance to novel desulfurization strategies.

Indiana University
Bloomington, IN 47405

Department of Chemistry

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

Caulton, K.C. **$113,400**
812-855-4798

A molecular prerequisite for CVD or sol/gel conversion from molecular precursors $M_aM'_b(OR)_n$ to ceramic materials $M_aM'_bO_{n/2}$ is the synthesis of the binary metal alkoxides $M(OR)_m$ and also rational methods for linking these together at a controlled stoichiometry. Synthetic efforts have culminated in the synthesis and characterization of $Y_2(OSiPh_3)_6$ in the solid state and in solution. The anhydrous compound $Y(acac)_3$ is not monomeric, but gives deceptively simple ^{89}Y and ^1H NMR spectra at 25 °C. A new catalytic procedure for production of the barium precursor $[BaN(SiMe_3)_2]_n \cdot mTHF$ was developed and used to synthesize $[Ba(OSiPh_3)_2] \cdot nTHF$. Procedures were developed for coupling different metals together to produce soluble and volatile precursors. For example, $ClCuZr_2(OR)_9$ and also $Cu_4Zr_4O_3(OR)_{18}$ ($R = {}^iPr$) were prepared and characterized. The latter displays certain structural features found in $YBa_2Cu_3O_7$, and magnetic studies show both ferromagnetic and antiferromagnetic interactions between the copper centers in this cluster. Also under investigation is the chemical basis for volatility enhancement by organofluoro groups in CVD precursors. The compound $Na_2Zr[OR']_6$ ($R' = CH(CF_3)_2$) is volatile, a consequence of its molecular character: the structure is described as $Na(\mu\text{-}OR')_2ZR(OR')_2(\mu\text{-}OR')_2Na$. Of special interest is the discovery that organofluoro groups bond to Na^+ via fluorine lone pairs. Such structural features explain why CVD with organofluoro precursors can leave inorganic fluoride in the resulting deposits.

279. *Metal Alkoxides: Models for Metal Oxides*

Chisholm, M.H. **$119,500**
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 ene–ynes are also under investigation in the light of recent developments in the chemistry of $W_2(OR)_6$ compounds. A study of the reactions of hydridometal alkoxide clusters is also proposed with regard to their stoichiometric reactions and their potential involvement in catalytic cycles. Building upon the complementary nature of carbonyl and alkoxide supported clusters of the late and early transition metals, it is proposed to investigate the activation of thiophene, benzothiophone, and related model compounds for the hydrodesulfurization (HDS) process. Also proposed is a study of the chemistry, particularly reactivity, of heterometallic hybrid clusters, that is, those formed from or involving mixed metal alkoxide/ligand systems.

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

Christou, G. **$103,400**
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.

281. *Free-Radical and Concerted Reactions in Coal Liquefaction*

Gajewski, J.J.
812-855-1192

Efforts are continuing to understand the high-temperature cleavage reaction of alkyl-aromatic coal liquefaction model compounds. In addition, the pyrolysis of 5-methylenespiro[3,5]nonane was studied. This material undergoes a retro 2 + 2 cleavage and a 1,3-shift to $\Delta^{1,2}$-octalin in a 1:2 ratio, respectively. Comparison of the activation parameters suggests that the rearrangement in unbiased systems results from an unfavorable entropy of activation and the secondary deuterium kinetic isotope effect at the exomethylene carbon is normal at 1.086 for two deuteriums, all of which is consistent with a concerted reaction. The 5-methylenespiro[3,5]nona-1-ene was prepared, and its thermal rearrangement to $\Delta^{1-2,3}$-hexalin was examined. Also formed is a triene resulting from cyclobutene ring opening. Kinetic modeling suggests that the triene reverts to either starting spirodiene or gives the hexalin directly. It is likely that both possible trienes are formed, but the *cis* material cyclizes immediately to hexalin, and the *trans* isomer is the visible component. Work continues on developing a force-field appropriate to organometallic systems. The model assumes that all metal ligand bond distances are a function of the ligand and the covalent radius of the metal, and it ignores bond angle and torsion potentials. Simplex optimization has allowed refinement of the original set to more accurately reproduce a vast array of organometallic structures provided that the metal is coordinately saturated and is not early in the periodic table.

University of Iowa
Iowa City, IA 52242

Department of Chemistry

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

Jordan, R.F. **$89,500**
319-335-2212

The objective of this research is to design and synthesize new types of electrophilic metal alkyl complexes for use in fundamental studies of olefin polymerization and C–H activation chemistry. Earlier studies of cationic $Cp_2Zr(R)(L)^+$ complexes (L = labile ligand) support recent proposals that $Cp_2M(R)^+$ ions are the active species in Cp_2MX_2-based olefin polymerization catalysts. Recent studies of these systems have focused on solution structures and dynamics. X-ray diffraction and spectroscopic studies establish that the alkyl ligands of the $Cp_2Zr(R)(L)^+$ (L = PMe_3, CH_3CN) complexes are distorted by β–agostic interactions. The alkyl ligand of $(C_5H_4Me)_2Zr(CH_2CH_2SiMe_3)(L)^+$ (L = THF, PMe_3, CH_3CN) is distorted by a strong Zr–β–C interaction. These studies suggest that the alkyl ligands of the $Cp_2Zr(R)^+$ and $Cp_2Zr(R)(olefin)^+$ ions in olefin polymerization reactions also adopt distorted (ground state) structures. Efforts are under way to probe how/whether these structural features influence insertion reactivity and/or stereochemistry. Studies of new group 4 metal complexes which incorporate ancillary ligand systems other than Cp_2M have been initiated to test the generality of the conclusions of the $Cp_2M(R)^+$ studies. To probe the influence of charge on reactivity, neutral d^0 $(C_2B_9H_{11})(Cp^*)M(R)$ (M = Zr, Hf) complexes which incorporate the dinegative, 6-electron donor ligand $C_2B_9H_{11}{}^{2-}$ (dicarbollide) in place of the uninegative Cp^- were prepared. This formal substitution reduces the metal charge by one unit but does not greatly change the metal frontier orbital properties. The reactivity of these new systems is comparable to that of their cationic $Cp_2Zr(R)^+$ analogues: $(C_2B_9H_{11})(Cp^*)MR$ complexes polymerize ethylene, oligomerize propene, insert acetylenes, and undergo internal C–H activation/CH_4 elimination to yield μ–CH_2 complexes $[(C_2B_9H_{11})(Cp^*)M]_2(\mu\text{–}CH_2)$. These results suggest that metal unsaturation may be more important than charge for high insertion and σ–bond metathesis reactivity. More recent studies have focused on early metal alkyls incorporating N_4-macrocyclic ligands.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

283. *Homogeneous Models of Ammoxidation Catalysis*

Maatta, E. **$118,260**
913-532-6687

Transition metal complexes bearing nitrogenous ligands of relevance to commercial ammoxidation processes are being prepared and their reactivity patterns are being explored. Allylimido systems $[L_nM{\equiv}N{-}CH_2{-}CH{=}CH_2]$ and allylideneamido systems $[L_nM{=}N{=}CH{-}CH{=}CH_2]$ are of particular interest with respect to propylene ammoxidation while analogous benzylimido and benzylideneamido species are relevant in the ammoxidation of aromatic substrates. The project has provided examples of these ligand systems bound in various monometallic complexes as well as in a new class of complexes derived from certain polyoxometalate anions. Results indicate that the α-hydrogen atoms in the allylimido and benzylimido systems are very acidic and readily removable, thus mimicking a key proposal in the currently accepted mechanism for ammoxidation. The possibility of forming various nitriles under mild conditions in solution from such species is being explored.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

284. *Infrared Study of Carbon Deposits on Bimetallic Catalysts*

Eischens, R.P. **$84,976**
215-758-3600

The objective of this research program is to determine how the addition of a second metal (such as rhenium, iridium, or tin) to a platinum/alumina reforming catalyst affects the nature of carbon deposition on the catalyst. Carbon deposition is followed by in situ measurement of weight increases and changes in the IR spectra. In each case the added component (rhenium, iridium, or tin) lowers the formation of a carboxylate species, which is detected by IR bands at 1585 and 1460 cm^{-1}. Current emphasis is on the study of the mechanism of carboxylate formation. The higher frequency (i.e., the more basic), surface hydroxyls of alumina provide the oxygen for carboxylate formation. Carboxylates are not formed on amorphous or crystalline silica alumina. Thus, mechanisms which postulate Al–O–Al linkages appear to be supported.

285. *Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane*

Klier, K. **$117,500**
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. Comparative studies of the activation of oxygen and methane on Pd(100) and Pd(679) have been carried out, and analogous research has been initiated with Pd(311), Pd(110), and Pd(111) to further probe the pressure gap and structure sensitivity of these activation reactions. The reaction of methane with Pd(679) was studied using a high-pressure cell installed in the ultrahigh vacuum (UHV) apparatus and Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and temperature programmed desorption (TPD) techniques. Methane was dissociatively adsorbed at 1 torr and >400 K with the formation of surface C and H species, with the latter diffusing into the Pd bulk. The initial dissociative sticking coefficient of methane was of the order of 10^{-7}–10^{-9} with an activation energy of 44.7 kJ/mol. The extent of the methane decomposition was strongly temperature dependent in that the formed surface C was in fractional monolayers for reaction at 400–500 K but in disordered agglomerated multilayers (i.e., 10 ML), at 600 K. Postsaturation of the C- and H-covered surfaces with oxygen followed by TPD indicated that clustered C species were primarily located in the vicinity of stepped and kinked sites on the Pd(679) surface after methane adsorption. The reaction of hydrogen, carbon monoxide, and oxygen with Pd(679) was also studied and combined AES and TPD results indicated that the 300 K adsorption of these molecules was primarily at the (111) terrace sites with the estimated saturation surface coverages of 0.86 ML, 0.28 ML, and 0.20 ML, respectively. Thermal desorption spectra of H_2 and CO resemble those on the low-index Pd single crystals with the activation energies of 63 and 134 kJ/mol, respectively, for the adsorbed phases. The results of this study indicate that the step and kink sites of the Pd(679) surface play a role in influencing the adsorption states only for the oxygen (and methane). The surface sensitive techniques of angle resolved X-ray photoelectron spectroscopy (XPS), involving strong forward focusing of photoelectrons, and angle resolved ultraviolet photoelectron spectroscopy (UPS) have been used to confirm the surface structure and to map the electronic structure, respectively, of Pd(100) prior to analyses following chemisorption of reactants.

Louisiana State University
Baton Rouge, LA 70803

Department of Chemical Engineering

286. *Gallium Zeolites for Light Paraffin Aromatization*

Price, J.L. **$109,953**
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 both laboratory and synchrotron-based 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

287. *Studies of Metal–Ammonia Interactions with Aromatic Substrates*

Rabideau, P.W. **$84,000**
504-388-8859

The dissolving metal reduction of coal, or related polymeric materials, promotes solubilization and depolymerization which are important to liquefaction as well as to structure characterization. This program has sought to understand the reduction pathway using polynuclear aromatics (PAs) as model compounds. This includes studies of the reaction mechanisms and delineation of the structural and geometric features of the anionic intermediates. For example, using theoretical calculations and NMR spectroscopy, the position of the metal counterions in the 7,12-dihydropleiadene dianion has been elucidated. Ion triplets represent the preferred arrangement; that is, one metal cation (sodium, potassium, or lithium) is located above the aromatic rings and the other below. In contrast, a theoretical study of dilithiobenzene by ab initio calculations predicts a structure with the lithiums on the same side as the global minimum. This is surprising and studies are under way to explore similar possibilities for polynuclear aromatics. This will be done initially by calculation and later by experiment (NMR and X-ray crystallography). Studies on the conformational analysis of hydroaromatics, which serve as hydrogen donors during thermal liquefaction, continue by both experimental and theoretical methods. This includes the detailed pathway by which carbocyclic rings in hydroaromatics undergo dynamic ring inversions.

University of Louisville
Louisville, KY 40292

Department of Chemistry

288. *Metallocarboxylate Chemistry*

Gibson, D.H. **$99,750**
502-588-5977

This research program is focused on the synthesis and studies of the chemistry of homogeneous models for catalytic intermediates in CO_2 activation/fixation processes. Current work is centered on bimetallic (transition metals) compounds having a CO_2 or CO_2-containing bridging group. The previously characterized metallocarboxylate anion, $CpFe(CO)(PPh_3)COO^-K^+$, has been used together with highly electrophilic metal complexes possessing a weakly coordinated anion $[Re(CO)_4(L)(F{-}BF)_3$; L=CO, PPh_3, $P(OPh)_3]$ to generate $\mu_2{-}\eta^2{-}CO_2$-bridged compounds. One of these (L=PPh_3) has recently been characterized by X-ray crystallography. All members of this class of compounds lose CO upon heating to yield examples of a second class of CO_2-bridged complexes; these are presently formulated with $\mu_2{-}\eta^3{-}CO_2$ bridges of the dimetallated dioxycarbene type based on their IR and NMR spectral properties. Two of the $\mu_2{-}\eta^3$ complexes [L=CO, $P(OPh)_3$] lose CO upon further thermolysis to give compounds which are formulated as heterobimetallic complexes with an oxo ligand on the rhenium center. Efforts are in progress to characterize the $\mu_2{-}\eta^3$ complexes and the oxo derivatives structurally. Reactions between the metallocarboxylate anion and the ethylene-coordinated cations, $CpFe(CO)(L)(C_2H_4)^+BF_4^-$[L=$PPh_3$, $P(OPh)_3$], yield bimetallic compounds with a carboxyethylene bridging group. These represent the first examples of compounds resulting from the coupling of coordinated carbon dioxide and ethylene through C–O bond formation. Efforts to define the characteristic reactions of all these classes of compounds are in progress.

University of Maryland at College Park
College Park, MD 20742

Department of Chemistry and Biochemistry

289. *Odd-Electron Organometallic Chemistry of Relevance to Hydrocarbon Functionalization*

Poli, R. **$81,303**
301-405-1809

The general objective of this project is to test the feasibility of the C–H oxidative addition to low-valent, unsaturated 15-electron organometallic intermediates, as well as to explore the general reactivity of these intermediates, which are isolobal fragments with methylidyne. Parallels with known C–H oxidative addition chemistry of 16-electron intermediates indicate that the sought intermediates may be obtained from electron-rich compounds having a 17-electron configuration by either (1) photochemically assisted reductive elimination of dihydrogen or (2) thermal or photochemical elimination of a neutral 2-electron donor ligand. The use of sterically demanding ligands is supposed to facilitate this process. Thus, the synthesis, characterization, and reactivity of these 17-electron precursors will be investigated in the first phase of the project. Subsequently, the generation and in situ characterization of the 15-electron intermediates will be attempted, as well as the analysis of the oxidative addition products when carrying out these reactions in the presence of a variety of X–Y substrates. Currently, efforts have just started toward the generation of $CpMoH_2L_2$ complexes (Cp = cyclopentadienyl, L = tertiary phosphine).

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

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

Ceyer, S.T. **$98,000**
617-253-4537

The major thrust of this proposed research is to carry out for the first time a heterogeneous catalytic reaction that normally is observed only at high pressures ($\gtrsim$1 atm) of reactant gas at low pressures ($\lesssim 10^{-4}$ torr) in an ultrahigh vacuum environment (UHV) on a Ni(111) crystal surface. This is possible using a scheme that couples molecular beam techniques with high-resolution electron energy loss spectroscopy (HREELS). Two molecular beams provide a means to activate each of the two reactants, and the HREELS is a sensitive and chemically specific detector of the reaction progress. These studies will verify the principles behind the lack of reactivity at low pressures. The ability to carry out a "high-pressure" reaction, such as the steam reforming of CH_4, in a UHV environment enables the use of surface-sensitive electron spectroscopies such as HREELS to identify unambiguously the reaction intermediates, thereby testing the mechanisms proposed from high-pressure kinetics measurements. Work has begun on the design of the apparatus.

291. *Controlled Synthesis of Polyenes by Catalytic Methods*

Schrock, R.R. **$126,000**
617-253-1596

In this project polyenes of a specific length are being prepared through stoichiometric reactions of molybdenum complexes that have been previously used in catalytic reactions. This approach has been dropped, since a way was 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

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

The proposed research is an experimental and modeling study of oxidation reactions involving CO as a reactant, adsorbed intermediate, and/or partial oxidation product. Reaction systems of current interest include Pt-catalyzed CO and methanol oxidation by O_2, CO oxidation by NO, and ethylene oxidation on metal (Cu, V) oxide catalysts. Each of these reactions can exhibit complex steady-state and dynamic behavior, including multiple rate-controlling steps, multiple rate states, and oscillatory phenomena. The overall project objective is to formulate elementary step kinetic models that can predict the correct experimentally measured features, including the basic kinetic trends, the location and shape of the operating condition region for which the rate is multivalued or periodic, and the trends in the adsorbed state composition. Successfully meeting this objective requires an integration of basic kinetic measurements, in situ catalyst surface monitoring, and nonlinear analysis tools. Catalytic rates are measured over a wide range of operating conditions in order to establish basic kinetic features, and to map the conditions in which the rate is multivalued and/or periodic. Surface measurements are made with Fourier transform infrared emission spectroscopy (FTIRES). The capability of using FTIRES to monitor both surface species and metal–oxygen bonds is being developed. Initial discrimination between rival kinetic models is based on their ability to predict reaction orders and activation energy in different kinetic regimes. Nonlinear regression schemes can be used to estimate kinetic parameters based on a fit of the operating condition region within which multiplicity or oscillations are observed. Rival kinetic models are then screened by testing their ability to predict kinetic and surface IR data over a wide range of conditions.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

293. *Hydrogen Induced C–C, C–N, and C–S Bond Activation on Pt and Ni Surfaces*
Gland, J.L. **$162,000**
313-764-7354 **(18 months)**

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

294. *Homogeneous–Heterogeneous Combustion: Chemical and Thermal Coupling*
Schmidt, L.D. **$89,700**
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

295. *Late Transition Metal Oxo and Imido Complexes*
Sharp, P.R. **$109,372**
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 bimolecularly decompose to gold clusters by elimination of tetrazenes, modeling recombination of atomic oxygen on metal surfaces.

University of Nevada at Reno
Reno, NV 89557

Department of Chemistry

296. *High-Temperature Chemistry of Aromatic Hydrocarbons*
Scott, L.T. **$107,400**
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 the high temperatures, such as those employed in the uncatalyzed gasification and liquefaction of coal. This year has brought new insight into the puzzling mechanism by which carbon atoms become thermally scrambled in PAHs. Isotopic labeling studies on the thermal conversion of benzofulvene to naphthalene implicate benzofulvene as an obligatory intermediate in the automerization reaction of naphthalene. A spectacularly short and convenient synthesis of corannulene, the bowl-shaped twenty-carbon subunit of spheroidal C_{60}, was also achieved by high-temperature chemical methods, and the energy barrier for its bowl-to-bowl inversion was measured. 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.

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

Work in two major areas is being pursued. New carbyne chemistry is being addressed and initiatives in metal nitrene chemistry are under way. A conceptual link between these two projects is provided by the isoelectronic relationship between $Tp'(CO)_2W{\equiv}CH$ and $Tp'(CO)_2W{\equiv}NH^+$. Both of these complexes have now been isolated and characterized. Dimerization of $Tp'(CO)_2M{\equiv}CH$ for both molybdenum and tungsten to form an unusual vinylidene bridged complex is a facile decomposition route which consumes the carbyne monomer. Reduction of coordinated phenylacetylene in $Tp'(CO)_2W(PhC{\equiv}CH)^+$ by stepwise addition of H^- and then H^+ yields an η^2-vinyl and then an agostic methylphenylcarbene. Using $Tp'(CO)W(Ph{\equiv}CH)_2^+$ as a reagent forms simple vinyl and carbene ligands in this sequence. Another agostic species has been formed by protonation of the rare dinuclear carbide, $Tp'(CO)_2Mo{\equiv}C{-}Fe(CO)_2Cp$. A rich chemistry with nitrogen donor ligands is unfolding in the $Tp'(CO)_2WNR_2$ system where $Tp'(CO)_2W{=}NHR$ can be easily generated and $Tp'(CO)_2WNR^+$, $Tp'(CO)_2WNR^-$, and $Tp'(CO)_2WN$ are all accessible, at least as reactive intermediates.

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Department of Chemical Engineering

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

Kung, H.H. **$112,000**
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. The relationship between surface atomic structure and bulk structure of an oxide with the catalytic properties is being studied using the oxidation of light alkanes as a test reaction. Earlier work has shown that the selectivity for oxidative dehydrogenation of butane over orthovanadates can be correlated with the reducibility of the second cation. It was proposed that the redox property of M in the M–O–V bonds in these oxides was a significant factor that affected selectivity. One consequence of this concept is that catalysts of very well dispersed vanadium oxide on a support, where most of the vanadium ions are bonded to the support oxide and therefore possess different M–O–V bonds depending on the chemical nature of the support, would have different catalytic properties. Indeed, this concept was confirmed with silica-supported vanadia. It was found that such catalysts containing one weight percent of vanadia were much more selective for oxidative dehydrogenation of butane than the five or ten weight percent samples. Control experiments have shown that the differences were not due to impurities present in the support. Since the Raman spectra showed that the one weight percent sample contained a much larger fraction of vanadia bonded to the support, these species must be more selective in the reaction.

Department of Chemistry

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

Marks, T.J. **$111,431**
708-491-5658 **(10 months)**

The project objective is to elucidate pathways effecting 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 probes, while catalytic transformations (e.g., olefin hydrogenation) are studied by kinetic measurements, isotopic labeling, product stereochemistry, and in situ spectroscopic probes. 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 and functionally modeled in solution by $Cp_2MR^+ X^-$ complexes, where X^- is a weakly coordinating anion such as $B(C_6F_5)_4^-$ (e.g., crystallographically characterized $[(CH_3)_5C_5]_2 ThCH_3^+ B(C_6F_5)_4^-$). The adsorption process as well as the means by which methylalumoxane, “$[Al(CH_3O]_n$” activates organo-group 4 complexes for homogeneous olefin polymerization can be modeled using $B(C_6F_5)_3$ as an alkide abstraction reagent. Finally, adsorption of $Th(\eta^3\text{-allyl})_4$ on Al_2O_3 yields heterogeneous arene hydrogenation catalysts which rival or surpass conventional platinum metal catalysts in activity.

300. Chemical Interactions in Multimetal–Zeolite Catalysts

Sachtler, W.M.H. **$108,100**
708-491-5263

Cobalt, nickel, copper, and gallium ions can be exchanged into zeolites, but their reduction requires severe conditions and often remains incomplete. The reducibility of cobalt, nickel, and copper can be dramatically enhanced by (1) washing at high pH and/or (2) adding platinum or palladium ions and placing them into specific zeolite cavities. At elevated temperature metal reduction is partially reversible: Cu in PtCu or PdCu particles and Ni in PdNi are selectively oxidized by zeolite protons to Cu^{2+} or Ni^{2+} ions which escape to smaller zeolite cavities. The resulting Pd particles are identified by their ability to form a hydride. Zeolite Y encaged PdNi particles are found to be much more active methanation catalysts than either of the pure elements in Y. PdCo/NaY catalysts display a higher selectivity for the isomerization of 2,2-dimethylbutane than Pd/NaY or Co/SiO_2. Ga/H-ZSM5 is active in converting alkanes (e.g., C_3) into aromatics. TPR reveals that reduction of Ga starts at a significantly lower temperature in H-ZSM5 than on SiO_2. Pt enhances the reduction of Ga^{3+} to Ga^{1+}, but no PtGa alloy appears to be formed. A novel method has been developed to produce active Ga/H-Z5M5 catalysts. It is based on the sublimation of $GaCl_3$ onto H-ZSM5, followed by reduction with H_2.

301. Organometallic and Surface Chemistry of Mixed-Metal Systems

Shriver, D.F. **$112,000**
708-491-5655

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, carbido, and hybrido ligands and their derivatives. Extensive 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 unit using a CCO ligand as the carbon course. 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. Also under study is the activation of H_2 by clusters. Facile reactions of H_2 with cluster-bound ligands have been found.

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Department of Chemistry and Biochemistry

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

Nicholas, K.M. **$112,993**
402-325-4811

The focus of this project is on the thermal (dark) and photochemical reactivity of carbon dioxide coordinated to transition-metal centers. Efforts are centered on defining the fundamental reactivity patterns of selected, structurally characterized η^2–mononuclear CO_2 complexes (1) under thermal (dark) conditions toward external reagents including electrophiles, nucleophiles, and radical reagents and (2) under photolytic conditions. Following discovery of the remarkably facile reactions of $Cp_2Mo(\eta^2\text{–}CO_2)$ with various electrophilic reagents (E–Nu) which afford $\{Cp_2Mo(CO)Nu\}$ + Nu^- and E–O–E, it was found that **1** reacts with acidic transition-metal hydrides ($HM'_x(CO)_y$) to produce $[Cp_2MoH(CO)]M'_x(CO)_y$ and H_2O. The reactivity of transition-metal hydrides towards **1** follows the trend of the metal hydride's acidity (i.e., $HCo(CO)_4 > H_2Fe(CO)_4 \gg HMCp(CO)_3$, Cp_2MoH_2). The capability of the hydrides $HCo(CO)_4$ and $H_2Fe(CO)_4$ to be produced from molecular hydrogen raises the attractive possibility of their serving as agents for catalytic CO_2 reduction. Studies were initiated on modeling CO_2 insertion reactions into M–C bonds using $(MeC_5H_4)_2Nb(\eta^2\text{–}CO_2)CH_2SiMe_3$ (**2**), the only established example of a complex containing both CO_2 and alkyl ligands. Surprisingly, **2** undergoes decarbonylation rather than insertion when heated at 60 °C, efficiently producing the oxo complex $(MeC_5H_4)_2Nb(O)CH_2SiMe_3$. Furthermore, this decarbonylation is dramatically accelerated by ultraviolet irradiation. Recent efforts to promote insertion reactions of **2** are centered on reactions with Lewis acids and external ligands. Finally, a series of remarkable rhodium-catalyzed H-transfer reductions of CO_2 to formic acid under very mild conditions was discovered. Either H_2 or H-donor substrates (e.g., ethers) can serve as reductants. In the latter mode added O_2 induces substrate oxidation with concomitant CO_2 reduction. Studies to elucidate and expand these novel initial results are under way. A number of new systems are also under investigation including the thermal and photochemical reactions of $Mo(CO_2)_2(PMe_3)_4$ and $(R_3P)_2Ni(CO_2)$.

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Department of Chemistry

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

Finke, R.G. **$115,112**
503-346-4622

The goal of this research is to develop a chemical paradigm for polyoxoanion-supported transition-metal catalysis (e.g., from the novel catalyst precursor $[(Bu_4N)_5Na_3][(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$), with an emphasis on small molecule (H_2, O_2, CH_4) catalytic activation and functionalization (CH_4, RH). Considerable success here was reported last year, and mechanistic studies of the $[(Bu_4N)_5Na_3][(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ system are continuing. A second goal of the DOE-supported research is to develop polyoxoanion-incorporated catalysts, such as $P_2W_{17}MO_{61}{}^{n-}$ [M = Mn(III), Fe(II), Co(II), Ni(II), and Cu(II)], for alkene, alkane, and aromatic C–H bond activation and functionalization. Kinetic and mechanistic studies are again an integral part of this work, since they provide both the best and fastest way to establish the strengths and weaknesses of such catalyst materials reliably. During the past year, two papers were published detailing highly active $P_2W_{17}MO_{61}{}^{n-}$ catalysts for olefin, alkane, and aromatic oxidations using PhIO as the terminal oxidant. Direct comparisons showed that these catalysts are almost as effective as the best metalloporphyrin catalysts developed to date. Future studies of these polyoxoanion-incorporated catalysts will focus in two areas: expansion of the list of metals (M) in the $P_2W_{17}MO_{61}{}^{n-}$ catalyst series, and kinetic and mechanistic studies of the best catalysts systems [especially M = Mn(III)].

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Department of Chemical Engineering

304. Enhancement of Activity and Selectivity by Metal–Support Interactions

Vannice, M.A. **$130,000**
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 rate enhancements greater than 100-fold for CO and acetone hydrogenation and an increase in selectivity from zero to over 35% for crotyl alcohol formation from crotonaldehyde, rather than butyraldehyde, when titania was used to disperse Pt. A model invoking special active sites at the metal–support interface has been proposed to explain this behavior. It is now being tested further by studying the selectivity of acetophenone hydrogenation over Pt. A study of Au/TiO_2 catalysts has clearly shown that Frost's model invoking O vacancies on the titania surface cannot explain this behavior because these catalysts were inactive in these hydrogenation reactions. However, they were found to be excellent CO oxidation catalysts at room temperature, and a study of this activity is continuing. 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 Pt and TiO_2 single crystals and a Pt-covered TiO_2 single crystal.

Studies of benzene, toluene, and xylene have shown that turnover frequencies (TOFs) on Pd can be increased using acidic supports. A similar enhancement occurs with Pt but to a lesser extent as Pt is more active than Pd. The addition of methyl groups to the ring decreases TOF values on both Pd and Pt. The presence of additional acidic adsorption sites on the support near the Pd or Pt crystallites has been proposed to explain this behavior. Characterization of these adsorbed molecules using infrared spectroscopy may also be accomplished if time permits.

Department of Chemistry

305. *Highly Nucleophilic Acetylide, Vinyl, and Vinylidene Complexes*

Geoffroy, G.L. **$115,500**
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.

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

Sen, A. **$110,000**
814-863-2460

The catalysis of organic transformations by transition metals, especially in solution, is of great practical and scientific importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The current research is focused primarily on three areas of transition metal catalyzed transformations of small molecules. The first encompasses metal catalyzed processes for the synthesis of several classes of carbon monoxide containing polymers. These include (1) new alternating copolymers of carbon monoxide with olefins and (2) polyureas and polyoxamides. The second area involves the examination of the chemistry of metal complexes incorporating oxo and hydrocarbyl ligands as a model for the heterogeneous oxidation of olefins and alkanes by metal oxides. The third area of research is concerned with the development of hybrid catalyst systems involving both homogeneous and heterogeneous metal components for the oxidative functionalization of alkanes. Finally, somewhat smaller effort is being devoted to the synthesis of well-defined nanoclusters (size <1–10 nm) of metals, metal oxides, and metal sulfides. It is anticipated that such species would exhibit size-dependent catalytic properties.

Department of Materials Science and Engineering

307. *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 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. A major problem in this field is that the previously used Flory–Rehner equation for the swelling of networks is now known to be incorrect. A model is being developed and applied that is based on disinterspersion and that appears to be far more promising. The ability of this model to account for coal structural characteristics is being probed using a novel dilatometric technique.

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Department of Chemical Engineering

308. *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 catalysts is being examined. Specifically, model catalysts are being used to understand two important classes of supported catalysts: supported noble metals for emissions-control catalysts and mixed oxides for acid catalysis. Model catalysts are chosen so that surface techniques like temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) can be utilized to understand the changes that occur on the catalyst caused by the support. These changes are being correlated to reaction properties in order to understand what can be done to optimize catalyst performance.

Department of Chemistry

309. *Catalytic Synthesis of Silicon Carbide Preceramic Polymers: Polycarbosilanes*

Berry, D.H. **$92,508**
215-898-2705

The first homogeneous transition metal catalysts for the dehydrogenative coupling of simple alkyl silanes to oligomeric and polymeric carbosilanes, $H{-}(SiR_2CR'_2)_n{-}SiR_3$, have been developed and are under investigation. 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. Well-characterized ruthenium complexes of the type $(PR_3)_3Ru(H)_3(SiR'_3)$ catalyze the dehydrogenation of trialkyl silanes at 150 °C to produce a distribution of linear and branched carbosilanes. Mechanistic studies suggest that transient metal silaolefin complexes of the type $L_nRu(\eta^2{-}R_2Si{=}CR'_2)$ are generated by β-hydrogen elimination from silyl ligands and play a key role in the catalytic silane dehydrogenation and carbosilane formation. Competing α-elimination from silyl ligands appears to lead to catalytic silane redistribution reactions. The addition of hindered olefins as hydrogen acceptors leads to a dramatic increase in the rate of silane coupling, and permits catalysis at 80 °C. Current studies include detailed elucidation of the catalytic mechanism and development of more active catalyst systems.

310. Synthesis and Properties of New Preceramic Materials

Sneddon, L.G. **$105,000**
215-898-8632

The goal of this project is to develop new selective high yield synthetic routes to important boron-based solid-state materials that allow the production of these materials in forms, such as fibers, coatings, and shaped bodies, unattainable using conventional powder processing techniques. This project has already resulted in the discovery of new boron polymer systems, including polyborazylene and polyvinylborazine, that have proven to give high yields of boron nitride ceramics. Ongoing work is now centered on the design and synthesis of new generations of boron nitrogen polymers, hybrid boron–silicon and boron–carbon polymers and the use of these polymers as reagents for the production of metal-boride and metal-boride/metal-nitride nanocomposites. The continued development of the fundamental reaction chemistry and synthetic methodology needed to produce both new molecular and polymeric inorganic polymers is also an integral component of this project.

311. Catalytic Hydrogenation of Carbon Monoxide

Wayland, B.B. **$120,300**
215-898-8633

This project is focused on developing strategies to accomplish the reduction and hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. The approaches to this issue are based on the recognition that rhodium macrocycles have unusually favorable thermodynamic values for producing a series of intermediates implicated in the catalytic hydrogenation of CO. Observations of metalloformyl complexes produced by reactions of H_2 and 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 overall process. Variation of the electronic and steric effects associated with the ligand arrays along with the influences of the reaction medium provide the chemical tools for tuning these factors. Recent studies have focused on the use of rhodium(II) metalloradicals in 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 applications for this new range of CO reactivity in forming organic oxygenates are being exploited through the use of multifunctional catalyst systems designed to couple the 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

312. Studies of Supported Hydrodesulfurization Catalysts

Hercules, D.M. **$85,000**
412-624-8300

The aim of the research is to investigate the Mo oxidation state/catalytic activity relationship in reduced Mo/Al_2O_3, Mo/SiO_2, and Mo/TiO_2 catalysts. The ultimate objective of the study is to identify required Mo oxidation states for various catalytic functions. To achieve the stated objective, a parallel study was conducted on Mo allyl-based "model" catalysts reportedly containing discrete Mo oxidation states and conventionally prepared catalysts that usually form mixed Mo oxidation states on reduction. The distribution of Mo oxidation states was determined by X-ray photoelectron spectroscopy, electron spectroscopy for chemical analysis (XPS, ESCA). For "model" catalysts, the results indicated that reduction of allyl-based Mo/SiO_2 at 550 °C may indeed lead to the formation of discrete Mo(+2) oxidation state as previously proposed. However, the reported formation of discrete Mo(+4) upon oxidation of the reduced catalyst at room temperature could not be substantiated by ESCA. ESCA study of conventionally prepared Mo/Al_2O_3 catalysts (8 wt % Mo prepared by impregnation) showed that Mo oxidation states ranging from +6 to 0 are produced on reduction between 200 and 900 °C. The catalytic activity of the reduced catalysts for propene hydrogenation and propane hydrogenolysis was measured as a function of the reduction temperature. The variation of catalytic activity of the reduced catalysts was compared with the distribution of Mo oxidation states obtained from ESCA. The results indicated that Mo oxidation states $\leq +4$ are required for propene hydrogenation. Propane hydrogenolysis required a more severe reduction treatment. The catalytic activity correlated with the change in the abundance of Mo metal.

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

Yates, J.T., Jr. **$159,000**
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) the activation and poisoning of CO-based and N_2-based surface chemistry; (2) the influence of electric fields on CO bonding to metals; (3) the thermal activation of methane, discriminating between activation of weakly bound methane and activation of methane in the gas phase above the surface; (4) fundamental studies of ethylene chemistry on supported Pt; (5) fundamental studies of the role of atomic steps on Pt single crystals on chemisorption; (6) spectroscopic FT-IRAS studies on C–H bond softening in hydrocarbons interacting with single crystal metal surfaces; and (7) 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 (7).

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314. Anchoring Strategies for Bimetallic Species in Zeolites

Bein, T. **$91,995**
317-494-5495

This research program is aimed at understanding new immobilization concepts for organometallic fragments in the crystalline pore structure of zeolites. The approach taken is to introduce heterobinuclear organometallic compounds containing appropriate ligands as candidates for linking a catalytic function to zeolite frameworks. The bimetallic complexes, $Cl_2(THF)GeM(CO)_5$ (M = Mo, W) and $X_3SnMn(CO)_5$ (X = Me, Cl), have been reacted with different acidic, large pore zeolites. Extended X-ray absorption fine structure (EXAFS) studies reveal that the precursors are attached to the zeolite oxygen framework via the Ge or Sn moiety by loss of chloride or methyl ligands, while the carbonyl moiety remains largely intact at moderate temperatures. At higher temperatures, cleavage of the metal–metal bonds is observed. A comprehensive combination of analytical techniques is used to probe local structural changes at the molecular level. These techniques include EXAFS spectroscopy utilizing synchrotron radiation, in situ Fourier transform infrared (FT-IR) coupled to thermodesorption, and Raman and reflectance UV-vis spectroscopies. 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. The long-term goal is also to prepare intrazeolite bimetallic clusters through controlled decomposition of zeolite-anchored heterobimetallic compounds.

315. Catalytic Arene Hydrogenation Using Early Transition-Metal Hydride Compounds

Rothwell, I.P. **$110,000**
317-494-7012

This project is for the study of a new series of transition-metal compounds capable of catalyzing the homogeneous hydrogenation of arene rings. The objective of this project is to characterize the activity of niobium- and tantalum-based catalysts for the hydrogenation of polyaromatic hydrocarbons and aryl–phosphine ligands. This includes the catalytic synthesis of new cyclohexyl–phosphine compounds. Preliminary work has shown that Group 5 metal aryloxide systems are capable of hydrogenating arene rings in both an inter- and intra-molecular fashion. It has been shown that it is possible to isolate stable mononuclear polyhydride compounds containing aryloxide ancillary ligation. Another useful reaction reported is the hydrogenation of arene rings on phosphines and polyphosphine ligands leading to cyclohexyl phosphines. A variety of polyaromatic hydrocarbons have been hydrogenated to mixed saturated–unsaturated systems with a high degree of selectivity using a niobium complex. Additional preliminary work on the catalytic activity of similar tantalum complexes has also been done.

316. Fundamental Studies of Reactive Intermediates in Homogeneous Catalysis

Squires, R.R. **$75,000**
317-494-7322

The thermochemistry and intrinsic reactivity of organometallic species relevant to catalysis are being investigated in the gas phase through use of a flowing afterglow triple quadrupole instrument. Measurement of reaction rates and collision-induced dissociation thresholds for organometallic ions yields metal–ligand bond strengths, reaction barriers, and mechanistic information. An extensive set of metal–carbonyl bond strengths has been measured, and is currently being extended and refined. The metal–ligand bond strengths in $M(CO)_n^-$ ions vary widely in the 29–44 kcal/mol range, emphasizing the importance of measuring sequential rather than average bond strengths. A pattern is emerging where metal–carbonyl bond strengths in 14- and 16-electron complexes are on average $\approx$ 10 kcal/mol weaker than those in 13-, 15-, and 17-electron complexes. The anion bond energies can be combined with literature data to derive neutral metal–carbonyl bond strengths, ionization potentials, and metal–alkene bond energies, and other physical data. These results indicate that bonds from iron to 1–4 olefinic groups are somewhat weaker than bonds to the same number of carbonyl ligands. Collisional activation of $Fe(CO)_4COOH^-$ leads to loss of CO and CO_2 with low efficiencies and barriers of $\approx$ 20 kcal/mol, although the reactions are essentially thermoneutral. These and other results are being used to determine a potential energy surface for the $Fe(CO)_4COOH^-$ system, a model species in the water–gas shift reaction.

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Department of Chemistry

317. Selective Transformations of Carbonyl Ligands to Organic Molecules

Cutler, A.R. **$126,500**
518-276-8447

Studies on the carbonylation of (η^5-indenyl)(L)(CO)Ru–R complexes (L = CO, PPh_3; R = CH_2OMe, CH_3) have been completed. Particularly noteworthy is that the methoxymethyl complexes readily transform to their acyl derivatives under mild conditions that leave their iron congeners inert toward CO. Surprisingly, even (η^5-indenyl)(PPh_3)$_2$Ru–CH_3 carbonylates and gives (η^5-indenyl)(PPh_3)(CO)Ru–C(O)CH_3. Attempts to carbonylate α-alkoxyethyl analogs (η^5-indenyl)(L)(CO)Ru–CH(OR)CH_3 [L = PPh_3, PEt_3, P(OMe)$_3$] afford (η^5-indenyl)(L) (CO)Ru–C(O)CH_2CH_2OR, which are isomeric to the expected α-alkoxypropionyl complexes [Ru]–C(O)CH(OR)CH_3. Attempts to use this rearrangement for incorporating additional CO into the ligand 'chain' are in progress. Mechanistic studies on the "noncatalyzed" hydrosilation of the manganese acyls $(CO)_5$Mn–C(O)CH_2R (R = H, OCH_3, CH_3) with Et_3SiH and of cobalt acetyls $(CO)_3(PR_3)$CoC(O)CH_3 with several monohydrosilanes have been completed. The cobalt acetyls cleanly give ethoxysilanes (not acetaldehyde), and the manganese acyls provide α-siloxyvinyl complexes Z–$(CO)_5$Mn–C($OSiEt_3$)=CHR (R = H, CH_3, OCH_3). Carbonylation and protolytic cleavage of the latter generate pyruvoyl complexes $(CO)_5$Mn–COCOR (R = CH_3, CH_2CH_3), formally the products of net "double carbonylation" sequences. Studies in progress are concerned with how manganese complexes as diverse as $(CO)_5$Mn–Y [Y = C(O)R, R, Br, but not $SiMe_3$ or $Mn(CO)_5$] and (η^3-C_3H_5)Mn$(CO)_2$L [but not CpMn$(CO)_3$ or CpMn$(CO)_2$ (η^2HSiR_3)] function as efficient hydrosilation catalysts toward Cp$(CO)_2$FeC(O)CH_3, for example. These reactions cleanly afford fully characterized α-siloxyethyl complexes Fp–CH($OSiR_3$)CH_3 under conditions where typical Rh(I) hydrosilation catalysts are inactive. Several of these manganese complexes also catalytically hydrosilate organic esters, including lactones, to their ethers R–CH_2OR′; these novel ester reductions occur quantitatively at room temperature and appear to be general in scope. Efforts to develop a phosphide–phosphine "switch" for controlling the reactivity (and stereochemistry) of acyl ligand reduction on Cp(PPh_2H)(CO)FeC(O)CH_3/Cp(PPh_2)(CO)FeC(O)$CH_3{}^{-1}$ have been completed. These studies involved attempts to generate (and reduce) siloxycarbene complexes Cp(PPh_2)(CO)Fe=C($OSiR_3$)CH_3 and Cp(PPh_2R)(CO)Fe=C($OSiR_3$)$CH_3{}^+$.

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318. Transition Metal Activation and Functionalization of Carbon–Hydrogen Bonds

Jones, W.D. **$112,200**
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 η^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. Also examined were the reactions of a series of trispyrazolylborate complexes of rhodium. 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 loses 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. The microscopic reverse of this elimination implies that thermal oxidative addition would occur by coordination of arene prior to loss of the isocyanide (i.e., and associative pathway for C–H activation). 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). Further studies of functionalization reactions are under way.

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

Department of Chemistry

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

Goldman, A.S. **$79,000**
908-932-5232

Significant progress has been made toward the goal of efficient transition-metal catalyzed systems for alkane functionalization. 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, including Rh(PMe_3)$_2$(P^iPr_3)Cl and [Rh(PMe_3)$_2$Cl]$_2$ have been developed. The latter systems require only moderate pressures of dihydrogen. It was demonstrated that the role of hydrogen in all cases is to add to the complexes which then dissociate to afford the species H_2Rh(PMe_3)$_2$Cl. The dihydride then reacts with hydrogen acceptor to give the fragment Rh(PMe_3)$_2$Cl which reacts with alkanes. It was also found that ketones and various d^8 metal carbonyls (including Ir(PMe_3)$_2$(CO)$_2$Cl and Ru(CO)$_3$(dmpe) as well as Rh(PMe_3)$_2$(CO)Cl) will cocatalyze the photochemical carbonylation of alkanes. It has been demonstrated that this catalysis involves formation of alkyl radicals via hydrogen abstraction by photoexcited ketones; radical attack on the metal carbonyls then affords acylmetalloradicals. In addition, a mechanistic study of Rh(pyridine)(CO)$_2$Cl-catalyzed aldehyde decarbonylation under CO atmosphere has been completed; in principle this complex must also catalyze the endoergic back-reaction, alkane carbonylation.

Department of Physics and Astronomy

320. Structure and Reactivity of Model Thin Film Catalysts

Madey, T.E. **$93,100**
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 bcc(111) and fcc(210) single crystal surfaces. 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), 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. Both LEED and scanning tunneling microscopy (STM) are used to characterize surface morphology. In contrast, ultrathin films of Ti, Co, Ni, Cu, and Ag grow pseudomorphically and do not induce faceting. The faceting occurs for overlayer elements having Pauling electronegativities greater than 2.0, suggesting that electronic effects are playing a role in structure changes. When CO is used as a probe molecule for Pt/W(111) changes in thermal desorption spectra are seen to correlate with faceting.

University of South Carolina
Columbia, SC 29208

Department of Chemistry

321. The Transformations of Organic Amines by Transition Metal Cluster Compounds

Adams, R.D. **$112,000**
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 ynamines and strained ring heterocycles containing nitrogen that result in the cleavage of carbon–nitrogen bonds by cluster complexes are also under study.

University of Southern California
Los Angeles, CA 90089

Department of Chemistry

322. Chemistry of Bimetallic and Alloy Surfaces

Koel, B.E. **$89,865**
213-740-4126

This research is focused on elucidating the underlying principles that govern chemical reactions occurring on bimetallic and alloy surfaces. This understanding will aid in the atomic level explanation of the reactivity and selectivity of alloy and bimetallic cluster catalysts and will be important for the design of new catalysts with improved performance. Using a battery of surface science methods, fundamental data on the thermochemistry, and kinetics of the adsorption and reaction of molecules on extensively characterized, single-crystal bimetallic surfaces will be obtained. Changes in chemisorption bond strengths, adsorption site distributions, and hydrocarbon fragment stability and reactivity are correlated with the geometric and electronic structure of the metal atoms on the surface. Careful design of experiments can isolate factors (e.g., ensemble and ligand effects) that control surface chemistry and catalysis on bimetallic and alloy surfaces. Alkali promoters strongly affect the reactions of hydrocarbons on Pt and Ni surfaces by altering the electronic structure and inducing significant site-blocking effects. Bismuth coadsorption provides benchmark data on ensemble sizes required for chemical reactions on Pt and Ni surfaces. Surface alloys, for example Sn/Pt, are used for detailed probing of ensemble sizes and also reactive site requirements.

Southern Illinois University
Carbondale, IL 62901

Department of Chemistry

323. Studies of the Stabilities and Reactions of Solution Phase Organic Radicals

Bausch, M. **$137,000**
618-453-6461 **(18 months)**

The project objective is to develop a more complete understanding of the stabilities and reactions of relatively large (molar mass > 100 g) organic radicals. Specifically, the research will aid in clarifying factors that affect the thermodynamic and kinetic stabilities of selected organic radicals, probe the acidic nature of organic radicals and the stabilities of their respective radical anionic conjugate bases, and determine bond strengths in organic radicals and radical anions. Analyses of the data that result from completion of these experiments will 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. Many of the data in this study will be collected with the aid of colorimetric and electrochemical protocols. Of particular interest is the use of high-speed cyclic voltammetric techniques in evaluations of the solution phase kinetics of carbon- and nitrogen-centered radical dimerizations.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

324. *The Dynamics of Adsorption on Clean and Adsorbate-Modified Transition Metal Surfaces*
Madix, R.J. **$140,000**
415-723-2402

Catalytic reactions often occur on surfaces covered with nonreactive species that block reactive sites and clutter the surface. These species may significantly affect the adsorption of reactive species through the formation of weakly bound adsorbed species, referred to as precursor states. These precursor states lead to adsorption kinetics that differ markedly from simple site blocking, and they can promote adsorption even with high surface coverages of the nonreactive intermediates. Adsorption into the precursor state is effected by energy exchange between the incoming molecule and the adsorbed species, leading to loss of translational energy and trapping of the incident species in a potential minimum at the surface. The dynamics of this process have been studied for alkane adsorption on Pt(111), a catalytic metal widely used for hydrocarbon oxidation, reforming, and dehydrogenation, in order to determine the effect of the dynamical state of the adsorbed nonreactive species on the trapping probability. Sulfur atoms, ethylidyne fragment, and molecular ethane all increase the trapping probability of ethane on Pt(111) compared to the clean surface. At the same incident kinetic energy the trapping probabilities for ethane increase from sulfur, ethylidyne to ethane covered surfaces, reflecting the increasing number of degrees of freedom accessible for energy absorption in the adsorbed species.

State University of New York at Binghamton
Binghamton, NY 13902

Department of Chemistry

325. *Photochemistry of Intermolecular C–H Bond Activation*
Lees, A.J. **$79,560**
607-777-4478

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 $Cp^*Rh(CO)_2$ ($Cp = \eta^5–C_5H_5$; $Cp^* = \eta^5–C_5Me_5$) 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 are providing insights into the nature of the electronically excited states and photophysical processes for $(HBPz^*_3)Rh(CO)_2$ and the mechanism for intermolecular C–H bond activation in this system.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

326. *Mechanistic Examination of Organometallic Electron-Transfer Reactions*
Atwood, J.D. **$84,500**
716-831-2122

Studies of the transfer of electrons and groups (H^+, $H\cdot$, H^-, CH_3^+, $CH_3\cdot$, CH_3^-, CO^{2+}, and so forth) between organometallic complexes have continued with the goal of understanding the role of such reactions in catalysis. Outer sphere processes have been identified for reaction of metal carbonyl monoanions with metal carbonyl dimers, metal carbonyl clusters and coordination complexes and even for the super nucleophile, $Fe(CO)_4^{2-}$ with $Mn_2(CO)_{10}$. Outer sphere reactions that lead to odd electron complexes have direct applicability to the activation of metal centers through electron transfer catalysis. Transfer of groups (H^+, CH_3^+, Et^+, and so forth) from neutral complexes to $CpFe(CO)_2^-$ has also been examined. The order of reactivity ($H^+ > CH_2C_6H_5^+ > CH_3^+ > Et^+ > Ph^+$) is consistent with nucleophilic attack. A proton is transferred much more readily than an alkyl group. Transfer of the groups as the anions (H^-, CH_3^-) from $RFe(CO)_4^-$ to metal carbonyl cations producing RM and $Fe(CO)_5$ shows much less difference in rates. Understanding these group transfer processes has potential for enhancing the selectivity of catalytic reactions.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering

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

Schwarz, J.A. **$80,000**
315-443-4575

The design of supported metal catalysts demands a thorough understanding of metallic complex adsorption phenomena on oxides. Hydroxyl groups on oxide surfaces can act as either exchange sites or adsorption sites if the metallic complex conforms to an electrostatically driven adsorption process. Sites which are not "titrated" by the metallic complex can serve as acid centers, which participate in the bifunctional properties of the resulting catalyst. The properties of oxides carrying different inventories of hydroxyl groups will be studied. The objective is to determine the relationship between these hydroxyl groups, the acidity of the oxide, and the resultant effects on the properties of catalytic metals formed by adsorption/impregnation onto these hydroxyl sites during catalyst preparation. The selective hydrogenation of acetylene serves as a practical as well as fundamental model reaction system. Palladium(II) cationic and anionic complexes will titrate Lewis and Brönsted sites, respectively, and thus potential differences in metal–support interactions formed during preparation can be assessed. Regulating the pH of the impregnation solution will leave a "residue" of untitrated sites which can serve as acid centers, thus regulating the activity and selectivity of the catalytic reaction. The strategy that is adopted to quantify the impact of hydroxyl sites on catalytic performance is accomplished by modeling the adsorption reaction of metallic precursors during catalyst preparation.

Texas A & M University
College Station, TX 77843

Department of Chemistry

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

Goodman, D.W. **$200,000**
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).

329. *Catalysts and Mechanisms in Synthesis Reactions*

Lunsford, J.H. **$105,400**
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 carbon dioxide, a by-product of the coupling reaction, has a poisoning effect on the production of methyl radicals. As a result, it strongly influences the activation energy for the formation of methyl radicals and, hence, for the overall coupling reaction. The LIF method has demonstrated for the first time that hydroxyl radicals may be generated on the surface of a strongly basic oxide, such as lanthanum oxide. These surface-generated radicals are formed not only during the reaction of methane with oxygen, but also during the reaction of water with oxygen. The activation energy for hydroxyl radical formation is essentially the same for both sets of reactants. Apparently, reactive surface oxygen ions abstract hydrogen atoms from water and release the resulting hydroxyl radicals into the gas phase. The rotational temperature of the hydroxyl radicals is much less than the surface temperature. These hydroxyl radicals may play an important role in catalytic combustion.

University of Texas at Austin
Austin, TX 78712

Department of Chemical Engineering

330. *Model Catalytic Oxidation Studies Using Supported Monometallic and Heterobimetallic 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, zirconia, and magnesia supports. 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 and metathesis reactions.

Department of Chemistry

331. Morphological Aspects of Surface Reactions

White, J.M. **$132,000**
512-471-3704

The long-range goal of this project is to establish correlations between the morphology of metals and their catalytic activity over a broad range of conditions. Silver and rhodium, individually and together, are of particular interest. Single crystals, thin films, and supported particles are all being used in surface chemical and model catalytic studies. Photon- and electron-stimulated, as well as thermal, chemistries are being developed. For example, the tools of surface science have been used to explore the formation and subsequent reactions of vinyl species, derived from vinyl iodide, in the presence of unavoidably coadsorbed atomic iodine. While some vinyl exists up to 450 K, there are two important and competitive lower temperature reaction channels which lead to ethylidyne (CCH_3) and ethylene (CH_2CH_2). In other work, TPD, XPS, UPS, and $\Delta\Phi$ have been used to study the chemistry, induced by 50 eV electrons, of C_2H_5Cl on clean, Cl-covered, and D-covered Ag(111) at 100 K. For coverages up to 1 ML, C_2H_5 radicals and C_2H_6 and C_2H_4 molecules, but no H_2 or Cl-containing species, desorb during electron exposure and, on the surface, there is no evidence for electron-driven C–C bond breaking, except at very-high electron doses. This demonstrates that bond-specific chemistry can be realized with controlled doses of low-energy electrons. The structures of oxide surfaces, and metal particles on them, are being explored with scanning tunneling microscopy. For example, annealing TiO_2(001), rutile, to 510 °C gives mainly (011) and stepped (011) facets with a smaller number of (114) and (111) planes.

Tulane University
New Orleans, LA 70118

Department of Chemical Engineering

332. The Formation of Supported Bimetallic Clusters: The Effect of Support–Metal Precursor Interactions

Gonzalez, R.D. **$71,395**
504-865-5772

The controlling variables in the preparation of Pt–Ru supported bimetallic clusters are currently under study. Variables which appear to have a significant effect on the surface composition of the resulting bimetallic clusters include (1) pretreatment in oxygen prior to reduction in H_2, (2) impregnation sequence for clusters prepared by sequential impregnation or ion exchange, (3) the control of pH during catalyst preparation, (4) the speciation of the metal precursors at the preparation pH, and (5) the relative mobility of the precursors under the synthetic conditions. Characterization studies of the resulting bimetallic clusters are currently performed using (1) differential scanning calorimetry, (2) diffuse UV spectroscopy, (3) selective chemisorption, (4) transmission electron microscopy, and (5) energy dispersive X-ray spectroscopy. The formation of mobile oxide species under oxygen flow has been established. In particular, the formation of volatile RuO_4 leads not only to metal sintering and phase separation but more importantly, to Ru loss as measured using intercoupled plasma spectroscopy. Pretreatment in O_2 prior to reduction in H_2 results in high dispersion for Pt and Pd catalysts but poor dispersion for Ru and Rh. Omission of the oxygen treatment results in high dispersions for Ru and Rh but poor dispersions for Pt and Pd. Ru demetallation was found to be inhibited when Ru was encapsulated within the silica framework through the use of the sol–gel preparative technique. BET surface areas approaching 100 m^2/g have been obtained for supported Pt and Ru catalysts prepared by the sol–gel method. Silica suported catalysts were found to have surface areas slightly larger than alumina. Present studies are directed at establishing a trade-off between BET surface areas and pore size distributions.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

333. Ligand Intermediates in Metal-Catalyzed Reactions

Gladysz, J.A. **$117,300**
801-581-4300

The first project goal is the synthesis, isolation, and characterization of homogeneous complexes containing ligand types ($-CHO$, $=CHOH$, $-CH_2OH$, $\equiv C$, $=CH_2$, $H_2C{=}O$, $-OCHO$, CO_2, and so forth) 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 is sought. The following topics are under active investigation: (1) new, facile base-induced carbon–hydrogen bond activation reactions of coordinated alkenes; (2) nonconventional coordination modes of alkenes involving carbon–hydrogen σ bonds; (3) the synthesis and physical characterization of new metal complexes of carbon, C_x ($x = 1,2,3,4$); (4) the detailed chemical characterization of C_x complexes as models for carbide intermediates in heterogeneously catalyzed processes; (5) elucidation of the factors that determine η^2 vs. η^1 coordination for aldehyde, ketone, and related ligands, and the comparative chemistry of the binding modes; (6) the synthesis and physical and chemical characterization of alkoxy, hydroxy, and oxo complexes in low metal oxidation states, including new OC–H bond activation processes in the former; (7) the study of thermal C–H bond rearrangements of alkylidene and vinylidene ligands, including unusual new bis(alkylidene) complexes $L_nM{=}CH(CH_2)_xHC{=}ML_n$.

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

Grant, D.M.; Pugmire, R.J. **$114,002**
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

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

Cox, D.F. **$65,000**
703-231-6829

The purpose of this 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 it 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 different surface properties on the catalytic reaction pathways of C_1 to C_3 oxygenates (alcohols, aldehydes, and carboxylic acids) are being examined. The reactivities of C_1 oxygenates (methanol, formaldehyde, and formic acid) have been examined. The most stoichiometric and the most defective surfaces give the lowest oxygenate conversion. The stoichiometric surface exposing five-coordinate cations (one vacant coordination site) and two coordinate anions (one vacant coordination site) is nearly inert. As the amount of bridging oxygen on the surface is decreased and the number of exposed four-coordinate cations increased, the conversion increases. The most active surface is that with the highest concentration of bridging oxygen vacancies, but the lowest number of in-plane oxygen vacancies that are associated with three-coordinate cations. The most highly defective surfaces show little activity for oxygenate conversion.

University of Washington
Seattle, WA 98195

Department of Chemistry

336. *Model Cu–ZnO Catalysts for Methanol Synthesis: The Role of Surface Structure*

Campbell, C.T. **$96,900**
206-543-3287

Copper/zinc oxide catalysts are highly active and selective for several reactions of importance in energy technologies: methanol synthesis, water–gas shift, and methanol steam reforming. These reactions are studied here using ultrahigh vacuum surface science combined with reaction kinetics at high pressure (1 to 10^4 torr). These experiments apply surface analytical techniques to investigate the relationship between catalytic activity and the atomic-level surface structure of model catalysts based on Cu and ZnO single crystals. The structural and electronic properties of adsorbed intermediates are correlated with their kinetics in individual steps, which in turn are compared to the overall reaction rates. In this way, a detailed understanding of the active site involved in each step is developed. The kinetics of the forward and reverse water–gas shift reactions and many elementary steps have been measured on the clean and cesium-doped Cu(110) surfaces. These results have clarified the reaction mechanism and the role of cesium promoters. A full kinetic model for the water–gas shift reaction which includes rates and energetics for all the elementary steps has been developed which successfully reproduces rate data not only on copper single crystals but also on practical catalysts over a large range of conditions. Detailed studies of cesium promoters have shown that the main form of the promoter is a surface carbonate, and have characterized the kinetics of the many reactions involved in determining the equilibrium composition of this carbonate and the other, less abundant forms of surface cesium. The interactions of water and CO with well-defined copper overlayers on the oxygen-terminated ZnO single-crystal surface have been clarified, and methanol synthesis kinetics on these model catalysts are being studied.

337. Homolytic Activation of Hydrocarbons and Hydrogen by Persistent Metal Radicals

Heinekey, M. **$75,000**
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

338. Novel Selective Heterogeneous Catalysts

Brenner, A. **$80,000**
313-577-2503

The primary goal of this research is to create a new type of selective heterogeneous catalyst. Heterogeneous catalysts are widely used in the chemical industry for hydrogenation reactions, and in some cases have poor performance because they are nonselective. Homogeneous catalysts can be more selective. A novel interpretation of this difference has been developed which focuses on the fact that the individual active sites in a homogeneous catalyst are noninteracting, whereas they can interact on a metal surface. The new catalysts will mainly consist of supported metals which 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 which can combine the advantages of a heterogeneous catalyst (different phase from reactants, high thermal stability, and low cost) and a homogeneous catalyst (improved selectivity). During the past year some of these catalysts have been synthesized, their unusual selectivity assessed by a model reaction, and some of the parameters which are important in creating high selectivity determined. In particular, whereas conventional catalysts of Ni, Pt, and Cu–Ni alloys show substantial scrambling during olefin hydrogenation, appropriately poisoned forms show very-high (homogeneous-like) selectivity.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemical Engineering

339. Experimental and Kinetic Modeling of Acid/Base and Redox Reactions over Oxide Catalysts

Dumesic, J.A. **$107,000**
608-262-1092

Research in the general area of acid catalysis involves the characterization of solid acidity and the corresponding assessment of catalytic performance of acidic materials. Acid characterization studies are required to provide essential information about the type of acid site (i.e., Lewis versus Brönsted), the strength of the sites, and the mobility of molecules adsorbed on the acid sites. An accurate measure of acid strength is given by the heat of adsorption of a basic probe molecule on the acid site. A thermodynamic representation of the mobility of adsorbed species on these sites is given by the entropy of adsorption. Important techniques used in these acid site characterization studies include microcalorimetry, thermogravimetric measurements, temperature programmed desorption, infrared spectroscopy, and solid-state nuclear magnetic resonance. The combination of these acid site characterization studies with reaction kinetics measurements of selected catalytic processes allows the elucidation of possible relationships between surface thermodynamic and kinetic properties of acidic sites. Such relationships would be important milestones in formulating effective strategies for the effective utilization of solid acid catalysts. Current work in this direction involves methylamine syntheses over various zeolites, and the basic probe molecules employed include ammonia, methanol, water, and mono-, di-, and tri-methylamines.

Department of Chemistry

340. Organometallic Chemistry of Bimetallic Compounds

Casey, C.P. **$125,000**
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. Three 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) 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 bypyramids. 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

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

Fripiat, J. **$84,607**
414-229-5852

In a project aimed at determining the Al coordination number in selected transition aluminas and zeolites, the assignment of the ^{27}Al resonance line near 30 ppm (with respect to Al^{3+} aq) to pentacoordinated Al (Al^V) has been confirmed in mechanically treated aluminas and in steamed or dealuminated zeolites using a two-dimensional nutation NMR technique. Further, EPR of chemisorbed probe molecules (aniline on zeolites and dimethylaniline on aluminas) has shown that the hyperfine splitting of the radical cation spectrum is a function of the strength of the Lewis sites associated with Al^V, and/or tetracoordinated Al^{IV}. Solids containing Al^V are more acid. For the first time it was observed that O_2 adsorbed on the surfaces containing the radical cations forms O_2^- with a sextet set of lines arising from the coupling with Al ($I = 5/2$). The hyperfine splitting of the O_2^- spectrum correlates also with the strength of Lewis sites. ^{1}H-^{22}Al cross polarization NMR spectra with increasing contact times have proved that Al^V and Al^{IV} are located near the surface while the ^{31}P chemical shift of adsorbed $P(CH_3)_3$ goes downfield with increasing Lewis acidity. The most downfield shifted line has been observed for Al^V-$P(CH_3)_3$ adducts. Finally, a study of the 1-butene isomerization in 2 *cis*-2*trans* butene has revealed that aluminas with Al^V are the most active for the 2 *cis* ⇄ 2 *trans* conversion.

342. An Investigation of Molybdenum Oxide Catalyzed Hydrocarbon Formation Reactions

Tysoe, W.L. **$116,447**
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 complimented 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

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

Haller, G.L. **$113,248**
203-432-4378

Active catalytic phases (metal, mixed metals, oxide or mixed oxides) interacting with oxide support on which the active phase is dispersed can affect the percentage exposed, the morphology of supported particles, the degree of reducibility of cations, and so forth, in a variety of ways. The project objective is to characterize the physical chemistry of the active phase–oxide support interaction by spectroscopic methods and to correlate this structure with catalytic function. An important corollary to this objective is an understanding of the interaction chemistry between the active phase precursors and the oxide supports using the same spectroscopies used to characterize the final active phase. The three specific systems recently investigated are SiO_2/Al_2O_3, Pd/L-zeolite, and Pt–Ni/L-zeolite. The investigation of acidity of SiO_2/Al_2O_3 used magic angle spinning NMR and infrared Fourier transform spectroscopies and 2-methyl-2-pentene isomerization as a test reaction. The test reaction for the Pd/L-zeolite system was the isomerization/hydrogenolysis of neopentane and the principal spectroscopy was X-ray absorption (EXAFS). In the case of Pt–Ni/L-zeolite, the hydrogenation/hydrogenolysis of cyclopropane was used to detect surface Ni sites and X-ray absorption was used to determine the geometric (EXAFS) and electronic (XANES) interaction between Pt and Ni.

Department of Chemistry

344. *Catalytic Oxidation of Hydrocarbons by Binuclear Fe Complexes*
Caradonna, J.P. **$112,599**
203-432-5221

This project pursues a study of the catalytic oxidation of alkane/arene molecules for the formation of oxygen insertion products. Of specific interest is the formation of methanol from methane. The objective of this project is to characterize the reactivity of nonheme dinuclear iron complexes and the intermediates formed and to elucidate the mechanisms and specificity of the reactions. Additionally, comparisons and contrasts with heme systems will be elucidated. Dinuclear Fe complexes were synthesized using a simple multidentate polyamide ligand, and voltammetry characterization indicates the redox behavior of mixed ferrous/ferric metal centers. The direct synthesis of the ferrous/ferric and the ferric/ferric complexes has been achieved and their reactivity characterized.

345. *Alkane Photoreactions with Mercury Vapor*
Crabtree, R.H. **$91,667**
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 H_2 to give H atoms. These, in turn, react with a variety of organic compounds to give dehydrodimers. A large variety of functional groups are tolerated including amino, fluoroalkyl, epoxy, and carboxyalkyl. The products are formed in multigram quantities. The intermediate radicals can be trapped by any of a wide variety of traps to give functionalized derivatives (e.g., CO, SO_2, and O_2).

Separations and Analysis

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

346. *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 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 micellization 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

347. *Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport*
Lamb, J.D. **$107,877**
801-378-3841

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. Studies of these membrane systems also include modeling of both cation transport and membrane stability under various initial phase conditions.

Brown University
Providence, RI 02912

Department of Chemistry

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

The properties of the photoacoustic effect in isotropic solid bodies are being investigated. This work is an extension of previous research on fluid bodies. In solids, however, shear waves profoundly affect the character of the photoacoustic waveforms. The theory has been completed, and experiments are being conducted using the Q-switched output of a Nd:YAG laser to irradiate solid targets. The effect of viscosity on the shape of photoacoustic waveforms from fluid bodies is being studied as well. This work is motivated by the observation of deviations of the experimental waveforms from what has been predicted by solutions to the wave equation for pressure. At this point, the theory is being developed based on a wave equation for pressure that has been modified to take viscosity into account. Experiments will be conducted using the same general methods employed in the past for fluid bodies, following completion of the theory. Also under investigation is the influence of viscosity and viscous relaxation acoustic waves generated by deposition of heat by picosecond optical standing waves. Experiments in ethylene glycol have shown that the zero and infinite frequency sound speeds, as well as the viscous relaxation time can be determined.

Columbia University
New York, NY 10027

Department of Chemistry

349. Utilization of Magnetic Effects as a Means of Isotope Enrichment
Turro, N.J. **$88,000**
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. **$157,382**
302-831-6771 **(24 months)**

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 liquid crystal stationary phases to understand the fundamental basis of liquid crystallinity at monolayer dimensions, as well as the principles of solvation by liquid crystal monolayers.

Duke University
Durham, NC 27706

Department of Chemistry

351. Studies of Multifrequency Phase-Resolved Fluorescence Spectroscopy for Spectral Fingerprinting
McGown, L.B. **$70,000**
919-660-1545

This project approaches the analysis of complex samples, such as humic substances, coal liquids, crude oils, and biological fluids, 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. Multiway chemometric techniques, also under development, are essential to the analysis and interpretation of multidimensional PRFS data. The second direction addresses the inaccuracies that may occur in quantitation of an analyte caused by 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. Exploration is under way of a different approach to this problem 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. Moreover, the possibility exists for modifying the binding microenvironment to maximize the sensitivity or selectivity of the determination.

Emory University
Atlanta, GA 30322

Department of Chemistry

352. Sensitized Luminescence in Organized Media

Warner, I.M. **$190,970**
404-727-6623 **(24 months)**

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 coinclusion 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.

University of Florida
Gainesville, FL 32611

Department of Chemistry

353. 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 element analysis of solid samples by atomic emission, atomic absorption, and mass spectroscopies. Major emphasis will be on glow discharge mass spectrometry (GDMS) to study the fundamental processes in the plasma and at the sample surface. Research continues on the analysis of rare earth materials and the many analyt cal problems that the analyst encounters in attempting t obtain mass spectra, namely the many oxide contribution that may interfere with elemental ion signals. Two meth ods are under investigation to decrease or eliminate thes interferents: (1) By use of getter agents added to the sam ple, gas phase chemistry can be carried out in the plasm to reduce the magnitude of the oxide species. (2) A coi surrounding the negative glow region, has bee constructed from 1/8 in. stainless steel tubing to accom modate the flow of liquid nitrogen. The coil aids in th removal of oxidizing species (e.g., water vapor) from th glow discharge, providing a simpler mass spectrum wit less interfering species. Fundamental studies of the e fects of water vapor on the processes in the glow discharg are also being conducted. These experiments reveal th detrimental effects that water vapor has on both atomiza tion and ionization processes in the plasma. The variou reaction mechanisms of water in the plasma are under in vestigation. Interest continues in the studies of pulsed d glow discharges and the advantages obtained by discrimi nating against molecular ions using time resolution Relative sensitivity factor values are being studied at var ious portions on the pulsed ion signal profile (i.e., th afterpeak region, where elemental ion signals dominate or the plateau, which should be similar to dc) in an effor to understand any variations in the ionization processes.

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

Winefordner, J.D. **$91,00**
904-392-0556

Laser-excited atomic spectrometric methods are being in vestigated in order to achieve high spectral selectivity an detection power. The techniques being studied involv laser-enhanced ionization in flames, atmospheric furnaces and low-pressure environments; laser-enhanced fluores cence in flames, inductively coupled plasmas (ICPs), an furnaces; and double resonance fluorescence in flames an ICPs for nonmetals. The techniques are used for both di agnostic measurements of spectral characteristics c atomic and ionic species in flames, plasmas, and furnace as well as for analytical measurements. The emphasis i to achieve extremely high detection powers (subpart pe trillion concentrations or femtogram amounts of elements with extremely high spectral selectivities and very hig freedom from matrix interferences. The diagnostic studie are directed toward (1) a more thorough understanding c the mechanisms of atomization, ionization, and dissocia tion of analyte species in plasmas and furnaces; (2) th optimization of experimental conditions to obtain the bes analytical results by means of laser fluorescence dip spec troscopy; and (3) the development of resonance ionizatio detectors for ultrahigh photon detection sensitivity.

The George Washington University
Washington, DC 20052

Department of Chemistry

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

Montaser, A. **$73,653**
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; (6) simulation and computer modeling of He ICPs and mixed-gas discharges to predict the behavior of plasmas on a fundamental basis; and (7) development of a new ICP-mass spectrometer capable of sampling a variety of ICP discharges. 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

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

Browner, R.F. **$86,000**
404-894-4020

Recent studies with the particle beam interface have shown some highly interesting properties to exist with respect to the thermal degradation of thermally labile species. In comparison with stable species, such as high molecular weight polynuclear aromatic species, unstable species, such as carboxylic acid pesticides, show specific thermal degradation patterns which are highly specific to the chemical form of the molecule. This may lead to peak tailing for specific ions, but not necessarily for all ions. The study of very high rates of vaporization, using a 3W argon ion laser, has indicated that thermal degradation may be reduced to extremely low levels for model compounds, such as cholesterol. A ratio of the 386/368 m/z peaks for this molecule of 5:1 has been obtained, compared to a previous high value of 3.5:1 using normal heating processes. The extent of nonlinearity in the calibration process has been examined through transport measurements of analyte, in an attempt to correlate the lack of linearity with the volatility of the species in the interface. Attempts to redesign the interface to eliminate these nonlinearity problems are under way.

Hampton University
Hampton, VA 23668

Department of Chemistry

357. Use of Ion Chromatography–DC Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals

Urasa, I.T. **$55,997**
804-727-5398

The program involves the use of direct current 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 when the sample is acidified.

University of Houston
Houston, TX 77204

Department of Chemical Engineering

358. 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

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

Carleson, T.E. **$37,468**
208-885-7652 **(24 months)**

In certain cases droplet direct contact heat transfer rates can be significantly enhanced by the application of an alternating electric field. This field can produce shape oscillations in a droplet that will enhance mixing. The theoretical evaluation of the effect of the interaction of the field with drop charge on the hydrodynamics has been completed for small amplitude oscillations. Previous work with a zero order perturbation method was followed up with a first order perturbation method to evaluate the effect of drop distortion on drop charge and field distribution. The first order perturbation results show secondary drop oscillations of four modes and two frequencies in each mode. The most significant secondary oscillation has the same mode and frequency as the second mode oscillation predicted from the first order perturbation work. The resonant frequencies of all oscillations decrease with increasing electric field strength and drop charge. Work is currently under way to evaluate the heat transfer enhancement from an applied alternating electric field.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Chemistry

360. *Molecular Aspects of Transport in Thin Films of Controlled Architecture*

Bohn, P.W. **$82,000**
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. Specific studies include (1) using the spatial localization of the electric field in thin Ag or Au layers interspersed at different points within a polymer 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); (2) using the near-surface electric field localization provided by surface plasmon excitation in the Kretschmann configuration to probe the alignment and segment density in thin (100–1000 Å) polymer layers on Ag and Au films; and (3) applying optical waveguide eigenmode excitation of polarized fluorescence to the study of composite microstructures by characterizing the effect of number density and alignment of amphiphilic layers on gross transport rates.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

361. *Hadamard Transform Spectrometry: A New Analytical Technique*

Fateley, W.G. **$82,000**
913-532-6298

A Hadamard transform spectrometer (HTS) has been developed for the visible and near-infrared (NIR) spectral regions. A new generation of stationary Hadamard encoding masks has been developed for the no-moving-part near-infrared Hadamard transform (HT) Raman spectrometer. These new masks utilize polymer dispersed liquid crystal (PDLC) materials and avoid the use of NIR polarizers. Thus, NIR Raman spectra free from attenuation of strong polarized Raman bands caused by absorption by the NIR polarizers are now available. Demonstrations of spectral subtractions, the theoretical multiplex advantage, and a new selective multiplex technique have all been accomplished. The next efforts include improving the detection system electronics, decreasing the time required for the PDLC material to switch from one state to another, and seeking new materials for a third generation stationary Hadamard encoding mask. New directions in addition to development of the Hadamard transform Raman spectrometer include the development of a Hadamard transform spectrometer to depth profile solids using photoacoustic detection and the use of a stationary two-dimensional Hadamard encoding mask to perform imaging studies using either laser induced fluorescence (LIF) or Raman scattering.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

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

This research is aimed at creating fundamentally new classes of membranes, based on the use of two-dimensional assemblies of molecular pores. The ultimate goal is to design synthetic membranes rationally, at the molecular level, which will provide an energy- and capital-efficient means of separating small molecules and ions on the basis of their size, shape, and polarity. An experimental method has been developed for making permeation measurements through monolayer films at the air–water interface, and is now being used to characterize the membrane properties of a series of polymerized assemblies made from amphiphilic calix[n]arenes.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemical Engineering

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

The objectives of this program are to develop and characterize a novel concept for the removal of trace contaminants from aqueous solutions with applications in environmental technology. Specifically, it is proposed to exploit the strong solubilizing powers of block copolymer micellar solutions to remove and/or recover halogenated and nonhalogenated, aromatic and polyaromatic hydrocarbons from aqueous solutions. The work will consist of the following tasks: (1) experimental determination of the solubilization capacities, or distribution coefficients, of a representative range of solutes in block copolymer micelle systems; (2) characterization of different block copolymer micelle systems using quasi-elastic light, small-angle X-ray and neutron scattering techniques, with attention to the structural changes induced by the solubilizate; (3) detailed statistical thermodynamic analysis of solubilization in block copolymer micelles using self-consistent field theories to describe the polymer segment distributions within the micelles, and linear solvation energy relationships to characterize solute-polymer interactions; and (4) experimental and theoretical analysis of the use of hollow fiber membrane extractors for large-scale applications in the cleanup of natural water sources and industrial effluents. The primary benefit of this work will be an increased understanding of the basic chemical and physical phenomena associated with solubilization in micellar aggregate structures.

Michigan State University
East Lansing, MI 48824

Department of Chemistry

364. Direct Probing of Chromatography Columns by Laser-Induced Fluorescence
McGuffin, V.L. **$80,000**
517-355-9715

A novel detection system has been developed that allows the direct examination of separation processes in chromatography. This system employs a single laser together with parallel detection optics and electronics to collect fluorescence emission at several points along an optically transparent packed capillary column. This detection scheme has been employed to examine the influence of temperature and pressure on retention processes in reversed-phase liquid chromatography. A homologous series of linear, saturated fatty acids, labeled with the fluorescent probe 4-bromomethyl-7-methoxycoumarin, have been chosen as model solutes. When separated on an octadecylsilica stationary phase using methanol as the mobile phase, these ideal solutes exhibit the theoretically expected logarithmic dependence of the partition coefficient on carbon number. As the temperature is increased from 10 to 60 °C while maintaining constant pressure (1700 psi), a nonlinear decrease in partition coefficient is observed (61 to 88% for C_{10} to C_{20}, respectively). Likewise, as the average pressure is increased from 1000 to 4400 psi while maintaining constant temperature (28 °C), a substantial increase in the partition coefficient is observed (10 to 25% for C_{10} to C_{20}, respectively). An abrupt change in the partition coefficient for all solutes is observed at 28 °C temperature and 1700 psi average pressure, which is attributed to a liquid–solid transition in the octadecylsilica stationary phase. The slope (dP/dT) of the phase diagram determined for octadecylsilica (430 psi/°C) appears to be approximately halfway between the literature values for octadecane (580 psi/°C) and dimyristoylphosphatidylcholine (360 psi/°C) at their respective melting points. These results suggest that the chromatographic stationary phase is intermediate in thermodynamic properties between a randomly oriented bulk alkane solvent and a highly ordered phospholipid membrane. Because the phase transition occurs within the normal range of operating conditions, the effect of temperature and pressure on solute retention cannot be considered negligible in liquid chromatography.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

365. Hadamard Transform Imaging
Morris, M.D. **$96,000**
313-764-7360

Hadamard multiplexing is used to generate spatially and spectrally resolved Raman microscope images. Global illumination allows high incident laser power, and rapid (2 to 10 min typical) image acquisition time. The current design of a Hadamard Raman microscope employs a research microscope, single channel spectrograph, and charge-coupled device (CCD) detection system. The multichannel CCD detector is used for simultaneous acquisition of up to 14 Raman images, thus allowing efficient examination of multicomponent materials and providing some background subtraction capability. The instrument is used for multispectral examination of polymer laminates and other composites. Chemometric techniques are used to evaluate spectrally overlapped images. Serial sectioning is used for three-dimensional Raman imaging. Nearest-neighbor deblurring has been implemented for reconstruction of three-dimensional images, and has been demonstrated to provide depth resolved images of organic crystals, polymers, and biological tissues. Iterative deconvolution is used to provide three-dimensional Raman images with much higher signal/noise ratio than is otherwise available.

University of Minnesota
Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

366. Continuous Reaction Chromatography
Carr, R.W. **$86,700**
612-625-9568

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. It is the relative motion of the feedstream and the chromatographic bed that is required for this to be achieved and one configuration meeting this criterion is the countercurrent moving bed. An experimental investigation has recently demonstrated that the predictions of high purity and high conversion that came out of previous theoretical studies are readily attained. The practical difficulties of moving a bed of granular solid against a gas stream have led to the consideration of a countercurrency which is simulated in a discontinuous manner 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, 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 been undertaken. Exploratory investigations of the application of simulated countercurrency to natural gas conversions have been started. Preliminary results indicate that in the case of oxidative coupling, high selectivity for ethane and ethylene and high methane conversions are possible.

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. **$72,000**
314-341-4429

(R)- and (S)-naphthylethylcarbamate-β-cyclodextrin bonded liquid chromatographic phases were originally developed for the normal phase separation of enantiomers. Although their selectivity resembled that of some of the earlier substituted cellulosic phases, the functionalized cyclodextrin stationary phases were much more stable as they were bonded to the silica support and not adsorbed. Because of their stability, the naphthylethylcarbamate-β-CD stationary phase was utilized in reversed phase separations. It was found that a completely different set of enantiomers was resolved by this column in the reversed phase mode. This included racemic pesticides such as Dyfonate, Ruelene, Ancymidol, and Coumachlor; as well as a variety of pharmacologically active compounds such as Tropicamide, Indapamide, Althiazide, Tolperisone, a sulfonamid from Merck Sharp & Dohme that has been resolved only by indirect methods, and over twenty others. It appears that the naphthylethylcarbamate-β-CD bonded phase is a highly effective, multimodal chiral stationary phase (CSP). A series of liquid cyclodextrin derivatives, 2,6-di-O-pentyl-3-O-trifluoroacetyl α-, β-, and γ-cyclodextrins (DP-TFA α-, β-, and γ-CD), have been used as highly selective chiral stationary phases for capillary gas chromatography. More than 150 pairs of enantiomers were resolved; 120 on DP-TFA-γ-CD, which is the first reported γ-cyclodextrin stationary phase that is more widely useful than the β-cyclodextrin analogue. The enantiomers resolved include chiral alcohols, diols, polyols, amines, amino alcohols, halohydrocarbons, lactones, α-halocarboxylic acid esters, carbohydrates, epoxides, nicotine compounds, pyrans, furans, and so on. Identical α values were observed for diol, amine, and γ-halocarboxylic acid ester homologues, respectively. The relationship between the unusual selectivity behavior and separation mechanism is discussed.

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. **$143,000**
301-975-2563

This project involves the measurement of fundamental properties of gas phase ions. The National Institute of Standards and Technology (NIST) pulsed electron beam mass spectrometer (MS) is the prime experimental facility, and a Fourier transform ion cyclotron resonance

(FTICR) instrument and triple MS system are also available. Emphasis is in two areas. One area is definition of the thermochemistry of 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. **$117,500**
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.

University of Oklahoma
Norman, OK 73019

Department of Chemical Engineering and Materials Science

370. *A Study of Micellar-Enhanced Ultrafiltration*
Scamehorn, J.F.; Christian, S.D. **$71,400**
405-325-4382

Colloid-enhanced ultrafiltration methods are being developed to purify polluted wastewater or groundwater. In micellar-enhanced ultrafiltration (MEUF), surfactant is added to polluted water. The micelles (aggregates containing approximately 100 molecules) formed by the surfactants tend to solubilize the organics and bind the multivalent ions (e.g., heavy metals) if the surfactant is of opposite charge to these ions. In polyelectrolyte-enhanced ultrafiltration (PEUF), polyelectrolyte is added to the water and multivalent ions bind to the oppositely charged polyelectrolyte. In ion-expulsion ultrafiltration (IEUF), either surfactant micelles or polyelectrolyte of the same charge as the multivalent target ion is added to the water. The solution from each of these techniques is treated using ultrafiltration with membrane pore sizes small enough to block the passage of the colloid. In MEUF or PEUF, extremely pure permeate streams have been produced. In IEUF a permeate solution of high target ion concentration is produced and simultaneously separated from the colloid. Problems that have recently been addressed include the recovery of colloid from MEUF or PEUF for recycle to the process for economical operation, and the use of polymer/surfactant mixtures or polysoaps in MEUF for organic solute removal to reduce the concentration of surfactant in the permeate.

Oregon State University
Corvallis, OR 97331

Department of Chemistry

371. *A Mechanistic Study of Molecular Survey Inorganic Membranes for Gas Separations*
Way, D.J. **$84,506**
503-737-3406

The objectives of this research effort are to investigate the transport mechanisms in a microporous, silica hollow-fiber membrane and to examine the relationship between the microstructure of the membrane, the membrane surface chemistry, and its separation performance. A further objective is to solve a general mathematical model of multicomponent separation and compare model predictions to multicomponent gas mixture permeation data. Characterization studies of the inorganic membrane will include pore size distribution and measurement of pure gas adsorption isotherms for gases of industrial and environmental interest which include NH_3, CO_2, NO, SO_2, O_2, N_2, CH_4, CO, and CCl_2F_2 at pressures up to 35 atmospheres and temperatures up to 300 °C. The transport and adsorption data will be used to determine the mechanism controlling molecular motion through the membrane, whether it is molecular sieving or surface diffusion controlled. A general multicomponent mathematical model of surface diffusion and molecular sieving transport mechanisms will be developed. This model will be compared with experimental gas mixture permeability data to gain a fundamental insight into the transport mechanisms controlling gas permeation in inorganic membranes.

Purdue University
West Lafayette, IN 47907

Department of Chemistry

372. *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	

Work continues using laser desorption Fourier transform/mass spectrometry (FT/MS) to study the gas-phase chemistry and photochemistry of transition-metal-containing ions. A recent thrust has been to investigate the properties of a series of doubly charged species including Nb^{2+}, V^{2+}, Ta^{2+}, Zr^{2+}, and La^{2+}. Because early transition metals have relatively low second ionization potentials, their reactions with simple hydrocarbons yield interesting doubly charged products in addition to charge-transfer products. Studies on the ligated doubly charged ions are aimed at obtaining thermochemical information for comparison to their singly charged analogues. Surprisingly, the bond energy of M^{2+} to a particular ligand can be either greater or less than that of M^{+}. An ongoing collaboration with Dr. Charles Bauschlicher at the NASA Ames Laboratory, has been particularly fruitful in providing theoretical insight into the nature of the stability and bonding of these interesting species. Techniques originally developed to measure ion kinetic energies in ion cyclotron resonance (ICR) spectrometry have been adapted to the FT/MS to study the single charge-transfer reaction of M^{2+} with benzene. In this way detailed information about the partitioning of reaction exothermicity among the internal and translational modes can be obtained.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemical Engineering

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

Belfort, G.	**$85,000**
518-276-6948	

The objective of the research is to measure the intermolecular forces between interacting layers of proteins including bovine pancreas ribonuclease A, lysozyme, cytochrome C, and human serum albumin, and ultrathin commercially relevant polymeric membranes. Polymers for these membranes include seven different types of cellulose acetate, in order to obtain a series of varying polarity membranes. The surface force apparatus is being used to obtain the intermolecular forces as a function of distance and solution conditions. The results of this study will provide a quantitative measure of the amplitude and extent of the interacting forces between proteins and polymeric membranes. This information is of interest in bioseparations, biocatalysis, biocompatibility, fouling of ship hulls, and biocolloid stability. With an understanding of these intermolecular forces, it should eventually be possible to choose polymer chemistries and operating conditions that minimize protein–membrane interactions and, hence, membrane fouling, a major cause of the decline in performance in membrane separation processes.

Department of Chemistry

374. *Macrocyclic Ligands for Uranium Complexation*

Potts, K.T.	**$98,000**
518-276-8460	**(24 months)**

A series of macrocyclic hosts for the uranyl ion, designed using computer modeling techniques, has been synthesized using a combination of acyl isocyanate chemistry and cyclocondensations. Examples include both partially preorganized and preorganized systems which contain six ligating oxygen atoms arranged in a symmetrical manner in the macrocycle and capable of binding in the equatorial plan of the uranyl ion. Variables were introduced by inclusion of sulfur as a ligating atom, and by using functional groups such as urea, biuret, thiobiuret, and pyridine rings in the macrocycle periphery. Difficulty in accurately controlling the cavity diameter in the partially preorganized systems has been encountered on metal complexation and, with the highly preorganized systems, some decomposition of the macrocycle has been observed. These problems are being addressed by systematic changes of the functional groups in the macrocyclic periphery as well as by the inclusion of groups likely to enhance solubility in a positive manner.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

375. *Determination of Solvation Kinetics in Supercritical Fluids*

Bright, F.V.	**$118,708**
716-831-3615	**(24 months)**

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 (molecular charisma, density augmentation) on the rates of chemical reactions; (4) investigation of 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; and (6) effects of fluid density and temperature on solute–solute interactions. This information is leading to a more detailed molecular understanding of supercritical fluid solvation.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering and Materials Science

376. Mechanisms of Gas Permeation through Polymer Membranes

Stern, S.A. **$88,000**
315-443-4469

A previously developed relation which describes the solubility behavior of plasticizing gases in glassy polymers was tested experimentally. This relation was found to represent satisfactorily the solubility of C_2H_6 in poly(ethyl methacrylate) (T_g = 69 °C) at 35.0 °C and in poly(vinyl benzoate) (T_g = 65 °C) at 5.0 °C over a range of elevated pressures. A new relation was also derived to describe the diffusivity of plasticizing gases in glassy polymers, and was found to be in good agreement with published data on the diffusion of CO_2 in several types of glassy polymers. In addition, a study was initiated on the dependence of the gas permeability of glassy polymers on the intrasegmental mobility of polymer chains. The polymers studied were the polyimides isomers PMDA-3,3′-ODA and PMDA-4,4′-ODA. The isomer with the *para*-phenyl diamine moiety (PMDA-4,4′-ODA) has a higher gas permeability but a lower selectivity to different gases than the isomer with the *meta*-phenyl diamine moiety (PMDA-3,3′-ODA). A dynamic mechanical analysis and molecular simulations indicate that this behavior is due to the fact that the phenyl rings in the diamine moiety of the *para*-isomer possess a measure of rotational mobility, albeit hindered (ΔE = 6.5 kcal/mol), even below the T_g (= 400 °C) of the polymer. Gas transport in this isomer is assisted by its intrasegmental rotational mobility. By contrast, the *meta*-isomer does not possess rotational mobility below its T_g (= 280 °C).

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

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

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

Current research focuses on the design and synthesis of polymer-supported reagents that can selectively complex targeted metal ions and neutral molecules. The approach taken in this research is to prepare bifunctional polymers and explore the conditions under which both types of ligands, operating together, can complex far higher levels of a given substrate than either could alone. A comprehensive study of such polymers has recently been published, and a supported ligand synergistic interaction has been defined. The bifunctional monoethyl/diethyl ester resin complexes silver ions to a much greater extent than the monofunctional monoester or diester polymers: for example, the bifunctional polymer has a Ag(I) distribution coefficient of 2924 (from 4N nitric acid solution) compared to values of 439 and 463 for the monoester and diester polymers, respectively. An alternative technique for preparing bifunctional polymers based on interpenetrating polymer networks (IPNs) has been published. A network, comprised of one or more monomers, is formed within an initial support structure such as polystyrene; when two monomers are used, a bifunctional IPN forms. Ion exchange/coordination polymers with carboxylate/pyridine and carboxylate imidazole ligands have been synthesized. Metal ion binding constants are being evaluated.

378. Study of the Surface Properties of Ceramic Materials by Chromatography

Guiochon, G. **$83,000**
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. This work is relevant to the production of advanced ceramic materials and provides new methods for the quality control of the powders used to make green bodies. A correlation between the measured distribution and the quality of a series of lots of alumina powders has been established. The procedure developed involves the determination of the distribution of the adsorption energy on a surface for a series of selected probes. This determination is made by measuring the adsorption isotherms of the selected probes by ECP, using a porous layer open tubular column. The integral equation which relates the adsorption energy distribution, the adsorption isotherm on each type of site (assumed to be homogeneous), and the measured isotherm can then be solved. Programs have been developed permitting this calculation and carrying out systematic determination on various samples of alumina. The adsorption energy distribution of a surface depends much on the nature of the probe used, so a series of probes is needed to characterize a surface. Silica particles are currently being studied.

379. Capillary Liquid Chromatography Using Laser-Based and Mass Spectrometric Detection

Sepaniak, M.J. **$82,500**
615-974-8023

The focus of this research is the fundamental and practical development of capillary electrokinetic separation techniques for analyses of complex samples and difficult-to-resolve mixtures. Work has continued with characterization and utilization of micellar electrokinetic capillary chromatography (MECC). With this technique, neutral compounds are separated based on differential partitioning between electrokinetically migrating aqueous and micellar components in the mobile phase. In addition, new applications and variations of capillary zone electrophoresis (CZE) are investigated for separations of ionic species. Three projects are currently in progress. The major project involves characterizing the PAH components in energy-related samples. To address problems associated with efficiently and selectively separating these hydrophobic compounds, MECC with mobile phases containing organic solvents and nontraditional organized media is used. Selectivity is further enhanced by employing laser fluorimetry with photodiode array detectors. Preliminary work involving the development of a chemiluminescence detector for this application is in progress. Systems for post-capillary electrokinetic mixing of reagents and CL flow cells have been constructed. Efforts to further refine retention programming techniques for MECC are continuing with simplex optimization of separations of PAH standard mixtures. In a minor project area, the separations of heavy metals with CZE are being investigated employing detection based on either on-column fluorescence labeling using chelating agents or indirect optical methods. As a final project area, exploratory evaluations of the merits of two distinct organized assemblies as mobile phase additives for CZE are being conducted. Both fundamental and practical investigations into the uses of soluble polymer additives for separations of biopolymers are beginning. The testing of the feasibility of developing the MECC analog of normal phase high-performance liquid chromatography (HPLC), using nonaqueous mobile phases containing carbon cluster additives, is also in progress.

Texas A & M University
College Station, TX 77843

Department of Chemistry

380. Development of Laser-Ion Beam Photodissociation Methods

Russell, D.H. **$84,000**
409-845-3345

This project uses laser-ion beam photodissociation methods 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 photodissociation apparatus is now completed and used routinely for a range of tandem mass spectrometry research. The instrument consists of a high-resolution magnetic sector instrument (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 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 laser. The primary objective of the current research is to improve the sensitivity of MS-MS experiments by 100 times (10 to 100 femtomole) and the mass resolution of MS-II by 5 to 10 times (1,000 to 10,000). The focus of the current work is on fundamental studies of protonated peptides and organo-alkali metal ions of peptides and nucleotides. In addition, laser-ion beam photodissociation 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

381. Metal Ion Complexation by Ionizable Crown Ethers

Bartsch, R.A. **$91,000**
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. These novel compounds are being tested in solvent extraction and in polymer-supported liquid membrane transport of alkali metal and alkaline earth cations. Novel ion exchange resins are being prepared from ionizable crown ethers. In addition to ion exchange sites, these resins also possess crown ether units. 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.

382. 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

383. *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 polysulfone 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. 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. This rule, while qualitative, has been invaluable for identifying structures with potential as advanced membrane materials. 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. The testing includes studies up to 1000 psia, so realistic conditions like those encountered in actual field conditions can be simulated. The high pressure range of the studies allows ranking the materials not only according to their intrinsic properties, but also according to their ability to resist plasticization-induced softening and selectivity loss.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

384. *Pulsed Laser Kinetic Studies of Liquids under High Pressures*

Eyring, E.M. **$77,000**
801-581-8658

Volume changes along the reaction coordinate profile can be obtained for processes in liquids by measuring rates with the liquid under high pressure. This information permits deduction of the reaction mechanism. Pulsed laser photolysis of $Mo(CO)_6$ in the presence of bidentate ligands L such as 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen) and their substituted analogues has been carried out under high pressures up to 150 MPa. The species $Mo(CO)_5L$ produced by a laser flash undergoes thermal elimination of CO to yield $Mo(CO)_4L$. The volumes of activation determined for the ring closure from high-pressure kinetic data indicate a changeover from an associative interchange mechanism denoted by I_a to a dissociative interchange mechanism denoted by I_d as steric hindrance in the bpy ligands is increased. When L is a rigid molecule like phen, the activation volume is almost the same for different substituted phens and is close to zero suggesting an interchange mechanism denoted by I with no subscript. A high-pressure laser flash photolysis study involving the formation of group VIb transition metal silane adducts from $M(CO)_6$ and R_3SiH [where M is Cr, Mo, or W; R is an alkyl group] is also under way. Hydrosilation reactions are important in the preparation of monomers for manufacture of silicone rubber.

Department of Metallurgical Engineering

385. *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

In situ Fourier transform infrared (FTIR) spectroscopy has been used to monitor in real time the adsorption of surfactants common to the froth flotation process. Using mineral crystals machined into internal reflection elements (IREs), in what are termed "reactive IREs," the adsorption of surfactants at dilute equilibrium concentrations has been monitored in real time by internal reflection spectroscopy (IRS). Mineral/surfactant systems studied by this method include fluorite (CaF_2)/sodium oleate, sylvite (KCl)/octylamine hydrochloride, and sapphire (Al_2O_3)/sodium dodecyl sulfate. This novel approach to the study of adsorption processes has allowed determination of the surfactant orientation, bonding characteristics at the surface, and adsorption density. Recently, conformational changes in the hydrocarbon chain of the adsorbed surfactant have been detected. These thermotropic transitions at the surface of mineral crystals clearly show when the adsorbed surfactant is in a micelle-like state or in a more condensed state by spectral changes corresponding to the number of gauche bonds in the hydrocarbon chain. Future research should establish how these conformational changes at the interface influence the hydrophobicity of a particular system. Finally, the oxidation/polymerization reaction of adsorbed oleate monomers, found in previous transmission work, is being studied in situ by this innovative FTIR/IRS technique. This oxidation/polymerization phenomenon is being investigated as a function of system variables (oxygen concentration, temperature, and applied electrochemical potential). In addition to the FTIR/IRS technique, laser Raman spectroscopy is being used to examine systems in which the mineral substrate is opaque. For example, $CaCO_3$ does not transmit in the mid IR and thus surfactant adsorption reactions have been studied in the near IR. These studies are being complemented by laser Raman spectroscopy using charge-coupled device (CCD) detectors. Finally the significance of surface charge in soluble salt flotation systems is being examined by nonequilibrium laser Doppler electrophoresis. The results suggest that the adsorption of oppositely charged collector colloids from the saturated brine is an important consideration in the flotation of soluble salt minerals.

Virginia Commonwealth University
Richmond, VA 23284

Department of Chemistry

386. *Enhancement of Fluorescence Detection in Chromatographic Methods by Computer Analysis of Second Order Data*
Rutan, S.C. **$79,000**
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

387. *UV Laser–Surface Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials*
Dickinson, J.T. **$84,999**
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

388. *Solid-Surface Luminescence Analysis*
Hurtubise, R.J. **$111,000**
307-766-6241

The primary goal of this project is to acquire a fundamental understanding of the physical and chemical interactions that are responsible for the room-temperature fluorescence and room-temperature phosphorescence of organic compounds adsorbed on solid matrices. Several spectral techniques are used to study the interactions. Filter paper, sodium acetate, and cyclodextrin/salt mixtures are being used as solid matrices for the adsorbed luminescent compounds. Experiments are carried out to obtain luminescence polarization, lifetime, and quantum yield data for a variety of compounds adsorbed on solid matrices. Also, experiments are performed to determine the modulus of filter paper as a function of temperature and humidity. From the luminescence data acquired, several photophysical parameters are calculated. The luminescence data and calculated photophysical parameters for the adsorbed compounds and properties of the solid matrices are correlated to develop interaction models. For example, a recent theory on the modulus of paper relates the water content of paper to the number of effective hydrogen bonds in paper. By using this theory with data from humidity experiments and the solid-matrix luminescence data of model compounds, it is possible to derive equations that directly relate the modulus of filter paper to the luminescence quenching phenomena of model compounds adsorbed on filter paper.

Heavy Element Chemistry

Florida State University
Tallahassee, FL 32306

Department of Chemistry

389. *Research in Actinide Chemistry*
Choppin, G.R. **$114,000**
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

390. Development of Immobilized Ligands for Actinide Separations

Paine, R.T. **$226,991**
505-277-1661 **(24 months)**

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

391. Molecular Orbital Studies of the Bonding in Heavy-Element Organometallics

Bursten, B.E. **$98,200**
614-292-1866 **(18 months)**

The ongoing investigation into the bonding in cyclopentadienyl actinide organometallics Cp_3An ($Cp = \eta^5-C_5H_5$; An = Th through Cf) via quasi-relativistic Xα–SW molecular orbital calculations has led to a new understanding of the changes in An–Cp bonding as a function of actinide element. These studies have also suggested new ventures in the organometallic chemistry of zirconium, which should parallel that of thorium to a certain extent. The Xα–SW calculations are being augmented with more sophisticated electronic structure methods that will allow for better spectroscopic correlations and the potential for geometry calculations. To this end, fully relativistic DV–Xα calculations have been carried out for a series of trivalent uranium and plutonium complexes, such as $An(CH_3)_3$, $An(NH_2)_3$, and Cp_3An (An = U, Pu). Preliminary investigations into the bonding in binary actinide carbonyl complexes have also been initiated. These studies provide a much clearer picture of the interplay between ligand-field and spin-orbit effects on the electronic structures of the complexes. Ab initio calculations with relativistic effective core potentials have been carried out for the diatomic molecule U_2. These studies show conclusively that relativistic effects will be the key in determining molecular architectures that could support direct actinide-to-actinide bonds.

University of Tennessee at Knoxville
Knoxville, TN 37996

Department of Chemistry

392. Physical–Chemical Studies of Transuranium Elements

Peterson, J.R. **$154,691**
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 fluorescence 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

393. *Premixed Turbulent Combustion*
Libby, P.A. **$60,000**
619-534-3168

This project involves several areas of research concerned with premixed turbulent combustion. The first relates to the characteristics of laminar flamelets as they arise in turbulent flames. A study of such flamelets in counterflowing streams subject to swirl is presently under way. The analysis for low rates of swirl has been completed. Beyond a critical rate of rotation, multiple stagnation planes appear and the situation calls for an entirely different asymptotic analysis which has been completed. The second area of research concerns counterflowing premixed turbulent flames. These flames are under experimental investigation at several institutions and are becoming recognized as providing a convenient vehicle for the study of a variety of phenomena connected with such flames. The portion of this work dealing with extinction is being combined with experiments carried out at Cambridge. The formulation for a third approach based on the Bray–Moss–Libby model, presumably the most realistic, is being reassessed because preliminary numerical results suggested that the modeling used to close the equations was seriously flawed. The numerical analysis of highly idealized premixed flames in a duct is progressing.

Clarkson University
Potsdam, NY 13699

Department of Chemical Engineering

394. *Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures*
Lucia, A. **$57,706**
315-268-6674

The analysis framework for multistage binary separators has been expanded to include both direct and indirect composition specifications as well as internal flow rate (i.e., reflux and boilup) specifications. Solution uniqueness has been rigorously established for all sets of product composition specifications. The potential for multiplicity has been rigorously established for internal flow specifications. These and previous analyses have been reclassified through the development of a general concept known as constrained separation. The algebraic analysis for several sets of specification have been interpreted graphically by using Ponchon–Savarit diagrams. Practical aspects of all analyses have been related to process design, simulation, operation, and control considerations. The behavior of Newton's method has been studied in the complex domain and has been shown to be qualitatively similar to its behavior in the single variable case. Complicated periodic and chaotic behavior on several common separation process models has been observed. Traditional dogleg strategies have been found to replace this nonconvergent behavior with convergence to a singular point. A multivariable extension of the dogleg strategy to the complex domain has been developed and 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

395. *Composition Dependence of Fluid Thermophysical Properties: Theory and Modeling*
Ely, J.F. **$109,591**
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

396. *Study of Improved Methods for Predicting Chemical Equilibria*
Lenz, T.G.; Vaughan, J.D. **$101,000**
303-491-7871

This project involves studies to develop computational methods capable of accurately predicting condensed-state chemical equilibria. Thermodynamic property computation for isolated molecules as well as condensed-state computational model development are thus central to this work. A specific computational goal is to assemble a single force-field program for calculating thermodynamic properties that combines accuracy and applicability to a wide variety of hydrocarbon and heteroatomic compounds. Currently, development of a program that calculates standard enthalpies of formation and thermodynamic functions of saturated and unsaturated isolated hydrocarbons is nearly complete. Recent calculations on a large variety of cyclic and acyclic -enes and -dienes and on various aromatic compounds using this program yielded thermodynamic properties in excellent agreement with experimental values. The program includes improved torsional potential energy functions for single bonds that lead to correspondingly improved barriers to internal rotation, and to improved contributions of hindered internal rotational to thermodynamic functions. In addition to the isolated molecule computational model, force-field/molecular dynamics (MD) studies of the condensed state are being conducted to help develop a full understanding of condensed state chemically reactive systems. An entirely new constant (N,P,T) MD simulation method for flexible molecules, which constrains pressure and temperature, has been developed for this purpose. Thus far calculations for CO_2 at 273 K, 1000 atm and 173 K, 1 atm employing varying cell sizes, have shown capability to predict good liquid thermodynamic properties from gas and crystal parameterization.

Cornell University
Ithaca, NY 14853

School of Chemical Engineering

397. *Theory and Simulation of Fluids of Associating Chain Molecules*
Gubbins, K.E. **$275,000**
607-255-4385

This work will develop a new equation of state for chain molecules that takes molecular size into consideration. Computer simulations of hard spheres and hard sphere chains with multiple bonding sites will be used to predict phase equilibria and to test the theory. Quantitative predictions are being made for the phase diagrams of binary and ternary mixtures of industrial interest, with components such as alkanes, alcohols, water, and benzene. Later in the research, the adsorption of associating chain molecules at vapor–liquid, liquid–liquid, and solid–liquid surfaces will be studied. New work on fluids in pores is being initiated. Molecular simulations and theoretical calculations are being made to study the adsorption of methane and other simple fluids in porous carbons and other inorganic materials.

398. *Exact Calculations of Phase and Membrane Equilibria for Complex Fluids by Monte Carlo Simulation*
Panagiotopoulos, A.Z. **$99,425**
607-255-8243

The central theme of this project is the investigation of phase equilibria for complex fluids using a novel methodology, Monte Carlo simulation in the Gibbs ensemble. The methodology enables the direct determination of the properties of any number of coexisting fluid phases from a single computer experiment, and is applicable to multicomponent systems with arbitrary equilibrium constraints. Current work focuses on the determination of equilibria in ionic and polymeric systems. The first Gibbs-ensemble calculations of the critical point and phase envelope for the restricted primitive model for ionic solutions have recently been performed. The calculations are being extended to asymmetric electrolytes and mixtures of electrolytes and nonelectrolytes. In the area of polymeric systems, a novel methodology has been developed based on insertion of test segments in a dense polymeric melt, that allows the calculation of chemical potentials (and thus phase behavior) for polymers of arbitrary chain length. The results of the simulations are being compared with theoretical models and phenomenological correlations, in order to determine the range of applicability of existing techniques and provide the data necessary for systematic improvements.

Department of Mechanical and Aerospace Engineering

399. *Reaction and Diffusion in Turbulent Combustion*
Pope, S.B. **$94,964**
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. Work has progressed on the first and third of these topics. The parameter range that can be accessed by DNS has been established, and the initial simulations are revealing the phenomena that will subsequently be quantified. DNS has also been performed of molecular motion in turbulence. It is found that an existing theory is remarkably accurate.

University of Delaware
Newark, DE 19716

Department of Chemical Engineering

400. *The Generalized van der Waals Theory of Pure Fluids and Mixtures*
Sandler, S.I. **$88,514**
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. This is the subject of this research activity. 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 uses computational quantum mechanics to identify groups in a nonambiguous way. The same computational techniques will also be 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 involves the use of molecular dynamics computer simulation and statistical mechanical theory to develop a correct description of chain molecules ranging from small hydrocarbons to long chain polymers.

University of Illinois at Chicago
Chicago, IL 60680

Department of Chemical Engineering

401. ***Transport Properties of Dense Fluid Mixtures Using Nonequilibrium Molecular Dynamics***
Murad, S. **$70,000**
708-996-5593

A method developed previously to study the thermal conductivity of rigid polyatomic fluids, has been extended to mixtures and then used to investigate a range of pure fluids (polyatomic) and mixtures. In these studies special attention was paid to the internal rotational contributions to thermal conductivity. Such contributions are needed in many theories for thermal conductivity of polyatomic fluids. Based on these results a method that is much more accurate than the currently used Eucken-theory based techniques has been developed for predicting these contributions. In addition, an examination of transport properties of fluids with flow constraints is being initiated. In these initial studies membranes, slits, and pores are being investigated. Later these studies will be extended to more complex geometries.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemical Engineering

402. ***Prediction of Thermodynamic Properties of Coal Derivatives***
Donohue, M.D. **$87,000**
410-516-7761

Changes in the chemical, petroleum, and energy industries have led to the need to predict properties for substances and mixtures which are complex in both their chemical structures and in terms of their intermolecular potential functions. While the field of molecular thermodynamics has made tremendous advances over the last twenty years, there is still no theory that can predict accurately the properties of multicomponent mixtures when the components differ greatly in size and in the nature of their potential functions. The work on this project includes experimental measurements of macroscopic behavior, spectroscopic measurements of molecular behavior, computer simulations of model compounds, and theoretical calculations based on chemical, perturbation, and lattice theories. Spectroscopic measurements show that the models developed from chemical theory are in good agreement with experimental data 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

403. ***Thermophysical Properties of Supercritical Fluids and Fluid Mixtures***
Sengers, J.V. **$126,400**
301-405-4805

The project is concerned with the development of theoretically based equations for the thermodynamic and transport properties of fluid and fluid mixtures that incorporate the proper singular asymptotic behavior near critical points as well as the crossover to classical behavior very far away from critical points. For the thermodynamic properties of one-component fluids such an equation has been developed on the basis of a renormalized Landau expansion and it has been applied to represent the thermodynamic properties of a variety of fluids including, most recently, ethane and methane. The relationship with previous asymptotic parametric equations of state has been elucidated. The current efforts emphasize the extension of the theory to fluid mixtures. Theories for the effect of critical fluctuations on the transport properties of fluid mixtures are also being developed. In conjunction with this effort an internationally coordinated program has been organized to measure the transport properties of mixtures of carbon dioxide and methane in the vicinity of the vapor–liquid critical line. This work has revealed an unexpected anomalous behavior of the thermal conductivity of fluid mixtures in the vicinity of a plait point which needs to be further investigated.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

404. ***Theoretical Studies of Solid–Fluid Phase Equilibria***
Monson, P.A. **$85,000**
413-545-0661

This project is concerned with 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 problems such as (1) the prediction of the melting line for anisotropic molecules and development of an understanding of the departures from the principle of corresponding states for solid–fluid equilibria; (2) the prediction variations of solubility of solids in liquids with details of the molecular interactions; and (3) the prediction of solid phase miscibility on the basis of the intermolecular forces. 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. The simulation results are providing data for rigorous testing of the theoretical predictions and providing physical insight into the development of approximations. Earlier an extensive study of the solid phase thermodynamics and solid–fluid equilibria of hard dumbbell systems was completed. This is an important reference point for understanding the freezing properties of real molecules. The results are being used to develop a generalized van der Waals theory for the freezing of molecular liquids.

National Institute for Petroleum and Energy Research
Bartlesville, OK 74005

Department of Fuels Research

405. ***Thermodynamic Properties by Noncalorimetric Methods***
Steele, W.V. **$200,000**
918-337-4210

This research complements the experimental programs currently in progress at the National Institute for Petroleum and Energy Research (NIPER) for other divisions of the Department of Energy. Those experimental programs are focused on the calorimetric determination of thermodynamic properties of key polynuclear heteroatom-containing aromatic molecules. This program focuses on the noncalorimetric determination of thermodynamic properties through the extension of existing correlation methodologies and through molecular spectroscopy with statistical mechanics. Important advances made in the program include the following: (1) Group-contribution parameters for estimation of thermodynamic properties for polycyclic heteroatom-containing aromatic hydrocarbons were derived. The group parameters were used to confirm a new experimentally determined value for the enthalpy of formation of phenanthrene, to estimate thermodynamic properties for several previously unstudied benzoquinolines, and to derive equilibria in the biphenyl/phenylcyclohexane/bicyclohexane/hydrogen system. (2) A method was developed to calculate the kinetic energy expansions as a function of the coordinate for the ring-puckering, ring-twisting (in-phase), and ring-twisting (out-of-phase) for molecules containing large amplitude anharmonic vibrations. The developed method was used to calculate thermodynamic functions for cyclopentene, 2,5-dihydrofuran, 2,3-dihydrofuran, 2,5-dihydrothiophene, and 2,3-dihydrothiophene to 1000 K.

National Institute of Standards and Technology, Boulder
Boulder, CO 80303

Thermophysics Divison

406. ***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

407. ***Theoretical Treatment of the Bulk and Surface Properties of Fluids Containing Long, Flexible Molecules***
Hall, C.K. **$222,167**
919-515-3571 **(24 months)**

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 which 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. The Generalized Flory Theory (which was previously applicable only to pure fluids containing chain-like molecules which interact via repulsions) has been extended to pure fluids containing chain-like molecules which interact via attractions as well as repulsions. This theory is in excellent agreement with computer simulation results for the pressure. Current activities include the extension of this theory to binary fluid mixtures of chain-like molecules. 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

408. Thermodynamics and Transport in Microporous Media
Glandt, E.D. **$99,000**
215-898-6928

This is a computational project concerned with the structural and topological properties of model porous materials, and with how these determine the transport behavior of a medium and the partitioning of compact and of chain macromolecular solutes into it. Complete sets of geometric, connectedness, and transport information will be generated on low-porosity sintered structures by random-walk, first-passage methods. New acceleration techniques have been developed for the solution of the diffusion equation within random boundaries rather efficiently. Percolation phase diagrams for both the solid and pore phases will be mapped for varying degrees of interpenetrability of the sintered particles constituting the body. The determination of the distribution coefficient for random flight chain molecules in the pore space (including the case of branched polymers) can be computed with analogous methods. The physical adsorption of repeat units of the polymer onto the walls of the solid matrix is also considered.

Princeton University
Princeton, NJ 08544

Department of Chemical Engineering

409. Molecular Interactions in Dilute Supercritical Mixtures: Molecular Dynamics Investigation
Debenedetti, P.G. **$79,000**
609-258-5480

The project aims at gaining molecular-level understanding of solute–solvent and solute–solute interactions in supercritical mixtures. Integral equations and molecular dynamics simulations are used to understand the influence of molecular shape, size, and interaction energy upon the local environment surrounding solute molecules, and hence upon their chemical potential in the supercritical mixture. The first direct comparison between fluorescence spectroscopy and simulation calculations of local density enhancements around solute molecules in attractive supercritical mixtures has been performed. The results show good agreement between experiments and simulations, and suggest that the spectroscopic measurements probe first-shell interactions. A new expression for the solute–solute pair correlation function integral has been derived: It shows that, in the limit of infinite dilution and close to the solvent's critical point, this quantity is positively divergent, regardless of the type of mixture (attractive or repulsive). A molecular dynamics study of solute–solute distributions in attractive and repulsive mixtures has confirmed this theoretical prediction, and has revealed dramatic enhancements in the first peak of the solute–solute distribution function in model attractive mixtures. Future work will address the lifetime and equilibrium distribution of solute–solute aggregates, as well as solute-cosolvent interactions.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

410. Fundamental Studies of Fluid Mechanics and Stability in Porous Media
Homsy, G.M. **$109,277**
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 in heterogeneous systems, 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 resonance between flow fields driven by heterogeneity and viscosity when the characteristic lengths are commensurate. 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

411. Thermophysical Properties of Fluids and Fluid Mixtures
Stell, G.R. **$116,000**
516-632-7899

A mathematically rigorous study of a very general family of kinetic theories has been made that includes the kinetic variational theories (KVTs) that have already been quantitatively evaluated. The study of a new transport theory has also been initiated. It is based upon a kinetic equation in which a stochastic term appears, and will facilitate the description of fluids of soft-core molecules as well as providing the basis of a new dense-fluid theory that wil reduce to a Boltzmann-equation description at low densities. An extension of the KVTs to models of chemically reacting fluids has also been started to supplement an ongoing study of diffusion-limited chemical reaction rates. Equilibrium research includes a long-term study of phase separation in models of ionic fluids, which focuses on both the exact phase-equilibria properties of such fluids as wel as critical appraisal of the predictions of some widely used approximations. An investigation of the thermodynamics and structure of a Hamiltonian model of microemulsions continues. In particular, percolation theory is used to help describe the special features of the bicontinuous microemulsion phase that distinguish it from a simple isotropic mixture.

University of Virginia
Charlottesville, VA 22903

Chemical Engineering Department

412. ***Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems***
Cummings, P.T.; **$167,038**
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: molecular simulation of vapor–liquid phase equilibria in ethanol/water, water/salt, and ethanol/water/salt systems; molecular simulation of supercritical aqueous systems; development of statistical mechanical theory of mixed solvent and mixed salt electrolyte solutions; and additional experimental measurements of phase equilibria and densities in mixed solvent electrolyte systems.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemical Engineering

413. ***Interphase Transport and Multistage Separations***
Stewart, W.E. **$87,000**
608-262-0188

This project deals with the mathematical modeling of mass transfer processes, including transport theory, computational methods, and correlations of system performance. An initial correlation study has been completed on sieve-tray heat and mass transfer, applying boundary layer theory, dimensional analysis, and statistical model-building methods to published fractionation experiments. An experimental design capability has been added to the parameter estimation package GREG, and an improved objective function for nonlinear parameter estimation from multiresponse data has been derived and implemented. Work continues on analysis of mass transfer in wall turbulence, and on an improved strategy for parameter estimation from multiresponse data with incomplete arrays of observations.

Yale University
New Haven, CT 06520

Department of Mechanical Engineering

414. ***Computational and Experimental Study of Laminar Premixed and Diffusion Flames***
Smooke, M.D.; Long, M.B. **$194,273**
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.

Small Business Innovation Research

The following projects were funded during FY 1992 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 and ongoing Phase II projects are given on the following page. New Phase II projects were started too late for inclusion in this section of the summary book. A list of them appears in the back of the book.

Advanced Fuel Research, Inc.
East Hartford, CT 06108

415. On-Line Diagnostics for Fullerene Synthesis

Serio, M.A. **$49,951**
203-528-9806 **(6.5 months)**

It has recently been shown that caged carbon clusters, fullerenes, are produced in significant quantities in a carbon arc in an atmosphere of about 150 torr He. It was also shown that the fullerenes are soluble in common organic solvents. These two discoveries opened the door to several possible applications of carbon fullerenes. Examples would include coatings, lubricants, composite materials, molecular sieve carbons, catalysts, and superconducting films. However, the yields of fullerenes reported by different laboratories using this procedure vary over a large range, from less than 5% to as much as 40% of the carbon soot, as does the selectivity to C_{60}. The overall objective of this program is to develop an optimized carbon arc process for the manufacture of bulk quantities of fullerenes. The Phase I program will have the following specific objectives: (1) Construct a carbon arc reactor with continuous gas flow and provision for the use of online Fourier transform infrared (FT-IR) diagnostics to make measurements of soot and gas species concentrations and temperatures. (2) Study how variations in the reactor physics (geometry, fluid mechanics, heat transfer) affect the selectivity and yield of C_{60} and other fullerenes. (3) Study how variations in the reactor chemistry (addition of H_2, O_2, N_2 or presence of contaminants like H_2O or hydrocarbons) affect the yield and selectivity. (4) Obtain a preliminary online UV-vis spectrum and design a more optimal reactor system which would allow additional diagnostics.

Bend Research, Inc.
Bend, OR 97701

416. Development of High-Selectivity, High-Permeability, Flexible, Plasma-Polymer Membranes

Friesen, D.T. **$50,000**
503-382-4100 **(6.5 months)**

The potential advantages of membrane-based processes for separations are well-known, but current membranes do not offer the combination of high selectivity and high flux required for many applications. Plasma polymerization is, in principle, an attractive process for making exceedingly thin, defect-free polymer films that have high selectivity. Unfortunately, most of the plasma-polymer membranes investigated thus far suffer from low permeability, which means that, to attain practical fluxes, they must be made so thin that conventional membrane structures cannot support them. Furthermore, conventional plasma polymers are brittle and prone to cracking. The goal of this program is to produce plasma-polymer membranes that overcome the dual problems of low flux and brittleness through a novel multilayer membrane structure. These new plasma-polymer membranes should have the high selectivities associated with the conventional single-layer plasma polymers investigated thus far, but have fluxes comparable to or better than any membranes that are currently available. In addition, these new plasma-polymer membranes should be more flexible, allowing their use in practical applications. In Phase I the feasibility of the approach will be demonstrated by preparing multilayer membranes with the characteristics described above.

417. Development of Novel Reverse-Osmosis Membranes with High Rejections for Organic Compounds

McCray, S.B. **$49,954**
503-382-4100 **(6.5 months)**

Many chemical process industry separations involve removing organic compounds from aqueous process streams. Several types of conventional unit operations are used to remove or destroy organics in aqueous process streams or to clean up contaminated groundwater. However, these operations (e.g., carbon absorption, steam stripping, liquid/liquid extraction) can be energy intensive or produce a secondary waste stream that must be disposed of. Some of these processes also destroy the organic compounds, precluding the possibility of recovering or recycling them. Reverse osmosis (RO) is a membrane-based process that has the potential to improve and simplify water treatment technology significantly. Although commercial RO membranes desalt water efficiently, they are not effective at removing many industrially important organics from water. A new class of RO membranes must be designed which remove high percentages of organic contaminants. Phase I will demonstrate the feasibility of developing RO membranes capable of high rejections of organic molecules and high water fluxes. Small membrane samples that have a water flux of 15 L/m^2-h (at 55 atm) and a rejection of phenol (the target contaminant) of at least 98% will be prepared.

Cape Cod Research, Inc.
Buzzards Bay, MA 02532

418. Selective Ceramic Membranes from Hybrid Templates

Dixon, B.G. **$50,000**
508-759-5911 **(6.5 months)**

A new microstructural composition is described which promises to yield high-performance ceramic membranes with molecular transport properties that can be tailored for a specific separation. The overall approach takes advantage of the highly structured order of hybrid organic/inorganic template materials to form previously unknown membranes that will be useful in the design of systems for selective chemical separations of many kinds.

Chromex, Inc.
Albuquerque, NM 87107

419. The Development of a Multiple-Input Spectrometer for Process Monitoring Applications

Bret, G.G. **$499,004**
505-344-6270 **(24 months)**

Recent years have seen significant advances in light detection technology and computer processing power. There are two-dimensional array detectors (e.g., CCD arrays) that are entirely capable of performing as scientific detectors. Modern small computers are capable of handling the vast quantities of data produced almost instantaneously by these detectors. The missing building block in the development of a spectrometer that can take advantage of these developments is an optical system capable of two-dimensional imaging. A proprietary method of producing high quality aspheric optics will be used to produce a high resolution stigmatic flat-focal-field spectrograph that, when coupled with array detection, can be the basis for a multiple fiber-optic input spectrophotometer. The resulting multiple spectrochemical measurements can be used to simultaneously determine target analyte concentrations at several locations. Such an application might be combustion diagnostics where numerous locations within a combustion chamber could be simultaneously monitored or a plasma reactor where spectral analysis could be made simultaneously at a number of discrete spatial locations within the reactor.

EIC Laboratories, Inc.
Norwood, MA 02062

420. A New Class of Ionomer Membranes

Rose, T.L. **$50,000**
617-769-9450 **(6.5 months)**

Ionomer membranes are presently used in desalination waste water cleanup and chemical production. Use of a membrane material with lower ionic resistivity than is currently available would reduce the energy expenditure in all of these processes. In addition, lower production cost and improved stability would accelerate their incorporation into new industrial processes. In this program a new class of ionomer membrane-containing polymers made from monomers of superacids with pK_a <-1.0 and low molecular weight of about 200 g/mol will be developed. In Phase I monomers will be synthesized to make two polymers of the new class from low-cost, readily available starting materials. The monomers will be polymerized by radical polymerization and hydrolyzed to form ionomer membranes. One polymer will have a hydrocarbon and the other a perfluorinated backbone. The ionic resistivity; equivalent weight; sorption; and thermal, chemical, and oxidative stability of these membranes will be evaluated.

Eltron Research, Inc.
Aurora, IL 60504

421. Stoichiometric Precursors for Preparation of Advanced Metal Oxide Solid Electrolytes

Sammells, A.F. **$49,996**
708-898-1593 **(6.5 months)**

This research program is directed toward development of an experimental synthesis approach that addresses the reliable achievement of precise initial precursor ceramic metal oxide composition control for oxide particles in the nanometer to several angstrom diameter range. The experimental approach relies upon initial electrochemical dissolution of sacrificial metal anodes in anhydrous alcohol electrolytes leading to formation of mixed metal alkoxides. Following the formation of the desired metal alkoxide composition, ultrasonic atomization of solutions will be performed to provide a mist of fine droplets. These will be hydrolyzed to the corresponding oxides by introduction into either a jet of dry steam at temperatures between 100 and 200 °C or into an aqueous alkaline solution (~ 3N KOH) at temperatures between 75 and 200 °C. The ability to control the composition of metal oxide ceramic precursor particles precisely and uniformly should have significant impact on the final quality of high-density ceramics obtained after their subsequent sintering. Of immediate interest is the application of this approach for the subsequent preparation of advanced solid electrolytes for both fuel cell and electrolytic applications.

INRAD, Inc.
Northvale, NJ 07647

422. Development of a Selective Sensor for Organic Contaminants in Groundwater Using a Molecular Imprinting Technique

Zhang, Z. **$49,929**
201-767-1910 **(6.5 months)**

The widespread presence of chlorinated and nonchlorinated organics in groundwater at many installations poses a serious environmental and health problem, with particular attention being drawn to trichloroethylene (TCE) as a common carcinogenic contaminant. Currently, monitoring the TCE contaminant level in groundwater comprises the collection of samples at the site, transportation of the samples to an analytic laboratory, and subsequent analysis in the laboratory. Such a procedure is labor-intensive, expensive, and time-consuming. In addition, the analysis gives only one concentration data point in time and space, with the chance that the removal and transportation of the sample may have altered its composition. A molecular imprinting technique will be used to prepare a TCE-selective polystyrene film that will then be applied to a surface acoustic wave (SAW) device to detect and quantify the TCE concentration in groundwater. A TCE-sensitive SAW microsensor would provide a highly sensitive, low-cost, online, and real-time means for monitoring TCE in groundwater.

Jet Process Corporation
New Haven, CT 06511

423. Thin Solid Film Electrochemical Oxygen Partial Pressure Sensor for Control of Low Vacuum Inert Gas Processes

Halpern, B.L. **$50,000**
203-786-5130 **(6.5 months)**

An essential element for high quality, high yield, low cost manufacture of advanced materials and components for use in the aerospace, electronics, biomedical, energy, and automotive industries is "intelligent" control of process parameters. One new process with technological and commercial potential is the Jet Vapor Deposition (JVD) process, which, like other advanced process technologies, uses a low vacuum, inert gas environment. Control of process purity, especially prevention of oxygen contamination, is integral to reliable, quality manufacturing in JVD and other low vacuum processes. There is currently a need for improved low cost sensors to monitor low vacuum process purity. An innovative, vacuum-compatible, low-temperature, thin solid film, electrochemical oxygen partial pressure sensor will be designed to monitor and verify low vacuum inert gas process purity.

Laser Photonics Technology, Inc.
Amherst, NY 14228

424. *Novel Durable Sol-Gel Fiber-Optic Sensors for Use in Elevated Temperature and/or Pressure Environments*

Casstevens, M. **$50,000**
716-636-3626 **(6.5 months)**

This program aims to demonstrate the utility of employing novel fiber-optic sensors for use in high-pressure and high-temperature environments. The sensor design employs a novel "surface composite" containing sol–gel coatings and immobilized fluorescent organic compounds. The first goal is to discover and characterize what factors govern the analytical figure of merit. Two specific sensor types are planned which are expected to reveal the unique functional properties of the design. The microporous nature of the nondensified sol–gel preparations provides a unique local environment that is environmentally stable and is expected to permit greater selectivity and sensitivity. Sample films are being prepared and analyzed to determine their uniformity and optical quality. These samples will then be tested in a variety of conditions whereupon their physical and spectroscopic responses will be assessed. The results will be critically reviewed with respect to the potential of this design (and these materials) to function under nonambient conditions.

Materials and Electrochemical Research Corp.
Tucson, AZ 85706

425. *The Development of a Process to Synthesize Tubular Fullerenes*

Withers, J.C. **$50,000**
602-574-1980 **(6.5 months)**

Fullerenes have been the subject of very intense scientific investigations during the past year since the announcement of their discovery and isolation. Recent evidence suggests that it may be possible to tailor the dimensions and configurations to tubular shapes. It has been demonstrated that such a tubular shape can be synthesized, isolated, and characterized. This program will further develop the synthesis by a detailed investigation of the mechanism of synthesis of these tubular fullerene geometries, and the separation, isolation, and characterization of these materials for a variety of applications.

Membrane Technology & Research, Inc.
Menlo Park, CA 94025

426. *Ultrathin Metal Membranes*

Athayde, A.L. **$500,000**
415-328-2228 **(24 months)**

The Phase I program demonstrated the feasibility of preparing ultrathin composite metal membranes with high selectivity and high hydrogen flux. The membrane consist of a permselective palladium/silver layer on a microporous polymer support layer, overcoated with polymer sealing layer. The Phase II program will bring ultrathin composite metal membranes to the point o readiness for pilot-scale testing. With palladium/silve membranes as the model system techniques for membrane preparation will be refined with the goal of continuous production process for rolls of membrane materials. Membranes will be evaluated for selectivity an flux in a bench-scale test unit, using typical industrial ga mixtures. The problems of membrane poisoning will be investigated. Based on these results, a pilot scale membran gas separation system will be designed.

427. *Molecular-Sieve-Modified Polymeric Membranes for Gas and Vapor Separation*

Pinnau, I. **$50,00**
415-328-2228 **(6.5 months**

Current commercial gas separation membranes are mad from glassy or rubbery polymers. Transport through thes membranes occurs by a solution-diffusion mechanism Most polymers show a trade-off between selectivity an permeability (i.e., high selectivities are coupled with lov permeabilities and vice versa). Recently developed highl rigid, glassy polymers have shown dramatic increases o permeabilities without sacrificing the selectivity for th separation of permanent gas mixtures such as oxygen nitrogen, hydrogen/methane, and carbon dioxide/methane However, the selectivities of current membrane material for other industrially important gas separation applications, such as hydrocarbon removal from natural gas carbon dioxide separation from hydrogen-containin streams, or the recovery of certain organic vapors fro air, are insufficient for a feasible membrane separatio process. The goal of this project is to develop a new approach to improving the selectivity of membranes for th separation of gas streams containing condensible gase and vapors. The membranes will consist of polymers modified with molecular sieves such as zeolites. Recen experimental data indicate that zeolite-modified polydimethylsiloxane or cellulose acetate membranes sho enhanced permselectivity for gas separations. A detaile investigation of such membranes for gas and vapor separation has not been undertaken. A systematic study o molecular-sieve-modified polymer membranes could lea to novel applications for membrane-based separations.

Pacific Fullerene Specialties
Sunnyvale, CA 94086

428. *Low-Cost Process for Manufacture of Fullerenes*

Lane, D. **$40,56**
408-293-0830 **(6.5 months)**

The recently discovered materials known as fullerenes have unique chemical and physical properties that have generated great interest in the scientific and technical research communities. Several applications have been proposed for these materials such as: superconductors, nucleation of diamond films, nonlinear optical materials, and catalysts. Development of commercial applications for these materials will require that they be readily available at a reasonable price. The currently used arc process is unable to satisfy these requirements. A new process for the continuous synthesis of fullerenes from carbonaceous feedstocks will be explored. In Phase I the commercial viability of this process will be assessed by determining production rates and operating costs.

Southwest Sciences, Inc.
Santa Fe, NM 87501

429. A Novel Mass Spectrometer for Combustion Studies

Bomse, D.S. **$497,531**
505-984-1322 **(24 months)**

This project uses a novel scheme, ionization energy modulation, to increase the amount of chemical information obtained from mass spectroscopy and uses the added information to support automated computerized deconvolution of the mass spectra of combustion mixtures. The Phase I research successfully demonstrated the ability of the method to enhance the information content obtainable from the mass spectra. In particular, it clearly distinguished among different species at the same parent ion mass, and could separate isomeric forms of the same compound. In Phase II, a prototype mass spectrometer using ionization energy modulation will be tested by quantifying the components in complex combustion mixtures above methane/oxygen and butane/oxygen flames. The Phase II instrument, now under construction, uses a time-of-flight mass spectrometer and is designed to have five times better energy resolution and 100,000 times greater sensitivity than the instrument that was used in Phase I.

TDA Research, Inc.
Wheat Ridge, CO 80033

430. Preparation of Low-Density Microcellular Materials from Fullerenes

Bell, W.L. **$50,000**
303-420-4329 **(6.5 months)**

Low density microcellular materials (LDMMs) are carbon- or silicon-based porous solids with high specific surface area. These materials have been developed extensively over the last decade, and they are moving toward substantial commercial development in a variety of applications. An opportunity to prepare novel LDMMs with improved properties now arises with the recent discovery of fullerene carbon. By combining reactions that yield organic LDMMs with recently reported reactions of fullerenes, porous monolithic solids containing fullerenes will be prepared. Fullerenes are particularly suited as building blocks for LDMMs because of their low density, inherent stiffness, thermal stability, and their tendency to react at multiple sites (which favors crosslinking reactions). Phase I will demonstrate the feasibility of the proposed preparation and characterize the products by determining specific surface area, porosity, cell size distribution, and the compressive strength and modulus. Adsorption and desorption of selected adsorbates on these materials will be measured. Potential applications of the new materials and the structural properties required for improved performance will be considered. Fullerene carbon can then be prepared in forms suitable for uses similar to that of activated carbon in adsorption or vitreous carbon in electrodes.

431. Continuous Production of Fullerenes from Hydrocarbon Precursors

Wright, J.D. **$50,000**
303-422-7918 **(6.5 months)**

Fullerenes and their derivatives have been suggested for use as three-dimensional organic conductors, high-temperature superconductors, nonlinear optical materials, high-current-density battery materials, catalyst supports, sorbents, polymer building blocks, reinforcing agents in composite materials, and lubricants. However, no matter how interesting their properties, no applications will be practical at current fullerene prices. For most applications a two to four order-of-magnitude reduction in cost is required. The current carbon-arc method is inherently a small-scale batch process, difficult to monitor and control accurately and to scale up. In this program a continuous process is being developed using hydrocarbon precursors to produce large quantities of low-cost fullerenes. Thermodynamic analyses have shown that the process has the potential for very high yields and low operating costs and offers much better and more direct control over the synthesis conditions. As a result the new process should be considerably less expensive than the current arc process. During Phase I the effects of temperature, pressure, hydrocarbon concentration, and carbon to hydrogen ratio on the fullerene yield will be investigated, and these data will be used to analyze the production costs of the new process.

ADDENDUM

Information on the following grants was received too late for their inclusion in the body of this book.

Atomic Physics

Michigan Technological University
Houghton, MI 49931

Department of Physics

432. ***Theoretical Hyperfine Structure Constants for Transition Metal Atoms and Ions***	
Beck, D. R.	**$65,532**

University of Notre Dame
Notre Dame, IN 46556

Department of Physics

433. ***Rydberg States in Multiply Charged Ions***	
Livingston, A. E.	**$80,973**

Tulane University
New Orleans, LA 70118

Department of Physics

434. ***Few Electron Transitions in Atomic Collisions***	
McGuire, J. H.	**$60,000**

SBIR PHASE II

Eltron Research, Inc.
Aurora, IL 60504

435. ***Distributed Fiber Optic Sensor for Reversible Detection of Atmospheric CO_2***	
Sammells, A. F.	**$499,954**
708-898-1583	**(24 months)**

Moltech Corporation
Stony Brook, NY 11794

436. ***Advanced Biosensors for Analytical Chemical Measurements***	
Skotheim, T.	**$499,958**
516-632-7565	**(24 months)**

Southwest Sciences, Inc.
Santa Fe, NM 87501

437. ***Measurement of Combustion Radicals Using Visible/Near-Infrared Diode Lasers***	
Silver, J. A.	**$499,042**
505-984-1322	**(24 months)**

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	$ 7,140,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	26,500,000
	Radiochemical Engineering Development Center	7,800,000
Sandia National Laboratories, Livermore	Combustion Research Facility	4,390,000
Stanford University	Stanford Synchrotron Radiation Laboratory	11,220,000

4.5-MV DYNAMITRON ACCELERATOR (KC-03-01-03)

Physics Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne Physics Division operates a high-current 4.5-MV Dynamitron accelerator which delivers magnetically analyzed beams of most atomic ions and many molecular ions. Among the unique facilities associated with the Dynamitron are (1) a beam line capable of providing "supercollimated" ion beams that permit angular measurements to accuracies of 0.1 mrad, (2) a beam-foil measurement system capable of measuring lifetimes to a few tenths of a nanosecond, (3) a 28-inch-diameter general-purpose scattering chamber, (4) a laser-ion beam system where an argon pumped dye laser beam is coaxial with the ion beam, (5) a variety of electrostatic and magnetic electron spectrometers, (6) large-area multiwire proportional counters capable of detecting up to eight particles simultaneously with submillimeter position and subnanosecond time resolution, and (7) a postacceleration chopper system giving beam pulses with widths that can be varied from 1 ns to several ms at repetition rates variable up to 8 MHz. A VAX 11/750 computer system with direct links to Argonne's central computing facility is used for on-line data acquisition, analysis, and the control of experiments.

COLLABORATIVE USE

Visiting scientists use the accelerator either in collaboration with Argonne investigators or as independent groups.

PERSON TO CONTACT FOR INFORMATION

E. P. Kanter Phone: (708) 252-4050
Physics Division
Argonne National
Laboratory
9700 South Cass Avenue
Argonne, IL 60439

TECHNICAL DATA

Range of terminal voltages attainable	0.3 to 4.8 MV
Range of ion beam currents attainable	10 aA to 500 μA
Monatomic singly charged ion beams available	Most elements
Monatomic multiply charged ion beams available	Rare gases, transition metals
Typical molecular-ion beams available	H_2^+, H_3^+, HeH^+, CH_n^+ $C_2H_n^+$, $C_3H_n^+$ ($n = 0 - 5$), CO^+, O_2^+, etc.
Pulse mode (postchopper)	
Pulse width	1 ns to 10 ms
Repetition rate	0 MHz to 8 MHz

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 636 shipments totaling over 19,000 ampoules have been made. A Users Handbook is updated annually and available from the Manager.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres
Chemistry Division, Bldg. 211
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone: (708) 252-7374
FAX: (708) 252-4470
Telex: TWX 910-258-3285 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 μ*M* can be generated with the 25-ps pulse, and concentrations in excess of 10 m*M* 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. Simultaneous multiwavelength kinetic spectrophotometric measurements are possible, and 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

Charles D. Jonah
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Computer address: Jonah@ ANLCHM.bitnet

Phone: (708) 252-3471
FAX: (708) 972-4993

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 30 experimental ports and the VUV ring accommodates 17. Each of these ports is split into two to four beam lines. By the end of 1991, the Light Source had 82 operational experimental beam lines. Of these 12 lines are dedicated to beam diagnostics and R&D.

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 underway 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. By March 1, 1992, 2300 scientists from 390 universities, laboratories, corporations, and foreign institutions were using 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. In FY 1991, six corporations conducted proprietary research at the Light Source.

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 75. 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. Two hundred and nineteen new General User proposals were submitted during FY 1991. A total of 1961 days of beam time were allocated to General Users on the X-ray and UV rings during FY 1991.

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-eight scientists, 30 faculty and 38 students representing 20 universities, participated in this program in FY 1991. One hundred and eight institutions have now participated in this program since its inception in 1984.

PERSON TO CONTACT FOR INFORMATION

Susan White-DePace	Phone:	(516) 282-7114
NSLS, Bldg. 725B	FAX:	(516) 282-7206
Brookhaven National Laboratory	E-mail:	swd@bnl.bitnet swd@bnl.gov bnl::swd
Upton, NY 11973		

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
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

TECHNICAL DATA (Continued)

Research area	Wavelength range (Å)	Energy range (eV)	Number of instruments
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

WB = White Beam
*from 1991 NSLS User's Manual

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, and Ar
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) 239-6117

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 6.5 MV. A wide variety of ion species is available. Two 90° magnets with a stripper (gas or 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 Elbeck magnetic spectrograph 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.

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Oak Ridge, TN 37831-6377
Phone: (615) 574-4789

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 6.5 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 ($cm^2 \cdot sec$). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory or other qualified users. Four beam tubes are used for neutron-diffraction experiments, and a small-angle neutron scattering facility sponsored by the National Science Foundation is available for use by researchers from universities, industry, and other national laboratories. Management of this facility has been transferred to the Assistant Secretary for Nuclear Energy. The funding remains in the Office of Energy Research.

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

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

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

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

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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 Applied Mathematical Sciences 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.

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or

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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	Laser fluorescence laboratory
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 23 experimental stations on 9 beam lines covering the spectrum from 5 to 45,000 eV. Specialized facilities for protein crystallography and lithography are available.

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, 2172 proposals for research have been received. Demand for experimental time is approximately twice that which can be accommodated.

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CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution ΔE/E	Approximate spot size, hgt × wdth, mm	Dedicated instrumentation
				Insertion Devices Stations			
Wiggler Lines–X-ray							
End stations							
4-2 (8 pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
6-2 (54 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
7-2 (8 pole)							Six-circle diffractometer
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
10-2 (31 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
Side stations							
4-1	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	2.0 × 20.0	
4-3							Two-circle diffractometer vertically focusing mirror
Focused	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	.5 × 20	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
7-1	1.0		Curved crystal	6,000 to 13,000	$\sim 8 \times 10^{-4}$	0.6 × 3.0	Rotation camera
7-3	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
Undulator Lines–VUV/soft X-ray							
5-2	1.5		Rowland circle-multiple grating	10 to 1,200	≥7% (raw undulator)	6.0 × 8.0	Angle integrated e-spectrometer
				Bending Magnet Stations			
X-ray							
1-4	2.0		Curved crystal	6,700 to 10,800	0.3×10^{-3}	0.25 × 0.5	Small angle scattering detector
1-5	1.0		Double crystal	2,800 to 30,000	$\sim 10^{-4}$	3 × 20	Area detector/CAD-4
2-1 (focused)	4.8	8.9	Double crystal	2,800 to 8,900	$\sim 5 \times 10^{-4}$	1 × 4	
2-2	1.0 to 6.1		None	3,200 to 30,000		4 × 22 to 4 × 134	
2-3	1.0		Double crystal	2,800 to 30,000	$\sim 5 \times 10^{-4}$	3 × 20	

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS (Continued)

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution ΔE/E	Approximate spot size, hgt × wdth, mm	Dedicated instrumentation
				Bending Magnet Stations			
VUV/soft X-ray							
1-1	2.0		Grasshopper	64 to 1,000	$\Delta\lambda = 0.1$ to 0.2 Å	1.0 × 1.0	
1-2	4.0		6m TGM	8 to 90	$\sim 2 \times 10^{-3}$	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	$\sim 5 \times 10^{-4}$	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	$\sim 9 \times 10^{-3}$	≤1 mm^2	Angle resolved e-spectrometer
8-2	5		6m SGM	50 to 1,000	$E/\Delta E \leq 22{,}000$	≤1 mm^2	Angle resolved e-spectrometer

FY 1992 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 contractors are used for all costs, including purchase of necessary equipment.) FY 1992 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds
Ames Laboratory	$ 460,000
Argonne National Laboratory	3,950,000
Brookhaven National Laboratory	2,080,000
Idaho National Engineering Laboratory	20,000
Lawrence Berkeley Laboratory	1,160,000
Los Alamos National Laboratory	50,000
National Renewable Energy Laboratory	115,000
Notre Dame Radiation Laboratory	265,000
Oak Ridge National Laboratory	3,490,000
Pacific Northwest Laboratories	1,000,000
Sandia National Laboratories, Albuquerque	15,000
Sandia National Laboratories, Livermore	1,132,000
Stanford Synchrotron Radiation Laboratory	700,000

SELECTED TOPICS OF GENERAL INTEREST

INSTITUTION INDEX

This index lists the institutions responsible for the projects cited in this publication. The corporate names are entered in standardized forms found in the authority listing *International Energy: Research Organizations* (ETDE/PUB-3). Each entry includes the project title and citation number.

INVESTIGATOR INDEX

Investigators' surnames are indexed in the form appearing in the citation; given names generally have been reduced to initials. For projects with multiple investigators, each name is indexed. Accent marks are not input because of computer alphabetization. Spelling and transliteration follow standard conventions.