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Summaries of FY 1990 Research in the Chemical Sciences

August 1990

U.S. Department of Energy
Office of Energy Research
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 separate section of this publication.

A separate section of this publication includes summaries of projects funded during FY 1990 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
Office of Energy Research
U.S. Department of Energy
Washington, DC 20585

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*On leave from Combustion Research Facility, Sandia National Laboratories, Livermore.
†On leave from West Virginia University.
‡On leave from 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.

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 electricity 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 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.

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 Combustion Research Facility (CRF) at Sandia/Livermore, the High Flux Isotope Reactor (HFIR) at Oak Ridge, 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 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 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, bio-, inorganic, physical, thermo-, and electrochemistry are central to these programs. The emphasis is on understanding the 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, anions, and isotopes. The program covers a broad spectrum of separations concepts, including membrane processes, extraction at both standard and supercritical conditions, adsorption, chromatography, photodissociation, complexation, etc. The research involves elucidating fundamental chemical phenomena for improved separations rather than developing specific processes for the separation of a particular species from particular matrices.

The analysis part of the program supports research on analytical techniques where a better understanding of chemical phenomena may facilitate improvements in sensitivity, reliability, and ease of operation and/or lower the costs of analytical determinations. Entirely new approaches to chemical analysis are investigated also, although this program does not support instrument development. Research progress is quickly reported 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 an analytical technique so that its utility can be improved, rather than developing techniques to unravel the composition of a particular sample or to analyze particular chemical species or sample types.

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 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) the measurement of crystal structures, melting points, magnetic susceptibilities, and the behavior of actinide metals and compounds 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 the more specific and energy-related aspects of chemically related engineering topics, including thermodynamics 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 turbulence research related to combustion. 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: Commercial (515) 294-9924

Chemical Sciences—Processes and Techniques

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NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **$580,000**

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

The goal of this project is to develop model systems of the bacterial photosynthetic reaction center through the use of monolayer and multilayer constructs; the primary tools of characterization are electrochemistry and Raman spectroscopy. It has become increasingly apparent that many more realistic simulacra of the *in vivo* membrane can be attained than previously thought, by the use of such monolayer model systems. Additionally, use of appropriate compounds in such model systems can result in increased chemical and physical stability. An example is the use of synthetic, covalently bound, double-ended phospholipids of lengths comparable to that of the cell membrane thickness. Such compounds are found in the thermophilic, archaic bacteria which thrive at high (80°C) temperatures. Using these compounds as the matrix material simulating that of the cell membrane, the essential pigments and other components present in the electron transfer chain of the reaction center can be readily incorporated. Use of monolayer techniques allows modulation of distances, orientations, and concentrations within the ranges seen in photosynthetic organisms. Any realistic model must approach the rates of photoinduced electron transfer seen *in vivo* and recent acquisition of time-resolved Raman instrumentation will allow measurements on model systems to be extended to the subnanosecond time scale. Raman identification of the bacteriochlorophyll and bacteriopheophytin ion radicals is essential in such studies. [2.0 FTE]

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

This research concerns two of the important rate determining factors in electron-transfer reactions, the orientation of the electron donor and acceptor and the thermodynamic driving force. Complexes consisting of the iron protein cytochrome c and the copper protein plastocyanin have been chosen for study because the redox-active metal ions in them are fully characterized, fixed in three dimensions, and replaceable with various nonbiological metals. The proteins (the donor and acceptor) are associated flexibly by electrostatic forces, and both rigidly and flexibly by covalent cross-links. The rates of electron-transfer within these complexes have been determined by laser flash photolysis. The experiments are designed to show whether ground state electron-transfer reactions require rearrangement of the donor and the acceptor into an optical configuration. Replacement of iron in cytochrome c with zinc has yielded a donor with a long-lived excited state, whose reaction with the plastocyanin acceptor has also been examined by laser flash photolysis. 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 effects of the thermodynamic driving force on the electron-transfer rate. [2.2 FTE]

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

The project objective is to develop a firm understanding of the early time electronic excitation and electron-transfer events of photosynthesis. This understanding will depend on knowledge of protein-pigment structure and the static and dynamical roles of the protein in transport phenomena that occur on a picosecond or shorter time scale. Both state-of-the-art frequency and time domain laser optical spectroscopies are essential for providing the data required for elucidating the crucial link between structure and dynamics. Laser-based high-resolution line-narrowing spectroscopies, developed in this laboratory for biological applications, are being used to study excitation transport and electron transfer in photosynthetic antenna (light-harvesting) and reaction center protein complexes. The spectroscopies include spectral hole burning and fluorescence line narrowing. They are ideally suited for elucidating both the excited electronic state structures of photosynthetic pigment complexes and the transport dynamics (including the role of the protein). The novel data generated are used to test existing theoretical models and to develop new theories. Data obtained have provided new insights into the role of coherence and the protein in electronic excitation transport and the types of charge-transfer states that may be important for the initial charge separation step in the reaction center (photosynthetic bacteria). The resulting theoretical models are being tested experimentally. [2.2 FTE]

4. ***Ultrafast Spectroscopy and Reaction Dynamics***
Struve, W.S.
Comm. 515-294-6342

Excitation and electron transfer in photosynthetic systems are studied using ultrafast fluorescence and pump-probe spectroscopies. Current issues being addressed include (1) the temperature dependence of single excitation hops in the chlorophyll *a* core antenna of photosystem I, which reflects directly on the extent of phonon participation in excitation transport; (2) the nature of excitation transport between the P670 and P680 chromophores in the photosystem II reaction center (which closely resembles the known reaction center structures in *sphaeroides* and *viridis*); and (3) the adequacy of the Förster dipole–dipole mechanism for describing excitation transport in strongly coupled photosynthetic systems. The latter question will be resolved in a subpicosecond pump-probe study of the Q_y absorption system of the bacteriochlorophyll *a* antenna protein complex from *Prosthecochloris aesturarii*. Additional systems of interest include those whose antenna function may turn out to be easily replicated in artificial systems. [2.2 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $5,115,000

5. *Electron Transfer and Energy Conversion*

Miller, J.R.; Meisel, D.; Schmidt, K.H.
Comm. 708-972-3481; FTS 972-3481

The project explores fundamental questions of electron-transfer reactions and redox catalysis that could lay foundations for new energy technologies. Special experimental tools enable measurements of how rates of electron transfer between molecules depend on distance, energy, polarity, and angular orientation. These measurements are unusual in their ability to investigate the effect of each of these critical variables without interference from the others and in a quantitative way which enables fundamental examination and development of theory, as exemplified in the recent striking success of theory in predicting temperature dependence. Redox catalysis by small semiconductor particles received fundamental support from knowledge of the electron and surface properties of the particles. Careful measurements of particle sizes, their absorption and emission spectra, and the dynamics of charge transfer in these particles allow insights into present, rudimentary theories, which relate size to bandgap. Stability and reactivity are partially controllable by chemical modification of the particle surface. Chemistry of d- and f-transition elements is investigated with emphasis on electron-transfer reactions and formation of colloids by these elements. [6.3 FTE]

6. *Characterization of Photosynthetic Components*

Norris, J.R.; Bowman, M.K.; Tiede, D.M.
Comm. 708-972-3544; FTS 972-3544

The project objective is to develop systems for use in studies of solar energy conversion. 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 antenna are required. The emphasis of these studies is on the three following categories: (1) transfer of excitation energy prior to charge separation, (2) properties of isolated molecules relevant to electron transfer, and (3) interactions responsible for noncovalent binding. Normal and isotopically altered chemicals or special assemblies are also provided to enhance the utility of the spectroscopies used in the study of photoinduced charge separation. [0.8 FTE]

7. *Photosynthesis Research*

Norris, J.R.; Tang, J.; Thurnauer, M.; Bowman, M.K.; Tiede, D.M.; Wasielewski, M.R.
Comm. 708-972-3544; FTS 972-3544

The project objective is to elucidate the chemistry and physics of the rapid and efficient photoinduced charge separation observed in natural photosynthesis. With such information artificial assemblages for solar energy conversion can be designed and constructed. The systems being studied include normal, isotopically substituted, and chemically manipulated photoactive assemblies, solutions, and compounds. The intrinsic photochemistry and photophysics are examined by spectroscopies tailored to probe the mechanisms of photochemistry, with an emphasis on optical and magnetic resonance spectroscopies. Perturbations, such as externally applied electric and magnetic fields, are designed to alter the photochemistry and spectroscopy. This eclectic approach characterizes the photochemical charge-separation process in a manner that allows both the development of theoretical understanding and the synthesis of laboratory asssemblies. [6.0 FTE]

8. *Reactive Intermediates in Condensed Phases: Radiation and Photochemistry*

Trifunac, A.D.; Jonah, C.D.; Sauer, M.C., Jr.; Bartels, D.M.; Schmidt, K.H.; Werst, D.W.; Lin, T.
Comm. 708-972-3483; FTS 972-3483

This project studies short-lived species whose transformations and dynamics define the chemistry of ionization and photoionization. The objective is to determine how the energy of particles or photons is transformed and partitioned into the variety of species produced. The observed diversity of consequences of ionizing radiation found in chemical and biological systems can be understood by considering fundamental processes involving charge transport, proton transfer, and excited states. The detailed study of short-lived species such as radical cations and electrons provides paradigms for understanding a wide range of fundamental issues of chemical reactivity and is relevant to many technologically important chemical processes. The role of the solvent in modulating the reactivity of such highly reactive species is exemplified by studies of electrons and ions in condensed phase. In a new direction of study, molecular segregation is achieved in low-temperature matrices, or "micro-reactors" such as zeolites, allowing detailed studies of condensed phase reactivity of radical cations. This research is conducted using specialized state-of-the-art techniques which include a picosecond linac, femtosecond laser and time-domain magnetic resonance and optical detection methods. [9.3 FTE]

9. *Artificial Photosynthesis*

Wasielewski, M.R.
Comm. 708-972-3538; FTS 972-3538

The purpose of artificial photosynthesis research is to design and prepare molecules that will convert light energy into useful chemical energy in the laboratory. The primary photochemistry of natural photosynthesis serves as a model of how highly-efficient conversion of light energy into chemical energy can take place. Natural photosynthetic charge separation may be improved by producing a more rugged molecular system that can function as a good photocatalyst in harsher chemical environments than those encountered with proteins. The initial events of photosynthesis consist of a sequence of picosecond electron transfer reactions between donor and acceptors that are positioned at critical distances and orientations relative to one another within a large protein. Thus, donor–acceptor molecules that maintain well-defined structural relationships between the various donors and acceptors are synthesized and studied. Molecules containing two or more covalently linked electron and/or energy donors and acceptors are synthesized to serve as models for the donor–acceptor configuration in photosynthetic proteins. The photophysics and photochemistry of these molecules are examined with primary emphasis on ultrafast light-induced energy and electron-transfer reactions. [4.0 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $1,015,000

10. *Porphyrin Chemistry*
Fajer, J.; Barkigia, K.M.; Renner, M.
Comm. 516-282-4521; FTS 666-4521

Porphyrin derivatives mediate a wide spectrum of bioenergetic reactions ranging from light-harvesting and energy conversion in photosynthesis to multielectron transfers in reactions as diverse as nitrogen assimilation, regiospecific syntheses and conversion of carbon dioxide to methane. This project seeks to define the electronic configurations that control these multifaceted mechanisms by a combination of experimental, structural, and theoretical approaches that considers the cumulative effects of macrocycle, substituents, metal, ligands, conformations, and environment (protein or solvent) in fine-tuning the photophysics, photochemistry, and electron-transfer properties of porphyrins. The work encompasses photochemistry, spectroelectrochemistry, magnetic resonance (ESR, ENDOR, NMR), X-ray diffraction, and synchrotron radiation techniques that are closely supported by several theoretical methods (extended Hückel, INDO, and molecular dynamics). The goals of the work are to identify and characterize the transients and mechanisms in these photosynthetic and biocatalytic reactions, and to provide specific guidelines for the development of synthetic photocatalytic systems. [5.7 FTE]

11. *Electrochemistry and Photoelectrochemistry*
Feldberg, S.W.; Smalley, J.F.
Comm. 516-282-4480; FTS 666-4480

The project comprises experimental and theoretical studies of electrochemical and photoelectrochemical phenomena. The major experimental effort focuses on studies of fast interfacial rate processes associated with electron transfer, ion transfer, and surface reconstruction or reorganization. A laser-induced-temperature-jump technique developed in an earlier phase of this work is one of the tools being used to characterize processes which can occur in the microsecond and submicrosecond time domain. Results in this previously inaccessible time domain will help to elucidate the mechanisms of these heterogeneous phenomena. Computer simulation of electrochemical and photoelectrochemical problems is a continuing contribution of this project. A new approach to computer simulation has been developed that greatly enhances the power of the commonly used explicit-finite-difference methodology without compromising its simplicity and flexibility. Some applications include simulations of the cyclic voltametric behavior of a variety of electrochemical mechanisms, of diffusion–migration effects at ultramicroelectrodes, and of photoresponses of semiconductor electrodes. [2.7 FTE]

Chemistry Department $3,035,000

12. *Thermal and Photoinduced Reactions in Solution*
Creutz, C.; Newton, M.; Seltzer, S.; Sutin, N.; Brunschwig, B.S.; Fujita, E.; Winkler, J.
Comm. 516-282-4359; FTS 666-4359

This project addresses three areas of fundamental importance 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. Both theoretical and experimental efforts are elucidating the factors controlling electron-transfer rates and excited-state lifetimes; the roles of electronic factors, nuclear configuration and free-energy changes, and solvent dynamics are being investigated through studies of transition-metal complexes. Theoretical approaches used include *ab initio* and semi-empirical electronic structure calculations and quantum and semiclassical rate calculations. Photoinduced electron-transfer reactions are probed by time-resolved absorption and emission measurements in the picosecond to millisecond time range. Efficient long-term chemical storage of the light energy requires coupling of light absorption and chemical transformation processes. Mechanistic studies of photoinduced and thermal olefin *cis-trans* isomerization address the nature of this coupling in the purple membrane proton pump. Chemical and mechanistic studies of transition-metal centers in high and low oxidation states are conducted because such centers can couple photoinduced electron transfer to the bond-forming reactions required in the photodecomposition of water or the photoreduction of carbon dioxide to useful chemicals. [13.9 FTE]

13. *Radiation Chemistry*
Schwarz, H.A.; Bielski, B.H.J.; Holroyd, R.A.; Cabelli, D.E.; Wishart, J.F.
Comm. 516-282-4330; FTS 666-4330

This project uses pulse radiolysis and photolysis to study the behavior of transient chemical species. Principal areas of investigation are (1) the properties and reactions of electrons in dielectric fluids, (2) photoionization in dielectric fluids, (3) the formation and reactions of transition metal complexes in unusual oxidation states, (4) intramolecular electron-transfer rates, (5) the nature of transition metal hydroperoxyl radical complexes, and (6) other reactions of the hydroperoxyl radical. 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 and hydroperoxyl radical reactions are important in developing and understanding certain homogeneous catalysis systems and methods of chemical storage of solar energy. [8.0 FTE]

14. *Hot Atom Chemistry*
Wolf, A.P.; Ferrieri, R.A.
Comm. 516-282-4397; FTS 666-4397

The project objective is to investigate the unusual chemical reactions that can be promoted through the interaction of translationally and, in some instances, electronically excited atoms with substrate molecules. The primary concern is how excess kinetic energy affects the fundamental chemistry of these species. A secondary concern is whether hot atoms can be used as a source for generating unusual and sometimes unique reaction intermediates for chemical studies. Studies of this nature can aid in the understanding of the complex chemistry involved, not only in numerous photochemical processes, but in discharge-induced plasmas, and in high-temperature combustion as well. Recently a new sputtering atom source was developed for generating hot oxygen atoms. The present system enables both transient species and stable end products to be monitored in the gas phase using mass spectrometry. This provides a broad range of information that can be related not only to the primary chemical interactions between the atoms and substrate molecules, but to the chemical fate of the reaction intermediates as well. Nucleogenic methods are also implemented within the program to investigate atom–molecule reactions of a different nature. Active areas of research include studies into the effect of kinetic energy on the quenching mechanisms for electronically excited nitrogen atoms, the stereochemical consequences of hot homolytic halogen atom substitution reactions, and the mechanisms of carbon atom reactions. [1.5 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Biodynamics Division $675,000

15. *Artificial Photosynthesis*
Calvin, M.; Otvos, J.W.
Comm. 415-486-4321; FTS 451-4321

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 our 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, advancement must be made in two areas. (1) The quantum yield of the initial photochemical reaction must be improved. One method of improvement is to compartmentalize the oxidized and reduced products of the initial photoreaction in order to prevent back-reaction. Studies use flash photolysis to determine which reactions are limiting the achievable quantum yield. (2) Soluble catalysts must be found for the final conversion of the intermediate products on both sides of the electron-transfer assembly. For the oxidation side, the most attractive catalysts being studied are complexes or oligomers of transition metal elements, which can exist in several oxidation states and might, therefore, be useful in the multielectron oxidation of water to oxygen. [2.6 FTE]

16. *Chemistry with Near-Infrared Photons*
Frei, H.
Comm. 415-486-4325; FTS 451-4325

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 lend a basis for 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 stereocontrolled photooxidation of alkenes and alkynes by red light excited nitrogen dioxide. These studies form the basis of controlled chemical synthesis 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. Most recent examples are elucidation of the mechanism of photooxidation of iodide at dye-sensitized TiO_2 colloids and achievement of direct reduction of singlet delta O_2 at a p-type Si electrode. The latter constitutes an important step towards conversion of the one eV electronic energy of singlet excited O_2 into electrical energy. [2.1 FTE]

17. *Chemistry of Electronically Excited Molecules*
Kim, S.-H.
Comm. 415-486-4333; FTS 451-4333

Both natural and artificial photosynthetic processes depend on the special chemistry of electronically excited molecules. Consequently, a full understanding of chemistry and energy movement on electronic hypersurfaces is key to the development of better processes for the storage of photon energy in the form of chemical bonds. Cryogenic solids permit light initiated study and differentiation between primary photolysis products, normally transient intermediates and secondary photolysis products. Progress has been made in controlling reaction branching with the matrix environment via controlled singlet–triplet surface crossing through external atom spin–orbit coupling. Fluorescence and phosphorescence spectra and lifetimes again reveal singlet–triplet crossing. Nanosecond infrared spectroscopy permits direct detection and kinetic study of electronically excited molecules. Chemical systems under matrix study include mercury, cadmium, and zinc atom photoreactions with haloalkenes and haloalkanes, photochromic molecules, tuned laser mapping of electronic hypersurfaces, fluorescence and phosphorescence of dimethylaminobenzonitrile, and spectra and kinetics of gaseous free radicals and excited-state molecules. [3.6 FTE]

Materials and Chemical Sciences Division $240,000

18. *Photochemistry of Materials in the Stratosphere*

Johnston, H.S.
Comm. 415-642-3674

This research is concerned with global change in the atmosphere, including photochemical modeling and experimental gas-phase photochemistry. In collaboration with Lawrence Livermore National Laboratory, theoretical studies are made of atmospheric transport, radiation balance, and photochemistry. One goal of the experimental work is to obtain optical and kinetic data in the laboratory that are needed by modelers of the atmosphere. Another goal is to study molecular dynamics. The experimental methods include laser flash photolysis, laser resonance absorption, resonance fluorescence, and dispersed chemiluminescence from photolysis products. [1.3 FTE]

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

Radiation Laboratory $3,125,000

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

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

Advanced techiques of modern electronic structure theory are employed to characterize the microscopic properties of matter, emphasizing applications to transient species such as free radicals and molecular excited states which dominate the early processes following radiolysis or photolysis of various media and also occur as important intermediates in many chemical reactions. The molecular structures and properties of individual radicals are theoretically determined by *ab initio* methods to facilitate the interpretation of experimental studies on such systems. Economical methods have been developed for accurate determination of the important spin polarization contributions and electron correlation corrections to hyperfine coupling constants observed in open shell molecular systems. These theoretical tools are applied to aid analysis of experimental electron paramagnetic resonance studies of a variety of small organic and inorganic free radicals. Force fields and excited state geometry changes are calculated to provide an explanation for the dramatic alterations in intensity patterns found in resonance Raman studies on various benzosemiquinone and phenoxyl radicals at different excitation wavelengths. New computational procedures are developed to investigate energies and autoionization lifetimes of highly excited resonance states to aid in understanding energy relaxation mechanisms in irradiated media. [2.9 FTE]

20. *Inorganic Photochemical Processes*

Ferraudi, G.J.
Comm. 219-239-7676

The dynamic effects of magnetic fields on the luminescence and photochemical reactions of coordination complexes are investigated at intensities up to 90,000 Gauss. With fields of this magnitude, coupling of the field to the electronic angular momentum results in significant perturbations of electronic states. Perturbations of excited and ground state electron transfer rates can be attributed to both a dynamic perturbation along the reaction coordinate and a Zeeman perturbation of the orbitally degenerated electronic levels in reactants and products. The flash-induced magnetic circular dichroism spectra of excited states are determined to provide insight concerning the nature of magnetodynamic effects in reactions of coordination compounds. Since these studies yield information concerning the splitting and energy shifts in those electronic levels above the lowest lying excited states, they will also be useful in characterizing upper electronic states usually associated with the observed photoreactivity in sequential biphotonic excitations. The photochemical reactivity of these "phantom" states in coordination complexes, namely states which cannot be populated directly from the ground state, is investigated by using time-resolved sequential biphotonic excitations. The ground and excited state properties of some compounds considered (e.g., metal clusters, macrocyclic complexes and metal carbonyls) are further characterized by pulse radiolysis and flash photolysis. [6.4 FTE]

21. *Microwave Studies of Radiation-Produced Radicals*

Fessenden, R.W.; Madden, K.P.
Comm. 219-239-5354

The structures, reaction mechanisms, kinetics, and interactions in nonreactive encounters of free radical reaction intermediates are being investigated by electron resonance (EPR). Both steady state as well as time resolved radiolysis and photolysis techniques are being used. Analysis of EPR spectra gives definitive electronic and geometric structures as well as acid-base properties. Rates of radical reactions and the importance of nonreactive encounters are determined from the time dependence of EPR absorption in pulse radiolysis and flash photolysis. Of particular interest are measurements of trapping rates for various reactions between radicals and spin traps. The stability of resultant radicals is also determined. These data provide a kinetic basis for interpreting the spin-trapping of hard-to-detect free radicals in biological and other complex systems. The time dependence of microwave dielectric absorption by photochemical intermediates is used to map their charge distribution and help explain variations in reaction mechanism as a function of solvent polarity. Rates of rapid internal charge rearrangements in excited states are determined from the dispersive component of the microwave signal. The yields, decay kinetics, and trapping depth of photoinduced charge carriers in semiconductor particles, films and crystals are also measured by microwave absorption. [10.7 FTE]

22. *Organic Photochemical Processes*

Hug, G.L.
Comm. 219-239-6527

Time-resolved and steady-state investigations are being conducted to determine mechanistic parameters for photochemically induced organic reactions in solution, such as: photoinduced electron transfer, ionization, homolytic and heterolytic bond cleavage and photoextrusions. Reactive intermediates and electronically excited states are typically generated by picosecond and nanosecond laser flash photolysis. Time-resolved absorption and fluorescence techniques are used for detection. Fluorescent free radical probes, for example, are being used to determine the mechanistic details of deactivation of electronically excited states by paramagnetic species. These probes are also used to characterize spin-statistic restrictions in a variety of bimolecular processes. High intensity uv laser photolysis of organic solutions which mimics the effects observed following ionizing radiolysis, is under investigation. For instance, the reactions of chlorine atoms in carbon tetrachloride, and in fluorochlorocarbons are being directly measured by their charge-transfer absorption spectra. Additionally, picosecond flash photolysis is being used as an alternate route for the study of geminate processes involving hydrated electrons. [6.4 FTE]

23. *Photochemical and Photoelectrochemical Processes for Energy Conversion*

Kamat, P.V.
Comm. 219-239-5411

Direct bandgap excitation as well as charge injection from excited dyes and from short bandgap semiconductors into the conduction band of a large bandgap semiconductor are being probed to elucidate the primary photophysical and photochemical processes that occur for these systems in the ps–ns time regime. Ultrasmall semiconductor particles that exhibit size quantization effects are synthesized and characterized in various heterogeneous media (e.g. polymer films). Optical effects due to trapped charge carriers in semiconductor colloids (e.g., metal sulfides and selenides) and coupled semiconductors (e.g., TiO_2–CdS) are characterized with picosecond and nanosecond laser flash photolysis, single photon counting, and pulse radiolysis. Investigation of these trapped charged carriers is important because they can greatly influence the photocatalytic activity and surface corrosion of the semiconductor. Support materials such as silica, alumina and zeolites are also being used for the effective control of excited state charge transfer processes. The behavior of excited states and photochemical transients in opaque particulate systems is characterized with front face emission and diffuse reflectance spectroscopy. Mechanistic and kinetic details obtained from these studies will be used to design organized molecular assemblies for improving the efficiency of photoinitiated redox events. [3.4 FTE]

24. *Track Effects in Radiation Chemistry*

LaVerne, J.A.; Mozumder, A.; Green, N.J.B.; Schuler, R.H.
Comm. 219-239-5563

Chemical effects of the track structure of ionizing radiation are being studied using experimental and theoretical methods. Experimental studies include heavy ion radiolysis measurements in water and liquid hydrocarbons from which the dependence of product yields on particle charge, energy, and linear energy transfer (LET) are determined. These studies have been expanded to obtain the time dependence of luminescence in hydrocarbons and liquified rare gases. An improved understanding of particle track structure in these systems should result. A wide variety of particles with energies up to 150 MeV/nucleon and LETs of 3 to 5000 eV/nm has been obtained using the facilities of the Notre Dame Nuclear Structure Laboratory, the ATLAS facility at Argonne National Laboratory and the BEVALAC at Lawrence Berkeley Laboratory. Theoretical studies have concentrated on determining the distributions of energy, ionization, and excitation in isolated spurs produced by fast electrons and heavy ions in water. These studies also examine ionization and scintillation processes in liquefied rare gases. Stochastic diffusion-kinetic models are being used to elucidate the initial distribution and temporal variation of radical species in water. Similar models are being applied to electron-ion pairs in alkanes. A comparable formalism is being used to obtain escape yields in anisotropic media such as crystalline anthracene. [7.8 FTE]

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

Patterson, L.K.
Comm. 219-239-5403

The effects of molecular organization on the chemistry of excited states and free radicals are investigated to determine the mechanisms by which such organization may be used to exercise kinetic control over reactions of interest. Particular attention is given those processes related to solar energy storage. Spread lipid monolayers at the gas–water interface are extensively utilized in this work to characterize, in ordered media, the behavior of chromophores such as: pyrene, porphyrins, benzophenone and cyanine dyes. With these systems, it is possible to alter molecular organization by physical means and simultaneously monitor changes in the thermodynamic state of the system. Time resolved and steady state fluorescence are used to measure energy transfer, self quenching, diffusion, monolayer permeability, and interfacial polarity as functions of layer organization. Photochemical reaction products from lipid reactions at the gas–water interface are analyzed by HPLC using scintillation counting or optical absorbance. Multiple monolayers are also deposited on solid surface for the study of processes, such as energy transfer, which cross layer boundaries. While not currently practical in monolayers, flash photolysis and pulse radiolysis measurements are carried out in micellar systems to characterize effects of the microenvironment on behavior of triplet excited states and lipid radicals. [4.3 FTE]

26. *Radiation Chemistry Data Center*

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

The Radiation Chemistry Data Center (RCDC) collects data on photochemical, photophysical, and radiation chemical processes. Kinetic, spectroscopic, and thermodynamic data for primary processes involving excited states and radicals in solution are compiled and evaluated in collaboration with scientists from other laboratories. Databases are assembled and used to prepare publications and to provide reference services. A chemical registry file (RCDCreg) is maintained for chemical species represented in the numeric data files. The RCDC Bibliographic Database (RCDCbib), containing over 100,000 references, is used to produce the current-awareness publication, *The Biweekly List of Papers on Radiation Chemistry and Photochemistry*. On-line access is available to RCDCbib and to numeric databases covering (1) rate constants for about 6500 reactions involving inorganic radicals in aqueous solution and (2) triplet–triplet absorption spectral data for over 1100 organic molecules in condensed phases. A current data compilation project covers the kinetics and energetics of condensed phase photochemical processes. A wide range of photophysical properties of the excited singlet and triplet states of organic molecules is being compiled, including kinetic data for first-order decay and bimolecular quenching reactions. [4.1 FTE]

27. *Radiation-Induced Chemical Reactions*

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

Time resolved absorption and resonance Raman methods are being used to study the radicals produced by oxidation, reduction, and electron transfer reactions in aqueous systems. Recent studies have largely focused on nitrogen and sulfur containing prototype radicals such as those produced radiolytically from phenylene diamines and thioaromatics. Raman studies, which are unique to this laboratory, provide structural information on a variety of important reaction intermediates. Studies in very acid media (below pH 0) are being conducted to characterize protonation of these radicals. Coupled pulse radiolysis and flash photolysis methods are used to examine photochemical properties of short-lived intermediates. Information on the reaction kinetics of intermediates acquired by these pulse methods and that on product formation obtained by modern chromatographic methods is integrated to provide a well-defined picture of both the primary and secondary radiolytic reactions of simple organic systems. These studies in turn provide a sound basis for examining the distribution of lifetimes of hydrated electrons and hydroxyl radicals which occur in the radiolysis of water. Product studies with high-intensity pulses also provide important information on the competition between second-order reactions of radicals and electron-transfer processes. [10.5 FTE]

Solar Energy Research Institute
Golden, CO 80401

Solar Fuels Research Division $1,185,000

28. *Photosynthetic Reaction Centers: Chromophore-Modified Polymer Systems and Photosystem II Preparations*

Connolly, J.S.; Seibert, M.
Comm. 303-231-1873; FTS 327-1873

This project focuses on fundamental aspects of light-induced electron transfer in molecular systems leading to the design and assembly of a synthetic photoreaction center. To date, the work has concentrated on electron-transfer interactions in porphyrin-containing molecular assemblies. Current investigations are concerned with tightly linked porphyrin–quinone molecules in which strong electronic coupling between the donor and acceptor moieties is highly sensitive to small changes in the dielectric properties of the host matrix. Local environments are probed in various media, including liquid mixtures, vesicles, and polymers. Studies are being carried out on the temperature dependence of charge-transfer (CT) interactions by picosecond measurements of the kinetics and, where possible, time-resolved optoacoustic measurements of the energetics. The goal is to understand the specific properties of protein membranes that facilitate electron transfer *in vivo* and to stabilize the resulting redox products. [2.8 FTE]

29. *Modified Semiconductor Electrodes for Solar Energy Utilization*

Frank, A.J.
Comm. 303-231-1962; FTS 327-1962

Charge-carrier dynamics and interfacial processes in semiconductor and metallic conjugated polymer films are being investigated from the perspective of photoelectrochemistry. Electroanalytical and spectrophotometric techniques are used to investigate the effect of the dopant anion, the solvent, and the applied bias on charge transport, lattice relaxation, electroactivity, hysteresis, and ion trapping in electronically conductive PMeT [PMeT = poly(3-methylthiophene)] films on electrodes. Optical absorption and theoretical studies are elucidating the roles of novel excitations, such as polarons and bipolarons, in solid-state films of PMeT as a function of the dopant and the solvent used in film preparation. These studies are raising fundamental questions about the validity of current theories of intrachain charge carrier generation and are yielding important insight into the charge-transport phenomenon. Light-induced electron spin resonance along with photoinduced absorption measurements indicate that bipolarons, and not polarons, are the predominant photoinduced charge carriers in undoped PMeT. [2.5 FTE]

30. *Basic Photoelectrochemistry Research*

Nozik, A.J.; Turner, J.A.
Comm. 303-231-1953; FTS 327-1953

Quantization effects in one-dimensional structures (semiconductor superlattices, multiple quantum wells, and single quantum wells) and three-dimensional structures (semiconductor particles) are being investigated with respect to basic problems in photoelectrochemistry, including hot carrier processes. Time-resolved and time-averaged hot luminescence has been found to depend upon barrier thickness in superlattices with miniband formation. Single quantum wells with exceptionally well-behaved properties have been prepared with p-doped buffer layers. The solid-state and photoelectrochemical properties of these single-well electrodes can be completely characterized; they are very promising structures for investigating hot electron injection. Novel quantized semiconductor colloids were prepared starting from crystalline powders. Future work will involve detailed studies of hot carrier relaxation and transport processes in one-dimensional and three-dimensional systems using a variety of time-resolved and steady-state spectroscopies. [5.7 FTE]

Chemical Physics

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program $705,000

31. *Chemical Theory*
DePristo, A.E.
Comm. 515-294-9924

The general focus of this research is the theoretical description of the structure and dynamics of chemically reactive systems in terms of their fundamental atomic and electronic constituents. Research is designed to describe, calculate, predict, and understand properties of such unusual chemical systems. One particular focus is the area of metal cluster chemistry. The goal is to determine the structure and energy of various metal clusters, and to investigate the relationship between these properties and the reactivity of clusters with different gas-phase molecules. 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. [1.75 FTE]

32. *Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals*
Ng, C.Y.
Comm. 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. 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. [3.75 FTE]

33. *Molecular Bonding Theory*
Ruedenberg, K.
Comm. 515-294-5253

Fundamental nonempirical quantum mechanical theory is used to determine properties of molecules and chemical reactions. Since the unifying concept for the understanding of molecular structure and dynamics is the molecular energy surface, a major objective is the global mapping of such surfaces by accurate *ab initio* calculations as functions of the atomic positions, and the determination of those critical surface features that determine directions and rates of chemical reactions. The resulting predictions of reaction paths, transition states, reaction energies, activation energies, and unstable intermediates provide information that, in most cases, is inaccessible by nontheoretical means. In this context, methods for calculating many-electron molecular wave functions are developed that include the correlations between electronic motions required for yielding the pertinent relative energy changes with sufficient accuracy. Because most distinctive energy surface modulations (e.g., minima, saddles, valleys, bifurcations) cannot be simply rationalized, rigorous explanations in terms of electronic rearrangements are needed. Consistent general methods are therefore developed for an in-depth analysis of *ab initio* electronic wave functions, leading to the relations between energetic interactions and electronic rearrangements. Oxidation-reduction reactions, exchange reactions, and isomerizations relevant to combustion, hydrogenation, or atmospheric problems are investigated. Currently, global potential energy surfaces are being established for the CO_2 molecule. [2.25 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $3,863,000

34. *Photoionization–Photoelectron Research*
Berkowitz, J.
Comm. 708-972-4086; FTS 972-4086

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, chemical reaction, or laser photolysis. 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, such as previously undetected COOH. The extraordinary chemistry of boron compounds is being explored by studying B_2H_5 and B_2H_4, for which no previous experimental measurements exist. *Ab initio* calculations are ambiguous as to the structure and stability of these species. The C_2H_5 radical has been studied, and an accurate H_5C_2–H bond energy determined. Studies are in progress on the important GeH_n system, for which very limited prior information exists. Unusual geometrical structures such as hydrogen-bridged $C_2H_5^+$ and GeH_4^+ highly distorted from tetrahedral structure are inferred from these studies. Conventional He I and threshold photoelectron spectroscopy are used to measure the spectroscopic properties of molecular ions. Another apparatus is used to study directly the spectroscopy and dynamics of molecular–ion decomposition by analyzing the fragments ensuing from ultraviolet laser irradiation of selected molecular ions. One recent application of this device is to distinguish clearly between isomeric molecular ions. [4.0 FTE]

35. Metal Cluster Chemistry Research
Riley, S.J.; Parks, E.K.; Jellinek, J.; Knickelbein, M.B.
Comm. 708-972-6793; FTS 972-6793

The chemical and physical properties of isolated transition-metal clusters are studied. Clusters of from two to several hundred atoms are generated by pulsed lasers and detected by laser-ionization mass spectrometry. Metals studied include iron, cobalt, nickel, niobium, aluminum, chromium, vanadium, rhodium, titanium, copper, and platinum. Chemical properties are studied in a unique continuous gas-flow tube reactor. The dependence of cluster reactivity on size is determined and shows correlation to other chemical and physical properties. Adsorbate uptake patterns are measured and give information about cluster structure, changes in structure with cluster size, and the nature of adsorbate-binding sites. Adsorbate-binding energies are measured and are compared to those of the bulk metal. Mechanisms for adsorbate decomposition on cluster surfaces are characterized. In another apparatus, cluster physical properties such as ionization potentials, electron affinities, and photophysical processes are probed. These experimentally determined cluster properties are correlated with theoretical calculations. Additional theoretical effort is aimed at developing tools for studying cluster dynamics. Ultimately, these studies will provide a better understanding of surface chemistry and heterogeneous catalysis. [9.2 FTE]

36. Chemical Dynamics in the Gas Phase
Wagner, A.; Davis, M.; Harding, L.; Harrison, R; Shepard, R.; Liu, K.; MacDonald, R.; Michael, J.; Hessler, J.
Comm. 708-972-3597

The project objective is to characterize the energetics, dynamics, and mechanisms of elementary reactions in a comprehensive manner, emphasizing reactions of importance in the oxidation of simple hydrocarbon fuels. The project combines theoretical and experimental efforts in chemical dynamics and kinetics. The theoretical effort focuses on the calculation of accurate reaction energetics and potential energy surfaces, reaction dynamics on the computed (or other realistic) surfaces, and development of theoretical/computational techniques needed to model chemical reactions accurately. In the latter area, this includes a project to develop chemistry codes for use on high-performance, shared-memory parallel computer systems. The experimental effort emphasizes (1) studies of reaction kinetics using both flash photolysis-resonance absorption and tunable laser-flash absorption techniques in shock tubes and (2) studies of state-resolved reaction dynamics using crossed, pulsed molecular beams, and laser spectroscopic detection techniques. A new project has been initiated to obtain state-resolved product distributions for radical–radical reactions in a flow tube. [17.1 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $580,000

37. Combustion Kinetics and Reaction Pathways
Klemm, R.B.; Sutherland, J.W.
Comm. 516-282-4022; FTS 666-4022

The project objectives are (1) to measure absolute rate constants for combustion-related reactions of fuels and intermediates and (2) to determine pathways of multichannel reactions. With a multitechnique approach that features three independent experiments, the project has unique capabilities in performing reliable kinetics measurements over an exceptionally wide temperature range, 200 to 2500 K. Recent kinetic investigations include: O + NH_3, 2100 to 2500 K, H + CH_4, 900 to 1700 K, O + H_2O, 1050 to 2000 K, and O + C_2H_6, 400 to 1400 K. A new discharge flow-photoionization mass spectrometer (DF-PIMS) experiment is used to determine branching ratios for multichannel reactions and to measure ionization potentials of free radicals. The DF-PIMS apparatus was designed to be operated on the U-11 beam line at the National Synchrotron Light Source. Two distinct advantages of performing PIMS with tunable vacuum ultraviolet light are improved detection sensitivity and improved selectivity in monitoring radical species. Recent DF-PIMS studies include (1) branching-ratio measurements for the O + C_3H_6 reaction and (2) direct ionization-potential measurements for HCO, CH_3CO, and H_2CN. [5.1 FTE]

Chemistry Department $2,835,000

38. Energy Transfer Studies in Cluster Impacts
Friedman, L.; Beuhler, R.J.
Comm. 516-282-4325; FTS 666-4325

Accelerated water cluster ions with kinetic energy on the order of a few keV/atom are used to investigate energy transfer in impacts on solid surfaces. Upon impact, these clusters produce assemblies of energetic atoms at very high transient temperatures and pressures. Experiments have been devised to detect energetic charged products of D–D fusion reactions when accelerated heavy-water cluster ions are used to bombard solid targets containing deuterium. Energetic protons, tritons, and He^3 particles can be detected with a geometric efficiency of approximately 10%. The studies of D–D fusion reactions are designed as a dynamic diagnostic approach to the investigation of the properties of transient particle densities and energy densities in assemblies of hot atoms produced by cluster impact. Results obtained so far indicate much higher probabilities of fusion reaction than predicted by relatively simple physical models. The investigation of reactions as a function of cluster size and cluster energy should provide answers to questions dealing with rates of energy transfer, equilibration of transitional energy on fuel atom assemblies, and basic mechanisms of fusion reactions in these dense energetic atomic assemblies. [3.1 FTE]

39. Gas-Phase Molecular Dynamics
Weston, R.E.; Muckerman, J.T.; Sears, T.J.; Preses, J.; Hall, G.E.
Comm. 516-282-4373; FTS 666-4373

Research in this project 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. The objective is a fundamental understanding of transient species and chemical processes, especially those related to combustion. 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. 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 wave packet descriptions for different degrees of freedom, are developed and applied to prototypical chemical systems. Since the merging of the scientific programs previously on beam lines U9A and U11 at the National Synchrotron Light Source, this program provides assistance to some of the outside users of beam line U11. [10.0 FTE]

40. Gas-Phase Photoionization of Molecules and Molecular Complexes
White, M.; Grover, J.R.; DiMauro, L.
Comm. 516-282-4345; FTS 666-4345

The general aim of this project is the experimental characterization of the dynamics of optically prepared excited and ionic states of molecules and molecular complexes and their nonradiative decay dynamics. Intense synchrotron and laser radiation sources are used to induce such processes as dissociation, dissociative rearrangement, and autoionization, the products of which are probed by a variety of photoionization-based techniques. Particular emphasis is placed on elucidating the decay dynamics of neutral or ionic molecular species with high internal energy content. For isolated molecules, these studies focus on "super-excited" neutral levels lying above the ionization potential and their coupling to the ionization and dissociation continue. Parallel investigations of weak molecular complexes are aimed at obtaining mechanistic 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. [4.0 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Applied Science Division $175,000

41. Combustion Chemistry
Brown, N.J.
Comm. 415-486-4241; FTS 451-4241

Combustion processes are governed by chemical kinetics, energy transfer, transport, and fluid mechanics, and the complex interactions among these. Understanding chemical kinetics and energy transfer offers the possibility of better understanding combustion so that it can be controlled. In all chemical changes, the pathways for energy movement are determining factors. Competition among these pathways, including energy dissipation, determines product yields, product state distributions, and the rate at which reaction proceeds. In this project the dependence of reactivity and energy-transfer processes on various types of energy, angular momentum, and potential energy characteristics is investigated. Dynamical and statistical theoretical approaches are being pursued using realistic potential energy surfaces for prototypical molecular systems important in combustion systems. Recent research has been concerned with the application of functional sensitivity analysis to determine the relationship between dynamic observables and the potential energy surface. This has revealed important information about energy-transfer processes. [1.0 FTE]

Materials and Chemical Sciences Division $2,410,000

42. Energy Transfer and Structural Studies of Molecules on Surfaces
Harris, C.B.
Comm. 415-642-2814

The goals of this research are the study of mechanisms responsible for the transfer of energy from the excited states of molecules to metal surfaces and the development of new laser techniques for probing molecule–surface interactions. The research is both theoretical and experimental in character, and includes nonlinear optical and picosecond laser techniques in addition to a variety of standard surface science tools for characterizing molecule–surface interactions. Recent work has centered on the development of picosecond infrared lasers, the elucidation of the mechanisms of surface-enhanced photochemistry, surface-enhanced photoelectron emission and the breakdown of classical dielectric response theory for explaining energy transfer from molecules to noble metal surfaces, and the development of new techniques for studying the dynamics of electrons at interfaces on femtosecond time scales. The results of this project 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. [1.8 FTE]

43. *Chemical Dynamics*

Lee, Y.T.; Lester, W.A.; Miller, W.H.;
Moore, C.B.; Saykally, R.J.; Neumark, D.
Comm. 415-486-6154; FTS 451-6154

The Chemical Dynamics program at MCSD is a multi-investigator effort involving strongly coupled experiments and theory. The research emphasizes the development of basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions. Specific projects include studies of primary photodissociation processes and of the structure and chemical behavior of reactive molecules, including highly reactive polyatomic radicals and unusual transient species. The nature of intra- and intermolecular relaxation will be probed. Searches will be made for bond- and mode-specific chemistry. Experimental approaches use modern laser, molecular beam, and various microscopic and state-specific detection techniques for excitation and probing of molecular processes. Advanced instrumentation, such as new photon sources and next-generation molecular-beam machines, are used as they become available. *Ab initio* calculations are carried out to provide complementary information and data to advance experimental efforts. Dynamical theories are developed and tested for these processes. The fundamental data obtained provide the basis for reliable modeling of complex chemical processes. This research project serves to foster the scientific understanding of the basic chemical processes underlying combustion, waste disposal, surface chemistry, and energy storage. [14.5 FTE]

44. *Physical Chemistry with Emphasis on Thermodynamic Properties*

Pitzer, K.S.
Comm. 415-642-3472

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 ionized systems, electrolyte solutions, and plasmas, with particular attention to fluid–fluid phase equilibria and critical behavior. While the critical region has been carefully studied for pure fluids and mixtures of neutral molecules, there has been little attention to critical behavior for ionic systems. The alternating charge and long-range nature of ionic forces requires a separate theoretical treatment. Recent contributions of this project have included treatments of the critical properties of pure ionic fluids and of NaCl at very high temperature in both steam and brine (liquid) phases. Also, liquid-salt, polar solvent systems have been discovered that have sufficiently moderate critical temperatures that measurements were made of various properties including conductance and critical exponents. Investigations of aqueous NaCl and other salts at high temperature and pressure are being carried out in collaboration with U.S. Geological Survey, Menlo Park, California. These systems, and especially NaCl–H_2O, are of both geological and industrial importance. [1.8 FTE]

45. *Chemical Physics at High Photon Energies*

Shirley, D.A.
Comm. 415-486-5666; FTS 451-5666

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, identified in "Opportunities in Chemistry" (the Pimental Report), 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). In fact, development and extension of the ARPEFS method, which is complementary to surface extended X-ray absorption fine structure (EXAFS) and other surface structural tools, is a major activity of this project. [9.0 FTE]

Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

Division of Computational Physics **$40,000**

46. *Chemical Kinetics Modeling*

Westbrook, C.K.
Comm. 415-422-4108; FTS 532-4108

This project involves computer modeling of the chemical kinetics of combustion of hydrocarbon and other fuels. Both the development of kinetic reaction mechanisms and the use of those mechanisms to analyze practical combustion systems are combined in this effort. The emphasis is primarily on fuels that are used in practical combustion systems such as furnaces, internal combustion engines, and other common environments. During the past year, modeling efforts have emphasized the roles that fuel size and structure play in determining the tendency of different fuels to knock in internal combustion engines. Fuels examined include isomers of butane, pentane, hexane, heptane, and octane. Other fuels examined have included silane and carbon tetrachloride which are analogs of methane. Model calculations are used to determine those reactions whose rates and products have particularly strong influences on the overall rates of combustion. These results then suggest reactions whose properties are of particular interest for others to pursue in theoretical and experimental kinetic studies. [0.3 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Molecular Science Research Center $2,700,000

47. *Chemical Kinetics and Dynamics at Interfaces*

Colson, S.D.
Comm. 509-375-6882

As a major component of the Molecular Science Research Center (MSRC) program, this project is designed to provide a molecular-level understanding of the mechanisms, dynamics, and kinetics of condensed-phase reactions controlling groundwater and atmospheric processes as they relate to the environment. To achieve this end, experimental studies are proposed on exemplary chemical reactions at interfaces in condensed media and the explicit incorportion of the results of these studies into models of environmental phenomena. Elements of this program include (1) real-time observations of molecular dynamics at interfaces, (2) optical spectroscopy of chemical reactions at interfaces, (3) development of clusters as models for molecular interface studies, and (4) integration of the proposed experimental approach with theoretical studies by the MSRC Theory group on the quantum chemistry and chemical dynamics of interfacial phenomena in condensed media. The anticipated results of this project are the achievement of a quantitative understanding of chemical reactions at interfaces in condensed media, the development of new techniques for detecting surface species at such interfaces and for following the course of chemical reactions among these species, and the interpretation of the observations in terms of a unified theory of interfacial reactions. [9.4 FTE]

48. *Molecular Theory, Modeling, and Simulation*

Dunning, T.H., Jr.
Comm. 509-375-6863

The molecular theory, modeling, and simulation project is designed to provide a molecular-level understanding of chemical processes in the atmospheric, terrestrial, and subsurface environments. This knowledge is critical to the development of reliable models of contaminant transport and transformation in the air, groundwater, and soil. The project is focused on studies of molecules and their interactions in isolation (gas phase) and in liquids, on surfaces, and at interfaces (condensed phase). Two activities have been initiated: (1) theory of molecular processes in the gas and condensed phases, with an emphasis on fundamental chemical processes that are important in the environment; and (2) development of software to facilitate, optimize, and extend the application of computational chemistry techniques to environmental problems, with an emphasis on graphical user interfaces, molecular visualization, and parallelization of computational chemistry codes. In the future, the theory, modeling, and simulation project will be expanded to include the computer simulation of molecular processes in the complex multispecies, multiphase geo- and biochemical systems prevalent in the environment. [4.7 FTE]

Sandia National Laboratories
Livermore, CA 94550

Combustion Research Facility $2,300,000

49. *Flame Chemistry: Modeling and Experiments*

Miller, J.A.; Kee, R.J.; Durant, J.L.; Fisk, G.A.
Comm. 415-294-2759; FTS 234-2759

The goal of this research is to determine the predominant chemical reactions that transform reactants to products in flames. Much of the work focuses on pollutants. A recent, exhaustive study of nitrogen's combustion chemistry has led to a kinetic model that predicts quantitatively the formation and destruction of nitrogenous pollutants under a wide variety of conditions. Current emphasis is on the chemistry of carbon-containing species in rich oxygen/acetylene flames, particularly the reactions that form soot precursors. Recent experiments and modeling have led to improved understanding of the growth of higher hydrocarbons and the formation of aromatic rings. Low-pressure flame experiments use laser diagnostics to yield temperature and the concentration profiles of radicals such as OH, CH, and H. Mass-spectrometric techniques give concentrations of stable species in the flames. A crucial element of the work is extensive modeling using computer programs that include transport phenomena and chemical kinetics. The recently extended model now predicts the major features of lean to lightly sooting acetylene/oxygen flames. In addition to studying laminar flames, this research is developing computational techniques for treating turbulent combustion. Present research is developing a chemical kinetics model for turbulent jet flames. [4.0 FTE]

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

Palmer, R.E.; Farrow, R.L.; Rahn, L.A.;
Lucht, R.P.
Comm. 415-294-3126; FTS 234-3126

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 Spectroscopy (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, and elastic vibrational dephasing. In particular, a new theory, based on speed-dependent collisional shifts, has been developed to account for asymmetric inhomogeneous line shapes observed in hydrogen. A high-resolution CARS system is used to examine saturation of Doppler-broadened line shapes, to perform pump-probe experiments for measuring inelastic rotational state-to-state transfer rates directly in nitrogen and hydrogen, and to measure high-temperature linewidths in high-pressure lamps. The modification of CARS spectra at high pressure caused by collisional narrowing is quantified in detail using high-resolution CARS and high-resolution inverse Raman spectroscopy, so that measurements in high-pressure environments (e.g., internal combustion engines) can provide more accurate results. Inverse Raman spectroscopy is also used to develop a high-resolution data base of spectral parameters for important combustion species such as nitrogen, carbon monoxide, hydrogen, and water vapor. A computer code for analyzing CARS spectra and for determining temperatures and concentrations is maintained and upgraded to incorporate advancements in spectral models. This project is supported through KC-03-01-04. [5.0 FTE]

51. Combustion Research Facility (CRF) Diagnostics Research: Advanced Methods

Palmer, R.E.; Goldsmith, J.E.; Koszykowski, M.L.; Rakestraw, D.J.; Trebino, F.P.
Comm. 415-294-3126; FTS 234-3126

This project supports the development and theoretical interpretation of new, nonlinear, laser-based techniques for detecting trace species and for studying collision-induced processes in combustion environments in support of Combustion Research Facility (CRF) projects. Absolutely calibrated profiles of hydrogen atoms in hydrogen/oxygen and hydrocarbon flames have been obtained. Photochemical effects as a source of interference in measurements of hydrogen and oxygen atoms in flames have been identified. Stimulated emission following multiphoton excitation of flame radicals is currently under investigation. Temperature measurements and imaging of OH, CH, and nitric oxide have been achieved using a promising new combustion diagnostic, degenerate four-wave mixing. A new technique for velocity measurement based on dephasing of induced gratings has been devised. In the area of theoretical studies, hydrogen linewidths have been modeled using various scaling theories. Three-level models have been developed and calculations performed to understand the many processes affecting transient femtosecond excite-probe experiments, including saturated absorption, free-induction decay, coherent artifacts (transient gratings), perturbed free-induction decay, photon echo, accumulated photon echo, orientational relaxation, and probe-beam saturation. A model has been developed to determine ultrafast laser pulse widths, self-phase modulation, and chirp from measurements based on induced thermal gratings. Such measurement techniques are more robust than second-harmonic generation or autocorrelation techniques. This project is supported through KC-03-01-04. [4.0 FTE]

52. Turbulent Reacting Flow Research

Schefer, R.W.; Lucht, R.P.; Chen, J.-Y.
Comm. 415-294-2681; FTS 234-2681

This research is directed toward an increased understanding of the coupling and competition between the chemical kinetic and mixing processes in turbulent reacting flows. This research project features close coupling between theory and experiment. The turbulent jet flame experiment is the simplest configuration of nonpremixed reactants that retains the fundamental ingredients of chemical reaction and turbulence. By adjusting velocities or by changing reactants, an important range of chemical kinetic and mixing rates can be explored. The mixing rates and chemical kinetic rates are quantified by using simultaneous multispecies laser Raman scattering and OH laser-induced fluorescence from which major species concentrations, temperature, and OH concentration are obtained on each laser pulse. The OH radical concentration is an excellent measure of the degree of chemical nonequilibrium in the flow. Ensembles of these measurements are directly compared with predicted ensembles of data from Monte Carlo numerical modeling of this flow. The Monte Carlo calculations of probability density functions are performed using the Sandia CRAY X-MP supercomputer. A major focus of the numerical efforts is the incorporation of reduced chemical kinetic schemes in turbulent flame codes. Chemical kinetic and mixing interactions in the more complicated flow configuration of the bluff-body flame are also being explored. Quantitative images of fuel concentration and fuel zone structure have been obtained from simultaneous, two-dimensional imaging of CH and CH_4. These images have allowed a critical comparison of the predictions of two different models of combustion: the flamelet and dissipative-eddy models. The experimental data are predicted more accurately by the dissipative-eddy model. OH imaging measurements in these flows have recently been performed as well as simultaneous CH, CH_4, and OH imaging measurements. The imaging data are being used to guide the development of a large-eddy simulation model of the recirculating bluff-body flow. The unique feature of the large-eddy simulation code is that renormalized group theory predictions are used to model the interactions of large and small scales. [4.0 FTE]

53. 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.
Comm. 415-294-2316; FTS 234-2316

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 CN and hydrocarbons. Recent experiments have discovered a catalytic mechanism for the dehydration of alcohols. A versatile flow-tube kinetics apparatus nearing completion will have both laser and mass-spectrometric diagnostics. Recent theoretical studies have treated reactions such as that between H and NH_3 and that of H with HNCO 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 have clarified the dynamics of the process and the partitioning of excess energy. Recently initiated investigations of processes that occur on femtosecond time scales are providing insight about how energy moves throughout molecules. Studies of carbonaceous clusters produced by laser vaporization are a focus of research 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 $1,532,000

54. *High-Resolution Laser-RF Spectroscopy with Atomic and Molecular Beams*
Childs, W.J.
Comm. 312-972-4042; FTS 972-4042

This program is directed toward increasing understanding of atomic and molecular structures through high-resolution laser and radiofrequency studies of many-electron atoms and small molecules. The emphasis throughout is on making the studies both systematic and of high precision. The double resonance experiments are able to provide hyperfine level information that, in turn, tests relativistic corrections in theories of atomic structure. [1.1 FTE]

55. *Atomic Physics at ATLAS*
Dunford, R.W.; Berry, H.G.
Comm. 312-972-4502; FTS 972-4502

The Argonne tandem-linac accelerator system (ATLAS) heavy-ion facility offers excellent opportunities for the study of the atomic physics of highly charged ions. The ATLAS uranium upgrade will provide greatly improved beam intensities and thereby further increase the potential of ATLAS for atomic physics experiments. The electron cyclotron resonance (ECR) ion source, which is part of the uranium upgrade of ATLAS, also affords an excellent opportunity for atomic physics. It produces slow, intense beams of moderately charged ions. A unique property of the source is that it is on a 350-kV high-voltage platform thereby increasing the range of ion velocities that are available. Atomic physics research at ATLAS includes both in-house experiments and experiments in collaboration with several outside groups. The program includes studies of ion–atom collisions and atomic structure. The atomic structure work includes precision tests of quantum electrodynamics and relativistic quantum theory of few-electron ions. The uranium upgrade of ATLAS makes possible studies of collisions where the two nuclei of the collision partners in close proximity can produce fields above those needed for spontaneous production of positrons. A collaboration with a nuclear physics group to prepare an experiment to study such collisions is in progress. [3.2 FTE]

56. *Interactions of Fast Atomic and Molecular Ions with Solid and Gaseous Targets*
Kanter, E.P.
Comm. 312-972-4050; FTS 972-4050

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. New multiparticle imaging detector systems have been developed which allow detection of multiparticle events consisting of up to 12 particles. The main objective is 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. This feature is that each molecular ion forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target. These techniques allow the direct determination of the geometrical structures of the molecular ions entering the target. Molecular systems such as $C_2H_3^+$ and CH_4^+ have been investigated. These measurements provide the first direct measurements of not only the spatial probability densities of the nuclei, but also their correlations in small polyatomic molecules. [4.8 FTE]

57. *Fast Ion-Beam/Laser Studies of Atomic and Molecular Structure*
Young, L.
Comm. 312-972-5029; FTS 972-5029

Atomic and molecular-ion structures by resonant laser excitation of fast ion beams are studied with high spectral resolution. The resolution is achieved by collinear excitation of the fast beams with continuous-wave (CW) narrow-frequency laser beams, using fluorescence and other detection techniques. The atomic structure measurements provide experimental tests of *ab initio* theoretical understanding of hyperfine structure in rare-earth and metallic ions, plus the fundamental calculations of relativistic quantum mechanics and quantum electrodynamics (QED) in few-electron systems. Research aimed at achieving a detailed understanding of both electronic and geometrical structure of simple molecular ion systems is in progress. [4.7 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $240,000

58. *Atomic Physics Research*
Jones, K.W.; Johnson, B.M.
Comm. 516-345-4588; FTS 666-4588

Studies of the physics of multiply charged ions use synchrotron radiation from the Brookhaven National Synchrotron Light Source (NSLS). Ions produced using the X-ray beams are stored in an ion trap and then used for further experiments. Interactions of the ions with gas in the trap make it feasible to measure rate coefficients for ions at energies of around 40 meV or an equivalent temperature of 500 K. Studies are in progress with argon and other noble gases as the primary target and with a variety of other gases as the neutral collision partner. The trapped ions can also be used as the target for further photoionization by the synchrotron beam. Early indications of positive results indicate that extensive experiments of the photoionization of ions can be performed. Development of experiments that extract the ions from the production region for measurement of collision cross sections at variable energies is in progress. An experiment to photoionize beams of singly charged ions from an ion source and to measure cross sections from near-thermal energies to keV energies is now being instrumented. [2.3 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Materials and Chemical Sciences Division **$465,000**

59. *High-Energy Atomic Physics*
Gould, H.A.
Comm. 415-486-4976; FTS 451-4976

The goals of this project are to understand atomic collisions of relativistic ions, to test quantum electrodynamics (QED) and relativistic many-body calculations in the strong Coulomb field of very-high atomic number (Z) atoms, and to search for a CP nonconserving electron electric dipole movement (EDM). Relativistic collisions and high-Z QED experiments can only be conducted with relativistic heavy ions. These experiments are conducted at the Lawrence Berkeley Laboratory's BEVALAC. Recent results include a 500 part per million measurement of the energy of the $2^2P_{1/2}$–$2^2S_{1/2}$ transition in lithiumlike uranium (U^{89+}). This is an exacting test that challenges new relativistic many-body calculations in the most relativistic, most quantum electrodynamic, and least many-body system available. When the calculations are complete, this measurement will yield a 0.25% determination of the electron self-energy in uranium. Present activities include measurement of screening-antiscreening effects in relativistic ionization, an attempt to observe a new capture mechanism (electron capture from the production of electron-positron pairs by the motional Coulomb fields of relativistic nuclei passing within atomic distances of each other), and an experiment to set a stringent upper bound on the electron EDM. [2.2 FTE]

60. *Atomic Physics*
Prior, M.H.
Comm. 415-486-5088; FTS 451-5088

This experimental atomic physics project carries out wide-ranging collision and spectroscopic studies of unique, highly charged atomic systems. Emphasis is placed upon topics that challenge current understanding of atomic structure and interactions and that have relevance to processes present in fusion, astrophysical, or advanced laser plasmas. Examples of such studies include electron capture by highly charged low-energy ions, Auger spectroscopy of excited high-charged-state ions, and the measurement of forbidden-line spectra from metastable ions. The approach to this work takes advantage of unique facilities and expertise available at Lawrence Berkeley Laboratory (LBL). Currently the effort is concentrated on the use of high-intensity, highly charged continuous-ion beams from the LBL Electron Cyclotron Resonance ion sources and beam line facilities. The project benefits substantially from collaborative efforts with colleagues from outside LBL. [1.2 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831-6377

Physics Division **$1,469,000**

61. *Theoretical Atomic Physics at Oak Ridge National Laboratory (ORNL)*
Becker, R.L.; Bottcher, C.
Comm. 615-574-4580; FTS 624-4580

The computational and mathematical techniques of modern theoretical physics are applied to interactions between atoms, ions, electrons, and photons over a wide range of energies, from a few electron volts to ultrarelativistic energies. Emphasis is placed 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 Schroedinger and Hartree–Fock equations by basis-spline collocation methods, coupled channel calculations, Monte Carlo evaluation of Feynman diagrams, and Born expansion and distorted wave techniques. A major new thrust is to convert several large codes to run on a massively parallel computer, with a view to performing realistic simulations of atomic and molecular processes in plasma and surface environments. Applications have been made to processes at nonrelativistic energies such as capture and ionization, in ion–atom collisions, including K- and L-shell ionization, and multiphoton ionization by intense laser beams. Recent studies include secondary electron spectra in proton–hydrogen and bare carbon–neon collisions at intermediate energies, laser multiphoton ionization by circularly polarized light, and sum rules for coincident particle–hole production processes. Successful interpretations have been provided for recent experiments on cusp electrons and post-collisions 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 are made of perturbative and nonperturbative treatments of pair production. [1.0 FTE]

62. *Accelerator Atomic Physics*
Datz, S.; Dittner, P.F.; Vane, C.R.
Comm. 615-574-4984; FTS 624-4984

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 beamline on Holifield Heavy Ion Research Facility (HHIRF). Experiments are being conducted to test whether the electrons contained in a crystal channel can be quantitatively treated as an almost free dense electron gas target. Using the HHIRF 25-MV tandem, beams of H-like, He-like, and Li-like calcium and titanium are produced and channeled at energies starting below, and proceeding through resonances for dielectronic excitation. The resulting X rays, from the decay of the dielectronically excited state, are measured in coincidence with ions that have captured an electron as a function of the ion energy. Since the cross sections are delta functions at the resonance energy, the energy width of the excitation function should reflect the Compton profile of the electrons in the channel. Correlated inelasticity and impact parameter dependence for 10-MeV carbon ions incident on neon and argon have been measured as a function of recoil-ion charge state for various combinations of ingoing and outgoing charge state of the carbon ions. Energy resolution of 1.2 keV and simultaneous angular resolution of 0.005° were achieved using the Elbek magnetic spectrograph. The double excitation of helium by fast, bare ions is being measured as a function of the charge of the projectile. The variation of the cross section of different doubly excited states as a function of the projectile charge elucidates the differing excitation mechanisms. [6.6 FTE]

63. *EN Tandem Operations*

Dittner, P.F.
Comm. 615-574-4789; FTS 624-4789

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, and beams of many heavier ions including nickel, iodine, gold, and uranium. A VAX-750/CAMAC-based data acquisition system, the Elbek magnetic spectrograph, and a high-resolution electron spectrometer are available to users. Recent major beam usage has included inelasticity and impact parameter dependence studies of charge-correlated multiple ionization of neon and argon by carbon ions, double excitation of helium by fast bare ions, convoy electron studies, electron–electron interactions in transfer and excitation, and angular distribution of Auger electrons following the collision of highly charged ions with an helium target gas. [1.3 FTE]

64. *Collisions of Low-Energy Multiply Charged Ions*

Phaneuf, R.A.; Meyer, F.W.; Havener, C.C.
Comm. 615-574-4707; FTS 624-4707

Experimental studies of interactions of multiply charged ions with neutral atoms, molecules, and solid surfaces are performed at kinetic energies ranging from less than 1 eV/amu to several keV/amu. In this energy range, the electronic potential energy of the reactants is an appreciable fraction of the total interaction energy, and inelastic collision cross sections depend strongly on the electronic structure of the colliding systems. Quantitative studies of such processes yield important information about collision mechanisms and quasi-molecular structure, providing benchmarks for developing theoretical models. An ion-atom merged-beams apparatus has been used in conjunction with the ORNL-ECR multicharged ion source to measure absolute total electron-capture cross sections from keV/amu down to 1 eV/amu relative energy. Recently completed measurements for O^{4+} and O^{3+} colliding with H or D atoms diverge from theoretical calculations at energies below 100 eV/amu, suggesting that the theory overestimates the contribution because of capture into the 3p state. Exploratory studies have also been made of the neutralization of multiply charged ions in grazing collisions with a solid surface at keV energies. Measurements of the energies of ejected electrons show definitive evidence for the transfer of electrons directly from inner shells of the solid to inner shells of the projectile ion. The ejected-electron spectra have also been used to quantify the metastable ion fractions in beams produced by the ECR ion source. [1.2 FTE]

Sandia National Laboratories
Albuquerque, NM 87185

Department of Advanced Laser and Optoelectronic Technologies — $155,000

65. *Atomic Processes*

Smith, A.V.
Comm. 505-846-6308; FTS 846-6308

The goals of this project are (1) the development of efficient coherent vacuum ultraviolet sources and (2) the application of advanced laser sources to the spectroscopy of atomic oxygen. Toward the first goal, a 5% efficient 130 nm source using Hg has been demonstrated and a model that accurately predicts its performance has been developed. The model is currently being refined to include additional nonlinear mechanisms. Simultaneously, continuously scannable, single-mode pulsed lasers are being developed that can be used both in narrow bandwidth sum-frequency mixing as well as in high-resolution spectroscopy. These lasers are based on active cavity-length stabilization of short, grazing-incidence grating-tuned resonators. With dyes or Ti:sapphire as the gain medium, continuous single-mode tunability over the red and near ir with linewidths of 0.01 cm^{-1} has been demonstrated. These new laser sources are being used to locate and characterize the even-parity autoionizing levels of atomic oxygen. In addition measurements of several key oscillator strengths between excited states of the oxygen atom will be made. [1.0 FTE]

Chemical Energy

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program — $1,217,000

66. *Organometallic Complexes in Homogeneous Catalysis*

Angelici, R.J.
Comm. 515-294-2603

Several new complexes containing thiophene have been synthesized with the goal of understanding possible modes of thiophene coordination to metal sites on hydrodesulfurization (HDS) catalysts. In an iron–rhenium complex the thiophene binds to the two metals by coordinating to rhenium via the sulfur and to the iron via the diene system. One further metal atom can be added to the sulfur that gives a complex in which thiophene is bonded to three metal atoms. Several modes of thiophene coordination to one metal center have also been observed: (1) via all five atoms in the π-thiophene ring, (2) via the four carbon atoms, and (3) via the sulfur only. In all three types of complexes the thiophene is activated to react in ways which account for the reactivity of thiophene on HDS catalysts. These fundamental types of thiophene reactivity suggest new mechanisms for thiophene HDS. [2.0 FTE]

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

Espenson, J.H.
Comm. 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 $L_nM\text{-}R \rightarrow L_nM + R\cdot$, and its reverse, radical capture. 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 radical capture 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 bond 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. Electron transfer reactions of excited-state complexes are also under investigation for $Cr(polypyridyl)_3^{3+}$ and $Cu(cyclam)(NH_3)_2^{3+}$. [4.2 FTE]

68. *Multiple Pulse NMR Studies: Catalysis and the Chemical Constitution of Coal*

Gerstein, B.C.
Comm. 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; and (3) use of dipolar oscillation NMR to determine internuclear distances in unstable organic molecules trapped in frozen matrices at 80 K; and use of variable-angle spinning to narrow the central transition of quadrupolar nuclei such as ^{17}O in active catalysts. [2.9 FTE]

69. *Fundamental Investigations of Supported Metal Catalysts*

King, T.S.
Comm. 515-294-9479

The major focus of this program is the investigation of the relationship between chemical and structural properties of highly dispersed, supported transition metal particles and their catalytic behavior. Much of this work deals with understanding the synergistic effects of adding a second element or material to a supported metal catalyst. Bimetallic catalysts, composed of two intimately mixed metals, often display behavior not observed with the pure metals. By systematically varying catalyst composition, characterizing in detail the surface of the material, understanding chemisorption behavior of various molecules, and correlating the above information with catalytic activity and selectivity, a number of fundamental research problems are addressed. For example, for a given bimetallic catalyst determine whether the catalytic behavior for a specific reaction is dominated by geometric (ensemble size) or electronic effects. Determine the extent to which the metal crystalline morphology is a factor in the catalytic processes and how this is modified by combining other constitutents. Determine the mode of interaction of molecules adsorbed on these catalysts and how it changes with relative composition of materials. Determine the mechanism of promotion and poisoning effects. In order to elucidate these research problems, the catalyst surface and species adsorbed on the surface are investigated by solid-state NMR in combination with more traditional adsorption and kinetic studies. Solid-state NMR of ^{1}H, ^{13}C, ^{65}Cu, and ^{133}Cs and various other nuclei is used to probe the local structual and chemical environment of surface metal atoms and adsorbed series. [1.9 FTE]

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

Schrader, G.L.
Comm. 515-294-0519

In this research, a fundamental understanding is being developed of the mechanisms of catalytic reactions, the structure and composition of catalysts, and the surface properties associated with metal oxides and sulfides. The catalysts being examined are used industrially for selective oxidation and hydrodesulfurization. Specific applications include paraffin oxidation and the hydroprocessing of organic sulfur compounds found in coal-derived liquids and petroleum. A complement of experimental approaches is used in this research involving kinetic measurements and comprehensive catalyst characterization. *In situ* spectroscopic techniques, such as laser Raman and Fourier transform infrared spectroscopy, are emphasized since they can be used to examine functioning catalysts at elevated temperatures and pressures. New techniques such as solid-state NMR and reflectance–absorbance spectroscopies also have important applications in the current activities. The goal of this research program is to provide fundamental relationships between catalyst structure, composition, and surface properties and the activity and selectivity of metal oxide and sulfide catalysts. [2.2 FTE]

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

Trahanovsky, W.S.
Comm. 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. Work focuses on reactive molecules that are products of primary thermal reactions. The approach includes (1) developing new methods to prepare these molecules, (2) developing new spectroscopic techniques to characterize them, and (3) studying their reactions to characterize their chemistry. Reactions being studied include their self reactions (oligomerization and polymerization), reaction with other species, and reactions in which they are transient intermediates. The work involves extensive use of flash vacuum pyrolysis, a convenient and effective technique for the study of the primary thermal reactions of organic compounds. Studies have concentrated on quinodimethanes, a large class of reactive molecules. A major objective of this work is to obtain a thorough understanding of the factors that affect the reactivity of *ortho*-quinodimethanes. Specific reactive molecules being studied include *ortho*-quinodimethanes derived from benzene, naphthalene, phenanthrene, furan, thiophene, and pyridine. A flow nuclear magnetic resonance (NMR) technique has been developed which allowed the ^{1}H NMR spectra of several very reactive *ortho*-quinodimethanes to be obtained for the first time. Other special techniques required to obtain the NMR spectra of reactive molecules are under development. In addition to studies involving model compounds, some studies involve the pyrolysis of coal itself. The objective of these studies is to identify by low-temperature ^{1}H and ^{13}C NMR spectroscopy the reactive molecules or types of reactive molecules produced by the pyrolysis of coal. [2.0 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemical Technology Division $587,000

72. *Fluid Catalysis*
Rathke, J.W.; Chen, M.J.; Klingler, R.J.
Comm. 708-972-4549; FTS 972-4549

This research is designed to determine reaction mechanisms and to explore new catalytic chemistry associated with molecular energy resources. An array of real-time high-pressure kinetic and spectroscopic techniques is used to determine the chemistry of small molecules derived from coal, natural gas, and petroleum. Maximal concentrations of reactive gases are achieved by making use of their complete miscibilities with supercritical fluids. Thus, the potential energy profiles for the activation of dihydrogen by several metal carbonyl catalysts in supercritical carbon dioxide solution were determined using high-pressure NMR spectroscopy. These studies were facilitated by finding a new type of NMR detector, an elongated toroid, which achieves greatly improved sensitivity in metal pressure probes for nuclei associated with organometallic systems. In other research, solution-phase oxide-catalyzed hydrogenation and water–gas shift processes that seem to parallel metal oxide surface chemistry are explored. Also investigated is the organometallic chemistry of extremely robust metallophthalocyanines designed to achieve stereoselective homogeneous hydrogenation and oxidation catalyses at unusually high temperatures. [3.7 FTE]

Chemistry Division $1,833,000

73. *Chemical Constitution of a Low-Volatile Bituminous Coal*
Stock, L.M.
Comm. 708-972-3570; FTS 972-3570

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. An investigation of the use of Sm(II) iodide for the removal of unpaired electron spin density from this coal has been completed. It was established that 90% of the organic carbon atoms are visible in the solid-state nuclear magnetic resonance (NMR) spectrum and that there are 87% aromatic sp^2 carbon atoms and 13% aliphatic carbon atoms. The 11 of the 13 aliphatic carbon atoms have been identified by selective oxidation with Ru(VIII) and isotope dilution MS analyses of the products. They are distributed among eight methyl groups and several two- and three-carbon-atom units. Excellent evidence for the occurrence of biaryl linkages between aromatic clusters in this coal was obtained. Initial work on the depolymerization of this coal by basic reagents at low temperature has been reasonably successful. Pocahontas No. 3 coal, which is quite insoluble in pyridine, undergoes C-alkylation with methyl, butyl, and octyl groups to yield mildly transformed products that are up to 60% soluble in pyridine. [0.8 FTE]

74. *Premium Coal Sample Program*
Vorres, K.S.
Comm. 708-972-7374; FTS 972-7374

The most pure samples available to the basic coal science community were prepared. Eight U.S. coals have been collected, processed, and packaged to preserve the properties of the original coal as much as possible. Over 390 orders have been filled with shipments of more than 11,000 ampoules. The material in ampoules will meet the demand for another three years, and the reserves in the carboys will continue to meet the current demand level for several decades. The gas atmosphere is monitored for stability. Microbes grew from cultures prepared from the three youngest samples, but not the oldest five. A users handbook has been updated for recipients of the samples, and an international symposium on "Research with Argonne Premium Coal Samples" has been organized in conjunction with the Pacifichem89 meeting. [0.5 FTE]

75. *Separation of Coal Macerals*
Winans, R.E.; Dyrkacz, G.R.; Bloomquist, C.A.A.
Comm. 708-972-7479; FTS 972-7479

Novel methods for the separation and characterization of coal macerals are being developed to obtain a better understanding of the heterogeneity of coal. The project focuses on two objectives: (1) the ultraresolution of maceral or submaceral components of coal using multicycle separations involving chemical modification and density gradient separation and (2) the development and study of potentially large-scale maceral separation systems. [2.8 FTE]

76. *Characterization and Reactivity of Coals and Coal Macerals*
Winans, R.E.; Hayatsu, R.; Botto, R.E.; Carrado, K.A.; McBeth, R.L.; Melnicoff, P.E.
Comm. 708-972-7479; FTS 972-7479

The global objective of this project is to provide fundamental information on chemical structures in coals and coal macerals in order to predict chemical, thermal, and biological reactivity. Selective chemical modification and solubilization techniques are used on the Argonne Premium Coal Samples, their separated macerals, and on synthetic coal maceral models. Characterization by a large array of traditional instrumental techniques is being augmented by nuclear magnetic resonance (NMR) solid imaging, tandem mass spectrometry, and synchrotron X-ray absorption spectroscopy (XAS) methods. These approaches are being extended to the characterization of synthetic layered molecules with catalytic potential. Information provided by these studies should help in the development of advanced processes for utilization of fossil fuels. [8.0 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $688,000

77. ***High-Temperature Chemistry***
Egan, J.J.
Comm. 516-282-4488; FTS 666-4488

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 that 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 used 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 electron 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. [3.2 FTE]

78. ***Metal Hydrides***
Reilly, J.J.; Johnson, J.R.
Comm. 516-282-4502; FTS 666-4502

Knowledge of the behavior and properties of hydrogen/metal systems is an essential element 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 of metallic-hydrogen systems. A particular goal is to relate all pertinent data and hypotheses to develop a predictive capability regarding the behavior of any given system. Current topics of interest are crystal structure of hydride phases, improved powder-diffraction methods and structural refinement calculations, reaction kinetics and catalytic properties of metal hydrides in liquid suspensions, and preparation of novel hydrogen bronze phases. The major experimental tools and/or techniques are X-ray and neutron diffraction, equilibrium pressure/temperature/composition measurements, and high-pressure autoclaves to study the kinetic behavior of metal-hydride suspensions. [3.1 FTE]

Chemistry Department $1,555,000

79. ***Structure and Reactivity in Catalysis and Advanced Materials***
Koetzle, T.F.; Kvick, A.; McMullan, R.K.; Andrews, M.; Bullock, R.M.; Hrbek, J.
Comm. 516-282-4384; FTS 666-4384

Research conducted in this project seeks fundamental understanding of the chemical and physical properties of substances relevant to energy conversion and transmission. The broad emphases include both advanced materials and homogeneous and heterogeneous catalysts. A number of the program's activities take advantage of Brookhaven National Laboratory's unique facilities—the National Synchrotron Light Source and the High Flux Beam Reactor–often in conjunction with outside collaborators. For example, the structures of zeolite microcrystals and dielectrics and the nature of the complex catalytic intermediates on single-crystal metal surfaces are being explored using X rays at the National Synchrotron Light Source, while the structures of metal hydrides, high-T_c superconductors, fast-ion conductors, and gas clathrate hydrates are being elucidated through neutron diffraction studies at the High Flux Beam Reactor. Investigations of transition metal hydride complexes comprise one of the program's specific focal points in the area of homogeneous catalysis. The work includes studies of the diverse reactivity patterns of metal hydrides (H^+ ion, H· atom, or H^- ion sources), correlation of these and other properties with accurate structural data exclusively available from neutron diffraction, and the application of metal hydrides to new areas of homogeneous catalysis, such as biomass-related carbohydrate conversion reactions. A growing component of the project is the study of metal surfaces and zeolites and their relationships to heterogeneous catalysis. Studies focus on the difficult structural problems encountered and on the determination of active sites and how they are affected by promoters and poisons. [9.8 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Applied Science Division $204,000

80. ***Homogeneous Catalytic Hydrogenation of Mono- and Polynuclear Heteroaromatic Nitrogen Compounds: Mechanistic Studies***
Fish, R.H.
Comm. 415-486-4850; FTS 451-4850

Mono- and polynuclear heteroaromatic nitrogen compounds, an important class of model coal compounds, are the focus of fundamental studies with homogeneous rhodium and ruthenium metal complexes. Since this class of model coal compounds is directly involved in the hydrodenitrogenation (HDN) process, it is important that these studies include the mode of bonding of the nitrogen compounds to the metal centers, i.e., N- versus π-bonding, and the utilization of organorhodium and ruthenium complexes as catalysts for the regioselective nitrogen heterocyclic ring hydrogenation reaction, the first step in the HDN process of nitrogen atom removal. Recently reported results with (η^5-pentamethylcyclopentadienyl)rhodium dication (Cp^*Rh^{2+}) and several heteroaromatic nitrogen compounds, such as 2-methyl, 2,4-dimethyl, and 2,4,6-trimethylpyridines, quinoline, isoquinoline, 1,2,3,4-tetrahydroquinoline, 2-methylquinoline, N-methylindole, N-methylpyrrole, acridine, phenathridine, 5,6- and 7,8-benzoquinolines clearly indicated that N- versus π-bonding to the metal center depends on the structure of the nitrogen ligand and the availability of lone pair electrons on the nitrogen atom. Two complexes, $Cp^*Rh(p\text{-xylene})^{2+}$ and $Cp^*Rh(\text{acetonitrile})_3{}^{2+}$, have been shown to be excellent catalyst precursors in the regioselective hydrogenation of quinoline, 2-methylquinoline, and isoquinoline to their corresponding tetrahydro analogues. This latter result clearly defines the role of N-bonding to the rhodium center as critical for selective nitrogen ring hydrogenation, since these nitrogen ligands all provided N-bonded complexes with Cp^*Rh^{2+}. The mechanism of this selective hydrogenation was studied with a relatively new high-pressure nuclear magnetic resonance (NMR) spectroscopy technique using $Cp^*Rh(\eta^1, \text{N-quinoline})(\text{acetonitrile})_2{}^{2+}$ as the catalyst precursor and provided information on reversible hydrogenation of the 1,2-N=C and stereoselectivity in the reduction of the 3,4-C=C. Similar bonding studies with (η^5 cyclopentadienyl)ruthenium cation ($CpRu^+$) and pyridine, 2-methylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, quinoline, 2-methylquinoline, and 1,2,3,4-tetrahydroquinoline revealed that N- and π-bonding to the metal center for these ligands also depends on steric and electronic effects; however, the $CpRu^+(\eta^1, N)$-bonded 2-methyl and 2,4, dimethyl-substituted pyridine complexes and the corresponding quinoline complex with the $CpRu(\eta^1, N)(CH_3CN)_2{}^+$ formula undergo a novel intramolecular N to π rearrangement. Several new exchange reactions of η^1 and η^6-bonded nitrogen ligands with free nitrogen ligands and an exchange reaction between two different η^1, N-bonded complexes were discovered. The scope of the selective hydrogenation reaction with mono, di, and trinuclear heteroaromatic nitrogen compounds using $Cp^*Rh(CH_3CN)_3{}^{2+}$ as the catalyst precursor is also being studied. [1.5 FTE]

Materials and Chemical Sciences Division $1,078,000

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

Bartlett, N.
Comm. 415-642-7259; FTS 451-5320

The main 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. [4.5 FTE]

82. *Catalytic Hydrogenation of Carbon Monoxide*

Bell, A.T.
Comm. 415-486-7095; FTS 451-7095

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. [3.5 FTE]

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

Bergman, R.G.
Comm. 415-642-2156

The central objectives of this program are (1) to discover new chemical reactions between organic compounds and organotransition metals, (2) to understand how these reactions work, and (3) to examine the applicability of the new transformations to the preparation of potentially useful materials such as fuels, commodity chemicals, and fine chemicals. Several years ago a major discovery on this project was the finding that certain iridium complexes undergo oxidative addition into the carbon–hydrogen bonds of saturated hydrocarbons (alkanes). This was the first example of this long-sought C–H activation reaction. Research carried out following this discovery has extended the C–H insertion reaction to other metals and provided information on its mechanism. One of the most significant recent discoveries in the project is that liquefied xenon and krypton can be used as inert solvents for C–H activation. Current work is directed toward using these unique noble gas solvents for (1) activating a range of new substrates, such as solids and gases that are difficult to liquefy (e.g., methane); (2) developing methods for detecting and studying directly the transient intermediates responsible for the critical C–H insertion step; (3) understanding the thermodynamics and kinetics of C–H activation; (4) extending the process to O–H, N–H, and C–F activation; and (5) developing better methods for using C–H activation to convert alkanes into functionalized organic compounds. [3.4 FTE]

84. *Formation of Oxyacids of Sulfur from SO_2*

Connick, R.E.
Comm. 415-642-4981; FTS 458-4981

Stimulus for the research is the existence of acid rain. Coal-burning power plants produce sulfur dioxide, which is oxidized in air to form sulfuric acid, the principal component of acid rain. In most commercial flue-gas desulfurization processes the sulfur dioxide is absorbed in an aqueous solution of low acidity where it may be oxidized by O_2. Control of the rate of this latter reaction is of major importance to these processes. While recent research has been concentrated on this reaction, investigation of the fundamental chemistry of species formed from sulfur dioxide and reactions of these species remains the primary goal. The oxidation-reduction chemistry of sulfur should be studied, particularly reactions between two oxidation states of the element (e.g., reactions involving HSO_3^-, H_2S, S_8, and the polythionates). 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, and configurations of activated complexes have been determined. The usual concept of a transition state with reflection coefficient near unity is quite inadequate. [0.5 FTE]

85. *Potentially Catalytic and Conducting Oligo-Organometallics*

Vollhardt, K.P.C.
Comm. 415-642-0286

This project involves the synthesis and evaluation of new, multimetallic molecules, designed to exhibit novel chemical behavior, particularly (1) the catalysis of organic transformations of synthetic and industrial importance and (2) potential conductivity. It centers on the development and execution of synthetic methodology aimed at allowing access to sequences of extended strong π-ligands to multiple transition metals. Although new work has as its target a variety of novel organic systems, most of the investigations so far have focused on the exploitation of a new, iterative strategy that allows the continued elaboration of linked cyclopentadienyl chains and their complexation with control of the resulting oligometallic sequence. In this way, a number of unknown transition-metal arrays have become available in which the metallic centers adopt "unnatural" linear and angular configurations. These structures give rise to unprecedented reactivity when exposed to small molecules, pointing toward applications in catalysis. They also provide ideal models with which to probe the elementary steps of multimetallic ligand and electron transfer. The discovery of exciting preliminary chemistry of these systems, including thermally and photochemically induced intramolecular transfer of organic fragments, has justified the original premise of this research. Current efforts concentrate on exploring the reactivity patterns of the structures under investigation and expanding the range of available ligand chains. [3.6 FTE]

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

Isotope and Nuclear Chemistry Division — $372,000

86. *Transition Metal Mediated Reactions of SO_2*

Kubas, G.J.; Burns, C.J.
Comm. 505-667-5846; FTS 843-5846

This research has focused on the basic chemistry of 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. Catalytic hydrogen reduction of SO_2 and NO on organometallic molybdenum sulfide complexes has been achieved, and mechanistic studies indicate that SO_2 undergoes oxygen transfer reactions that may be relevant to the catalytic cycle. Disproportionation of SO_2 to sulfur and SO_3 (as SSO_3 or SO_3H groups) occurs on reaction with $Cp'_2Mo_2S_4$ catalyst and also with $Cp'Ru(CO)_2H$ ($Cp' = C_5Me_5$). Reactive thiosulfate ligands such as those in $Cp'_2Mo_2(S_2)(S)(SSO_3)$ have now been observed to be formed from SO_2 in several systems and appear to be intermediates in the catalysis. Catalytic hydrogenation of NO on the Mo–S complexes was promoted by sulfur, whereby H_2S generated *in situ* is apparently the actual reducing agent, producing NH_3, N_2O, and H_2O. The discovery in this laboratory 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). Studies of these complexes, both experimentally and theoretically, provide an extremely detailed picture of bond rupture on a metal center. Protonation and deprotonation reactions of H_2 complexes such as $W(CO)_3(PR_3)_2(H_2)$ and $FeH_2(H_2)(PR_3)_3$ are being carried out to determine whether they can directly transfer hydrogen in catalysis. Activation of O–H bonds in H_2O and alcohols on the same complexes that bind H_2 is also being investigated. [1.5 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831-6194

Chemical Technology Division — $526,000

87. *Kinetics of Enzyme-Catalyzed Processes*

Greenbaum, E.; Woodward, J.
Comm. 615-574-6835; FTS 624-6835

During the current fiscal year a novel photophysical phenomenon was observed in isolated spinach chloroplasts that were metallized by precipitating colloidal platinum onto the surfaces of the thylakoid membranes. A two-point irradiation and detection system was constructed in which a helium–neon laser was used to irradiate the platinized chloroplasts at varying perpendicular distances from a single linear platinum electrode in pressure contact with the platinized chloroplasts. No external voltage bias was applied to the system. The key objective of the experiment was to measure the relative photoconductivity of the chloroplast–metal composite matrix. Unlike conventional photosynthetic electrochemical cells where irradiated chloroplasts are in close proximity to an electrode or linked to the electrode by an electrode-active mediator, in the present experiments the flow of photocurrent was through the biocomposite material. A sustained steady-state vectorial flow of current in the plane of the entrapped composite from the point of laser irradiation to the wire electrode was measured. The absolute value of the measured photocurrent and the maximum perpendicular distance between the point of irradiation and the linear electrode for which sustained current could be measured depended critically on the experimental procedure used to prepare the platinized chloroplasts. The effect of guanidine hydrochloride on the hydrolytic activity and tryptophan fluorescence of the major cellulase component, cellobiohydrolase I, has also been studied. [4.0 FTE]

Chemistry Division $2,636,000

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

Buchanan, A.C.; Britt, P.F.; Hagaman, E.W.; Chambers, R.R.
Comm. 615-576-2168; FTS 626-2168

This program constitutes a fundamental investigation of the relationship between the structure of coal and its reactivity under chemical or thermal conditions. The major structural tool being used is solid-state nuclear magnetic resonance (NMR) spectroscopy. A primary emphasis is on the development of double cross polarization (DCP) methodologies, ^{1}H–X–^{13}C, which only highlight carbon atoms within a small volume element ($\leq$4 Å) from an NMR active nucleus X. Current research is exploring the development of selective chemical reactions for the introduction of X = P or F into coal which, when coupled with DCP–NMR of the derivative, provides new details concerning the chemical structure of coals. The new studies on fluorine chemistry are initially examining the use of *N*-fluoro-*N*-alkylsulfonamides to fluorinate carbanion sites generated in coal. The mechanistic influences underlying the thermal reactivity of coal are also being studied. Other research focuses on the use of surface-attached model compounds to examine the impact of restricted diffusional and conformational mobility in pyrolysis induced free-radical reactions. The role of hydrogen shuttling reactions in allowing radical centers to migrate in a diffusionally constrained environment is being revealed through studies of two-component surfaces containing $Ph(CH_2)_nPh$ [n = 3,4] and a co-attached hydrogen donor. Insights gained from these fundamental investigations will contribute to the scientific base of knowledge necessary for the development of novel methods for the conversion of coal to chemicals or fuels in an environmentally acceptable manner. [6.3 FTE]

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

Mesmer, R.E.; Holmes, H.F.; Marshall, W.L.; Palmer, D.A.; Simonson, J.M.
Comm. 615-574-4958; FTS 624-4958

The goal of this program is to advance experimental methods and theoretical models to elucidate and describe the chemical and thermodynamic behavior of broad classes of solutes in water at high temperatures and pressures. The scope includes pretransition, transition, and heavy elements, along with selected actinides, and focuses on speciation, homogeneous and heterogeneous equilibria, and excess thermodynamic properties. Current emphasis is on the change from strong to weak electrolyte behavior, the application of the ion-interaction theory to the separation of mass action and electrostatic interactions, complexation, and electrolyte partitioning to steam. In this program multiple techniques are applied to the study of a given system to strengthen the species assignments and the associated thermodynamics. Advancements are being made in the use of calorimetry; electrical conductance; densimetry; and isopiestic, electrochemical, and spectroscopic methods to attain more extreme conditions and to obtain more definitive chemical and thermodynamic information. Recent progress has been made in the study of: gibbsite solubility and aluminum speciation; bisulfate ionization; mixing effects for acids, bases, and salts; deuterium isotope effects; near-critical enthalpies of mixing; complexation of metals by organic and chloride ions; and Raman spectra of phosphate and uranyl solutions. Results have important applications in power plant coolant and steam systems, waste disposal, environmental chemistry and restoration activities, and hydrothermal geochemistry. [4.2 FTE]

90. *Heterogeneous Catalysis Related to Energy Systems*

Overbury, S.H.; Huntley, D.R.; Mullins, D.R.; Krause, M.O.
Comm. 615-574-5040; FTS 624-5040

The interaction of molecules on single-crystal metal surfaces is the primary focus of this project, with particular emphasis on model hydrodesulfurization systems. Using high-resolution electron energy loss spectroscopy, Auger and photoelectron spectroscopies, and temperature-programmed reaction studies, the adsorption, reaction, decomposition, and desorption of methanethiol and hydrogen sulfide on clean and modified Ni(110) have been studied, including the reaction of hydrogen sulfide with surface oxygen to form water. Similar studies of benzenethiol and benzene on Ni(110) are in progress. The orientation and thermally induced reactions of hydrogen sulfide, thiophene, methanethiol, and benzenethiol on Ru(0001) are under analysis by photoelectron spectroscopy and near-edge X-ray absorption fine structure using either laboratory photon or synchrotron sources. To provide a structural basis for observed chemical reactivity, angle-dependent ion scattering has been applied to O, C, and S overlayers on Mo and W surfaces, and to ultrathin metal overlayers such as Ni and Cu on W(001), Sn on Pt(111), and Cu on Ru(0001). The structure and composition of various faces of NiAl have also been determined. Another project focuses on atomic spectroscopy and dynamics of excitation and relaxation of free atomic species using synchrotron radiation. Open-shell atoms including O, Mg, Cd, Be, and Ga are of particular interest. [4.4 FTE]

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

Zingg, S.P.; Dworkin, A.S.; Pagni, R.M.
Comm. 615-576-7325; FTS 626-7325

This research program constitutes a fundamental investigation of the photoreactions of organic substrates in heterogeneous systems. The approach is to first investigate the photochemistry of a series of polycyclic aromatic hydrocarbons (PAHs) both in homogeneous solution and sorbed to surfaces in solvent/solid slurries, by product analyses and *in situ* spectroscopic techniques. The study of photoreactions on surfaces for PAHs would be of value not only in advancing basic understanding, but in providing insight into the transformations of these chemicals in the environment and the roles which sunlight and sorption to solids play. Anthracene was chosen as the substrate in the initial investigations, since it undergoes a variety of well-known solution photochemical reactions including energy transfer, electron transfer, photooxygenation, and photodimerization. A greatly enhanced rate of photooxygenation of anthracene when sorbed on SiO_2 in cyclohexane/SiO_2 slurries was observed. Possible contributing factors that are being investigated include increased irradiance caused by light scattering by SiO_2, the role of the more polar environment of the SiO_2 surface, the role of solution and sorbed O_2, and surface coverage. An enhanced rate of photooxidation of anthracene in water as compared to organic solvents, which appears to proceed by a different mechanism, was also observed. The photochemistry of PAHs in aqueous media, though of significant environmental concern, is not well understood. [2.3 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $592,000

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

The objective of this project is to determine kinetics and mechanisms of key radical rearrangements and atom transfer reactions important to thermal degradation of coal. Efforts include determination of bond strengths of key C–H, S–H, and C–S bonds; absolute rates of organic free-radical rearrangements; rate expressions for hydrogen atom transfer between heteroatom-centered radicals and heteroatom hydrogen donors; and absolute rate expressions for hydrogen atom transfer to carbon-centered radicals from CH, PH, SH, MoH, and other heteroatom donors. Methods include nanosecond kinetic laser flash photolysis, kinetic electron paramagnetic resonance spectroscopy, and laser photoacoustic calorimetry. Homolytic cleavage of carbon–sulfur and carbon–selenium bonds in reactions with carbon, phosphorus, and metal-centered radicals are under investigation. *Ab initio* quantum chemical calculations at various levels of electron correlation are being investigated to examine excited state and open shell potential surfaces of organosulfur intermediates. A theoretical and experimental study of the radical hydrogen transfer mechanism for the cleavage of aryl–alkyl bonds is under way. Procedures for the quantitative application of ultrahigh speed magic angle spinning CPMAS NMR and solid-state ^{195}Pt and ^{15}N NMR to the determination of carbon and sulfur structure in coal are under development. [4.1 FTE]

Solar Energy Research Institute
Golden, CO 80401

Solar Fuels Research Division $324,000

93. *Basic Research in Synthesis and Catalysis*
DuBois, D.L.; Curtis, C.J.
Comm. 303-231-7371; FTS 327-7371

The synthesis and the characterization of new inorganic and organometallic complexes for evaluation as catalysts for the electrochemical reduction of CO_2 and CO to methanol are under investigation. Palladium complexes containing triphosphine ligands that catalyze the electrochemical reduction of CO_2 to CO have been synthesized. Mechanistic studies have resulted in a detailed understanding of the fundamental steps involved in the catalytic cycle. Minor structural modifications of the triphosphine ligand have significant effects on catalytic rates, turnover numbers, and mode of catalyst deactivation. The objective is to determine those structural features necessary for the design of very active and long-lived catalysts. Similar studies are in progress to develop homogeneous catalysts for the electrochemical reduction of CO. In this effort stoichiometric reactions of electrochemically generated transition metal hydride complexes with electrophilic metal carbonyl complexes resulting in the formation of metal formyl complexes have been demonstrated. The objective is to understand the electronic and steric features required for the intermolecular hydride transfer from the metal hydride to the carbonyl ligand. The understanding of this fundamental reaction will be important in the development of catalysts for CO reduction. [1.8 FTE]

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, IA 50011

Processes and Techniques Program $1,076,000

94. *Analytical Separations and Chemical Analysis*
Fritz, J.S.
Comm. 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. A modern adaptation of steam distillation is coupled with solid phase extraction for preconcentration of organic compounds from a variety of aqueous samples. 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]

95. *Analytical Spectroscopy*

Houk, R.S.; D'Silva, A.P.
Comm. 515-294-9317

The project objective is the development of new techniques for ultratrace analysis. Excitation sources for atomic spectroscopy, such as inductively coupled plasmas (ICPs), inert gas afterglows, and laser-produced microplasmas, are studied by both optical and mass spectroscopy. Typical studies include characterization of the noise behavior of ICPs, investigation of the extraction process and interferences in ICP mass spectrometry, and elucidation of energy transfer processes in ICPs and afterglows. These atomic excitation sources are coupled with chromatographic separations to provide element-selective detection for elemental speciation. New methods for ion trapping and time-of-flight mass spectrometry are also investigated. [4.21 FTE]

96. *Chemical Analysis at Liquid–Solid Interfaces*

Porter, M.D.
Comm. 515-294-6433

This project examines new approaches for the construction and characterization of monomolecular films at liquid–solid interfaces. Recent efforts have focused on (1) probing solvent-monolayer interactions of n-alkanethiol monolayers with aqueous and various nonaqueous solvents with *in situ* Fourier transform infrared reflection spectroscopy, (2) examining the fabrication for molecular recognition monolayers with organosulfur derivatized cyclodextrin monolayers, and (3) developing molecular level descriptions of the head group chemistry for the above monolayers at Au and Ag. The molecular level descriptions are derived primarily from infrared reflection spectroscopy, optical ellipsometry, scanning tunneling microscopy, 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 also examines the incorporation of size selective channels in long alkyl chain monolayers. [2.2 FTE]

97. *Lasers in Analytical Chemistry*

Yeung, E.S.
Comm. 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) nonlinear Raman and magneto rotation techniques for selective measurements in solutions; (3) detectors for liquid chromatography and for thin-layer chromatography that are more sensitive and more reliable; and (4) laser-initiated chemiluminescence for trace gas and for surface analysis. [4.1 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $1,193,000

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

Horwitz, E.P.
Comm. 708-972-3653; FTS 972-3653

The primary objectives of this project are: (1) to design, synthesize, and characterize new classes of aqueous-soluble 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 less environmentally noxious species; (2) to study extractant–diluent interactions with the objective of improving the solubility of highly polar extractants in hydrocarbons; and (3) to develop improved methods for synthesizing new and existing organophosphorus extractants and complexants by studying the basic mechanisms 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. [5.6 FTE]

99. *Particle-Induced Desorption/Ionization Mass Spectrometry*

Hunt, J.E.
Comm. 708-972-3517; FTS 972-3517

The particle-induced desorption mass spectrometry program is a basic research program focused on the study of processes that occur in the emission of charged and neutral species as a result of particle impact. The research involves the study of the interaction of fast atomic and molecular ions and photons with organic surfaces. The goal of these studies is to elucidate the processes that occur, and thus provide new knowledge relevant to analytical particle-induced desorption mass spectrometry techniques, such as fast-atom bombardment (FAB), secondary ion mass spectrometry (SIMS), and ^{252}Cf-PDMS. Particle-induced desorption (PID) mass spectrometry, which began about a decade ago, has revolutionized mass spectrometry. Nonvolatile compounds, once considered intractable, are now routinely analyzed by PID techniques. The underlying physical processes that occur in desorption, however, are by no means yet fully understood. A comprehensive understanding of the interaction of fast particles with materials is important since these interactions represent the first and most fundamental steps in the desorption process. The chemical and physical processes of desorption are studied in an effort to understand the fundamentals of particle/solid interactions related to desorption of intact organic molecules. [1.1 FTE]

Brookhaven National Laboratory
Upton, Long Island, NY 11973

Department of Applied Science $458,000

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

Jones, K.W.; Gordon, B.M.
Comm. 516-282-4588; FTS 666-4588

This project investigates new analytical techniques for elemental determinations and chemical speciation using synchrotron radiation from the Brookhaven National Synchrotron Light Source (NSLS). X-ray fluorescence methods are used to identify specific elements. The X-ray beams are reduced to micrometer dimensions by use of focusing mirrors and collimators. The aim is to produce an instrument that can make measurements with a spatial resolution of 1 micrometer and that has a minimum detection limit of less than .5 parts per million (ppm) for a 300-s acquisition time. These values represent an improvement of a factor of 3 to 10 over present achievements. Computed microtomography methods are used to make non-destructive measurements on materials. Present spatial resolution is about 5 micrometers, and the aim is to improve this to 1 micrometer or less. The addition of extended X-ray absorption fine structure (EXAFS) or X-ray absorption near-edge spectroscopy (XANES) to the instrumentation is in progress. The instrumentation developed in this project is in active use in catalysis and coal research projects. Complementary measurements are made with MeV ion beams using nuclear reaction analysis and related methods. [2.7 FTE]

101. *Microparticle Analysis by Laser Spectroscopy*

Tang, I.N.; Fung, K.H.
Comm. 516-282-4517; FTS 666-4517

The project focuses on building a fundamental understanding and exploring new applications of novel laser-based spectroscopic methods for chemical analysis of microparticles. Suspensions of micro-sized particles are abundant in nature, and in numerous 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 analytical measurement techniques for *in situ* monitoring of these suspended particles. Such a task has always been a formidable one, since the mass of an individual particle is only in the order of nanograms and the composition is often complex. Areas of current interest include (1) elucidation of the transient states that result in Raman intensity enhancement by resonance absorption, (2) studies of time-resolved spectroscopy as applied to microparticles in order to reduce the fluorescence background in Raman emissions, (3) fundamental understanding of the fractionation processes taking place during phase transformation of multicomponent solution droplets in order to quantify Raman signals, and (4) studies of other potentially important nonlinear optical processes such as stimulated emission and multiphoton absorption in droplets. [1.9 FTE]

EG&G Mound Applied Technologies
Miamisburg, OH 45343

Operations Department $200,000

102. *Isotope Separation Research and Development*

Jepson, B.E.; Eppley, R.E.; Wilkes, W.R.
Comm. 513-865-3893; FTS 774-3893

This project will investigate chemical exchange chromatography as a technique for stable isotope separation. The work is directed toward finding metal isotope exchange systems that possess equilibrium single-stage separation factors sufficiently large for practical application to metal isotope enrichment processes. Recently, adequate separation with macrocyclic ligands chemically bonded to or immobilized on solid supports has been demonstrated. Three factors are important in determining the practicality of a separation process: the separation factor, the average concentration of the element being separated, and the rate of exchange. Each depends upon the nature of the bond between the ligand and the solid support. Current emphasis is on optimizing the specific separative capacity of selected ligands by varying the "tether" that binds the ligand to the solid support. [1.9 FTE]

Idaho National Engineering Laboratory
Idaho Falls, ID 83415

$279,000

103. *Negative Ionization Mass Spectrometry*

Delmore, J.E.; Appelhans, A.D.; Dahl, D.A.
Comm. 208-526-2820; FTS 583-2820

Gas/solid negative ion formation processes are being studied to elucidate the ion formation/decomposition pathways. An example is the formation of sulfur hexafluoride anions and the subsequent decomposition back to the neutral species, a process used to produce well-focused beams of high energy neutral molecules. Another type of system produces a variety of negative ions when electrons impact an adsorbate on an electrode. The hydride ion forms in good yield when hydrogen is adsorbed on the electrode in a certain chemical state. This is another potentially important analytical system, and the ion formation mechanism is only partially understood. Other systems are being studied to explore the chemical interactions between ad/absorbates and the substrates as they pertain to gas-phase ion formation both for understanding of the chemistry and better understanding of the ion formation process. To develop understanding of these processes, it is necessary to accurately model the motion of ions in electrical/magnetic fields. Mathematical algorithms have been developed and converted into computer codes for modeling such systems. These codes have been essential to the success of this project, are also in use by many other scientists at other facilities for related purposes, and are now being developed into three-dimensional algorithms that operate on 386 class PC's. [1.0 FTE]

Lawrence Berkeley Laboratory University of California Berkeley, CA 94720

Applied Science Division $148,000

104. Repetitively Pulsed Laser: Material Interaction

Russo, R.E.
Comm. 415-486-4258; FTS 451-4258

A comprehensive program is under way to study the mechanisms that describe the explosive removal of material induced by high-power pulsed-laser irradiation. Acoustic monitoring, optical probe beam deflection, and atomic emission spectroscopy are studied to indicate distinct mechanisms occurring during the interaction. Piezoelectrics are used to study the propagation of acoustic waves induced in the material by pulsed laser irradiation. Changes in the acoustic response 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 heating and cooling rates, the onset of material removal, and the formation of a laser initiated surface plasma. Atomic emission spectroscopy is used to monitor the composition and quantity of the laser-sampled material. This material is transported to an inductively coupled plasma (ICP) for excitation to emission. This work emphasizes the use of a repetitively pulsed-laser material interaction for producing steady-state emission intensity in the ICP. For chemical analysis, steady-state laser sampling can provide improved precision over transient sampling, direct solid analysis, simultaneous multielement analysis, microanalysis, and spatial characterization. [1.7 FTE]

Oak Ridge National Laboratory Oak Ridge, TN 37831-6365

Analytical Chemistry Division $1,754,000

105. R&D in Secondary Ion Mass Spectrometry

Christie, W.H.; Todd, P.J.; Valiga, R.E.
Comm. 615-574-2455; FTS 624-2455

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. [1.9 FTE]

106. Mass Spectrometry R&D for Organic Analyses

Glish, G.L.; McLuckey, S.A.; Van Berkel, G.J.; Goeringer, D.E.
Comm. 615-574-2456; FTS 624-2456

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. A better understanding of the fundamental processes involved in ionization, ion activation, and unimolecular and bimolecular reactions provides a stronger base from which to develop analytical methods. In the area of ionization, specific research efforts include: electrospray ionization, glow discharge ionization, ionization with positrons, and ionization via controlled ion/molecule reactions. Topics of interest in ion activation include collision-induced dissociation in various energy regimes, electron-induced dissociation, and photodissociation. Mass spectrometry/mass spectrometry (MS/MS) is used as a tool in most of these studies as well as in the study of unimolecular and bimolecular reactions. The information gained from these experiments is then used to improve the analytical capabilities of MS/MS. The results of this work will be of benefit in that they will provide improved methods of analyzing organic compounds and of probing the fundamental properties of molecules. [2.6 FTE]

107. Advanced Spectroscopic Methods for Chemical Analysis

Hulett, L.D.; Donohue, D.L.; Rosseel, T.M.;
Comm. 615-574-8955; FTS 624-8955

High-resolution heavy-ion-induced X-ray satellite emission (HIXSE) spectroscopy has been used to study the chemical environment of ions implanted in a range of matrices. Measurements of the sensitive satellite lines are obtained with a specially designed highly efficient, high-resolution X-ray spectrometer operating at the 6-MV EN-tandem accelerator. The positron beam line at the Oak Ridge Electron Linear Accelerator (ORELA) has been in continuous operation for nearly two years. The primary tungsten moderator assembly has been replaced by a new design that is easier to fabricate and install and improves the positron flux. Positron ionization mass spectrometry has been improved with a thin-film tungsten re-moderator and mini-penning trap ion source for the positronium formation mechanism that produces selective and highly controlled fragmentation of the sample molecules. Equipment has been acquired to measure the Doppler broadening of the positron annihilation radiation as a probe of the electron momentum distribution in high-temperature oxide superconductor films as a function of depth. [2.8 FTE]

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

Ramsey, J.M.; Ross, H.H.; Shaw, R.W.; Whitten, W.B.; Young, J.P.; Klatt, L.N.
Comm. 615-574-5662; FTS 624-5662

The objective of this research program is to develop techniques for spectrochemical analysis with enhanced specificity and sensitivity. The emphasis is on high-resolution laser spectroscopy. This project involves a number of experimental efforts including work on new laser sources, measurement schemes, and sampling techniques. Continuous-wave (CW) dye lasers employing photorefractive optical elements are being studied in addition to the application of diode lasers to high-resolution optical spectroscopy. Advances in this area may find application in the area of field-portable instrumentation using laser-based measurement schemes. Resonance-enhanced multiphoton ionization (REMPI) spectroscopy is employed in several experiments for high-resolution, high-sensitivity measurements. These experiments include resonance ionization mass spectroscopy (RIMS) in magnetic sector instruments, RIMS in ion trap mass spectrometers, and REMPI in low-pressure sampling cells. The RIMS experiments are primarily directed toward isotope ratio measurements while the low-pressure sampling cell apparatus is applicable to elemental analysis in general. The latter experiment can provide isotope ratio information as well when Doppler-free spectroscopy is used. The use of diode laser excitation with the low-pressure sampling cell may provide a convenient instrument for radionuclide survey measurements when interfaced to a conventional atomization source. Work is also being initiated on measurement schemes that have application to global environmental studies. [3.0 FTE]

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

Smith, D.H.; Donohue, D.L.; May, M.P.
Comm. 615-574-2449; FTS 624-2449

The objective of this work is to advance the state of the art in inorganic mass spectrometry with emphasis on the analysis of the lanthanide and actinide elements. Improvements are sought in both instrumentation and sample preparation methodology in order to gain enhanced precision, accuracy, specificity, and sensitivity. Isotope dilution techniques are used extensively. Laser-based resonance ionization is studied as a means for vastly improving specificity. Improved methodology for determining various difficult-to-measure elements is investigated. For improved sensitivity and more accurate measurements in survey analyses, new work is under way in glow-discharge mass spectrometry. Its ability to deliver quantitative results over a wide dynamic range is being evaluated with respect to the effect of sample matrix. Its ability to measure isotopic ratios is presently being evaluated, and a radio frequency (rf) probe for analysis of nonconducting samples is being developed in collaboration with researchers at Clemson University. [2.3 FTE]

Chemical Technology Division $1,223,000

110. *Chemical and Physical Principles in Multiphase Separations*

Byers, C.H.; Basaran, O.A.; Scott, T.C.; Perona, J.J.
Comm. 615-574-4653; FTS 624-4653

This project comprises several fundamental studies that address the use of electromagnetic fields to enhance the efficiency of separation processes. Focus is on improving mass transfer in liquid–liquid solvent extraction and on analysis of electric field effects on drops in liquid–liquid systems. New thrusts for this work will employ electric fields to enhance vapor–liquid equilibria utilizing understanding gained in liquid–liquid systems. A secondary focus is on exploring the use of high-gradient magnetic fields in separation processes. Investigations in the area of solvent extraction include mechanics and fluid mechanics of drop formation, large-amplitude drop oscillations and break-up to form interfacial surface area, effects of external electric fields upon drop-continuum hydrodynamics, interaction and coalescence of two or more drops, and mass transfer to free and forming drops. Investigations in the area of magnetic fields in separations include novel means for isolating macromolecules and use of ferrofluids as the continuous phase. [2.8 FTE]

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

Cochran, H.D.; Byers, C.H.
Comm. 615-574-6821; FTS 624-6821

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 commercial technologies such as supercritical extraction and supercritical fluid chromatography. New developments based on distribution function theory and Kirkwood–Buff solution theory predict the important effects of added third components such as cosolvents in supercritical extraction, from the pair correlation functions and molecular interactions. Related work permits determination of chemical potential from solution of integral equation theories at only the state of interest. A new solution algorithm for integral equation theories will permit calculations much closer to the critical point than previously possible. Calculations on dilute, repulsive supercritical solutions led to the discovery of a new separation concept which is being explored in a related program. Following completion of solubility measurements for simple solids in simple supercritical solvents, current experiments aim toward direct observation of the fluid microstructure by neutron scattering. Studies of the system solid Ar in supercritical Ne will permit a direct test of the new theoretical developments. Studies of Ne in supercritical Ar, to follow, will similarly illuminate the structure of repulsive solutions. [1.0 FTE]

112. *Chemistry of Actinides and Fission Products*

Toth, L.M.; Sherrow, S.A.
Comm. 615-574-5021; FTS 624-5021

The primary purpose of this project is to explore the fundamental chemistry of the actinide elements and their fission products. Emphasis is placed on the photochemistry, coordination chemistry, and separations chemistry of these elements, especially as they relate to problems in waste management, environmental control, and the nuclear fuel cycle. The chemistry of other elements is often examined in parallel with that of the actinides and fission products in order to develop a better understanding of the periodic behavior of the elements. The current interests are (1) low-temperature spectroscopy/photochemistry (including matrix isolation methods to isolate and identify reactive intermediates) and (2) neutron/X-ray small-angle scattering experiments of hydrolytic polymers (to define sizes and geometries of colloidal species and those factors controlling their formation, reactivity and ultimate size). [1.5 FTE]

Chemistry Division $835,000

113. *Chemical and Structural Principles in Solvent Extraction*

Moyer, B.A.; Sachleben, R.A.; Burns, J.H.
Comm. 615-574-6718; FTS 624-6718

The purpose of this project is to provide an understanding of the fundamental role of molecular structure and bonding in determining the separative and chemical properties of solvent-extraction and related systems of relevance to energy technologies. Questions of interest pertain to the bonding requirements of organophilic polydentate ligands as hosts for metal cations. The approach involves the synthesis of potential extractants and the investigation of their properties by (1) X-ray structure determination of crystalline model compounds; (2) NMR, UV/vis, FTIR, and other physical measurements; (3) molecular mechanics calculations; and (4) acquisition of separations data followed by computer-aided equilibrium analysis. A central strategy involves coupling the selective process of coordination involving encirclement of the metal cation by the polydentate ligand with the pH-driven process of cation exchange involving the deprotonation of an organophilic acid. A major thrust concerns the question of how these functions may all be advantageously incorporated into one molecule as represented by the class of ionizable dibenzo-14-crown-4 lariat ethers. Systems of continued interest are those containing polydentate oxa and thia ligands combined synergistically with organophilic sulfonic and carboxylic acids. Computer techniques for analyzing liquid–liquid extraction equilibria are being developed and initially tested on extraction data involving a sulfoxide extractant. [5.0 FTE]

Pacific Northwest Laboratory
Richland, WA 99352

Chemical Sciences Department $1,224,000

114. *Analytical Mass Spectrometry Research*

Baer, D.R.; Hubbard, C.W.; Ballou, N.E.; Styris, D.L.
Comm. 509-376-1907; FTS 444-1907

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 composite rhenium surfaces is being investigated by surface work function measurements, Auger electron spectroscopy, and ultraviolet photoelectron spectroscopy. The development of new mass spectrometric techniques addresses a broadly applicable mass spectrometry based on concurrent vaporization and plasma ionization in a graphite furnace. [2.8 FTE]

115. *Laser-Based Analytical Techniques*

Glab, W.L.; Bushaw, B.A.; Cannon, B.D.
Comm. 509-376-3956; FTS 444-3956

The objective of this program is to provide a scientific basis for the design of laser-based detection techniques that will have applications in a wide variety of fields related to energy production. Ultrasensitive isotopic analysis of metastable noble gas atoms has been the primary focus of this work. The research has demonstrated that high-resolution continuous-wave (CW) laser-based techniques can detect metastable krypton atoms with high isotopic selectivity. The scope of this program will broaden to include optical techniques for metastable-state generation. Studies of atomic and molecular systems will be initiated. The use of high-resolution single-mode pulsed lasers in the far ultraviolet (UV) and vacuum ultraviolet (VUV) to drive multiphoton excitation processes will be investigated as a means for producing the metastable states of a variety of species. Multiphoton photodissociation of small molecules, leading to the production of ground and excited state fragments, will be studied. Spectroscopic studies of radical species that are of interest in the analysis of plasmas and flames are planned. The production of negative ions via collisions between molecules and Rydberg atoms will also be examined. [1.3 FTE]

116. *Fundamental Phase Partitioning in Supercritical Fluid Chromatography*

Smith, R.D.; Yonker, C.R.; Fulton, J.L.
Comm. 509-376-0723; FTS 444-0723

The goal of this project is a fundamental understanding of the kinetic, thermodynamic, and molecular level phenomena related to structure in supercritical fluid solutions relevant to separation and chromatographic processes. In the most general sense, this project is exploring supercritical fluid phenomena in order to bridge the gap between understanding the gas and liquid states. One aspect of this project is focused on gaining an understanding of solvation phenomena supercritical fluid systems, and the kinetic and thermodynamic limitations upon separations using supercritical media. A second area involves local molecular structure and organized molecular assemblies (e.g., micelles and microemulsions) in supercritical fluid solutions, and the changes in intermolecular forces upon variation in fluid density between the gas and liquid limits. Both normal and reverse micelle and microemulsion systems, where the nonpolar phase is a supercritical fluid, are being investigated as the basis for new separation methods caused by the unusual pressure dependence of phase behavior for these systems. Novel pressure-dependent bicontinuous fluid-structure systems have also been discovered. Experimental results are being compared with theoretical methods for prediction of fluid-phase structure in the solvation region about a solute molecule. Spectroscopic studies for simple micelle systems, where fluids such as xenon constitute the continuous fluid phase, are being conducted to facilitate understanding of various organized structures in fluids. Light- and neutron-scattering studies are exploring the structure and attractive (i.e., micelle–micelle) interactions in fluids and providing new insight into the forces dictating phase behavior. It is anticipated that this research will form the basis for new separation methods as well as improve understanding of solvation and structure in both the supercritical and liquid phases. [2.4 FTE]

117. Mechanisms of High-Temperature Atomization in Chemical Analysis

Styris, D.L.; Prell, L.J.
Comm. 509-376-1907; FTS 444-1907

This project uses mass spectrometry and atomic absorption spectrometry techniques to elucidate mechanisms that control atomization on high-temperature surfaces; unique applications are developed and refined. These mechanisms form the basis needed to broaden and improve applications of spectrometries that rely on thermal atomization sources. The atoms and molecular species that evolve from high-temperature surfaces, during rapid thermal ramping, are monitored in real time. Surface state theory and available thermodynamic and kinetic data are then used to help identify and characterize the controlling chemical and physical processes. The work primarily involves pyrolytic graphite surfaces because of the extensive use of this material for thermal atomization sources. However, atomization on high-temperature quartz surfaces, such as those used in hydride generation spectroscopy, is also investigated. Atomization mechanisms of Group II-A elements and mechanisms responsible for chemical matrix effects, such as interference effects of calcium and stabilizing effects of palladium, are elucidated. The project is also providing, through investigations of Group III-A elements, the carbide formation data essential to establishing validity of existing atomization models. Mechanisms associated with the unique hollow-anode plasma furnace atomization nonthermal excitation spectroscopy source are also being investigated. [1.7 FTE]

Heavy Element Chemistry

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division $1,611,000

118. Heavy Element Chemistry Research

Morss, L.R.; Appelman, E.H.; Beitz, J.V.; Carnall, W.T.; Soderholm, L.; Sullivan, J.C.
Comm. 208-972-3667; FTS 972-3667

The project conducts fundamental studies that determine electronic, bonding, and dynamic properties of the f elements, especially the transuranium elements in solids, solutions, and gases. The objectives are (1) to understand how the unique properties of f electrons influence the behavior of heavy elements (especially transuranium elements) and (2) to apply this understanding to solve key problems in energy, materials, and nuclear fuel cycle research. Syntheses of novel transuranium oxides and halides probe the limits of stability of oxidation states of these ions and provide pure materials for the project. Research in the photophysics and photochemistry of the transuranium elements, using techniques such as laser-induced fluorescence, provides new insight into the chemical consequences of excited-state formation and the dynamics of relaxation modes, addressing DOE needs in the separation and recovery of actinides. New ultrasensitive spectroscopic detection methods such as laser photoacoustic spectroscopy support DOE interest in monitoring nuclear wastes. Electronic structure models are developed to identify newly synthesized species and to guide the interpretations of bonding and magnetic interactions. Systematic comparisons among 4f and 5f ions in parallel oxidation states and coordination sites in solids by neutron scattering and X-ray absorption spectroscopy aid in explaining and predicting the electronic and bonding properties of novel materials such as the new high-T_c superconductors. The dynamic and thermodynamic parameters that characterize dissolution, electron-transfer, and complex-formation reactions are measured with specialized pulse radiolysis, stopped-flow, and calorimetric instrumentation in order to gain a predictive understanding of the energetics and mechanisms of actinide ion reactions in process chemistry and in heterogeneous aquatic systems. [10.2 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Materials and Chemical Sciences Division $1,237,000

119. Actinide Chemistry

Edelstein, N.M.
Comm. 415-486-5624; FTS 451-5624

The purpose of this project is to study actinide materials in order to provide the basic knowledge necessary for their safe and economic use in present and future technology.

The program includes preparation of new gaseous, liquid, and solid phases and studies of their physical and chemical properties. Techniques for characterization include X-ray diffraction, optical and vibrational spectroscopy, magnetic resonance, and magnetic susceptibility. Equilibrium and kinetic data for complex formation are measured. From these complementary studies, new insights into the structural and chemical principles of actinide compounds are obtained with which to design new synthetic schemes to produce new materials. A major aspect of the program is the design and synthesis of sequestering agents for actinide ions. These compounds are intended for use in the treatment of actinide poisoning and for possible application in the treatment of spent reactor fuels. Preparative, structural, and physical studies of new types of organoactinide, related organolanthanide, and new actinide inorganic complexes are continuing. Studies on optical spectra of actinide ions in crystals and in molecules are being pursued in order to understand their electronic structure. [14.0 FTE]

Nuclear Science Division $128,000

120. Chemistry of the Heaviest Elements
Hoffman, D.C.
Comm. 415-486-4474; FTS 451-4474

The objective of this project is the determination of the fundamental 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 on these chemical properties. 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. A program to investigate some of the most basic chemical properties of elements 102 through 106 is being undertaken. The chemical properties being investigated include the determination of range and stability of oxidation states, measurement of ionic radii, and anionic halide complex formation. Atoms of the heaviest elements are produced at the LBL 88-inch Cyclotron by irradiation of heavy actinide targets, such as ^{248}Cm, ^{249}Bk, or ^{249}Cf. These chemical properties can be determined using "atom-at-a-time" techniques, even though production rates can be as low as a few atoms per hour. Some chemical properties of No, Lr, Rf, and Ha have been measured using both aqueous phase and gas-phase techniques. Preparations are under way for large multinational collaborations to study the chemical properties of Rf and Ha. Chemical studies using 44-m ^{261}Lr are in progress using 65-s ^{261}Rf for studies of anionic chloride complex formation. There is a continuing effort to produce and identify new, longer-lived isotopes of the heaviest elements, such as ^{263}Rf and ^{265}106, which may permit more detailed studies of their chemical properties. [1.0 FTE]

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

Isotope and Nuclear Chemistry Division $351,000

121. Actinide Chemistry in Near-Neutral Solutions
Hobart, D.E.
Comm. 505-667-9313; FTS 843-9313

Efforts to provide fundamental physicochemical knowledge pertinent to the behavior of plutonium and other actinides in the environment, in reprocessing and purification, and in nuclear waste isolation and storage are continuing. Investigations of hard oxygen-donor-type ligands for actinide complexation in near-neutral solutions are continuing with the spectral and X-ray diffraction characterization of the actinide oxalates. The oxalate ion, though not common in the environment, serves as a prototype for other common ligands found in groundwaters. Studies of the preparation and characterization of the actinide silicates have been initiated. Silicate ions are the major component of most rocks and minerals and are expected to be a major potential complexing agent for actinides under conditions above ambient temperatures and pressures (e.g., near a highly radioactive, elevated temperature nuclear waste package). The structures of the transamericium oxalates and silicates have not been previously reported. Carbon-13/oxygen-17 nuclear magnetic resonance studies have been initiated to determine the carbonate complexation quotients for Pu(IV). Preliminary results with 99.9% ^{13}C-enriched uranium carbonate solutions reveal that different carbonate species can be readily distinguished with high-field solution NMR on isotopically labeled complexes. This method provides a species-sensitive detection method for unequivocally unravelling the complicated actinide carbonate systems. Major progress is reported in a collaboration with Life Sciences and the Los Alamos Neutron Scattering Center (LANSCE)–Physics Divisions in studying the behavior of Pu(III) in near-neutral human physiological pH regimes and determining the solution structure of the protein calmodulin by neutron resonance scattering from plutonium-240. Photoacoustic spectroscopy (PAS), photothermal deflection spectroscopy (PDS), and laser-induced fluorescence (LIF) and Raman spectroscopies are now operational. [0.6 FTE]

122. Actinide Organometallic Chemistry
Sattelberger, A.P.
Comm. 505-667-1604; FTS 843-1604

The project objective is to study fundamental aspects of early actinide organometallic chemistry. The current focus is on: (1) the synthesis and characterization of new classes of early actinide complexes containing nonclassical ligands, such as alkyls, amides, imides, phosphides, phosphinidenes, and thiolates; (2) investigations of actinide-mediated reactions of unsaturated inorganic and organic substrates; (3) variable temperature magnetic and electronic spectroscopic studies; (4) actinide alkoxide and oxo/alkoxide complexes as models for aqueous-phase hydroxo and oxo/hydroxo species; (5) the development of low-temperature solution and gas-phase routes to solid-state actinide materials. Recent results include (1) the synthesis of actnide(III) triiodide complexes of the type AnI_3L_4, where An = Np, Pu and L = tetrahydrofuran, pyridine, and dimethylsulfoxide; (2) the preparation of new neptunium(III) and plutonium(III) complexes: $Np[N(SiMe_3)_2]_3$, $Np(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$, $Pu[N(SiMe_3)_2]_3$, and $Pu(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$; (3) the synthesis and X-ray structure of $C_6H_5N{\equiv}U[N(SiMe_3)_2]_3(F)$, a uranium(VI) organoimido complex; (4) the synthesis and structural characterization of the uranium(IV) alcoholate $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ and its reaction with oxygen-free water to give the triangular uranium(IV) cluster compound $U_3O(O\text{-}t\text{-}Bu)_{10}$; (5) the neutron diffraction structure of $(C_5Me_5)(C_8H_8)Th[N(SiMe_3)_2]$, a molecule that exhibits an agostic Th–H–C interaction; and (6) the preparation of binary uranium nitrides from the reaction of $U[N(SiMe_3)_2]_3$ with anhydrous ammonia in hexane solution. [0.8 FTE]

Nuclear Materials Technology Division \$122,000

123. *Actinide High-Temperature Thermodynamics*

Kleinschmidt, P.D.
Comm. 505-667-6945; FTS 843-6945

The goal of this project is the thermochemical characterization of actinide compounds and molecules by measuring gas-solid and gas-phase equilibria. The Knudsen effusion mass spectrometry technique is used to measure the partial pressures of the gas-phase species. Thermochemical quantities derived from these pressures are the enthalpy, entropy, and free energy. Currently the bond dissociation energies of gaseous neptunium and plutonium fluorides are being measured as well as the decomposition mechanisms of their oxyfluorides. The stability of mixed salts of plutonium trichloride with the alkali chlorides is also being measured with this technique. Ultimately, systematic trends in bonding of the actinide series will be established with this data as well as applications of the data to such problems as waste storage and disposal, scrap recovery, radioisotope heat sources, metal production schemes, isotope separation processes, and waste minimization schemes. [0.6 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Chemistry Division \$1,212,000

124. *Chemistry of Transuranium Elements and Compounds*

Moyer, B.A.; Gibson, J.K.; Johnson, E.;
Haire, R.G.; Payne, G.F.
Comm. 615-574-6718; FTS 624-6718

Understanding the chemical effects of 5f electrons is the principal focus of this program. Broad contributions are made to the understanding of bonding, relativistic electronic effects, and periodicity. Emphasis is placed on the reactor-produced transplutonium elements through fermium plus selected accelerator-produced elements such as mendelevium. To study small quantities of these highly radioactive elements, specialized techniques involving mass spectrometry, calorimetry, X-ray diffraction, magnetic-susceptibility determination, spectroscopies (Raman, UV-vis, and luminescence), and organometallic synthesis are employed. Questions concerning 5f-orbital interactions have led recently to the examination of properties of americium–curium alloys and $CfCl_3$ under high pressure, revealing evidence for delocalization in the americium–curium system. Interactions of 5f electrons are also reflected in the magnetic and specific-heat properties of californium oxides, americium halides, and neptunium alloys and in vibrational and electronic spectra of lanthanide and actinide dipicolinate complexes. High-temperature studies carried out by mass spectrometry are yielding basic thermodynamic properties (e.g., ΔH_v for californium metal, alloys, and oxides) and allowing the identification of high oxidation states (e.g., AmF_4). Stabilization of the low oxidation states is being attempted through synthesis of divalent organometallic complexes of lanthanide and eventually actinide metals. Accurate ionization potentials and radii of element 104 and its ions to the 4+ state have recently been derived from relativistic quantum-mechanical calculations. [7.0 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Applied Science Division \$335,000

125. *Turbulent Combustion*

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

The interaction between fluid mechanical turbulence and chemical reactions in laboratory-scale premixed and non-premixed turbulent flames is studied experimentally using laser diagnostic techniques. A theoretical study of premixed turbulent flames using the vortex dynamics method is also being conducted. The objective is to obtain a better fundamental physical understanding of the interaction processes and to develop theoretical models with predictive capabilities. Currently, three experimental premixed flame configurations are used: (1) a rod-stabilized turbulent v-flame, (2) a Bunsen-type conical turbulent flame, and (3) a turbulent flame stabilized in stagnation flow. The experimental configuration for the nonpremixed turbulent flame study consists of a jet flame burner. Space- and time-resolved statistical data on scalar and velocity fluctuations are measured to study the effects of large heat release on the turbulent flow field, in particular, the role of combustion in generating turbulence. Also determined are empirical parameters (such as mean reaction rates and turbulent burning speed) significant to theories of turbulent combustion. In addition, two-dimensional laser imaging techniques are being developed to determine the scales of the flame structures. The experimental results are used to validate predictions made by a deterministic theoretical simulation of premixed turbulent flames developed by Lawrence Berkeley Laboratory and predictions obtained from the statistical model of Bray and Libby. [3.0 FTE]

Materials and Chemical Sciences Division $164,000

126. High-Pressure Phase Equilibria in Hydrocarbon–Water (Brine) Systems

Prausnitz, J.M.
Comm. 415-642-3592

Phase equilibria are required for design of efficient large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries. In this context, "efficient" refers to optimum use of raw materials and conservation of energy. Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all desired 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. Particular attention is given to those systems that are of interest in energy-related industries, e.g., those concerned with fossil fuels and fossil fuel–water mixtures, (including aqueous waste streams) and those concerned with specialty chemicals and with high-value chemicals produced by enzyme-catalyzed processes (biotechnology). Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it demands simultaneous awareness of progress in molecular science and of realistic requirements for engineering design. [1.8 FTE]

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

Theoretical Division $85,000

127. Thermophysical Properties of Mixtures

Erpenbeck, J.J.
Comm. 505-667-7195; FTS 843-7195

The thermophysical properties of mixtures of particles interacting through the hard-sphere potential (and other simple interactions) are evaluated, using the equilibrium techniques of Monte Carlo (MC) and molecular dynamics (MD), as well as nonequilibrium molecular dynamics (NEMD). Properties under investigation include both the equation-of-state and transport properties. The latter include 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" seem appropriate. In addition, the merits of the various numerical techniques are considered in providing thermophysical properties. MCMD calculations have been initiated for binary hard-sphere mixtures (50–50) having a mass ratio of 0.03 and a diameter ratio of 0.4. These values match those for mixtures of helium and xenon. Both equation-of-state and transport properties have been obtained for fluid densities ranging from low to moderate, establishing that the results approach the theoretical low-density limit, as a necessary condition in establishing the reliability of the calculations. The mode-coupling theory has been applied to mixtures to obtain the longtime behavior of the time-correlation functions which enter the Green–Kubo formulae for mutual diffusion, thermal conductivity, thermal diffusion, and viscosity. These theoretical estimates are needed to make longtime corrections to the Green–Kubo integrands for the transport coefficients. [0.5 FTE]

Sandia National Laboratories
Livermore, CA 94551-0969

Combustion Research Facility $357,000

128. Analysis of Turbulent Reacting Flows

Ashurst, W.; Kerstein, A.R.; Marx, K.D.
Comm. 415-294-2274; FTS 234-2274

The goal of this project is to develop numerical simulation techniques for the understanding of turbulent reacting 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 have revealed vorticity generation in a premixed flame–vortex interaction which may be the source of increased turbulence in the product gases. Simulations of a diffusion flame near a vortex indicate that a flame tip is formed and the tip may have the highest temperature. Pollutant formation may thus be larger in the flame tip region. Computational modeling of multiphase reacting flow focuses on the development and validation of finite-difference solutions of the Reynolds-averaged Navier–Stokes equations with a Lagrangian model for multiphase flows, including the large-scale behavior of swirling flows with sprays. Results from these tasks 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

129. *Dynamics of Charge Transfer Excited States Relevant to Photochemical Energy Conversion*

Lim, E.C. **$93,669**
Comm. 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, etc.). Novel biphotonic, as well as more conventional monophotonic, laser excitation schemes are used to create intramolecular ion pairs in these species. The time- and energy-resolved spectra of the ion pairs 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

130. *Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids*

Kispert, L.D. **$78,624**
Comm. 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. Recent 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. Studies of isotopic substitution indicate that the short lifetime is a result of nonradiative decay mechanisms within the carotenoids. Additionally it was discovered that the lifetimes of electrochemically prepared carotenoid cation radicals as studied by EPR techniques are critically dependent on solvent and are longest in CH_2Cl_2. Semiempirical molecular orbital calculations of the minimum energy structure of the carotenoid cation radicals, singlet and triplet excited states, have been completed and are being used to interpret electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) measurements. 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

131. *Photoinitiated Electron Transfer in Multichromophoric Species: Synthetic Tetrads and Pentads Featuring Diquinone Moieties*

Gust, J.D., Jr.; Moore, T.A.; **$157,000**
Moore, A.L.
Comm. 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

132. *Photochemical Energy Conversion by Membrane-Bound Photoredox Systems*

Tollin, G. **$103,530**
Comm. 602-621-3447

Mechanisms of photochemical electron transfer in chlorophyll-containing lipid bilayer vesicles are being investigated using laser flash photolysis techniques. Current effort is being spent on developing strategies for use of redox proteins as electron donors and acceptors, and on studies of the mode of interaction of such proteins with lipid bilayers using nuclear magnetic resonance (NMR) 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 mediators and several redox proteins in a linear sequence. 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.

Boston University
Boston, MA 02215

Department of Chemistry

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

Hoffman, M.Z. **$93,670**
Comm. 617-353-2494

Coordination complexes of Ru(II), especially those possessing aromatic α-diimine ligands, play an important role 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, and continuous and pulsed photolysis and radiolysis, 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) preparation and characterization of Ru(II)-tris-homo- and heteroleptic complexes containing bpy (= 2,2′-bipyridine), bpz (= 2,2′-bipyrazine), bpm (= 2,2′-bipyrimidine), bpd (3,3′-bipyridazine), and bpr (4,4′-bipyrimidine); (2) cage escape yields in the oxidative and reductive quenching of the excited states of Ru(II) complexes as a function of the energy gap between the redox products and the nature of the solution medium; (3) comparison of analogous Ru(II) and Cr(III) complexes; (4) the acid-base, electron-transfer, and electrochemical properties of one-electron reduced Ru(II) complexes; and (5) ion-pairing of Ru(II) complexes studied by NMR.

134. *Photoinduced Electron Transfer in Ordered Polymers*

Jones, G. **$98,600**
Comm. 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 which 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.

Bowling Green State University
Bowling Green, OH 43403

Center for Photochemical Sciences

135. *Photoinduced Charge Separation by Polymer-Bound Chromophores*

Rodgers, M.A.J. **$55,000**
Comm. 419-372-7606

Photoinduced charge separation between amphiphilic copolymers composed of methacrylic acid with covalently bound chromophore residues of diphenylanthracene and pyrene at 1% loading, and methylviologen are the subject of this work. Previous work has shown that in acidic aqueous solution where the polymer chain assumes a coiled conformation, significant charge separation occurs on the submicrosecond time scale for the diphenylanthracene copolymer, but not for the pyrene copolymer. However, in basic solution, where the polymer becomes an extended chain polyelectrolyte, neither copolymer shows any charge separation on the sub-microsecond time scale. The major effort to date has been to examine the above systems on the sub-nanosecond time scale using a picosecond absorption spectrometer. The experimental data obtained thus far confirm earlier observations. The diphenylanthracene copolymer in acidic solution displays a time-dependent formation of the initial ion pair, which has a rise time of ca 400 ps. The pyrene copolymer shows no formation of charge-separated products. In basic solution both systems show an immediate reduction in the absorption caused by the S_1 state with no formation of charge-separated products. This implies a static quenching mechanism that occurs within the time resolution of the apparatus.

Brandeis University
Waltham, MA 02254

Department of Chemistry

136. Mechanistic Studies of Excited State Chemical Reactions

Linschitz, H. **$88,740**
Comm. 617-736-2506

This research is designed to clarify the factors that control the efficiency of the primary stages of energy conversion in photochemical electron-transfer reactions. This involves the measurement of primary quantum yields of redox photoproducts in homogeneous solution, as functions of such relevant parameters as the free enthalpy of the excited state reaction (ΔG^*), solvent polarity and viscosity, spin-orbit coupling in the intermediate exciplex, temperature, and external fields. The current emphasis concerns the role of ΔG^* and solvent polarity. Laser flash photolysis is used to identify excited (triplet) intermediates and transient photoproducts and to determine yields. Necessary experimental parameters (transient spectra and molar extinctions) are measured by appropriate means. Test systems include porphyrins and oxidants (quinones and nitroaromatics) and arylketones and reductants (amines and anisoles).

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

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

Lewis, N.S. **$138,000**
Comm. 818-356-6335

The focus of the research is in three areas: (1) to understand the chemical nature of the semiconductor/liquid interface; (2) to develop working curves for the cyclic voltammetric behavior of semiconductor electrodes; and (3) to understand the short wavelength spectral response of n-Si/liquid junctions. In the first area, the chemical modification of the electrically active trap sites at important semiconductor surfaces has been investigated. Angle-resolved X-ray photoelectron spectroscopy (XPS) experiments were performed on single crystal (100) n-GaAs surfaces treated with a series of aqueous cobalt metal complexes at pH > 9. The XPS results demonstrated that Co(III) complexes were reduced to the Co(II) state. Cobalt K adsorption edge and Extended X-ray Absorption Fine Structure (EXAFS) studies on powers of GaAs exposed to aqueous Co(III) amine complexes at pH > 9 were performed. The edge adsorption position and structure are consistent with an assignment of Co(II). The EXAFS results were extremely similar to EXAFS data taken on bulk $Co(OH)_2$. The second area of research involves the cyclic voltammetry of semiconductors. Simulations were performed using a model circuit under varying levels of illumination and for different values of the diode barrier height and voltage scan rate. It has been demonstrated that the key parameter is the impedance ratio of the open circuit impedance of the diode to the maximum faradaic impedance in the circuit. A general set of working curves was derived. The third area of research utilized short wavelength photons to study the interfacial kinetics of semiconductors. The interfacial properties of an n-Si/MeOH-$LiClO_4$-Me_2Fc^+\0) liquid junction are different from that of an n-Si Schottky barrier device. All data agree with the theoretical formulation for interface kinetics proposed by Reichmann and Green.

University of California
Berkeley, CA 94720

Department of Chemistry

138. Theoretical Studies of Electron Transfer in Complex Media

Chandler, D.
Comm. 415-643-6821

The structures, distributions, 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.

University of California
Irvine, CA 92717

Department of Chemistry

139. Research in Chemical Kinetics

Rowland, F.S. **$175,000**
Comm. 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, ^{38}Cl, and ^{18}F 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. These non-RRKM systems furnish excellent illustrations of the heavy-atom effect, in which a large central atom (Sn, As) makes energy transfer from one ligand to another extremely difficult. Additional experiments on ^{38}Cl reactions with polyvinyl compounds are planned for molecules containing central atoms ranging in mass from silicon to lead. Experiments are also being conducted with thermalized tritium atom addition reactions to look for possible non-RRKM intramolecular energy transfer in similar systems. Laser analytical detection is being tested for isotopic variants of CH_4 and CO in typical atmospheric concentrations to determine whether $^{13}C/^{12}C$ ratio data are useful in such studies. Separation procedures are being developed to provide purified 100 to 200 microgram quantities of carbonaceous atmospheric molecules suitable for ^{14}C determination with accelerator mass spectrometry.

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

Valentini, J.J. **$83,810**
Comm. 714-856-6142

This research project focuses on studies of the dynamics of chemical reactions and energy transfer collisions at hyperthermal energy. This effort is primarily experimental, with an emphasis on measurements of the state-to-state dynamics of the hyperthermal collisions. A smaller component of the program involves calculations aimed at providing a theoretical description of the collision dynamics. Among the systems that are currently under investigation in this laboratory are the hydrogen atom abstraction reactions, $H + RH — R + H$, where RH = methane, ethane, or propane, the accompanying energy transfer processes, $H + RH \rightarrow RH^{\dagger} + H$, where the dagger indicates internal excitation, and the reaction of $OH + H_2 \rightarrow H_2O + H$. In these experiments translationally hot atomic and molecular free radical reactants are generated via pulsed-laser photolysis. The collision energy is selected by variation of the photolysis wavelength and the identity of the precursor. The quantum state distributions of the products of the reactions are detected under single-collision conditions by highly time-resolved pulsed-laser spectroscopy. Anticipated experiments will use stimulated Raman excitation to prepare the molecular reactant in a specific vibrational excited state. The computational part of the work, which uses quasi-classical trajectory calculations, is designed to complement the experimental studies, providing a means to interpret in detail the experimental results.

University of California
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

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

El-Sayed, M.A. **$128,180**
Comm. 213-825-1352

The conversion of solar energy into chemical energy (ATP) by the other photosynthetic system in nature, bacteriorhodopsin (bR), involves five main steps: (1) 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 (ADP → ATP) transformation. These studies deal with steps one to three. The function of the protein during the photocycle has been examined in a systematic (but indirect) study of fluorescent protein molecules (i.e., tryptophan, TRP). The observed intensity and lifetimes of the TRP molecules in bR have been studied using picosecond streak camera fluorescence techniques. The number of different TRP sites is determined and their intensity changes are followed for bR and under different perturbations (e.g., temperature and pH changes, removing lipids and metal cations). All the observed changes are found to be controlled by the protein conformation changes under the different perturbations. From the results of these and other studies, the conclusion is reached that the deprotonation process [process (3) above] involving site-selective mutagenic substitution of different amino acids, which is found to strongly correlate with the strongest quenching of the TRP fluorescence, is controlled by the interaction between the surface potential and the internal structure of the protein at the active site.

University of California
Santa Barbara, CA 93106

Department of Chemistry

142. *Energy Transformations in Organometallic Complexes*

Watts, R.J. **$123,250**
Comm. 805-961-2032

This research identifies metal complexes that could have application as photocatalysts in photoconversion processes. Primary emphasis is placed on the preparation and characterization of new organometallic species formed in ortho-metalation processes, including studies of complexes of d^6 metal ions including Ir(III), Rh(III), and Ru(II) as well as d^8 metal ions such as Pt(II), Pd(II), and Au(III). Additional research to explore the preparation and characterization of complexes containing metal–silicon bonds has recently been undertaken. This work is focused on complexes that are structurally similar to the organometallic species under study and is intended to provide insight into what new photocatalytic properties might be associated with metal–silicon-bonded species in comparison to those that contain metal–carbon bonds. Chemical synthesis is used as a starting point in preparing ligands that are then used to form complexes containing either metal–carbon or metal–silicon bonds. These ligands are generally intended to explore the manner in which particular properties of a metal complex (such as redox potential, photoreactivity, luminescence lifetime, solubility, etc.) can be modified by the ligand. Once prepared and purified, these species are structurally characterized by a variety of physical techniques, including NMR and infrared spectroscopies as well as X-ray crystallography. Structural information regarding excited states is sought largely with laser-based spectroscopic techniques including emission, time-resolved emission, and excited-state absorption spectroscopies. After their excited-state properties have been established, these materials are excited in the presence of selected substrates in order to establish their excited-state reactivities. Studies of excited-state electron transfer processes are emphasized because of the importance of these types of reactions in many known photoconversion schemes. In this context, several of the ortho-metalated complexes of Ir(III) that are being studied are among the strongest photoreducing agents presently known.

Clemson University
Clemson, SC 29634-1905

Department of Chemistry

143. *Intramolecular Energy Transfer Reactions in Polymetallic Complexes*
Petersen, J.D. **$78,880**
Comm. 803-656-3220

Preparation of the complexes $RhH_2(PPh_3)_2L^+$, $[RhH_2(PPh_3)_2]_2L^{2+}$, and $(bpy)_2RuLRhH_2(PPh_3)_2^{3+}$ where L is 2,2′-bipyrimidine (bpm), 2,3-bis(2′-pyridyl)pyrazine (dpp), and (2,3-bipyridyl) quinoxaline (dpq), as well as the monometallic analogs $RhH_2(PPh_3)_2en^+$ and $RhH_2(PPh_3)_2bpy^+$ (en = ethylenediamine and bpy = 2,2′-bipyridine) have been completed. All of the complexes undergo photochemically induced reductive elimination of molecular hydrogen when irradiation at wavelengths equal to or shorter than 405 nm for the monometallic complexes and equal to or shorter than 436 nm for the bimetallic complexes. In addition the monometallic rhodium complexes and the heterobimetallic (RuLRh) complexes undergo emission in fluid solution at room temperature from a state different than the photoactive state. In the case of the heterobimetallic complexes, the photoemissive state is best described as a Ru-based metal-to-ligand charge transfer (MLCT) state while the photoreaction is assigned as a Rh-based ligand-field (LF) state in all of the complexes studied. Luminactive (luminescent and photoactive) monometallic and bimetallic complexes involving the ligand 3,5-bis(2′-pyridyl)-1,2,4-triazole (Hbpt) and its deprotonated form have also been studied. In the case of the monometallic complexes, $[RhH_2(PPh_3)_2H_nbpt](PF_6)_n$ (n = 0 and 1), both display luminescence and undergo loss of H_2 at room temperature in ethanol. The bimetallic complex, $(bpy)_2Ru(bpt)RhH_2(PPh_3)_2^{2+}$, undergoes photochemistry from a rhodium-based, ligand-field (LF) excited state and emission from a ruthenium-based metal-to-ligand charge-transfer (MLCT) excited state.

University of Colorado
Boulder, CO 80309

Department of Chemistry and Biochemistry

144. *Investigation of Redox Processes at Semiconductor Electrode/Liquid Junctions*
Koval, C.A. **$83,810**
Comm. 303-492-5564

Three subjects relating to electron transfer reactions that occur at semiconductor-solution interfaces (SEI) are being investigated: (1) development of solution redox systems capable of detecting hot electron reactions, (2) current measurements at ideal SEI interfaces to determine factors that control dark currents, and (3) theoretical formulations of image potentials and reorganization energies for ions near the SEI. Multivariate experiments involving reduction of a Cu(I) complex ion to copper metal at the p–InP/acetonitrile interface were used to demonstrate that this process appears to involve direct reaction of hot electrons with Cu(I). Current research involves reduction of organotin compounds, which form soluble products, at rotating ring/disk p–InP photocathodes. An electrochemical microcell for investigating dark electron transfer at ideal, metal chalcogenide semiconducting electrodes has been constructed and tested. Rates for reduction of metallocenes at n-type tungsten selenide and tin sulfide are being compared. Nonlocal electrostatics were used to investigate the image potential at the SEI theoretically. These results are being incorporated into a computer simulation of interfacial electron transfer.

Columbia University
New York, NY 10027

Department of Chemistry

145. *Laser-Enhanced Chemical Reaction Studies*
Flynn, G.W. **$123,250**
Comm. 212-854-4162

This project employs extremely high resolution infrared diode lasers to study fundamental combustion and collision dynamics and photochemical reaction processes. High-energy atoms and chemically reactive radicals, produced by excimer laser photolysis, are used as reagents to investigate collisional excitation 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 infrared transitions. Chemical reactions between hot Cl atoms and stable molecules are monitored with quantum state resolution using this diode laser probe method. Reaction between deuterated cyclohexane and Cl atoms produces a DCl product with cold rotational but hot translational degrees of freedom. This suggests a reaction mechanism in which the DCl recoils collinearly along the C–D–Cl axis. Such a mechanism has been observed previously for combustion reactions involving H atom abstraction from hydrocarbons by O atoms. A similar experimental approach is being used to investigate the chemical dynamics of the reaction between OH radicals and CO moelcules to give CO_2 and H atoms. Highly energetic and reactive O(^{1}D) atoms with 0.67 eV of translational energy are quenched by CO_2 through a variety of physical and chemical mechanisms. A significant fraction of the electron energy of the atom appears to be funnelled into rotational and translational degrees of freedom. A very small amount of the electronic energy goes into CO_2 asymmetric stretch vibrational excitation, and a slightly larger amount goes into CO_2 bending vibrational excitation.

Department of Electrical Engineering and Applied Physics

146. *Photogenerated Carrier-Induced Reactions of Semiconductor Surfaces*

Osgood, R.M., Jr. **$49,300**
Comm. 212-854-4462

The objective is to study solid-gas reactions initiated by photogenerated carriers. Focus is on the GaAs/Cl_2 system, since dry laser etching of GaAs has been demonstrated in ambient Cl_2 gas. This work will be done on clean, well-defined, GaAs single crystal in ultrahigh vacuum. Time-of-flight mass spectrometry will be used to study the products emitted to the gas phase, as a function of photon energy and laser light polarization. The reaction dependence on wavelength will help determine whether it occurs via excitation of the adsorbed chlorine or the substrate's bulk. If carriers are indeed involved, the question of whether or not they have to be hot will be addressed. The dependence on laser polarization should tell whether their initial direction in k space is of any importance. Photoreflectance measurements will be used to estimate the band bending near the surface with and without adsorbed chlorine at different crystal temperatures and crystal dopings. Temperature desorption spectroscopy (TDS) will be used to distinguish between physisorbed and chemisorbed chlorine species and to determine energy barriers to chlorine desorption as a function of coverage. These barriers will be compared with the barrier for carrier transport to the surface caused by band bending. The ratio between the amount of chemisorbed to physisorbed species, after illumination of chlorine-covered GaAs sample, will be studied as well. Additional effort will be directed toward studying the carrier transport across a thin metal layer deposited on a semiconductor face. The ultraviolet laser-induced reaction of dimethyl cadmium, chemisorbed on thin cadmium film that has been evaporated on GaAs and Si samples, will be examined.

Dartmouth College
Hanover, NH 03755

Department of Chemistry

147. *Photoexcited Charge Pair Escape and Recombination*

Braun, C.L. **$73,950**
Comm. 603-646-2500

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is studied in solids and liquids. Two experimental approaches are used to resolve the picosecond time scale recombination of the geminate charge pairs formed by laser photoionization of solute molecules in liquid hexane. A pump-probe conductivity technique gives useful results but appears to introduce modest measurement bias when compared with decay kinetics recorded by the less-sensitive transient absorption method. 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 ionization does not originate from the relaxed charge-transfer excited state that is observed by fluorescence to have a lifetime of 12 nanoseconds. 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 77204-5641

Department of Chemistry

148. *Charge Separation in Photoredox Reactions*

Kevan, L. **$118,320**
Comm. 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 chlorophyll, metalloporphyrins, phenothiazines, phenothiazine sulfonates 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. In the last year a newly synthesized series of alkylphenothiazine sulfonates has been studied. Changes in location can be monitored by electron spin echo modulation spectroscopy. The photoionization efficiency is being assessed by electron spin resonance intensities. This work is leading to the general objective of molecular control of the photoinduced charge separation efficiency.

Louisiana State University Baton Rouge, LA 70803-0301

Department of Chemistry

149. *Theoretical Studies of Electrons and Electron Transfer Processes in Fluids*
Kestner, N.R. **$65,000**
Comm. 504-388-1528

This research project studies electrons and electron-transfer processes in fluids, especially those important in energy conversion and storage. Some of the studies deal with small clusters of various polar molecules (water, ammonia, alcohols) where the calculations can be more accurate. These are then related to properties and reactivities in bulk liquids. Current work focuses on the role of temperature and pressure on mobility and reactivity, and on time dependence as well as the role of other hydrated ions like sodium which are often present in solution. Related research is also under way to calculate the structure and electron-transfer rates for hydrated and ammoniated transition-metal ions such as iron and ruthenium. The distortions of their ligand structure obtained in molecular simulations appear to confirm the geometry found in differential neutron diffraction studies. As part of this work, fast Fourier transform techniques for solving one-electron Hamiltonians are being coupled to molecular dynamics routines to obtain media effects on a variety of electronic and vibrational spectra.

Marquette University Milwaukee, WI 53233

Department of Chemistry

150. *Resonance Raman and Photophysical Studies of Transition Metal Complexes in Solution and Entrapped in Zeolites*
Kincaid, J.R. **$82,000**
Comm. 414-288-3539

Normal coordinate calculations for both the ground and ^{3}MLCT (metal-to-ligand charge transfer) excited states of the parent complex, $Ru(bpy)_3^{2+}$ have been completed. The results were used, in conjunction with a recently developed procedure for decomposition of normal modes into individual diatomic stretching coordinates, to extract ground-to-excited-state bond length changes. The results are in excellent agreement with predictions based on theoretical considerations and comparison with ^{3}MLCT-state model compounds. A systematic resonance Raman and time-resolved resonance Raman study of the two bis-heteroleptic, tris-ligated Ru^{2+} complexes comprised of bipyridine and bipyrazine has been completed. The results clearly demonstrate specific population of bipyrazine-localized excited states for both heteroleptic analogues. Similar studies of other heteroleptic complexes with various bipyridine analogues are continuing. In addition, the detailed characterization of the ground- and excited-state structures and reactivity of complexes in organized media have been initiated.

Massachusetts Institute of Technology Cambridge, MA 02139

Department of Chemistry

151. *Interfacial Systems for Photochemical Energy Conversion*
Wrighton, M.S. **$266,220**
Comm. 617-253-1597

The objective of this research project 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) surface-confined biocatalysts (to exploit and understand multielectron-transfer processes of importance in fuel-forming photoreactions); (3) multicomponent redox molecules (to mimic the essential functions of natural photosynthesis of light absorption, charge separation, and charge transport); and (4) surface modification reagents (to tailor the properties of electrodes used in photoconversion processes). Unique surface chemistry of semiconductors has led to efficient photoconversion devices. Preliminary results show promising leads in molecular approaches to photoconversion which theoretically will be no less efficient than semiconductor-based devices. Molecular systems under study include donor–chromophore–acceptor molecules such as covalently linked ferrocene–porphyrin–viologen systems capable of being linked to electrode surfaces.

University of Massachusetts Boston, MA 02125

Department of Chemistry

152. *Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions*
van Willigen, H. **$90,000**
Comm. 617-287-6147

The factors that affect the rate of photoinduced electron transfer from excited-state porphyrin molecules to acceptor molecules are studied with the aid of electron spin resonance (ESR) techniques. Measurements give information on the structure of precursor porphyrin photoexcited triplets, aid the identification of redox ion products, and provide kinetic data. Electron donor molecules being studied are tetraphenyl porphyrin (TPP), various metal substituted TPPs, and water-soluble TPPs. Acceptor molecules of interest include various benzoquinones and potassium ferricyanide. To be able to investigate the kinetics, equipment was built for the performance of time-resolved ESR measurements on transient free radicals with a lifetime as short as 1 microsecond. With this equipment, it is possible to investigate the factors that affect reactions that proceed at close to diffusion-controlled rates. During the past year a Fourier Transform (FT) ESR spectrometer has been constructed. With this instrument the dynamics of excited-state electron transfer can be followed with nanosecond time resolution. FT-ESR measurements give data on the kinetics of redox product formation and decay. The measurements also give information on spin-state dynamics in transient intermediates.

Of particular interest is that the FT-ESR spectra give data on the characteristics of radical pairs involved in the electron-transfer process.

University of Minnesota
Minneapolis, MN 55455

Department of Chemistry

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

Lipsky, S. **$92,688**
Comm. 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 fluoresence induced by pulsed vacuum ultraviolet excitation of cyclohexane + anthracene solutions (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 neopentane + anthracene solutions. From this data are developed for theoretical modeling of the nature of the ionizing transition in liquids.

National Institute of Standards and Technology
Gaithersburg, MD 20899

Chemical Kinetics Division

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

Neta, P. **$192,270**
Comm. 301-975-5635

The pulse radiolysis technique is applied to the study of electron transfer processes in a variety of chemical systems. Reactive intermediates are produced in solution by electron pulse irradiation and the kinetics of their reactions are followed by time-resolved absorption spectrophotometry. These studies are concerned with mechanisms, kinetics, and thermodynamics of reactions of organic and inorganic radicals and unstable oxidation states, in aqueous and nonaqueous solutions. For studies of aqueous solutions, emphasis is focused 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. For studies in nonaqueous solutions, pulse radiolysis is used for kinetic measurements as well as for unraveling the basic radiation chemistry of certain solvents. 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 one-electron reduction and oxidation of metalloporphyrins to radical-anions and -cations or to unstable oxidation states and the subsequent reactions of the resultant species. Important reactions of these species are those with colloidal catalysts that may lead to solar energy storage (e.g., to decomposition of water to hydrogen and oxygen). For these studies, pulse radiolysis is used to characterize specific reactions and photochemical experiments are carried out on the whole system to measure the yields of products.

University of North Carolina at Charlotte
Charlotte, NC 28223

Department of Chemistry

155. *Oligomer and Mixed-Metal Compounds, Potential Multielectron Transfer Agents*

Rillema, D.P. **$93,000**
Comm. 704-547-4445

The design and synthesis of potential solar energy photocatalysts is the focus of the investigation. New classes of photoactive complexes have been isolated. These are tetracarbonyl complexes of rhenium(I), biphenyl complexes of platinum(II), and a bimetallic complex of rhenium(I) and ruthenium(II). The rhenium(I) tetracarbonyl complexes contained the ligands 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, 2,2′-bipyridine and 2,2′-bipyrimidine. The excited state lifetimes of these complexes in fluid solution at room temperature ranged from 390 to 4050 ns. The platinum(II) biphenyl complexes containing the ancillary ligands diethylsulfide, acetonitrile, pyridine, and ethylenediamine also luminesced in fluid solution at room temperature and their excited state lifetimes varied from 4 to 14 μs. Emission in the rhenium(I) complexes was ^{3}MLCT based; emission in the platinum(II) complexes was ^{3}CT based. Both the rhenium(I) and platinum(II) complexes underwent excited state electron transfer. A system that appears to be a model for energy transfer was isolated and contained the metals ruthenium(II) and rhenium(I). The metals were bridged by 1,2-bis(4,′-methyl-2,2′-bipyridyl-4-yl)ethane. The bimetallic complex luminesces at 540 and 610 nm in methylene chloride at room temperature. The luminescence at 540 nm was derived from the rhenium component and the one at 610 nm was derived from the ruthenium component. Enhanced luminescence at the ruthenium site was noted at the expense of the rhenium component.

University of North Carolina
Chapel Hill, NC 27599-3290

Department of Chemistry

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

Meyer, T.J. **$145,000**
Comm. 919-962-6319 **(14 months)**

The photochemistry of transition-metal complexes is being explored with respect to energy conversion processes at the molecular level. It has been possible to incorporate sensitizers and quenchers (e.g., transition metal polypyridyl complexes and/or organic fragments) into soluble polymers with control of loading via chemical binding to the backbone. Studies on these complex arrays indicate that it is possible to design polymers in which light-induced energy and electron-transfer events on a polymer can be initiated. The considerable synthetic versatility of these systems makes it possible to tune their excited-state properties and to control their energy/electron transfer processes. A related theme is the detailed study of the underlying photophysics of transition metal complex sensitizers. A systematic understanding of medium and solvent effects on excited-state properties is leading to the design of more ideal sensitizers. Analysis of emission spectral profiles and resonance Raman data are providing considerable insight into excited-state properties (e.g., nature of structural distortions in the excited-state, preference for radiative vs nonradiative decay, etc.).

Northwestern University
Evanston, IL 60208-3113

Department of Chemistry

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

Hupp, J.T.
Comm. 708-491-3504

This project involves: (1) construction of pulsed-accelerated flow and pulsed-laser instruments for fast electron-transfer rate measurements; (2) invention and synthesis of multiple-site target molecules for intramolecular rate studies; (3) application of time-dependent Raman scattering theory to the question of inner-shell reorganization in charge-transfer reactions; and (4) further development of electrochemical methods for gauging electronic coupling. A key accomplishment in the past year has been the direct measurement of intramolecular electron transfer (ET) rates in $(bpy)_2ClOs^{III}$–4,4′bpy–$Ru^{II}(NH_3)_5^{4+}$ (bpy is 2,2′bipyridine; 4,4′-bpy is 4,4′bipyridine). The measurements were based on optical intervalence pumping in the near infrared to give Os^{II}–4,4′bpy–Ru^{III}; this species then relaxes back in a thermal ET process which can be followed by visible-region transient absorbance. The results are significant, in part, because they permit both optical and thermal charge-transfer events to be monitored within the same chemical system. It another area, Raman spectroscopy, the first observations of surface intervalence enhanced scattering (not SERS) have been made. The system is $Os(CN)_6^{4-}$ bound to colloidal TiO_2. From the experiment and subsequent time-dependent analysis one obtains a remarkable result: a complete mode-by-mode description of the vibrational Franck–Condon barrier for interfacial transfer of an electron from Os^{II} to the semiconductor.

Ohio State University
Columbus, OH 43210

Department of Chemistry

158. *Photoinduced Electron Transfer Reactions in Zeolite Cages*

Dutta, P.K. **$84,000**
Comm. 614-292-4532

Zeolites are crystalline aluminosilicates containing channels and cavities of dimensions varying from 2 to 13Å. The structure and reactivity of molecules within the zeolite are influenced by the architecture, electrostatics, and mobilities in the unique microreactor environment. The aim of this study is to understand the influence of the zeolite on the photoelectron transfer between $Ru(bpy)_3^{2+}$ and methylviologen occurring within its cages. The interest in this reaction stems from the possibility of using visible light to bring about a redox reaction. However, the problem that needs to be solved is the separation of the redox products before the wasteful and efficient back reaction can occur. The strategy outlined here will be to trap the $Ru(bpy)_3^{2+}$ in the supercages of zeolite Y, where translational mobility is nonexistent, but where the molecules do have the freedom to rotate. Photoelectron transfer from these trapped $Ru(bpy)_3^{2+}$ to methylviologen in neighboring cages separated by a 7Å window will be examined. The environment in the zeolite can be readily altered by changing levels of hydration, presence of nonpolar solvents, cations of varying charge, and Si/Al ratio. The influence of these parameters on the photoelectron transfer reaction will be examined. Various spectroscopic techniques, including steady-state and time-resolved absorption, emission, Raman, and lifetime measurements are being used to probe the structure and kinetics of the $Ru(bpy)_3^{2+}$-methylviologen system.

Oregon Graduate Institute of Science and Technology
Beaverton, OR 97006

Department of Chemical and Biological Sciences

159. *Fundamental Studies in Oxidation-Reduction in Relation to Water Photolysis*

Hurst, J.K. **$100,000**
Comm. 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.

Pennsylvania State University
University Park, PA 16802

Department of Chemistry

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

Lampe, F.W. **$83,810**
Comm. 814-865-3029

This research project includes four activities. The first activity will develop an understanding of the chemical kinetics and mechanisms involved in the gas-phase photochemical decompositions of silane, germane, and phosphine systems. Emphasis is on the reactions of silylene, silyl, germylene, and germyl radicals with silane, germane, and phosphine, as well as with each other and with various inorganic and organic substrates. The second activity involves (1) elucidation of the ion–molecule reactions characteristic of ionized silane, germane, and phosphine, and silane–germane, silane–carbon monoxide, germane–phosphine, germane–hydrogen, and germane–water mixtures and (2) measurement of the pertinent rate coefficients and cross sections. Such knowledge is critically important in understanding and modeling the immensely complex chemistry involved in electrical discharge and plasma chemistry. The third activity involves (1) acquisition of kinetic and thermochemical data, particularly in regard to silanes, germanes, and phosphines and (2) advancement of understanding of the kinetics and kinematics of elementary chemical reactions in general. The fourth activity will investigate the formation of thin films of amorphous silicon (a-Si:H) produced by the low-intensity γ-ray irradiation of silane admixed with noble gases.

161. Experimental and Computational Studies of Polar Solvation

Maroncelli, M. **$83,810**
Comm. 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

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

Waldeck, D.H. **$105,000**
Comm. 412-624-8430 **(15 months)**

This research program addresses the kinetics of charge carrier relaxation at the semiconductor-electrolyte interface. Because of the complexity of this interface a variety of tools, both optical and electrical, are used to characterize its structural properties in conjunction with the kinetic studies. The main emphasis of the research is on the relaxation of charge carriers at a semiconductor surface in contact with an inert electrolyte. The fundamental processes in this relaxation are characteristic of the processes that occur in heterogeneous redox chemistry and a second aspect of this project is to study heterogeneous redox chemistry. The initial studies have focused on the carrier relaxation in n–CdSe [a direct gap material (1.75eV)] in contact with 0.5M KOH solution. Preliminary studies have been performed under high injection conditions under which the band bending is minimized. A simple diffusion model for the hole dynamics is not appropriate for the material under these conditions. Computer simulation studies in conjunction with the experimental studies indicate that a finite lifetime of surface state traps could explain these observations. Before concluding that this process is present other possibilities are being explored such as the role of ambipolar diffusion and recombination of carriers in the space charge region.

Portland State University
Portland, OR 97207-0751

Department of Chemistry

163. *Asymmetric, Interfacially Polymerized Porphyrin Films for Artificial Photosynthesis*

Wamser, C.C. **$110,000**
Comm. 503-464-3811

This research 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-aminophenyl)porphyrin (TAPP) in DMSO with tetra(p-chlorocarbonylphenyl)porphyrin (TCCPP) in ethyl acetate, or from tetra(p-hydroxyphenyl) porphyrin (THPP) in aqueous base with TCCPP in chloroform, or from various aliphatic diamines in water with TCCPP in chloroform. Typical film thicknesses are in the range of 0.01 to 10 μm 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

164. *Surface Chemistry at Semiconductor-Electrolyte Interfaces*

Bocarsly, A.B. **$82,823**
Comm. 609-258-3888

This study involves the deliberate chemical modification of cadmium chalconide-based photoelectrochemical cell interfaces in order to arrest photodecomposition processes while enhancing the efficiency of light to electricity conversion. Recent work has focused on the surface chemistry of n–CdX (X = S or Se) photoelectrodes in a cyanometallate-containing electrolyte. Illumination of such interfaces produces a layer of cadmium metallocyanide on the electrode surface. This overlayer has alkali cation exchange properties. If $Fe(CN)_6^{4-/3-}$ is employed as the electrolyte, then iron sites in this layer are electroactive and support mediated charge transfer from the semiconductor to solution electroactive species. 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 the 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. However, the limiting photocurrent is found to be affected negatively by the variation. Formation of an overlayer containing both $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ appears to yield an optional result, producing maximum power conversion efficiencies. Once the cyanometallate overlayer has been formed and stabilized, substitution of ascorbate for the cyanometallate electrolyte produces an optically transparent electrolyte suitable for conversion of white light to electricity. To date, electricity conversion efficiencies of 6% have been observed for solar irradiation.

165. *Photochemistry of Metalloporphyrins*

Spiro, T.G. **$128,180**
Comm. 609-258-3907

The photochemistry of metalloporphyrins is being explored with a view toward developing new photoenergy transfer catalysts. Porphyrin cation radicals, the primary products of electron-transfer reactions, have been studied by resonance Raman spectroscopy. Band assignments have been secured via isotope shifts. They demonstrate distinctive vibrational patterns for radicals of different orbital character, a_{1u} and a_{2u}, and establish conclusively that octaethylporphyrins give a_{1u} radicals while tetraphenylporphyrins give a_{2u} radicals. Evidence of pseudo-Jahn–Teller mixing of ground and low-lying excited states (A_{1u} and A_{2u}) is provided by the appearance of anomalously polarized Raman bands that are strongly shifted from those of the neutral porphyrins. Time-resolved Raman techniques are under development in order to monitor the spectra of porphyrin excited states. The spectrum of triplet zinc tetraphenylporphyrin has been obtained, and assigned with the aid of isotopic data. Modified porphyrins have been synthesized in which donor and acceptor substituents are expected to stabilize charge transfer excited states having transiently reduced or oxidized central metal ions. Redox chemistry of these transient states, particularly hydrogen and oxygen atom transfer reactions, are being developed.

University of Rochester
Rochester, NY 14627

Department of Chemistry

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

Eisenberg, R. **$100,000**
Comm. 716-275-5573

This project focuses on the synthesis, characterization, and photochemistry of new square planar complexes of the platinum group elements which luminesce in fluid solution. Mononuclear complexes of this type are extremely rare, but would be useful as photocatalysts because of their inherent coordinative unsaturation. Current efforts have concentrated on Pt(II) complexes of the formula Pt(N–N)(S–S) where N–N is a diamine, bipyridine, or o-phenanthroline derivative and S–S is a 1,1- or 1,2-dithiolate ligand. The complexes are prepared from the corresponding $PtCl_2$(N–N) species and an alkali metal salt of the dithiolate. The absorption spectra of these systems exhibit an intense band at 450 to 490 nm which is highly solvatochromic and assigned as a charge transfer transition. The emission spectra for the 1,1-dithiolate systems in fluid solution are broad and asymmetric. At low temperature, evidence of multiple emitting states is obtained with the emergence of new emission bands ascribable to a diamine $\pi\pi^*$ state. Both lifetime and quantum yield measurements as functions of temperature have been performed for several of the complexes. The emitting state in these complexes, while not unambiguously established, appears to be a charge transfer state involving the metal and the dithiolate ligand. The ecda complexes (ecda = ethyl-2-cyano-3,3-dithioacrylate) have been studied most extensively because of their greater solubility. Electron transfer quenching of the emission of some ecda complexes has been observed to follow good Stern–Volmer kinetics using either a dialkylaniline donor or a nitrobenzaldehyde acceptor.

167. Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Solutions

Whitten, D.G. **$123,250**
Comm. 716-275-4231

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. In several cases, suitable location of the 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. Other areas of these investigations include a study of photochemically driven two-electron redox processes that can be thermally reversed on relatively long (hours or days) time scales.

University of South Florida
Tampa, FL 33620

Department of Chemistry

168. Frontier Orbital Symmetry Control of Intermolecular Electron Transfer

Stevens, B. **$78,880**
Comm. 813-974-2896

The synthesis and photophysical parameterization of linked electron–donor–acceptor (EDA) systems is being actively pursued. Typical donor and acceptor groups are $-NH_2$ and –CN respectively while –terphenyl or 9,9′–bianthryl are used as linkages. Several of these systems have an additional long-wave absorption band, absent in the unsubstituted linking molecules, and exhibit dual fluorescence characteristic of twist internal charge transfer (TICT) states. However, contrary to reported TICT state behavior, the long-wave fluorescence band is selectively quenched by polar molecules, including water, and the dynamics of this quenching process are currently under investigation to determine its physical (reversible) or chemical (irreversible) nature. Relative quantum yield data for electron acceptor fluorescence in the presence of electron donor quenchers (at concentration c) continue to be accumulated for analysis in terms of the Finite Sink Model expression for the quenching rate constant $k_Q(c)$, to obtain intrinsic rate constants k° for (electron transfer) quenching of the encountered donor–acceptor pair. Preliminary results indicate that k° is sensitive to both the dielectric constant and the viscosity of the supporting medium and the design of systems permitting the selective variation of one of these parameters now has priority. From the theoretical standpoint it has been shown that transient (van der Waals) intermolecular vibrations of appropriate symmetry in odd quantum states provide vibronically adiabatic channels for intermolecular electron transfer that is electronically diabatic in intermediate complexes belonging to the C_{2v} point group. Complexes of higher and lower symmetry are also being examined in this context, and the role of optically excited intramolecular vibrational modes of different symmetry will be explored.

Stanford University
Stanford, CA 94305

Department of Chemistry

169. Energy Transfer Processes in Solar Energy Conversion

Fayer, M.D. **$185,000**
Comm. 415-723-4446

Experimental and theoretical studies are being used to investigate fundamental problems in solar energy conversion. Electronic excitation transport and photoinduced electron transfer are examined with picosecond fluorescence and transient grating experiments. Dispersive excitation transport has been observed, for the first time, in a room-temperature system. Excitation transport has been described using the Foerster mechanism for room temperature and near-room-temperature samples for 40 years. Dispersive transport has only been observed at low temperatures (4 K). It was believed that dispersive transport could not exist in a room-temperature sample. By carefully studying the time dependence of fluorescence depolarization as a function of the excitation wavelength in an energy transport sample, it has been demonstrated that transport is dispersive. A detailed statistical mechanical theory has been developed which is capable of describing dispersive transport at or near room temperature with no adjustable parameters. The theory was compared to experiments for a variety of wavelengths and temperatures and was found to give a good representation of the data. The theory is capable of handling complex chromophore spatial distributions, and there is a "magic wavelength" at which the manifestations of dispersive transport vanish.

Syracuse University
Syracuse, NY 13244-1200

Department of Chemistry

170. *Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane Mimetic Systems*

Fendler, J.H. **$118,320**
Comm. 315-443-4146

Conversion of solar energy to chemical energy continues to be the main objective of this project. Components of the photosynthetic apparatus are being reconstructed in organized surfactant assemblies. Emphasis is on the development of separate sacrificial reduction and oxidation systems which result in the photodecomposition of water to hydrogen and oxygen, respectively. Colloidal semiconductor particles in surfactant vesicles and bilayer lipid membranes are used as sensitizers and catalysts, while advantage is taken of viologens as relays.

University of Tennessee
Knoxville, TN 37996-1501

Department of Chemistry

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

Williams, T.F. **$113,390**
Comm. 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. Radical cations are generated radiolytically in Freon matrices at low temperatures, while radical anions are similarly produced and stabilized in hydrocarbon matrices, the pertinent reactions involving positive-hole transfer and electron capture, respectively. Radical ions can also be generated photochemically by electron transfer to excited states of strong electron acceptors or by redox reactions on surfaces of semiconductor colloid particles such as titanium dioxide. Electron spin resonance (ESR) and optical spectroscopy are used to characterize these paramagnetic species; measurements of g factors and hyperfine coupling constants are being made on isotopically labeled radicals to obtain information about molecular geometry and spin density distribution. Specific projects include studies of (1) radical cation structure and solvent interactions; (2) unimolecular rearrangements (ring opening, hydrogen transfer, cyclization) and ion-molecule reactions of radical cations; (3) fluorocarbon and Freon negative ions, including dissociative processes leading to neutral radical formation; (4) the photogeneration of radical ions in solution and at colloidal semiconductor surfaces; and (5) photoinduced electrocyclic reactions of radical cations.

University of Texas
Austin, TX 78712

Department of Chemistry

172. *Organic Redox Phototransformations at Chemically Modified Surfaces*

Fox, M.A. **$108,460**
Comm. 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 N-alkylated nicotinamide derivatives 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 are being synthesized as vehicles for efficient light collection and vectorial energy migration.

173. *Electron Transfer Reactions in Microporous Solids*

Mallouk, T.E. **$100,000**
Comm. 512-471-5903

The purpose of this project is to explore the use of microporous crystalline solids as organizing media for vectorial electron-transport assemblies. In these systems, self-assembly of an artificial photosynthetic system from its molecular components is driven by ion-exchange equilibria, size-exclusion effects, and specific adsorption. Aluminosilicate particles (zeolites and pillared clays) have been covalently attached, by means of a cationic silane, to electrode surfaces. Ion-exchange with the appropriate combination of electroactive anions and cations, and with size-excluded cationic photosensitizers, gives an electrode that behaves electrochemically like a diode, transistor, or photodiode. The factors that determine the photocurrent efficiency of the latter are being studied. The photochemistry and electrochemistry of zeolites ion-exchanged with cationic electron acceptors and covalently linked photosensitizer-acceptor complexes are presently being investigated. In these systems attempts are being made to improve upon a previously demonstrated ca 15% quantum efficiency for long-lived light-induced charge separation, by varying the separation distances and energetics of the redox-active components. Quantum-size TiO_2/zeolite composites have been prepared in an effort to create systems in which the TiO_2 mediates light-induced electron transfer between surface-bound sensitizers and electron acceptors within the zeolite cavities. This work also involves fundamental studies of long distance electron transfer between molecules co-adsorbed on oxide semiconductor particles. The role that tunneling and/or superexchange via delocalized semiconductor orbitals plays in accelerating intermolecular electron transfer rates is being investigated.

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

Webber, S.E. **$100,000**
Comm. 512-471-3633

In this project polymethacrylic acid was prepared with small loadings of the aromatic chromophores phenanthrene and naphthalene (PMA-Ph and PMA-Naph respectively) and the quenching of the triplet state by the zwitterionic viologen (4,4′-bipyridinium-1,1′-bis(trimethylene sulfonate, SPV)) has been characterized. It was found that the quantum yield for separation of ion-pair states (i.e., $Ar^{+\cdot}$ and $SPV^{-\cdot}$) per electron-transfer quenching event (Φ_{ce}) exceeded 0.4 in all cases and, for favorable cases, approached unity. The optimal pH for *ion-pair separation was 6 for PMA-Ph* ($\Phi_{ce} = 0.9$) *and 11* for PMA-Naph ($\Phi_{ce} = 1.0$). The triplet yield was found to decrease dramatically with increased chromophore loading, which is believed to be the result of singlet-state self-quenching. PMA-Ph polymers with 0.6 mole % covalently bound anthracenes were examined and it was found that the sensitized triplet state of anthracene was also capable of efficient ion-pair separation following redox quenching. However it was also found that for high phenanthrene loadings the sensitization of the anthracene *triplet state was inefficient, despite a high efficiency of* singlet-state sensitization. In all cases the $SPV^{-\cdot}$ species was long-lived, in excess of 500 μs. The fate of the aromatic cation radical ($Ar^{+\cdot}$) is not clear but it seems likely that these species react irreversibly with water.

Washington State University
Pullman, WA 99164-4630

Department of Chemistry

175. Investigations of Charge-Separation Processes in Metal Complexes

Crosby, G.A. **$93,670**
Comm. 509-335-5605

Complexes of Zn(II), Cd(II), Pt(II), and Cu(I) are under *spectroscopic investigation. The systems contain both* donor and acceptor ligands coordinated to the same metal ion. One goal of the project is to determine the nature of the low-lying electronic excited states, which are assigned to be ligand-to-ligand charge-transfer in nature. The methods used are primarily luminescence spectroscopy, both time-resolved and steady-state, applied on the substances in various physical states over a range of temperatures. Thermal modulation is used for probing near-degenerate excited states (50 to 500 cm^{-1}). An important feature of these substances is the occurrence of multiple phases that exhibit widely different optical properties. X-ray structure determinations reveal the incidence of phenyl ring twisting. Extensive calculations are under way to ascertain the electron origins of the changes in luminescence and relate them to the phase changes. The goal is to relate these structural changes to the charge-separation process.

Wayne State University
Detroit, MI 48202

Department of Chemistry

176. Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates

Endicott, J.F. **$98,600**
Comm. 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 the migration of energy between donor and acceptors transition metal complexes. Research involves the design and synthesis of molecular systems to be used as mechanistic probes and the characterization of 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, 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 cyano-linked Rh(III) ammine 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 a 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. The behavior of the potential electron transfer systems, with Co(III) or Ru(III) am(m)ine acceptors, is more complex and the rate of regeneration of ground states in the Ru(III) ammine acceptor complexes is so rapid ($\leq$25ps) that discrete electron transfer steps may not be a feature of the relaxation sequence.

Chemical Physics

Aerospace Corporation
Los Angeles, CA 90009

Aerophysics Laboratory

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

Bott, J.; Cohen, N. **$78,771**
Comm. 213-336-7427

The project objective is to measure the rate coefficients for OH reactions of special importance 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 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. Experimental data on the rate of reaction of OH radicals with H_2, CH_4, i–C_4H_{10}, and c–C_5H_{10} have been determined. Rate coefficients have also been measured for the reactions of OH with acetone, methanol, ethylene, and ethanol. Experiments have been performed to determine the rate coefficient for the reaction of OH with methyl radicals (CH_3) and to determine the reaction path.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

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

Balasubramanian, K. **$89,726**
Comm. 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, and so forth, of these clusters and their reactivities vary dramatically with size. Many main group and transition metal clusters are under investigation. In particular, theoretical investigations of Au_4, In_4, Rh_3, Ag_4, Cu_4, and Pt_3 are being conducted. The properties investigated are geometries, ionization energies, electron affinities, and the separations of the low-lying electronic states. The electronic properties of metal dimers, such as Rh_2, Zr_2, Au_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 $M + H_2$ and $M_2 + H_2$. The potential energy surfaces of TcH_2, NbH_2, YH_2^+, ZrH_2^+, RuH_2, and so forth, are being determined with the objective of understanding the reactivities of these atoms with H_2. The $Pt_2 + H_2$ and $Pd_2 + H_2$ 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.

University of Arizona
Tucson, AZ 85721

Department of Chemistry

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

Lichtenberger, D.L. **$92,683**
Comm. 602-621-4749

This project is directed toward understanding the relationships between molecular ionization energies and the bond energies and reactivity of transition metal complexes. The formal relationship between 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. The relationship is being used to clarify the activation of small organic molecules by transition metals, such as in the investigations in this program of the activiation of C–H bonds by metals. Complete oxidative addition of an aliphatic C–H bond to a metal center has not been investigated yet by these techniques, but the principles have been illustrated in the related study of Si–H and Ge–H bond addition to metals. The transfer of these electronic features to other chemical systems is being investigated in terms of the principle of additivity of ligand electronic effects, with studies of numerous small molecules bound to metals. The electronic effects of intermolecular interactions have been observed by comparing the ionizations of metal complexes in the gas phase with the ionizations of thin solid organometallic films. Most significantly, scanning tunneling microscope imaging of these thin films has allowed the determination of intermolecular packing.

Brown University
Providence, RI 02912

Department of Chemistry

180. *Interactions of Molecules with Surfaces*

Greene, E.F. **$80,852**
Comm. 401-863-1193

The variation with kinetic energy of the yield of ions formed when alkali atoms strike surfaces of Si(111) and polycrystalline Pt permits a deduction of the probability of electron transfer from the atoms to the surfaces as z, their distance of separation, changes. At z = 5Å for Na and K near a Si surface it is $10^{12\pm0.2}s^{-1}$ while for Cs it is three times less. For Na on Pt it is $10^{12.9\pm0.1}s^{-1}$. Measurement of the temperature rise at steady state when beams of He, Ar, N_2, H_2, and SF_6 strike a Pt surface can be extrapolated to a condition in which heat conduction and radiation losses are negligible. These limiting values are interpreted to give a quantity, like an accommodation coefficient, that shows the efficiency of energy transfer from the molecules to the surface. The transfer of internal energy is studied also by exciting SF_6 molecules with an infrared laser before they strike the surface. The diffraction of a beam of He atoms by surfaces of Si(111) and Si(100) and by Ge(111) allows study of the surface phase transitions that occur as the crystals are heated. These are transitions near 1140 K for Si(111), 930 K for Si(100), and 550 K for Ge(111).

University of California
Davis, CA 95616

Department of Chemistry

181. *Laser Studies of the Dynamics of Free-Radical Reactions*

Jackson, W.M. **$34,576**
Comm. 916-752-6310

Transient infrared (IR) spectra of vibrationally excited HCN has been observed in the room temperature reaction of CN radicals with methane, ethane, and propane. Rate constants for the production of HCN molecules in a specific vibrational level were obtained by fitting a kinetic model to the transient emission curve. In all cases a population inversion is seen in the observed vibrational distribution. The fractional populations for the production of HCN from the reaction of CN with ethane and propane in the $V'' = 2$, 1, and 0 were found to be 0.80/0.18/0.02, but for methane these ratios were 0.2/0.8/0.0. These observations can be rationalized in this heavy–light–heavy system if the radical fragment acts as a spectator during the reaction. Transient IR emission from trace amounts of vibrationally excited hydrogen isocyanide have also been observed, but only in the $V'' = 1$ level. Experiments are continuing to determine if vibrationally excited HCN and HNC are also produced in the reaction of CN with neopentane and cyclopropane in an effort to determine how the dynamics correlate with whether the abstracted hydrogen is primary, secondary, or tertiary.

University of California
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

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

Felker, P.M. **$71,371**
Comm. 213-206-1274

Mass-selective, ionization-detected stimulated Raman spectroscopy (IDSRS) methods, and Fourier transform versions thereof, have been applied to the study of the vibrational resonances of weakly bound species in molecular beams. These methods rely on resonantly enhanced multiphoton ionization to probe the shifts in state populations induced by stimulated Raman scattering processes. Much of the effort thus far has been directed toward the Raman spectroscopy of benzene dimer and isotopically substituted dimers in the region of the ν_1 totally symmetric C–C stretch fundamental. In addition to benzene dimers higher benzene clusters (i.e., the trimer and tetramer) have also been studied. For all of these species information has been obtained about the lifetimes of the excited vibrational states prepared by ν_1 excitation. High-resolution (0.05 cm^{-1}) Raman spectra have also been obtained for the species. In this regard frequency shifts and splittings caused by the interaction between benzene moieties have been observed. Mixed one-to-one complexes of benzene with atoms or molecules have also been studied. The ν_1 line position shifts of benzene-Ar, benzene-N_2, benzene-CH_4, and others have been measured. Each of these species upon ν_1 excitation lives for nsec or longer, despite the fact that the vibrational excitation is significantly higher in energy than that required to dissociate these weakly bound species. In conjunction with the study of benzene-N_2 and benzene-phenol, the possibility of studying vibrational spectroscopy of solvent species in solute–$(solvent)_n$ complexes with IDSRS methods has been demonstrated, even though probe photoionization proceeds through a solute-localized transition.

Catholic University of America
Washington, DC 20064

Department of Chemistry

183. *Studies of Combustion Kinetics and Mechanisms*

Gutman, D. **$147,900**
Comm. 202-635-5385

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., $CH_3 + CH_3$), reactions of free radicals with atomic oxygen (e.g., $O + C_2H_5$ and $O + C_3H_5$), 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

184. *Quantum Dynamics of Fast Chemical Reactions*
Light, J.C. **\$85,000**
Comm. 312-702-7197 **(9 months)**

The objectives of this research have been the quantum formulation and accurate evaluation of cross sections and rate constants of fast gas phase reactions. These objectives are now being reached for the first time for specific chemical reactions, namely the hydrogen isotopic exchange thermal rate constants. This is now possible because an accurate L^2 representation of three atom systems (in three dimensions) in the interaction region can be obtained using discrete variable representations. Using this representation and the technique of sequential diagonalization and truncation one can solve explicitly for the eigenvectors of the Hamiltonian, the Green's function, and the flux operators. The thermal rate constants for the $H + H_2$, $D + H_2$, and $H + D_2$ reactions have recently been determined via the flux-flux correlation function approach and the state-to-state cross sections are now being evaluated. Generalization to other systems (of more interest) will be straightforward. Ultimately these techniques will be combined with more approximate (probably classical or reaction path) techniques to treat the reactions of larger molecules.

University of Colorado
Boulder, CO 80309-0215

Department of Chemistry and Biochemistry

185. *Laser Photoelectron Spectroscopy of Ions*
Ellison, G.B. **\$132,263**
Comm. 303-492-8603

This project involves the study of radicals likely to be reactive intermediates in combustion processes using photoelectron spectroscopy. Photoelectron spectra are obtained by measuring the kinetic energy of electrons photodetached from mass-selected ion beams. Recent improvements in the sensitivity and resolution of the spectrometer have allowed the determination of the electron affinity of O_2 (0.451 ± 0.007 eV) and NO (0.026 ± 0.005 eV) with unprecedented accuracy. The analysis of the photoelectron spectra also provided bond lengths and fundamental vibrational frequencies of the parent anions. The electron affinity of the amino radical, NH_2, along with the angular distribution of electrons ejected from various rotational states have been measured. Within experimental error, the electrons from the Q, P, and R branches all exhibited the same angular distribution. A complete determination of the strengths of all the bonds in ethylene and acetylene has been made from photoelectron spectroscopy and gas-phase ion chemistry: from photoelectron spectra the electron affinities for $CH_2{=}CH_2$, $CH_2{=}CH$, and $HC{\equiv}CH$ were determined. From proton transfer kinetics in a flow-tube reactor the gas phase acidities of $CH_2{=}CH_2$, $CH_2{=}CH$, and $HC{\equiv}CH$ were determined. These experimental values were combined with heats of formation for related species to give the CH bond dissociation energies in $CH_2{=}CH_2$, $CH_2{=}CH$, and $HC{\equiv}CH$. In addition, the enthalpy of the rearrangement of $HC{\equiv}CH$ to $CH_2{=}C$ was determined to be 46.4 ± 5.5 kcal/mol.

186. *Time-Resolved FTIR Emission Studies of Laser Photofragmentation and Chain Reactions*
Leone, S.R. **\$88,750**
Comm. 303-492-5128

A time-resolved Fourier transform infrared (FTIR) emission experiment has been developed for the study of photofragmentation and chain reactions by uniting a commercial FTIR spectrometer with a high-repetition rate laser. High-resolution emission spectra from excited molecular and radical fragments are recorded at time delays down to a few microseconds after the laser pulse. Internal state distributions have been characterized for the products of photo fragmentation, in collisional energy transfer, and for radical reactions. The dynamics of these processes are also explored. A modification of the apparatus allows multiple time traces to be obtained after each laser pulse and time resolutions of 10's of nanoseconds for the study of chain reaction systems.

Columbia University
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Department of Chemistry

187. *Energy Partitioning in Elementary Gas-Phase Reactions*
Bersohn, R. **\$85,780**
Comm. 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. Recent experiments have focused on the photodissociation of two series of homologous molecules (i.e., monomethylbenzene, dimethylbenzene, trimethylbenzene and tetramethylbenzene and mono, di, and trimethylpyrazine). A laser photon of known energy is absorbed by the molecule, and the electronic energy is very quickly converted into vibrational energy. Energy is redistributed within the molecule until ultimately on the time scale of microseconds enough accumulates in a methyl C–H bond to eject a hydrogen atom. A key finding is that the hydrogen atoms have a translational temperature (determined from the Doppler width of the atomic absorption line) that is within experimental error the same as the internal vibrational temperature. The measurement of both H atom kinetic energy and dissociation rate as a function of both internal energy and molecular complexity while the transition state remains fixed has enabled a thorough test of RRKM theory.

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Department of Applied and Engineering Physics

188. Mass Resolved Resonance Ionization Spectroscopy of Combustion Radicals

Cool, T.A. **$86,768**
Comm. 607-255-4191

Resonance-enhanced multiphoton ionization (REMPI) spectroscopy offers very low detection limits for nonperturbative, *in situ*, spatially resolved density measurements of combustion radicals. The REMPI approach is the only method currently available for ultrasensitive (sub part-per-million) monitoring of weakly fluorescing species. Even though REMPI spectroscopy has provided a remarkable body of new spectroscopic data on previously unobserved states of many molecules, the widespread application of REMPI for flame diagnostics is presently limited by the scarcity of spectroscopic data for Rydberg states of combustion radicals. The primary goal of this research is the discovery and characterization of such electronic states. A molecular beam/resonance ionization/mass spectrometer (MB/REMPI/TOFMS) apparatus was used to observe transitions to new electronic states in HCO, C_2, and the elusive ethynyl radical C_2H. REMPI spectra for C_2 and C_2H were obtained with a tunable dye laser focused within the molecular beam following the two-step 193 nm photolysis of jet-cooled C_2H_2. A new apparatus, nearing completion, will be used for direct sampling and mass resolved detection of REMPI ions, formed *in situ*, from laboratory flames. This will permit the correlation of mass spectra with a rich library of presently unidentified REMPI electron spectra obtained with an electron collection probe. This will enable unambiguous assignment of the REMPI electron spectra to the originating flame species, thereby overcoming the primary difficulty presently limiting more widespread use of the REMPI method.

Department of Chemistry

189. State-Resolved Studies of the Methyl Radical

Houston, P.L. **$86,767**
Comm. 607-255-4303

Methyl radicals are important in combustion, in atmospheric chemistry, and in the decomposition of energetic materials. This project is developing two new techniques for characterizing methyl fragments, one to measure three-dimensional velocity distributions, and another to measure vector correlations between the methyl velocity and its angular momentum. These two techniques are being used to characterize the internal energy, velocity, and alignment distributions of methyl radicals produced by photodissociation of a variety of precursors at several wavelengths, including CH_3I, acetone, nitromethane, CH_3COI, and $(CH_3)_2M$ (M = Cd, Zn, Hg) at 266, 248, and 193 nm. Work on acetone, and nitromethane is now completed. The methyl fragments from these dissociations will be used to investigate the rates of two important combustion reactions. The $CH_3 + O_2$ reaction will be investigated to learn how the rate depends on the reacting methyl distribution, while the $H + CH_4$ reaction will be investigated to learn what methyl distributions are produced.

Emory University
Atlanta, GA 30322

Department of Chemistry

190. Theoretical Studies of Combustion Dynamics

Bowman, J.M. **$82,483**
Comm. 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. 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. Also completed are L^2 simulations of the photodetachment spectra of IHI^- and $ClHCl^-$ for zero total angular momentum.

Georgia Institute of Technology
Atlanta, GA 30332-0430

School of Physics

191. Reactive Collisions of High-Temperature Systems

Graff, M.M. **$81,500**
Comm. 404-894-8255

A newly developed experimental technique examines reactivity of neutral systems with large activation barriers using a fast neutral beam. The initial system under investigation is the basic oxygen–hydrogen combustion system $O + H_2 \rightarrow OH + H$. A fast beam of neutrals is produced by photodetachment of the corresponding negative ions within the extended cavity of an argon ion laser. Energetic neutrals then collide with a stable reactant gas in a collision cell. Reaction products are detected by ionization and mass analysis, providing the total (relative) reaction cross section. The beam-cell geometry isolates the contribution of reagent internal excitation from that of translational energy. A temperature-controlled reaction cell minimizes thermal energy, thus allowing a precise study of the structure of the reaction cross section. The effect of rotational excitation will be studied by comparing reactivity for cold para- and normal H_2. This study significantly augments experimental capabilities for the study of neutral systems with activation barriers.

University of Georgia
Athens, GA 30602

Center for Computational Quantum Chemistry

192. Potential Energy Surfaces for Chemical Reactions

Schaefer, H.F., III **$98,600**
Comm. 404-542-2067

In recent years theoretical chemistry has become 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* quantum mechanics include CH_3 + O_2, CH_4 + O_2, C_2H_5 + O_2, and C_2H_6 + O_2. Other problems of current interest include the reactions of triplet methylene with saturated hydrocarbons, the heats of formation of the C_2H and C_2H_3 radicals, the infrared spectra of CH_5^+ and $C_2H_5^+$, quantitative theoretical predictions of infrared and Raman spectral intensities, the characterization of keto-carbenes, the understanding of the relationship between the two nearly degenerate isomers of the HO_2 dimer, hydrocarbon rearrangements on small metal clusters (especially aluminum), and the nature of hydrated hydronium clusters.

Harvard University
Cambridge, MA 02138

Division of Applied Sciences

193. Fundamental Studies of Carbenes and Hydrocarbon Radicals

Thaddeus, P.; Gottlieb, C. **$70,992**
Comm. 617-495-7340

This project comprises fundamental millimeter-wave spectroscopy of the carbenes, carbon-chain radicals, and ring-chain hybrids involved in reactions of hydrocarbon combustion. Reactive hydrocarbons are produced in low-pressure dc glow discharges through flowing mixtures of combustion gases, such as acetylene, allene, and 1,3-butadiene. Those previously detected in this laboratory at millimeter wavelengths are the linear carbon-chain radicals C_2H through C_6H and the three-membered carbene ring cyclopropenylidene (C_3H_2); the Japanese detected cyclic-C_3H. Presently, the program emphasis is on the spectroscopic assignment of the fairly large number of lines now being found with a new spectrometer that allows accurate determination of the temperature dependence of the reactive hydrocarbons. Given the excellent quality of the spectra, the following molecules may now be detectable in hydrocarbon discharges: propadienylidene and prop-2-ynylidene, two isomers of cyclopropenylidene; the linear carbon-chain radicals C_7H and C_8H; cyclopentadienylidene (C_5H_4), a five-membered carbene closely related to the cyclopentadienyl radical (C_5H_5) frequently mentioned in gas-phase oxidation studies of benzene; and C_5H_2, a ring-chain carbene whose structure was recently calculated *ab initio*.

Department of Chemistry

194. Laser Spectroscopy of Hydrocarbon Radicals

Chen, P. **$82,169**
Comm. 617-495-1842

Supersonic jet-flash pyrolysis of tert-butyl peroxyesters are used to generate cold organic free radicals in the gas phase for spectroscopic characterization. Current species of interest include the ethynyl ($HC{\equiv}C$), vinyl ($CH_2{=}CH$), and cyclopropenylidene ($-CCH{=}CH-$) radicals. These radicals have been selected for study because of their involvement in pyrolysis reactions leading to soot formation in combustion processes. In the supersonic pulsed jet-flash pyrolysis source, precursor molecules, mixed with an inert carrier gas, pass through a heated zone where pyrolysis occurs. The pyrolysis products then expand from a pulsed nozzle and cool. The pulsing assures adequate mixing of the products upstream and rotational temperatures of 40 K are obtained downstream from the pulsed nozzle. The spectroscopic technique used for the characterization of the free radicals is resonant multiphoton ionization (MPI) spectroscopy with mass spectrometric detection for species identification. From these studies ionization potentials of radical species are obtained from which heats of formation of the neutral species can be calculated. The MPI spectra can also be used for flame diagnostics.

University of Illinois
Chicago, IL 60680

Department of Chemical Engineering

195. Kinetics of Combustion-Related Processes at High Temperatures

Kiefer, J.H. **$88,740**
Comm. 312-996-3469

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, and 1,3-butadiene. Flash absorption measurements at 220 nm have now confirmed the rate for 1, 3-butadiene dissociation. A study of the dissociation of vinylacetylene has led to the proposal of a new mechanism for acetylene polymerization, and this mechanism has now been employed in a successful modeling of previous shock tube data on this reaction. Current work centers on the study of allene/propyne pyrolysis, the decomposition of formaldehyde, and further investigation of falloff effects in large-molecule dissociation.

Department of Chemistry

196. *Kinetics of Elementary Atom and Molecule Reactions*

Gordon, R.J. **$93,665**
Comm. 312-996-3280

The project objective is to study the chemical reactions and energy transfer rates of atoms and small molecules. Recent efforts have dealt with the photodissociation of carbon dioxide, the production and relaxation of multiplet states of oxygen atoms, and the quenching of electronically excited carbon monoxide. When CO_2 is excited with 157 nm radiation, it dissociates to produce both ground state, triplet oxygen atoms and electronically excited, singlet oxygen atoms. The fraction of triplet oxygen atoms produced is 6%. This finding can be explained by a nonadiabatic transition from an excited singlet potential energy surface to the ground state triplet surface. In a second study, the multiplet state distribution of triplet oxygen atoms produced by the photodissociation of sulfur dioxide was measured. A statistical distribution of multiplet populations was observed which is consistent with the high-energy recoil limit for photodissociation. In a third study the fluorescence of CO excited to the Rydberg B state at 115 nm was monitored in real time, and the rate of quenching of this state by H_2, D_2, He, Ne, Ar, Kr, Xe, N_2, O_2, HF, and HCl as collision partners was measured. Various mechanisms are proposed, including long-range energy transfer, charge transfer, internal conversion, and exciplex formation.

University of Iowa
Iowa City, IA 52242

Department of Chemistry

197. *Determination of Step-Size Parameters for Intermolecular Vibrational Energy Transfer*

Tardy, D.C. **$45,656**
Comm. 319-335-1355

Collisional vibrational energy transfer is an important component in any mechanism in which either highly vibrationally excited molecules must be stabilized or generated. Specific applications involve pyrolysis, combustion, and laser-induced chemistry. The primary objective of this project is to perform a sufficiently diverse set of experiments (laboratory and computer) so that the relative importance of substrate excitation energy, molecular complexity of substrate and heat bath, interaction energy, temperature, and so forth, can be determined. Experimental results have been obtained using optoacoustic and interferometric techniques for a homologous series of hydrocarbons and deactivators. It is found that the rate constants for deactivation are independent of substrate excitation energy (30 to 60 kcal/mole) and decrease as hydrogen atoms are replaced with fluorine atoms. The collision efficiency decreases as the number of carbon atoms in the substrate increases while increasing when the heat bath changes from helium to argon and decreasing slightly in going to xenon. Computer experiments are being performed to understand these observations. The experimental results for the thermal unimolecular decomposition of cyclohexene were modeled; contrary to the results that were previously published the inversion temperature is important and the average energy removed per collision is independent of temperature.

Jackson State University
Jackson, MS 39217

Department of Chemistry

198. *Infrared and Visible Laser Double Resonance Studies of Vibrational Energy Transfer Processes in Polyatomic Molecules*

Bhatnagar, R. **$50,567**
Comm. 601-968-2171

The wavelength and time-resolved excitation spectra of selected compounds are monitored in the presence of vibrationally excited donor compounds. Some compounds are directly excited by an unfocused pulsed CO_2 laser while others are collisionally pumped by the CO_2 laser excited donor molecules such as SF_6 and CH_3F. The time-resolved fluorescence measurements provide information on the intra- and inter-molecular energy flow in the compound. The wavelength-resolved excitation spectra with and without the CO_2 laser excitation illustrate changes in thermal population of various ground state vibrational levels in the compound. Measurements are made as functions of pressure, degree of excitation of the energy-donor compounds, and time delay between the pump and probe lasers. The species being studied include chromylchloride and S-tetrazine.

University of Kentucky
Lexington, KY 40506-0055

Department of Chemistry

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

Clouthier, D.J. **$62,118**
Comm. 606-257-1790

The spectroscopy and excited-state dynamics of transient species formed by pyrolysis reactions are currently under investigation. The major experimental technique is pyrolysis jet spectroscopy, in which precursor molecules are pyrolyzed in the throat of a supersonic nozzle and then rapidly expelled into a vacuum. Laser-induced fluorescence is used to detect and characterize the jet-cooled pyrolysis products. A major study of the S_1–S_0 and T_1–S_0 spectra of thioformaldehyde has been completed and excited state bending potentials determined. The S_1 state decay dynamics have also been extensively studied under collision-free conditions. Spectra of the HCCS and DCCS free radicals have been acquired and are being analyzed. Rotationally resolved spectra of dichlorocarbene have yielded the ground and excited state geometries, symmetries, and multiplicities. Studies of the N_2S, C_2S, HCCO, and C_3O transient species are in progress.

Massachusetts Institute of Technology Cambridge, MA 02139

Department of Chemical Engineering

200. *Aromatics Oxidation and Soot Formation in Flames*

Howard, J.B. **$106,500**
Comm. 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 and soot particle size and number concentration through the reaction zone of low-pressure one-dimensional flames. The oxidation of benzene and other aromatic compounds by hydroxyl radicals and oxygen atoms is studied by introducing the aromatic compound as a fuel additive in hydrogen–oxygen flames whose OH and O concentrations profiles are experimentally well-known. A molecular-beam-sampling instrument, with on-line mass spectrometry and water-cooled probe sampling with cryogenic trapping followed by GC, GC/MS, FTIR, and NMR analyses, is being used to study gases including high molecular weight compounds. Soot particles are being studied by optical scattering and absorption measurements in the flame and 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.

Department of Chemistry

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

Field, R.W.; Silbey, R. **$137,500**
Comm. 617-253-1489

The high-resolution spectroscopic technique, stimulated emission pumping (SEP), has been employed to study the ground and first excited triplet potential energy surfaces of acetylene, with particular emphasis on isomeric forms such as vinylidene that become accessible only at high energies. Zeeman- and Stark-induced anticrossing spectroscopy provide additional information on the structure and dynamics of excited acetylene. Using these techniques, a new upper bound on the C–H bond dissociation energy in acetylene has been deduced, and evidence for large amplitude orbiting motion of hydrogen has been observed.

University of Massachusetts Amherst, MA 01003-0035

Department of Chemistry

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

Jackson, B.E. **$42,703**
Comm. 413-545-2583

Realistic quantum mechanical models are being developed for studying the dissociative adsorption of diatomic molecules on metals. Time-dependent techniques are used in which the molecular wave function is numerically evolved in time and reacted with the metal. The first quantum study of dissociative adsorption was implemented using an exactly solvable two-dimensional model. The dissociative sticking probability of H_2 and its isotopes on Ni was computed as a function of molecular kinetic energy. Techniques have been developed that extend time-dependent scattering theories to include finite surface temperature. This allows for energy exchange between the molecule and the vibrations of the solid, which are treated quantum mechanically. These models have been successfully used to study the scattering of He, Ne, and Ar from Cu and Ni. Six dimensional models for the dissociative adsorption of diatomics such as H_2, O_2, CO, and N_2 are being developed. They will be used to examine how dissociative sticking probabilities depend on molecular kinetic energy, rotational and vibrational state, angle of impact, and various features of the gas–surface interaction potential. With the inclusion of finite temperature and all molecular degrees of freedom, a complete comparison with experiment will be possible.

University of Michigan Ann Arbor, MI 48109-2143

Department of Atmospheric, Oceanic, and Space Sciences

203. *Energy-Transfer Properties and Mechanisms*

Barker, J.R. **$98,600**
Comm. 313-763-6239

This project studies the mechanisms and properties of collisional energy transfer involving moderate-sized molecules. The project objectives are to gain a fuller understanding of highly vibrationally excited molecules by a combination of experiments and theoretical investigations, and to develop a workable theoretical model of the energy-transfer process. In the experimental investigations, various techniques are used to monitor energy in the excited molecules, or energy transferred to a collision partner. The techniques include time- and wavelength-resolved infrared fluorescence, optoacoustics, and time-dependent thermal lensing. In order to determine the mechanisms of energy transfer, homologous series of molecules and isotopomers are investigated to examine the effects of dipole moments, symmetry properties, fundamental vibrational frequencies, internal rotors, and so forth. In the theoretical effort, improved methods are being developed for calculating internal state sums and densities for nonseparable degrees of freedom. Collisional/reaction master equation calculations are carried out to investigate the manifestations of energy transfer under extreme conditions, such as in shock-heated gases.

University of Minnesota
Minneapolis, MN 55455

Departments of Chemistry and Physics

204. ***State-to-State Dynamics of Molecular Energy Transfer***
Gentry, W.R.; Giese, C.F. **$108,460**
Comm. 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. Further work is in progress to extend these studies to a broader range of polyatomic molecules, and to incorporate 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 descriptions of the rotational dynamics in each system are under investigation using rigid-shell models of the molecular shape.

Department of Chemistry

205. ***Variational Transition State Theory***
Truhlar, D. **$88,740**
Comm. 612-624-7555

This project is concerned with the development and applications of generalized transition state theory and multidimensional tunneling approximations to chemical reaction rates. Several practical versions of variational transition state theory (VTST) have been developed and implemented, as have several accurate multidimensional semiclassical tunneling approximations. The methods have been applied to thermal rate constants, using transmission coefficients based on ground-state tunneling, and adiabatic and diabatic extensions have also been presented and applied to calculate rate constants for vibrationally excited reactants. 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. New methods for the analysis of secondary deuterium kinetic isotope effects are also being developed. Another important aspect of this work is the development of algorithms for calculating reaction rates on the basis of limited electronic structure information. Both interpolation procedures and direct dynamics methods are under development.

National Institute of Standards and Technology
Gaithersburg, MD 20899

Center for Atomic, Molecular, and Optical Physics

206. ***Laser Studies of Chemical Dynamics at the Gas–Solid Interface***
Cavanagh, R.R.; King, D.S. **$80,000**
Comm. 301-921-2368

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). The kinetic energy distributions observed for the two substrates are similar, each exhibiting a strong dependence on rotational states. The internal state and the vibrational level populations were consistently dependent on the wavelenth of the desorption laser, and were highly sensitive to coverage and substrate. Measurements that determine the population of internal states have revealed highly non-Boltzmann distributions and nonstatistical spin-orbit populations that are essentially independent of the desorption laser wavelength. 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 for more complex molecular adsorbates (such as $Mo(CO)_6$).

Center for Chemical Technology

207. ***Kinetics Database for Combustion Modeling***
Herron, J.T. **$95,640**
Comm. 301-975-2569

This project provides a reliable and consistent set of recommended rate constants on the elementary single-step thermal reactions relevant to the combustion of organic compounds. Data have been evaluated for over 1020 elementary chemical reactions involved in the combustion of methane, methanol, the C2-C4 saturated hydrocarbons, propene, trans-2-butene, and the allyl radical, and for the reactions of oxygen atoms with hydrocarbons, and oxygen-, halogen-, and sulfur-substituted hydrocarbons. The reactions included in the evaluation cover all possible reactions and all possible reaction types, and provide the basis for estimating reactivities for higher members of the alkane series. In addition, these evaluations include all of the reactions of H, O, OH, HO_2, O_2, CO, CO_2, and so forth, which are basic to all combustion systems. The data evaluations are being published in the *Journal of Physical and Chemical Reference Data*. As a supplement to the data evaluation work, data compilations are being published in the NSRDS-NBS series that cover a broader range of reactions than those covered to date in the evaluations. These data are included in a searchable PC database covering the literature from 1971–1989. Data for more than 2500 reactions are in this database, and additional data are being added continuously. Current activities involve the further expansion of the work to include a broader range of unsaturated structures. Work will continue on the compilation of chemical kinetic data for all thermal gas-phase reactions.

University of New Orleans
New Orleans, LA 70148

Department of Chemistry

208. Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels

Kern, R.D., Jr. **$76,119**
Comm. 504-286-6847

The main focus of this work is the formulation of reaction mechanisms for pyrolytic reaction systems that pertain to the soot formation process. Establishment of a comprehensive mechanism for the thermal decomposition of acetylene is essential since it is an integral part of mechanisms that describe the pyrolyses of aromatic compounds, the later stages of hydrocarbon fuel combustion in rich mixtures, and as part of the soot formation reaction sequence. A shock tube coupled to a time-of-flight (TOF) mass spectrometer was used to obtain the dynamic reaction profiles for C_2H_2, C_4H_2, and C_6H_2 over the temperature range 1880 to 2620 K. The results were modeled satisfactorily with a new 40 step reaction mechanism. The experiments were performed with acetone-free mixtures. It was demonstrated that a fragment chain reaction mechanism is clearly dominant in this high-temperature region. The TOF technique was applied also to the role of chemi-ions in soot formation. Mixtures containing deuterated ethylene were used to prove the absence of chemi-ion formation in oxygen-free mixtures. It was concluded that a radical mechanism is solely operative for the formation of soot in pyrolytic reaction systems.

State University of New York/Buffalo
Buffalo, NY 14260

Department of Electrical and Computer Engineering

209. Picosecond CO_2 Laser Interactions with Polyatomic Molecules

Kwok, H.-S. **$76,908**
Comm. 716-636-3119

The goal of this project is to study the ultrafast dynamics of excited molecular states. Broadband incoherent light pulses are used to probe various molecules in a dynamic grating type arrangement. In this self-diffraction geometry, the signal is measured as a function of the delay time between the two pump pulses. The time resolution is <10 fs, which is very difficult to achieve with coherent light pulses. So far, the following effects have been observed: (1) molecular vibrational modulation (37 fs) of the self-diffraction signal in R-565 and CV-670 dyes, (2) 1.6 fs Michelson interference fringes in the photodissociation of NO_2, and (3) ultrafast photodissociation (<40 fs) in NO_2 using 400 nm laser excitation. The ultrafast photodissociation time in NO_2 is quite unexpected because the excess energy above the dissociation limit is quite small. Additionally, dephasing information of the upper level can also be obtained. T_2 times of 20 to 200 fs were observed in various dye molecules. The photodissociation experiment will be extended to other molecules in the future.

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

Department of Chemistry

210. Studies of Atmospheric Molecules by Multiphoton Spectroscopy

Johnson, P.M. **$78,880**
Comm. 516-632-7912

Resonance ionization spectroscopy is currently being applied to the investigation of the optical transitions and photochemistry of molecules, including metastables and radicals which are difficult to study using conventional techniques. New transitions of both familiar and unstable molecules provide additional information about their excited-state electronic structure and enable the detection of minute quantities in difficult environments. Normally the species under study are prepared in a supersonic beam, providing a collisionless and cold environment. Unstable molecules are created in the supersonic beam by means of a pulsed electric discharge at the exit of a pulsed valve. Current molecules being studied include carbon dioxide, metastable nitrogen, and pyrazine. Multilaser, multiphoton techniques, including mass spectroscopy and photoelectron spectroscopy, are being used. In carbon dioxide, the selectivity of multiphoton ionization for photochemically stable states enables the discrimination of detailed structure from a continuous background and provides a better understanding of the electronic structure and photodissociation of this important atmospheric constituent. In metastable nitrogen, new transitions between excited states enable a fresh look at some previously obscure electronic states, while in pyrazine, high-resolution resonant two-color photoelectron spectroscopy is providing extensive analysis of the ionic ground state vibronic structure and the mechanism of singlet-triplet coupling in S_1.

University of North Carolina
Chapel Hill, NC 27599-3290

Department of Chemistry

211. PEPICO Studies of Ion Dissociations: The Structure and Heats of Formation of Ions, Molecules, and Free Radicals

Baer, T. **$80,852**
Comm. 919-962-1580

This research is concerned with the development of photoelectron–photoion coincidence (PEPICO) spectroscopy and its application to two classes of compounds: fused rings and organic radicals. In the PEPICO technique, ions are generated by photoionization and detected in delayed coincidence with energy selected electrons. Ions are thus prepared with selected, known internal energies allowing the study of (1) the role of internal energy in the dissociation of metastable ions; (2) the manner in which internal energy is distributed in the products of dissociation; and (3) under certain conditions, the dynamics of dissociation. Compounds are vaporized and expanded in a supersonic nozzle to reduce the internal energy of the molecules so that the onset of ionization can be measured with a precision comparable to the resolution of the instrument. The heats of formation of parent ions, the fragment ions, or fragment neutrals are determined from the measured ionization energies and the fragment ion appearance energies. In some cases structural information is obtained through *ab initio* calculations.

University of Pennsylvania
Philadelphia, PA 19104-6323

Department of Chemistry

212. Unimolecular and Bimolecular Reactions Induced by State-Specific Vibrational Excitations

Dai, H.-L. **$98,600**
Comm. 215-898-5077

Using a recently developed transient vibrational spectroscopic method, Flash Photolysis Stimulated Emission Pumping, the high vibration–rotation levels of the CH_2 molecule, which is an important species in combustion processes, have been characterized. Vibrational levels as high as the third overtone of the bending mode of the lowest singlet state have been studied. In addition to the determination of the molecular constants associated with the bending vibrational levels, the barrier of the bending motion has been determined to be 9870 cm^{-1}. Abnormally strong $\Delta K_a = 3$ transitions in the $\tilde{a} \longleftarrow \tilde{b}$ band were observed. Fermi, Coriolis, and singlet–triplet couplings have all been identified in the spectra. Using Stark Level-Crossing Spectroscopy, the highly excited vibrational levels of formaldehyde near dissociation barrier (at 28,300 cm^{-1}) have been characterized with single quantum state resolution. Neighboring isoenergetic vibration–rotation eigenstates within 0.1 cm^{-1} of each other have been found to have dissociative lifetimes fluctuating between 1.4 and 130 nsec. The dissociation barrier of $H_2CO \rightarrow H_2 + CO$ is deduced to be 81.8 ± 1 kcal/mole. The vibrational level density at this high energy is measured to be 83 ± 27 per cm^{-1} and the vibrational levels were found, even for $J = 1$, to interact with each other through Coriolis coupling mechanisms. Through a chi-squared probability test, it was shown that while the fluctuation of the dissociation rates of the quasi-stationary eigenstates originates from mode-specific coupling to the reaction coordinate, the distribution of the rates indicates that the coupling is chaotic in nature.

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

Lester, M.I. **$151,000**
Comm. 215-898-4640

An experimental program is being pursued to provide a detailed picture of the interaction potentials between the open-shell hydroxyl radical and molecular partners. In these experiments, the collision partners are aggregated together in a van der Waals complex and probed through spectroscopic measurements and half-collision studies of the binary complexes. To date, laser-induced fluorescence and infrared overtone spectroscopy have been used to map directly the intermolecular potential between $Ar(^1S_0)$ and hydroxyl radicals in the excited $A\ ^2\Sigma^+$ and ground $X\ ^2\Pi_{3/2}$ electronic states. The radial portion of the intermolecular potential is strikingly different for OH in its ground and excited electronic states. The dynamics taking place on these potential energy surfaces is probed by vibrationally exciting the OH subunit, which induces dissociation of the OH–Ar complex. The rate of dissociation is evaluated through spectral line broadening and direct time-domain lifetime measurements. The lifetime changes by more than five orders of magnitude between the ground and excited electronic states, giving information on the couplings between vibrational degrees of freedom. The OH product rotational distribution reflects the bending wave function of the complex, providing a means to probe the angular variation (anisotropy) of the potential energy surface.

University of Pittsburgh
Pittsburgh, PA 15260

Department of Chemistry

214. Quantum State Resolved Desorption of CO from Solid Surfaces

Janda, K.C. **$86,768**
Comm. 412-624-8680

A study of the desorption kinetics of H_2 from the Si(100) surface has recently been completed. Recombinative desorption was found to occur via a first order kinetic mechanism for which the activation energy is less than the reaction enthalpy. Also, hydrogen atoms from the gas phase were found to react directly with D atoms on the surface. These results have been explained by invoking an unusual delocalized bound state intermediate. Work is currently in progress to study isotope mixing between CO molecules on a K-promoted Ni(111) surface. The laser-induced thermal desorption technique is being used to study the temperature dependence of the isotope mixing rate. The onset of mixing is found to occur at 450 K, 150 degrees below the thermal desorption temperature.

Princeton University
Princeton, NJ 08544

Department of Chemistry

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

Rabitz, H.A. **$132,000**
Comm. 609-258-3917

This research is concerned with elucidating the fundamental relations between structure at the atomic and molecular level and the structure of such laboratory observations as reaction kinetics and dynamics. The research is developing and making special use of advanced techniques in sensitivity analysis within an overall framework of molecular systems analysis. This line of research has most recently been extended to the most basic electronic level where the primary question concerns how electronic orbital structure steers or otherwise indirectly influences chemical reactivity. In contrast, starting with a Born–Oppenheimer electronic potential surface, features upon the surface can be explored for their effect on similar reactive energy transfer processes. In turn, the role of transport and chemical rate constants within a chemical mechanism can be explored for their contribution to overall bulk behavior or chemical species profiles. Particular applications of these concepts are being explored for combustion phenomena. Recent work has shown that the presence of sufficiently strong coupling, especially of a nonlinear nature, can lead to a considerable simplification of the relationship between the input and output in dynamical or kinetic systems. This observation has potentially significant implications for reducing or simplifying models to their essential structure. Most recently these tools are being extended to prepare algorithms for efficiently inverting laboratory spectral and molecular beam data.

Department of Mechanical and Aerospace Engineering

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

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

The experimental aspects of the project are conducted in a flow reactor facility that permits chemical kinetic observations at atmospheric pressure (at about 850 K to 1200 K) for reaction times on the order of 10 to 1000 msec. Sampling of stable reactant, intermediate, and product species concentrations provides substantial definition of the phenomenology of reaction mechanisms and a much more constrained set of pure kinetic information than can be derived in flames or shock tubes. The modeling aspects of the project emphasize (1) the use of hierarchical mechanistic construction as a means of developing kinetic mechanisms and (2) the comparison of model and experiment using elemental gradient sensitivity based techniques. Modeling using a well-defined and validated mechanism for the $CO/H_2/O_2$ system and perturbations of experimental oxidations by small amounts of additives is also used to derive absolute reaction rates and to investigate the compatibility of elementary kinetic rate information. Chemical issues of particular interest continue to include the $CO/H_2/O_2$ system and its perturbation by added species (to obtain elementary kinetic data involving a small amount of an added hydrocarbon), the formaldehyde pyrolysis and oxidation systems, the acetaldehyde pyrolysis and oxidation systems, and the pyrolysis and oxidation mechanisms of simple alcohols, including methanol. Efforts are currently being extended to include experimental research at pressures to 15 atmospheres.

217. Aromatic-Radical Oxidation Kinetics

Glassman, I.; Brezinsky, K. **$81,179**
Comm. 609-258-5199

Cyclopentadiene represents a class of species that appears frequently in the combustion of aromatics: long-lived resonantly stabilized compounds. Not only are the oxidation and thermal decomposition of such species interesting in their own right, but their presence in the reaction mixture greatly alters the rates and routes of the combustion process. The current high-temperature flow reactor study of the oxidation and pyrolysis of cyclopentadiene permits examination of the initial reaction steps of the stable parent and some of the postulated steps for the reaction of the cyclopentadienyl radical—an effort crucial to achieving one of the program's ongoing research goals: accurate modeling of aromatic oxidation processes. Complementary studies of the oxidation of phenol and multiple substituted aromatics perturbed by the addition of NO_2 are also important components of this program. An extensive phenol pyrolysis study, conducted as part of the program, has revealed the details of the oxygen-free decomposition of this molecule. The oxidation study of phenol, by providing a significantly different radical environment, will help confirm and contrast the mechanism for phenol pyrolysis already developed and the oxidation and pyrolysis mechanisms being developed, of cyclopentadiene, a decomposition product of phenol. In a similar way, perturbation of the oxidation mechanism of compounds (such as xylene) aid in the full understanding of the mechanistic steps necessary for modeling.

Rensselaer Polytechnic Institute
Troy, NY 12180-3590

Department of Chemical Engineering

218. Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions Over Wide Temperature Ranges

Fontijn, A. **$75,000**
Comm. 518-276-6508

The goal of this project is to provide accurate data on the temperature dependence of the kinetics of elementary combustion reactions, to gain a better fundamental understanding and predictive ability of the chemistry involved, and for use by 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 oxygen atoms with H_2, D_2, the C_2-hydrocarbon molecules, propylene, and hydrogen chloride have been completed. Quantum-mechanical tunneling is found to be an important contributing factor

Princeton University
Princeton, NJ 08544

Department of Chemistry

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

Rabitz, H.A. **$132,000**
Comm. 609-258-3917

This research is concerned with elucidating the fundamental relations between structure at the atomic and molecular level and the structure of such laboratory observations as reaction kinetics and dynamics. The research is developing and making special use of advanced techniques in sensitivity analysis within an overall framework of molecular systems analysis. This line of research has most recently been extended to the most basic electronic level where the primary question concerns how electronic orbital structure steers or otherwise indirectly influences chemical reactivity. In contrast, starting with a Born–Oppenheimer electronic potential surface, features upon the surface can be explored for their effect on similar reactive energy transfer processes. In turn, the role of transport and chemical rate constants within a chemical mechanism can be explored for their contribution to overall bulk behavior or chemical species profiles. Particular applications of these concepts are being explored for combustion phenomena. Recent work has shown that the presence of sufficiently strong coupling, especially of a nonlinear nature, can lead to a considerable simplification of the relationship between the input and output in dynamical or kinetic systems. This observation has potentially significant implications for reducing or simplifying models to their essential structure. Most recently these tools are being extended to prepare algorithms for efficiently inverting laboratory spectral and molecular beam data.

Department of Mechanical and Aerospace Engineering

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Comm. 609-258-5206

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Comm. 609-258-5199

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Rensselaer Polytechnic Institute
Troy, NY 12180-3590

Department of Chemical Engineering

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Comm. 518-276-6508

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Rice University
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Department of Chemistry

219. Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals

Curl, R.F., Jr.; Glass, G.P. **79,866**
Comm. 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. Recently, the rate constants for the reactions of the ethynyl radical (C_2H) with methane, ethylene, ethane, D_2, and CO have been determined by following the time decay of an ethynyl infrared transient absorption line originating from the ground vibronic state using diode laser spectroscopy. The ethynyl was created by excimer laser flash photolysis (ArF, 193 nm) of trifluoropropyne. Relaxation of excited states of ethynyl was achieved by buffering the photolysis cell with $\approx$ 20 Torr of He buffer and approximately 130 mTorr of sulfur hexafluoride. When possible, the dependence of the reaction rate on helium pressure was investigated over the range of 8 to 70 Torr. Second-order rate constants of $3.0(2) \times 10^{-12}$, $1.3(3) \times 10^{-10}$, $3.6(2) \times 10^{-11}$, and $2.3(3) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} were obtained for the reactions of ethynyl with methane, ethylene, ethane, and D_2 respectively. A third-order rate constant of $2.1(3) \times 10^{-30}$ cm^6 $molec^{-2}$ s^{-1} was obtained for the reaction of ethynyl with CO. Surprisingly, the rate constant for the reaction of ethane with ethynyl exhibited a linear dependence upon helium buffer gas although the rate extrapolated to zero helium pressure is about 1/2 the rate at 80 Torr of helium.

220. Supersonic Bare Metal Cluster Beams

Smalley, R.E. **$96,628**
Comm. 713-527-4845

Research into the physics and chemistry of bare metal clusters advanced considerably over this past year because of two major technical advances. First, the development of a much improved laser vaporization source involving twin pulsed nozzles with ultrafast rise times now permits metal cluster beams to be produced with much improved stability and cooling compared to the original "Smalley-type" source. This in turn has enabled the first detailed study of the evolution of the 3-D band copper clusters as a function of cluster size in the range from 1 to 410 atoms. Similar ultraviolet photoemission spectroscopic spectra (UPS) studies of gold clusters using the new source have revealed striking evidence of shell structure behavior, and dye laser scans near the photodetachment thresholds of the negative ions are revealing high-resolution spectral detail of some of the small clusters, particularly in the case of Au_6^-. The second major technical development has been the invention of a new direct-injection cluster source for use in ion-cyclotron resonance studies of clusters trapped in a superconducting magnetic field. This new device now permits the study of the surface chemistry of even very large metal clusters, containing well over 200 atoms, while they are trapped for many seconds without perturbation in an ultrahigh vacuum. These experiments are revealing fascinating size and structure-dependent reactivities which should provide vital data for detailed theoretical modeling efforts in understanding the chemistry of metal surfaces.

University of Rochester
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Department of Chemistry

221. Low-Energy Ion-Molecule Reactions and Chemi-Ionization Kinetics

Farrar, J.M. **$84,792**
Comm. 716-275-5834

Crossed ion beam–neutral beam reactive scattering experiments are being performed on several chemical systems with the goal of using energy disposal measurements and angular distributions to deduce dynamical information about reactive collisions and potential surface topology. By studying proton transfer and isotope exchange collisions and nonreactive energy-transfer collisions in systems such as $OH^- + D_2$, $OD^- + NH_3$, and $OD^- + CH_2{=}CH{=}CH_2$, the branching ratios yield quantitative information on isomerization barrier heights and the product recoil distributions assess the statistical nature of intramolecular energy transfer in the collision complex. Product state-resolved electron detachment reactions are also being studied. To test the theoretical foundations of such collisions, simple diatomic systems such as $Na^- + Na \rightarrow Na_2(v', J') + e^-$ and $H^- + Na \rightarrow NaH(v', J') + e^-$ are being examined. Rotational state-resolved detection of the products, using laser-induced fluorescence and multiphoton ionization, will yield the first opacity function measurements for detachment. Experimental methods and theoretical results from the diatomic systems will be applied to examine energy disposal in important combustion-related reactions such as $O^- + H_2$ and $O^- + C_2H_4$, as well as atmospheric reactions such as $O^- + N_2O$ and $O^- + CO$.

222. Double Resonance Reactant Preparation for State-to-State Unimolecular Reaction Studies

Rizzo, T.R. **$67,556**
Comm. 716-275-2304

This work is aimed at providing critical experimental tests of statistical and dynamical models of energy redistribution and unimolecular dissociation dynamics of molecules on the ground potential surface. The testing and refinement of these models is important for predicting the reaction rates of energy partitioning in combustion-related reactions. Two new spectroscopic techniques have been developed to probe the dynamics of molecules excited with chemically signifcant amounts of energy. In one case infrared-optical double resonance is used to prepare reactant molecules in quasi-bound states above the dissociation threshold with precisely specified energy and angular momentum. The dissociation process from this state into individual states of the products is monitored with laser-induced fluorescence. Application of this approach to H_2O_2 has served to distinguish clearly between competing statistical models of product energy partitioning. The linewidths of rotationally selected vibrational overtone transitions of H_2O_2 and HNO_3 are providing information on the rotational state dependence of the intramolecular energy redistribution process. A second spectroscopic approach uses an optical-infrared double resonance technique followed by laser-induced fluorescence of the dissociation products to measure the infrared spectrum of molecules subsequent to vibrational overtone excitation. Such spectra reveal the nature of the states that participate in energy redistribution.

SRI International
Menlo Park, CA 94025

Molecular Physics Laboratory

223. *Flame Studies, Laser Diagnostics, and Chemical Kinetics*

Crosley, D.R. **$124,974**
Comm. 415-859-2395

This research project involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the chemistry of pollutant formation in hydrocarbon and ammonia combustion processes. The research includes: (1) LIF probing of reactive intermediates in flames at atmospheric and reduced pressure; (2) the development of a spectroscopic and state-specific collisional database for LIF measurements; (3) development and application of rate constant estimation methods; (4) computer modeling of combustion chemistry networks; and (5) rate constant measurements, especially at higher temperature, using a laser pyrolysis/LIF technique. Collisional quenching of the $\tilde{A}^2A_1$ state of NH_2 depends on the rotational level. However this dependence varies with vibrational level so that collision dynamics are not responsible, as they are for the rotational level dependence of diatomic hydride quenching. RRKM calculations have been performed for the reaction t-C_4H_9 + H/DX (X = I, Br). Potential surfaces compatible with negative activation energies require an inverse isotope effect, contrary to observation. This has implications for many alkyl radical reaction rates important in combustion.

University of Southern California
Los Angeles, CA 90089-0482

Department of Chemistry

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

Beaudet, R.A. **$86,765**
Comm. 213-743-2997

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 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. Such complexes involving triplet state molecules have not yet been studied. 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 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 (e.g., O + HCl reaction has an activation energy of 22 kJ/mol), and the oxygen atom will lie in a shallow well just outside the barrier.

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

Reisler, H. **$81,128**
Comm. 213-743-7852

Reaction dynamics of carbon atoms in selected electronic states with various small molecules relevant to combustion systems are studied using crossed, pulsed atomic and molecular beams. Various photolytic means are used to produce the carbon atoms in well-defined electronic states from precursor molecules. Reactants and products are detected using laser-induced fluorescence or multiphoton ionization. The reactions of NO, NO_2, and SO_2 with carbon atoms are being investigated, and for each of the reactions studied, the branching ratios between various product channels are determined. These experiments are expected to provide detailed dynamical data for testing theoretical potential surfaces and reaction mechanisms. Preliminary results have been obtained for the reactions of carbon atoms with hydrogen, hydrochloric acid, and nitrous oxide. Vibrational and rotational populations, as well as lambda-doublet propensities and translational energy distributions generated from Doppler profiles were obtained. In the case of the reactions with HCl, both CH and CCl channels are observed with the latter being more probable. The reaction of ground state carbon atoms with nitrous oxides produces CN with an inverted vibrational distribution and a thermally 'hot' rotational distribution.

226. *Reactions of Small Molecular Systems*

Wittig, C. **$133,150**
Comm. 213-743-6389

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 → 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 velocity-aligned

Doppler 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 stimulated emission pumping of reactants (e.g., $OH + NO \rightarrow H + NO_2$, $\Delta H = 10{,}200\ cm^{-1}$, where either OH or NO can be pumped to high vibrational levels).

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Stanford, CA 94305

Department of Mechanical Engineering

227. Spectroscopy and Kinetics of Combustion Gases at High Temperatures

Hanson, R.K.; Bowman, C.T. **$133,110**
Comm. 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 for these species and (2) shock tube studies of radical–molecule and radical–radical reactions relevant to combustion. Species under investigation in the spectroscopic portion of the research include OH, NH, NH_2, NCO, and NO. A novel aspect of the shock tube reaction kinetics studies is the use of excimer laser photolysis to produce controlled levels of radical species in shock-heated gases. The primary excimer laser wavelength used in experiments thus far is 193 nm (argon fluoride), although other wavelengths are of interest. Radical species of interest in this work include OH, NH, NCO, O, H, and N. Source compounds employed for radical production are H_2O, NH_3, HNCO, N_2O, and NO. Reactions studied include the reactions of N-atom with NO, H_2 and CH_3, the reactions of NH with NO, O-atom and O_2, and the reaction of H-atom with O_2.

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Madison, WI 53706

Department of Chemistry

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

Crim, F.F. **$85,808**
Comm. 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 time-resolved spectroscopic detection of products and 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

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Fullerton, CA 92634

Department of Physics

229. Correlated Processes in Atomic Collisions

Feagin, J.M. **$43,352**
Comm. 714-773-3366

Recent efforts have concentrated on the development of a unified description of Wannier threshold effects in three- and four-particle systems. A set of collective coordinates especially appropriate for describing threshold breakup configurations has been devised. They facilitate a reformulation of the Wannier theory in terms of a familiar theory of small oscillations. In the case of four-particle breakup, the coordinates have led to the prediction of multiple unstable normal modes in the breakup configuration and thus to a new feature in the Wannier formalism: the occurrence of multiple Wannier power laws. This prediction has been found to be in accord with recent precision experimental observations of a break in the cross section near threshold for triple photoionization both in atomic oxygen and neon. These coordinates appear to have many novel and interesting features, including, for example, reduced masses that depend on parameters determined by the Coulomb potential, specifically, the "Wannier saddle." Because the Wannier saddle is known to characterize many kinds of Coulomb correlations, these coordinates are of interest in the general study of collective motions in few-body systems, as, for example, in reducing the number of coupled equations usually required. Ongoing efforts in this project include the application of a diatomic molecular description of atoms to calculate cross sections for electron-pair excitations in heavy ion collisions, the development of a quantum diffusion (Monte Carlo) code for two-electron excited states, and the development of a theory of electron transfer and excitation (RTE) in crystal-channel collisions.

Clark Atlanta University
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Department of Physics

230. *Theoretical Investigation of Electron–Ion Interaction*
Msezane, A.Z.
Comm. 404-880-8662

Dominant physical mechanisms underlying the processes of electron-impact excitation and ionization of ions and atoms of importance in astrophysical, laser, and laboratory fusion plasmas are identified and calculated. The R-matrix method and program NIEM of Henry et al. are used to obtain both differential and integral cross sections to guide measurements. In particular, detailed multistate photoionization calculations are performed of: (1) ground state atoms 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 inner shell to investigate and understand the recent experimental measurement of strong enhancement of shake-up satellites and many electron effects in sodium. Also, electron-impact excitation is studied from near threshold to about ten times threshold of core-excited atomic quartet and doublet states, particularly those quartet states that are metastable against autoionization (e.g., Na I) and atoms and singly and multiply charged positive ions to investigate target wave function effects and scattering approximations (e.g., e-Na^+ and e-N^{2+}). All calculations use extensive CI target wave functions, which take into account correlation and polarization effects.

University of Colorado
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Joint Institute for Laboratory Astrophysics

231. *Spectroscopic Diagnostics of Electron–Atom Collisions*
Gallagher, A.C.
Comm. 303-497-3936

Fully differential cross sections for electron collisional excitation of sodium have been measured by a unique new method based on high-resolution laser spectroscopy. The character of the excitation is detected through the Doppler-recoil spectra of the excited atoms, and the angular momentum and spin dependence are detected as intensities of spectroscopically resolved Zeeman line components. Angle differential cross sections for the different spin and angular-momentum changing components of the sodium resonance line excitation have been measured for low electron energies. A trochoidal electron monochrometer has been constructed to allow measurements with higher energy resolution. Measurements of electron excitation of high-lying states of the alkalis are under way.

232. *Near-Resonant Absorption by Atoms in Intense Fluctuating Fields*
Smith, S.J. **$103,500**
Comm. 303-492-7788

This research is an experimental investigation of the behavior of atoms coherently excited in a near-resonant very intense optical laser field, on which statistically well-characterized phase and frequency fluctuations have been imposed. The population of driven atoms constitutes a phased dipole array evolving in time in the presence of various perturbations. In this case, since the medium is quite diffuse, the important perturbations consist of the phase/frequency fluctuations of the optical field in which the atom is immersed. The parameters of the field fluctuations are determined by fully controlled experimental parameters. A comprehensive experimental investigation of the variance (fluctuations) of the fluorescence intensity, and of the spectrum of intensity fluctuations, from a two-level atom driven by such a phase-diffusing laser field is being completed. The results are being compared to recently developed theoretical predictions relating the observed quantitites to the magnitude and bandwidth of the phase fluctuations and to the laser field intensity. These investigations are being extended to the effects of phase-diffusing fields on the process of four-wave mixing in a diffuse medium in the vicinity of an optical resonance.

Cornell University
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Nuclear Science and Engineering Program

233. *Experimental Study of Interactions of Highly Charged Ions with Atoms at keV Energies*
Kostroun, V.O. **$286,348**
Comm. 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 temperatures and densities typical of thermonuclear plasmas. Fundamental processes being studied include single, double, and multiple electron capture by the projectile; transfer ionization (Auger decay in the quasi-molecule formed during the collision); radiative transitions in quasi-molecules; excitation and ionization of the target; and the decay of the highly excited two-electron states of the projectile formed in capture. Low-energy ($\leq$ keV/amu), multiply charged ions (O^{8+}, Ar^{16+}, Ar^{18+}, Kr^{33+}, Xe^{44+}) are crossed with H, He, H_2, O, Ne, etc. gas targets, and the reactions studied by energy gain/loss spectroscopy, collisional spectroscopy, and electron and photon (soft X-ray and visible) spectroscopies. The highly charged ions are produced by the Cornell Electron Beam Ion Source CEBIS II, a superconducting solenoid, cryogenic EBIS, designed and constructed in this laboratory. CEBIS-II produces such species by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam.

Georgia Institute of Technology
Atlanta, GA 30332-0430

School of Physics

234. *Statistical Fluctuations in Lasers*
Roy, R. **70,000**
Comm. 404-894-5265

The detection of extremely weak signals by the technique of super-regenerative detection has been investigated. These experiments are based on earlier work on statistical fluctuations in laser transients. A helium neon laser signal was detected by a tunable dye laser, and a dynamic range of over 70 dB and a sensitivity limit of 1 picoWatt were demonstrated. These experimentally achieved limits correspond well with theoretical estimates. The bandwidth of the receiver was determined to be 5 MHz for a signal strength of 1 microWatt. The effect of detuning of the external signal from the laser receiver wavelength was studied and compared with theory; very good agreement was obtained. An analytic theory of the transient dynamics of the injection-seeded laser was developed and agrees well with both numerical simulations and experiment. The effect of the injection field statistics on the transient dynamics has been evaluated. It was found that only fast phase fluctuations (on the time scale of the seeding process) alter the initiation times appreciably. It is predicted from initial studies that a solid-state tunable laser will lower the threshold of sensitivity to 1 femtoWatt. These predictions are being tested experimentally. Techniques have been extended for the simulation of stochastic fields to determine the spectrum of light scattered from an atom interacting simultaneously with a coherent and a chaotic field.

235. *Metastable Enhancement of C^+ and O^+ Capture Reactions*
Thomas, E.W. **$57,417**
Comm. 404-894-5200 **(24 months)**

It was demonstrated that low-energy (10 to 500 eV) metastable C and O ions exhibit charge transfer cross sections in H_2 that are ten times greater than the ground state. This can be related to an accidental resonance of these metastable states with vibrationally excited H_2^+. This observation resolves discrepancies between data by different groups where ion beams contained indeterminate fractions in the metastable state. The charge transfer of C^+ and O^+ in atomic H is now being studied. It is anticipated that a high cross section will be found for ground state oxygen ions in hydrogen where there is again an accidental resonance. Cross sections for ground state species and for metastable carbon ions are likely to be smaller because of a large energy defect. The results have implications for the understanding of how carbon and oxygen impurity ions are neutralized at the edge of a fusion plasma.

Harvard University
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Harvard-Smithsonian Center For Astrophysics

236. *Theoretical Studies of Highly Ionized Species*
Dalgarno, A. **$138,000**
Comm. 617-495-4403

The structure of the molecular ion HCl^+, its photoionization, its radiative and predissociation lifetimes, and the cross sections for charge transfer in the collision of protons with chlorine atoms are being calculated. The fine-structure excitation of singly charged sulfur ions induced by collisions with photons and with sulfur ions is being investigated. Geometric phases in atomic collisions are being explored. A time-dependent formulation of photon scattering is under development.

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Manhattan, KS 66506

Department of Physics

237. *Atomic Physics of Strongly Correlated Systems*
Lin, C.D. **$123,250**
Comm. 913-532-6786

This project is directed at the understanding of the formation and the properties of multiply excited states of atoms and related systems. The molecular properties of doubly excited states of atoms are being analyzed to investigate the origin of molecular behavior displayed by these states. The autoionization and radiative decay rates of double Rydberg states of multiply charged ions are being investigated. Applications of hyperspherical coordinates to three-body problems with arbitrary pair interaction potentials are being pursued. Cross sections for the formation of doubly excited states resulting from the collision of multiply charged ions with atoms via charge transfer as well as double excitation processes are being carried out to understand the role of electron correlation in ion–atom collisions. The close-coupling method with atomic orbitals as basis functions is used, and the results are compared to experiments where individual doubly charged states have been identified.

238. *Atomic Physics with Highly Charged Ions*
Richard, P. **$1,449,420**
Comm. 913-532-6783

Zero-degree electron spectroscopy has been used to measure processes including K shell ionization and excitation of lithiumlike F and O projectiles by quasi-free electrons in He and H_2 targets. Measurements of the zero-degree production of binary encounter electrons by F, O, N, and C ions with H_2 and He targets have revealed an anomalous projectile charge state dependence. Work on laser-pumped lithium for similar studies is under way. Cross sections for charge transfer and target ionization have been measured in coincidence experiments for bare F and O projectiles on

He and D_2 targets between 0.25 and 2 MeV/amu and compared to model calculations. Cross sections for recoil ion production by O^{+q} and F^{+q} [q = 2 to bare] at 1 MeV/amu on Ar were measured. For 0.53/amu Cu and F ions on Ne, delta electron spectral shapes have been measured in coincidence with charge-separated recoil ions, and the distribution of the transverse momentum transfer among projectile, recoil ion, and ionized electrons was investigated for the latter beam using coincidences between recoils and angle-resolved projectiles. Differential cross sections were measured for ionization of Ne and Ar by 3 and 6 MeV protons and a model constructed for the description of relevant ionization mechanisms. A cryogenic electron beam ion source (EBIS) was put into operation and produces up to Ar^{+18} beams. The EBIS was used to measure cross sections for dielectronic recombination of heliumlike Ar using both ion yields and Ar K X rays from the source. Theoretical calculations of these cross sections were made and some discrepancies with experiment were identified. Theoretical calculations, which take into account correlations in the initial and final state wave functions and both one- and two-step mechanisms, were carried out for the double excitation of helium by projectiles over a wide range in velocity and charge state. Cross sections for transfer ionization of helium by fast protons via two-step Thomas scatterings were calculated. Extensive calculations of Auger and radiative rates in highly charged lithiumlike and berylliumlike ions were carried out and applied to calculate dielectronic recombination rate coefficients and resonant transfer and excitation (RTE) cross sections for selected cases. Calculations for coherent electron capture from oriented molecular hydrogen targets were made.

University of Louisville
Louisville, KY 40292

Department of Physics

239. Spectroscopic Studies of Hydrogen Atom and Molecule Collisions
Kielkopf, J. **$76,906**
Comm. 502-588-6787

Low-energy collisions of the hydrogen atom with other atoms, ions, or molecules in excited electronic states are fundamental processes in collision physics. Bound states of the simplest combinations are well-understood. However, light may be emitted or absorbed during the course of collisions of a free H atom with one or more atoms, involving, for example, transient free and bound states of H_3 and H_3^+. This research is directed toward understanding such radiative processes and the broadening of atomic spectral lines by collisions. A plasma with a small volume (10^{-4} cm^{-3}) and short duration (10 nanoseconds) is created in hydrogen at the focus of an ArF or YAG laser, yielding a high density of excited atoms and ions on each laser pulse. During and following recombination the spectra of the emitted light is observed and the excited region is probed with a tunable vacuum ultraviolet laser. Topics of current work include a study of the continuum emission and absorption from three body collisions, and a determination of resonant multiphoton processes in atomic hydrogen. Newly discovered population inversion and stimulated emission that occur in Al and Tl when their vapor interacts with hydrogen in the presence of focused 193 nm ArF excimer laser light are also being investigated.

National Institute of Standards and Technology
Gaithersburg, MD 20899

Center for Atomic, Molecular, and Optical Physics

240. Electron–Atom Collision Studies Using Optically State Selected Beams
Celotta, R.J.; Kelley, M.H. **$86,250**
Comm. 301-975-3710

Scattering experiments are carried out using spin-polarized incident electrons and optically pumped sodium atoms. Optical pumping of the target atoms produces either spin-polarized ground state atoms, or spin-polarized, aligned, and/or oriented excited-state (3P) atoms. The scattered electrons are detected as a function of scattering angle and incident energy. Elastic scattering measurements have been carried out at incident energies of 70 eV, 54.4 eV, 20 eV, and 10 eV. At the higher energies, it is possible to probe the relative roles played by spin-orbit and exchange effects; while they both contribute to the scattering roughly equally, there is no evidence of so-called interference effects arising from the simultaneous presence of the two. At the lower energies, large effects caused by exchange are seen. Measurement of these has introduced a new level of detail to the comparison between experiment and state-of-the-art theory. A similar level of detail has been provided by inelastic measurements at 54.4 eV, 20 eV, and 4.1 eV. Here, exchange effects as well as effects caused by the orientation and alignment of the target atom affect the scattering in dramatic ways. The comparison between theory and experiment has led to new insights and exacting tests of the current understanding of electron–atom scattering.

University of Nebraska
Lincoln, NE 68588-0111

Department of Physics and Astronomy

241. Dynamics of Collision Process
Starace, A.F. **$63,100**
Comm. 402-472-2795

This project is concerned with collision processes that are governed by the dynamics of three interacting charged particles. Results for three such processes have recently been obtained. First, detailed theoretical analyses have been presented of the projectile energy dependence as well as the target dependence of the electron detachment collision processes, $H^- + T \rightarrow H(n = 1,2) + T^* + e^-$, for targets T = He, Ne, Ar, Kr, and Xe, and for incident H^- projectile energies of 0.1, 0.5, 1.0, and 1.5 MeV. Inclusion of H(n = 2) final states in the calculations gives marked improvement in the agreement with experimental data. Second, photodetachment of H^- with excitation of H(n = 2) has been calculated using an adiabatic hyperspherical approximation; good agreement with the experimental line shape for the ^1P shape resonance is obtained. Third, an asymptotic expansion in Sturmian functions of the wave functions for three-body break-up processes has been carried out. These expansions lead to polarized orbitals for two-electron systems and to improved dissociation channels for molecular ions. Among additional processes being studied are two photon detachments of H^- with excitation of $H(n = 2)$ and capture of thermal muons by H.

University of New Mexico
Albuquerque, NM 87131

Department of Physics and Astronomy

242. *Relativistic Atomic Beam Spectroscopy II*
Bryant, H.C. **$105,000**
Comm. 505-277-3044

The negative ion of hydrogen is one of the simplest three-body systems. Understanding its spectroscopy, in addition to intrinsic scientific interest, is important to fusion research, astrophysics, and accelerator physics. 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 can be Doppler-shifted to energies in the ion's rest frame ranging from 34 to 400 MeV, thereby allowing study of multiphoton electron detachment involving multiplicity from 2 to 22 photons at a 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, also at the linear accelerator at Los Alamos (LAMPF), concerns the high-lying, doubly excited states in the negative hydrogen ion leading to double detachment. A very interesting pattern of so-called "ridge-states," which seem to be related to the Wannier double detachment mechanism, is beginning to emerge. An extensive survey of the systematics of these states is planned. Further studies of electric field effects and passage through foils are also planned.

University of Oregon
Eugene, OR 97403

Department of Physics

243. *Nonlinear Dynamics of Broad-Band Lasers*
Raymer, M.G.
Comm. 503-346-4785

The dynamical behavior of lasers operating simultaneously in many longitudinal modes is being studied experimentally. Significant progress has been made in determining the origin of the apparently random fluctuations in the amplitudes of the lasing cavity modes in a continuous dye laser. It was found that coherent four-wave mixing in the gain medium continually couples energy from one mode into another and a steady state is never reached. Current work is directed toward understanding the influence of quantum mechanical noise (spontaneous emission) on the laser dynamics very near, but just above, the lasing threshold, where such effects are predicted to be significant. These studies will be carried out with titanium-sapphire lasers, recently developed room-temperature, solid-state lasers that are tunable in the visible, and with dye lasers. The longer upper-level lifetime in the titanium-sapphire compared to the dye laser will change the nature of the dynamics. Relaxation oscillations caused by level-population dynamics may have to be taken into account. These studies have potential to help in the understanding of intracavity laser spectroscopy, an extremely sensitive technique for detecting low-concentration species.

Pennsylvania State University
Lehman, PA 18627

Department of Physics

244. *Electron Transfer, Ionization, and Excitation in Atomic Collisions*
Winter, T.G.; Alston, S.G. **$62,000**
Comm. 717-675-9278

Cross sections are calculated for the processes of electron transfer, excitation, and ionization in ion–atom collisions at keV to MeV energies. Simple systems containing one or two electrons are considered, since the most control can then be exercised over the use of approximations. In the lower-energy range, where the probability of electron transfer is largest, coupled-state approaches are applied because of the strong coupling of many states. Earlier one-electron work is being extended to the two-electron proton–helium-atom system. Large coupled-Sturmian-state calculations are under way to study how electron correlation affects electron transfer—90% or more of the electron correlation of the target is included. As the energy increases, perturbative approaches become valid because the likelihood of transfer decreases and the inverse of the impact velocity offers a convenient expansion parameter. Recent work has centered on a second-order Faddeev approximation for proton collisions with hydrogen and helium atoms; excellent agreement with experiment is obtained at MeV energies. When one of the nuclear charges becomes much larger than the other one, a different perturbative approach, the strong-potential approximation, is applicable at sufficiently high energies. A comparison of numerical results of this method and the coupled-state approach is now under way, with the goal of obtaining a formal connection of the two methods.

University of Pittsburgh
Pittsburgh, PA 15260

Department of Physics and Astronomy

245. *New Infrared Photon Absorption Processes*
Bayfield, J.E.
Comm. 412-624-9280

The simultaneous application of resonant ultraviolet and nonresonant mid-infrared laser radiation is a possible approach for the subpicosecond noncollisional breakdown of gases. Experiments are being carried out on the carbon dioxide laser ionization of optically excited hydrogen atoms with principal quantum numbers selected between n = 5 to 10. At present, 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 infrared wavelengths and may feature laser ionization rates enhanced over perturbative values.

Rice University
Houston, TX 77005

Department of Physics

246. Theoretical Atomic and Molecular Physics

Lane, N.F. **$80,000**
Comm. 713-527-4026

Quantum mechanical and semiclassical collision theory has been applied to the calculation of differential and integral cross sections, and selected rates, for a variety of atomic collision processes that are important to advanced energy research and in other applications. Recent progress includes results for: (1) charge transfer in He$^+$/H and H$^+$/He collisions: spin effects; (2) excitation and charge transfer in He$^+$/Na collisions: comparative MO and AO studies; (3) two-electron excitation in Li$^+$/He collisions; (4) selective-state excitation via charge-transfer in He^{2+}/Na collisions; and (5) orientation and alignment of Li(2p) resulting from Li/He collisions. Research is continuing on similar processes and on the development of new theoretical methods.

St. John Fisher College
Rochester, NY 14618

Department of Physics

247. Multilevel Relaxation Phenomena and Population Trappings

Hioe, F.T. **$73,000**
Comm. 716-385-8162

This project is directed toward the studies of multiphoton and multilevel coherent effects in laser-induced excitation of atomic systems. Among the new results obtained are a novel method for a two-photon population transfer in a three-level system driven by two overlapping laser pulses, and specific conditions that give rise to population trapping and possibilities for multiple optical solution propagation in multilevel systems. The group theoretical approach to the studies of the problem of dynamic symmetries in the laser-atom interaction will be continued, and the question concerning population trapping in atomic ionization suppression will be studied.

University of Tennessee
Knoxville, TN 37996

Department of Physics and Astronomy

248. Production and Destruction of Metastable Negative Ions

Pegg, D.J. **$83,500**
Comm. 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. The negative ion of Ca has been found to be, contrary to earlier expectations, stably bound in the $4s^24p\,^2P$ state (electron affinity of 43 MeV). Partial cross sections for detaching either the 2s or the 2p electron from the metastable He$^-$(1s2s2p^{4}P) ion have been determined at several different photon energies in the visible. Spectral dependences of the asymmetry parameters, characterizing the shapes of the photoelectron emission patterns for He$^-$ photodetachment, have been found to have shapes that, as yet, are not fully understood. Measurements of cross sections for photodetaching B$^-$ ions are under way.

Texas A and M University
College Station, TX 77843

Cyclotron Institute

249. Excitation of Atoms and Molecules in Collisions With Fast, Highly Charged Ions

Watson, R.L. **$83,000**
Comm. 409-845-1411

The systematics of multiple ionization and electron capture have been examined for Ar recoil-ion production in 1 MeV/amu oxygen ion collisions involving the capture or loss of 0, 1, and 2 electrons by the projectile. The relative cross section for Ar^{1+} production by pure ionization decreased with projectile charge (q) while the relative cross sections for Ar^{2+} through Ar^{4+} increased. In the case of electron capture, the mean charge state of the Ar recoil-ions increased as $q^{0.43}$ and displayed a discontinuity at q = 7 with the onset of capture to the K-shell. The charge state distributions were bell-shaped for both electron capture and electron loss for the high q. For low q, the charge state distributions for electron loss were similar to those for pure ionization. Calculations using the independent electron approximation give fair agreement with the data for high q, but the correspondence between the calculated and measured cross sections becomes progressively worse as q decreases and the recoil-ion charge increases.

University of Texas at Austin
Austin, TX 78712

Department of Physics

250. *Kinetic Studies Following State-Selective Laser Excitation*
Keto, J.W. **$104,000**
Comm. 512-471-4151

State-to-state rates for reaction of excited rare gas atoms with halogen molecules in harpoon reactions are being measured. The atoms are excited in two-photon transitions using ultraviolet lasers. Accurate (±2%) measurements of the reaction rates from Xe* to Cl_2 have been recently published for states in $5p^5 5d$, $5p^5 6p$, and $5p^5 7p$ configurations. These states provide a range of ionization potentials to compare with a multichannel curve crossing model. The measurements are now being extended to HCl and F_2 reactants and to excited states of krypton and argon using vuv lasers. A large termolecular contribution has been observed for energy transfer in xenon buffers but not in argon buffers. A model has been developed that agrees with both sets of experiments and assumes that a collision between the excited state and a background atom transiently lowers the ionization potential of the excited state, thereby increasing the harpoon reaction rate. Termolecular reactions in krypton buffers and at higher pressures where the diffusive limit is expected are now being studied. In different experiments, the laser is tuned away from the xenon atomic resonance so as to excite only atoms that are perturbed by collisions. By changing the wavelength of the laser, the internuclear separation of the electronically excited collision pair can be varied. The question of how the initial configuration of the excited pair influences the final quantum state of the reaction is then studied.

University of Toledo
Toledo, OH 43606

Department of Physics and Astronomy

251. *Semiempirical Studies of Atomic Structure*
Curtis, L.J. **$52,000**
Comm. 419-537-2341

The energy level structures, transition probabilities, ionization potentials, polarizabilities, and other properties of highly ionized many-electron atoms 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 sources, and conventional light sources. The experimental studies are strengthened through large-scale *ab initio* calculations using the MFE Cray X-MP computer. The available database is extended and improved in accuracy by predictive systematization and parameterization along isoelectronic, homologous, isoionic, Rydberg, and yrast series. Projects conducted during this past year include: (1) the prediction of transition probabilities in two valence electron isoelectron sequences using semiempirically projected line strengths and singlet–triplet mixing angles obtained from spectroscopic data; (2) lifetime measurements of quintet states in neutral carbon, for which radiative and autoionization channels are in sensitive competition; (3) lifetime measurements by coincidence methods of two-photon emitting states in hydrogenlike and heliumlike nickel; and (4) high-precision predictions of the resonance transition wavelengths for the lithium isoeletronic sequence using semiempirical screening parameterizations of quantum electrodynamic contributions.

252. *Measurements of Scattering Processes in Negative Ion-Atom Collisions*
Kvale, T.J. **$60,947**
Comm. 419-537-2980

A new experimental facility will be used to study the collisions of negative ions with neutral atoms at intermediate impact energies. The initial series of experiments will concentrate of H^- + noble gas collisional systems for 0- to 44-mrad scattering in the 5- to 55-keV impact energy region. The measurements will be of absolute, angular differential cross sections (ADCS) for elastic scattering, electron detachment, and target excitation/ionization processes. The experimental technique is Ion Energy Loss Spectroscopy (IELS), which is useful in distinguishing elastic scattering from inelastic processes. These measurements will be conducted on the University of Toledo Negative Ion Energy Loss Spectrometer (UT-NIELS), which is scheduled for initial operation this year. In order to obtain state-resolved ADCS measurements, high energy resolutions and high angular resolutions are necessary, and the design goal of UT-NIELS is an energy resolution of 0.3 eV and an angular resolution of 0.10 mrad, with an angular step size of 0.01 mrad. The measurements of the ADCS for the processes listed above, in comparison with sophisticated theoretical models, will provide stringent tests of scattering in ion–atom collisions, and of the structure of negative ions.

Vanderbilt University
Nashville, TN 37235

Department of Computer Science

253. *Theoretical Studies of Atomic Transitions*
Fischer, C.F. **$118,320**
Comm. 615-322-2926

Atomic structure calculations are being performed to predict properties such as energy levels, binding energies, 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 in this work. Recent calculations have concentrated on core-excited states of sodium iodinelike ions in order to assist the identification of lines observed in beam-foil spectra. Of primary interest are the quartet levels in the 2500 to 4000 Å region. Both wavelengths and lifetimes need to be predicted. Because of spin-orbit interaction, autoionization is a possible mode of decay as well as radiative transitions. Another problem being investigated is the role of core-polarization in negative calcium. *Ab initio* calculations are difficult and lengthy so a semi-empirical core-polarization approach is being used. Also under development is a modification to the multiconfiguration Dirac–Fock code (GRASP), replacing the full matrix representation by a sparse one. The latter should make possible large relativistic calculations for some levels in Gd with a half-filled f-shell, and study correlation in U^{+4}.

University of Virginia
Charlottesville, VA 22901

Department of Physics

254. ***Studies of Autoionizing States Relevant to Dielectronic Recombination***
Gallagher, T.F. **$107,657**
Comm. 804-924-6817

Dielectronic recombination, the recombination of an impurity ion and an electron via an intermediate autoionizing state, contributes to the radiative power loss in fusion plasmas. While it is a real problem in a plasma, a plasma is not the best environment in which to study the process. The inverse process, the excitation of autoionizing states by multistep laser excitation, is under study. The intrinsic autoionization rates of a broad range of atomic states are studied and how the rates are affected by perturbations, such as the ionic microfields that are found in a plasma, is observed. During the past year the first measurements of the autoionization rates of the Mg 3pnl states were made. Specifically, the excitation spectra of the 3pns and 3pnd $J = 1$ and 3 states were obtained. A quantum defect theory analysis of the data was carried out using the previously calculated K matrix and excellent agreement was found. Dielectronic recombination measurements have been made with magnesium, and as a result a series of measurements of autoionization rates in magnesium would provide a stringent test of the theories used to calculate the recombination rates.

Western Michigan University
Kalamazoo, MI 49008-5151

Department of Physics

255. ***Correlated Charge-Changing Ion–Atom Collisions***
Bernstein, E.M.; Tanis, J.A. **$86,000**
Comm. 616-387-4941

Experimental studies of fundamental atomic interactions are conducted for collisions of few-electron ions with neutral gas targets, single crystals, or electrons. Processes involving excitation, ionization, and charge transfer are investigated using coincidence techniques. A major emphasis of this research is the study of two-electron interactions, and particularly those in which the electron–electron interaction plays a role. Specific interaction mechanisms are isolated and identified by detecting charge-changed projectile ions emerging from the collision region in coincidence with X rays, recoiling target ions, or electrons. The studies typically involve ions with $2 \leq Z \leq 92$ in charge states $q \geq Z/2$ and energies ranging from 5 keV/u to 1000 MeV/u. Accelerator facilities at Lawrence Berkeley Laboratory, Argonne National Laboratory, Western Michigan University, and Indiana University are used in this work. Principal areas of investigation are: (1) resonant capture and recombination processes, (2) double ionization mechanisms at intermediate and high velocities, and (3) continuum or Rydberg capture accompanied by inner-shell bound-state capture.

The College of William and Mary
Williamsburg, VA 23185

Department of Physics

256. ***Collisional Detachment of Negative Ions***
Champion, R.L.; Doverspike, L.D. **$98,600**
Comm. 804-221-3510

The goal of this research project is to develop an understanding of the dynamics of atomic and molecular collisions for systems involving negative ions. The experimental studies are designed to investigate gas-phase, two-body collisions for energies that range from a few electron volts up to several hundred electron volts. These experiments include measurements of total and differential cross sections for a number of exit channels. Mechanisms under investigation include collisional and associative detachment, charge transfer, and ion–molecule reactions. Systems currently being studied include the negative ions of hydrogen, deuterium, oxygen, and several halogen anions in collisions with atomic hydrogen and deuterium. A separate study of negative ion desorption from surfaces that are illuminated with ultraviolet light is also under way. In this latter experiment, it is observed that some molecules that impinge upon surfaces can fragment, attach an electron generated by the photon, and desorb from that surface as negative ions. The mechanism that drives this phenomenon is being examined.

Chemical Energy

Auburn University
Auburn, AL 36849

Department of Chemical Engineering

257. ***Carbon Deposition and Deactivation of Metallic Catalysts***
Baker, T.K. **$179,967**
Comm. 205-844-2007 **(18 months)**

Recent macro-scale studies have revealed some dramatic effects with regard to carbon deposition on alumina-supported cobalt particles that have been preheated in a critical concentration of H_2S prior to exposure to a hydrocarbon environment. With trace amounts of H_2S, subsequent yields of catalytically produced carbon were extremely high, whereas effective inhibition of carbon deposition was achieved when cobalt was preheated in significant amounts of H_2S. It is possible that surface construction of the cobalt crystallites occurs following adsorption of a critical amount of H_2S, resulting in the creation of a new surface that is particularly active towards hydrocarbon decomposition to produce carbon. Another series of experiments under investigation concerns the possibility of removing carbonaceous deposits from a deactivated catalyst system by treatment in atomic oxygen. It was found that two forms of deposit, filamentous and graphitic, are readily gasified in 2.0 Torr atomic oxygen at 50°C. In order to achieve the same rates of gasification in 2.0 Torr molecular oxygen it is necessary to heat the specimen to around 700°C. These studies indicate that there are fundamental differences in the mechanism by which atomic and molecular oxygen species interact with carbonaceous materials.

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

258. Hydrocarbon Rearrangements Promoted by Highly Electrophilic Transition Metal Complexes

Bercaw, J.E. **$133,110**
Comm. 818-356-6577

The scope, mechanism, and thermodynamics of α-olefin and butadiene polymerizations using well-defined, single-component organoscandium catalysts are under study. It was established that sterically crowded scandocene derivatives of the type $(\eta^5\text{–}C_5Me_5)_2Sc\text{–}R$, $[(\eta^5\text{–}C_5Me_4)_2SiMe_2]Sc\text{–}R$, and $[(\eta^5\text{–}C_5H_3CMe_3)_2SiMe_2]Sc\text{–}R$ (R = H, alkyl, and so forth) catalyze the dimerization of α-olefins to the "head-to-tail" dimers with remarkable selectivities (>99% for >50 turnovers in the case of 1-butene). The α,ω-dienes undergo clean cyclization to the corresponding methylenecycloalkane. Under present investigation are the mechanisms of the chain propagating (olefin insertion into [Sc–R] bonds) and chain transfer steps (βH and βalkyl elimination). The possibility that specific "agostic" C–H interactions are assisting some of these processes is being explored using kinetic and thermodynamic deuterium isotope effects as probes. With new linked cyclopentadienyl-amide ligands systems (e.g.,$[(\eta^5\text{–}C_5Me_4)SiMe_2(NCMe_3)]Sc\text{–}R$ and $[(\eta^5\text{–}C_5Me_3CMe_3)SiMe_2(NCMe_3)](Sc\text{–}R)$, polymerization of α-olefins is observed, and the kinetics of this clean catalytic system are being measured to establish the identity of the true catalyst. Modifications of these ligand systems are being made in hopes of obtaining a truly "living" Ziegler–Natta olefin polymerization system. The results of these studies are providing an understanding of some of the fundamental steps in olefin metathesis, dimerization, polymerization, hydroformylation and hydrogenation, hydrocarbon cracking, branching, and isomerization.

University of California
Irvine, CA 92717

Department of Chemistry

259. Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes

Evans, W.J. **$106,000**
Comm. 714-856-5174

The special chemical, physical, and catalytic properties of yttrium and the lanthanide elements, a unique group of metals that are abundant in the U.S., are under investigation. The utility of alkoxide ligands to provide soluble, reactive complexes of these metals which can be used under a variety of reaction conditions is being explored. It was found that syntheses involving the tert-butoxide ligand readily give trimetallic compounds such as $Y_3(OCMe_3)_7Cl_2(THF)_2$. This complex has a terminal chloride ligand which can be substituted to make reactive alkyl and hydride derivatives. This complex is also being used to study processes by which alkoxide compounds form polymetallic oxide materials (e.g., it converts under mild conditions to the tetradecametallic alkoxide complex $Y_{14}(OCMe_3)_{28}Cl_{10}O_2(THF)_4$). Syntheses involving the 2,6-dimethylphenoxide ligand (OAr′) yield monometallic and bimetallic complexes such as $Y(OAr')_3(THF)_3$ and $Y_2(OAr')_6(THF)_2$. The interconversion and derivatization chemistry of these complexes is being studied to generate mixed alkoxide alkyl complexes and to understand how polymetallic species are formed. Collectively, these complexes offer the opportunity to evaluate the effect of several types of three-dimensional alkoxide ligand frameworks on the chemistry of yttrium and the lanthanides. These results will allow the special properties of these metals to be exploited more effectively.

University of California
Santa Barbara, CA 93106

Department of Chemical and Nuclear Engineering

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

Weinberg, W.H. **$127,000**
Comm. 805-961-3525 **(18 months)**

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 clean and chemically modified 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). Selected measurements are planned to quantify the effects of adsorbed hydrogen and adsorbed oxygen on the surface reactions. 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.

Department of Chemistry

261. Studies Relevant to the Catalytic Activation of Carbon Monoxide

Ford, P.C. **$120,292**
Comm. 805-893-2443

This research project involves continuing investigations of fundamental reactions relevant to the catalytic activation of carbon monoxide. These involve mechanistic studies of the water gas shift and related CO reactions, including hydrocarbon carbonylations, as catalyzed by metal complexes dissolved in homogeneous solution or immobilized by functionalized polymers. Studies in progress include quantitative elucidation of reaction mechanisms for nucleophile-carbonyl adducts of mononuclear and cluster metal carbonyls and for ligand transformations on metal clusters related to the catalytic utilization of C_1 fragments, use of thermal and photochemical techniques to prepare and study reactive intermediates relevant to catalytic processes, and batch and flow reactor kinetic studies of working catalysts. The goals are to delineate the mechanistic principles that dictate effective conversions of C_1 compounds, thus to establish and extend chemical guidelines for molecular engineering of selective and efficient new catalysts for the utilization of coal and biomass as feedstocks for the production of fuels and high-value chemicals.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

262. Chemically Modified Electrodes and Related Solution Chemistry

Elliott, C.M. **$88,750**
Comm. 303-491-5204

The primary goal is the development of polymer-coated electrodes containing electroactive materials which alter the chemical and/or physical properties of the electrode-solution interface in useful ways. Several such electrodes have been prepared, and 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 was developed and this material is undergoing further study. There are two aspects to the studies of chemically modified electrodes. One is developing schemes for incorporating electroactive systems of interest into polymers; the other, developing and studying molecules that are of potential interest (e.g., catalysts) for incorporation into polymer films. 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 that 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.

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

Norton, J.R. **$166,951**
Comm. 303-491-5609 **(19 months)**

This project is investigating the stereochemistry of the formation of diosmacyclobutanes from olefins. This reaction models the chemisorption of olefins onto metal surfaces. 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). This project has also developed methods to use NMR in liquid crystal solvents to determine the structure of mononuclear and dinuclear ethylene complexes in solution. For the dinuclear ethylene complex, an 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

264. Lewis Acid Modified Molybdenum Sulfide Complexes

DuBois, M.R. **$69,045**
Comm. 303-492-5039

The objective is to identify how electronic effects of protic and Lewis acids alter the reactivity of molybdenum (Mo) sulfide sites in discrete dinuclear complexes. The project may provide a basis for evaluating the role of acids in the reactions of supported metal–sulfide catalysts. For example, derivatives with the formula $[C_5H_5Mo(\mu\text{-}SR)_2]_2$ (R = alkyl) react with protic acid at −77°C to form products tentatively identified as Mo hydrides. Upon warming to room temperature these metal-protonated complexes undergo a one-electron oxidation to form paramagnetic cations $[C_5H_5Mo(\mu\text{-}SR)_2]^+$ and H_2. When complexes of the same general formula contain substituents with electron-withdrawing groups, protonation at low temperature results in rapid S–R bond cleavage. Attempts to identify the initial site of protonation in the latter systems are in progress. Characterization of these protonated Mo(III) derivatives will provide mechanistic insight into the reversible heterolytic activation of H observed for related systems: $[(C_5H_5Mo)_2(\mu\text{-}S)(\mu\text{-}SR)_3]^+ + H_2 \rightleftharpoons (C_5H_5Mo)_2(\mu\text{-}SR)_3(\mu\text{-}SH) + H^+$. Reactions with Lewis acids are also being studied. Neutral Mo(IV) derivatives containing bridging sulfide ligands, $[(C_5H_5Mo)(\mu\text{-}S)(\mu\text{-}SR)]_2$, do not form stable adducts with trialkyl Al reagents despite the established nucleophilicity of these ligands. The role of steric interactions in these systems is being investigated.

University of Connecticut
Storrs, CT 06269-3060

Department of Chemistry

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

Suib, S.L. **$72,964**
Comm. 203-486-2797

The goals of this research program are (1) to prepare bimetallic and alloy phases of Co in zeolites; (2) to characterize the sizes, shapes, compositions, and structures of such species; and (3) to study the structure sensitivity of these metals in reactions of cyclopropane and H_2. The bimetallic and alloy species are prepared by codepositing two separate volatile metal complexes in the large pores of zeolite NaX followed by microwave plasma decomposition of these complexes. The resultant metal and bimetal particles are characterized by transmission electron microscopy (TEM), ferromagnetic resonance (FMR), chemisorption, and spin echo nuclear magnetic resonance (SENMR) to determine the relative particle sizes of the particles. The structure of the metal phases are determined by electron diffraction, X-ray powder diffraction, FMR, and SENMR. Bulk compositions are determined with atomic absorption and energy dispersive X-ray analyses. The shapes of the particles can be observed with TEM, SENMR, and FMR experiments. The catalytic activity and selectivity of these metal particles are tested for ring opening, hydrogenation, hydrogenolysis, and oligomerization reactions of cyclopropane and hydrogen. Both steady state and transient kinetic studies are used to characterize intermediates and final products. After initial reactivity of cyclopropane and hydrogen at the surface, titrations with H_2 and O_2 are done to determine the number, amount, and type of surface intermediate carbon and hydrogen species, respectively. Correlations among the sizes, shapes, and structures of metal particles and the turnover frequencies and selectivities of these catalysts are sought.

University of Delaware
Newark, DE 19716

Center for Catalytic Science and Technology

266. Selectivity of the Reactions of Oxygenates on Transition Metal Surfaces

Barteau, M.A. **$79,866**
Comm. 302-451-8905

This research focuses on the reactions of oxygenates (of interest as clean-burning, high-octane fuels) on transition metal surfaces, with emphasis on determining the influence of surface modifiers and surface structure on the interactions of oxygenates with rhodium and palladium surfaces. On palladium, higher alcohols and aldehydes decompose via a common sequence of reactions to CO, H_2, and lower hydrocarbons. This sequence involves surface alkoxide, η^2-aldehyde and acyl species. Reactions on rhodium differ in several important respects. First, although much of the oxygenate reaction network is identical to that on palladium, the kinetics of individual steps and thus the identities of the most abundant surface intermediates differ from those on palladium. Second, higher alcohols exhibit lower selectivities for hydrocarbon formation than do aldehydes on rhodium; spectroscopic studies suggest that alcohol and aldehyde synthesis pathways may diverge early in the network. These results are supported by mechanistic information about CO insertion from investigations of rhodium and palladium catalysts. These studies serve to illustrate the pathways, intermediates, and energetics of oxygenate reactions on group VIII metal surfaces and thus provide insights into the mechanisms of olefin hydroformylation and oxygenate synthesis from CO and H_2.

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

Gates, B.C. **$91,698**
Comm. 302-451-2347

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 and NMR spectroscopies. These "molecular" precursors are treated to give highly dispersed metals and are characterized by the same techniques. Thorough results have been obtained for tungsten and rhenium carbonyls on alumina and magnesia. $HRe(CO)_5$ forms a surface complex formulated as $Re(CO)_3(HOMg)(OMg)_2$. Similar complexes are formed from $H_3Re_3(CO)_{12}$ on alumina, and when these are treated in hydrogen at 400°C, they form small trirhenium monolayer rafts. Re is in a high oxidation state (about +6); each Re has two oxygen neighbors of the support, and the average Re–Re distance is 0.267 nm, which is less than the distance in bulk Re metal (0.274 nm) and about the same as the O–O distance in the (111) face of alumina. The results suggest metal–metal bonding in the cationic rafts. 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 spectroscopy. For each, Ir–Mg and Ir–O distances have been determined and used to construct models of the metal-support interface.

Harvard University
Cambridge, MA 02138

Department of Chemistry

268. Model Studies of Hydrodesulfurization and Hydrodenitrogenation on Molybdenum Surfaces

Friend, C.M. **$82,824**
Comm. 617-495-4052

The Mo-induced deoxygenation of alcohols and cyclic oxides and the desulfurization of thiols and cyclic sulfides have been investigated because of their importance in the catalytic deoxygenation of synthetic fuels and desulfurization of fuel feedstocks, respectively. These reactions were investigated on well-characterized single-crystal surfaces using state-of-the-art surface spectroscopies. This recent work suggests that adsorbed alkoxide (RO-) and thiolate (RS-) intermediates decompose via a transition state in which there is a substantial amount of C–X (X=O,S) bond cleavage. The kinetics for alkoxide decomposition correlate with the stability of the corresponding radicals formed via C–O bond cleavage. Similarly, the reactivity of the corresponding thiolates parallels alkyl stabilities. They also react more rapidly than the analogous alkoxides, as anticipated since the C–S bond is substantially weaker than corresponding C–O bonds. Surface sulfur and oxygen both inhibit nonselective decomposition, resulting in higher selectivity albeit slower reaction rates. There is not a change in mechanism on the modified surfaces since similar trends in reactivity are observed on clean, oxygen-precovered, and sulfur-modified Mo(110).

University of Illinois
Chicago, IL 60680

Department of Chemical Engineering

269. The Formation of Supported Bimetallic Clusters: The Effect of Support - Metal Precursor Interactions

Gonzalez, R.D. **$69,010**
Comm. 312-996-9430

The effect of catalyst pretreatment on the surface composition of supported bimetallic clusters is currently being studied using the following techniques: (1) *in situ* diffuse ultraviolet spectroscopy, (2) differential scanning calorimetry, and (3) electron microscopy. *In situ* diffuse ultraviolet reflectance spectroscopy is being used to probe the nature of the interactions between the metal precursors and the support. Current interest is on structural differences between catalysts prepared by impregnation and those prepared by ion exchange. Quantitative differential scanning calorimetry is being used to measure heats of reduction during the preparation of supported Pt–Ru bimetallic cluster catalysts. The reductive sequence is of current interest. Scanning transmission electron microscopy (STEM) is being used to measure individual particle compositions using (1) an imaging defocusing technique and (2) electron diffuse angle X-ray scattering (EDAX). For a series of supported Pt–Ru bimetallic cluster catalysts, the smaller bimetallic particles are alloyed. Larger ruthenium particles in addition to platinum particles are also present. True bimetallic clusters are favored for Pt–Ru compositions that are close to 50%.

Indiana University
Bloomington, IN 47405

Department of Chemistry

270. The Molecular Precursor Strategy for the Production of Superconducting Oxides

Caulton, K.C. **$103,530**
Comm. 812-855-4798

The project objective is to use the general principles of molecular metal alkoxide chemistry to synthesize mixed-metal (ternary) alkoxides $M_aM'_bM''_c(OR)_n$ and to convert these at low temperatures to ternary metal oxides of the general type shown to be high-temperature superconductors. The method is generalized to the synthesis of heterometallic oxo/alkoxides. Yttrium silyloxides $Y(OSiPh_3)_3L_n$ where n = 2 or 3 have been prepared. For a less bulky silyloxide, the product was $Y_2(OSiMe_2{}^tBu)_6({}^tBuMe_2SiOH)$. The acidic hydrogen in this molecule is a functional group that can be employed to introduce another metal. As another route to coupling yttrium to a second metal (e.g., Cu), the anionic $Y(OSiPh_3)_4(MeOC_2H_4OMe)^{-1}$ was prepared. These compounds have been characterized by ^{89}Y and ^{29}Si NMR, and by X-ray diffraction. Thermogravimetric studies are under way to understand how alkoxide composition influences conversion from molecular precursor to final solid. In addition, nontraditional energy sources such as photolysis and ultrasonication will be employed. In this fashion, conversion to bulk solid and direct formation of thin superconducting oxide layers is enabled, the latter from dip-coated substrates.

271. Metal Alkoxides: Models for Metal Oxides

Chisholm, M.H. **$111,418**
Comm. 812-855-6606

Structural analogies between polynuclear metal alkoxides and metal oxides have been noted, with the former providing models for subunits within the lattice structures of the latter. The choice of specific alkoxide ligand allows the design of unsaturation and substrate selectivity by alkoxide clusters. For molybdenum and tungsten alkoxide clusters, there exist analogies in structure and bonding with carbonyl clusters of the later transition elements based on isolobal relationships: $W(OR)_3 \longleftrightarrow Co(CO)_3$ and $Fe(CO)_3{}^-$ leads to similarities in the compounds $W_3(\mu_3 - CR')(OR)_9/Co(\mu_3 - CR')(CO)_9$ and $W_4(\mu_4 - C)(O)(OR)_{12}/Fe_4(\mu_4 - C)(CO)_{13}$. Current studies of alkoxide clusters of molybdenum and tungsten are focused on (1) the mode and mechanism of cleavage of C≡O and N≡N to carbide oxide/nitride; (2) the reactivity of hydrido/carbido and nitrido ligands; and (3) the reactions of unsaturated hydrocarbons (olefins, dienes, ene-ynes) with alkoxide clusters. Detailed studies by nuclear magnetic resonance (NMR) spectroscopy employing a variety of labels, solvents, and temperatures allow insight into fundamental reaction processes that parallel those observed in surface science.

272. *A Model Approach to Vanadium in Crude Oils and Their Refining*

Christou, G. **$98,600**
Comm. 812-855-2399

This research is directed toward (1) identifying the types of nonporphyrin vanadium (VO^{2+}) impurities in crude oils and (2) determining the mechanistic pathways by which they are reduced, de-ligated, and sulfided under hydrometallization (HDM) and hydrodesulfurization (HDS) conditions. As part of this identification process, investigation is continuing into the reactivity characteristics of VO^{2+} complexes under reducing conditions, extending the work from just thiolate ligands to mixed O/S and O/N ligands also, to better model the true oil impurities. In all cases, vanadium(III) complexes of various nuclearities are the products, with either partial or complete loss of the VO^{2+} oxygen. The neutral complex $V(SC_4H_9)_4$ has been obtained and fully characterized, and employed as a model for high-energy intermediates to V_2S_3 during HDS; its mass spectrum has been recorded and its fragmentation modes elucidated. The predominant process observed is C–S bond cleavage.

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

Gajewski, J.J.; Gilbert, K.E. **$90,000**
Comm. 812-855-1192

Efforts are continuing to understand the high-temperature cleavage reactions of alkyl-aromatic coal liquefaction model compounds. Gas phase pyrolysis of tetralin results in dehydrogenation, neophyl rearrangement, and ethyl benzene and styrene in an initiated reaction. Rearrangement and dehydrogenation must have the same kinetic order since their ratio is concentration independent. Pyrolysis of liquid tetralin is five times faster than the gas phase reaction and gives mostly naphthalene at low conversions but more 1-methylidan at longer reaction times. The 5-methylene-1,3-cyclohexadien-6,6-spirocyclobutane 1,4-adduct of CO loses CO in a first order reaction to give the methylene spiro triene and this rearranges to tetralin and *o* allyl toluene. The 1,3-shift of carbon occurs with a threefold preference for retention of configuration at the migrating carbon. The fact that no cleavage products (C_2 loss) are obtained in the ketone pyrolysis and the fact that the allyl toluene fraction decreases with temperature suggest that the species responsible for products is not that which is involved in the high-temperature pyrolysis of tetralin. Many organometallic structures in the Cambridge Crystallographic Database were minimized with a molecular mechanics program to assess the quality of the metal–ligand bond distance parameters. Simplex optimization has allowed refinement of the original set to more accurately reproduce a vast array of organometallic structures.

Indiana University–Purdue University Indianapolis, IN 46205

Department of Chemistry

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

Rabideau, P.W. **$79,865**
Comm. 317-274-6888

Dissolving metal reduction and alkylation reactions are important because they promote the solubilization and depolymerization of coal. Solubilization is important to liquefaction, as well as to the characterization of coal structure because the soluble fractions can be analyzed spectroscopically. This research seeks a better understanding of the reduction pathway using polynuclear aromatics (PAs) as model compounds. Two particularly attractive systems involve PAs separated by (1) inactive spacers (methylene groups) or (2) active spacers (benzene rings). In the first category, the reduction of dinaphthylethanes in ether and ammonia solvents was studied. The cleavage of the ethane bridge only occurs at higher temperatures regardless of solvent suggesting that solubilization of coals by reduction methods at low temperatures does not result from the cleavage of this type of bond. The second case included an investigation of a number of dinaphthylbenzenes and found that, unlike the related terphenyls, these compounds show no propensity for inner ring reduction. Moreover, reduction of the outer rings appears to occur without synergism, with a number of products isolated containing dihydro- or tetrahydroaromatic rings in the naphthalene moiety. Future studies will involve PAs within a polymer chain or as pendant groups. The focus of interest is how reduction in one ring affects the other, and how many alkyl groups can be incorporated with reductive alkylation.

University of Iowa Iowa City, IA 52242

Department of Chemistry

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

Jordan, R.F. **$87,755**
Comm. 319-335-2212

The objective of this research is to synthesize and understand the chemistry of new types of cationic d^0 organometallic complexes of Group IV-VI metals that incorporate important features of heterogeneous catalysts, such as high steric and electronic unsaturation, reactive alkyl ligands, and terminal and bridging oxo groups. Several new classes of highly unsaturated alkyl complexes have been prepared including $(C_5R_5)Zr(R)_2(THF)_2^+$ and $(C_5R_5)Zr(R)_2(dmpe)(THF)^+$ which have been characterized crystallographically, and $Zr(R)_3(THF)_3^+$. The scope and mechanisms of the olefin reactions of these complexes, and their relevance to Ziegler–Natta polymerization catalysis are being explored. The C–H activation chemistry of related bis-Cp cations $(C_5H_5)_2Zr(R)(L)^+$ is being studied from both a synthetic and a mechanistic perspective. These complexes react with pyridines and related substrates via ortho C–H activation to yield reactive Zr pyridyl species with three-membered Zr–N–C rings. Cationic pyridyl complexes produced in this manner undergo insertion of olefins, acetylenes, and other unsaturated substrates. The regiochemical trends and mechanistic details of these reactions have been studied in detail. A catalytic productive C–H activation reaction which effects overall insertion of olefins into the ortho C–H bond of pyridines and other heteroaromatic substrates has been developed based on these studies.

University of Kentucky
Lexington, KY 40506-0055

Department of Chemistry

276. Metallacumulenes and Carbide Complexes

Selegue, J.P. **$115,402**
Comm. 606-257-3484

The synthesis, structure, and reactivity of metallacumulenes and carbide complexes are being studied, with a long-term goal of obtaining a better understanding of the behavior of reactive carbon-rich fragments formed from carbon monoxide and acetylene on heterogeneous catalysts. The tautomerization of *tert*-butyl acetylene to *tert*-butyl vinylidene on molybdenum was studied using a variety of techniques. Exposure of $[Mo(HC{\equiv}CCMe_3)L_2(Cp)][BF_4]$ (L = PMe_3, PMe_2Ph) to CO effects conversion to *trans*-$[Mo(C{=}CHCMe_3)(CO)L_2(Cp)][BF_4]$. Small basic, monodentate phosphine ancillary ligands (L), and carbon monoxide as incoming ligand promote this rearrangement. Cyclic voltammetry and theoretical studies suggest that alkyne to vinylidene rearrangement should occur for anions $[Mo(HC{\equiv}CCMe_3)L_2(Cp)]^-$. However, only for $[Mo(HC[{\equiv}CCMe_3)(CO)(PPh_3)(Cp)][BF_4]$ did two-electron reduction, followed by protonation, lead to alkylidyne $[Mo({\equiv}CCH_2CMe_3)(CO)(PPh_3)(Cp)][BF_4]$ (in very low yield). Bis(alkyne) complexes $[M(HC{\equiv}CR)_2(CO)(Cp*)]^+$ (M = Mo, W; Cp* = η^5–C_5Me_5, R = CMe_3) are converted by stepwise deprotonation, methylation and deprotonation to alkynyl vinylidene complexes $[M(C{\equiv}CR)(C{=}CMeR)(CO)_2(Cp*)]$, potential precursors to bis(vinylidene) complexes. Reactions of ethyne with $[MXL_2(Cp)]$ (M = Fe, Ru) lead to η^2–ethyne complexes $[M(\eta^2\text{–}HC{\equiv}CH)L_2(Cp)]^+$ as kinetic products for the small ancillary ligands PMe_3, $P(OMe)_3$ and o–$C_6H_4(PMe_3)_2$. The rate of conversion of η^2–$HC{\equiv}CH$ to $C{=}CH_2$ decreases according to Fe > Ru and $P(OMe)_3 \geq o$–$C_6H_4(PMe_3)_2 > PMe_3$, whereas the rate of displacement of ethyne by acetonitrile decreases according to Fe > Ru and $PMe_3 > o$–$C_6H_4(PMe_3)_2 > P(OMe)_3$. The crystal structure of $[Ru(C{=}C{=}CHFc)(PPh_3)_2(Cp)][PF_6]$ (Fc = ferrocenyl) confirms that it is a monosubstituted allenylidene complex, with resonance contributions from both allenylidene and progargyl forms.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

277. Infrared Study of Carbon Deposits on Bimetallic Catalysts

Eischens, R.P. **$88,740**
Comm. 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 infrared spectra. In each case the added component (rhenium, iridium, or tin) lowers the formation of a carboxylate species, which is detected by infrared bands at 1585 and 1460 cm^{-1}. However, the tin–platinum/alumina catalyst shows a large synergistic increase in both total carbon and carboxylate. This effect is unexpected because it is not consistent with the use of tin–platinum catalysts in commercial processing. Attempts are being made to understand the enhanced carbon deposition by modifications in the catalyst preparation procedures and by studies of the effect of tin on the adsorptive properties of platinum.

278. Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane

Klier, K.; Simmons, G.W.; Herman, R.G. **$150,000**
Comm. 215-758-3577

Surfaces that are active for the activation of methane on palladium and involve $O/CH_2Cl_2/Pd(100)$ overlayers were studied by AES/LEED/TDS and HREELS. With oxygen adsorbed on the Pd surface, the previously observed disproportionation of the c(2 × 2)-0 structure into a mixture of a dense phase, $(\sqrt{5}\times\sqrt{5})R27^\circ$-0, and a rare phase, "(2 × 2)", is accounted for by a reconstruction–relaxation process of the Pd(100) surface that arises as a response to a critical coverage at a critical temperature. The O/Pd(100) study suggests that the rare adsorbed oxygen phase with a surface coverage $\theta_O \leq 0.25$ monolayer (ML), achievable at 650 K and low partial pressure of oxygen, is the most reactive state for oxidation reactions. This rare phase features adsorbed oxygen with a suitable chemisorption strength while leaving part of the Pd surface uncovered for breaking the C–H bond in methane. Dichloromethane, used to control oxidation of methane to formaldehyde over supported Pd catalysts, is adsorbed dissociatively on the Pd(100) surface. The CH_2Cl_2 adsorption proceeded with a near-unity initial sticking coefficient and reached saturation with Cl coverage of 0.22 ML. The surface structures formed, as well as their interactions with O, have been modeled and fitted to the CH_2Cl_2 adsorption data, and the best features are obtained with surface Cl–C–Cl ensembles, having 90° Cl–C–Cl angles, that exclude nearest-neighbor adsorption and Cl–Cl next-nearest-neighbor adsorption. A Monte Carlo simulation of the oxidation of surface carbon by surface oxygen atoms resulted in semiquantitative agreement with the observed rates of production of CO and CO_2 as a function of Cl coverage. The model explains selective oxidation to CO_2 on Cl-free Pd and to CO on Pd covered by some 20% Cl atoms in terms of a restricted supply of oxygen partially Cl-covered surfaces that can be regarded as ensemble control of the oxidation reaction.

University of Louisville
Louisville, KY 40292

Department of Chemistry

279. *Metallocarboxylate Chemistry*
Gibson, D.H. **$94,601**
Comm. 502-588-5977

Metallocarboxylates are implicated as intermediates in transition metal-catalyzed water–gas shift reactions and in catalytic processes leading to CO_2 fixation. Work is presently focused on the chemistry of metallocarboxylate anions, $LFe(CO)(PPh_3)CO_2^-M^+$ (L = Cp or Cp*; M = K, Li). An aqueous synthetic route that was developed for these anions leads to hydrated products (typically the trihydrate) that hydrolyze readily in nonaqueous media to the corresponding metallocarboxylic acids. The facility of this reaction limits the synthetic uses that can be made of the anions. Several routes have been explored that might provide the corresponding water-free products; the best route, thus far, involves dehydration of the hydrated ions. The resulting anhydrous metallocarboxylates have been characterized spectroscopically and are more thermally stable than the hydrated ones. Furthermore, they are stable enough in organic solvents to allow studies of their chemical properties. Their reactions with alkylating agents (and Ph_3SnCl) are similar to those of the hydrated anions and they exhibit oxide-transfer behavior toward some other electrophiles. Efforts are in progress to use these compounds as synthons for a variety of bimetallic CO_2-bridged complexes.

Massachusetts Institute of Technology
Cambridge, MA 02139

Department of Chemistry

280. *High-Pressure Heterogeneous Catalysis in a Low-Pressure, Ultrahigh Vacuum Environment*
Ceyer, S.T. **$200,000**
Comm. 617-253-4537 **(18 months)**

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 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.

281. *Controlled Synthesis of Polyenes by Catalytic Methods*
Schrock, R.R. **$118,375**
Comm. 617-253-1596

This project concerns the synthesis of organic conductors and related nonlinear optical materials, specifically polyenes at this stage, using well-defined transition metal complexes. It was shown that 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (TCDT-F6) can be ring-opened in a controlled manner by $M(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$($M$ = Mo or W; Ar = 2,6-C_6H_3-i-Pr_2) to give living oligomers from which the metal can be removed in a Wittig-like reaction with pivaldehyde or 4,4-dimethyl-*trans*-2-pentenal. Heating the oligomer yields a distribution of t-butyl-capped polyenes, $(t\text{-}Bu)(CH{=}CH)_x(t\text{-}Bu)$, where x is odd if pivaldehyde is used in the cleavage reaction, or even if 4,4-dimethyl-*trans*-2-pentenal is used. The retro Diels–Alder reaction was carried out on the living TCDT-F6 oligomers to give "living polyenes," $W[(CHCH)_x(CH\text{-}t\text{-}Bu)](NAr)(O\text{-}t\text{-}Bu)_2$, that are stable toward "back-biting" to give benzene, and thermally stable up to x = 10-12. These are now being used as reagents in Wittig-like reactions with unsaturated dialdehydes such as OHCCH=CHCH=CHCHO and OHCCH=CHCH=CHCH=CHCHO in order to prepare long polyenes. Living polyenes can also be prepared by the direct controlled polymerization of acetylene itself. The possibility of polymerizing substituted acetylenes in a controlled fashion is under investigation. The goals include a complete understanding of why and how polyenes of intermediate conjugation length (15 to 20 double bonds) crosslink, and an understanding of the relevance of that behavior to the nature of classical polyacetylene. Physical measurements on materials that are being made include (through collaborations) third-order nonlinear optical behavior, spectroscopy of radical cations in low-temperature matrices, and conductivity via microelectrode techniques.

University of Massachusetts
Amherst, MA 01003

Department of Chemical Engineering

282. *Surface Analyses and Modeling of Rate Multiplicity and Instabilities in Catalytic Reactions*
Harold, M.P. **$69,020**
Comm. 413-545-2507

Isothermal rate multiplicity can arise from interactions of mass transport and chemical rate processes. Knowledge of the multiplicity mechanism for platinum catalyzed carbon monoxide oxidation is crucial for understanding the more complex reactions which involve an adsorbed CO species. To address these issues, experimental and modeling studies of platinum catalyzed reactions with CO are being conducted; specifically, CO oxidation by both O_2 and NO. The first part of the research involves kinetic studies on an electrically heated platinum wire over a large temperature and pressure range. Operating regimes in which rate multiplicity exists are determined. Modifications of the commonly proposed three-step CO oxidation reaction sequence have been determined that are necessary in order to predict the basic kinetic and multiplicity features observed over a wide range of conditions. Model discrimination of three new models is based on the ability to simulate CO oxidation over a wide range of temperature, CO/oxygen ratio, and total pressure. Complicating features due to mass transport limitations and catalyst hot spots are also modeled. The simulations of CO oxidation over a wide pressure range help to bridge the gap between surface science and atmospheric pressure. The second part of the research involves the development of a novel scanning Fourier transform infrared emission technique to study catalytic reaction dynamics. Emission spectra obtained for CO chemisorbed on Pt/Al_2O_3 samples reveal linear- and bridge-bonded CO and gas phase CO. The emission spectra agree well with transmission spectra obtained with the same catalyst. Three important factors which influence the spectra quality have been identified: background radiation, sample thickness, and metal loading. Emission FTIR studies for NO chemisorption, and CO oxidation by NO on the same catalyst are currently under way.

University of Minnesota
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Department of Chemical Engineering and Materials Science

283. *Homogeneous–Heterogeneous Combustion: Chemical and Thermal Coupling*
Schmidt, L.D. **$85,486**
Comm. 612-625-9391

The roles of homogeneous and heterogeneous reactions in combustion processes are being studied experimentally and theoretically by examining the 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 the $NH_3 + O_2 \rightarrow NO$, $CH_4 + O_2 \rightarrow CO$, and $CH_4 + NH_3 + O_2 \rightarrow HCN$ 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 bifurcation behavior (occurrence of multiple steady states and oscillations) for various models of homogeneous–heterogeneous processes. Reaction rate expressions for individual surface and homogeneous reactions will also be used to simulate behavior observed experimentally. 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.

University of Missouri
Columbia, MO 65211

Department of Chemistry

284. *Late Transition Metal μ-Oxo and μ-Imido Complexes*
Sharp, P.R. **$100,448**
Comm. 314-882-7715

The synthesis and reactions of oxo, imido, dioxygen, and nitrosoarene complexes of the late transition metals are being studied. 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. The exploration of the versatility of these synthetic procedures and the reaction chemistry of the complexes is continuing. Unique reactivity leading to C–C bond formation associated with the high basicity of arene imido complexes has been found and may have applications in synthetic organic chemistry. Also being explored is the possibility of a dioxygen-to-dioxo pathway to the oxo complexes. This would amount to molecular oxygen activation and would mimic another property of the metal surfaces. An important part of this effort is the synthesis, using already established methods, of oxo (and imido) complexes that can be targeted for formation from dioxygen.

University of Nevada
Reno, NV 89557

Department of Chemistry

285. *High-Temperature Chemistry of Aromatic Hydrocarbons*
Scott, L.T. **$93,670**
Comm. 702-784-6683

This work focuses on some of the elementary chemical processes that occur during the uncatalyzed conversions of coal, particularly its gasification and liquefaction. The molecular reaction chemistry occurring during the heating of coals to high temperatures will be studied, as it pertains to the thermal transformations of primary subunits in coal comprised of benzenoid rings and related aromatic structures (all prominent in the molecular architecture of coal). The work aims to uncover the principal reaction channels available to polycyclic aromatic hydrocarbons, and to understand the rearrangements and interconversions that occur upon thermal activation.

State University of New York/Binghamton
Binghamton, NY 13901

Department of Chemistry

286. *Photochemistry of Intermolecular C–H Bond Activation*
Lees, A.J. **$75,333**
Comm. 607-777-2362

This research encompasses detailed study of the photochemistry of several organometallic complexes which, on light excitation, activate hydrocarbon C–H bonds. Low-temperature spectroscopic and steady-state laser photolysis measurements are being performed for the complexes (η^5–C_5R_5)M(CO)$_2$ (M = Rh, Ir; R = M, Me), (η^5–C_9H_7)Ir(CO)$_2$ (η^5–C_9H_7 = indenyl) and (η^5–C_5H_5)Re(CO)$_2$L (L = a pyridine derivative) under dilute solution conditions in deoxygenated alkane and aromatic solvents. In each system the solution photoreaction has been carefully monitored by diode-array UV-visible and FTIR spectroscopy and photoproducts have been further characterized by mass spectrometry. The solution photochemistry (laser excitation at 458 nm) of (η^5–C_5H_5)Rh(CO)$_2$ has also been monitored in the presence of excess PPh$_3$ scavenging ligand. FTIR spectral sequences recorded over the time of photolysis illustrate that the photoreaction involves clean and complete conversion to the *(η^5–C_5H_5)Rh(CO)(PPh$_3$)* complex. Photochemical quantum efficiencies have been determined and they show a linear dependence on entering PPh$_3$ ligand concentration in the 0.05 to 0.3 M range. This result reveals that the photosubstitution reaction does not take place via a dissociative mechanism, as currently understood, but rather it involves an associative process.

State University of New York/Buffalo
Buffalo, NY 14214

Department of Chemistry

287. *Mechanistic Examination of Organometallic Electron-Transfer Reactions*
Atwood, J.D. **$82,825**
Comm. 716-831-2122

Research designed to provide a mechanistic understanding of the transfer of electrons between organometallic complexes is being pursued. This understanding should prove very useful in applications of electron-transfer catalysis. It was established that metal-based anionic species undergo a variety of reactions with at least three distinct mechanisms. Reactions of anions with cations result in a two-electron process (CO^{2+} transfer); a similar reaction is operative in reactions of dianions with neutral complexes. A nucelophilic attack mechanism is operative in reactions of anions with dimeric complexes and with MeI. An outer sphere mechanism is operative in reactions between metal carbonyl anions and coordination complexes and between cluster ions and clusters. All of these reactions are examined kinetically by stopped-flow infrared spectroscopy and by isotope-labeling experiments. An understanding of the reactivity patterns of metal-based anions as models for electron transfer in organometallic reactions is being developed.

University of North Carolina
Chapel Hill, NC 27599-3290

Department of Chemistry

288. *Reductive Coupling of Carbon Monoxide to C_2 Products*
Templeton, J.L. **$110,919**
Comm. 919-966-4575

Coupling reactions involving carbon monoxide and carbyne ligands are being explored. A rare aryloxycarbyne complex has been prepared by nucleophilic attack on a phosphonium carbyne unit with a substituted phenoxide reagent, and the reaction chemistry of the metal-carbon triple bond is being extended to additional heteroatom carbynes. Electrophilic attack at the oxygen of a terminal carbonyl ligand to generate related alkoxycarbyne ligands is a long-term goal. In modeling this chemistry it was found that electrophilic addition to isonitrile ligands can generate aminocarbyne products or η^2–iminoacyl complexes. The η^2–iminoacyl complexes are sufficiently acidic at the Cβ position that deprotonation/alkylation sequences succeed in elaborating the η^2–iminoacyl substituent. The aminocarbyne monomers can be protonated in the presence of phenylacetylene to form η^2–vinyl products. These results are compatible with formation of a cationic carbene by carbyne protonation followed by alkyne insertion to form the η^2–vinyl iminium complex. Hydride addition to the iminium carbon is easily accomplished and a neutral-amine-substituted η^2–vinyl complex is the final product.

Northwestern University
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Department of Chemical Engineering

289. *Solid-State, Surface, and Catalytic Studies of Oxides*
Kung, H.H. **$150,000**
Comm. 708-491-7492

The selective conversion of low-priced saturated hydrocarbons to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher values can be of great technological importance. The emphasis of this project is to elucidate the properties of oxidic catalysts that could achieve these conversions efficiently by selective oxidation. For practical purposes, the ability to produce only one desired product among many possibilities, some of which are extremely thermodynamically favorable, is important. 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 showed that in a mixed vanadium–magnesium oxide catalyst, the high activity and selectivity in the oxidation of butane can be correlated to the presence of magnesium orthovanadate. It was then found that whereas samarium and neodymium orthovanadates were also selective catalysts, europium orthovanadate was less selective, and magnesium pyrovanadate and metavanadate were nonselective. The differences among these vanadates can be attributed to the different nature of M in the M–O–V bonds in these oxides, and particularly the different redox properties of the cation M. In addition to butane, the mixed magnesium–vanadium oxide was also quite selective in the oxidation of propane, 2-methylpropane, and cyclohexane. It was found that when the selectivities for alkenes were plotted as a function of alkane conversion, propane and 2-methylpropane showed very similar behavior, while butane and cyclohexane showed a different behavior. Their differences can be correlated with the subsequent reactions of the pi-allyl intermediates in the reactions of the alkenes.

Department of Chemistry

290. *Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, and Catalysis*

Marks, T.J. **$97,548**
Comm. 708-491-5658

The project objective is to understand the dramatic and technologically important changes in catalytic activity that occur when metal hydrocarbyl molecules are adsorbed on metal oxide and metal halide surfaces. The approaches involve integrated surface chemical (product analysis, isotopic labeling), catalytic (chemoselectivity, kinetics), and spectroscopic (CPMAS NMR, FT-IR) studies of selected actinide, lanthanide, and group 4 organometallic molecules adsorbed on high surface area Al_2O_3, SiO_2, $MgCl_2$, and other supports. A parallel solution chemistry effort focuses on the synthesis and structural characterization of complexes that spectroscopically and chemically model the surface environment and test ideas about the chemistry. A detailed kinetic/mechanistic study has been completed on hydrogenation of a variety of olefins by $Cp'_2Th(CH_3)_2/Al_2O_3$ and $Cp'_2Th(CH_3)_2/MgCl_2$, where $Cp' = (CH_3)_5C_5$. There are striking mechanistic similarities to f-element reaction patterns in solution. Furthermore, NMR studies reveal that unsaturated cationic complexes of the type $Cp'_2ThCH_3^+$ and $Cp_2ZrCH_3^+$ ($Cp = C_5H_5$) are formed in large quantities on Al_2O_3 and $MgCl_2$ surfaces. Rational synthetic routes to such f-element cations have now been developed in solution. Cationic organothorium species have also been identified on other Lewis acid supports, and dosing with various reagents affords a detailed, *in situ* picture of the surface reaction chemistry. Good agreement is found between the percentage of active sites deduced by catalytic poisoning and NMR studies.

291. *Chemical Interactions in Multimetal–Zeolite Catalysts*

Sachtler, W.M.H. **$103,500**
Comm. 708-491-5263

The chemistry controlling the formation, composition, and size of bimetallic particles in zeolite cages has been studied. The position and coordination of ions and the size of reduced particles have been examined by diffuse reflectance spectroscopy and X-ray absorption fine structure, extended (EXAFS). It is found that the most effective way of producing zeolite-encaged PtRe particles is a two-step process: Pt is deposited by ion exchange, calcination, and reduction; subsequently a volatile rhenium carbonyl is deposited and decomposed in a hydrogen flow. Activity and selectivity of such catalysts for hydrocarbon conversion reactions differ significantly from those of samples prepared from bimetallic PtRe carbonyl clusters. Zeolite-encaged combinations of Pd with Co, Ni, or Fe reveal interactions of the unreduced ions with each other or with reduced particles. The reducibility of Co in NaY is dramatically enhanced by Pd; this enhancement is largest when Pd and Co ions are located in each other's proximity, which is contrary to simple hydrogen spill-over models. Moessbauer data and Fourier transform infrared (FTIR) of adsorbed CO show that Fe ions decorate zeolite-encaged Pd particles. Catalytic superactivity of Pd/NaY is observed and attributed to "electron-deficient" adducts of protons and Pd clusters.

292. *Organometallic Surface Chemistry*

Shriver, D.F. **$101,700**
Comm. 708-491-5655

The overall objective is to develop a greater understanding of the way in which metal clusters activate ligands and the relation between these processes in cluster compounds and similar transformations on metal surfaces. The reactions of metal oxide supports with metal clusters containing the ketenylidene (CCO) ligand are being studied. Another area of investigation is the formation, structural chemistry, and reactivity of organometallic clusters containing the oxo ligand. This is of interest for comparing the chemistry and structures of these compounds with that of oxygen on surfaces.

University of Oklahoma
Norman, OK 73019

Department of Chemistry

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

Nicholas, K.M. **$100,819**
Comm. 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 photochemical conditions. The first extensive reactivity study of an η^2–CO_2 complex: $Cp_2Mo(\eta^2–CO_2)$ was begun. Following the reported discovery of the remarkable photochemical reactivity of this complex, this compound was found to react readily in the dark with a variety of electrophilic reagents including R_3SiCl, HCl,RC(=O)Cl, and BX_3 to afford cationic carbonyl complexes of the type $[Cp_2Mo(CO)Nu]^+Nu^-$ and E–O–E, the result of CO_2-splitting with oxygen transfer to the electrophile. The reactions of the previously cited complex with various group and transition metal hydrides, designed to induce reduction of coordinated CO_2, are now under investigation. Studies were also initiated directed towards modeling CO_2 insertion reactions into M–C bonds using $(MeC_5H_4)_2Nb(\eta^2–CO_2)CH_2SiMe_3$, the only established example of a complex containing both coordinated CO_2 and alkyl ligands.

University of Oregon Eugene, OR 97403

Department of Chemistry

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

Finke, R.G. **$85,375**
Comm. 503-346-4622

The goal of this research is to develop a chemical paradigm for polyoxoanion-supported transition-metal catalysis, with an emphasis on small molecule (H_2, O_2, CH_4) catalytic activation and functionalization (CH_4, RH). Kinetic and mechanistic studies are an integral part of this work, since they provide both the best and fastest way to reliably establish the strengths and weaknesses of this previously unknown class of catalytic materials. The first example of a polyoxoanion-supported catalyst has been reported. That work employs the novel, second-generation catalyst precursor $[(Bu_4N)_5Na_3][(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$, the best polyoxoanion-support material to date, and describes *H_2 activation and related chemistry. A mechanistic study* providing the needed evidence that the true catalyst is indeed polyoxoanion-supported, has also been reported. The mechanistic studies noted above pointed towards a preference for oxidative addition of substrates like H_2 and O_2, and led to studies of cyclohexene catalytic oxidations by O_2 and $[(Bu_4N)_5Na_3][(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$. This work provides the first example of oxidative catalysis by a polyoxoanion-supported metal and only the second example of polyoxoanion-supported catalysis of any type. The turnover rates and turnover numbers are better than any previous Ir-catalyzed oxygenation of cyclohexene using dioxygen.

Pennsylvania State University University Park, PA 16802

Department of Chemical Engineering

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

Vannice, M.A. **$111,418**
Comm. 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 and (2) to use these effects to favorably alter hydrogenation reactions. Focus is on characterizing adsorbed molecules and the chemical and physical state of the metal and support. Early studies found rate enhancements greater than 100-fold for CO and acetone hydrogenation (to isopropyl alcohol), 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 and the effect, if any, of supporting gold on titania. In addition, an ultra high vacuum (UHV) system with high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and a high-pressure reaction chamber is being set up to investigate CO and acetone adsorbed on Pt and TiO_2 single crystals and a Pt-covered TiO_2 single crystal. Studies of BTXs have shown that turnover frequencies (TOFs) can be increased using acidic supports, with the greatest enhancements occurring with benzene. The addition of methyl groups to the ring decreases TOF values in the order benzene $\gtrsim$toluene $\geq$p-xylene $\geq$m-xylene $\gtrsim$o-xylene. The presence of additional acidic adsorption sites on the support near the Pd crystallites has been proposed to explain this behavior. Emphasis is now on the characterization of these adsorbed molecules using infrared spectroscopy.

Department of Chemistry

296. Mechanistic Studies of Carbon Monoxide Insertion into Metal–Nitrene and Metal–Carbene Bonds

Geoffroy, G.L. **$122,264**
Comm. 814-865-9591

The reactivity of nitrene, carbene, and ketene ligands on metal clusters is being studied. The overall goal of the nitrene research is to understand the mechanism by which Ru complexes catalyze the carbonylation of nitroaromatics to form isocyanates, carbamates, azo, and azoxy compounds. Insight into the mechanism by which halides promote these reactions has been provided, and unique bimetallic Fe/Ru catalysts for nitroaromatic carbonylation have been discovered. The data indicate that the initial activation of the nitroaromatic occurs via electron transfer from a reducing metal complex to the nitroaromatic molecule, and this line of investigation is being pursued. The reaction of diiron methylene compounds with phosphinimines gives rise to unprecedented transformations that lead to the formation of binuclear ferra-pyrrolinone and ferra-azetine complexes. These complexes in turn react with alkynes to give binuclear ferrapyridine complexes from which free organic pyrrolinones can be released by heating under a CO atmosphere. Protonation of the binuclear ferra-azetine complexes leads to the synthesis of binuclear azaallylidene complexes which in turn react with alkynes to give binuclear ferrole complexes. These latter compounds possess an unprecedented example of a fluorine atom bridging between carbon and boron atoms. The chemistry of these and related binuclear complexes is currently under exploration. In other work, a series of chiral anionic manganese acetylide complexes have been discovered. These compounds are remarkably nucleophilic and undergo a number of unusual addition and cycloaddition reactions with organic substrates, generally with high stereospecificity.

297. Transition-Metal-Mediated Transformations of Small Molecules

Sen, A. **$86,768**
Comm. 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 these processes. The project objectives are: (1) to achieve a fundamental understanding of a number of processes of this type and (2) to use this knowledge to develop new and useful catalytic processes. The project encompasses research in three specific areas of catalysis. The first involves the catalytic synthesis of new alternating copolymers of carbon monoxide and olefins, and a new catalytic route to polycarbonates, polyesters, and polyamides. The second area of research involves the examination of the chemistry of metal complexes incorporating oxo and alkyl ligands as a model for the industrially important heterogeneous oxidation of olefins and alkanes by metal oxides. Specific plans are to mimic in solution two proposed key steps in the heterogeneous oxidations. These are, respectively, the heterolytic cleavage of an alkyl C–H bond that is assisted by an oxo ligand, and the transfer of an oxo group to the resultant metal-bound alkyl ligand. The final research area is concerned with the development of a hybrid catalyst system involving both homogeneous and heterogeneous components for the oxidation of alkanes. The basic idea is to employ a transition-metal in the elemental state to activate an alkane C–H bond and form a surface alkyl group. A second transition-metal species that will oxidize the surface alkyl group to form oxidized organic products will be present in solution.

Department of Materials Science and Engineering

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

Painter, P.C. **$98,600**
Comm. 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 fundamental knowledge of coal structure both at the level of local composition and at the larger scale of the effect of the balance of intermolecular forces on solution and swelling behavior. In recent work previous methods of relating swelling measurements have been modified to account for hydrogen bonding and a new theoretical model has been proposed. On this basis it has been predicted that the number of aromatic clusters between cross-links is small and that swollen coal gels will exhibit a phenomenon called gel collapse at certain solvent concentrations and/or temperatures.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemical Engineering

299. *Support Effects Studied on Model Supported Catalysts*

Gorte, R.J. **$90,712**
Comm. 215-898-4439

Model catalysts consisting of thin films of Group VIII metals deposited on alumina, zirconia, and zinc oxide substrates are being used to study the properties of supported metal catalysts. Samples are prepared under ultrahigh vacuum conditions and can be characterized using standard surface science techniques, including Auger electron spectroscopy, photoelectron spectroscopy, and temperature-programmed desorption of simple gases. Transmission electron microscopy is being used to characterize selected samples, and reaction rates for CO hydrogenation and NO reduction by CO are being used on some samples to relate the spectroscopic results to the catalytic properties. Preparation conditions and metal loading are being varied in order to separate effects caused by oxide and particle size. The results of these experiments are being used to understand how the oxide substrate affects the structure and properties of supported metal particles.

Department of Chemistry

300. *Synthesis and Properties of New Preceramic Materials*

Sneddon, L.G. **$98,600**
Comm. 215-898-8632

This project is focused on the development of new molecular and polymeric precursors to nonoxide ceramics. The use of such chemical precursors may allow ceramic formation under milder conditions and in different forms than possible with conventional high-temperature powder techniques. Boron-based ceramics, such as boron carbide and boron nitride, are materials of particular interest, because of both their hard refractory nature and their useful electronic properties. For example, boron carbide has been shown to have excellent promise as a high-temperature thermoelectric material, while boron nitride has applications as both a dielectric material in semiconductor devices and as a fiber coating that will improve the strength of ceramic composites. This work has resulted in the development of new selective routes to boron carbide and boron nitride based on the use of a series of new boron polymer systems that have been synthesized. Under current investigation are the properties of thin-film and coated materials derived from these polymers, the development of new polymeric precursors to both boron carbide and boron nitride, and an extension of these techniques to the formation of metal borides ceramics.

301. *Catalytic Hydrogenation of Carbon Monoxide*

Wayland, B.B. **$118,000**
Comm. 215-898-8633

The primary focus of this program is to explore potential strategies for the hydrogenation of carbon monoxide to form organic oxygenates. Metal promoted reactions of CO and H_2 to form intermediate metalloformyl (M–CHO) and hydroxymethyl ($M–CH_2OH$) complexes is the most widely accepted route to oxygenates. Alternate pathways that use reductive coupling of CO as the initial step and subsequent hydrogenation may be important in selective formation of two carbon products. Rhodium porphyrin and related macrocycle complexes are being used to probe the formation of intermediates in these diverse CO hydrogenation mechanisms. Favorable thermodynamic factors for producing formyl complexes (M–CHO) from H_2 and CO and reductive coupling of CO to form α-diketone species (M–C(O)C(O)–M) provide an unusual opportunity to evaluate these types of complexes as productive intermediates in organic oxygenate formation. 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. Studies are directed toward the use of nonmacrocyclic ligand complexes that emulate the favorable thermodynamic features associated with rhodium macrocycles, but that also manifest improved reaction kinetics. 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 are promising candidates to accomplish CO hydrogenation at mild conditions.

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Department of Chemistry

302. Studies of the Fundamental Nature of Catalytic Acidity, Sites, and Intermediates

Hall, W.K. **$104,000**
Comm. 412-624-8360

This research has been directed toward understanding the factors that govern catalyst acidity and its influence on activity and selectivity. Two approaches have been used. The first involved spectroscopic measurements of chemisorbed species to test the ability of various preparations to form carbenium ions and other protonated bases. The second was studies of reactions of model compounds. A motivation was to determine whether any of the preparations (mainly zeolites) were superacids. Carbon-13-MASNMR studies of adsorbed alcohols and olefins showed that carbenium ions are formed as transient metastable species, not as stable intermediates. Ways of assaying the acid strength using Hammett and H_R indicators, adsorbed alcohols, and heterocyclics were developed. An objective was to determine the strength required to stabilize a given ion and how the catalytic properties are affected by the "acidity." Thus, amorphous silica–aluminas were characterized as equivalent to 70% to 80% H_2SO_4, the HY-zeolites as 90% to 98% H_2SO_4, and the H-mordenites as mild superacids. The effects on the reaction chemistry of isobutane and neopentane over solid acids were determined for these materials. These model compounds may be protonated forming primary decomposition products, which can then undergo secondary carbenium ion chemistry. Means were found to separate these processes. New insight into the reaction chemistry in acid catalysis and into the nature of catalyst acidity was thus obtained. These results were supplemented by poisoning experiments with NH_3 (NH_4^+) and Na^+. The poisoning was similar for both ions; it was nonlinear. An amount of NH_3 equivalent to less than 10% of the potential Broensted sites reduced the catalytic activity by over an order of magnitude. The data suggest that the chemisorption on a few sites reduced the activity of all the remaining ones.

303. Studies of Supported Metal Catalysts

Hercules, D.M. **$100,079**
Comm. 412-624-8300

A systematic study of the reduction of a Mo/Al_2O_3 catalyst (8% Mo) has been conducted. The reduction conditions were varied to obtain Mo oxidation states ranging from Mo^{+6} to Mo metal. The distribution of Mo oxidation states in the reduced catalysts was determined by electron spectroscopy for chemical analysis (ESCA). The following Mo oxidation states Mo^{+6}, Mo^{+5}, Mo^{+4}, Mo^{+3}, Mo^{+2}, and Mo metal were detected. The distributions of Mo oxidation states were correlated with the catalytic activity for propene and benzene hydrogenation. The results show that Mo^{+5} is not relevant for propene hydrogenation. The onset of the catalyst activity for this reaction appears to coincide Mo^{+4} formation. Benzene hydrogenation requires deeper reduction of the Mo phase (Mo^{+2}, Mo metal). This is consistent with a previous study of Mo/TiO_2 system. The influence of Ti (1 to 4 wt %) addition on the surface structure of a Mo/Al_2O_3 catalyst (8 wt % Mo) following sulfidation with thiophene/H_2 mixture has been investigated by ESCA. The results were correlated with the catalyst activity for thiophene hydrodesulfurization. Molybdenum remains highly dispersed following sulfidation in thiophene. An increase in sulfidability with increasing additive loading was observed by ESCA. The increase in sulfidability can be attributed to formation of octahedral Mo–O–Ti species. The hydrodesulfurization (HDS) activity of the titania-modified Mo/Al_2O_3 catalysts increased with increasing Ti loading. The increase in HDS activity of the titania-modified catalysts was correlated with formation of octahedral Mo–O–Ti species on the oxidic precursor.

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

Yates, J.T., Jr. **$152,932**
Comm. 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 (FT)-infrared reflection absorption spectroscopy, high-resolution electron energy loss spectroscopy, and transmission infrared spectroscopy, with the latter method being employed to study actual high area catalysts. Current problems include: (1) the activation and poisoning of CO-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; and (5) fundamental studies of the metal-support interaction on model catalysts prepared by thin film (Angstrom thickness) deposition on Al_2O_3 surfaces, using high-resolution electron energy loss spectroscopy (HREELS).

Purdue University
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Department of Chemistry

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

Squires, R.R. **$100,000**
Comm. 317-494-7322 **(18 months)**

Gas phase ion chemistry techniques are being used to investigate the thermochemistry and intrinsic reactivity of transition metal ion complexes that are proposed as reactive intermediates in homogeneously catalyzed water–gas shift reactions, catalytic hydrogenations, hydroformylations, and dioxygen activation reactions. With the use of a selected-ion-flow tube equipped with a triple quadrupole analyzer, a variety of reactive metal ion complexes may be generated in the gas phase. These include hydroxycarbonyls, coordinatively unsaturated metal hydrides, and metal peroxo complexes, and it is possible to characterize their structures, unimolecular reactions, and reactivity with small molecules. Research includes (1) the determination of metal ligand bond dissociation energies for simple metal carbonyl ions and their derivatives through collision-induced dissociation threshold energy measurements; (2) the characterization of metal formates, hydroxycarbonyls, and related metal acyl anion complexes that are formed by nucelophilic addition of negative ions to volatile metal carbonyls, and the direct measurement of activation energies for thermal and base-catalyzed decarboxylation; (3) the investigation of the kinetics and mechanism of olefin insertion reactions of coordinatively unsaturated metal hydride ions, and the role of vinyl insertion; and (4) an analysis of the sequential oxidation reactions of metal carbonylates and simple organometallic anion complexes with dioxygen and identification of the oxo-, peroxo- and superoxo intermediates that are involved.

Rensselaer Polytechnic Institute
Troy, NY 12180

Department of Chemistry

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

Cutler, A.R. **$118,320**
Comm. 518-276-8447

Three objectives in the catalytic hydrosilylation of organotransition metal acyl complexes have been attained. First, efficient catalysts and near optimal reaction conditions supersede previous procedures using $(PPh_3)_3RhCl$. Manganese acyl compounds $L(CO)_4MnCOR$ [L = CO /R = Me, Ph; L = PPh_3, PEt_3 /R = Me] as catalysts (0.1 to 10%) promote addition of R'_2SiH_2 (R′ = Et, Ph) and R'_3SiH (R'_3 = Et_3, Me_2Ph) across FpCOR″ (R″ = Me, Ph), the test substrates. Reductive dehydrogenative coupling of R'_2SiH_2 and the lower reactivity of R'_3SiH are no longer problems. All α-siloxyalkyl iron complexes Fp–CH(OSiR$'_3$R″, Fp–CH(OSiHR$'_2$)R″, and [Fp–CH(CH_3)O]$_2$ SiR$'_2$ are fully characterized. Results of control studies using other $(CO)_5Mn$–X pre-catalysts (X = CH_3, CH(CH_3)OSiHR$'_3$, $SiMe_3$, $Mn(CO)_5$, and $COCD_3$–^{2}H NMR spectral monitoring), solvent effects, and CO pressure are available. Second, diastereoselective hydrosilylation [$(PPh_3)_3RhCl$ catalysis /R'_2SiH_2] of chiral Fe and Ru acetyl complexes Cp(L)(CO)M-$COCH_3$ (L = $P(OMe)_3$, PEt_3, PPh_3) has been achieved. Studies in progress focus on comparing this diastereoselectivity with that observed in generating corresponding α-alkoxyethyl complexes from reduction of Cp(L)(CO)M=C(OEt)CH_3^+ and on minimizing the subsequent conversion of the resulting siloxyethyl complexes to their vinyl derivatives, Cp(L)(CO)M–CH=CH_2. Third, coupling hydrosilylation and subsequent carbonylation steps have been achieved using $(CO)_5Mn$ acyl complexes. Thus, $(CO)_5Mn$–COR″ rapidly adds R'_2SiH_2 and R'_3SiH (autocatalytically) and forms α-siloxyalkyl compounds $(CO)_5Mn$–CH(R″OSiR$'_3$, $(CO)_5Mn$–CH(R″)OSiHR$'_2$, and [$(CO)_5Mn$–CH(CH_3)O]$_2$SiR$'_2$ (which are characterized by NMR spectroscopy and in some cases by elemental analyses). Carbonylation of one siloxyethyl complex (at 85 psig CO), thus far, affords $(CO)_5Mn$–COCH(CH_3)OSiMe$_2$Ph. Satisfactory progress is being made on the hydrosilylation (catalytic potentially diastereoselective) then carbonylation of (η^5-indenyl)Ru acetyl compounds, In(L)(CO)Ru–$COCH_3$.

University of Rochester
Rochester, NY 14627

Department of Chemistry

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

Jones, W.D. **$113,390**
Comm. 716-275-5493

The investigation of homogeneous C–H bond activation by $(C_5Me_5)Rh(PMe_3)$ has been continued. Earlier studies have shown that the increased stability of metal phenyl hydride complexes relative to metal alkyl hydride complexes can be attributed to the stronger metal–phenyl bond. Other aromatic C–M bonds are also found to be strong. The preference for $(C_5Me_5)Rh(PMe_3)$(2-furanyl)H over an η^2-furan complex indicates that the aromaticity of the group activated may play an important part in the strength of the carbon–metal bond. A variety of new η^2-arene complexes of the type $(C_5Me_5)Rh(PMe_3)(\eta^2$-arene) where the arene is a fused, polycyclic aromatic has been discovered. The dynamics of the η^2-arene to aryl hydride interconversions are being examined, as are the electronic effects upon the site of η^2-binding. It has also been found that thiophene undergoes selective C–S bond cleavage via insertion of the metal. Mechanistic studies suggest that the insertion reaction proceeds by way of initial S-coordination. A series of $RhCl(PR_3)_2(CNR)$ complexes catalyze the insertion of isonitrile into aromatic C–H bonds. Light is used to dissociate an isonitrile ligand from the complex, and low concentrations of added isonitrile are used to increase efficiency. The reaction is believed to occur by way of initial phosphine dissociation.

Rutgers University
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Department of Chemistry

308. Carbon–Hydrogen Bond Functionalization Catalyzed by Transition Metal Systems
Goldman, A. **$52,500**
Comm. 201-932-5232

The objective of this project is to understand the factors that determine the ability of transition metal systems to catalyze the functionalization of C–H bonds. Initial efforts are focused on expanding the scope and elucidating the mechanisms of several hydrocarbon functionalization reactions catalyzed by $Rh(PMe_3)_2(CO)Cl$; these include photohydrogenation, transfer-dehydrogenation, carbonylation, and the insertion of unsaturates (e.g., acetylenes) into C–H bonds. The mechanistic understanding obtained will be tested and applied in the development and study of related late-transition metal systems. In the case of photochemical reactions, the development of related thermal systems will be attempted. The applicability of these systems to organic synthesis as well as alkane conversion will be explored. One particular goal is the development of an efficient thermal transfer-dehydrogenation system; the high efficiency (>5000 turnovers) of the photodehydrogenation reaction suggests that this is feasible. Catalytic aldehyde decarbonylation systems will be developed and studied particularly with a view toward the design of catalysts for the reverse reaction, alkane carbonylation. The mechanistic study of two such decarbonylation systems is presently under way: $Rh(p\text{-}NCC_6H_4N)(CO)_2Cl$ and $[Rh(PMe_3)(CO)Cl]_2$. Other systems, chosen based on the conclusions of mechanistic work, will be developed and studied. Transition metal polyhydrides and complexes of organo-f-block elements are likely candidates.

Department of Physics and Astronomy

309. Structure and Reactivity of Model Thin Film Catalysts
Madey, T.E. **$90,000**
Comm. 201-932-5185

The relationship between microscopic surface structure and chemical reactivity is being studied for model bimetallic catalysts (i.e., ultrathin films of metals on metals). The focus of the work is on atomically rough unstable single-crystal surfaces that undergo massive reconstruction and faceting when covered with ultrathin metal films (~1 monolayer thick), upon annealing to elevated temperatures. Such surfaces include the bcc(111) and the fcc(210) surfaces. Present studies are focused on ultrathin films of Pt and Au on the W(111)surface. This surface reconstructs to form microscopic facets upon annealing to $T > 800$ K, and LEED and scanning tunneling microscopy (STM) are used to characterize surface morphology. This group is currently characterizing the adsorption behavior and catalytic activity of these films, and will determine the effect of adsorption and reaction on the stability of ultrathin Pt films on W. Future studies will focus on the growth, thermal stability, and reactivity of metal films on atomically rough surfaces of fcc and hcp metals.

University of South Carolina
Columbia, SC 29208

Department of Chemistry

310. The Transformations of Organic Amines by Transition Metal Cluster Compounds
Adams, R.D. **$108,460**
Comm. 803-777-7187

This research is focused on the nature of the activation and transformation of tertiary amines by transition 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. Triosmium carbonyl cluster complexes are the focus of attention. Additional studies are focused on reactions of cluster complexes containing activated amines with hydrogen and on the determination of the mechanism of cluster-catalyzed tertiary amine metathesis.

University of Southern California
Los Angeles, CA 90089-0482

Department of Chemistry

311. Chemistry of Bimetallic and Alloy Surfaces
Koel, B.E. **$119,500**
Comm. 213-743-6201 **(18 months)**

This project explores the chemisorption and reactions of hydrocarbons on well-characterized, single-crystal bimetallic surfaces in order to understand the role of electronic and geometric effects in modifying the chemistry of these surfaces. Recent work has included studies of several important systems: (1) C_2H_4–K–Pt(111); (2) C_2H_4–Bi–Pt(111); (3) C_2H_4–Sn–Pt(111); and (4) C_2H_4 and C_2H_2–C–Ni(100), and O–Pt(111). Potassium coadsorption causes the formation of a new, weakly bound, π-bonded state of ethylene. At high potassium coverages, the mechanism for ethylene decomposition passes through a stable $CHCH_3$ species. Bismuth and tin coadsorption acts to block platinum sites for ethylene adsorption and decomposition but does not affect the ethylene binding energy. Work is in progress to model these results in order to determine surface ensemble requirements for ethylene reactions on platinum. Studies have been initiated on the reactions of C_2H_4 and C_2H_2 on Ni(100) with the aim of explaining the structure sensitivity of this surface relative to Ni(111) on the decomposition mechanisms. Work related to studies of the chemical modification of surface properties has also been done on the reaction kinetics of high coverages of atomic oxygen, $\theta_o \leq 0.75$ ML, on Pt(111).

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

312. *Catalytic Steam Gasification of Carbon*
Boudart, M. **$90,000**
Comm. 415-723-4748 **(19 months)**

The use of ^{129}Xe NMR as a probe of catalytic surfaces has been explored. The sample was in the form of a few large pellets of platinum supported on alumina. When successive doses of H_2 or O_2 are chemisorbed on a pre-reduced and evacuated sample, the NMR spectrum consists of one or two lines. With O_2, only two lines are observed irrespective of temperature, each one at a constant value of chemical shift σ. With H_2, there is one line for adsorption at 450 K, with σ shifting to lower values with successive doses. But with H_2 at room temperature (RT), there are two lines: one at constant σ, the other with σ shifting to lower values with more gas adsorbed. These results can be explained as follows. With O_2, the gas is chemisorbed irreversibly as it penetrates into the pores of the pellets and Xe probes two environments separated by a sharp interface: Pt saturated with adsorbed O and bare Pt. With H_2 at 450 K, adsorbed H atoms are uniformly distributed throughout the pellet. But at RT, Xe sees two environments, one corresponding to a monolayer of H on Pt, the other to a Pt surface progressively filled with adsorbed H. In this way, Xe NMR provides a valuable new tool to probe the penetration of gases in a porous adsorbent. It can also probe the penetration of H_2 into a pellet where the metal has been previously saturated with O. This is a promising new use of Xe NMR. Applications to catalysis are being explored.

313. *Molecular Beam Studies of Activated Adsorption and Heterogeneous Kinetics on Transition Metal Surfaces*
Madix, R.J. **$139,685**
Comm. 415-723-2402

Activated adsorption of gases on metal surfaces plays an important role in heterogeneously catalyzed reactions. In direct collisional activation of molecules at surfaces, energy may be supplied to the reaction coordinate by translational and vibrational energy of the colliding molecule. In addition to the energy necessary to clear the potential energy barrier to reaction, energy is dissipated into nonreactive channels in the collision. These dissipative channels may involve energy transfer to vibrational modes of the metal or to internal modes of the gas, particularly if the colliding molecule is translationally hot. Alkanes with kinetic energies between about 50 and 100 kJ/mol have been observed to dissociate with reaction probabilities between 0.001 and 1.0 upon direct collision with Ni(100) and Pt(111) surfaces. For a given incident kinetic energy the reaction probability decreases with increasing molecular weight of the alkane, suggesting that dissipative channels drain more energy from the reactive collision for the heavier molecules. Consequently, the dependence of the adsorption probabilities of small molecules on Pt(111) has been studied in order to better understand the collisional energy transfer of alkanes with surfaces. In the initial study of methane adsorption on Pt(111), the adsorption probability was determined to increase from 0.16 to 0.94 between incident kinetic energies of 3.4 and 20.2 kJ/mol at a surface temperature of 95 K. Although the adsorption probability varied smoothly with incident normal kinetic energy, the high trapping probabilities observed at high incident kinetic energies belie the one-dimensional theories of trapping. Indeed, subsequent model experiments performed with xenon show that a relatively complex three-dimensional potential function is necessary to adequately model the energy exchange that leads to adsorption. Experiments are in progress for more complex alkanes in order to better relate trapping dynamics and energy exchange to the energetics of collisionally activated adsorption.

Syracuse University
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Department of Chemical Engineering and Materials Science

314. *Metal–Support Interactions: The Effect of Catalyst Preparation on Catalytic Activity*
Schwarz, J.A. **$78,880**
Comm. 315-443-4575

The structure and activity of composite oxide (Al_2O_3 on TiO_2 and TiO_2 on Al_2O_3) supported monometal (Pt, Ir) and bimetal (Pt–Ir) catalysts have been studied. Catalyst precursors were prepared for H_2PtCl_6 and H_2IrCl_6. The adsorption rates on different supports were determined. The calcined precursors prepared by dry impregnation were characterized by temperature-programmed reaction (TPR) and temperature-programmed desorption (TPD) and by a structure-sensitive reaction, the hydrogenolysis of ethane. The dried precursors were characterized by TPR and TPD and by studying the thermal decomposition gravimetrically. The metal weight loading was adjusted to 3% for monometal catalysts and 3% each for the bimetal catalysts. Pure-oxide-supported monometal catalysts were used as standards to compare the behavior of composite-oxide-supported catalysts. Bimetal formation was observed on all supports. Varying degrees of H_2 chemisorption occurred on composite-oxide-supported catalysts. The effect of the strong metal-support interaction (SMSI) carrier (TiO_2) on H_2 chemisorption suppression is dependent on the composition of the composite oxide. The dissolution characteristics of alumina have been studied. The dissolved/readsorbed Al^{3+} species have been observed to play a major role in altering the reducibility, morphology, and activity of the composite-oxide-supported catalysts. The reducibility and activity of the Al_2O_3–TiO_2–supported Ir catalysts can be simulated by precursors prepared by the impregnation of TiO_2 with a solution of H_2IrCl_6 containing dissolved aluminum nitrates. This work now involves the formulation of a model for the effect of pH on divalent metal ion adsorption on amphoteric surfaces. The elements of any comprehensive model require a quantitative description of how the surface charge density changes with the pH and how the ionized forms of the solute adsorb. The end result of such a formulation should provide direct information on the strength of interaction of catalytic precursors with oxide supports. Characterization and performance studies of the catalysts derived from adsorption/desorption should be consistent with the parameters derived from the model. The overall objective of this research is to provide a basis for design of catalyst systems that includes the intrinsic properties of the supports and electrolytes used in the preparation of supported metal catalysts.

Texas A and M University
College Station, TX 77843-3255

Department of Chemistry

315. Correlations Between Surface Structure and Catalytic Activity/Selectivity

Goodman, D.W. **$180,438**
Comm. 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. These issues are germane to understanding the origins of the enhanced catalytic properties of mixed-metal catalysts. The principal objectives of this project are: (1) the study of the unique catalytic properties of monolayer and submonolayer metal films of "active" catalytic metals on "inactive" substrates; (2) the investigation of methanation, ethane hydrogenolysis, and cyclohexane dehydrogenation of two-dimensional overlayers with emphasis on the critical ensemble size requirements for each of these key probe reactions; and (3) the simulation of small-particle catalysts using corrugated single crystal surfaces.

316. Catalysts and Mechanisms in Synthesis Reactions

Lunsford, J.H. **$103,296**
Comm. 409-845-3455

The objective of this research is to understand the role of surface-generated gas-phase radicals in catalytic oxidation reactions, with emphasis on the conversion of methane to more useful fuels and chemicals. A matrix isolation electron spin resonance (MIESR) system is used to analyze the radicals that emanate from a hot metal oxide surface during a catalytic reaction. It has been demonstrated that, even over metal oxides containing transition metal ions, the coupling of gas-phase methyl radicals is a major pathway for the formation of ethane during the partial oxidation of methane. While present in the catalyst bed, the radicals undergo many collisions with the surface before they encounter another methyl radical, and if these collisions result in reactions, the product will ultimately be carbon dioxide. Recent research has focused on the reactions of methyl radicals with various metal oxides, including members of the lanthanide oxide series, for which very large variations in reactivity have been found. Lanthanum oxide, for example, is relatively unreactive, whereas cerium oxide is highly reactive. The radicals presumably react by reductive addition to oxides having multiple oxidation states. Cerium oxide, which is a nonselective methane oxidation catalyst, can be modified by the addition of sodium carbonate, and the resulting material becomes a good catalyst for the oxidative dimerization reaction. Similarly, the modified catalyst becomes a poor radical scavenger and a good radical generator. Recent studies have shown that the sodium carbonate when added to the lanthanide oxides essentially covers the surface, and it appears that a form of sodium oxide is responsible for the activation of methane. These results illustrate the potential of the MIESR system in providing detailed mechanistic information on these important oxidation reactions.

University of Texas
Austin, TX 78712

Department of Chemical Engineering

317. Model Catalytic Oxidation Studies Using Supported Monometallic and Heterobimetallic Oxides

Ekerdt, J.G. **$76,343**
Comm. 512-471-4689

This research program is directed toward a more fundamental understanding of the effects of catalyst composition and structure on 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 η^3–C_3H_5, cyclopentadienyl, or CO ligands are bound to silica, alumina, titania, and magnesia supports by exchange of these ligands with surface hydroxyl groups. The anchored complex is subsequently oxidized to generate a supported oxide. Attempts will be made to support molybdenum and tungsten as isolated monomeric cations, isolated monometallic MoMo and WW dimers or cation pairs, isolated bimetallic MoW dimers or cation pairs, and polymolybdate or polytungstate clusters. The research involves characterization of the organometallic deposition process, characterization of the resulting oxides using spectroscopic and structure sensitive molecular probes, and use of these oxides in catalytic studies. The majority of the effort has focused on molybdenum; Raman spectroscopic studies of structure, CO adsorption and photoreduction activity, and methanol oxidation activity have been performed and used to relate catalytic activity to molybdenum (VI) structure and oxygen ligand type. Current work is continuing with Mo, W, and Mo–W systems.

Department of Chemistry

318. Morphological Aspects of Surface Reactions

White, J.M. **$185,000**
Comm. 512-471-3704 **(18 months)**

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. A systematic photochemical study of ethyl chloride, methyl bromide, and methyl iodide on Ag(111) has been completed. Adsorbed alkyl fragments, formed by photodissociation at 100 K, thermally recombine during subsequent heating to form either butane or ethane; there is neither C–C nor C–H bond cleavage. Scanning tunneling microscopy is being used to study the morphology of vapor-deposited Rh supported on thin silicon dioxide (on silicon) films. *Ab initio* electronic structures of Rh clusters, with and without chemisorbed small molecules, are being calculated.

Potassium-promoted activation of carbon dioxide is under experimental investigation.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

319. *Ligand Intermediates in Metal-Catalyzed Reactions*

Gladysz, J.A. **$115,000**
Comm. 801-581-4300

The project goal is the synthesis and study of homogeneous complexes containing ligand types ($–CHO$, $=CHOH$, $–CH_2OH$, C, $=CH_2$, $H_2C=O$, $–OCHO$, CO_2, and so forth) intermediate in C_1/C_2 catalytic reactions. Mechanistic understanding of key steps and insight needed for the design of new catalysts is sought. The reaction of the chlorobenzene complex $[(\eta^5–C_5H_5)Re(NO)(PPh_3)–(ClC_6H_5)]^+\ BF_4^-$ and $RC\equiv CR$ gives alkyne complexes $[(\eta^5–C_5H_5)Re(NO)(PPh_3)(RC\equiv CR)]^+\ BF_4^-$. When R = H, subsequent reaction with base gives C_2 acetylide complex $(\eta^5–C_5H_5)Re(NO)(PPh_3)(C\equiv CH)$. Conditions for the deprotonation of the latter (which was previously available only by a multistep route) to lithiocarbon complex $(\eta^5–C_5H_5)Re(NO)(PPh_3)(C\equiv CLi)$ were found. The synthesis of heterobimetallic C_2 complexes $(\eta^5–C_5H_5)Re(NO)(PPh_3)(C\equiv CM'L_{\underline{n}})$ is under investigation. The reaction of the phenyl complex $(\eta^5–C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ and $HBF_4 \cdot OEt_2$ at −80°C in CH_2Cl_2 gives η^2–benzene complex $[(\eta^5–C_5H_5)Re(NO)(PPh_3)–(\eta^2–C_6H_6)]^+\ BF_4^-$, and the benzene ligand is displaced by CH_2Cl_2 at −40°C. Interestingly, Ph_3C^+ attacks the para position of the phenyl ligand to give an alkyl idene complex. It was found that reactions of the dichloromethane complex $[(\eta^5–C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+\ BF_4^-$ with ethers (ROR) and alcohols (ROH) give isolable ether and alcohol complexes $[(\eta^5–C_5H_5)Re(NO)(PPh_3)(ROR')]^+\ BF_4^-$. Subsequent reactions establish the order of $O=CHR > ROH > ROR > CH_2Cl_2 > C_6H_6$ for ligand-binding affinities to the 16-electron fragment $[(\eta^5–C_5H_5)Re(NO)(PPh_3)]^+$. It was also found that amide complexes $(\eta^5–C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ undergo racemization at rhenium (40 to 60°C) by a mechanism involving initial and rate determining PPh_3 dissociation; the $–\ddot{N}RR'$ lone pair provides anchimeric assistance, giving an intermediate with a planar, trigonal rhenium.

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

Grant, D.M.; Pugmire, R.M. **$110,925**
Comm. 801-581-8854

This 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. The use of the flipper probe on noncrystalline solids has made significant progress during the past year. The study of motional and preferential ordering effects upon methylene tensors in hydrocarbon chains in amorphous organic solids is now possible. The method has application to the study of anisotropic samples ordered by the bedding plane. Variable angle spin offers a way to separate overlapping chemical shift bands in condensed aromatic samples. Carbon-13 NMR shielding tensors have been determined for two anthracite coals and a fusinite maceral, using this variable angle spinning technique along with a variety of other NMR spectroscopic methods. Theoretical calculations on the model compounds such as coronene and circumcoronene support these interpretations. 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.

University of Washington
Seattle, WA 98195

Department of Chemistry

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

Campbell, C.T. **$95,000**
Comm. 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 (1-10^4 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 water–gas shift reaction and many elementary steps have been measured on the clean and cesium-doped Cu(110) surface. An ultralow-cast surface-vibrational spectrometer was also built. Future work will involve the kinetics of methanol synthesis and its individual steps on clean and Cs-doped Cu crystals and on structurally characterized Cu and Cs films on ZnO (.0001). These results should improve the fundamental understanding in Cu/ZnO catalysis and also in phenomena generic to catalysis such as interactions at metal/oxide supports.

Wayne State University
Detroit, MI 48202

Department of Chemistry

322. Reactive Characterization as a Probe of the Nature of Catalytic Sites

Brenner, A. **$103,530**
Comm. 313-577-2503

This research is primarily concerned with achieving a better understanding of the nature of active sites on heterogeneous catalysts. It is extremely rare that the identity of an active site is known and the density of active sites is also known. Active sites frequently account for a small fraction of the surface of a catalyst. In addition to the classical method of selective poisoning to obtain an upper limit for the number of active sites, a novel technique involving the exchange of surface OH groups with $D^2(g)$ has been developed to obtain a lower bound to the number of active sites. Patterns of activities and product distributions are also used to gain information on the nature of active sites, a technique termed reactive characterization. A large amount of data has been collected on the H_2–D_2 exchange reaction over metals and metal oxides. A unified mechanism for H_2–D_2 exchange on metal oxides has been proposed. The isotopic product distribution from the deuterogenation of ethylene has been used to show that the catalytic sites on NiO are isolated, and that the adsorption of CO on a Ni catalyst causes the surface of the Ni to be broken into small patches which are also noninteracting.

University of Wisconsin
Madison, WI 53706

Department of Chemical Engineering

323. Experimental and Kinetic Modeling of Acid/Base and Redox Reactions Over Oxide Catalysts

Dumesic, J.A. **$130,000**
Comm. 608-262-1092

Microcalorimetric measurements have been used to study surface acidity for silica-supported oxides and H–Y zeolites. The entropy change of adsorption can be calculated through Gibbs free energy and enthalpy relationships by measuring the heat of pyridine adsorption calorimetrically and the adsorption isotherm volumetrically. Accordingly, it has been found that the activation energy for surface diffusion on silica is about 20 kJ/mol, compared to the heat of adsorption determined to be 95 kJ/mol. Surface diffusion thus provides an effective equilibration pathway for adsorbed basic molecules. It is estimated that acid sites with heats of adsorption as high as 220 kJ/mol at 473 K can be titrated calorimetrically in an equilibrium manner. Calorimetric studies on H–Y zeolite cracking catalysts have shown that gasoline selectivity can be correlated with the presence of acid sites of intermediate strength, with sites near 150 kJ/mol being particularly effective. Catalysts containing strong acid sites with heats of pyridine adsorption near 220 kJ/mol show excessive cracking and coke formation. Another direction of research has been the study of the selective catalytic reduction of nitric oxide over thin-film vanadia/titania surfaces. Temperature programmed reaction spectroscopy has been employed to determine the kinetics of NO, N_2O, NH_3, and H_2O desorption, and N_2 formation. These measurements allow prediction of the performance of a working vanadia/titania catalyst.

Department of Chemistry

324. Organometallic Chemistry of Bimetallic Compounds

Casey, C.P. **$118,320**
Comm. 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. The synthesis of heterobimetallic dihydrides in which one hydrogen atom is bonded to each metal is one target. The oxidative addition of a rhenium dihydride to platinum(O) complexes has provided a new route to heterobimetallic dihydrides. The kinetics and mechanism of the reaction of $C_5H_5(CO)_2(H)RePt(H)(PPh_3)_2$ with alkynes to produce rhenium–alkene complexes is being studied. The use of such compounds as catalysts for the hydrogenation of CO, alkenes, and alkynes is being investigated. Bimetallic compounds with one early and one late transition metal will be investigated since the resulting dihydrides are expected to have one hydridic and one acidic metal–hydrogen bond, and may act as powerful reducing agents for polar molecules such as CO. The synthesis and reactions of new zirconium–ruthenium and zirconium–rhenium compounds that possess highly polar metal–metal bonds are being studied. The use of diphosphines with unusually wide bite angles (P–M–P, 110 to 150°) as ligands on hydroformylation and other catalysts is being studied in a search for more regioselective catalysts.

Yale University
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Department of Applied Physics

325. Model Catalyst Studies of Active Sites and Metal–Support Interactions on Vanadia and Vanadia-Supported Catalysts

Henrich, V. **$83,060**
Comm. 203-432-4399

This project involves experimental investigations of the surface properties of vanadia catalysts, the nature of active sites on those catalysts, and the interaction between catalyst metal atoms and oxide supports. Experimental techniques employed include ultraviolet photoemission spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), Auger spectroscopy, inverse photoelectron spectroscopy, and the use of the tunable photon sources available at the National Synchrotron Light Source. Work on the electronic properties of vanadia surfaces involves studies of single-crystal V_2O_5 and V_2O_3, oxidation of V metal, and the deposition of V atoms onto single-crystal TiO_2 supports. The single-crystal model catalyst work addresses what types of sites are the active ones in real vanadia catalysts. The model-supported V experiments will try to determine the interactions that take place between V, Ti, and O ions in titania-supported vanadia catalysts. Ways to adapt Dr. Tony Cox's (Inorganic Chemistry Laboratory, Oxford University) Fourier transform method of removing surface phonon overtones from HREELS spectra to the cases of oxides that are supporting small metal particles and of very thin oxide layers on a different oxide have been considered collaboratively with him. Work at the National Synchrotron Light Source involves resonant photoemission experiments on both stoichiometric and reduced TiO_2 (110) surfaces in order to obtain information about the hybridization of cation and anion electronic states on the surface. This research program is yielding valuable information about active sites on vanadia-based catalysts and on the interaction between vanadia and transition-metal-oxide supports.

Department of Chemical Engineering

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

Haller, G.L. **$103,500**
Comm. 203-432-4378

The interaction of small Pt metal particles supported in L-zeolite were probed for changes in electronic character using the relative adsorption constants of benzene and toluene (which have different electron donation properties) as a measure of this character. It was observed that the apparent electronic charge on the particles increased as the zeolite support was made more basic. Extended X-ray absorption fine structure is being used to study both the metal support interaction and the metal–metal interaction in bimetallic catalysts. The application of discrete prolate spheroidal wave functions as tapering windows has been developed for the EXAFS Fourier transforms. These have been demonstrated to improve the spectral estimates and, in turn, the structural parameters of the catalysts under study. It would be useful to have a physical measurement of the acid site density and strength of amorphous silica–alumina catalysts. The chemical shift and intensity of NMR spectra of ^{29}Si and ^{27}Al can potentially be such a measure. A correlation of the ^{29}Si NMR chemical shifts with the catalytic activity has been observed for Bronsted catalyzed cumene cracking.

Department of Chemistry

327. Alkane Photoreactions With Mercury Vapor

Crabtree, R.H. **$108,460**
Comm. 203-432-3925

The Hg* reaction has been extended to substrates that do not dimerize under the conditions previously described. For example, Hg* reacts with the C=O group of ketones to give conventional triplet state products. H_2 has now been added so that the Hg* is quenched by H_2 and the resulting H atoms are the principal abstractors. This leads to dehydrodimers from ketones. Hydrogen atoms add to C=C double bonds to give dehydrodimers regioselectively. The addition of N_2O to the system allows reactions of methane and ethane, in which case O atoms are the principal abstractors. Initial results on oxygen suggest that hydroxylation of alkanes will be possible. The same chemistry also allows a polymer surface to be modified.

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

Heinekey, M.D. **$100,000**
Comm. 203-432-3917

Methods for the thermal synthesis and isolation of rhenium(0) radicals of the general form $Re(CO)_3(PR_3)_2$ (R = cyclohexyl, isopropyl, cyclopentyl) have been developed. The structure of the PCy_3 complex has been determined by X-ray crystallography. Characterization of transient radical species with less bulky ligands (such as PPh_3) by electron paramagnetic resonance spectroscopy has been undertaken. These novel seventeen electron species are very reactive toward a variety of small molecules including hydrogen and methane, to afford products of homolytic cleavage of H–H and C–H bonds. The mechanism of these reactions is under investigation. Future work will include the synthesis of persistent biradicals through the use of spanning bidentate ligands and investigation of their structural and spectroscopic properties.

329. Energies of Organic Compounds

Wiberg, K.B. **$105,117**
Comm. 203-432-5160

This research project is designed to provide information on energies and conformations of organic molecules via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semiempirical schemes (e.g., molecular mechanics) for estimating the properties of organic compounds. Because of its importance in organic chemistry, a major effort is being made to understand the factors that control the structures, energies, and reactivity of carbonyl groups. The equilibrium constants for hydration, hemiacetel, and acetal formation are being determined as a function of temperature in order to obtain more quantitative information on the differences between aldehyde, ketones, and other carbonyl compounds. Parallel theoretical calculations are being carried out. A method has been developed for determining the heats of reduction of carbonyl compounds, and it is now being applied to a number of methyl substituted norbornanones in order to see how alkyl groups interact with carbonyl groups. It is also being applied to a series of monocyclic lactones in order to obtain information on strain effects in these compounds. Measurements of heats of hydration of alkenes also is continuing, as well as theoretical calculations on rotational barriers that are needed for molecular modeling.

Separations and Analysis

Aerospace Corporation
Los Angeles, CA 90009

Chemistry and Physics Laboratory

330. *Isotopically Selective, Two-Step, Laser Photodissociation of Triatomic Molecules in Cryogenic Solutions*
Zittel, P.F. **$137,825**
Comm. 213-336-6642

The project ojective is to understand photophysical, energy transfer, and chemical reaction processes relevant to isotope separation by two-step laser photodissociation of small molecules in cryogenic solution. The two-step technique involves the excitation of molecules containing a chosen atomic isotope to an excited vibrational state by an infrared laser, followed by ultraviolet laser photodissociation and chemical scavenging of the photofragments. Focus is on the two-step photodissociation of OCS dissolved in liquid rare gases and liquid oxygen. An FTIR spectrometer is used to measure vibrational band centers, widths, strengths, and isotope shifts for OCS in the different cryogenic solvents. A laser induced fluorescence method is being used to determine relaxation rates of several low-energy vibrational states of OCS by liquid Ar, Kr, Xe and O_2. Two-step photodissociation of OCS in liquid Ar has enriched oxygen-17 and oxygen-18 isotopes by a factor of four. The dependence of isotope enrichment on experimental variables is also used to probe vibrational relaxation and chemical reaction processes in the cryogenic solutions. The cryogenic solution work is complemented by gas phase experiments designed to measure cross sections for photodissociation of molecules in specific excited vibrational states. Of increasing interest are photodissociation cross sections and vibrational relaxation rates for very-highly excited vibrational states of various small molecules in both the gas phase and in cryogenic solution.

Auburn University
Auburn, AL 36849-5128

Department of Chemical Engineering

331. *Interfacial Chemistry in Solvent Extraction Systems*
Neuman, R.D. **$104,000**
Comm. 205-844-2017

Significant questions remain to be resolved pertaining to the interfacial chemistry in the solvent extraction of metal ions for a detailed understanding of the extraction mechanism in hydrometallurgical and nuclear industries. Present research emphasizes characterization of the macroscopic and microscopic interfaces that occur in acidic organophosphorus solvent extraction systems associated with Ni^{2+}, Co^{2+}, Zn^{2+}, and UO_2^{2+}. Recent advances in laser and spectroscopic techniques provide novel tools to investigate interfacial extractant films from a microscopic point of view. A pulsed Nd:YAG/dye laser system is being assembled to obtain unique structural and dynamical information on liquid–liquid interfacial systems in conjunction with a Brooks' frame for manipulating model extractant films. Laser-induced fluorescence, optical second-harmonic generation (SHG), and Raman techniques will provide information about the dynamic properties and the structual organization of extractant molecules in the interfacial zone. Laser fluorescence studies also will permit probing the nature of the microenvironment about the polar head groups of extractant films. The physicochemical nature of the molecular aggregates or microstructures that form in the bulk organic phase of organophosphorus extractant systems is also being examined using various spectroscopic and scattering techniques to improve upon a recently proposed model for aggregation of metal-extractant complexes in solvent-extraction systems.

Brigham Young University
Provo, UT 84602

Department of Chemistry

332. *Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport*
Lamb, J.D. **$88,377**
Comm. 801-378-3841

The macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems is being investigated. Potential macrocyclic carriers are screened by measuring pKa values and extraction equilibrium constants and partition coefficients for various metal cations. Macrocycles of particular interest are then studied in the potentially practical emulsion and hollow fiber supported liquid membrane systems. A two-module hollow fiber system has been successfully implemented for use with less hydrophobic and proton-ionizable macrocycles. 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. 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

333. *Photochemical Generation of the Optoacoustic Effect*
Diebold, G.J. **$79,000**
Comm. 401-863-3586

The production of acoustic waves in a conventional photoacoustic cell when heat conduction to the walls plays a role is under investigation. At present the most sophisticated method solves the coupled equations for pressure and temperature in the cell and includes conduction of heat to the walls. The agreement of this approach with the experimental data is quite good given that there are no adjustable parameters in the theory. A solution that includes the effects of viscosity has also been obtained. The results depend critically on the Prantl number. Some additional experimentation may be warranted to explore the effects predicted by the new theory. The acoustic waveforms generated by laser irradiation of particles are also being investigated. It has been shown that the photoacoustic effect gives information about the geometry of the particle and its acoustic properties relative to the surrounding fluid. For example, rapid heating of a weakly absorbing spherical solid particle or a fluid droplet gives a photoacoustic waveform from which the density, sound speed, and diameter of the particle can be determined.

University of California
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

334. Multiheteromacrocycles That Complex Metal Ions

Cram, D.J. **$128,810**
Comm. 213-825-1562

The goals of this research are to design, synthesize, and test organic multiheteromacrocycles for their abilities to complex metal anions and inorganic cations. The liganding systems are highly preorganized for binding during their synthesis rather than during their complexing acts (principle of preorganization). Most of the functional groups of organic chemistry are being tested as ligating sites. Ion specificity in binding of Li^+ and $UO_2\ (CO_3)_3{}^{4-}$ is a special goal that makes use of stereoelectronic complementarity between host and guest (principle of complementarity). Systems that simultaneously bind and lipophilize both anions and cations of salts are of particular interest. Correlations between host–guest structures, binding free energies, rates of complexation–decomplexation, and solvation effects are being studied.

Columbia University
New York, NY 10027

Department of Chemistry

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

Turro, N.J. **$82,919**
Comm. 212-854-2175

The project objective is to provide a theoretical and experimental framework for the enrichment and separation of isotopes based on their magnetic properties. The radical pair theory of chemically induced dynamic polarization of electrons and nuclei has been employed as a basis to design and to drive experiments. The theory assumes that the chemical reactivity of triplet radical pairs can be controlled by nuclear magnetic moments which interact with the unpaired electrons of the radical pair through the nuclear spin/electron spin hyperfine coupling. Under the appropriate circumstances triplet pairs containing nuclei that possess magnetic moments are more reactive than triplet pairs that contain nuclei with no magnetic moments. An important feature of the radical pair theory is the need for a restricted reaction space or a microscopic reactor to control the rate and extent of separations and returns of the radical pairs. The efficient separation of 13-C (a magnetic isotope) from 12-C (a nonmagnetic isotope, i.e., of spin 0) has been demonstrated in the photolysis of dibenzyl ketone in several microheterogeneous environments that serve as microscopic reactors (e.g., micelles, porous solids, zeolites and flexible chain biradicals). These results allow the design of experimental conditions that will optimize the efficiency of isotope separation based on magnetic effects and produce knowledge that is pertinent to a variety of areas of importance to the energy sciences, including photochemistry, interface chemistry, magnetic resonance and reactive intermediates.

University of Delaware
Newark, DE 19716

Department of Chemistry

336. Studies of the Analyte–Carrier Interface in Multicomponent Flow Injection Analysis

Brown, S.D. **$78,880**
Comm. 302-451-6861

Separation by a physical or chemical step is the most common route to analysis of complex samples. However, separation steps are difficult to optimize and are highly matrix dependent. Thus, it is of considerable interest to examine novel methods for the analysis of complex mixtures, such as ones based on competitive kinetic assay or on mathematical methods for resolution of cointerfering responses. This project involves the study of real-time digital filters developed for kinetic analysis of materials in flowing media and filters for enhancing the resolution of transient responses, such as those found in kinetic analysis, flow injection analysis, and liquid chromatographic separations. Real-time analysis of transient species and factor analysis of flow data are being used to study the spatial distribution of species in the flow reaction zone. Theoretical profiles are being developed from simulation of mass transfer and kinetic effects. Experimental profiles are compared with those from theory. The goal is a better understanding of homogeneous and heterogeneous chemical reactions.

Duke University
Durham, NC 27706

Department of Chemistry

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

McGown, L.B. **$64,090**
Comm. 919-684-3668

The use of phase-resolved fluorescence spectroscopy for spectral characterizing of complex samples is being studied. The addition of fluorescence lifetime information to spectral arrays through phase resolution provides greater selectivity and allows observation of subsets of the total spectral features as a function of fluorescence lifetime, by scanning modulation frequency. The goal is to relate spectral and lifetime features to both composition of a sample and dynamic behavior of sample constituents (aggregation, quenching, energy transfer, distribution between different microenvironments, and so forth). The multifrequency phase-resolved fluorescence data arrays can be represented as tensors or three-way arrays. Novel data analysis strategies are being developed for these arrays, for noise-reduction, rank estimation, and spectral resolution. Pattern recognition techniques for comparison of different samples are also being explored. Organized bile salt media are being investigated for use in complex samples to solubilize and isolate fluorescent molecules from each other and from sample matrix constituents.

University of Florida
Gainesville, FL 32611

Department of Chemistry

338. The Glow Discharge as an Atomization and Ionization Source

Harrison, W. **$93,670**
Comm. 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. Increased emphasis will be on glow discharge mass spectrometry (GDMS) in current activity. Work is also conducted to improve understanding of the sputtering process by ablation of material from a metal alloy into a glow discharge using lasers and fast-atom sources. An rf discharge is being studied to develop methods for direct analysis of nonconducting materials without the need to mix these materials with conducting matrix, such as powdered copper. A comparison of rf and dc systems will be made with respect to sputter rates, ion yields, and ratios of sputtered to discharge gas ions. Methods for pulsing the rf discharge are also under investigation. Another active project deals with pulsed dc glow discharges and the advantages obtainable in discriminating against molecular ions by time resolution. Setting a data gate in the trailing edge of the pulse causes the signal to consist of primarily ions from the sputtered sample material. Interest continues in earth materials and the many analytical problems that the analyst encounters in attempting to obtain mass spectra, namely the many oxide contributions. By use of getter agents added to the sample, gas phase chemistry can be carried out in the plasma to reduce the magnitude of oxide signals. Differing degrees of success have been found with tantalum, rhenium, and titanium. Studies of electrochemial vaporization into a glow discharge have recently been initiated, aiming for the ability to analyze solution samples of very small volumes.

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

Winefordner, J.D. **$93,670**
Comm. 904-392-0556

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

The George Washington University
Washington, DC 20052

Department of Chemistry

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

Montaser, A. **$69,361**
Comm. 202-994-6480

New high-temperature plasmas, new sample introduction systems, 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 in the fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is 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 powers of a number of elements; (2) development and characterization of low-cost sample introduction systems that consume microliter or microgram quantities of samples; (3) investigation of dual-beam, light-scattering interferometry for simultaneous measurements of droplet-size and velocity distributions of aerosols from various nebulizers; (4) simulation and computer modelings of He ICPs to predict the behavior of plasmas on a fundamental basis; and (5) development of a new ICP-mass spectrometer capable of sampling a variety of ICP discharges. Investigations address 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

341. Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)
Browner, R.F. **$83,810**
Comm. 404-894-4020

Fundamental studies with the monodisperse aerosol generation interface have been directed at two primary issues: (1) increasing the mass range of compounds to which the interface is applicable and (2) enhancing the vaporization properties of thermally labile compounds in order to reduce thermal degradation at the sample vaporization step. A fast atom bombardment version of the interface has been developed, which has proved very successful for obtaining mass spectra of high mass molecules, such as erythromycin (m.w. 735) and several environmentally important azo dyes, which are incapable of normal electron impact ionization. The ability to flash vaporize, in a very short time scale, the small (typically <50 nm) particles which are generated by the interface has proved to reduce the extent of thermal degradation experienced by thermally labile compounds such as cholesterol. By maintaining such small particles and ensuring a very rapid temperature ramp in the mass spectrometer ion source area, excellent freedom from thermal degradation has been accomplished. Additionally, further studies of the transport properties of the interface have been carried out, in an effort to further improve its transport efficiency and solvent handling capabilities.

Hampton University
Hampton, VA 23668

Department of Chemistry

342. Use of Ion Chromatography–DC Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals
Urasa, I.T. **$54,230**
Comm. 804-727-5398

This research involves trace metal speciation by using a combination of ion chromatography with dc plasma atomic emission spectrometry. Presently, focus is on the development of an efficient mechanism for introducing the ion chromatographic effluents into the dc plasma system. By employing a high-efficiency nebulizer coupled with modifications on the plasma geometry, it is hoped that a mechanism will be developed that will allow the introduction of 90 to 100% of the analyte eluting from the chromatographic column into the excitation zone of the plasma. In this way, the detection power of the dc plasma detector will be improved considerably. This will result in the reduction of detection limits to below 1.0 ppb concentration level. This research is also concerned with the elucidation of the solution chemistry of trace metals. The behavior of metal ions in different aqueous media can have a great influence on their speciation. The aim is to use the Ion Chromatograph–DC Plasma Atomic Emission Spectrometer (IC)–(DCPAES) approach to study the changes that metal ions undergo as a result of changing solution properties.

University of Houston
Houston, TX 77204-4792

Department of Chemical Engineering

343. Mechanisms of Thickening, Cake Filtration, Centrifugation, Expression, and Ceramic Processing
Tiller, F.M. **$105,000**
Comm. 713-749-4316

The project objective is the provision of an improved qualitative and quantitative framework covering the relative flow of liquid and solids in suspensions and compacting particulate beds. Application is made to the industrially important fluid/particle separation operations of sedimentation, thickening, cake filtration, centrifugation, expression, and deliquoring. Specific areas of focus include environmental separations, ceramic processing, formation damage in reservoirs, and mineral engineering. Development models and the accompanying differential equations related to sedimentation, compaction of particulate beds, and flow rates as a function of various driving forces constitute the theoretical part of this research. Among areas under investigation are particle movement in suspensions and sediments, centrifugal filtration, thickening, optimal operation of filters, and testing procedures related to determination of porosity and permeability. Determination of local and microscopic characteristics of sediments and cakes is being carried out by (1) CATSCAN analysis of local concentrations and (2) liquid-pressure distribution during flow. Macroscopic phenomena under investigation include the formation and compaction of sediments and cakes. The effect of flocculation and dispersion on the properties of suspensions and particulate beds is under study.

University of Idaho
Moscow, ID 83843

Department of Chemical Engineering

344. Drop Oscillation and Mass Transfer in Alternating Electric Fields
Carleson, T.E. **$37,468**
Comm. 208-885-7652

An analytical solution was obtained for the flow field produced by a charged drop suspended in an alternating electric field. The model is part of an effort to predict observed enhancements in mass transfer for drops in alternating electric fields. These enhancements are not predicted by standard mass transfer models such as the surface stretch or surface renewal models. The model assumes creeping flow of Newtonian fluids and a small oscillation amplitude. Good qualitative agreement with the experimental results of others as well as other models was obtained. Based upon the model results, the amplitude of droplet oscillation passes through a maximum as a function of frequency. Thus it is expected that the heat and mass transfer rate would pass through a maximum as a function of the applied frequency, as observed experimentally. Experimental work has been started on the verification of these results. A method has been established for recording drop movement in the electric field by taking pictures at high speed with an ordinary camera and a stroboscope. Mass transfer rates will be measured by analyzing the drop phase composition so that the effect of the electric field on the mass transfer rate can be assessed.

University of Illinois
Urbana, IL 61801

Department of Chemistry

345. Thin Films Under Chemical Stress

Bohn, P.W. **$83,810**
Comm. 217-333-0676

This project is aimed at the study of static and dynamic structure in thin organic films of nonuniform composition. Raman scattering and fluorescence measurements are excited with optical waveguide eigenmodes, and information about the spatial distributions of active sites is recovered from the observed spectra. Currently the Case II and Fickian diffusion contributions to mass transport of linear and branched alkanes in 1 to 5 μm-thick poly(styrene) films are under investigation. In addition the mass transport properties of structures in which thin (i.e., one or at most a few molecular layers) barrier layers are incorporated by self-assembly or by Langmuir–Blodgett techniques are being examined. The understanding gained will allow processes involving differential solubility in a macromolecular matrix (e.g., photoresist removal in microlithography) to be operated more efficiently.

346. Theta Pinch Discharges for Emission Spectrochemical Analysis

Scheeline, A. **$77,000**
Comm. 217-333-2999

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. Optimization of energy coupling from the discharge circuit into the pinch plasma, and thence to the sample, is the focus of half of this project's current work. Assorted discharge induction coils that can control the relative magnitude of the electric and magnetic fields have been constructed. Characterization of sampling and excitation produced by 4 tesla peak field discharges is under way. Early indications are that large electric fields are needed for efficient sampling. A second current thrust is to excite powdered samples and determine what biases in sampling and excitation may exist. Emission line selection is a crucial part of the set of experiments, as resonance lines are frequently self-reversed. This in turn means that line selections that are appropriate for other discharges are decidedly inappropriate for use with the pinch. Lastly, the pinch's emitted light is being coupled into a locally fabricated echelle spectrometer, with the goal of using a charge-coupled array detector for simultaneous multielement analysis. Considerable improvement in radio frequency noise containment will be required for success in this part of the research.

Kansas State University
Manhattan, KS 66506

Department of Chemistry

347. Development of a Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry

Fateley, W.G. **$86,768**
Comm. 913-532-6298

A Hadamard transform spectrometer (HTS) has been developed that can be used for visible, near-infrared (NIR) and Raman spectroscopy. A new liquid crystal electro-optic shutter is used as a stationary Hadamard encoding mask. This Hadamard NIR Raman instrument is able to do simultaneous multiwavelength detection with a single diode as the detector. Hadamard transform spectrometers (HTS) have many advantages similar to Fourier transform spectrometers and also have the advantage of no continuously moving parts. In addition to these advantages, the HTS has previously demonstrated a selective multiplex advantage. By simply shutting off certain elements of the encoding mask, unwanted solvent bands can be eliminated. Also, because of the frequency precision of HTS, spectral subtraction can be performed. It has been shown that this HTS instrument can be used for Raman spectroscopy in the visible region using an Ar^+ (514.5 nm) laser. Rejection of the Rayleigh line is accomplished by simply adjusting the grating so that the Rayleigh line does not fall on the spectral window of the encoding mask. Thus, the requirement for the optical filter system, needed for Fourier transform Raman spectrometry, is eliminated in Hadamard transform Raman spectrometry. Development is continuing on the installation of a Hadamard mask in a stationary interferometer. The advantage found in using the mask is that all radiation from the stationary interferometer is Hadamard encoded and impinges upon one detector. Previously an array of detectors has been used to record the interferogram. The advantages found in the use of the Hadamard mask are actively being investigated.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

348. Perforated Monolayers

Regen, S.L. **$70,992**
Comm. 215-758-4842

This research is aimed at creating a fundamentally new class of membranes, based on the construction of organized, two-dimensional assemblies of molecular pores. The immediate objectives of this work are to prepare first-generation perforated monolayer composite membranes and to define their permeation properties. The ultimate goal is to rationally design synthetic membranes, 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. Specific porous surfactants that are now being examined as building blocks for such assemblies are mercurated calix[n]arenes.

Michigan State University
East Lansing, MI 48824

Department of Chemistry

349. *Direct Probing of Chromatography Columns by Laser-Induced Fluorescence*
McGuffin, V.L. **$120,000**
Comm. 517-353-4511 **(18 months)**

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 capillary column. By measuring solute zone characteristics directly on the column, quantitative information concerning the separation process can be obtained as a function of spatial position. Any changes in solute zone characteristics, such as area, velocity, variance, asymmetry, etc., which occur between the detectors are the result of retention and dispersion processes in that region alone. Hence, this detection scheme effectively isolates the specific column regions of interest, affording a view of hydrodynamic and physicochemical processes not previously possible. This detection scheme has been applied to examine solute zone retention and dispersion in reversed-phase liquid chromatography. A homologous series of linear, saturated fatty acids (C_{10} to C_{24}), labeled with the fluorescent probe 4-bromomethyl-7-methoxycoumarin, have been chosen as model solutes. When separated on a spherical octadecylsilica stationary phase, these ideal solutes exhibit the theoretically expected logarithmic dependence of the partition coefficient on carbon number. The retention and dispersion of these solutes have been compared with classical chromatographic theory under isocratic (steady state) and gradient (stepwise or continuous nonequilibrium) conditions. In addition, nonequilibrium processes occurring abruptly upon injection and elution of the solute zone have been systematically investigated and show excellent agreement with theoretical models derived in our laboratory. Although these results are limited to liquid chromatographic applications, this detection scheme should also be compatible with gas and supercritical fluid chromatography as well as high-voltage capillary electrophoresis.

University of Michigan
Ann Arbor, MI 48109

Department of Chemistry

350. *Hadamard Transform Imaging*
Morris, M.D. **$204,896**
Comm. 313-764-7360 **(18 months)**

Hadamard multiplexing is used to generate spatially and spectrally resolved Raman and photothermal images using unfocused laser radiation. Hadamard multiplexing reduces local power density by 10^2 to 10^5 enabling use of high-power pulsed or continuous-wave (CW) lasers. Source-encoded imaging is performed by masking a laser beam with a series of Hadamard masks. The encoded beam is condensed to the desired dimensions and used to excite the sample. Source encoding is used if an image of the signal cannot be formed. Signal-encoded imaging is performed by masking the magnified signal image, formed with unfocused laser radiation. Signal encoding is preferred with Raman scattering and fluorescence. The Hadamard-encoded Raman microscope uses signal encoding. The system provides diffraction-limited images using pulsed or CW lasers. With an array detector, spectral and spatial resolution are obtained. The system is used to provide images of biological tissues, analytical electrodes, and catalysts. The Hadamard-encoded photothermal deflection system uses source encoding to generate line images. It is used to provide rapid scans of proteins on electrophoretic blots and gels.

University of Minnesota
Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

351. *Continuous Reaction Chromatography*
Aris, R.; Carr, R.W. **$83,810**
Comm. 612-625-9568

The motivating principle behind this research has been to explore the advantages of doing the separation of products at the same time as the reaction that is forming them takes place. Thus the thermodynamic limitations of the reversible reaction in a fixed bed can be overcome and conversions far beyond the static equilibrium obtained. The difficulties of moving a bed of granular solid against a gas stream have motivated consideration of the switched column in which the counter currency is attained discontinuously by switching the feed point to a fixed bed in a cyclic manner. The value of this scheme was first tested for separations using a small unit of four columns. A computer-controlled switching device cycles the carrier to the first column, adds the feed at the second, taking off the least adsorbed components before the third bed, and the most strongly held at the fourth. This set up is now being run as a reactor and currently being enlarged to an eight-column unit. Model calculations, using data obtained in previous experiments, predict 99.7% conversion with 98.5% purity for mesitylene hydrogenation under conditions that would give less than 62% conversion in a fixed bed.

University of Missouri
Rolla, MO 65401

Department of Chemistry

352. *Use of Functionalized Surfactants and Cyclodextrins in Chemical Analysis*
Armstrong, D.W. **$71,978**
Comm. 314-341-4429

Cyclodextrin-bonded phases have been used for the reversed-phase separation of a variety of enantiomers, diastereoisomers, structural isomers, enzymes, and routine compounds. Of these, the enantiomeric separations probably have received the greatest attention. In order to evaluate the mechanism of enantioselective chromatography, a number of empirical and theoretical studies have been done. In specific cases involving cyclodextrins, the formation of an inclusion complex seems to be a fundamental part of the chiral recognition and separation process. As yet, there have been no reports of normal phase, enantiomeric separations on cyclodextrin-bonded phase columns. Indeed the fact that facile enantiomeric resolution obtained in the reversed-phase mode could not be duplicated in the normal-phase mode has been used as indirect evidence that inclusion complexation is necessary for enantioselectivity. However, cyclodextrin-bonded phases have been used successfully in normal-phase liquid chromatography for a number of achiral separations. The retention behavior was somewhat like that of a diol column. It is believed that the nonpolar portion of the mobile phase (e.g., hexane, heptane, etc.) occupies the cavity of cylodextrin and that solute retention was mainly the result of interaction with the external hydroxyl groups that line the top and bottom of the cyclodextrin torus. Four different derivatized β-cyclodextrins were synthesized and used as chiral stationary phases in normal-phase liquid chromatography. The multiply substituted derivatives were made with acetic anhydride, (R)-(-)-1-(1-naphthyl)ethylisocyanate, 2,6-dimethylphenylisocyanate and p-toluoyl chloride. The first successful cyclodextrin-based, normal-phase separation of enantiomers was accomplished on these derivative phases. In contrast to chiral separations on the native β-cyclodextrin stationary phase, the enantiomeric separation mechanism on these new phases is not thought to be dependent on inclusion complexation. The similarities and differences between the derivatized cyclodextrin stationary phases and the cellulosic stationary phases are being evaluated.

National Institute of Standards and Technology
Gaithersburg, MD 20899

Chemical Kinetics Division

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

Sieck, L.W. **$146,322**
Comm. 301-975-2563

This project involves the measurement of fundamental properties of gas phase ions. The project uses the NBS pulsed electron beam mass spectrometer as the prime experimental facility, and an ICR instrument and triple MS system are also available. Emphasis is in two areas. One area is definition of the thermochemistry of anionic association and cluster ions via variable-temperature equilibrium measurements. Correlation lines, which express the dependence of the bond strengths upon the differences between the acidities of the two interacting partners, are then developed for predictive purposes for various classes of ligands and anions. The temperature dependence of various particle transfer reactions is also under investigation. The most extensive aspect of this project involves measurement of proton transfer equilibria of the type $A^- + BH \rightleftharpoons B^- + AH$ as a function of temperature in order to accurately define the acidity difference between A and B. Interlocking ladders of relative ΔH and ΔS are then referenced to primary standards in order to provide an absolute gas phase acidity scale. Other studies include the pyrolysis of protonated alcohols and definition of an absolute proton affinity scale, again using variable-temperature equilibrium measurements.

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

Department of Chemistry

354. *Stable Isotope Studies*

Ishida, T. **$98,728**
Comm. 516-632-7894

The goal of this project is development of a hydrophobic heterogeneous catalyst for exchange reaction of hydrogen isotopes, such as protium, deuterium, and tritium, between hydrogen gas and liquid water (Reaction I) for which the catalytic activity is *in situ* regeneratable and the hydrophobicity is *in situ* variable. Platinum-group metals dispersed on a conductive substrate are rendered variable degrees of hydrophobicity via chemical surface modifications by electropolymerization of benzene derivatives and fluorinated aromatic compounds and/or by silanization. The following properties of the catalyst surface and the correlation of these properties to the surface preparation techniques are being studied: (1) regeneratability of catalyst activity by electrochemical potential programs; (2) chemical and electrochemical stabilities of the surface modifier, in particular, the reversibility of electrochemical oxidation/reduction in the potential range used for the regeneration in the presence of the platinum group metals; (3) absence or presence of poisoning of surfaces of the catalytic metal due to the modifier molecules; (4) surface tension in aqueous media as a function of electrode potential; (5) catalytic activity for Reaction I; (6) mechanical durability of the metal deposit-modifier-substrate entity in realistic industrial environment. To gain insight into the chemistry of isotope separations in general, vapor pressure isotope effects and kinetic isotope effects are studied and theoretical tools such as normal coordinate analysis, molecular dynamics, and orthogonal polynomial approximations are used.

University of North Carolina
Chapel Hill, NC 27514

Department of Chemistry

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

Murray, R.W. **$117,000**
Comm. 919-962-6296

Miniaturized electrochemical cells suitable for electrochemical voltammetry of electroactive materials dissolved in or affixed to thin ionically conducting polymer films have been designed and tested. The cells are based on microdisk electrodes sealed in glass capillaries or are fashioned as microband electrodes microlithographically. Experiments with these cells are aimed at developing a range of electrochemical methodologies, with appropriate boundary value theory, to bring the diagnostic power developed for electrochemical voltammetry in fluid electrolytes to rigid polymeric media experiments. Secondly, the polymer solvent film can be exposed to a bathing gas whose constituents can interact in a plasticizing or in a chemically reactive way with the polymer solution, altering the observed electrochemical voltammetry. Such interactions presently form the basis for investigation of the molecular aspects of polymer plasticization effects and chemical reactivity in polymer phases, and may be applied to design sensors for bathing gas constituents.

Oklahoma State University
Stillwater, OK 74078-0447

Department of Chemistry

356. Unsegmented Continuous Flow Sample Processing and Electrochemical Detection and Determination of Gaseous Species

Mottola, H.A. **$75,000**
Comm. 405-744-5936

Three basic ways of producing modified conducting surfaces (based on metal complex redox couples and polymeric films with or without redox mediators) are studied: (1) direct admixing of relatively insoluble salts of a complex cation (or an immobilized enzyme preparation) with carbon pastes, (2) covalent binding of the modifier to graphite or binding liquids, and (3) oxidative electropolymerizations. Completed work has resulted in the development of a family of amperometric sensors based on Fe(II)/Fe(III) redox centers anchored as complexes with ligands derived from the 1,10-phenanthroline moiety. Glassy carbon surfaces modified with electropolymerized tris[5-amino-1,10-phenanthroline]iron(II/III) perchlorate provide, for example, competitive limits of detection for NO_2(g) in rugged, stable, and compact sensors. Incorporation of the enzyme sulfite oxidase to carbon pastes (via immobilization to crosslinked agarose) results in surfaces for selective and satisfactory detection of SO_2(g). A new family of surfaces is being developed by electropolymerization of resole prepolymer mixtures. Resole mixtures based on 4-hydroxybenzaldehyde result in conducting films that can be used for direct detection or for attachment of enzyme molecules to enhance selectivity and sensitivity. Resole mixtures based on 4-hydroxybenzoate do not conduct but can be used for attachment of other chemical species (e.g., enzymes) via carbodiimide-mediated linkages. These preparations can be incorporated into continuous-flow systems as thin-layer electrochemical cells or as chemical reactors for repetitive/continuous detection of ppm/ppb (v/v) level of gaseous species. Electrochemical cells take advantage that the continuous-flow operation (under laminar flow conditions) ensures the presence of an unbroken film of ionic solution that supports electrical migration and satisfies electroneutrality.

University of Oklahoma
Norman, OK 73019

Department of Chemical Engineering and Materials Science

357. A Study of Micellar-Enhanced Ultrafiltration

Scamehorn, J.F.; Christian, S.D. **$68,800**
Comm. 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 in MEUF for organic solute removal to reduce the concentration of surfactant in the permeate.

Purdue University
West Lafayette, IN 47907

Department of Chemistry

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

Freiser, B.S. **$103,530**
Comm. 317-494-5270

This work continues using laser desorption Fourier transform mass spectrometry (FTMS) on the gas-phase chemistry and photochemistry of transition-metal-containing ions. Two areas of focus this past year have included the study of (1) MgL^+($L = O$, OH) species and (2) M^+–benzyne ($M = Fe$, Fe_2, Sc) species. The goal of the MgL^+ work was to provide accurate thermodynamic data, important for modeling upper atmospheric chemistry, since several values were in question. Benzyne is a highly reactive ligand that can be stabilized by a metal center. These studies have revealed information on the effect of the benzyne ligand on the chemistry of the metal center. Progress was also made on studies involving doubly charged metal ions and electron-deficient ions. In particular it was demonstrated that $NbCH_2^{2+}$ and $NbC_2H_4^{2+}$ are thermodynamically stable, and the surprising result that alkanes can displace alkenes from selected doubly charged metals, a result that is supported by theory, was obtained. Ions such as YCH_3^+, which has 1-valence electron on yttrium, and $Sc(CH_3)_2^+$, which has none, cannot undergo direct insertion. It was observed that σ-metathesis reactions for these species, as proposed recently by Bercaw, explain analogous solution reactions. Finally, studies of the ir multiphoton dissociation of these species have been initiated to obtain dynamic and structural information.

Rensselaer Polytechnic Institute
Troy, NY 12180-3590

Department of Chemical Engineering

359. Direct Measurements of Protein–Polymer Membrane Interactions in Solution with Relevance to Fouling and Reducing Energy Utilization

Belfort, G. **$140,000**
Comm. 518-276-6948 **(18 months)**

The objective of the research is to measure the intermolecular forces between interacting layers of proteins including bovine pancreas ribonuclease A, lysozyme, myoglobin, and human serum albumin, and ultrathin commercially relevant polymeric membranes. Polymers for these membranes include cellulose acetate, aromatic polyamide, polysulphone, and a copolymer mixture of polysulphone and poly(pyrrolidone) in order to obtain a series of varying polarity membranes. The Surface Force Apparatus will be 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, and biocolloid stability. With an understanding of these intermolecular forces, it should eventually be possible to choose membrane 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

360. Macrocyclic Ligands for Uranium Complexation

Potts, K.T. **$94,656**
Comm. 518-276-8460

A series of macrocyclic hosts for the uranyl ion has been designed using computer modeling techniques. These macrocycles contain six ligating oxygen atoms capable of binding in the equatorial plane of the uranyl ion arranged in a symmetrical manner in the macrocycle, and variables are introduced by inclusion of sulfur as a ligating atom, and by inclusion of peripheral subunits containing functional groups such as urea, biuret, thiobiuret, 1,3-diketone, and pyridine moieties. In the macrocycles prepared to date with alkane subunits in the periphery, it was not possible to control cavity diameters with sufficient accuracy (4.7 to 5.2 angstrom) to form uranyl complexes of adequate stability because of conformational flexibility in the macrocycle periphery. This is being addressed by the synthesis of more highly preorganized macrocycles containing pyridine and other aromatic subunits. The introduction of functional groups to influence solubility in a positive manner as well as to allow incorporation into polymer systems is also being studied. Single-crystal X-ray data obtained on several uranyl complexes prepared in the study show cavity diameters between 4.88 and 5.02 angstrom, in good agreement with those predicted in the modeling studies.

San Diego State University
San Diego, CA 92182-0328

Department of Chemistry

361. Synthesis and Characterization of Mesomorphic and Other Stationary Phases

Laub, R.J. **$80,000**
Comm. 619-594-5572

This work is concerned with studies of the synthesis and physicochemical characterization of mesomorphic side-chain (liquid-crystalline) and other stationary phases that offer unprecedented selectivity in the chromatographic separation and analysis of complex organic mixtures. In particular, mesomorphic polysiloxane (MEPSIL) solvents are being synthesized that yield crystalline-to-nematic transition temperatures of less than ambient and nematic-to-isotropic transitions that approach 350°C. Characterization of the phases is being conducted in terms of the measurement and interpretation of probe-solute specific retention volumes, activity coefficients, and interaction parameters. "Family-plot" slopes (the equivalent of specific heats of solution) are also being determined and interpreted for a wide variety of hydrocarbon solutes with small-molecule as well as polymeric solvents.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering and Materials Science

362. Mechanisms of Gas Permeation Through Polymer Membranes

Stern, S.A. **$126,000**
Comm. 315-443-4469 **(18 months)**

Solubility, diffusion, and permeability coefficients of light gases in polymers generally become strong functions of pressure, or concentration, when the temperature is lowered below the glass-transition temperature (Tg) of the polymers. This behavior is generally interpreted in terms of a "dual-mode sorption" (DMS) model. Previous solubility studies in this laboratory have shown that the onset of DMS behavior may occur only at temperatures 40 to 50°C below Tg if the "excess" free volume of the polymers in the glassy state is sufficiently small [e.g., as in the case of poly(alkyl methacrylates)]. These observations have now been confirmed for CO_2 in poly(ethyl methacrylate) by means of a sensitive high-pressure electromicrobalance. It was also found that by first exposing the glassy polymer to an elevated CO_2 pressure, thereby increasing the "excess" free volume of the polymer, the onset temperature of DMS behavior is raised to just below Tg, as is commonly observed. Additionally, a new theoretical representation of gas solubility and transport in glassy polymers has been developed based on a "concentration–temperature superposition" principle. This representation requires only two adjustable parameters, both of which have a well-defined physical meaning. The new model describes satisfactorily the solubility behavior of gases in glassy polymers even when the polymer is highly plasticized by the penetrant gas.

363. *Particle Deposition in Granular Media*

Tien, C. **$98,599**
Comm. 315-443-4050

This study is concerned with the analysis and examination of the various phenomena arising from the deposition of particles from gas–solid suspensions flowing through granular media. Both experimental and analytical studies are being conducted. The specific topics of investigation include: (1) experimental measurements of collection efficiencies of particles as a function of the extent of deposition and their correlations, (2) computer simulation of particle deposition and determination of deposit morphology under various operating conditions, and (3) development of algorithms for predicting the pressure drop increase across a clogging granular medium.

University of Tennessee
Knoxville, TN 37996-1600

Department of Chemistry

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

Alexandratos, S.D. **$81,390**
Comm. 615-974-3399

Fundamental studies are in progress that will determine the variables most important to preparing polymer-supported reagents with high levels of complexing specificity for target ions and molecules. Polymer bifunctionality has been found to be a critical variable in metal ion recognition. A "Principle of Ionic Recognition" has been derived from the results: "Ionic recognition is an inherent property of polymers which couple an access mechanism with a recognition mechanism subject to reaction or steric control." The access mechanism is the relatively aspecific ion exchange reaction that allows ions entry into the polymer network. Reaction control of the recognition mechanism entails a polymer/ion interaction wherein the ion loses its ionic character (as in reduction to the free metal or precipitation as an insoluble metal salt) or changes its coordination sphere to that of a coordinating ligand on the polymer. Steric control applies to polymers that display specificity through steric hindrance to complexation for all but the target ion. The fundamental interactions between polymers and molecules are being investigated. Linear free energy relationship studies have been used to define the degree of molecular recognition displayed by polymer-supported phosphinic acid, sulfonic acid, and tertiary amine ligands in the complexation of neutral phenols, anilines, and benzoic acids. The total amount complexed is an additive function of an active site interaction and a solvent interaction. No solvent effect is observed when the solute/solvent solubility parameters are comparable. The phosphinic polymer has the greatest degree of selectivity in its absorption of substituted anilines (25% to 75% absorbed) with electron donating substituents increasing the percent absorbed.

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

Guiochon, G. **$86,755**
Comm. 615-974-0733

The project objective is to better understand some aspects of the firing of ceramics. The production of advanced ceramic material is hampered by the lack of methods permitting the timely elimination of lots that result in the production of faulty parts. The chemical composition of the surface of various samples of raw ceramic powders will be characterized by determining their energy distribution function for selected gases and vapors and correlating these functions with the performance of test ceramic parts prepared with that material. The surface chemical composition controls the wettability of the particles by, and their adhesion to, the organic materials used during the molding process, such as binders, dispersants, or solvents. Rapid methods have been developed for the calibration of chromatographic detectors and for the derivation of the adsorption isotherms of vapors on the surface of raw ceramic powders. For this purpose, a porous layer open tubular column is prepared with the powder. The energy distribution function can be derived from the isotherm and can be used for the calculation of other important data, such as the monolayer formation energy. Combining the energies determined for a set of probe vapors should permit a classification of the surface of a new material with respect to similar ones and possibly predict behavior of the new powder lot in the firing process.

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

Sepaniak, M.J. **$100,000**
Comm. 615-974-8023 **(17 months)**

The focus of this research is the practical development of capillary electrokinetic separation techniques for the analyses of volume-limited, complex samples, and difficult-to-resolve mixtures. Emphasis has been on the development, characterization, and utilization of micellar electrokinetic capillary chromatography (MECC). With this technique, neutral compounds are separated based on differential partitioning between aqueous and micellar components in the mobile phase, which are transported through the capillary column at different velocities because of electrophoretic effects. The results of numerous studies of factors that influence separation performance have been reported. There are five research projects currently in progress. The first project involves investigating factors that influence efficiency and detectability of separated proteins. Laser-based natural protein fluorescence and precolumn and oncolumn fluorescence derivatization have unique advantages and disadvantages in the detection of proteins/peptides. The second project shows that metal ions present in real matrices have been separated and detected with ppb LODs using mobile phases that incorporate fluorescing chelates such as 8-hydroxyquinoline-5-sulfonic acid. In the third project, using retention and flow rate parameters obtained from isocratic separations, computer simulated elution profiles have been generated to determine optimum gradient elution conditions for separating standard mixtures. It is seen in project four that chiral-ordered surfactants (bile salts) have allowed the enantiomeric separations of binaphthyl compounds. The separation of isomeric PAH compounds is under study using these systems. The fifth project involves conducting preliminary investigations into the use of affinity reagents (e.g., antibodies) as mobile phase additives to provide highly selective electrokinetic-based affinity separations.

Texas A and M University
College Station, TX 77843

Department of Chemistry

367. Development of Laser-Ion Beam Photodissociation Methods

Russell, D.H. **$81,838**
Comm. 409-845-3345

This project emphasizes laser-ion beam photodissociation methods for probing the dynamics of dissociation reactions of highly activated ionic systems. The experimental hardware and methods are developed, and studies on the photochemistry and photophysics of ionized peptides and transition metal clusters are in progress. 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 under construction. 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. Photodissociation on this instrument 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 (1000 to 10,000). The focus of the current work is on structural characterization of peptides and organo-alkali metal ions of peptides and nucleotides.

Texas Tech University
Lubbock, TX 79409

Department of Chemistry and Biochemistry

368. Metal Ion Complexation by Ionizable Crown Ethers

Bartsch, R.A. **$93,670**
Comm. 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 bulk and 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. Applications of these resins in alkali metal and alkaline earth cation separation processes are being explored.

369. Novel Approaches to Ionic Chromatography

Dasgupta, P.K. **$85,377**
Comm. 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. Present work concentrates on on-line generation of ultrahigh purity acidic and basic eluent substances; gradient chromatography is possible by programming the eluent generator rather than programming proportionation of pumps. The superior eluent purity is expected to lead to minimum baseline excursion during the execution of gradient chromatography and to detection limits superior to those heretofore attained. In conjunction with the totally electrical suppressor developed earlier in this project, a fully recycled suppressed ion chromatograph is envisioned. A second aspect of this project is to make available continuous information on the identity and purity of the peaks eluting from an ion chromatographic system. With tandem two-channel conductimetric detection, it is envisioned that standardless calibration will also be possible and pKa of weak acid analyte ions can be measured.

University of Texas
Austin, TX 78712

Department of Chemical Engineering

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

Koros, W.; Paul, D. **$81,670**
Comm. 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 with high permeabilities for important commercial gases such as hydrogen, carbon dioxide, and oxygen have been identified by systematic variation in the structures of polycarbonates, polyimides, and polysulfones. 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. Current work is now expanding to consider the polyester family as well. 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 structure with potential as advanced membrane materials. 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

371. Pulsed Laser Kinetic Studies of Liquids Under High Pressures

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

The volume reaction coordinate profile can be obtained for processes in liquids by measuring the process rate with the liquid under high pressures. Knowledge of the volume profile aids in the deduction of the reaction mechanism of processes in liquids. A high-pressure spectrophotometer cell will be used in rate studies of three different liquid sample systems. A combination of pulsed photothermal beam deflection, thermal lens, and photoacoustic techniques will be used to examine radiationless decay processes occurring in liquid solutions of 4-(N,N,-dimethylamino)benzonitrile that is thought to form a twist internal charge transfer (TICT) triplet excited state. The photothermal measurements carried out at high pressures will shed new light on this controversial photophysical problem. In a second study, the volume profile will be determined for the pulsed laser-induced dissociation of pure liquid water into hydronium and hydroxide ions. The kinetics of complexation of lithium ion by nitrite ion in aqueous solution will also be investigated under high pressures using an ultrasonic absorption technique. This last sample system is one that lends itself to computer simulations of the dynamics of the complexation process. Thus the reaction mechanism deduced from high-pressure kinetic measurements will be interesting to compare with a detailed theoretical model of the complexation reaction.

Department of Metallurgy and Metallurgical Engineering

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

Miller, J.D. **$160,000**
Comm. 801-581-5160 **(18 months)**

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. Research has focused primarily on the fluorite/sodium oleate system. Specifically, it has been shown that the first monolayer of chemisorbed oleate has a distinctly different infrared spectrum than subsequent precipitated layers of calcium oleate. Also, complete adsorption isotherms for oleate on a reactive fluorite IRE have been determined at various temperatures. These isotherms were constructed from spectra in the mid-infrared region (3050 to 2800 cm^{-1}) of the electromagnetic spectrum. Adsorption measurements have also been made in the near-infrared using a combination band between 4400 and 4000 cm^{-1}. Results obtained using these different regions of the infrared are in excellent agreement. This use of internal reflection spectroscopy in the near-infrared allows for the extension of this technique to many systems where the desired IRE is not transparent in the mid-infrared, such as calcite ($CaCO_3$)and dolomite ($CaMg(CO_3)_2$). 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).

Virginia Commonwealth University
Richmond, VA 23284

Department of Chemistry

373. Compensation for Peak Shifts and Variable Background Responses in Fluorescence Spectroscopy

Rutan, S.C. **$77,401**
Comm. 804-367-1298

The fluorescence responses observed for polyaromatic hydrocarbon compounds are susceptible to changes in the chemical surroundings of the molecules. Perturbations to the spectral responses arising from the presence of variable background components or solvent-dependent spectral shifts cause errors in algorithms developed for the identification and quantification of fluorescent species. The purpose of these studies is the development of mathematical methods that allow determination of fluorescent species, despite errors caused by these perturbations to the spectra. Current work is focused in two areas. The first area is the development of an on-line fluorescence spectroscopic detector for high performance liquid chromatography, based on an intensified diode array. Window programs that allow for control of the liquid chromatography gradient conditions, which can be run concurrently with the diode array manufacturers software, have been developed. This allows collection of fluorescence spectra "on-the-fly" from liquid chromatographic eluants. Data analysis algorithms can then be implemented which can correct for sample dependent background responses and solvent dependent response shifts. These methods allow fluorescence spectral detection to be used reliably in the detection of polyaromatic hydrocarbon compounds.

University of Wyoming
Laramie, WY 82071

Department of Chemistry

374. Solid-Surface Luminescence Analysis

Hurtubise, R.J. **$93,670**
Comm. 307-766-6241

The objective of this project is to acquire a basic 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. The main spectral techniques used to study the interactions are luminescence, reflectance, and Fourier transform infrared spectrometry. Filter paper, sodium acetate, and B-cyclodextrin/NaCl mixtures are being used as solid matrices in studying the interactions of adsorbed compounds. Several experiments are being performed in which the temperature or humidity is varied, and experiments are being carried out to study the solution fluorescence properties of B-cyclodextrin/solute complexes. From the data acquired, quantum yields, photophysical rate constants, and rotational relaxation times are calculated. The calculated parameters are primarily related to adsorbed fluorophors, adsorbed phosphors, and the properties of the solid matrices. For example, by comparing heat capacity data for sodium acetate and the luminescence properties of p-aminobenzoate adsorbed on sodium acetate, it is concluded that the triplet energy of p-aminobenzoate is lost via skeletal vibrations of sodium acetate. Also, an important discovery is that the B-cyclodextrin/NaCl matrices give very high room-temperature luminescence quantum yields from adsorbed compounds.

Heavy Element Chemistry

Florida State University
Tallahassee, FL 32306

Department of Chemistry

375. Research in Actinide Chemistry

Choppin, G.R. **$112,000**
Comm. 904-644-3875

This research emphasizes the chemical behavior in aqueous systems of the actinide and lanthanide elements. The complexation of NpO_2^+ with a series of aliphatic dicarboxylic and aromatic polycarboxylic ligands was studied by spectrophotometry. The data were valuable in clarifying the role of chelate ring size, statistical effects of multiple binding sites and of protonated species. The hydrolysis constants of UO_2OH^+ and $UO_2(OH)_2$ formation were obtained as well as the binding constants of UO_2^{2+} and NpO_2^{2+} with $H_2PO_4^-$ and HPO_4^{2-}. These are necessary for modeling actinide behavior in the far-field areas of nuclear repositories. The ΔH of formation of NpO_2OH was obtained by calorimetry and used to estimate the hydrolysis of AnO_2^+ at waste repository temperatures. The results from luminescence and NMR spectroscopy are combined with thermodynamic data from solvent extraction, potentiometry, and calorimetry to define the structure, residual hydration, and so forth of inorganic and organic ligand complexes. The kinetics of reduction of NpO_2^{2+} by organic ligands were determined as a model for reduction by humic substances of NpO_2^{2+} and PuO_2^{2+}. The dissociation kinetics of actinide and lanthanide complexes with ligands of interest environmentally (e.g., humics), medically (MRI agents) or in separations (phosphonates) have also been major areas of study. The humic dissociation kinetics showed that migration of actinides in humic bearing soils would be retarded kinetically in a complex fashion.

University of New Mexico
Albuquerque, NM 87131

Department of Chemistry

376. Development of Immobilized Ligands for Actinide Separations

Paine, R.T. **$110,437**
Comm. 505-277-1661

The primary goals of this project are (1) to establish fundamental data for the design of new families of organic extractants suited for the separation of lanthanide and actinide ions from complex matrices and (2) to develop methods for preparing separations agents covalently attached to solid supports. In particular, synthetic schemes are devised that provide two or more functional groups in 1,2 positions on a carbon backbone, and preference is given to saturated carbon backbones with high orientational flexibility. Functional groups most commonly employed are organo-phosphoryl, nitrosyl, sulfinyl, sulfonyl, and carbonyl. The coordination chemistry of new ligand types is studied and systematized, and the extraction properties of selected ligands are characterized by radio-chemical methods. Ligands that demonstrate favorable separations properties are further functionalized in order to provide for covalent attachment of the ligands to solid organic and inorganic supports. Steric and electronic factors that subsequently influence the separation properties of immobilized ligands are examined.

Ohio State University
Columbus, OH 43210

Department of Chemistry

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

Bursten, B.E. **$59,160**
Comm. 614-292-1866

This project continues to investigate the electronic structure and bonding in organoactinide complexes, particularly those that contain pentahaptocyclopentadienyl (Cp) ligands. Significant progress has been made in understanding the bonding in complexes that contain three Cp ligands coordinated to an actinide center. A detailed analysis of the bonding in $(\eta^5\text{–}C_5H_5)_3U\text{–}X$ and $(\eta^5\text{–}C_5H_5)_3U\text{–}L$ complexes has been reported, and the electronic structural differences induced when no fourth ancillary ligand is coordinated (so-called "base-free" complexes) have been investigated. The first electronic structure calculations on organometallics of the transplutonium elements have been reported. While the quasi-relativistic Xα–SW molecular orbital method continues to be the primary method of analysis, recent access to the Cray Y–MP supercomputer at the Ohio Supercomputer Center has allowed the expansion of the theoretical methodology to include the DV–Xα method and *ab initio* method. Both of these methods are allowing the investigation of the magnitude of spin-orbit effects on the bonding in these systems. The latter is currently being used to explore the potential surface of UH_3 as a model of the homoleptic U(III) alkyl complex $U[CH(SiMe_3)_2]_3$ that was synthesized recently at Los Alamos National Laboratory (LANL). The potential energy surface of the diuranium (U_2) molecule is also being examined.

SRI International
Menlo Park, CA 94025

Physical Sciences Division

378. *Chemistry of Gaseous Lower-Valent Actinide Halides*

Hildenbrand, D.L.; Lau, K.H. **$104,437**
Comm. 415-859-3436

The project objective is to provide accurate thermochemical information for key actinide halide, oxyhalide, and related systems, starting with the uranium and thorium halides, so that the basic factors underlying the energetic and structural aspects of the chemical bonding in these systems can be elucidated in a systematic way. The principal focus is on the gaseous lower-valent halides, since there is little thermodynamic or spectroscopic information on these species. Bond dissociation energy and absolute entropy data are derived from chemical equilibrium measurements made primarily by high-temperature mass spectrometry. Current studies are concerned with the gaseous tetrabromides and tetraiodides of uranium and thorium, the neptunium fluorides and oxyfluorides, and the equilibrium thermal ionization of urania vapor. Sublimation entropies indicate that the gaseous uranium tetrahalides and some thorium tetrahalides most likely have distorted tetrahedral structures, while other thorium tetrahalides are regular tetrahedra. Bond energy patterns also show significant differences in the two series. Clarification of these trends will be useful in modeling the thermochemistry of the heavier actinides, which will be much more difficult to study experimentally.

University of Tennessee
Knoxville, TN 37996-1600

Department of Chemistry

379. *Physical–Chemical Studies of the Transuranium Elements*

Peterson, J.R. **$152,830**
Comm. 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 extent and magnitude of the actinide contraction; (3) the spectroscopic, crystallographic, thermodynamic, and magnetic properties of these materials as related to general theories; (4) the chemical and physical consequences of radioactive decay in the bulk-phase solid state; and (5) 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) X-ray diffraction of actinide materials under pressure; (4) absorption and Raman spectrophotometry of lanthanide and actinide materials under pressure; (5) measurement of the enthalpies of solution of actinide compounds; (6) direct or indirect (via radioactive decay) synthesis of actinide compounds containing unusual oxidation states; (7) broader applications of studies to determine the physical and chemical consequences of radioactive decay in the bulk-phase solid state; (8) study of the relationship of natural ion implantation to artificial ion implantation; and (9) growing single crystals of actinide elements and compounds on the milligram scale.

Department of Physics and Astronomy

380. *Magnetic Measurements of the Transuranium Elements*

Nave, S.E. **$104,516**
Comm. 615-574-5013

This project involves a study of the magnetic properties of transuranium metals, alloys, and compounds. Currently research is focused on determining the validity of a crystal-field modified, free ion model to explain the susceptibility of the actinide trihalide and sesquioxide compounds. A computer code has been developed for calculation of the susceptibility based on a crystal-field model using intermediate coupling wave functions and including j-mixing effects. Magnetic actinides have been diluted with nonmagnetic americium to determine the effect of separation of the magnetic species on the low-temperature magnetic ordering. Experiments are also in progress on the heavy fermion class of compounds, to study the change from a heavy fermion state to a local moment state with increasing atomic number. A technique has been developed to grow single crystals of actinide halides with milligram masses without loss of material. Research continues on other lossless crystal growth techniques applicable to compounds, metals, and alloys of the heavy actinides, to allow magnetic measurements as a function of orientation and to provide samples large enough to allow neutron diffraction studies. Work is also in progress to develop new microinstruments for determining the electronic properties of the heavy actinides that are obtained in submilligram sizes because of their scarcity and high specific radioactivity.

Chemical Engineering Sciences

American University
Washington, DC 20016

Department of Physics

381. *Theory of Condensable Gases*
White, J.A. **$104,170**
Comm. 202-885-2747 **(18 months)**

A statistical mechanical theory of fluids that takes into account effects of fluctuating attraction among molecules neglected in the mean field approximation has been formulated for use over a wide range of densities that includes the critical point density. Increments of free energy resulting from fluctuations with wavelengths comparable to and greater than the range of attractive forces between the molecules are evaluated recursively in the phase space cell approximation of K. Wilson, with results at the critical point that agree with those of Wilson. When away from the critical point, the recursion equations have been evaluated numerically for a simple model gas of hard spheres that attract one another with forces of moderately short range. For particular choices of the three model gas parameters, determined uniquely by the critical point pressure, temperature, and density, compressibility factors predicted by the theory are found to agree to ~1% with those measured at the critical point temperature in simple fluids, Ar, Xe, CH_4, and so forth, for densities in the range approximately 0.3 to 1.6 times the critical point density. The model is currently being extended to other temperatures and densities and to other thermal properties; future work will explore its suitability for systems other than simple fluids.

University of California
Santa Barbara, CA 93106

Department of Chemical and Nuclear Engineering

382. *Reaction Enhancement of Heterogeneously Catalyzed Reactions by Concentration Forcing*
Rinker, R.G. **$71,000**
Comm. 805-961-2610

Experimental and theoretical studies are under way to examine the behavior of nonlinear reacting systems, both isothermal and nonisothermal, under conditions of forced concentration oscillations (FCO) at constant total pressure. Compared to optimal steady-state operation, concentration forcing can provide higher time-averaged production rates, increased catalyst life, improved selectivity, and lower energy requirements. This study focuses on the synthesis reactions of methanol and methane from carbon monoxide and hydrogen, and has provided new insight into how surface concentrations of these reactants on commercial catalyst surfaces can be manipulated, under conditions of practical interest, to kinetically accelerate the overall rates of conversion to desirable products. Methanol synthesis is being conducted in fixed-bed reactors with well-mixed and nonmixed gas phases, whereas the methane synthesis studies are limited currently to a fixed-bed reactor with well-mixed gas phase. For both systems, commercial catalysts at essentially commercial conditions are being used, namely, a copper/cuprous oxide/zinc oxide synthesis catalyst for methanol and a nickel/aluminum oxide methanation catalyst. Preliminary FCO studies, using pure-component cycling for ranges of cycle times and cycle splits, have given production-rate improvements for methanol as high as 25% relative to optimal steady state and for methane as high as 12%. However, considerably higher improvements are expected, particularly for methanation.

University of California/San Diego
La Jolla, CA 92093

Department of Applied Mechanics and Engineering Sciences

383. *Premixed Turbulent Combustion*
Libby, P.A. **$56,349**
Comm. 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 subject to swirl is presently under way. The configuration considered involves counterflowing reactant streams with swirl about an axis of rotation. The analysis for low rates of swirl is straightforward and has been completed. Beyond a critical rate of rotation, multiple stagnation planes appear and the situation calls for an entirely different asymptotic analysis. A tentative treatment has been completed and is being explored numerically. 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. Two analyses of these flames have been completed; one involves a simple algebraic model for turbulent transport while a second uses the well-known k-ϵ model. The portion of this work dealing with extinction was combined with experiments carried out at Cambridge. The formulation for a third approach based on the Bray–Moss–Libby model, presumably the most realistic, has been completed but the numerical treatment that is formidable is giving trouble.

Clarkson University
Potsdam, NY 13699-5705

Department of Chemical Engineering

384. ***Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures***
Lucia, A. **$49,612**
Comm. 315-268-6674

A unified analysis framework has been developed for separation processes involving either homogeneous or heterogeneous multicomponent mixtures. Results show that when the mixture involved is homogeneous, the solution to the process model is unique for a variety of specifications. For mixtures that are heterogeneous, the analysis indicates that two-phase solution multiplicity can occur and simple examples that illustrate turning points and bifurcations in these solutions have been constructed. The analysis has been used to study the convergence behavior of certain existing algorithms and develop new methods for multicomponent, multistage separation process simulation. As a consequence, new sum-rates and bubble-point methods have been developed. A numerical study was conducted and shows that these new sum-rates methods are considerably more reliable in practice than traditional methods. Periodic and chaotic behavior of equation-tearing and equation-solving methods have been illustrated on problems involving heterogeneous mixtures. Current research includes an analysis of the singularities in two-phase solutions for heterogeneous mixtures, a study of the numerical performance of new bubble-point methods, continued investigation of periodic and chaotic behavior of fixed-point methods, and analysis of the number of three-phase solutions.

Colorado State University
Fort Collins, CO 80523

Department of Chemical Engineering

385. ***Study of Improved Methods for Predicting Chemical Equilibria***
Lenz, T.G.; Vaughan, J.D. **$95,642**
Comm. 303-491-7871

The equilibrium composition of chemically reactive systems can be determined experimentally, but considering the extremely large number of potentially valuable reactions, relying solely on measurements would be prohibitively expensive. This project involves computational and experimental studies to develop methods capable of accurately predicting condensed-state chemical equilibria. Computed gas-phase isolated molecule thermodynamic properties for reactants and products are extended to liquid-phase values by means of vapor pressure data. Detailed studies of the thermodynamics of the dimerizations of both 1,3-cyclopentadiene and 1,3-butadiene, the reaction of ethene with 1,3-butadiene and 1,3-cyclopentadiene, and the reaction of ethyne with 1,3-cyclopentadiene have been carried out by the application of three force-field programs. In all instances the calculated equilibrium data were as accurate as the best literature data. Currently, the 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. To this end the QCFF/PI program of Warshel and Levitt, modified to calculate thermodynamic functions, is being further modified to calculate standard enthalpy of formation, barriers to internal rotation, and hindered internal rotational contributions to thermodynamic functions. Recent experimental studies supporting development of this computational model have included obtaining X-ray crystallographic structures for 3-phenylmaleic anhydride and the Diels–Alder adduct of 3-phenylmaleic anhydride/anthracene.

Cornell University
Ithaca, NY 14853-5201

School of Chemical Engineering

386. ***Theory and Simulation of Fluids of Associating Chain Molecules***
Gubbins, K.E. **$238,485**
Comm. 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 will be 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.

387. ***Exact Calculations of Phase and Membrane Equilibria for Complex Fluids by Monte Carlo Simulation***
Panagiotopoulos, A.Z. **$146,528**
Comm. 607-255-8243 **(18 months)**

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 systems. The first exact calculation of the critical point and phase envelope was obtained for the restricted primitive model for ionic solutions, and calculations are being extended to asymmetric electrolytes and mixtures of electrolytes and nonelectrolytes. Planned work includes extension of the Gibbs methodology to other strongly interacting systems such as chain molecules and highly asymmetric mixtures with large differences in size and potential energy of interaction. A combination of techniques such as species identity exchange and gradual particle insertions will be used. The results of these 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.

388. *Experimental and Theoretical Studies of Dense Fluid Mixtures*

Zollweg, J.A. **$121,000**
Comm. 607-255-1101 **(18 months)**

The primary goals of this research are: (1) to carry out a comprehensive thermophysical property measurement program on a few strategic pure fluids and mixtures and (2) to develop methods for correlating, extrapolating, and predicting dense fluid properties using statistical mechanics and intermolecular potential theory. The measurements are performed in a direct-weighing PVT apparatus that is designed to work from room temperature to 600°C and from 0 to 2000 bar, and a pulse-echo overlap speed-of-sound apparatus that is designed for work from −150 to 250°C and from 0 to 4000 bar. Theoretical work has included using a multiproperty fitting method to find thermodynamic functions that simultaneously describe PVT, speed-of-sound, and heat capacity data. New speed-of-sound measurements have been made on a specially purified sample of R-134a to be used in developing an equation of state for a promising environmentally safe refrigerant. These results were found to be representable by a two-variable rational approximant with a relative error of less than 0.1%.

Department of Chemistry

389. *Reaction and Diffusion in Turbulent Combustion*

Pope, S.B. **$174,992**
Comm. 607-255-4314 **(19 months)**

The project objectives are model development for turbulent, nonpremixed combustion, and increase in the range of such model development by the incorporation of more of the essential physics. The work is divided into (1) direct numerical simulations (DNS) of reactions in constant-density, homogeneous, isotropic, statistically stationary turbulence; (2) stochastic modeling which mimics the results of the DNS calculations; and (3) the study of mixing as molecular motion. The latter is a long-standing problem which has not as yet yielded to molecular analysis.

University of Delaware
Newark, DE 19716

Department of Chemical Engineering

390. *The Generalized van der Waals Theory of Pure Fluids and Mixtures*

Sandler, S.I. **$68,669**
Comm. 302-451-2945

A computer simulation of model molecules (on a CRAY supercomputer) and a form of the canonical partition function, developed previously and referred to as the generalized van der Waals partition function, has been successfully used to test the basis of current thermodynamic models, and to develop new ones. This work has provided detailed insight into the molecular basis of thermodynamic modeling and local composition effects. In particular, a better understanding of the temperature and density dependence of various terms in the equation of state has been obtained, and new equations have been developed, such as the simplified perturbed hard chain equation. Local composition models based on computer simulations have been used in the generalized van der Waals partition function to obtain new activity coefficient models and equation of state mixing rules. Work is currently extending to nonspherical chain molecules, and to mixtures of molecules that differ greatly in size and functionality. Research completed on the effect of molecular polydispersivity on phase equilibrium has resulted in new, more efficient descriptions of mixtures as varied as petroleum reservoir fluids and polymer solutions used in biological separations. A polymer fractionation phenomenon in this work has been discovered and has been experimentally verified.

University of Illinois
Chicago, IL 60680

Department of Chemical Engineering

391. *Evaluation of Mixing Rules for Viscosity and Thermal Conductivity Using Nonequilibrium Molecular Dynamics*

Murad, S. **$68,034**
Comm. 312-996-5593

A nonequilibrium molecular dynamics method was developed to investigate the thermal conductivity of nonspherical fluids; no such technique was previously available. The method has been used to predict the thermal conductivity of hydrogen chloride, using potential models developed previously, to demonstrate the feasibility of the method. This method is now being used to investigate the thermal conductivity of homonuclear and heteronuclear linear molecules and their mixtures. In a related study the viscosity of linear homonuclear diatomic fluids and their mixtures was examined. This study enabled the effect of bond length on viscosity to be investigated and mixing rules suitable for such mixtures to be developed. Such a study is now being conducted for heteronuclear diatomic systems. This will then complete a comprehensive study of diatomic fluids.

Johns Hopkins University
Baltimore, MD 21218

Department of Chemical Engineering

392. *Prediction of Thermodynamic Properties of Coal Derivatives*

Donohue, M.D. **$86,768**
Comm. 301-338-7761

It is quite difficult to predict the properties of streams found in coal processing operations. There are two primary reasons for this difficulty. The first is that the species encountered in coal processes are quite complex in both their physical structure and in terms of their intermolecular potential functions. In contrast to the species found in petroleum-based processes, a wide variety of compounds are encountered in coal-derived products with more aromatic species and more compounds with functional groups containing oxygen, nitrogen, and sulfur. The second difficulty concerns a lack of knowledge of multicomponent mixtures—especially when the species involved differ significantly. There are few thermodynamic theories (either equation of state or activity coefficient) that can yield accurate predictions of even binary phase behavior without the use of large binary interaction parameters. In general, there is no reason to believe that these parameters will be valid in ternary and multicomponent mixtures without additional ternary and quaternary parameters. A multifaceted approach to addressing these problems is being taken. A semitheoretical equation of state has been developed which attempts to take into account polarity, hydrogen bonding, and molecular size. This equation of state has been systematically evaluated against experimental data for a wide variety of compounds and mixtures. From the lessons learned concerning the successes and failures of this equation, molecular simulations have been devised to help guide the next generation of theory. Current efforts are concerned with simulations at low densities where, it appears, many properties do not scale linearly with molecular size.

University of Maryland College Park, MD 20742

Institute for Physical Science and Technology

393. *Thermophysical Properties of Supercritical Fluids and Fluid Mixtures*

Sengers, J.V. **$85,782**
Comm. 301-454-4117

This research project is concerned with the development of scientifically based representative equations for the thermophysical properties of fluids and fluid mixtures. A procedure was constructed on how a classical Landau expansion can be transformed into an expansion that incorporates the crossover from Ising-like singular behavior near the critical point to the regular behavior far away from the critical point. The procedure is based on the renormalization-group theory of critical phenomena and yields an accurate representation of the thermodynamic properties of fluids in a large range of densities and temperatures around the critical point as illustrated for such fluids as carbon dioxide, steam, ethylene, and ethane. Attempts are made to continue the research in two directions, namely to extend the theory to fluid mixtures and to investigate how the procedure can be combined with cubic equations and hard-sphere perturbed equations often used in chemical engineering applications. Also in collaboration with the University of Amsterdam new, accurate thermal conductivity data were obtained for ethane. These data appeared to be in good agreement with a crossover description for the transport properties of fluids obtained on the basis of the mode-coupling theory of dynamic critical phenomena.

Massachusetts Institute of Technology Cambridge, MA 02139

Department of Chemistry

394. *Thermodynamics and Kinetics of Complex Organic Systems*

Alberty, R.A. **$88,740**
Comm. 617-253-2456

The objectives of the project are to make thermodynamic calculations on complex organic systems in new ways and to compute the approach to equilibrium using simple rate equations. The new methods involve the use of isomer groups, homologous series groups, new thermodynamic potentials obtained by Legendre transforms, matrix methods, and distribution functions for equilibrium distributions. Since the isomer group properties of the successive isomers in a homologous series are linear in carbon number after the first one or two members, the standard Gibbs energy of formation of an isomer group with carbon number n can be represented by A + Bn, where A and B are only functions of temperature for a given homologous series. If the partial pressure of molecular hydrogen is specified, the equilibrium distribution of the successive isomer groups in a homologous series is given by a geometric distribution that depends only on A. If the partial pressure of ethylene is specified for an equilibrium calculation, the equilibrium distribution depends only on B. Equilibrium distributions of benzenoid polycyclic aromatic hydrocarbons are also found to be geometric distributions which are functions of the partial pressures of acetylene and molecular hydrogen in the benzene flame studied by Bittner and Howard.

National Institute for Petroleum and Energy Research (NIPER) Bartlesville, OK 74003

Processing and Thermodynamics Division

395. *Thermodynamic Properties by Noncalorimetric Methods*

Steele, W.V. **$185,358**
Comm. 918-337-4210

This research program provides a valuable complement to 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 to date include: (1) Group-contribution parameters were derived for estimation of thermodynamic properties for polycyclic aromatic nitrogen-, oxygen-, and sulfur-containing compounds. Initial results show a regular difference between the thermodynamic properties for compounds containing an oxygen or sulfur atom within five-membered rings. Provisional group parameters for nitrogen heterocycles were used to estimate properties for several benzoquinolines not studied calorimetrically. (2) A long pathlength, far-infrared sample cell was operated successfully in the collection of vapor-phase spectra of polycyclic compounds (up to three rings) with low vapor pressure. Previously only one- and two-ring molecules could be studied. (3) A method was developed to predict the vibrational frequencies of two- and three-ring polycyclic molecules to an accuracy sufficient for identification of fundamental vibrations in experimental spectra. (4) A method developed in this project was applied 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) modes for molecules containing large amplitude anharmonic vibrations. It was found that the direct summation of calculated energy levels to obtain the partition function for the vibration must be extended to near 10,000 cm^{-1} before the contribution from subsequent levels becomes negligible. (5) Correlation of critical properties for heteroatom-containing polycyclic aromatic compounds was begun. Key to the correlation are new experimental values obtained in complementary projects at NIPER. This is an initial step in the development of a new theoretical vapor-pressure equation applicable between the critical and triple-point pressures.

National Institute of Standards and Technology
Boulder, CO 80303

Thermophysics Divison

396. Integrated Theoretical and Experimental Study of the Thermophysical Properties of Fluid Mixtures

Ely, J.F. **$281,010**
Comm. 303-497-5467

The major objective of this research is the development of theoretically based predictive models for complex fluid mixtures. The research consists of three main elements: (1) development of predictive procedures for the properties of fluids and fluid mixtures, (2) basic understanding of fluid behavior through advances in theory and computer simulation, and (3) development of theoretically based correlations. Acquisition of experimental data to support theoretical and modeling efforts is also anticipated. Emphasis is placed on development of predictive models in the form of computer codes which can be readily transported to engineering users and which are easily incorporated into industrial design packages. In the development of predictive procedures, advanced corresponding states theories are being used, including the extended corresponding states concept and field space corresponding states ideas. Computer simulations will be performed for systems in equilibrium and out of equilibrium (e.g., under shear). The computer simulation results are used to test and extend the theoretically based models. Finally, correlations of near critical transport properties of mixtures and multicomponent-multiphase mixtures are being developed using crossover theory and field space concepts.

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

Department of Chemistry

397. Thermophysical Properties of Fluids and Fluid Mixtures

Stell, G.R. **$111,418**
Comm. 516-632-7899

Transport coefficients from the most highly developed version of kinetic theory (KVTIII) have been compared with the coefficients found from computer experiments and simple-fluid experiments over a wide range of temperatures in the dense-fluid regime. The agreement is good; the approach appears to represent the most quantitatively successful analytic "first-principles" approach yet developed. An analysis of the linearized theory, which facilitates comparison with important earlier work by others, has also been made. New results of an exact analytic study of a dilute gas diffusing through a highly porous medium of scatterers have been published. The gas-scatterer interaction was taken to be hard sphere plus square well, permitting a detailed study of the effects of gas-scatterer attraction. A detailed study of the viscosity of a polydisperse solute (not necessarily dilute) in a monodisperse solvent has also been conducted. A general theory of liquids in pores was introduced via an integral-equation approach to the problem. These initial results focused on the hard-sphere-fluid model in hard-walled pores. A closely related theory of liquid structure in the vicinity of membrane and vesicle surfaces was also developed. An equilibrium theory of molecular association and of the association of weak electrolytes has been developed and applied to the case of diatomics that dissociate into either monatomic atoms or ions, depending upon the details of the model. Extensive numerical results for association constants and related quantities have been obtained.

University of Pennsylvania
Philadelphia, PA 19104

Department of Chemical Engineering

398. Thermodynamics of Systems of Very Many Components

Glandt, E.D. **$96,666**
Comm. 215-898-6928

This research deals with the equilibrium properties of dense (liquid) mixtures, and with extreme cases with a high number of components, such as petroleum fluids and polymer solutions and melts. The study of phase equilibrium in such systems is usually a laborious task, with the difficulty increasing proportionally to the number of species. Highly efficient methods have been developed for the theoretical calculation and computer simulation of phase equilibrium, which essentially reduce the difficulty to that of the study of a pure substance, regardless of the number of components. The current objective is focused on the limit of very wide distributions. A predictive theory was also developed in which the properties of a mixture are obtained as a perturbation expansion about the case of an infinitely polydisperse system. Unlike other perturbation approaches, many terms of this expansion can be computed.

Princeton University
Princeton, NJ 08544

Department of Chemical Engineering

399. Anisotropy, Charge Distribution, and the Properties of Dense CO_2: Molecular Dynamics Studies
Debenedetti, P.G. **$52,545**
Comm. 609-258-5480

In this project, efficient algorithms are developed for the molecular-based study of fluids through computer simulations. The improved techniques are then applied to the investigation of the influence of molecular length and electrical charge upon the transport and thermodynamic properties of linear, quadrupolar molecules, such as carbon dioxide. Existing methods for the calculation of shear viscosity via equilibrium molecular dynamics are compared. The displacement approach, in its McQuarrie version, has substantial statistical and computational advantages over the commonly used Green–Kubo technique and leads to significant time and memory savings. A new, automatic-update neighbor list algorithm was developed which always allocates time optimally between list updates and force evaluations. Substantial time savings with respect to conventional neighbor list approaches are obtained. Using these algorithms, the dependence of shear viscosity, rotational and translational diffusion, pressure, and internal energy upon length, density, temperature, and quadrupole strength in carbon dioxide and model fluids were studied. These fluids were obtained by separate perturbations of length and quadrupole strength about the reference case. The individual effects of density, temperature, length, and quadrupole strength were isolated.

Purdue University Research Foundation
West Lafayette, IN 47907

School of Chemical Engineering

400. Gas–Liquid–Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons
Chao, K.-C. **$82,824**
Comm. 317-494-4088

An equation of state called the Augmented BACK equation was obtained by combining the Boublick–Alder–Chen–Kreglewski (BACK) equation with the steam table equation of Keenan, Keyes, Hill, and Moore. The equation gives a good description of phase equilibrium of water + hydrocarbon mixtures, but is lengthy, containing 107 terms. To facilitate application, the equation was simplified to two less complicated versions. The focus is now on the interpretation of liquid–liquid solubility data with the simplified equations. The fluid-phase equilibria of water + n-decane mixtures has been experimentally observed at elevated temperatures and pressures. High miscibility and complete miscibility are found to exist. Vapor–liquid critical states are found to be connected to the three-phase coexistent states on the one hand, and to the critical state of n-decane on the other, but not to the critical state of pure water.

Stanford University
Stanford, CA 94305

Department of Chemical Engineering

401. Fundamental Studies of Fluid Mechanics and Stability in Porous Media
Homsy, G.M. **$118,375**
Comm. 415-723-2419

This research treats problems in flow and transport in porous media of interest in energy recovery processes. A recent major focus has been in the study of instabilities that occur during displacements that are driven by differences between the properties of the displaced and displacing fluids. Both experiments and large-scale simulations are carried out in these studies. Either density differences (when coupled with gravity) or viscosity differences may drive such instabilities and the fluids may be either immiscible or miscible. Important recent results include the description of the coupling between instabilities and fluctuations in flow driven by permeability heterogeneity. Results indicate that mutual enhancement of the two mechanisms occurs when the intrinsic length scales of instability are commensurate with the correlation scale of the heterogeneities. Current research is focused on the description of miscible fingering in the presence of anisotropic dispersion, such as occurs in porous materials or model Hele–Shaw cells. Results indicate that a new mechanism, associated with the merging or coalescence of fingers, is expressed when the anisotropy is large. The ability of two-dimensional simulations to model the averaged macroscopic behavior seen in experiments, which are necessarily three-dimensional in nature, is currently being assessed.

University of Virginia
Charlottesville, VA 22903-2442

Chemical Engineering Department

402. Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems
Cummings, P.T.; **$108,221**
O'Connell, J.P.
Comm. 804-924-6248

The objective of this project is to develop fundamentally based predictive theories for the thermodynamic properties and phase equilibria of mixed solvent electrolyte systems. The approach used in this project involves a combination of molecular simulation, statistical mechanics, and experimental studies. During the past year, molecular simulation codes were developed for phase equilibria in aqueous systems, preliminary experimental studies were performed on mixtures of water and isopropanol with tetrabutyl ammonium bromide, and with tetramethyl ammonium bromide, and a simple statistical mechanical model for hydrogen-bonded water was developed. Goals for the current year include extension of the molecular simulation codes to electrolyte solutions; development of an equation of state for mixed solvent electrolytes based on an analytically solved statistical mechanical theory, numerical solution of a detailed statistical mechanical model for electrolyte solutions; and more accurate experimental characterization of the mixtures of water, alcohol, and tetra-alkyl ammonium salts.

University of Wisconsin
Madison, WI 53706

Department of Chemical Engineering

403. *Interphase Transport and Multistage Separations*
Stewart, W.E. **$96,628**
Comm. 608-262-0188

This project has two complementary goals: (1) to provide new predictive capabilities for mass transfer processes and (2) to develop efficient new approaches for computer-aided engineering of these processes. Recently published asymptotic scaling analysis of laminar and turbulent mass transfer operations has now been implemented as part of a collocation simulator for multicomponent fractionation stages. This computational model is being applied to fractionation data collected from the literature to develop predictive correlations of tray performance. An efficient variable-property transport calculation method is being developed based on optimal reference states calculated from perturbation theory. A Fourier-transform analysis of turbulent mass transport from solid surfaces at high Schmidt numbers is under way, and is being compared against available measurements of mass transfer power spectra.

Yale University
New Haven, CT 06520

Department of Mechanical Engineering

404. *Computational and Experimental Study of Laminar Premixed and Diffusion Flames*
Smooke, M.D.; Long, M.B. **$118,000**
Comm. 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. An important part of the computational work is the ability to predict extinction limits, flame shape, and space heating rates as a function of various parameters. 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 1990 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 $6\frac{1}{2}$ months and are designed to evaluate the merits and feasibility of the ideas proposed. Proposals are considered as a result of a solicitation and awards are made after 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 or 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.

Advanced Technology Materials, Inc.
New Milford, CT 06776

405. *Thin Film WSe_2 Photoelectrodes*
Kosar, W.P. **$50,000**
Comm. 203-355-2681 **(6.5 months)**

A primary limitation of photoelectrochemical cells is photocorrosion of electrode materials. One solution to this problem has been to apply elaborate conducting polymeric coatings to sensitive electrodes. An alternative is to use corrosion resistant electrode materials. Group VI metal dichalcogenides, and tungsten diselenide (WSe_2) in particular, have shown promise as intrinsically corrosion resistant photoelectrode materials with good photoefficiences. Unfortunately, variable quality of the materials, resulting from current growth techniques, has resulted in reduced photoefficiencies caused by electron-hole recombination at grain boundaries. The materials quality problem currently afflicting these metal dichalcogenides has prevented their commercialization in photoelectrochemical systems. State-of-the-art capability in metalorganic chemical vapor deposition (MOCVD) is being used in Phase I to prepare high purity, single crystal WSe_2 thin films. These high quality single crystal films should have improved conversion efficiencies because of reduced surface grain boundaries. The single crystal WSe_2 films will then be used as photoelectrodes in a photoelectrochemical cell. In

Phase II, the process will be scaled up and the demonstration of improved photoefficiencies in WSe_2 cells will be confirmed.

Bend Research, Inc.
Bend, OR 97701-8599

406. Development of High-Performance Chemically Resistant Composite Membranes

McCray, S.B. **$50,000**
Comm. 503-382-4100 **(6.5 months)**

The purpose of this project is to develop a new generation of chemically inert membranes. Specifically, these will be thin-film-composite (TFC) membranes in which conventional high-performance membrane films will be supported by a novel polymeric microporous support having chemical resistance far surpassing any polymer supports now available. This new support material will be insoluble in all normal solvents and will resist plasticization and other problems associated with current polymeric supports. Development of this support is the focus of this program. Phase I is aimed at proving that suitable supports (i.e., solvent-resistant supports with high permeability, strength, and characteristics necessary to support interfacial films) can be fabricated. Optimization of these supports and fabrication of TFC membranes and modules will be carried out in Phase II, along with testing that will establish module performance.

Chromex, Inc.
Albuquerque, NM 87123

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

Gobeli, G.W. **$49,800**
Comm. 505-294-6047 **(6.5 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 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.

Marko Materials, Inc.
North Billerica, MA 01862

408. Molecular Recognition in Metal Ion Sensors

Ray, R. **$50,000**
Comm. 508-663-2210 **(6.5 months)**

This project will demonstrate the feasibility of fabrication and characterization of novel metal-ion sensors for the real-time detection and *in situ* quantification of target metal ions. Specifically, polymers will be developed with molecular recognition properties for metal ions such as nickel, copper, cadmium, mercury, chromium, etc. The matrix of polymers will be imprinted with specific size cavities by means of templates which will be the same metal ions of interest. Reversible covalent, ionic or hydrogen bonds form between the template and the binding sites of the polymer chain. Upon polymerization the template will produce cavities specific for size, shape, and arrangement of the binding sites. To preserve the memory effects of the polymer, the template will be split off without altering the cavity. In Phase I, an all-solid-state sensor is being fabricated by the application of membranes containing ion-selective imprinted polymer on conducting filled epoxy layers of an ion electrode. The sensor will be tested and calibrated.

Membrane Technology & Research, Inc.
Menlo Park, CA 94025

409. Ultrathin Metal Membranes

Athayde, A. **$49,974**
Comm. 415-328-2228 **(6.5 months)**

This program focuses on the preparation technique of a new type of ultrathin metal membrane made by a metal sputtering technique. The membranes are extremely thin, in the range of 300 to 600 A. Because they are so thin, useful fluxes of permeable gases such as hydrogen can be obtained at room temperature. The best of these membranes is up to 10 times more permeable to hydrogen and significantly more selective to hydrogen over other gases than the best currently available polymeric membranes. Higher selectivities would be achievable if the membranes could be made defect-free. This project involves development of a technique for depositing ultrathin metal films on polymeric supports. The early development work will principally be performed using palladium silver alloys as a model membrane material. Some work may be performed with other metals, such as silver. Polymer/metal composite membranes that combine high selectivity with high flux would be an entirely new class of separation membranes. In the Phase I program the feasibility of a controlled technique for producing metal membranes is being determined. In Phase II, membrane modules will be assembled and evaluated in a test system.

Separation Systems Technology, Inc.
San Diego, CA 92117

410. *Development of Oxidation-Resistant Mosaic Membranes with Enhanced Transport Properties*

Riley, R.L. **$49,999**
Comm. 619-581-3765 **(6.5 months)**

This program is directed toward the development of a method of composite membrane preparation from organic polymers that can be tailored for a variety of separation processes, while producing a membrane flux considerably higher than presently attainable. Unlike traditional methods of composite membrane preparation, where the membrane barrier is formed on the surface of a porous membrane support, the planned method of membrane preparation involves the formation of the permselective barrier within the pores of the microporous support. This is accomplished by a process of occlusion or pore-filling, whereby the reverse side of a fabric-reinforced microporous membrane is contacted with a dilute solution of a polymer with desirable transport properties. The solution is subsequently drawn into the fine surface pores by capillary action, and the polymer is deposited within the pores as the solvent evaporates from the membrane surface. Thus, the membrane barrier does not cover the entire surface of the substrate, yielding a mosaic surface structure which eliminates flow restrictions resulting from barrier thickness. In addition, both the transport barrier polymer and the porous substrate polymer can be individually selected for their specific functions.

Southwest Sciences, Inc.
Santa Fe, NM 87501

411. *A Novel Mass Spectrometer for Combustion Studies*

Bomse, D.S. **$49,996**
Comm. 505-984-1322 **(6.5 months)**

This project uses a novel scheme to increase dramatically 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 results obtained in Phase I will provide directly the critical design information required to develop a prototype instrument. The Phase I program targets the mass spectrometer hardware and the computational software required for a completely self-contained system that would sample a combustion reaction, collect spectra, identify the species present, and maintain an expanded database. The innovation, as described in the proposal, shows significant advantages (at comparable cost) over commercially available computer controlled quadrupole mass spectrometer systems currently used for combustion diagnostics.

Spire Corporation
Bedford, MA 01730

412. *Novel Electrically Conductive Membranes for Enhanced Chemical Separation*

Wollam, J. **$500,000**
Comm. 617-275-6000 **(24 months)**

New concepts of separation processes based on electrochemical interactions have been developed through successful electromembrane development. This new electromembrane is different from conventional ion-exchange membranes because it conducts electrically while ion exchange membranes conduct ionically. This characteristic contributes to the unique applications for this new class of membrane. A variety of new applications based on this novel electromembrane are identified. The Phase I work has clearly demonstrated that an environmentally stable electromembrane can be synthesized. In the Phase II work, the process optimization necessary to support the synthesis on a commercial scale is being evaluated, the principles of separation by electromembranes are being examined, and potential applications are being explored.

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, D C 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	$6,107,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	$18,301,000
	Radiochemical Engineering Development Center	$6,851,000
Sandia National Laboratories, Livermore	Combustion Research Facility	$3,719,000
Stanford University	Stanford Synchrotron Radiation Laboratory	$8,781,000

ATOMIC SPECTROSCOPY FACILITY (KC-03-01-02)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne atomic spectroscopy facility is designed for high-resolution investigations of the spectroscopic and dynamic properties of atomic and molecular systems. A 5-m Czerny-Turner spectrograph equipped with a holographic grating forms the core of the facility. Both diode-array and standard detectors are directly interfaced to microcomputers for control of experiments and pulse-to-pulse normalization of signals which result from the excitation process.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Jan P. Hessler
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone: Comm. (708) 972-3717
or FTS 972-3717

BITNET: HESSLER @ ANLCHM
Facsimile: (708) 972-4470

TECHNICAL DATA

Resolving power: $>10^6$
Wavelength range: 120 to 500 nm

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
Physics Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone: Comm. (708) 972-4050
or FTS 972-4050

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 390 shipments totaling over 11,000 ampoules have been made.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres
Chemistry Division,
Bldg. 211
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone: Comm. (708) 972-7374
or FTS 972-7374
FAX (708) 972-4470

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 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

Phone: Comm. (708) 972-3471
or FTS 972-3471
or 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 1990, the Light Source will have 76 operational experimental beam lines and 10 lines dedicated to beam diagnostics and R&D.

A total of seven insertion devices are installed on the X-ray and VUV rings. These devices, known as either wigglers or undulators, are special magnets which produce synchrotron radiation orders of magnitude brighter than is available from conventional bending magnets. The insertion devices will be used for microscopy, medical research, materials sciences, spectroscopy, scattering, and Transverse Optical Klystron (TOK) experiments. By year end, all of the insertion device ports will be operational, supporting eleven Insertion Device Team (IDT) programs. The first General User programs using insertion device beam lines are expected to begin in FY 1991.

The NSLS facility offers a wide range of research techniques for use by biologists, chemists, solid state physicists, metallurgists, and engineers for basic and applied studies. In February 1990, 1350 scientists from 218 universities, laboratories, corporations and foreign institutions were registered at the Light Source. Some of the techniques available to these scientists are EXAFS (extended X-ray absorption fine structure), scattering, diffraction, topography, radiography, fluorescence, interferometry, gas phase spectroscopy, crystallography, photoemission, radiometry, lithography, microscopy, circular dichroism, photoabsorption, and infrared vibrational spectroscopy.

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.

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 85. 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. General Users are required to submit a General User Proposal for Beam Time Allocation for each cycle in which beam time is desired. 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. 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.

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. Eighty-three faculty/student research teams representing 29 universities participated in this program in FY 1989.

PERSON TO CONTACT FOR INFORMATION

Susan White-DePace
NSLS, Bldg. 725D
Brookhaven National
Laboratory
Upton, NY 11973

Phone: Comm. (516) 282-7114
or FTS 666-7114

TECHNICAL DATA

Facilities	Key features	Operating characteristics
VUV electron storage ring	High brightness; continuous wavelength range (λ_c = 25 Å); 17 ports	0.75-GeV electron energy
X-ray electron storage ring	High brightness; continuous wavelength range (λ_c = 2.5 Å); 30 beam ports	2.5-GeV electron energy

Research area	Wavelength range, Å	Number of instruments
Circular dichroism	1400 to 6000	1
Energy dispersive diffraction	0.1 to 2.5	3
EXAFS, NEXAFS, SEXAFS	0.1 to 250	22
Gas phase spectroscopy/ atomic physics	0.6 to 14.6	3
High pressure physics	White beam	2
Infrared spectroscopy	2.5×10^4 to 1.2×10^8	2
Lithography/microscopy/ tomography/radiography	0.6 to 15	8
Medical research	0.37	3
Nuclear physics	2.5×10^{-6} to 2.5×10^{-4}	1
Photoionization	0.6 to 12000	5
Radiometry	–	1
Reflectometry	20 to 55	1
Research & development/ diagnostics	White beam	9
Time resolved fluorescence	1000 to 12000	2
Topography	0.1 to 3	3
Transverse optical klystron	12.5 to 1250	1
VUV & X-ray photoemission spectroscopy	0.3 to 1280	29
X-ray crystallography	0.3 to 6.2	9
X-ray fluorescence	12.4 to 620	3
X-ray scattering/ diffraction	0.1 to 15.5	27

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

Department of Physics
Kansas State University
Manhattan, KS 66506

The laboratory operates a 6-MV tandem accelerator, a 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 CRYBEIS is operational for ions up to 4q keV/μ and the LINAC is expected to become operational in the spring of 1990. 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, Phone: (913) 532-6783
Director
James R. MacDonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506

TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 6 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 < 80μ 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
Phone:
Comm. (219) 239-6117
Notre Dame Radiation Laboratory
Notre Dame, IN 46556

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	MicroVAX II
Pulse width	5, 10, 20, 50 ns
Time resolution (RC)	2 ns
Pulse current	Up to 1 A
Repetition frequency	$0.2\ s^{-1}$
Optical absorption measurements	
Spectral region	210 to 750 nm
Sensitivity	±0.00002 absorbance
Conductivity	
pH range	3 to 11
Sensitivity	±5 mhos/cm

EN-TANDEM (KC-03-01-03)

Physics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 7.0 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.

PERSON TO CONTACT FOR INFORMATION

P. F. Dittner
Bldg. 5500
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6377

Phone: Comm. (615) 574-4789
or FTS 624-4789

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 7.0 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$^2 \cdot$ sec) is available to irradiate the curium target material. The HFIR is a beryllium-reflected light-water-cooled and -moderated, flux-trap reactor with a design power level of 85 MW. It burns 93% enriched ^{235}U fuel in aluminum-clad plates. Additional irradiation facilities are provided in the beryllium reflector around the fuel element to increase the production rate of the heavy isotopes.

The HFIR also has, as a secondary purpose, the performance of diverse irradiations, tests, and experiments which benefit from the exceptionally high neutron flux available. In the fuel element flux trap, a hydraulic-rabbit tube provides access to the maximum thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. The beryllium reflector contains numerous experiment facilities with thermal-neutron fluxes up to 1×10^{15} neutrons/(cm$^2 \cdot$ sec). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory Isotopes Group. 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.

PERSON TO CONTACT FOR INFORMATION

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Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831

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

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

The objective of this program is to supply transplutonium elements for use in research. This involves operation of the Radiochemical Engineering Development Center (REDC), which is the distribution center for the DOE 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.

PERSON TO CONTACT FOR INFORMATION

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Oak Ridge, TN 37831-6384

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

Sandia National Laboratories, Livermore
Livermore, CA 94551-0969

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, research in fundamental chemistry in combustion, as well as analytical studies of reacting turbulent flows. (These programs are individually described elsewhere in this publication.) The active program of visitors to the facility, including senior researchers, graduate students, and postdoctorals 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 nonpremixed 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 frequently 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 two-phase flow analysis, 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 18 independent experiments, special facility laser systems, a dedicated VAX computer, and access to a Cray computer.

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.

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.

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TECHNICAL DATA

Equipment	Key features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2-μs pulse length 5 J/pulse, 5 Hz Tunable 440 to 620 nm 0.3-nm bandwidth
Multipurpose pulsed laser system	High peak power, high resolution doubled YAG and tunable dye lasers: Single mode capability 10 to 500 mJ/pulse 10 to 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

TECHNICAL DATA (Continued)

High-pressure flame	Combination of diffusion flame burner with high pressure flow chamber: Pressures up to 20 atm Slot- or cylindrical-geometry burner 2-D axisymmetric laminar diffusion flame
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
Visitor laboratory	Rayleigh, Mie, and Raman 2-D imaging

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

Stanford Synchrotron Radiation Laboratory
Bin 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 both the 3.5 GeV storage ring, SPEAR, and the 15 GeV storage ring, PEP. SPEAR is dedicated to the production of synchrotron radiation half of its operating time. Operation on PEP is parasitic with the high energy physics program. Presently SSRL has 23 experimental stations on 9 beam lines covering the spectrum from 5 to 45,000 eV. Two additional undulator beam lines on PEP provide the world's most brilliant photon beam at X-ray wavelengths. 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 process in laser materials, lithography and microscopy, and static properties and dynamic processes of chemisorbed gases.

Research in the chemical and biological sciences includes: the structure and function of homo- 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: 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, 2107 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	~5×10^{-4}	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	~10^{-4}	2.0 × 20.0	
6-2 (54 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	~5×10^{-4}	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	~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	~5×10^{-4}	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	~10^{-4}	2.0 × 20.0	
10-2 (31 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	~5×10^{-4}	2.0 × 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	~10^{-4}	2.0 × 20.0	
Side stations							
4-1	1.0		Double crystal	2,800 to 45,000	~5×10^{-4}	2.0 × 20.0	
4-3							Two-circle diffractometer vertically focussing mirror
Focused	1.0		Double crystal	2,800 to 45,000	~5×10^{-4}	.5 × 20	
Unfocused	1.0		Double crystal	2,800 to 45,000	~10^{-4}	2.0 × 20.0	
7-1	1.0		Curved crystal	6,000 to 13,000	~8×10^{-4}	0.6 × 3.0	Rotation camera
7-3	1.0		Double crystal	2,800 to 45,000	~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
Undulator lines–X-ray							
PEP 1B							
Focused	1.7	22	Double crystal	12,000 to 22,000	2×10^{-5}	.5 × 3	
Unfocused	Full		Double crystal	12,000 to 42,000	~10^{-5}	0.6 × 6.0	Six-circle diffractometer
PEP 5B							
Focused	1.7	22	Double crystal	12,000 to 22,000	2×10^{-5}	.5 × 3	
Unfocused	Full		Double crystal	12,000 to 20,000	~10^{-5}	0.6 × 6.0	
				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

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution ΔE/E	Approximate spot size, hgt × wdth, *mm*	Dedicated instrumentation
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		None	3,200 to 30,000		4 × 22	
2-3	1.0		Double crystal	2,800 to 30,000	$\sim 5 \times 10^{-4}$	3 × 20	
VUV/soft X-ray							
1-1	2.0		Grasshopper	64 to 1,000	$\Delta\lambda$ = 0.1 to 0.2 Å	1.0 × 1.0	
1-2	4.0		6m TGM	8 to 180	$\Delta\lambda$ = 0.06 to 3 Å	TBD	
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	0.35 to 7 eV Å	2.0 × 4.0	
3-4	0.6		Multilayer	0 to 3,000	White or $\Delta\lambda/\lambda$ = 0.6%	2 × 8	Vacuum diffractometer/ lithography exposure station
8-1	12		6m TGM	8 to 180	$\Delta\lambda$= 0.06 to 3 Å	1mm^2	Angle resolved e-spectrometer
8-2	5		6m SGM	50 to 1,000	E/ΔE ≤ 22,000	1mm^2	Angle resolved e-spectrometer

*SSRL presently has 24 experimental stations, 22 of which are located on SPEAR and two on PEP. Eleven of these stations are based on insertion devices while the remainder use bending magnet radiation.

FY 1990 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 1990 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds
Ames Laboratory	$ 560,000
Argonne National Laboratory	4,150,000
Brookhaven National Laboratory	2,130,000
Idaho National Engineering Laboratory	30,000
Lawrence Berkeley Laboratory	860,000
Los Alamos National Laboratory	50,000
Notre Dame Radiation Laboratory	265,000
Oak Ridge National Laboratory	2,090,000
Pacific Northwest Laboratories	2,482,000
Sandia National Laboratories, Albuquerque	15,000
Sandia National Laboratories, Livermore	580,000
Solar Energy Research Institute	115,000
Stanford Synchrotron Radiation Laboratory	800,000

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 EDB Corporate Author Entries (DOE/TIC-4585).

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.