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# Summaries of FY 1989 Research in the Chemical Sciences

August 1989

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

Prepared by  
Office of Scientific and  
Technical Information

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

This report was compiled for the Office of Energy Research from project summaries contained in the Research-In-Progress (RIP) data base of the Office of Scientific and Technical Information, Oak Ridge, Tennessee. The RIP data base 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 six 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 energy technologies can evolve. As a result, scientific excellence is a major criterion applied to the selection of research supported by the Division of Chemical Sciences, but another important consideration is emphasis on sci-

ence 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 1989 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.

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†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. A growing program of photochemistry, spectroscopy, and related studies is centered at the National Synchrotron Light Source at Brookhaven National Laboratory.

#### **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 inter-

est. 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, two facilities at Oak Ridge are operated as a service to the scientific community: the Radiochemical Engineering Development Center (REDC) and the Electromagnetic Isotopes Separations Facility (Calutrons).

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 is directed toward improving our basic 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 program is technique oriented rather than species oriented; i.e., 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 isotope separation program emphasizes isotopic properties and isotope effects and is basic in nature.

The analysis part of the program is aimed at supporting research on analytical techniques where a better understanding of basic chemical phenomena may facilitate improvements in sensitivity, reliability, and ease of operation and/or lower the costs of analytical determinations. Entirely new analytical techniques are investigated also, although this program does not support instrument development. New techniques are quickly reported in the literature so that those interested in instrument development can build on work supported herein. The program is not geared to using existing techniques to unravel the composition of samples nor to developing techniques to analyze particular chemical species or sample types. Rather, it is aimed at obtaining a thorough understanding of the basic chemistry of an analytical technique so that others may use this understanding to improve its utility.

### **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 actinides in complex oxides and binary halides, (4) the chemistry of actinides in near-neutral aqueous solutions and the reactions of aqueous actinides 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 thermochemical and thermophysical properties and phase equilibria, especially of mixtures, including supercritical phenomena, and to turbulence research related to combustion. 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

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David K. Hoffman  
Phone: Commercial (515) 294-6342

#### Chemical Sciences—Processes and Techniques

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# NATIONAL LABORATORIES

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## Photochemical and Radiation Sciences

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**Ames Laboratory**  
**Iowa State University**  
**Ames, IA 50011**

**Fundamental Interactions Program**                      **\$425,000**

**1. Photoinduced Electron-Transfer Reactions in Protein Matrices**  
*Kostic, N.M.*

Photosynthesis and various artificial processes for conversion of light into chemical energy are based on electron-transfer reactions. Electron transfer processes are studied in cytochrome *c* (an iron protein) and plastocyanin (a copper protein). Chemical treatments of these proteins yield several new electron-transfer systems. In one, an inorganic chromophore is attached selectively to the surface of cytochrome *c*. In another system, up to three molecules of cytochrome *c* are aggregated by their attachment to a redox-active trimetallic cluster. In yet another system, cytochrome *c* and plastocyanin are attached to each other by electrostatic bonds alone or by electrostatic and covalent bonds simultaneously. Electron-transfer reactions are effected by different methods in all three systems, and the rates of these reactions are determined. In the first system, the chromophore enhances the effectiveness with which light causes reduction of iron. In the second one, electrons can be transferred from the trimetallic "core" to the protein "periphery" of the aggregate. In the third system, electron-transfer reactions can occur only if the protein molecules are allowed to rearrange into the optimal configuration. [2.2 FTE]

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

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. [1.7 FTE]

**3. Picosecond Spectroscopy and Reaction Dynamics**  
*Struve, W.S.*

Picosecond fluorescence and pump-probe spectroscopies are used to study electronic excitation transport (EET) in light-harvesting and core antenna complexes of green photosynthetic organisms. The principal issues being addressed are the random-walk versus excitonic nature of EET, the relationships between EET and chromophore architecture in structurally well-characterized complexes, and the possibility that mechanisms other than dipole-dipole coupling contribute to singlet EET. Systems currently studied include the bacteriochlorophyll *a*-protein complex from the sulfur bacterium *Prosthecochloris aestuarii* and the chlorophyll *a* core antenna complex in enriched P700 photosystem I particles; planned studies will deal with the chlorophyll *a/b* light-harvesting complex of photosystem II and with the light-harvesting complex of the purple bacterium *Rps. sphaeroides*. Dispersive excitation transport for chlorophyll *a* molecules in low-temperature glasses between 10 and 300 K is also being examined. [2.0 FTE]

## Argonne National Laboratory

**Argonne, IL 60439**

**Chemistry Division**    **\$5,410,000**

**4. Electron Transfer and Energy Conversion**  
*Miller, J.R.; Meisel, D.; Schmidt, K.H.*

A pulsed linear accelerator (linac) is used to examine the fundamental chemistry of charge-transfer processes and the structure of small colloidal particles by fast production of electrons or holes. The results lay the groundwork for possible new technologies in photochemical energy storage, and the processing of nuclear wastes and their motion if released into the environment. Experiments with the linac resolve chemical processes occurring in times as short as  $10^{-10}$ s and show that electrons can be transferred over considerable distances in that short a time. The linac-based experiments provide a capability not available with any other technique to produce reactive intermediates readily and under well-defined conditions. With this capability, it is possible to obtain clear answers to the questions of how electron-transfer rates depend on distance, energy, and solvent polarity. Current work measures "hole" transfer as well as electron

transfer to explore the relation of long-distance electron-tunneling processes to the electronic structure of materials, and further explores the effects of angular orientation of electron donor and acceptor groups. The linac also enables production of small colloidal particles of semiconducting materials. For some materials, it is possible to produce and examine the properties of particles having sizes from one atom to several thousand while keeping a narrow, well-defined distribution of sizes. Electronic properties of these small particles are examined, and the interplay with microparticle photochemistry and charge-injection processes is studied. [10.0 FTE]

#### 5. *Characterization of Photosynthetic Components*

Norris, J.R.; Bowman, M.K.; Tiede, D.M.

The project objective is to develop systems for solar energy conversion. As a result of attempts to understand and to develop highly efficient forms of solar energy conversion, the basic physical and chemical features of the separate, individual compounds, solvents, matrices, and light-harvesting antenna are required. In addition, certain nonphotoactive interactions among the components need to be characterized. These interactions are related to the three following, basic 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. [2.5 FTE]

#### 6. *Photosynthesis Research*

Norris, J.R.; Tang, J.; Thurnauer, M.; Bowman, M.K.; Tiede, D.M.; Wasielewski, M.R.

The project objective is to understand the basic principles of the chemistry and physics essential to rapid and efficient photoinduced charge separation. With such information artificial solar energy systems can be designed and constructed. The systems examined include normal, isotopically substituted, and chemically manipulated photoactive assemblies, solutions, or compounds. The intrinsic photochemistry and photophysics are examined by spectroscopy specifically tailored to probe the mechanisms of photochemistry. Such techniques emphasize modified optical and magnetic resonance. Perturbations such as electric and magnetic fields are designed to alter the photochemistry and spectroscopy. As a result, this approach characterizes the photochemical charge-separation process by enough methods to establish ultimately a unique theoretical description. [8.0 FTE]

#### 7. *Reactive Intermediates in Condensed Phases: Radiation and Photochemistry*

Trifunac, A.D.; Jonah, C.D.; Sauer, M.C., Jr.; Bartels, D.M.; Schmidt, K.H.

The overall project objective is to determine how energy determines chemistry by understanding the partition of energy into bond breaking and ionization; the kinetic energy of an electron; and the formation of excited electronic and vibrational states. These studies are carried out by observing short-lived entities such as radicals, ions, electrons, and excited states created by radiation or photoionization. Focus is on several principal directions.

First, the chemistry of reactive intermediates such as radical cations and highly excited states are identified. The dynamics of charge pair and radical pair processes are examined in detail to learn the intricacies of charge thermalization and localization and the nature of interaction between radicals. The second direction is the study of the role of solvent in chemical reactivity. The largest difference between gas- and condensed-phase chemistry is the role of the solvent as a heat sink to cool down excited molecules limiting the possible reaction channels and the effect of solvent on transport properties of reactants. A third direction of study is a new effort in the study of transient species in solid-state chemistry. Such experiments are made possible using state-of-the-art techniques such as magnetic resonance detection, a 5 picosecond linac, and a femtosecond laser. [13.0 FTE]

#### 8. *Artificial Photosynthesis*

Wasielewski, M.R.

The project objective is to construct and to characterize molecular assemblages that will perform photosynthetic energy conversion in the laboratory. The ultrafast photochemistry and photophysics is examined by femtosecond optical spectroscopy specifically designed to probe systematically the mechanisms of artificial charge separation. The initial events of natural photosynthesis consist of a sequence of subnanosecond electron-transfer reactions between chlorophyll, pheophytin, and quinone molecules that are positioned at critical distances and orientations relative to one another within a large protein reaction center. Thus, in order to understand the mechanism by which high quantum yield photochemical charge separation occurs within these reaction centers, it is necessary to study the ways in which these molecules or their derivatives interact with each other at specific distances and orientations. Since the photosynthetic pigments are photochemically labile when they are removed from their natural protein, the development of stable derivatives of these molecules is especially important if we hope to improve upon the natural photosynthetic charge separation process. [4.7 FTE]

### Brookhaven National Laboratory Upton, Long Island, NY 11973

Department of Applied Science      \$995,000

#### 9. *Porphyrim Chemistry*

Fajer, J.

Porphyrim 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 substitutions 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 redox, light-absorption properties, and rates of electron transfer. The work encompasses photochemistry, spectroelectrochemistry, magnetic resonance, (ESR,

spectroscopy (diode laser absorption, laser-induced fluorescence, or spontaneous infrared fluorescence) of the initially excited species or a collision partner measures the loss or gain of energy as a result of collisions. Doppler techniques are being developed to investigate orientational effects in inelastic collisions. In addition, vacuum-ultraviolet radiation from the dynamic spectroscopy beamline of the National Synchrotron Light Source (NSLS) is used to study electronically excited states of molecules and photoionization of atoms. Recent experiments at the NSLS have determined mechanisms of electronic energy relaxation in small saturated hydrocarbons in the solid phase or isolated in rare gas matrices. Assistance to outside users of the NSLS is also provided by this project. [6.1 FTE]

### 15. *Hot Atom Chemistry*

*Wolf, A.P.; Ferrieri, R.A.*

The project objective is to understand the roles translational and electronic energy play in promoting unusual chemistry between atoms or radicals and substrate molecules. Accomplishments include the development of a sputtering atom source for generating hot oxygen atoms in well-defined states. Recent interest is in the reactions involving hot  $O(^3P)$  atoms and formaldehyde, or other oxygen-bearing molecules. Quite often, the excess kinetic energy of these sputtered atoms can result in the formation of unusual reaction intermediates, sometimes unique in the sense that they cannot be generated by conventional methods. Studies focusing on the chemistry of the electronically excited dioxymethylene and peroxyethylene biradicals are examples of this behavior. Effusive beam sampling coupled with quadrupole mass spectrometry is an extremely effective means for monitoring the chemical fate of such species, particularly when combined with the use of oxygen-18 labeling either in the hot atom source or the substrate. Other active areas of research utilizing classical nucleogenic methods include studies on the effect of translational energy on the deactivation mechanisms for electronically excited nitrogen atoms, the stereochemical consequences of hot homolytic halogen atom substitution reactions, and the mechanisms of carbon atom reactions. [1.8 FTE]

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

Chemical Biodynamics Division      \$970,000

### 16. *Artificial Photosynthesis*

*Calvin, M.; Otvos, J.W.*

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 three areas. (1) The useful fraction of the total solar spectral irradiance must be increased. At present, with resonance absorbers like dyes and other chromophores, only narrow spectral regions are useful. It is obvious that a series of relatively narrow-band sensitizers could be arranged to take advantage of the full solar spectrum. (2) 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. (3) 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]

### 17. *Chemistry with Near-Infrared Photons*

*Frei, H.*

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. Emphasis is on the elucidation of elementary reaction steps, since the insight gained allows the identification of relevant chemical systems. Therefore, time-resolved emission and absorption spectroscopy are used for the study of redox chemistry in aqueous solution. The most recent example is the elucidation of the mechanism of oxidation iodide to iodine by singlet delta  $O_2$ , a reaction that may allow conversion of the electronic energy of the excited  $O_2$  into electrical energy. Other reactions are initiated in an inert gas matrix in order to elucidate reaction paths by trapping chemical intermediates. FT-infrared spectroscopy is used to determine structures of intermediates and final reaction products. With this technique, observations have been made of the first chemistry of singlet  $SO$ , and stereospecific photooxidation of alkenes to epoxides by nitrogen dioxide. [2.1 FTE]

### 18. *Chemistry of Electronically Excited Molecules*

*Pimentel, G.C.*

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

ENDOR, NMR), X-ray diffraction, and synchrotron radiation techniques that are closely supported by several theoretical methods (extended Hückel, INDO, molecular dynamics) in order 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. [6.1 FTE]

**10. Electrochemistry and Photoelectrochemistry**  
Feldberg, S.

The project comprises experimental and theoretical studies of electrochemical and photoelectrochemical phenomena. The major experimental effort has addressed the development and application of a laser-induced-temperature-jump perturbation of interfacial electrode temperature. This is a new technique for characterizing the rate processes associated with very fast heterogeneous (electrochemical) phenomena in the submicrosecond time domain. The dynamics of heterogeneous phenomena are not well understood and it is important to obtain high quality data in this previously inaccessible time domain. Several types of heterogeneous phenomena are being examined: heterogeneous electron transfer; ion adsorption/desorption; double-layer relaxation; and thermocouple effects (in particular, the response of electronically conducting polymer films). Computer simulations of a variety of electrochemical problems are a significant, continuing contribution of this project. This project studies (1) diffusional-migration effects at ultramicro-electrodes, (2) phototransients in semiconductors, (3) electron transfer in redox polymers, and (4) the mechanism of switching in conducting polymers. Recent work on the simulation methodology indicates that a simple variation of a well-known algorithm can provide a powerful approach to the solution of a variety of stiff problems. The approach is applicable to nonlinear problems involving diffusion-migration as well as a wide dynamic range of first- and second-order rate constants. [3.4 FTE]

**Chemistry Department** **\$3,320,000**

**11. Radiation Chemistry**  
Holroyd, R.A.; Schwarz, H.A.; Bielski, B.H.J.; Wishart, J.

In order to understand and control chemical reactions, it is essential to know the properties and reactions of any transient species that may be involved as intermediates. For instance, various forms of iron(IV) have been postulated as intermediates in catalytic processes, but little is known about these species. The high-energy physics community is showing rapidly increasing interest in the ionization of liquids and needs to know the behavior of the ions and electrons involved. These areas can be studied by pulse radiolysis. Current studies include: (1) the reaction kinetics and energy level of electrons in dielectric liquids under high pressures, which help explain the nature of electron capture and the role of electrostriction; (2) the hall mobility of electrons (mobility of electrons in the untrapped state) in mixtures of dielectric liquids, to ascertain the importance of the trap model of electron transport; (3) the stability of the various acid-base forms of Fe(IV) complexes in aqueous solutions; (4) the effect of macrocyclic ligand conformation on the kinetics of

formation and interconversion of cobalt hydrides, carbon dioxide, and carbon monoxide complexes in aqueous solution; and (5) long-distance electron transfer rates as a function of distance, driving force, and molecular configuration using both small molecules and large redox proteins. [7.7 FTE]

**12. Photochemical Transformations in Bacteriorhodopsin**  
Seltzer, S.

The aim of this research is to elucidate important factors in the mechanism used by the purple membrane for converting solar energy to chemical energy. When light is absorbed by bacteriorhodopsin, the protein pigment of the membrane, protons are pumped through the membrane, resulting in the formation of a proton gradient. The proton translocation process is completely dependent on reversible *cis-trans* isomerizations of retinal, the bound chromophore of the pigment. Photon absorption initiates a cycle wherein retinal is isomerized in the first step. Proton translocation and retinal reisomerization occur in subsequent nonphotolytic steps. The manner in which these *cis-trans* isomerizations are driven is currently being investigated. Theoretical calculations support the hypothesis that *cis-trans* isomerizations of bound retinal are catalyzed by a neighboring carboxylate anion of an aspartate residue of bacteriorhodopsin via an electrostatic or nucleophilic interaction mechanism. Compounds containing an amino group for Schiff base formation with retinal and a tethered carboxylate group have been synthesized to mimic the binding site of retinal in bacteriorhodopsin. These systems are being examined for activity in retinal isomerization. [2.2 FTE]

**13. Thermal and Photoinduced Reactions of Metal Complexes**  
Sutin, N.; Creutz, C.; Brunschwig, B.S.; Winkler, J.; Fujita, E.

The design of molecular systems that will efficiently generate and maintain a photoinduced charge separation requires a thorough understanding of the factors that control electron-transfer rates. This project involves fundamental, experimental, and theoretical studies of these factors. The roles of distance, nuclear configuration, free-energy changes, and solvent dynamics (in inter- and intramolecular electron-transfer processes) are being elucidated through studies of transition-metal complexes. The efficient photogeneration of fuels also requires the coupling of one- and multielectron transfer processes and the stabilization of reactive intermediate fragments. This project also encompasses fundamental chemical and mechanistic studies of catalytically promising transition metal centers in high and low oxidation states. The thermal- and photoinduced oxidation of water and the reduction of water and CO<sub>2</sub> are being studied. [10.3 FTE]

**14. Energy Transfer in Chemical Kinetics**  
Weston, R.E.; Preses, J.M.; Hall, G.

Rates and pathways of energy transfer in atomic and molecular collisions are important components of many reaction mechanisms. This project is directed toward the experimental study of energy flow in collisions and in photodissociation. Energetic atoms or molecules are prepared with excess translational, vibrational, or electronic energy by pulsed laser radiation. Time-resolved



**Notre Dame Radiation Laboratory  
University of Notre Dame  
Notre Dame, IN 46556****Radiation Laboratory****\$3,050,000****21. Quantum Mechanical Studies of  
Radiation-Produced Intermediates***Chipman, D.M.; Carmichael, I.C.; Bentley, J.*

Electronic structure calculations are being used to theoretically characterize the microscopic properties of matter, emphasizing applications to transient species such as free radicals and electronically excited molecules. These dominate the early processes initiated by radiolysis and photolysis of various media and also occur as important intermediates in many chemical reactions. As an aid to the interpretation of experimental studies on such systems, molecular structures and properties of individual radicals are being theoretically calculated by *ab initio* methods. Traditional coupled cluster methods of treating electron correlation have been used to compute hyperfine splittings for the important carboxyl radical anion and its protonated forms to aid interpretation of the effects of acid concentration on the ESR spectrum. Comparison with the pH dependence of the ESR splittings measured experimentally in this laboratory lends support to a recent redetermination of the dissociation constant. Currently, efficient Gaussian basis sets are being developed that are capable of fitting highly accurate numerical calculations of the important spin and orbital polarization contributions to spin densities in prototype atomic and diatomic radicals. These will be used to facilitate accurate computation of hyperfine coupling constants in large polyatomic radicals. [2.8 FTE]

**22. Inorganic Photochemical Processes***Ferraudi, G.J.*

The photochemical reactivity of coordination complexes is being investigated by using sequential biphotonic excitation to initiate photoprocesses involving excited states which, because of selection rules, cannot be populated directly from the ground state. Such studies allow characterization of these "phantom" states. Some of the compounds considered in these studies, e.g., metal clusters, macrocyclic complexes, and metal carbonyls, require further characterization of their ground and excited state properties. These mechanistic studies are conducted with pulse radiolysis and flash photolysis. The sequential biphotonic technique is also used for the generation and subsequent photolysis of complexes with metal ions in unusual oxidation states and species where metal ions are coordinated to ligand-radicals. The luminescence and photochemical reactions of transition metal compounds are investigated under magnetic fields with such intensities up to 90,000 Gauss such that coupling of the field to the electronic angular momentum results in significant perturbation of the electronic states. Dynamics of excited and ground-state electron transfer reactions are determined under such magnetic fields where the field effects can be regarded as both dynamic perturbation along the reaction coordinate and as a Zeeman perturbation of the orbitally degenerated electronic levels in reactants and products. [7.0 FTE]

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****\$331,000****19. Photochemistry of Materials in the Stratosphere***Johnston, H.S.*

This research is concerned with global atmospheric photochemical modeling and with 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 measure the distribution of excess energy in the fragments produced after a molecule is broken apart by an energetic pulse of light. The experimental methods include laser flash photolysis, laser resonance absorption, resonance fluorescence, dispersed chemiluminescence from photolysis products, and infrared diode lasers. This research has applications to molecular dynamics, to problems of atmospheric ozone, and to problems of global change of trace gases in the atmosphere. [2.2 FTE]

**20. Photon-Assisted Surface Reactions, Materials, and Mechanisms***Somorjai, G.A.*

This project explores the surface science of photocatalyzed chemical reactions that take place at the solid-vapor and solid-liquid interfaces. Focus is on processes that thermodynamically could not occur without the presence of light as the energy source. The photodissociation of water to produce hydrogen and oxygen, of nitrogen to form ammonia, and of carbon dioxide to produce formic acid is investigated. The catalysts are semiconductor surfaces that absorb and convert light to separated, excited electron-electron vacancy pairs that initiate the reduction and oxidation of adsorbed species. The materials that are being used include iron oxides, silicates, and silicon carbide. The purpose of these studies is to explore the elementary steps of the photon-assisted surface reaction by a combination of modern surface science techniques and then to establish the optimum conditions (of surface structure, composition, temperature, and reactant mixture) to maximize the rate of production of desired chemicals. [2.3 FTE]

**23. Microwave Studies of Radiation-Produced Radicals**

*Fessenden, R.W.; Madden, K.P.*

The structures, reaction mechanisms, kinetics, and interactions in nonreactive encounters of free radicals formed by radiolysis and photolysis are being studied by electron spin resonance (ESR). Definitive electronic and geometrical structures and acid-base properties are determined from the ESR spectra. Rates of radical reactions and nonreactive encounters are determined from the time dependence of the ESR absorption in experiments using pulse radiolysis. Of particular interest are measurements of the rates of spin trapping using a variety of radicals and spin traps. This technique makes possible quantitative and qualitative observation of free radicals that have very complex ESR spectra or negligible extinction coefficients. The time dependence of microwave dielectric absorption by photochemical intermediates maps their charge distribution to help explain variations in reaction mechanism in solvents of varying polarity. Rates of rapid internal charge rearrangements in excited states are determined from the dispersive component of the microwave signal. The yield, localization, and decay kinetics of photoinduced charge carriers in semiconductor particles and films are also measured by microwave absorption. [9.8 FTE]

**24. Photochemical and Photoelectrochemical Processes for Energy Conversion**

*Kamat, P.V.*

Primary photochemical and photophysical processes that directly influence the photocatalytic properties of the colloidal semiconductor particles are being investigated with transient absorption and emission spectroscopy. Ultrafast electronic processes associated with bandgap excitation of the semiconductor are being time resolved in the sub-nanosecond time domain to obtain information regarding kinetics of electron and hole transfer and the factors that control the charge transfer efficiency. Optical effects due to trapped charge carriers in semiconductor colloids, such as metal sulfides and selenides, 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. Photosensitized charge injection processes in opaque semiconductor powders and photochemical processes on opaque metal oxide surfaces are being investigated by diffuse reflectance laser flash photolysis. Such *in situ* measurements are important in obtaining mechanistic and kinetic details of photoelectrochemical reactions involving nontransparent photocatalysts. Spectroelectrochemical experiments in polymer films are being performed to elucidate the role of host polymer in the stabilization of photoinduced charge transfer products. [3.8 FTE]

**25. Track Effects in Radiation Chemistry**

*LaVerne, J.A.; Mozumder, A.; Green, N.J.B.; Schuler, R.H.*

Experimental and theoretical techniques are being used to study the chemical effects of the track structure produced by different types of ionizing radiation. Experiments focus on determining the radiolytic products in the

radiolysis of water and simple hydrocarbons with a variety of heavy ions having different energy, linear energy transfer (LET), and local energy deposition. Other studies examine luminescence in hydrocarbons caused by ion recombination in the particle track. These experiments are being conducted with ions of LETs between 10 to 5000 eV/nm using the facilities of the Notre Dame Nuclear Structure Laboratory, the ATLAS facility at Argonne National Laboratory, and the National Superconducting Cyclotron Facility at Michigan State University. Track models based on experimentally available cross sections are being developed to determine the distribution of energy loss events and subsequent production of ion pairs in isolated spurs in all phases of water. The temporal variation of radical species in water and electron-ion pairs in alkanes are examined with stochastic diffusion-kinetic models and comparisons are made with experiment when possible. Track models are being developed to explain ionization and scintillation processes generated by electrons and heavy ions in liquified rare gases. [8.0 FTE]

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

*Patterson, L.K.*

Photochemical and radiation chemical processes are investigated in ordered molecular systems such as micelles, vesicles, and monolayers. These studies are directed toward determining the mechanisms by which molecular organization may be used to exercise kinetic control over reactions of interest, especially those related to solar energy storage. Spread monolayers at the air-water interface are extensively utilized because these provide the best means for simultaneously controlling organization and monitoring the thermodynamic state of the system. Time-resolved and steady-state fluorescence techniques are used to measure lateral diffusion, rotational mobility, energy transfer, and monolayer permeability as functions of layer organization. Reflectance and absorption techniques may be used to monitor spectra of nonfluorescent species. Photochemical reaction products are analyzed by HPLC. Monolayers are also transferred to solid surfaces to build multilayer systems for the study of processes that cross layer boundaries. Flash photolysis and pulse radiolysis in micellar systems are used to characterize the pathways by which lipid structures, used for compartmentalization of reactions, may undergo peroxidative degradation induced by photolysis and high-energy radiation. [7.4 FTE]

**27. Radiation Chemistry Data Center**

*Ross, A.B.; Helman, W.P.; Hug, G.L.; Carmichael, I.C.*

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. Data bases 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 Data Base (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 data bases 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 the condensed phase. Other data compilations to be added to RCDC online include one-electron reduction potentials involving radicals in aqueous solution and quenching rates of excited states of metal complexes in solution. Assembly and evaluation of kinetic data for reactions of alkylperoxyl radicals in solution are in progress. A handbook of photochemistry is being prepared that will contain properties of the excited states of organic molecules, their quenching rates, and other photochemical information. [3.0 FTE]

**28. Radiation-Induced Chemical Reactions**  
*Schuler, R.H.; Tripathi, G.N.R.; Patterson, L.K.*

Pulse radiolysis with detection by absorption, conductivity, ESR, and laser Raman techniques on nanosecond and longer time scales is being used to characterize transients produced in radiolytic reactions and to examine their reaction kinetics. Considerable emphasis is being given to time-resolved resonance Raman measurements on nitrogen-containing radicals with focus on the proton and electron exchange properties of these radicals. Laser flash photolysis studies of radicals produced by pulse radiolysis are being conducted to examine photochemical properties of the excited states of radicals. The products generated by high-intensity pulses are being examined by chromatographic methods to provide information on the second-order reactions of radicals produced in aqueous solutions. Investigations of radiation-induced processes in hydrocarbons and other organic solvents are being conducted both by pulse radiolysis methods and by product analysis using gas chromatography with mass spectrometric detection. Scavenging studies are being conducted to examine the distribution of lifetimes for intermediates, both in aqueous solutions and in nonpolar solvents. [14.8 FTE]

**29. Organic Photochemical Processes**  
*Weir, D.; Hug, G.L.*

Kinetic rates and mechanisms for photochemically induced organic reactions in liquid and solid phases are being investigated. The reaction intermediates of these processes are studied by a variety of time-resolved methods including pulse radiolysis, picosecond and nanosecond laser flash photolysis, and diffuse reflectance. Diffuse reflectance studies provide direct optical detection of intermediates on solid surfaces and allow the measurement of molecular diffusion on two-dimensional surfaces. Novel organic photoreactions on organic oxides may also be characterized by this technique. Photoreactions (e.g., intramolecular rearrangements, electron transfer, and photoenolization) that cannot be studied by surface luminescence techniques are being explored. In solution, time-resolved light absorption techniques provide spectral identification and absolute reaction rates for short-lived organic reaction intermediates in a variety of organic reactions such as photoenolization, ring expansion, electron transfer, energy transfer, and radical hydrogen abstractions. Compounds utilized in these investigations include: alkyl- and aryl-ketones, substituted ethylenes, polyenes, aromatic hydrocarbons, and arylmethyl halides. The effects of unusual spin multiplicities are being pursued via the energy transfer, electron transfer, and hydrogen

abstraction properties of the excited states of organic radicals. [6.2 FTE]

**Solar Energy Research Institute**  
**Golden, CO 80401**

**Solar Fuels Research Division**      **\$1,010,000**

**30. Model Systems for Artificial Photosynthesis**  
*Connolly, J.S.*

This project focuses on fundamental aspects of light-induced electron transfer in donor-acceptor systems designed to mimic the primary photoprocesses in reaction centers of photosynthetic organisms. To date, the work has concentrated on studies of covalently linked porphyrin-quinone molecules and their unlinked constituents in order to sort out the effects of some of the factors that influence both forward and reverse electron transfer. These factors include the photophysical and spectroscopic properties of the donor, the redox potentials of the donor and acceptor, the distance and orientation imposed by the linking bridge, the nature of the surrounding medium, and the temperature. The emphasis of this research has been expanded to include studies of how the medium (solvent or solid-state matrix) influences the rates and mechanisms of excited-state quenching processes, specifically how the local dielectric environment affects the energetics for electron transfer. The molecular environments of interest include organic solvents of varying dielectric strength and polymer matrices, both synthetic and biological. The goal is to understand the specific properties of protein membranes that facilitate electron transfer and stabilize the resulting redox products in natural photosynthesis. [2.1 FTE]

**31. Modified Semiconductor Electrodes for Solar Energy Utilization**  
*Frank, A.J.*

Basic research is being conducted on the nature of the conductive polymer-semiconductor junction on the photoconduction mechanism of the polymer. Solid-state and electrochemical measurements have established that highly doped (metallic-like) and undoped (semiconductor-like) films of PMeT [PMeT = poly(3-methylthiophene)] give rise to a Schottky barrier and a p-n heterojunction, respectively, when the polymer makes electronic contact with n-CdS. The photovoltaic characteristics of the PMeT (doped):n-CdS junction compare favorably with those of metal:n-CdS Schottky barrier devices. The junction characteristics of the PMeT(doped):n-CdS junction are not altered appreciably by the redox electrolyte. Auger depth profile studies show that the doped (metallic-like) PMeT film is relatively impermeable to redox species in solution. An energy-band model is invoked to account for the experimental results. Solid-state studies of the p-n heterojunction imply that the depletion of PMeT can be predicted from simple theoretical equations in spite of the complex fibril morphology of the polymer. Resonance Raman scattering, photo-induced absorption spectroscopy, photoluminescence, and theoretical studies are being applied to elucidate the charge-transport mechanism and electronic properties induced by light in undoped PMeT. [1.8 FTE]

### 32. *Basic Photoelectrochemistry Research*

Nozik, A.J.; Turner, J.A.

Quantum size effects in superlattice photoelectrodes (one-dimensional quantization) and in small semiconductor particles (three-dimensional quantization) are being investigated in the context of photoelectrochemical applications and basic phenomena. For superlattice electrodes: (1) miniband formation has been characterized in detail using photomodulated reflectance spectroscopy, (2) single quantum wells have been used for the first time as photoelectrodes, (3) very high quality GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As epilayers and heterojunctions have been grown in our new MOCVD reactor, and (4) very long-lived (nanoseconds) hot electrons have been apparently observed at low light intensities. For semiconductor colloids and quantized particles: (1) picosecond pump-probe measurements on CdS colloids indicate the presence of a photoinduced blue shift caused by a dynamic Burstein-Moss effect, (2) quantized particles of MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub> can be formed with controlled particle size and stability via thermal ultrasonication, and (3) HgI<sub>2</sub> colloids can be formed from molecular HgI<sub>2</sub> in aqueous solutions. Future work will emphasize studies of hot electron transfer from superlattice and single quantum well photoelectrodes using supra-band-edge redox chemistry, time-resolved measurements of quantized systems in the picosecond and femtosecond regime to follow hot electron processes, and the use of resonant tunneling diode structures to create, for the first time, an electron energy spectroscopy for electrode-electrolyte interfaces. [5.5 FTE]

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## Chemical Physics

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Ames Laboratory  
Iowa State University  
Ames, IA 50011

Fundamental Interactions Program      \$675,000

### 33. *Statistical Mechanics of Nonequilibrium Systems*

Hoffman, D.K.

New classical, semiclassical, and quantum mechanical scattering theories for reactive collisions between gas-phase molecules are devised and incorporated into a statistical mechanical development of the kinetic theory of reactive polyatomic gases. This work provides powerful methods for investigating reaction dynamics in systems of importance in combustion. Another activity involves developing new, efficient methods for accurately predicting interaction energies in small and large molecular clusters. Finally, the dynamics and statistics of distributions of molecules adsorbed on surfaces under nonequilibrium conditions are analyzed via master equations and computer simulation. Such a theory is important for the appropriate interpretation of surface spectroscopic data. This analysis incorporates the effect of interactions between adsorbed surface species on the selection of binding sites, a study of island formation via direct adsorption

and surface migration mechanisms, and adsorbate effects on the catalytic properties of surfaces. [2.0 FTE]

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

Ng, C.Y.

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. [5.8 FTE]

### 35. *Molecular Bonding Theory*

Ruedenberg, K.

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. 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 developed for an in-depth analysis of *ab initio* electronic wave functions, leading to the recognition of atoms in molecules, to the identification of interatomic interactions, and 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. [3.0 FTE]

**Argonne National Laboratory**  
**Argonne, IL 60439****Chemistry Division****\$4,065,000****36. Photoionization—Photoelectron Research**  
*Berkowitz, J.*

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 clearly distinguish between isomeric molecular ions. [4.0 FTE]

**37. Chemical Dynamics in the Gas Phase**  
*Dunning, T., Jr.; Davis, M.; Harding, L.; Harrison, R.; Shepard, R.; Wagner, A.; Liu, K.; MacDonald, R.; Michael, J.; Hessler, J.*

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 an ongoing theoretical effort with a new experimental initiative in chemical dynamics and kinetics. The theoretical effort focuses on calculating accurate reaction energetics and potential energy surfaces, determining the reaction dynamics on the computed (or other realistic) surfaces, and developing the theoretical/computational techniques needed to model chemical reactions accurately. In the latter area a new project has been initiated to develop chemistry codes for use on high-performance, shared-memory parallel computer systems. The experimental initiative emphasizes (1) shock tube studies of the kinetics of reactions using both flash photolysis-resonance absorption and tunable laser-flash absorption techniques; and (2) molecular beam studies of the dynamics of reactions using crossed, pulsed beam, and laser spectroscopic techniques capable of both angle- and state-resolved measurements. [17.1 FTE]

**38. Metal Cluster Chemistry Research**  
*Riley, S.J.; Parks, E.K.; Jellinek, J.; Knickelbein, M.B.*

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, nickel, niobium, aluminum, chromium, vanadium, rhodium, titanium, 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]

**Brookhaven National Laboratory**  
**Upton, Long Island, NY 11973****Department of Applied Science****\$560,000****39. Combustion Kinetics and Reaction Mechanisms***Klemm, R.B.; Sutherland, J.W.*

This project consists of a multitechnique, experimental investigation of combustion kinetics and reaction pathways. The two main objectives are (1) the direct measurement of absolute rate constants for important combustion-related, elementary reactions of atoms and radicals with fuel molecules (hydrogen, alcohols, hydrocarbons) and combustion intermediates (aldehydes, olefins) over a wide temperature span (200 to 2500 K), and (2) the mechanistic study of combustion and pollutant formation processes to determine pathways for multichannel reactions. The project features three independent kinetics experiments: discharge flow-resonance fluorescence, 300 to 1200 K, flash photolysis-resonance fluorescence, 200 to 1100 K, flash photolysis-shock tube, 800 to 2500 K. With this multitechnique approach, the project has attained unique capabilities in performing reliable kinetic measurements over an exceptionally wide span in temperature. Recent kinetic results include reactions of atomic oxygen with: ethylene, 250 to 2300 K, nitric oxide (+Ar), 300 to 1300 K, and ammonia, 800 to 1800 K. An additional experimental technique, discharge, flow-photoionization mass spectrometry (DF-PIMS), is used in studies of multichannel reactions to determine branching ratios by identifying primary products that are sampled via a molecular beam from a flow tube. The device was designed specifically to be operated on the U-11 beam line at the National Synchrotron Light Source and thus uses the tunable-VUV and -XUV radiation available.

The advantages of tunable-VUV light to perform PIMS are: dissociative ionization may be avoided; auto-ionizing transitions may be probed to achieve enhanced sensitivity (for atom detection); and photoionization spectra with precise ionization thresholds may be obtained. [5.1 FTE]

**Chemistry Department** **\$3,030,000**

**40. Energy Transfer Studies in Cluster Impacts**

*Friedman, L.; Beuhler, R.J.*

This research project is concerned with energy transfer and related chemical processes in very high energy density assemblies generated by impacts of clusters on solid surfaces. Energy densities corresponding to temperatures as high as one million degrees K can be generated in assemblies of thousands of atoms by the impact and penetration of 300 keV clusters containing between 50 and 250 atoms. These atomic assemblies cool either by thermal conduction or by the ejection of hot atomic or molecular particles. A study of the gaseous products of cluster impact provides information on the relative importance and the mechanisms of the cooling processes. The initially formed collision spike, in cooling by conduction, creates a larger assembly of very energetic atoms that can participate in chemical reactions with very high kinetic barriers. Techniques have been developed for the determination of mass distributions and kinetic energies of gaseous products of cluster impacts. The sputtering of molecular ion fragments has been observed from carbon, copper, and gold targets, which indicates a correlation between fragment size and binding energy in these systems. Kinetic energy determinations on sputtered products should provide information on projectile stopping power and the magnitude of initial energy densities. [3.8 FTE]

**41. Gas-Phase Photoionization and Photoelectron Spectroscopy of Molecules and Clusters**

*Grover, J.R.; White, M.; DiMauro, L.*

The general aim of this project is the experimental characterization of the dynamics of optically prepared excited and ionic states of molecules, radicals, and clusters. 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. Current research activity is centered on: (1) application of resonant multiphoton ionization with photoelectron detection to provide internal state distributions (scalar correlations) and spatial alignment (vector correlations) of molecular fragments resulting from photodissociation or photodesorption from surfaces; (2) systematic investigations of superexcited Rydberg states of molecules by vibrationally resolved photoelectron and photoion fluorescence techniques; (3) elucidation of microscopic detail in chemical reactions via efficiency function, fluorescence, and final-state energy measurements in photoionization-induced dissociative rearrangement and self-reaction processes in van der Waals heterodimers and heterotrimers of known structure; (4) systematic study of the behavior of isolated atoms and molecules in an intense laser field, using angularly resolved electron spectroscopy to examine the nonresonant multiphoton ionization of alkaline earth atoms and diatomic molecules

in the intensity regime of  $10^{13}$  to  $10^{10}$  W/cm<sup>2</sup>; (5) development and construction of a laser-synchrotron radiation experiment at the NSLS which will couple the unique capabilities of dispersed synchrotron radiation (tunability, energy) and lasers (bandwidth, intensity) for the study of time- and state-resolved photochemical dynamics; and (6) the use of laser techniques to form and detect chemically transient species. [6.7 FTE]

**42. Chemical Crystallography**

*Koetzle, T.F.; Kvick, A.; McMullan, R.K.*

In the chemical crystallography project, the complementary techniques of neutron and X-ray diffraction are used to provide essential structural data for substances of importance to energy conversion and transmission, including homogeneous and heterogeneous catalysts, and advanced materials such as dielectrics and high-T<sub>c</sub> superconductors. The combined power of the National Synchrotron Light Source (NSLS) X-ray crystallography station and the High Flux Beam Reactor (HFBR) neutron diffraction facilities is being exploited to open up new areas of research. The ultimate objective is to provide theoretical and synthetic chemists with structural data required to understand the unique properties of substances used in energy conversion systems and to guide in the synthesis of new substances with specific functionality. In recent results at the NSLS, the special characteristics of this intense X-ray source have made possible the first structure determinations of extremely small zeolite single crystals, work that promises to allow the direct location of the active sites in these framework catalysts. Examples of neutron diffraction studies carried out at the HFBR include determination of the distinctive molecular structures of catalytically important transition metal hydride and dihydrogen complexes, and investigations of hydrocarbon gas clathrate hydrates of a type known to be important constituents of Arctic oil sands. [6.2 FTE]

**43. Theoretical Chemistry**

*Muckerman, J.T.; Newton, M.D.; Ehrenson, S.*

This work explores structure and dynamics pertinent to energy storage, solvation, and charge transfer in complex chemical systems, and the energetics and dynamics of molecular collision phenomena. One objective of this research is to formulate and implement techniques for elucidating structural, thermodynamic, and dynamical properties of complex chemical systems, relying heavily on large-scale *ab initio* electronic structure techniques and dielectric response theory. Emphasis is on mechanistic analysis of the trapping or transport of excess charge in condensed phases (especially electron transfer processes associated with transition metal complexes in polar fluids). Both the geometrical and electronic structural aspects of the theoretical research are strongly coupled to a variety of experimental probes, including those represented by the major structural facilities at Brookhaven National Laboratory. The theoretical studies help to interpret these experimental data, to facilitate their use in mechanistic kinetic analyses, and to suggest useful areas for new experiments. Another objective is to develop theoretical approaches and computational methods for elucidating state-to-state collision phenomena (with major emphasis on gas-phase reactive collisions involving a small number of atoms), and to apply these methods to systems of experimental interest in a variety of disciplines. An important facet of this work involves

point. Systems comprising fused salts mixed in any proportion with water or other polar solvents are being studied experimentally and theoretically. Current studies also include (1) dilute ionic solutions very close to the critical point of the solvent where anomalous properties are observed and (2) the representation of near-critical properties in an equation of state valid over the full range of temperature and density. Recent theoretical advances include treatments of the dielectric constant of H<sub>2</sub>O, the thermodynamics of ionic solutions in H<sub>2</sub>O above its critical temperature, and the critical properties of pure ionic fluids such as NaCl. Earlier advances yielded improved equations for electrolyte solutions, which are now being applied to a wide variety of systems of industrial or geological interest (including geothermal brines). Recent efforts also include relativistic quantum chemistry of molecules containing very heavy atoms. [1.8 FTE]

#### 49. Photoelectron Spectroscopy

Shirley, D.A.

This project addresses both experimental and theoretical aspects of electron spectroscopy to investigate the electronic structure of matter in the gaseous and condensed phases. Research uses both laboratory sources at Lawrence Berkeley Laboratory and synchrotron radiation in the 5 to 5000 eV energy range available at the Stanford Synchrotron Radiation Laboratory, where there is participation in developing the spectroscopy of this newly accessible range of the electromagnetic spectrum. Time-of-flight measurements with synchrotron radiation are used to measure angular distributions of photoelectrons and resonant photoemission phenomena in the gas phase. Ultrahigh-resolution photoelectron spectroscopy based on molecular beams is yielding new information about small molecules and about the transition from single metal atoms to behavior characteristic of a three-dimensional solid. This project examines the electron structure of solids by using angle-resolved, variable-energy photoemission, and electron-energy-loss spectroscopy. The project also studies the geometric and electronic structure of surface-adsorbate systems using photoelectron diffraction, angle-resolved photoemission extended fine structure (ARPEFS), and surface extended X-ray absorption fine structure (SEXAFS). [9.0 FTE]

### Lawrence Livermore National Laboratory University of California Livermore, CA 94550

Division of Computational Physics \$40,000

#### 50. Chemical Kinetics Modeling

Westbrook, C.K.

The project objective is computer modeling of the chemical kinetics of combustion in laboratory and practical systems. Experimental data provided by a number of collaborating laboratories are analyzed using the numerical models and detailed reaction mechanisms developed by this effort. Emphasis is on hydrocarbon fuels that are widely used in present combustion devices, such as furnaces and internal combustion engines. Construction and

validation of comprehensive reaction mechanisms for these fuels will identify those elementary reactions on which the computed results are most dependent and that therefore merit the closest attention from experimental and theoretical research. Fuels being examined include iso-octane, n-heptane, acetone, ethanol, and the isomers of hexane and pentane. A particular goal of the current work is to assess the role that fuel molecular structure plays in determining overall rates of oxidation in engines, in cool flames, and in multistage ignition. [0.3 FTE]

### Sandia National Laboratories Livermore, CA 94550

Combustion Research Facility \$2,160,000

#### 51. Turbulent Reacting Flow Research

Dibble, R.; Schefer, R.; Lucht, R.P.; Chen, J.-Y.

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 multi-species laser Raman scattering and OH laser-induced fluorescence from which we obtain major species concentrations, temperature, and OH concentration 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<sub>4</sub>. 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<sub>4</sub>, 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. [3.0 FTE]

the characterization of potential energy surfaces governing various chemical reactions. A new aspect of this research in molecular dynamics focuses on properties of molecules adsorbed on solid surfaces. [5.1 FTE]

#### 44. Spectroscopy and Structure of Short-Lived Intermediates Sears, T.

High-resolution molecular spectroscopy is used to measure the structure and reactivity of molecular fragments in gas phase chemical reactions. The data provide information on species whose reactions often govern the course and rate of gas phase processes. In addition, the spectroscopic data are necessary precursors to future precise measurements of chemical reactions on a state-by-state basis. Most recently, ultraviolet laser flash photolysis has been used as a clean source of small free radicals, in particular small hydrocarbon fragments such as methyl ( $\text{CH}_3$ ), ethyl ( $\text{C}_2\text{H}_5$ ), and methoxy ( $\text{CH}_3\text{O}$ ). The radicals formed in the photolysis reaction are detected by means of their infrared absorption spectrum, using a low-power tunable infrared laser source. This technique allows the measurement of the vibration-rotation spectrum of the radical with extremely high precision. The data obtained are used to estimate the detailed molecular structure, often including electron spin fine structure effects, and the intramolecular potential surface. The distribution of the available photoproduct energy among the energy levels of the radical also provides information on the nature of the surface on which the photoreaction is occurring. [3.6 FTE]

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

Applied Science Division \$155,000

#### 45. Combustion Chemistry Brown, N.J.

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, determine 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 \$2,360,000

#### 46. Energy Transfer and Structural Studies of Molecules on Surfaces Harris, C.B.

The goals of this research are (1) to study the mechanisms responsible for transfer of energy from the excited states of molecules to metal surfaces and (2) to develop new laser techniques for probing molecule-surface interactions. The research is both theoretical and experimental in character, and includes nonlinear optical, picosecond, and femtosecond 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, 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 timescales and the optical properties of thin films. [1.8 FTE]

#### 47. Molecular Structure and Chemical Dynamics

Lee, Y.T.; Lester, W.A.; Miller, W.H.;  
Moore, C.B.; Saykally, R.J.

The research goal is to develop basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions and 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. Bond- and mode-specific chemistry will be searched for. The goal is the characterization of the basic chemical processes underlying combustion, surface chemistry, and energy storage. 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 will be utilized as they become available. *Ab initio* calculations are performed to provide complimentary 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. [14.5 FTE]

#### 48. Physical Chemistry with Emphasis on Thermodynamic Properties Pitzer, K.S.

The project objective 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. Current emphasis is on novel ionic systems, and on properties close to the critical



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 be interpreted more accurately. 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. This project is supported through KC-03-01-04-0. [5.0 FTE]

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

Palmer, R.E.; Goldsmith, J.E.;  
Koszykowski, M.L.; Lau, A.M.F.; Trebino, F.P.

This project supports the development and theoretical understanding of new nonlinear laser-based techniques for detecting trace species and characterizing collision-induced processes in combustion environments. Profiles of hydrogen atoms in hydrogen/oxygen and hydrocarbon flames have been obtained. Photochemical effects in the measurement of hydrogen and oxygen atoms in flames have been observed. Detailed studies of Doppler-free spectra of OH and CO have been made. Collision-induced resonances, involving nonlinear mixing of up to fourteen photons, for transitions between hyperfine and Zeeman states in sodium aspirated into flames, have been detected. In the area of theoretical studies, collisional narrowing of nitrogen and CO are modeled both by semi-classical scattering calculations and by simple scaling theories based on fits to experimental data. Hydrogen linewidths are modeled with similar scaling theories. Models have been developed to predict Doppler-broadened saturated line shapes (both transient and steady-state) and pump laserphoto statistics. A new perturbation expansion and diagrammatic technique have been developed to interpret collision-induced, high-order resonances. This project is supported through KC-03-01-04-0. [4.0 FTE]

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## Atomic Physics

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### Argonne National Laboratory Argonne, IL 60439

Physics Division \$1,595,000

**57. Beam-Foil and Ion-Beam Laser Interactions**

Berry, H.G.; Young, L.

Resonant laser excitation is used to study molecular and atomic ion structures. High spectral resolution is achieved by collinear excitation of fast ion beams with CW narrow-frequency laser beams and the use of rf/laser double-resonance techniques. Work on molecular ions is aimed at achieving understanding of both electronic and geometrical structures of simple systems. Several double-resonance techniques are under way to study hyperfine structures in  $N_2^+$  and other simple molecular ions. *Ab initio* theoretical understanding of hyperfine structure in metallic and rare-earth ions is being tested. Other studies

include fundamental problems of relativistic quantum mechanics and QED in few-electron systems. New double-resonance measurements are in progress for all these systems. Some collision studies of fast ions in solids and gases are continuing. [4.7 FTE]

**58. High-Resolution Laser-RF Spectroscopy with Atomic and Molecular Beams**

Childs, W.J.

This program is directed toward increasing our understanding of atomic and molecular structure 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 with high precision. Comparison of the new hyperfine structure (hfs) studies of Ti I (and of recent results on La I and BLASE results on Sc II) with new *ab initio* calculations reveal systematic shortcomings in the multi-configuration Dirac-Fock (MCDF) approach. Work in the group IIIA monoxides has recently been extended to praseodymium monoxide, PrO, in which the metal-centered electron that characterized the group IIIA monoxides has been replaced by 4f electrons. Although the present studies solve this problem very cleanly, they also show the need for considerably more theoretical sophistication than is currently available. Experimental work on the hfs of many-electron atoms is also continuing. [1.1 FTE]

**59. Atomic Physics at ATLAS**

Dunford, R.W.; Berry, H.G.

The primary goal of the atomic physics project at ATLAS is to study atomic structure at a fundamental level. Recent experiments have included ultraviolet spectroscopy of two- and three-electron titanium and nickel, and measurement of the two photon decay rate of the  $2^1S_0$  level in heliumlike nickel. Plans are under way for precision X-ray spectroscopy of one- and two-electron calcium, ultraviolet spectroscopy of two-electron bromine, and measurement of the two-photon decay rate of one-electron nickel. Exploratory work was performed using an ECR ion source that is to be part of the ATLAS accelerator but is available to this project temporarily. Measurements include state-selected electron pick-up cross sections at low to intermediate velocities, and auger spectroscopy of highly-charged, slow ions. [3.2 FTE]

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

Kanter, E.P.; Vager, Z.

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) molecular ions with matter. 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 incident on a solid target forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target. A unique apparatus has been developed that permits three-dimensional imaging of the trajectories of fragment ions resulting from the collisional dissociation of fast molecular beams. The new multiparticle imaging detectors developed for this work have exceptionally high resolution ( $\approx 0.005^\circ$  and  $\approx 600$  psec) in

## 52. Flame Chemistry: Modeling and Experiments

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

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. Work on the flame chemistry of nitrogen-containing species contributed to the development of RAPRENOx, a chemical process for removing nitrogen oxides from exhausts. A recent, exhaustive study of nitrogen's combustion chemistry has improved the mechanistic understanding of RAPRENOx and 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 such as diacetylene. Experiments conducted in a low-pressure flame give useful spatial resolution through the reaction zone. Laser diagnostics yield temperature and the concentration profiles of radicals such as OH, CH, and CN. 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. Careful comparison of modeling with experimental results, aided by sensitivity analysis, enables extension and validation of the reaction mechanisms that govern flames. In addition to studying steady-state flames, this research is developing computational techniques for treating ignition in combustible mixtures. The effects of temperature and pressure perturbations on the ignition process are areas of present emphasis. [4.0 FTE]

## 53. Chemical Kinetics and Dynamics

*Fisk, G.A.; Tully, F.P.; Durant, J.L.; Chandler, D.W.; Miller, J.A.; Rohlfing, E.A.; Hayden, C.C.*

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. Fundamental studies of the kinetics of nitrogen-containing species recently led to the invention of RAPRENOx, a chemical process that removes the oxides of nitrogen from exhausts. Theoretical approaches augment experiments. Quantum chemical calculations define the potential-energy surfaces on which chemical reactions occur. Statistical theoretical methods are then used to calculate the rates of important reactions in regimes for which experimental results are not available. Recent theoretical work has furthered the understanding of the OH + acetylene and the O + ethyl reactions. Studies of dynamics emphasize collecting quantum-state-resolved data for elementary chemical processes. Photofragment imaging, recently developed in this project, is a valuable technique for collecting highly resolved data on the dynamics of processes such as photodissociation. Results obtained for molecules like methyl iodide are leading to a better understanding of how energy is released when a chemical bond breaks. 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. [5.0 FTE]

## 54. Flame Dynamics Research

*Flower, W.; Lucht, R.P.*

The project objective is to investigate the interactions among chemical species, temperature, and fluid motion as they relate to the formation of soot in flames. Local soot-formation rates have been determined using laser-velocimetry flow-field measurements and light-scattering measurements of soot size and number density. Laminar axisymmetric ethylene-air diffusion flames have been studied at pressures up to 1.0 MPa to examine how the balance between soot formation and oxidation processes changes with pressure. Turbulent jet diffusion flames have been examined at pressures up to 0.8 MPa to investigate the effect of turbulent mixing on soot formation. Peak time-averaged soot volume fractions are found on the centerline in these flames, unlike laminar coflowing flames where the peak soot concentration is located off-axis, just inside the position of the flame front. At any position and at all pressures, the turbulent flames consist of alternate soot-laden and soot-free zones. This is demonstrated by instantaneous planar Mie-scattering visualizations of the sooting regions that show that the soot is found in relatively narrow, intertwined layers. At low pressures, the axial time-averaged soot-volume-fraction profiles approach universal functions of normalized axial position for long characteristic flame residence time. At high pressures, lower-soot-volume-fraction profiles are observed for increasing characteristic flame residence time. A counter-flow diffusion flame has been used to study the impact on soot formation of dilution of the fuel, preferential diffusion, and oxygen addition to the fuel. When the fuel is diluted with a fixed inert gas and the flame temperature is held constant, the peak soot volume fraction varies in direct proportion to the initial fuel concentration. When the inert diluent added to the fuel is varied, the quantity of soot formed decreases as the diffusivity of the inert gas is increased, demonstrating that differential diffusion affects the soot formation process. [2.0 FTE]

## 55. Combustion Research Facility (CRF) Diagnostics Research: Coherent Raman Processes

*Palmer, R.E.; Farrow, R.L.; Rahn, L.A.; Lucht, R.P.*

This project develops coherent Raman diagnostic techniques in support of CRF programs. Detailed studies are made of the significance of several 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, pump laser photon statistics, laser line shape convolutions, and collisional narrowing of Q branch transitions. A high-resolution CARS system is used to examine saturation effects, to perform pump-probe experiments for measuring inelastic rotational state-to-state transfer rates directly, and to measure high-temperature linewidths in high-pressure lamps. The

angle and time-of-flight and allow detection of multiparticle events consisting of up to 8 particles. The use of this detector system, combined with ultrathin stripping films and low-excitation ion sources, has allowed the direct determination of the geometrical structures of the molecular ions entering the target. These experiments have provided the first direct measure of the nuclear densities within several small molecular and cluster ions. [4.8 FTE]

**Brookhaven National Laboratory  
Upton, Long Island, NY 11973**

**Department of Applied Science                      \$240,000**

**61. Atomic Physics Research**

*Jones, K.W.; Johnson, B.M.*

Studies of the physics of multiply charged heavy ions use synchrotron radiation from the Brookhaven National Synchrotron Light Source (NSLS). An X-ray beam line was improved by the addition of a 1:1 focusing mirror to increase the flux of white radiation delivered to the target by three orders of magnitude. A conversion to ultrahigh vacuum operation is under way to conduct windowless experiments with a greater photon flux. Monoenergetic radiation can be obtained by use of a monochromator in the experimental hutch, but it will not be operated in the windowless mode initially. Experiments to study photoionization of ions using traps were initiated. The beam-line changes made during the NSLS X-ray ring shutdown will make possible better signal-to-noise ratios and greatly enhance the quality of the data. The first experiments used argon gas and ion beam targets. [2.3 FTE]

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

**Materials and Chemical Sciences Division                      \$445,000**

**62. High-Energy Atomic Physics**

*Gould, H.A.*

The goals of this project are to understand atomic collisions of relativistic ions and to test quantum electrodynamics (QED) in very high atomic number atoms. These are new areas of research that involve physics not accessible at lower energies or with ions of lower atomic number. This research is conducted at the Lawrence Berkeley Laboratory's Bevalac, the world's only relativistic heavy ion accelerator. Recent results include the first measurement of electron impact ionization of highly ionized very heavy ions (U88+, U89+, U90+, and U91+). This measurement was done by channeling relativistic uranium ions through silicon single crystals. These and earlier experiments have led to an understanding of relativistic heavy-ion-atom collisions, which in most cases is now more complete than for nonrelativistic collisions. Present activities include measurement of screening-antiscreening effects in relativistic ionization and a precision (0.1%) measurement of the Lamb shift in uranium. Future experiments will 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. [2.2 FTE]

**63. Atomic Physics**

*Prior, M.H.*

This experimental atomic physics project carries out broad-ranging studies of collisions and spectroscopy of unique atomic systems. Emphasis is on topics that challenge current understanding of atomic structure and interactions and 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, and the measurement of forbidden-line spectra from highly charged 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 source and recently completed beam line facilities. The project benefits from valuable collaborative efforts with colleagues from outside LBL. [1.2 FTE]

**Oak Ridge National Laboratory  
Oak Ridge, TN 37831**

**Physics Division    \$1,525,000**

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

*Becker, R.L.; Bottcher, C.*

Theoretical predictions, interpretations of experimental results, and detailed calculations are made for atomic collision, radiation, and structure phenomena. Emphasis is placed on reactions of highly stripped ions with atoms, particularly those reactions of importance in fusion energy devices and those studied in atomic high-energy accelerator physics laboratories. Atomic excitation, ionization, and electron transfer (capture) are treated. Particular topics treated recently include coincident ionization and excitation of lithiumlike ions, a quantum scattering theory of electron-impact ionization of hydrogenic ions, single- and double-K shell vacancy production, and outer shell processes with multielectron projectiles. A major collaboration with the nuclear theory group at Oak Ridge National Laboratory helps develop highly efficient algorithms to conduct numerical solutions of systems in the strong fields produced in collisions of highly charged ions at relativistic speeds. In particular, these include the production of lepton pairs, i.e., ( $e^+e^-$ ), ( $\tau^+\tau^-$ ), and ( $\mu^+\mu^-$ ). The exact numerical solutions of the three-body ion-atom scattering system are studied. The "constraint dynamics" methods of Dirac are being applied to study the structure of the  $e^+e^-$  system at very short distances. Theoretical approaches include the one-and-a-half center version of coupled-channels theory, the unification of shakeoff theory with collision theory, and the use of basis spline and collocation methods in the numerical integration of time-dependent quantum equations such as the time-dependent Hartree-Fock theory. [1.0 FTE]

### 65. Accelerator Atomic Physics

*Datz, S.; Dittner, P.F.; Vane, C.R.*

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) for atomic physics research. Electron capture, ionization, and transfer ionization (TI) have been studied for 0.1 to 1.0 MeV/nucleon highly charged ions colliding with helium. Single and double charge transfer cross sections have been measured. Zero-degree electron spectroscopy has been studied in coincidence with transfer ionization, and vacuum ultraviolet photons have been detected in coincidence with capture and with TI. These measurements indicate charge transfer to lower  $n$  states with TI than with single capture, in qualitative accord with theory based on level transfer. Dielectronic recombination has been measured for the boronlike ions,  $N^{2+}$ ,  $O^{3+}$ , and  $F^{4+}$ . 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  $0.005^\circ$  were achieved using the Elbek magnetic spectrograph. Experiments are conducted to test the extent to which the electrons contained in a crystal channel can be quantitatively treated as a dense electron gas target. Beams of  $S^{15+}$  through silicon crystals are channeled at energies below and proceeding through thresholds for  $n = 1 \rightarrow n = 3$  excitation. Since excitation cross sections rise sharply at threshold, the energy width of the excitation function should reflect the Compton profile of the electrons in the channel. [5.0 FTE]

### 66. EN Tandem Operations

*Dittner, P.F.*

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, universities, and industry. Terminal voltages up to 6.5 MV are routinely available, and ion sources are sufficiently versatile to provide beams of (1) all ions from protons through fluorine and silicon through chlorine and (2) many heavier ions including nickel, iodine, gold, and uranium. A VAX-750/CAMAC-based data acquisition system and the Elbek magnetic spectrograph 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, ion channeling through silicon crystals, dielectronic recombination rate measurements for boronlike ions, convoy electron studies, and zero-degree Auger electron spectroscopy of highly charged ions. [2.2 FTE]

### 67. Collisions of Low-Energy Multiply Charged Ions

*Phaneuf, R.A.; Meyer, F.W.; Havener, C.C.*

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. Studies of such processes yield important information about collision mechanisms and quasi-molecular structure, providing tests of developing theoretical models. An ion-atom merged-beams apparatus has been developed for use 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  $O^{5+}$ ,  $N^{5+}$ ,  $N^{4+}$ , and  $N^{3+}$  colliding with H or D atoms demonstrate the effects of ion-induced-dipole attraction between the reactants. 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 the first evidence for the transfer of electrons directly from inner shells of the solid to inner shells of the projectile ion. [1.2 FTE]

## Sandia National Laboratories Albuquerque, NM 87185

Laser and Physical Chemistry  
Department-1164

\$155,000

### 68. Atomic Processes

*Smith, A.V.*

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  $0.01 \text{ cm}^{-1}$  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]

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## Chemical Energy

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Ames Laboratory  
Iowa State University  
Ames, IA 50011

Processes and Techniques Program      \$1,153,000

**69. Organometallic Complexes in Homogeneous Catalysis**  
*Angelici, R.J.*

The general goal of this project is to understand how transition metal catalysts adsorb and activate molecules in various catalytic reactions. Current studies are directed toward understanding hydrodesulfurization of thiophenes on heterogeneous catalysts. Evidence for the  $\pi$ -adsorption of thiophene to the catalyst surface comes from the very similar patterns of deuterium exchange of thiophene on HDS catalysts and of  $\pi$ -thiophene in  $(\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_4\text{H}_4\text{S})^+$ . The  $\pi$ -thiophene ligand in the latter complex is also activated to react with metal hydride sources which may be present on catalyst surfaces. These reactions lead to partially hydrogenated dihydrothiophenes which have been shown to eliminate sulfur and give desulfurized hydrocarbons. Thus, the dihydrothiophenes are key intermediates on the pathway to desulfurized products. They also react with transition metal cluster hydrides to give complexes which account for by-products in the HDS reactions. These reactivity studies provide a basis for understanding details of the mechanism for thiophene hydrodesulfurization. [3.0 FTE]

**70. Chemical Kinetics and Reactivity of Transition Metal Complexes**  
*Espenson, J.H.*

The general goal of this project is to understand the homogeneous chemistry that underlies catalytic processes including synthetic fuels formation. Thus 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  $L_n\text{M-R} \rightarrow L_n\text{M} + \text{R}\cdot$ , 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. The 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. Free radicals occur as intermediates in these reactions. Thus another aspect of this work concerns the kinetics and mechanisms of reactions in which alkyl radicals react with transition metal complexes. [3.7 FTE]

**71. Multiple Pulse NMR Studies: Catalysis and the Chemical Constitution of Coal**  
*Gerstein, B.C.*

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  $^{133}\text{Cs}$  and  $^{63}\text{Cu}$  to characterize the chemical states of catalysts such as zeolites and alkali metal-doped copper oxides, and the use of NMR of  $^{51}\text{V}$  and  $^{17}\text{O}$  to characterize possible active sites for  $\text{C}_4$  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. [3.3 FTE]

**72. Fundamental Investigations of Supported Metal Catalysts**  
*King, T.S.*

This project focuses primarily on supported, mono- and bimetallic catalysts with the intent of understanding how the chemical and structural properties of the highly dispersed transition metals affect catalytic performance. A variety of fundamental catalytic phenomena are investigated in this work by correlating chemisorption and surface reaction behavior with a detailed description of the catalyst surface. For example, the abundance and morphology of the surface metal atoms can play an important role in structure sensitive reactions. Likewise, the relative surface composition of metal constituents in a supported bimetallic catalyst has been postulated to influence reactions requiring groups of contiguous metal atoms (ensemble effect). Furthermore, delocalized or partially delocalized electronic interactions may play an important role in multimetallic catalysts. Similarly, promoters and poisons can alter the metal in a fundamental way by either perturbing the electronic structure of the surface or by imposing structured constraints. To understand the above phenomena, the chemical and structural properties of both 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  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{195}\text{Pt}$ , and various other nuclei is used to probe the local structural and chemical environment of surface metal atoms and adsorbed species. [2.3 FTE]

**73. Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts**  
*Schrader, G.L.*

The goal of this research is to provide a fundamental understanding 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 in selective oxidation and hydrodesulfurization. Specific applications include paraffin oxidation (such as the oxidative coupling of methane) and the hydroprocessing of organic sulfur compounds found in coal-derived liquids and petroleum. A complement of experimental approaches is used involving reaction engineering kinetic measurements and extensive

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. New techniques such as solid-state NMR also have important applications in current research into the active components and active sites of catalysts. The purpose of the experimental project is to provide fundamental relationships between catalyst structure, composition, and surface properties and catalytic activity and selectivity. [2.6 FTE]

**74. High-Temperature Gas-Phase Pyrolysis of Organic Compounds**  
Trahanovsky, W.S.

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 NMR technique has been developed which allowed the  $^1\text{H}$  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. [2.3 FTE]

**Argonne National Laboratory**  
Argonne, IL 60439

**Chemical Technology Division**      **\$575,000**

**75. Fluid Catalysis**  
Rathke, J.W.; Chen, M.J.; Klingler, R.J.

This research uses an array of high-pressure autoclave and *in situ* spectroscopic techniques to determine reaction mechanisms and to explore new catalytic chemistry of small molecules. Kinetic, structural, and thermochemical parameters of catalytic species are typically studied *in situ*, while the reaction is in progress, under forcing conditions of temperature and pressure. Currently investigated are soluble oxide catalysts that promote hydrogenation and water-gas shifting via catalytic mechanisms that are distinct from those of other homogeneous catalysts and that seem more relevant to suspected metal oxide surface chemistry. It has been discovered that oxide-based nucleophiles can activate hydrogen in the complete absence of a metal center. In other research, the chemistry of soluble phthalocyanines is developed to allow homogeneous

catalysis under extreme conditions of temperature and pressure. A synthetic approach was devised to incorporate trialkylsilyl groups onto the phthalocyanine rings, thereby imparting high solubility and other useful properties to the macrocycles. *In situ* kinetic and thermochemical studies are advanced by improvements in a new NMR detector, an elongated toroid, which achieves greatly improved sensitivity for  $^{13}\text{C}$  and other insensitive nuclei associated with organometallic systems. Because of its confined magnetic flux, this detector was found to be ideal for use in metal pressure probes. [4.9 FTE]

**Chemistry Division**      **\$2,125,000**

**76. Inorganic/Fluorine Chemistry**  
Appelman, E.H.

This project is directed toward (1) the synthesis and characterization of novel and aggressive oxidants and fluorinating agents, (2) the elucidation of the mechanisms of their chemical reactions, and (3) the development of applications of such compounds as synthetic and analytical reagents. Current projects include studies of the reactions of powerful oxidants and fluorinating agents with ions of the actinide elements in aqueous solution, and fluorination of cubane and its derivatives. Future studies include an extensive exploration of the aqueous reaction chemistry of fluorine and reactive fluorine compounds, and of the reactions of such compounds with a variety of organic substrates. [1.6 FTE]

**77. Chemical Constitution of a Low-Volatile Bituminous Coal**  
Stock, L.M.

This project is based on the idea that higher ranking bituminous coals, such as the Pocahontas No. 3 coal in the Premium Coal Sample Program, have chemical compositions that are significantly less complex than the compositions of the lower ranking oxygen-rich bituminous coals. Chemical and spectroscopic strategies are being employed to establish the constitution of this coal. The current year's work involves the exploitation of  $\text{Sm(II)}\text{I}_2$  to reduce the free-radical content and thereby to enhance the quantitative character of solid-state  $^{13}\text{C}$  NMR spectroscopy and the use of selective  $\text{Ru(VIII)}$  oxidation to define the aliphatic structural elements. Not less than 80% of the aliphatic carbon atoms in this coal have been identified. The connecting links and the aromatic structural elements are being elaborated. [0.8 FTE]

**78. Premium Coal Sample Program**  
Vorres, K.S.

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 270 orders have been filled with shipments of more than 8000 ampoules. The material in ampoules will meet the demand for another five years, and the reserves in carboys will continue to meet the current demand level for several decades. The gas atmosphere is monitored for stability. These measurements have also shown that the youngest coals evolve carbon dioxide while the oldest tend to evolve methane. A new users handbook has been prepared for recipients of the samples, and symposia on "Research with Argonne Premium Coal Samples" have

been organized in conjunction with American Chemical Society meetings. [0.5 FTE]

**79. Separation of Coal Macerals**

*Winans, R.E.; Dyrkacz, G.R.;  
Bloomquist, C.A.A.*

New techniques for the separation and characterization of coal macerals are being used to attack the problem of coal heterogeneity. The project focuses on two objectives: (1) the development and utilization of combined two-dimensional chemical modification and density gradient (DGC) separations to achieve the ultimate separation of macerals and (2) the development of large-scale flow-separation systems using both centrifugation and magnetohydrostatic separations. [2.8 FTE]

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

*Winans, R.E.; Hayatsu, R.; Botto, R.E.;  
Neill, P.H.; McBeth, R.L.; Melnicoff, P.E.*

The objective of this project is to develop a fundamental understanding of the chemical and physical nature of coals and their maceral constituents in order to predict their chemical, thermal, and biological reactivity. Studies focus on the Argonne Premium Coal Samples, on macerals separated from these coals, and on synthetic macerals prepared in this project. The approaches used include selective chemical modification and solubilization methods closely coupled with multiple instrumental characterization. Several high-resolution mass spectrometric and solid NMR techniques are being employed to characterize large molecules derived from coals. In addition, layered catalysts are being synthesized that should be effective for reducing these large molecules. The information developed in this study should help predict coal reactivity leading to the development of more efficient and cleaner uses of coals. [8.0 FTE]

**Brookhaven National Laboratory  
Upton, Long Island, NY 11973**

**Department of Applied Science      \$675,000**

**81. High-Temperature Chemistry**

*Egan, J.J.*

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<sub>2</sub> 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]

**82. Metal Hydrides**

*Reilly, J.J.*

The overall objective of this project is to investigate the kinetic, thermodynamic, and structural properties of hydrogen in metals or metalloids. A particular goal is to relate all pertinent data and observations to develop a predictive capability regarding the behavior of a given metal/hydrogen 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**

**\$632,000**

**83. Organometallics in Homogeneous Catalysis**

*Bullock, R.M.; Andrews, M.A.*

Reactions of transition metal hydrides and other organometallic complexes are being investigated to improve our fundamental understanding of how these complexes effect important transformations of organic compounds. Experimental studies encompass both exploratory synthetic reactions and mechanistic investigations that demonstrate new principles of reactivity of organometallic complexes. Novel catalytic transformations of carbohydrates are targeted at biomass conversion. Recent progress in this area includes the first demonstration of the catalytic hydrocracking of sugar C—C single bonds under mild conditions to provide glycols. Another accomplishment is the decarbonylation of unprotected aldose sugars. Studies of reactions of transition metal hydrides have led to the isolation of novel bimetallic  $\eta^1$ -aldehyde complexes. These aldehyde complexes may represent a previously unobserved intermediate in the catalytic hydroformylation of alkenes. Studies on the formation and reactions of these species have provided new understanding of the detailed mechanism of dinuclear elimination reactions. Metal-mediated interconversions of acetylene and vinylidene are also being studied. [4.6 FTE]

**84. Molecular Structure and Chemical Reactivity on Surfaces**

*Hrbek, J.*

The main objective is to develop and improve the understanding of molecular processes at the gas-solid interface, with emphasis on catalytically important systems. Focus is on the electronic and geometric effects of surface modifiers, such as alkali metals, electronegative elements, and second metals, on the coadsorbed molecules. Coadsorption of alkali metals and oxygen is studied in mono- and multilayer coverage ranges. Dissociatively adsorbed oxygen is found to stabilize thermally alkali metal overlayers. A new oxygen species with an O 1s binding energy above 532 eV was observed in the K-O and Cs-O systems, together with several intense O 2p levels in the valence

band region of photoemission spectra, indicating the formation of peroxo and superoxo species. All alkali metals studied (lithium, sodium, potassium, and cesium) show a negative binding energy shift of core levels upon oxidation, suggesting unusual electronic interactions in the surface complex. Currently, modified surfaces containing an alkali metal complex with weakly bonded oxygen are used in the oxidation studies of carbon monoxide and ethylene. This project uses an array of surface techniques, including photoemission spectroscopy, Auger spectroscopy, thermal desorption spectroscopy, vibrational spectroscopy, and electron diffraction and synchrotron radiation spectroscopies. [2.45 FTE]

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

**Applied Science Division \$200,000**

**85. Homogeneous Catalytic Hydrogenation of Mono- and Polynuclear Heteroaromatic Nitrogen Compounds: Mechanistic Studies**

*Fish, R.H.*

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, among others. Since this class of model coal compounds is directly involved in the hydrodenitrogenation (HDN) process, it is highly important that these fundamental studies include the mode of bonding of the nitrogen compounds to the metal centers, i.e., N- versus  $\pi$ -bonding, and the utilization of rhodium and ruthenium as well as other metal complexes as catalysts for the regioselective nitrogen heterocyclic ring hydrogenation reaction; this latter reaction being the first step in the HDN process of nitrogen atom removal. Recently reported results with pentamethylcyclopentadienylrhodium dication ( $\text{Cp}^*\text{Rh}^{2+}$ ) and several heteroaromatic nitrogen compounds, such as quinoline, isoquinoline, 1,2,3,4-tetrahydroquinoline, 2-methylquinoline, N-methylindole, and N-methylpyrrole, clearly indicated that N- versus  $\pi$ -bonding to the metal center depends on the structure of the nitrogen ligand and the availability of nonbonding electrons on the nitrogen atom. More importantly, two complexes,  $\text{Cp}^*\text{Rh}(\text{p-xylene})^{2+}$  and  $\text{Cp}^*\text{Rh}(\text{acetonitrile})_3^{2+}$ , have been shown to be excellent catalyst precursors in the regioselective hydrogenation of quinoline, 2-methylquinoline, and indole 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  $\text{Cp}^*\text{Rh}^{2+}$ . Similar studies with cyclopentadienylruthenium cation ( $\text{CpRu}^+$ ) and pyridine, 2-methylpyridine, 2,4-dimethylpyridine, and quinoline revealed N-bonding to the metal center; however, the  $\text{CpRu}^+$ -N-bonded methyl-substituted pyridine and quinoline complexes undergo a novel and unprecedented intramolecular N to  $\pi$  rearrangement that is deleterious to  $\text{CpRu}^+$  complexes being used as catalysts for selective nitrogen ring reduction. Finally, by utilizing the new

technique of high pressure nuclear magnetic resonance (NMR) spectroscopy, the mechanism of the selective nitrogen ring hydrogenation reaction directly with the above-mentioned catalyst precursor,  $\text{Cp}^*\text{Rh}(\text{acetonitrile})_3^{2+}$ , and the nitrogen ligand, quinoline, is being studied. This powerful new NMR technique will hopefully provide information on the formation of intermediate hydride, transfer of hydrogen to the N-bonded ring, and release of product. [1.5 FTE]

**Materials and Chemical Sciences Division \$1,027,000**

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

*Bartlett, N.*

The main aim of this project is the synthesis and characterization of new materials that may have value in electrochemical applications. The synthetic work tests models and theories that correlate physical properties (such as electrical conductivity) with chemical composition and structure. The present emphasis is on the study of two-dimensional extended atomic networks, such as those derived from graphite, layer-form boron nitride, and their relatives. Electron oxidation of such materials (with accompanying intercalation to form salts) generates durable and conductive materials (some conducting better than aluminum). Chemical, stoichiometric, and structural requirements for the best conductivity are being defined. The layered materials can often be oxidized (and intercalated) electrochemically in reversible processes. Some of these materials may be useful for high-energy electrodes. Physical and chemical studies are being applied to determine the structure and bonding changes that accompany oxidation and reduction. Salts that are either proton conductors or fluoride-ion conductors, and that are resistant to oxidation but are not metallic, are being sought as solid electrolytes for use with the metallic-layer-material salts. [4.5 FTE]

**87. Catalytic Hydrogenation of Carbon Monoxide**

*Bell, A.T.*

The purpose of this project 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 (LEED, AES, XPS, EELS, NMR, IRS, TPD) is 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]



**88. Transition Metal Catalyzed Conversion of CO, NO, H<sub>2</sub>, and Organic Molecules to Fuels and Petrochemicals**  
*Bergman, R.G.*

The goals of this project are the development of new chemical reactions in which transition metals interact with organic materials, and the understanding of how these reactions work. A recent discovery on this project was the finding that certain hydrido-iridium and -rhodium complexes undergo oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons ( $M + R-H \rightarrow R-M-H$ ). Since this finding was the first example of a long-sought alkane C-H activation reaction, research is now being directed at examining the scope, selectivity, and mechanism of the process and in developing ways to convert the activated metal complex R-M-H into functionalized organic molecules. Progress was made on the functionalization problem by uncovering a modified iridium system that effects dehydrogenation of the activated alkane. In a second study, activation of the very strong vinyl C-H bond in ethylene was investigated; evidence for the intervention of a transient intermediate other than the iridium-ethylene  $\pi$ -complex was obtained. Further progress was made toward understanding the thermodynamic driving force of the C-H oxidative addition process, and a flash kinetics spectrometer was constructed that is capable of infrared detection of transient organometallic species (similar to those involved in C-H activation) and measurement of the rates of their rapid reactions. [3.4 FTE]

**89. Formation of Oxyacids of Sulfur from SO<sub>2</sub>**  
*Connick, R.E.*

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<sub>2</sub>. Control of the rate of this latter reaction is of major importance to these processes. While 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<sub>3</sub><sup>-</sup>, H<sub>2</sub>S, S<sub>8</sub>, and the polythionates). A secondary goal is to determine 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]

**90. Potentially Catalytic and Conducting Oligo-Organometallics**  
*Vollhardt, K.P.C.*

This project involves the design and execution of organic methodology aimed at allowing access to sequences of linked strong  $\pi$ -ligands to transition metals. The synthetic approaches are designed to be efficient, readily performed, and to be so adaptable as to allow control over

the sequence of the attached metals. In this way, a number of novel transition metal arrays have become available in which the metallic centers adopt unnatural linear and angular configurations. It is anticipated that these structures will give rise to unobserved reactivity and potential catalytic activity when exposed to small organic molecules. Moreover, such transition metal chains provide ideal models for probing the elementary steps of multimetallic ligand and electron transfer. Novel systems were synthesized in which several cyclopentadienyl units have been linked and complexed to transition metals. The first total syntheses of ter- and quatercyclopentadienyl tri- and tetrametals have been announced, including a trisheterometallic system containing the sequence molybdenum, rhenium, and tungsten. The discovery of exciting preliminary chemistry of these systems, including thermally and photochemically induced intramolecular ligand transfers, has justified the original premise of this research. Current efforts are focused on exploring the reactivity patterns of the structures under investigation and on expanding the ligand chain. [3.6 FTE]

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

**Isotope and Nuclear Chemistry**                      **\$365,000**  
**Division**

**91. Transition Metal Mediated Reactions of SO<sub>2</sub>**  
*Kubas, G.J.; Ryan, R.R.*

This research has focused on the basic chemistry of energy-related small molecules, primarily SO<sub>2</sub> and H<sub>2</sub>, mediated by transition metal complexes. A fundamental understanding of the cleavage of S=O and H-H bonds will benefit efforts to control SO<sub>2</sub> emissions, providing new directions in metal-catalyzed reactions. Homogeneous catalytic reduction of SO<sub>2</sub> to sulfur and H<sub>2</sub>O by hydrogen on organometallic molybdenum sulfide complexes has been achieved and mechanistic studies are under way. SO<sub>2</sub> has been found to undergo oxygen transfer reactions that may be relevant to the catalytic cycle. Disproportionation of SO<sub>2</sub> to sulfur and SO<sub>3</sub> (as SSO<sub>3</sub> or SO<sub>3</sub>H ligands) occurs on reaction with Cp'<sub>2</sub>Mo<sub>2</sub>S<sub>4</sub> and Cp'<sub>2</sub>Ru(CO)<sub>2</sub>H (Cp' = C<sub>5</sub>Me<sub>5</sub>). Thiosulfate ligands such as those in the product Cp'<sub>2</sub>Mo<sub>2</sub>S<sub>3</sub>( $\mu$ -SSO<sub>3</sub>) have now been observed to be formed from SO<sub>2</sub> in several systems and appear to be intermediates in the catalytic SO<sub>2</sub> reduction. SO<sub>3</sub> can be readily stripped off the Mo-SSO<sub>3</sub> complex with weak organic bases such as amines and alcohols to regenerate starting complex, possibly leading to a catalytic cycle where SO<sub>2</sub> and organic compounds are converted to sulfur and sulfonylated organics. In regard to H<sub>2</sub> activation, the discovery of side-on bonding of H<sub>2</sub> molecules to metals represents the first stable  $\sigma$ -bond complex and serves as a prototype for other  $\sigma$ -bond activations (e.g., C-H in hydrocarbons). These complexes may be important in catalysis, and the reactivity of M-H<sub>2</sub> complexes (e.g. protonation, isotopic exchange) is being studied along with the thermodynamics and kinetics of H<sub>2</sub> reactions. Reaction of W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>) with HBF<sub>4</sub> results in loss of H<sub>2</sub> and formation of a novel new complex shown by crystallography to contain coordinated BF<sub>4</sub>

and an unusual disordered CO ligand possibly interacting with an unlocated hydrogen. [2.0 FTE]

## Oak Ridge National Laboratory Oak Ridge, TN 37831

Chemical Technology Division \$543,000

### 92. *Kinetics of Enzyme-Catalyzed Processes* Greenbaum, E.; Woodward, J.

Progress was made in the following areas: (1) kinetic measurements of interfacial vectorial photoelectric current generated at the photosynthetic membrane-metal colloid interface; (2) resolution of individual flash yields of photocurrent; (3) the role of electrode structure and symmetry on the origin of oriented photocurrent in platinized chloroplasts; and (4) further elucidation of the nature of synergism among the components of the cellulase enzyme system. Experiments performed during the current reporting period explored the kinetic and mechanistic aspects of the photoelectrochemistry of photosynthesis by saturating flash illumination and repetitive flash illumination of varying frequency. Electrode-contacted platinized chloroplasts were irradiated with brief flashes of light in the frequency range of 1 to 400 Hz. Repetitive flash illumination is a powerful technique for elucidating the rate-limiting step in the flow of photocurrent in this photobioelectrochemical cell. The turnover kinetics measured by this technique indicated that the rate limiting step has a kinetic time constant of 4 msec as defined by the role-off in flash yield per frequency interval. It has also been determined that synergism between cellulase components is dependent on the level of saturation of substrate. [4.0 FTE]

Chemistry Division \$2,740,000

### 93. *Organic Chemistry and the Chemistry of Fossil Fuels* Buchanan, A.C.; Britt, P.F.; Brown, L.L.; Hagaman, E.W.; Chambers, R.R.

The objective of this project is to conduct fundamental research that will advance current understanding of coal structure and reactivity. The development of novel processes for the selective production of liquid fuels or chemicals from coal in an environmentally acceptable manner will require input from such systematic molecular level knowledge. The development and application of advanced solid-state NMR techniques to the elucidation of coal structure is an integral part of this program. Double cross polarization (DCP) methodologies are being developed which, in concert with selective chemical derivatization, provide a direct spectroscopic view of the carbon bonding network in the immediate vicinity of the reaction centers in coal. Organic chemical reactions are being developed and applied to coals that are providing new insights into the underlying structural basis for coal chemical reactivity. A series of organo-lithium bases of defined strength has been developed that can probe acidic C-H structures in coal in the  $pK_a$  range of 12 to 33. Carbanions generated in the coal network in a specified  $pK_a$  range can be derivatized with carbon-13 and carbon-14 doubly labeled reagents (for NMR and quantitation purposes), or with a phosphorous labeled moiety for a more

detailed assessment of localized structure by  $^1H$ - $^{13}C$ - $^{31}P$  DCP/MAS  $^{13}C$  NMR. Principles underlying the thermal reactivity of coal are being investigated with current focus on the effects of restricted diffusion on thermolysis pathways, which could be operative in coal as a result of its cross-linked macromolecular structure. This feature is being explored by the thermolysis of model compounds that are covalently attached to an inert silica surface. [7.4 FTE]

### 94. *Basic Aqueous Chemistry to High Temperatures and Pressures* Mesmer, R.E.; Holmes, H.F.; Marshall, W.L.; Palmer, D.A.; Simonson, J.M.

The purpose of this research is to study chemical reactions and thermodynamic properties of electrolytes in water over wide ranges of temperature and pressure to better understand the interactions of a variety of solute types with each other and with the solvent, particularly at high temperatures and pressures. The research includes detailed physical chemical studies with emphasis on thermodynamics. Systems for study are selected as model substances from important classes of electrolytes that demonstrate characteristic behavior ranging from ionization, association, hydrolysis, oxidation-reduction, complexation, and precipitation. Specific systems generally have applicability in steam generation, coolant chemistry, waste treatment and isolation, environmental chemistry, geochemistry, geothermal energy extraction, and in the energy production and conservation technologies. New and unique equipment is being developed and utilized that involves flow calorimetry, electrical conductivity, electrochemical cells, isopiestic measurements, densimetry, spectrophotometry, Raman scattering, and phase studies. New results demonstrate the transition from strong-to-weak electrolyte behavior, excess properties of pure electrolytes and mixtures of a number of important classes, reaction enthalpies in the vicinity of the critical point, a model of ionization thermodynamics for weak acids in terms of the volumetric properties of the solvent, the use of a noncomplexing medium electrolyte to separate electrostatic and mass action effects, complexing with organic ligands, and speciation of aluminum, uranyl, and of phosphate ions. [5.0 FTE]

### 95. *Heterogeneous Catalysis Related to Energy Systems* Overbury, S.H.; Huntley, D.R.; Mullins, D.R.; Krause, M.O.

This project involves the study of adsorption and reaction of molecules at well-characterized metal surfaces, with particular emphasis on reactions related to surface-catalyzed hydrodesulfurization (HDS). Ultra-high vacuum techniques are used to prepare and maintain a single crystal surface in a desired state for exposure to adsorbates, and for subsequent analysis by various techniques including temperature programmed reaction, high-resolution electron energy loss, Auger electron and photoelectron spectroscopies, ion scattering, and near-edge X-ray absorption spectroscopy. The kinetics of adsorption, reaction, and product desorption of methanethiol and hydrogen sulfide on Ni(110) have been studied as model HDS systems. The formation of surface intermediates and the effects of surface oxygen and sulfur on these reactions have been characterized. The

structures of refractory (Mo and W) surfaces following reaction with various atomic adsorbates (oxygen, carbon, sulfur, copper, and nickel) have been analyzed using ion scattering techniques, to better understand the effects of modifiers and decomposition products on surface reactions. A new project has the goal of using synchrotron radiation to study bonding, orientation, and thermally induced changes of chemisorbed molecules by near edge X-ray absorption and angle-resolved photoemission. Existing capabilities to study electronic structure and photoelectron dynamics of gas phase species are used for reference to determine effects of adsorption on molecules and atoms. [4.6 FTE]

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

Zingg, S.P.; Dworkin, A.S.; Pagni, R.M.

This research program initiates a fundamental investigation of the photoreactions of organic substrates in heterogeneous systems. The potential results of this research are the discovery of new reactions and control of chemical reactivity by factors specific to interfaces. The investigation will provide mechanistic insight into the transformation of these chemicals in the environment, and the roles played by sunlight and sorption to solids. An approach in this program is to first investigate the photochemistry of a series of polycyclic aromatic hydrocarbons both in homogeneous solution and sorbed to surfaces in solvent/solid slurries, by product analyses and *in situ* spectroscopic techniques. For a more detailed understanding of the factors underlying these photochemical reactions, the photophysics of selected examples will be investigated by time-resolved emission spectroscopies. [2.9 FTE]

**Pacific Northwest Laboratory  
Richland, WA 99352**

**Chemical Sciences Department \$580,000**

**97. Free-Radical Chemistry of Coal**

Franz, J.A.; Alnajjar, M.S.; Autrey, S.T.; Linehan, J.C.

The objective of this project is to establish a quantitative mechanistic description of radical ion and radical mediated molecular rearrangements and atom transfer reactions important to thermal degradation of coal. Efforts include determination of absolute rates of organic free-radical rearrangements, rate expressions for hydrogen atom transfer between sulfur-centered radicals and thiols, and absolute rate expressions for hydrogen atom transfer to carbon-centered radicals from CH, PH, SH, MoH, and other heteroatom donors. 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  $^{195}\text{Pt}$  NMR to the determination of heteroatom structure in coal are under development. [4.1 FTE]

**Solar Energy Research Institute  
Golden, CO 80401**

**Solar Fuels Research Division \$281,000**

**98. Basic Research in Synthesis and Catalysis**  
DuBois, D.L.; Curtis, C.J.

The synthesis and characterization of new inorganic and organometallic complexes for evaluation as catalysts for the electrochemical reduction of  $\text{CO}_2$  and CO to methanol is under investigation. This research includes the elucidation of structural and electronic effects that are important in such catalytic processes. Palladium complexes containing triphosphine ligands were found to be capable of catalyzing the electrochemical reduction of  $\text{CO}_2$  to CO. The effect of structural modifications of the triphosphine ligand on catalytic rates, mechanism, turnover numbers, and mode of catalyst deactivation are being investigated. 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 are being examined, and the formation of a metal formyl complex in such a reaction has 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 \$1,055,000**

**99. Analytical Separations and Chemical Analysis**  
Fritz, J.S.

Work during the past year has led to two major developments, as well as solid progress in other areas. Small amounts of water in analytical samples can now be determined chromatographically in only 1.5 min. The mechanism of this unique detection system is now well understood and may pave the way for future improvements in chromatographic detectors. New chelating reagents now make it possible to determine several metal ions by complexation and chromatography. A modern adaptation of steam distillation is shown to be a very

attractive way to concentrate traces of many organic compounds from aqueous samples so that a chromatographic analysis is possible. [2.7 FTE]

### **100. Analytical Spectroscopy**

*Houck, R.S.; D'Silva, A.P.*

The general objective of this project 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, time-of-flight mass spectrometry, and ion implantation are also investigated. [5.0 FTE]

### **101. Chemical Analysis at Liquid-Solid Interfaces**

*Porter, M.D.*

This project examines new approaches for the construction and characterization of polymeric and monomolecular films at liquid-solid interfaces. Recent efforts have focused on: (1) probing the structure and reactivity of chemically modified polymer films with *in situ* Fourier transform infrared reflection spectroscopy and scanning tunneling microscopy; (2) examining the fabrication of artificial membranes as interfaces for molecular recognition; and (3) developing optical sensors with novel chemical analysis capabilities. The methodology based on infrared reflection spectroscopy and scanning tunneling microscopy relates the composition and molecular arrangement (spatial orientation and packing density) of the organic surface structures with their performance as barrier films to solvent penetration and electron transfer. The artificial membrane efforts examine the incorporation of size selective channels in long alkyl chain monomolecular assemblies. The sensor research explores new strategies for developing optical probes for remote-sensing and chemical analysis. [2.4 FTE]

### **102. Lasers in Analytical Chemistry**

*Yeung, E.S.*

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 transient atom sources, such as the laser microprobe, so that quantitation can become more reliable; (2) nonlinear Raman 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. [5.0 FTE]

## **Argonne National Laboratory Argonne, IL 60439**

**Chemistry Division**

**\$1,205,000**

### **103. Separations Science Related to Nuclear and Hydrometallurgical Technology**

*Horwitz, E.P.*

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 be used in conjunction with conventional extractants to achieve unique separations and to avoid waste disposal problems that are created by reagents used in the separation); (2) to determine quantitatively what structural features influence the solubility of carbamoylmethylphosphine oxide extractants in a normal paraffinic hydrocarbon; and (3) to develop improved methods for synthesizing new and existing organophosphorous extractants and complexants by studying the basic mechanisms for converting one or more phosphorous-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]

### **104. Particle-Induced Desorption/Ionization Mass Spectrometry**

*Hunt, J.E.*

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 with organic surfaces. The goal of these studies is to describe the processes that occur, and thus provide new knowledge relevant to analytical particle-induced desorption mass spectrometry techniques, such as FAB, SIMS, and <sup>252</sup>Cf-PDMS. Particle-induced desorption (PID) mass spectrometry, which began about a decade ago, has revolutionized mass spectrometry. Non-volatile compounds, once considered intractable, are now routinely analyzed by PID techniques. An exciting example is the recent mass determination of an intact protein of mass 34,000 amu. 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**      **\$490,000****105. Analytical Techniques with Synchrotron  
Radiation and Ion Beams***Jones, K.W.; Gordon, B.M.*

This project investigates new analytical techniques for elemental determinations and chemical speciation using synchrotron radiation from the National Synchrotron Light Source (NSLS). A beam line that will be used as an X-ray microscope/microprobe (XRM) beam line is now being installed. The new beam line is a major step beyond the one used for our initial work on XRM experiments. A monochromator and focusing mirror have been incorporated in the line, and the target position moved closer to the X-ray source point. The X-ray flux at the sample will be increased by approximately three orders of magnitude, and it will be possible to use either white light or monoenergetic photons. It should be possible to use either a collimator or secondary focusing system to make measurements with spatial resolutions below 10 micrometers and detection limits around 1 fg. Related work concerns improvements of detector systems and application of computed tomography and other imaging techniques to enhance the performance of the system. Measurements with ion beams are going on to develop accurate methods for assay of light elements with high sensitivity and excellent spatial resolution. The measurements include application of nuclear reaction methods, proton-induced X-ray emission, and accelerator mass spectrometry. [2.7 FTE]

**106. Analytical Techniques and Applications  
of Microparticles***Springston, S.R.; Tang, I.N.*

This project focuses on fundamental improvements in chromatographic separations and spectroscopic techniques for microanalysis. Cross-linked stationary phases are to be treated within capillary gas-chromatographic (GC) columns by using *in situ*-generated low-temperature plasmas to accomplish cleaning, deactivation, cross-linking, and modification of stationary-phase polarity. This research also fostered development of a novel cryogenic focusing injector. Since column performance in liquid chromatography (LC) is a sensitive function of the packing material characteristics, one novel strategy for enhancing performance is to isolate uniform fractions of silica-based material ranging from 1 to 2  $\mu\text{m}$ . Packing techniques will be studied. Peak symmetry, column permeability, and column efficiency will be related to packing structure. Other applications of this unique fractionation process may also be explored. In addition, a knowledge of the particle shape, size, and chemical composition of microscopic particles is vital to the understanding and control of the heterogeneous processes in which these suspended particles are playing a central role. Analytical techniques are being developed for *in situ* chemical analysis of suspended particles whose individual mass is only in the order of nanograms. Current effort centers on applying laser Raman spectroscopy to chemical characterization of a flowing particle stream. An investigation of Raman intensity enhancement by

resonance absorption will be undertaken in order to measure trace constituents in particles. Other advanced technologies such as Fourier transform (FT)-Raman spectroscopy employing the Nd:YAG laser and fluorescence spectroscopy using a tunable light source will also be investigated for chemical characterization of microscopic particles. One of the immediate applications of the present work is to couple the spectroscopic techniques developed here with an evaporative light-scattering detector, currently being developed elsewhere for liquid chromatography of high-molecular-weight organic compounds whose structural information cannot otherwise be obtained with conventional LC detectors. [1.9 FTE]

**Idaho National Engineering Lab  
Idaho Falls, ID 83415****\$225,000****107. Negative Ionization Mass Spectrometry***Delmore, J.E.; Appelhans, A.D.; Dahl, D.A.*

Several gas-phase and solid-phase 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 system currently being studied produces a variety of negative ions when electrons impact an adsorbate on an electrode. The hydride ion forms in good yield when hydrogen-containing molecules are adsorbed on the electrode. This is another potentially important analytical system, and the fundamental ion formation mechanism needs to be better understood. Other systems are being studied to understand the chemical interactions between adsorbates and the substrates as they pertain to gas-phase ion formation. Efforts are being made to relate this information to chemical reactions. In order to understand 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**      **\$100,000****108. Repetitively Pulsed Laser—Material Interaction***Russo, R.E.*

A repetitively pulsed laser-material interaction has been studied and developed as a direct solid sampling technique for chemical separations and analysis. The repetitively pulsed interaction can provide continuous, steady state atomic emission intensity from an analytical

excitation source. Steady state response provides improved precision over transient response and represents a controlled approach in which to study the laser-material interaction itself. This research focuses on studying the fundamental mechanisms underlying the repetitively pulsed interaction with condensed phase material and determining the parameters that influence continuous, steady state emission response in an analytical excitation source. Mechanisms of vaporization and ablation are investigated as to their influence on congruent sampling. Probe techniques, including acoustic (thermal expansion, shock wave) monitoring and optical probe beam deflection, are studied, developed, and tested to monitor the material surface during repetitive pulsing. [1.7 FTE]

**Mound Facility**  
**EG&G Mound Applied Technologies**  
**Miamisburg, OH 45343**

**Operations Department**                      **\$225,000**

**109. Isotope Separation Research and Development**

*Jepson, B.E.; Eppley, R.E.; Wilkes, W.R.*

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. The current emphasis is on macrocyclic ligands as metal ion hosts with the ligand immobilized on, or chemically bonded to, a solid support to enable the use of chromatographic separation techniques. The measurements of fundamental parameters are accomplished with column chromatography utilizing the breakthrough technique. This method yields accurate single stage separation factors, theoretical stage heights, packing capacities, and other information pertinent for evaluating applicability in practical enrichment processes. [1.9 FTE]

**Oak Ridge National Laboratory**  
**Oak Ridge, TN 37831**

**Analytical Chemistry Division**                      **\$1,813,000**

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

*Christie, W.H.; Todd, P.J.; Valiga, R.E.*

Secondary ionization mass spectrometry (SIMS) is an important analytical tool for both inorganic and organic chemical analysis. SIMS is noted for both its utility and extreme sensitivity. Research conducted here is directed toward understanding and taking advantage of matrix effects to improve performance and to obtain a better understanding of sputtering and secondary ionization in general. The yield and chemistry of secondary ions and sputtered neutrals are dominated by matrix effects, often in a complementary way. To study the various matrix effects, samples and the environment of the secondary ion source are first rigorously defined, and then changes in the behavior of secondary ions and sputtered neutral species conditions are observed as source conditions are

changed. Photoionization and electron impact ionization are employed to ionize sputtered neutral species. Both secondary ions and ionized sputtered neutrals transit the same mass analyzer but can be distinguished because the ion source optics are different for each. Organic research is conducted using a triple sector MS/MS spectrometer that permits isomeric distinction. Studies of inorganic samples are made on two virtually identical ion microprobes, for which the source optics of one are configured to transmit ionized sputtered neutrals while the other is configured for transmission of secondary ions. [1.9 FTE]

**111. Mass Spectrometry R&D for Organic Analyses**

*Glish, G.L.; Asano, K.G.; McLuckey, S.A.*

The study of gas phase ion chemistry and physics with the goal to develop techniques to analyze gas phase species is a focus of this work. Mass spectrometry/mass spectrometry is the primary technique used for these gas phase studies of unimolecular and bimolecular reaction processes. The work includes ionization methods, ion activation techniques, and protocols for analysis. The techniques being investigated and developed are primarily related to mass spectrometry. This work will lead to a better understanding of the intrinsic chemical properties of gas phase species, both neutral and ionic. The results will benefit mass spectrometry and other methods of charged particle analysis along with other techniques that probe fundamental properties of molecules. [2.6 FTE]

**112. Advanced Spectroscopic Methods for Chemical Analysis**

*Hulett, L.D.; Donohue, D.L.; Rosseel, T.M.; Dale, J.M.*

Positrons and heavy ions are being used in the development of new spectroscopic methods. The Oak Ridge Electron Linear Accelerator (ORELA) and the Holifield Heavy Ion Research Facility (HHIRF) provide a unique venue for this work. The ORELA has been retrofitted with a secondary target that collects waste gamma energy and produces a beam of monoenergetic positrons. Positrons are supplied on a 24-hour schedule 5 days per week. Extra costs for producing this new by-product are negligible; thus the facility constitutes the most practical source of monoenergetic positrons available. A high resolution X-ray spectrometer has been constructed and put into use. It operates in both the wavelength dispersive and energy dispersive modes and is capable of resolving subtle chemical shifts in ion-induced X-ray fluorescence spectra. In this past year's work, positrons have been used to ionize large molecules for purposes of mass spectrometry analysis. Mutagenic changes in DNA have been effected by positron irradiation. Future applications will include the characterization of superconductors, microscopy, and diffraction. Heavy ion induced X-ray satellite emission (HIXSE) has been used to study electronic structure in alloys and other solids. The most recent work dealt with chemical states of sulfur in ion implanted specimens. [2.8 FTE]

**113. 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.

The objective of this research project is to develop techniques for spectrochemical analysis with enhanced specificity and sensitivity. Emphasis is on high resolution laser spectroscopy. The project encompasses work on laser sources, measurement schemes, and sampling techniques for high spectral resolution and sensitivity. A low-pressure cell for atmospheric sampling is being developed. The combination of low pressure and Doppler-free laser spectroscopy provides a substantial reduction in homogeneous and inhomogeneous line broadening. Other studies with this sampling cell include atomic spectroscopy in supersonic expansions and resonance enhanced multiphoton ionization spectroscopy. Ion trap detection of CW laser ionization with unit mass resolution is under development. The use of photorefractive optical elements in CW dye lasers to narrow the linewidth and control the frequency is being explored. Other applications of photorefractive crystals in laser-based chemical analysis are being studied. [3.0 FTE]

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

Smith, D.H.; Walker, R.L.; Young, J.P.; May, M.P.; Shaw, R.W.

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. Examples are a high-precision method for determining calcium and the determination of promethium in the presence of excess samarium by resonance ionization mass spectrometry (RIMS). RIMS work provides much fundamental analytical spectroscopy data. For improved sensitivity and more accurate measurements, 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. [2.3 FTE]

**Chemical Technology Division**      **\$1,244,000**

**115. Chemical and Physical Principles in Multiphase Separations**

Byers, C.H.; Basaran, O.A.; Scott, T.C.; Perona, J.J.

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. 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. [3.9 FTE]

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

Cochran, H.D.; Byers, C.H.

Experimental and fundamental theoretical studies focus on relating macroscopic properties of mixtures to intermolecular interactions and molecular correlation functions for systems characteristic of extraction by supercritical fluids and adsorption from supercritical fluids. Studies based on distribution function theories from statistical mechanics have already led to new models for solubility and other equilibrium properties. Theoretical calculations have shown that a dissolved solute molecule is surrounded by a diffuse cluster of solvent molecules consistent with experimental observations; solute-solute aggregation is also predicted. Experimental studies of solubility of simple molecular solids,  $\text{CCl}_4$  and  $\text{MoF}_6$  in supercritical carbon tetrafluoride are nearing completion. [1.1 FTE]

**117. Chemistry of Actinides and Fission Products**

Toth, L.M.; Pruett, D.J.; Sherrow, S.A.

This project explores the fundamental chemistry of the actinide and fission product elements. Particular emphasis is given to those properties that determine chemical behavior in the various separations schemes currently in use, and to properties that may be exploited in the future. Within the project are three primary areas: (1) structure and chemical behavior of pure and mixed actinide hydrous polymers, (2) spectroscopy and photochemistry of actinide compounds, and (3) complex and redox behavior in aqueous and nonaqueous solvents. In the first area, small angle neutron/X-ray scattering measurements are used to determine the sizes and geometries of colloidal species; the polymer morphology is then correlated with its method of preparation and its properties, such as solubility and extractability. In the second area, matrix isolation spectroscopic/photochemical techniques are applied to the study of actinide reaction mechanisms. In the third area, a variety of techniques are used to investigate the thermodynamics and kinetics of complexation in solvent extraction schemes and in-room temperature molten salts. All three areas include mutually beneficial collaborative interactions with universities or other laboratories. [2.2 FTE]

**Chemistry Division**

**\$875,000**

**118. Chemical and Structural Principles in Solvent Extraction**

*Moyer, B.A.; Sachleben, R.A.; Burns, J.H.; McDowell, W.J.*

The purpose of this project is to elucidate 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. Specific attention is directed at recognition phenomena involving organophilic polydentate and macrocyclic ligands as hosts for metal cations. The approach involves synthesis of potential extractants and investigation of their properties by (1) X-ray structure determination of crystalline model compounds; (2) NMR, UV/vis, FTIR, and Raman spectral measurements; (3) molecular mechanics calculations; and (4) acquisition of equilibrium data by radiotracer and other analytical techniques followed by computer-aided equilibrium analysis. A major 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. This synergistic coupling is presently being studied in systems containing polydentate oxo and thia ligands combined with organophilic sulfonic and carboxylic acids. Selectivity is being assessed in the alkali, alkaline-earth, and first-row-transition metal series. The coupling of coordinating and cation-exchange groups contained in the same molecule is being examined in the coordination of alkali metals by ionizable dibenzo-14-crown-4 lariat ethers. [5.7 FTE]

**Pacific Northwest Laboratory  
Richland, WA 99352**

**Chemical Sciences Department**

**\$1,200,000**

**119. Analytical Mass Spectrometry Research**

*Baer, D.R.; Hubbard, C.W.; Kelley, J.M.; Stricklett, K.L.; Stoffel(s), J.J.; Ballou, N.E.; Styris, D.L.*

This project advances knowledge and techniques to improve and extend applications of mass spectrometry to problems in chemical and isotopic analyses. Elucidation of pertinent processes at the fundamental level is emphasized. The project (1) determines physicochemical mechanisms responsible for efficient ion production by surface ionization, and (2) develops methods for the control of surface work function of ion sources. Surface analysis and microchemical separations establish physical properties of surfaces and identify chemical pathways responsible for ion production. The new ionization source techniques that are being investigated include laser-assisted negative ionization and thermal vaporization with concurrent dc plasma ionization. [2.8 FTE]

**120. Laser-Based Analytical Techniques**

*Bushaw, B.A.; Cannon, B.D.*

The objective of this project is to develop and evaluate laser-based spectroscopic techniques for the measurement of trace materials produced in energy production. Recent

focus has been directed toward using metastable states of noble gas atoms as the basis for ultrasensitive isotopic analysis. Expected properties of the metastable atoms have been demonstrated including the measurement of isotope shifts in higher states, atomic beam deflection, isotope specific depletion of the metastables, and optical focusing of a beam of metastable atoms. The limitation to measurements using these techniques appears to be the efficiency with which the metastable states may be generated: production of ~0.05% metastables has been demonstrated using a dc discharge in a supersonic expansion, while calculations indicate a yield approaching 1% should be possible with this source. Accordingly, improving the yield of metastable production will be the emphasis of the project. Low-level detection via metastable state spectroscopy is attractive for other species besides the noble gases, particularly reactive atoms such as O, F, and P. Methods of metastable production other than electric discharges, including one- and two-photon laser schemes and resonance lamp excitation, will also be studied in an effort to maximize metastable production for a variety of species. [1.3 FTE]

**121. Fundamental Phase Partitioning in Supercritical Fluid Chromatography**

*Smith, R.D.; Yonker, C.R.; Fulton, J.L.*

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 chromatographic processes for polar and mixed supercritical fluid and solute systems, and the kinetic and thermodynamic limitations upon separations in supercritical media. A second area of concern is the exploration of local molecular structure and organized molecular assemblies (e.g., micelles and microemulsions) in supercritical fluid solutions and the effects related to 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 also being investigated as the basis for new separation methods caused by the unusual pressure dependence of phase behavior for these systems. Experimental results are being compared with theoretical methods for prediction of fluid-phase structure in the solvation region about a solute molecule. Experimental 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. 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]

**122. Mechanisms of High-Temperature Atomization in Chemical Analysis**

*Styris, D.L.; Prell, L.J.*

This project uses mass spectrometry and atomic absorption spectrometry techniques to elucidate mechanisms that control atomization on high-temperature surfaces. 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 these surfaces, during rapid thermal ramping, are monitored in real time. 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 being elucidated. The project is also providing the carbide formation data essential to establishing validity of existing atomization models. [1.7 FTE]

## Heavy Element Chemistry

**Argonne National Laboratory**  
**Argonne, IL 60439**

**Chemistry Division** **\$1,472,000**

### 123. Heavy Element Chemistry Research

*Morss, L.R.; Beitz, J.V.; Carnall, W.T.; Soderholm, L.; Sullivan, J.C.*

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 (especially in transuranium elements) influence the behavior of heavy 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** **\$1,318,000**

### 124. Actinide Chemistry

*Edelstein, N.M.*

The project objective is to study actinide materials to provide the basic knowledge necessary for their safe and economic use in present and future technology. The project 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 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 free ions and actinide ions in crystals are being pursued in order to understand their electronic structure. [14.0 FTE]

**Nuclear Science Division** **\$100,000**

### 125. Chemistry of the Heaviest Elements

*Hoffman, D.C.*

The objective of this project is to investigate some of the most fundamental chemical properties of elements 102 through 105, which are of particular interest in defining the architecture of the periodic table and in assessing the influence of relativistic effects. The actinide series ends with lawrencium (element 103), and the change in properties in going to elements 104 and 105 is especially important. In addition, relativistic effects have been predicted to become increasingly prominent for the higher Z elements and possible observable effects include anomalous trends in ionic radii and stabilization of different oxidation states relative to lighter homologs. These properties are being investigated for elements 102 through 105 on an "atom-at-a-time" basis by irradiation of heavy actinide targets such as  $^{248}\text{Cm}$  and  $^{249}\text{Bk}$  with light heavy ion beams at the Lawrence Berkeley Laboratory 88-inch Cyclotron. Recently, in a collaboration with German and Swiss scientists, automated separations systems were used to obtain important information about the aqueous and gas-phase chemistry of hahnium, (element 105) using 35-second  $^{262}\text{Ha}$ , the longest known isotope of hahnium. Methods are being developed to stabilize No(III) and deduce its ionic radius from measurements of its elution behavior relative to other actinides in reverse-phase chromatographic studies. Efforts to produce and identify new,

longer-lived isotopes of the heaviest elements which will permit more detailed studies of their chemical properties are continuing. [1.0 FTE]

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

**Isotope and Nuclear Chemistry Division**      **\$344,000**

**126. Actinide Chemistry in Near-Neutral Solutions**  
*Hobart, D.E.*

The efforts to provide fundamental physicochemical knowledge pertinent to the behavior of plutonium and other actinides under environmental conditions, in reprocessing and purification, and in nuclear waste isolation and storage are continuing. Several direct analytical methods have been reported for determination of the structure of plutonium(IV) colloid. For experimental reasons, all of these studies involved examination of the colloid in dried form. Recently, attempts have been made to deduce structural information for Pu(IV) colloid suspended in solution using Raman spectroscopy. Raman vibrational spectra have been obtained for concentrated hydrous samples of the colloid, and for powdered samples of high-fired plutonium dioxide. Although these samples are weak Raman scatterers, spectra were obtained for both samples. These spectra lend significant additional support to the previous conclusion that the molecular structure of Pu(IV) colloid is remarkably similar to that of the high-fired oxide. Investigations of the redox reactivity of plutonium(IV) colloid were continued and significant progress was made in studying the homogeneous oxidation reaction with cerium(IV) and in applying advanced voltammetric methods to study both oxidation and reduction of colloid at platinum and mercury electrodes. The reaction with Ce(IV) is quite complicated and the kinetics indicate at least three separate reactions. No voltammetric oxidation of colloid was observed, however, reduction waves were detected. The exact mechanism for this heterogeneous reaction is being investigated. New instrumentation is being applied to actinide speciation in near-neutral solutions. A state-of-the-art photoacoustic spectrometer is presently being constructed. In addition, a collaborative project with Stanford University uses X-ray absorption spectroscopy to study neptunium adsorbed on natural minerals such as goethite, a basic iron oxide. [0.6 FTE]

**127. Actinide Organometallic Chemistry**  
*Sattleberger, A.P.*

The project objective is to study fundamental aspects of early actinide (Th→Am) organometallic chemistry. Focus is on: (1) synthesis and characterization of new classes of actinide complexes containing nonclassical ligands, such as alkyls, silyls, amides, phosphides, and thiolates; (2) investigation of actinide-mediated small molecule chemistry, such as the insertion of carbon dioxide into actinide-alkyl, -amide, and -phosphide bonds; (3) variable temperature magnetic and electronic spectroscopic studies of three-coordinate  $AnX_3$  systems where X = alkoxide,

amide, or alkyl; (4) synthesis and characterization of actinide alkoxide and oxo/alkoxide cluster compounds that will serve as useful models for aqueous-phase actinide oxo/hydroxide complexes relevant to environmental speciation; and (5) development of low-temperature routes to known and new solid-state actinide materials from solution or the vapor phase. Recent results include (1) structural characterization of the first thermally stable homoleptic uranium alkyl complex,  $U[CH(SiMe_3)_2]_3$ ; (2) the synthesis and structural characterization of  $U_3(THF)_4$ , a valuable starting material for further explorations of uranium(III) chemistry; (3) the isolation and structure of the first uranium(IV) aryloxide complex,  $U(O-2,6-t-Bu_2C_6H_3)_4$ , and (4) the preparation and X-ray structure of  $Me_3SiN\equiv U[N(SiMe_3)_2]_3F$ , the first uranium(VI) complex with a multiple bond to a main group element other than oxygen. [0.8 FTE]

**Materials Science and Technology Division**      **\$120,000**

**128. Actinide High-Temperature Thermodynamics**  
*Kleinschmidt, P.D.*

The thermochemical parameters, bond dissociation energies, standard entropies, enthalpies and entropies of sublimation, and enthalpies of formation are being measured for the systems neptunium-fluorine and americium-fluorine. Both gas phase and solid species are studied. The parameters are measured primarily with Knudsen effusion mass spectrometry techniques. The parameters are systematically compared as a function of atomic number with the rest of the actinide series and with the lanthanide and transition metal series. Comparisons are made with other parameters such as spectroscopic and structural data and with the number of electrons available for bonding. [0.7 FTE]

**Oak Ridge National Laboratory**  
**Oak Ridge, TN 37831**

**Chemistry Division**      **\$1,258,000**

**129. Chemistry of Transuranium Elements and Compounds**  
*Keller, O.L.; Gibson, J.K.; Johnson, E.; Haire, R.G.; Payne, G.F.*

The studies in this project focus on Cm through Fm, the elements produced in the DOE National Transplutonium Production Program. Critical experiments are also performed on heavier elements (such as Md) made on heavy ion accelerators (such as the Lawrence Berkeley Laboratory 88-inch Cyclotron) using products of the Production Program (such as  $^{254}Es$ ) as targets. The two characteristics, which this project addresses theoretically and experimentally, that make the actinide series unique for understanding the periodic table are their 5f electrons and the large relativistic effects on their electrons. Of particular interest is the creation of bonds with the heavier actinides in which their usually localized, atomic 5f electrons become merged into shared-electron bonds with other atoms. Currently the only known way to bring

about such 5f orbital bonding is the application of extremely high pressures to the metals, which has been achieved in this project in the metals Am to Cf. Alloys and compounds will offer equally significant opportunities for high pressure studies. Organometallic compounds offer another possible avenue to 5f orbital bonding. Electron-rich, low valency, organometallic compounds are emphasized since they are more likely to allow electron-shared bonds than the highly oxidized, electron-poor ones. Compounds are characterized through optical and vibrational spectroscopy, magnetic susceptibility, and X-ray diffraction. The search for electron-rich compounds, such as CfO and CfS, will be pursued using a 1000 AMU Knudsen cell/mass spectrometer. For comparison with the opposite end of the redox scale, a 400 AMU Knudsen cell/mass spectrometer has been modified to withstand superoxidizing atmospheres for achieving new, highly oxidized, electron-poor species. Compounds such as AmF<sub>6</sub> and AmF<sub>7</sub> will be sought. Lower fluorides have already been studied. Relativistic quantum chemical calculations are being made and new theories are being developed to put these results in a form that has greater correlative and predictive power. [7.8 FTE]

## Chemical Engineering Sciences

Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

Applied Science Division \$328,000

### 130. Turbulent Combustion *Talbot, L; Cheng, R.K.*

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 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. The experiments use space- and time-resolved statistical data on scalar and velocity fluctuations to study the effects of large heat release on the turbulent flow field, in particular, the role of combustion in generating turbulence. Also studied 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 spatial 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 us and predictions obtained from the statistical model of Bray and Libby. [3.0 FTE]

Materials and Chemical Sciences Division \$161,000

### 131. High-Pressure Phase Equilibria in Hydrocarbon—Water (Brine) Systems *Prausnitz, J.M.*

Phase equilibria are required for the 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 selected data toward reliable general 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, especially those concerned with fossil fuels, fossil fuel-water mixtures, agricultural products, and 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 \$83,000

### 132. Thermophysical Properties of Mixtures *Erpenbeck, J.J.*

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 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. Merits of the various numerical techniques are considered in providing thermophysical properties. In the study of the "synthetic" NEMD technique, extensive MC-MD calculations, using the Green-Kubo method, have been made for the Lennard-Jones fluid near the triple point. Published Green-Kubo values of the viscosity coefficient are in sharp disagreement with the published NEMD results, being larger by about 40 percent. By studying both the dependence on system size and the contribution from the long-time tail of the stress autocorrelation function, it has been possible to bring all existing results on the subject into reasonable statistical agreement. The tail of correlation function is found to differ sharply from that predicted by simple mode-coupling theory, being larger by more than two orders of magnitude,

but supports the extended mode-coupling prediction of Kirkpatrick. The mode-coupling theory has also been applied to the thermal and viscous transport properties of mixtures, resolving previous problems associated with the choice of the fluxes and forces. While the long-time tail expressions are particularly simple when the isothermal gradient of the chemical potential is used as the driving force for diffusion, the tails have been evaluated for all three of the choices defined in the book by de Groot. For the case of an isotopic hard-sphere mixture at a volume of three times close packing, the long-time tails observed in MCMD calculations are found to be in close agreement with the mode-coupling predictions. [0.5 FTE]

## Sandia National Laboratories Livermore, CA 94550

Thermofluids Division-8363 \$350,000

### ***133. Analysis of Reacting, Turbulent Flows***

*Ashurst, W.; Kerstein, A.R.; Barr, R.K.;  
Marx, K.D.; Sanders, B.*

This project consists of the development of turbulence prediction methods for application to flows with high Reynolds numbers and large heat release. In each of the methods, emphasis is placed on understanding the detailed mechanisms of heat, mass, momentum, and species

transport in reacting flows. Four distinct modeling approaches are being studied, each focusing on a particular aspect of reacting turbulence. These four computational turbulence approaches, either directly or indirectly, impact the understanding of experimental data obtained in turbulent flow facilities at the Combustion Research Facility (CRF). Two of the approaches, time-averaged turbulence closure models and Vortex Dynamics, have been applied directly to combustion flows under experimental investigation at the CRF. The time-averaged closure studies have been extended to include the transport of a second phase, namely the vaporization and combustion of liquid fuel sprays in a turbulent flowfield. Vortex Dynamics continues to be a robust technique for studying the time-dependent evolution of turbulent flow structures in reacting and nonreacting flows, flows that cannot be treated by conventional time-averaged procedures. A third approach is based on a linear-eddy model of flame propagation in which a process of random exchanges between pockets of burned and unburned reactants provides turbulent burning velocities and other statistical properties. This procedure is showing remarkable ability to accurately predict differential molecular diffusion in CRF turbulent reacting flow experiments. A fourth approach involves the direct numerical simulation of the Navier-Stokes equations, where detailed fluid flow and species interactions provide new understanding of turbulent mixing phenomena. [2.0 FTE]

# OFFSITE INSTITUTIONS

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## Photochemical and Radiation Sciences

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**University of Akron**  
Akron, OH 44325

Department of Chemistry

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

This project involves fundamental studies of the factors that influence the rate of electron transfer. Current emphasis is on the study of charge neutralization and charge separation in diarylalkanes and  $b\pi$ - $a\pi$  charge-transfer complexes. A novel biphotonic laser excitation scheme is used to create intramolecular ion pairs in diarylmethanes via bicimers (dimeric species formed by the association of two identical, electronically excited molecules). The temporal characteristics of the ion pairs are then probed by laser kinetic spectroscopy to identify the mode and rate of their decays. The photophysical properties of electron donor-acceptor complexes in supersonic free jet are compared with those in condensed phase to obtain information concerning solvent and temperature dependence of nonradiative decay processes of charge-transfer excited states, including charge neutralization. The effects of vibrational and rotational degrees of freedom on the decay rates and conformational isomerization are also examined from the comparison.

**University of Alabama**  
Tuscaloosa, AL 35487

Department of Chemistry

**135. Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids**  
*Kispert, L.D.* **\$78,700**

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. Current studies involve electrochemical preparation of carotenoid cation radicals; ENDOR and ELDOR studies of carotenoid cation radical-polyiodide complexes; ENDOR studies of vinyl radicals in X-ray irradiated carotenoids and polyene cation radicals in X-ray irradiated Freon matrices; picosecond optical absorption measurements of carotenoids; CIDEP studies of carotenoid cation radicals; semiempirical molecular orbital calculations of carotenoid cation radicals, singlet

and triplet excited states; and photochemically generated carotenoid cation radicals. Attempts are being made to manipulate the host matrix so as to understand the carotenoid function (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

**136. Photoinitiated Electron Transfer in Multichromophoric Species: Synthetic Tetrads and Pentads**  
*Gust, J.D., Jr.; Moore, T.A.* **\$115,000**

The project objective is the synthesis and study of complex 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 tetrad C-P-Q<sub>A</sub>-Q<sub>B</sub> consisting of a porphyrin (P) linked to a carotenoid polyene (C) and a diquinone moiety (Q<sub>A</sub>-Q<sub>B</sub>) has recently been prepared. Absorption of light by this species results in the formation of an initial charge-separated state, C-P<sup>+</sup>-Q<sub>A</sub><sup>-</sup>-Q<sub>B</sub>, within 15 picoseconds of excitation. A series of electron transfer steps leads from this state to a final charge-separated state, C<sup>+</sup>-P-Q<sub>A</sub>-Q<sub>B</sub><sup>-</sup>, which is formed with a quantum yield of 0.50, and has a lifetime of up to 4 microseconds depending on conditions. The final state preserves about 1.1 eV of the energy inherent in the absorbed photon. Photophysical studies indicate that the high quantum yield is a consequence of the multistep nature of the electron transfer process. The knowledge gained from the studies of the tetrad is being used to design new tetrad and pentad artificial reaction centers in which the quantum yield, lifetime, and amount of stored energy have been further optimized. In addition, the tetrad is being incorporated into thin film monolayers deposited on conducting substrates in order to investigate the photoelectrochemical properties of these molecular devices.

**137. Particulate Models of Photosynthesis**  
*Seely, G.R.* **\$81,000**

The system under investigation consists of chlorophyll and other amphiphilic substances adsorbed to particles of polyethylene swollen with tetradecane and suspended in a thickened aqueous medium. Through the use of appropriate surfactants, the chlorophyll is rendered monomeric, and is capable of photosensitizing a number of redox reactions, including some in which the products are segregated into different phases (aqueous medium and particle interior). The scope of research has been expanded by investigation of recently discovered interaction

between chlorophyll and nonligating surfactants of the N-alkylpyridinium class, which has been demonstrated in toluene solution and apparently in the particles as well. The research is further extended by investigation of a photoreaction between chlorophyll and dithiobis (5-nitropyridine), first discovered in the particulate system, which apparently results in substitution of the pigment with an electron-accepting nitropyridinethiyl group. In photoreactions of these systems, emphasis is placed on reagents capable of reversible oxidation or reduction, especially when accompanied by a change of location in the system. Accurate fluorescence spectrometry continues to be an essential investigative tool.

**University of Arizona  
Tucson, AZ 85721**

**Department of Biochemistry**

**138. Photochemical Energy Conversion by  
Membrane-Bound Photoredox Systems**  
Tollin, G. **\$100,000**

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 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. 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. Systems that carry out vectorial electron transport across the bilayer and multistep electron transfer sequences are being developed. 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**

**139. Study of Intermediates from Transition  
Metal Excited-State Electron-Transfer Reactions**  
Hoffman, M.Z. **\$90,000**

Coordination complexes of Ru(II), especially those possessing aromatic  $\alpha$ -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) cage escape yields in the oxidative and reductive quenching of  $^*Ru(bpy)_3^{2+}$  (*bpy* = 2, 2'-bipyridine) and its derivatives and analogues; (2) the detailed photodynamics of the reductive quenching of  $^*Ru(bpz)_3^{2+}$  (*bpz* = 2,2'-bipyrazine) and  $^*Ru(bpm)_3^{2+}$  (*bpm* = 2, 2'-bipyrimidine) in the absence and presence of methylviologen (N, N'-dimethyl-4,4'-bipyridinium dication;  $MV^{2+}$ ); (3) the excited-state properties of Ru(II)-tris-heteroleptic complexes containing *bpy*, *bpz*, and *bpm*; (4) the acid-base, kinetic, and electrochemical properties of Ru(II) complexes possessing a reduced ligand-radical coordinated to the metal center; and (5) photophysics of new mono- and binuclear Ru(II) complexes containing ligands with extended structures.

**140. Photoinduced Electron Transfer in Ordered Polymers**  
Jones, G. **\$95,000**

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. Two dye/polymer systems have been chosen for investigation: (1) poly-L-tryptophan and its copolymers with poly-L-lysine, combined with the organic dye, eosin, and tertiary amine groups which can be attached, respectively, to N-terminal and C-terminal amino acids of the peptide chain; and (2) polyelectrolytes, including the derivatives of the naturally occurring polysaccharide, carrageenan, which have cyanine dye counter-ions electrostatically bound to the polymer surface as *J*-aggregates. Various electron transfer events are proposed including polymer end-to-end charge migration to traps that are synthetically introduced, or electron transfer along a chain of dye counter-ions. Emphasis is 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. Methods employed to study the bound dye systems include laser flash photolysis, NMR, circular dichroism, and cyclic voltammetry.

**Bowling Green State University**  
**Bowling Green, OH 43403****Center for Photochemical Sciences****141. Photoinduced Charge Separation by  
Polymer-Bound Chromophores**  
*Rodgers, M.A.J.* **\$42,500**

Amphiphilic polymers composed of methacrylic acid, styrene sulfonic acid, or pyrrolidone backbones with covalently linked chromophoric residues at a 1% or less loading are the subject of this work. Work to date has shown that in acidic aqueous media where the polymer chains assume a coiled conformation, significant charge separation occurs on sub-microsecond timescales when chromophore excited states interact with alkyl pyridinium ions contained in the aqueous phase. Picosecond laser flash spectrometry methods have been used to characterize the details of the yields of ion pair production at times below one nanosecond, on the premise that rapid charge annihilation is probably in competition with charge separation. The major effort to date has been installation and calibration of the picosecond absorption spectrometer. Preliminary experiments have indicated that efficient fluorescence quenching by alkyl viologens at high pH values is accompanied by charge separation that rapidly (ca 30ps) reduces to 50% of its initial value. This second component decays more slowly but is probably reduced to zero by a few nanoseconds. In acid solution (pH = 2.4), unquenched fluorescence has to date obscured clear indications of early ion production, but more needs to be done. Chromophores attached to the PMA or polystyrene sulfonate backbones have been anthracene and its phenyl and alkyl derivatives, pyrene and perylene. This project is conducted in collaboration with Professor S.E. Webber of the University of Texas at Austin.

**Brandeis University**  
**Waltham, MA 02254****Department of Chemistry****142. Mechanistic Studies of Excited State  
Chemical Reactions**  
*Linschitz, H.* **\$90,000**

This project is designed to clarify general mechanisms of energy-storing photochemical reactions. The research focuses on excited state electron-transfer reactions and the factors which control the yield of high-energy products in competition with dissipative quenching. These factors include spin-orbit coupling in an intermediate exciplex, solvent polarity and viscosity, the free energy change in the excited state reaction, and external magnetic fields. The main experimental technique is laser-flash photolysis, in which both reaction rates and product quantum yields are measured. The latter quantity requires determination also of extinction coefficients of transient species, triplet states, and radicals. Test systems include porphyrins, ketones, and inorganic ions whose thermodynamic and spectroscopic parameters are known.

**California Institute of Technology**  
**Pasadena, CA 91125****Department of Chemistry****143. Fundamental Electron Transfer Processes  
at the Single Crystal Semiconductor/Liquid Interface**  
*Lewis, N.S.* **\$105,000**

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 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 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)<sub>2</sub>. 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<sub>4</sub>-MeFc<sup>+10</sup> 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****144. Theoretical Studies of Electron Transfer  
in Complex Media**  
*Chandler, D.* **\$103,200**

The structures, distributions, and free energies of the transition states for the prototypical aqueous ferrous-ferrocyanide 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 quantum 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**

**145. Research in Chemical Kinetics**  
*Rowland, F.S.* **\$200,000**

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,  $^{38}\text{Cl}$ , and  $^{18}\text{F}$  atoms are studied with gaseous substrates. Thermalized tritium atoms added to olefinic positions in  $\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)_4$  and  $(\text{CH}_3)_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$  form excited radicals whose pressure-dependent decomposition indicates highly non-RRKM energy distribution because of restricted intramolecular energy flow. Similar studies with thermal  $^{18}\text{F}$  and  $^{38}\text{Cl}$  are being continued, with tests for the radiation-damage sensitivity of the reaction products. The mechanistic distinction between (1) "anti-Markownikoff" halogen atom addition to vinyl halides and (2) subsequent radical isomerization is under investigation with both  $^{35,37}\text{Cl}$  and isotopic substrates, and with  $^{38}\text{Cl}$ . Thermal  $^{35}\text{Cl}$  attack on C—C bonds is being explored with hydrocarbon and halocarbon substrates. Mechanistic studies of thermal  $^{18}\text{F}$  reactions with metallo-organic compounds are being extended to several silicon-based molecules. The reaction rates of bisulfide ion from aqueous hydrolysis of carbonyl sulfide toward metal precipitation, oxidation, and escape of  $\text{H}_2\text{S}$  to the gas phase are being studied in the laboratory, because of their significance toward such competition in oceanic environments. The mechanistic routes for product formation during HO oxidation are being studied with  $\text{O}^{14}\text{CS}$  and  $^{14}\text{CS}_2$ . Preliminary theoretical calculations are being conducted on the relative stability of various isomeric forms of  $\text{Cl}_2\text{O}_2$  because of their possible formation in dimerization reactions of gaseous ClO.

**146. Single-Collision Studies of Hot Atom Energy Transfer and Chemical Reaction**  
*Valentini, J.J.* **\$82,000**

This research project focuses primarily on experimental studies of the dynamics of chemical reactions and energy transfer in collisions at high energy. Among the systems that are now being emphasized are reactions of H atoms with  $\text{CD}_4$  to produce HD and  $\text{CH}_3\text{D}$  and the  $\text{H} + \text{CH}_3\text{Cl} \rightarrow \text{HCl} + \text{CH}_3$  reaction. Also being investigated is the  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  reaction. The experiments are state-to-state dynamics experiments, that is, the quantum states produced in the reaction are determined when selected energy states of the reactants are prepared. The experiments use pulsed-laser state preparation of the reactants, coupled with pulsed-laser spectroscopy to determine the quantum state distributions of the products. Simple theoretical models of the dynamics of these high energy reactions are developed using classical trajectory calculations, to help interpret the experimental results. Recently, these calculations have focused on reactions previously studied experimentally:  $\text{H} + \text{HX} \rightarrow \text{H}_2 + \text{X}$ , where X is a halogen atom (Cl, Br, or I). Some effort has

been expended on developing new sources of translationally hot reactants. Recent work on this topic has involved investigating the photodissociation of  $\text{CH}_3\text{I}$  as a source of fast  $\text{CH}_3$  radicals.

**University of California  
Los Angeles, CA 90024**

**Department of Chemistry and Biochemistry**

**147. Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin**  
*El-Sayed, M.A.* **\$127,000**

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 ( $\text{ADP} \rightarrow \text{ATP}$ ) transformation. These studies deal with the (1) to (3) steps. 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 has been studied using picosecond streak camera fluorescence techniques. The number of different TRP sites are 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), which is found to strongly correlate with the strongest quenching of the TRP fluorescence, is controlled by specific protein conformation changes, which are catalyzed by surface charges.

**University of California  
Santa Barbara, CA 93106**

**Department of Chemistry**

**148. Energy Transformations in Organometallic Complexes**  
*Watts, R.J.* **\$120,000**

Research identifies and characterizes species that could have application as photocatalysts in conversion of solar energy into chemical fuels. Chemical synthesis is used as a starting point in preparing organometallic species which, by prior related experience and chemical/physical intuition, might provide new insights into solar photocatalysis. Once prepared and purified, these species are structurally characterized by a variety of physical techniques, including NMR and infrared spectroscopies and 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. Once 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 electron transfer processes are emphasized because these types of processes occur in many known photoconversion schemes. Effects of environmental parameters such as temperature, solvent polarity, and viscosity are assessed in order to provide further insights into the environmental sensitivity of both intramolecular and intermolecular electron transfer and energy transfer processes. These types of studies also provide insight into the extent and relative location of charge separation caused by electronic excitation. Prior experience and chemical/physical intuition have led to an emphasis on studies of materials that contain metal-carbon sigma bonds formed as a result of ortho-metalation processes. Combination of the strong sigma-donor character of the carbon-bonded portion of ortho-metalating ligands with the pi-electron-accepting character that can be introduced in the coordinating portion leads to organometallic complexes in which low energy charge-transfer is promoted. The electron-rich nature of the metal center in these species renders them strong photoreducing agents in their excited states.

## Clemson University Clemson, SC 29634-1905

### Department of Chemistry

#### 149. Intramolecular Energy Transfer Reactions in Polymetallic Complexes

Petersen, J.D. **\$80,000**

Polymetallic complexes that are covalently bridged by aromatic, nitrogen, heterocyclic ligands display various amounts of electronic communication across the bridge. For bidentate bridging ligands, such as 2, 2'-bipyrimidine (bpm), 2,3-bis(2'-pyridyl)pyrazine (dpp), and 2,3-bis(2'-pyridyl)quinoxaline (dpq), the metal-metal distance is similar but the electronic communication in the ground and excited states is different. The ability of bpm to effectively couple excited states has been displayed by the emission quenching of the ruthenium center in  $(bpy)_2Ru(bpm)Fe(CN)_4^+$ , a process not observed for the analogous dpp bridged species. Metallocluster complexes with specific properties have been prepared with various bridging ligands to electronically couple the metal centers. For example, by controlling the nature of the three bridging ligands around a central ruthenium center, the initial metal-to-ligand charge-transfer excitation and the subsequent energy- or electron-transfer process that follows the excitation can be directed into a specific terminal metal center. These data suggest that molecular charge separation can take place in tetrametallic complexes with the correct selection of bridging ligands.

## University of Colorado Boulder, CO 80309

### Department of Chemistry and Biochemistry

#### 150. Investigation of Redox Processes at Semiconductor Electrode/Liquid Junctions

Koval, C.A. **\$80,000**

Fundamental aspects of electron transfer reactions that occur at the semiconductor/solution interface (SEI) are being investigated because understanding these reactions is essential for improvement of photoelectrochemical cells (PECs) and related devices. One area of current research is developing solution redox systems capable of detecting hot electron reactions. Recently, reduction of a Cu(I) complex ion to copper metal at the p-InP/acetonitrile interface was used to obtain the first distinct chemical evidence for a hot electron process in a PEC. Current research in this area is directed toward establishing the mechanism of this process as well as attempting to increase the quantum yield. The unique properties of metal chalcogenide semiconducting electrodes, such as tungsten diselenide, are used to determine factors that control dark currents in PECs. Recent research involves construction of a variable temperature microcell that will be used to investigate electron tunneling at the SEI. In order to analyze the results of these experiments from a theoretical standpoint, a nonlocal formulation for the image potential of ions near the SEI has been developed.

## Columbia University New York, NY 10027

### Department of Chemistry

#### 151. Laser-Enhanced Chemical Reaction Studies

Flynn, G.W. **\$121,000**

This project employs extremely high resolution infrared diode lasers to study fundamental combustion and collision dynamics and photochemical reaction processes. High-energy atoms are produced by excimer laser photolysis and are used as reagents to investigate collisional excitation of individual rotational and vibrational states of molecules and to study the chemical reaction processes occurring as a result of encounters between translationally hot atoms and molecules. Translational energy recoil of the target molecules is probed by measuring the time-dependent Doppler profile of the molecular infrared transitions. Infrared up-conversion with  $LiIO_3$  crystals is being used to extend the speed of the diode probe technique to the subnanosecond time domain. Chemical reactions between hot Cl atoms and stable molecules are probed with quantum state resolution using this diode laser probe method. The relative efficiency of quenching highly excited molecules such as azulene by different vibrational modes of bath gases is being studied. High frequency bath modes are generally inefficient compared to translational and rotational motions at quenching species with more than  $10,000\text{ cm}^{-1}$  of internal energy. Highly energetic and reactive  $O^1D$  atoms with 0.67 eV of translational energy are quenched by  $CO_2$  through a variety of physical and chemical mechanisms that include

electronic to vibrational and translational to vibrational energy exchange.

**Dartmouth College  
Hanover, NH 03755**

Department of Chemistry

**152. Photoexcited Charge Pair Escape and Recombination**  
*Braun, C.L.*

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; no hot electron effects are observed. In solid-state electron donor-acceptor materials, the escape and recombination mechanism is apparently quite different. The time-resolved current that arises from single-photon excitation in the charge-transfer absorption band of the 1:1 mixed crystal, phenanthrene:pyromelliticdianhydride, agrees with a model in which the free charges originate from thermal ionization of singlet-charge transfer excitons which live for many nanoseconds. A number of donor-acceptor geometries are explored in experiments to understand factors that limit efficient charge pair separation.

**University of Houston  
Houston, TX 77004**

Department of Chemistry

**153. Charge Separation in Photoredox Reactions**  
*Kevan, L.* **\$115,000**

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, tetramethylbenzidine, and phenothiazines in frozen vesicles and micelles to produce the cation radical is 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 radical cation with respect to the vesicular structure. Current emphasis is on location control of electron donors and electron acceptors relative to the assembly interface by attachment of variable length alkyl chains and by variation of the interface charge. The location is being probed 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

**154. Theoretical Studies of Electrons and Electron Transfer Processes in Fluids**  
*Kestner, N.R.* **\$75,000**

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, pressure, mobility and reactivity, and 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 studies. Various supporting projects are also under way to more accurately calculate the intermolecular interactions needed in this work and to eliminate the basis set superposition errors.

**Marquette University  
Milwaukee, WI 53233**

Department of Chemistry

**155. Resonance Raman and Photophysical Studies of Polypyridine Complexes of Ruthenium**  
*Kincaid, J.R.* **\$75,000**

The detailed studies of the vibrational spectra of the ground and <sup>3</sup>MLCT (metal-to-ligand charge transfer) excited states of the parent complex, Ru(bpy)<sub>3</sub><sup>2+</sup>, have been extended. Specifically, a normal coordinate calculation for the <sup>3</sup>MLCT state has been essentially completed. The lack of availability of excited state infrared active modes and the absence of effective enhancement for several mid-frequency modes in the excited state prompted the study of additional isotopically labeled species so as to provide a larger number of observed frequencies. Spectra have now been obtained for ten selectively deuterated analogues as well as the <sup>15</sup>N and doubly labeled <sup>15</sup>N, 3, 3'-deuterated species. Addition of these data reinforces the validity of the normal mode calculation and strengthens confidence in the derived force field. Systematic resonance Raman and time-resolved resonance Raman studies of several *bis*-heteroleptic complexes have continued. Previously initiated studies of the properties of specific complexes in organized media have also continued resulting in improved methods for the preparation,

analysis, and characterization of entrapped homogeneous complexes.

**Massachusetts Institute of Technology  
Cambridge, MA 02139**

**Department of Chemistry**

**156. Interfacial Systems for Photochemical Energy Conversion**  
*Wrighton, M.S.* **\$260,000**

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) multi-component 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 photoconversion devices with efficiencies in excess of 10% for conversion of sunlight to electricity or fuel (in the form of H<sub>2</sub> from H<sub>2</sub>O). Preliminary results show promising leads in molecular approaches to photoconversion which theoretically will be no less efficient than semiconductor-based devices.

**University of Massachusetts  
Boston, MA 02125**

**Department of Chemistry**

**157. Magnetic Resonance Studies of Photosynthetic Reaction Centers and Porphyrins**  
*van Willigen, H.* **\$84,500**

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. In addition to the time-resolved CW ESR measurements, the photoinduced electron transfer from porphyrins to quinones has been investigated with the novel Fourier Transform (FT) ESR technique. With this method the time resolution extends into the nanosecond domain. The time-resolved techniques are used to

measure electron transfer rates. Furthermore, the measurements give information on spin state evolution of paramagnetic transient intermediates. This provides an insight into the mechanism of the electron transfer process.

**University of Minnesota  
Minneapolis, MN 55455**

**Department of Chemistry**

**158. The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems**  
*Lipsky, S.* **\$91,959**

Photophysical properties of organic molecules are being studied that have relevance in determining their behavior when subjected to high-energy radiation. Because the formation of ion pairs appears to be an important precursor of chemical damage in irradiated liquids, recent studies have concentrated on ion-pair properties. These are generated by photoionization, and their decay is observed by (1) recombination (to give fluorescence) and (2) "escape" (to give photocurrent). These observations are made as functions of photon energy, nature of the liquid, concentration of electron scavenging impurities, and strength of externally applied electric and magnetic fields. Current work includes (1) measurement of the effect of low concentrations of highly electron-affinic scavengers to enhance ion-pair escape probabilities, (2) measurement of the photoionization yield and electron thermalization range spectra of aromatic solutes in nonpolar liquids, and (3) measurement of the transient displacement currents and transient fluorescence intensities induced by pulsed vacuum ultraviolet excitation of saturated hydrocarbon solutions. The magnetic field alters the yield of fluorescence by influencing the probability that recombining pairs are triplet or singlet. The magnitude of this effect provides information on loss-of-spin coherence because of electron attachment and spin thermalization processes.

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

**Chemical Kinetics Division**

**159. Pulse Radiolytic Studies of Electron Transfer Processes and Applications to Solar Photochemistry**  
*Neta, P.* **\$195,000**

Electron transfer processes involving reactive intermediates in aqueous and nonaqueous solutions are studied by the pulse radiolysis technique. Reactive intermediates are produced by an electron pulse, and their reactions are followed by time resolved absorption spectrophotometry. These studies are concerned with kinetics, thermodynamics, and mechanisms of reactions of organic and inorganic radicals and unstable oxidation states. Focus is on the study of electron transfer reactions of metalloporphyrins and other compounds that may be applicable to solar

energy conversion systems. These include one-electron reduction and oxidation to radical anions and cations and the subsequent reactions of these species. Of particular importance are the reactions with colloidal catalysts that lead to decomposition of water to hydrogen and oxygen. Current studies are concerned with the reaction between metalloporphyrin radical cations and iridium oxide colloids resulting in the oxidation of water to oxygen. The redox potential of the porphyrin, the electrostatic charges on both the porphyrin and the catalyst, and the solution pH exert a strong effect on the rate and outcome of these reactions. Similarly, metal colloids are studied as catalysts for hydrogen evolution from water, utilizing either a porphyrin radical anion or other reducing species. Studies are also conducted on organic peroxy radicals and inorganic radicals to understand the mechanisms of their reactions and to determine the fundamental properties.

**University of Nebraska  
Lincoln, NE 68588-0304**

**Department of Chemistry**

**160. Electrochemical and Optical Studies of  
Model Photosynthetic Systems**

*Cotton, T.M.*

**\$24,800**

In continuing efforts to model the photosynthetic reaction center by means of monolayer and multilayer constructions, current activities are directed at three specific goals. The first goal involves monolayer characterization of a number of different chlorophyll structures that will find appropriate compounds that have monolayer orientations different from that of bacteriochlorophyll. Use of such compounds will provide information regarding the influence of orientation on electron transfer. Covalently linked dimeric forms are of special interest in this regard. The second goal involves electron transfer in pigment-protein associations where a large (26 kDalton) channel protein has been formed into spread monolayers. This appears to be the first time such a structure has been observed to form ordered monolayers, and opens the possibility of manipulating the compound much in the manner that smaller, traditional monolayer-forming molecules have been employed. Attempts are being made to produce mixed monolayers of the protein and chlorophylls; in addition, a water-soluble electron acceptor will be incorporated into the interior hydrophilic core of the protein. The third goal uses covalently linked porphyrin dimers to produce template sites in self-assembled monolayers, with the aim of producing noncovalently associated chlorophyll dimers after reconstitution with chlorophyll itself. Such systems will be characterized by scanning tunneling microscopy, as well as by Raman and other optical techniques.

**161. High-Energy Halogen Atom Reactions Activated by Nuclear Transformations**

*Rack, E.P.*

**\$58,000**

The major objective of this project is to understand the stereochemistry, energetics, and systematics of highly energetic halogen atom homolytic bimolecular substitution reactions ( $^3\text{HH}^2$ ) at the chiral centers of enantiomeric and diastereomeric molecules in the gas and condensed phases. In an attempt to ascertain halogen atom kinetic

energy effects, the stereochemistry of exothermic thermalized fluorine and chlorine atom homolytic bimolecular substitution at chiral centers is studied. Specifically conventional nuclear methods are used to obtain information in the following areas: (1) energetic F, Cl, Br, and I stereochemistry and mechanisms with chiral 2-halopropionyl halides and related substrate molecules; (2) stereochemistry of energetic halogen-for-halogen substitution reactions with *d,l*, *meso*-2,3-dihalobutanes; (3) stereochemistry of thermalized F and Cl exothermic substitution reactions with chiral 2-halopropionyl halides and *d,l*, *meso*-2,3-dihalobutanes; and (4) calculations of conformational energies for 2-halopropionyl halides and 2,3-dihalobutanes (using molecular-mechanics techniques). Reactions of  $^{82}\text{Br}$  and  $^{130}\text{I}$ , activated by isomeric transition, are studied in liquid aqueous solutions of alkyl halides and halogenated biomolecules to determine the applicability of various models such as the Auger effect coulombic explosion model to liquid state systems. Practical applications of recoil atom chemistry to activation analysis of biological or environmental samples are conducted.

**University of North Carolina at Charlotte  
Charlotte, NC 28223**

**Department of Chemistry**

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

*Rillema, D.P.*

**\$87,500**

The photophysical properties of various monometallic and multimetallic complexes are being examined. A ruthenium(I) tetracarbonyl complex was isolated and an X-ray structure confirmed the presence of four carbonyl ligands. The complex luminesced in acetonitrile solution at  $\sim 540$  nm when excited at 355 nm. Similar energy excitation of  $[(\text{bpy})_2\text{Ru}(\text{Mebpy-Mebpy})\text{Re}(\text{CO})_3\text{py}]^{3+}$ —where bpy is 2, 2'-bipyridine, py is pyridine, and Mebpy-Mebpy is 1, 2-bis(4'-methyl-2,2'-bipyridyl-4-yl)ethane—in acetonitrile led to dual luminescence. Emission was observed at 538 and 604 nm. The multimetallic complexes studied were ruthenium(II)/ruthenium(II) species bridged by biimidazole and bibenzimidazole. In these complexes the  $\pi^*$  energy levels of the ligands remained relatively fixed, whereas the  $d\pi$  energy levels of the central ruthenium(II) core changed. The photosubstitution behavior of ruthenium(II) bipyridine complexes was also studied. The  $\text{Ru}(\text{bpy})(\text{bpz})^{2+}$  core was found to represent a photochemically stable unit which could be used to study charge transfer events to an electron acceptor ligand, such as  $\text{MeQ}^+$ , where  $\text{MeQ}^+$  is N-methyl-4,4'-bipyridine ion.

University of North Carolina  
 Chapel Hill, NC 27514

Department of Chemistry

**163. Energy Conversion Processes Based on  
 Molecular Excited States**  
 Meyer, T.J.

The photochemistry of transition metal complexes is being explored in energy conversion processes at the molecular level. New classes of metal complex sensitizers are being synthesized. Based on measurements of their photochemical and photophysical properties, it has been possible to design sensitizers that combine high light absorptivity with chemical stability and desirable excited state properties. Synthetic procedures have also been developed for the incorporation of transition metal complex sensitizers into soluble polymers by chemical binding. Even more complex molecular assemblies have been prepared that contain controlled loadings of light absorbers and quenchers. Initial studies on these complex systems show that it is possible to design polymers in which light-induced, intrapolymeric energy, and electron transfer events can be initiated and controlled.

Northwestern University  
 Evanston, IL 60201

Department of Chemistry

**164. Intramolecular Electron Transfer Rates**  
 Hupp, J.T.

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. New developments in the past year have come in the Raman project where the previous intramolecular studies have now been extended to selected intermolecular systems. Intervalence enhancement of Raman scattering has been detected for outer-sphere pairs like  $\text{Ru}(\text{NH}_3)_6^{3+}$ ,  $\text{Ru}(\text{CN})_6^{4-}$  and methylviologen,  $\text{Fe}(\text{CN})_6^{4-}$ . A time-dependent analysis of the enhanced scattering intensities can lead to complete (quantitative) mode-by-mode descriptions of vibrational reorganization for each of the redox couples. Other new work has come in the area of environmental effects upon intramolecular electron transfer. Here enormous optical-barrier effects (up to  $2000\text{ cm}^{-1}$ ) have been observed due to counter-ion coupling to electron transfer. Finally, in an exploratory effort, bimolecular photoredox studies (rhenium tricarbonyls with nitroaromatics) have been initiated in an unusual new reaction medium: supercritical  $\text{CF}_3\text{H}$ .

Oregon Graduate Center  
 Beaverton, OR 97006

Department of Chemical and Biological Sciences

**165. Fundamental Studies in Oxidation-  
 Reduction in Relation to Water Photolysis**  
 Hurst, J.K. **\$101,600**

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. Emphasis has been placed in recent studies on objectives (2) and (3). It has been demonstrated that methyl viologen ( $\text{MV}^{2+}$ ) bound to anionic dihexadecylphosphate vesicles is capable of mediating transmembrane oxidation-reduction by a mechanism that involves transverse diffusion of  $\text{MV}^{2+}$  radical cations. This demonstration constitutes a breakthrough which is crucial to developing a detailed understanding of reaction mechanisms in microphase-organized redox systems. Transmembrane electron exchange involving monoalkylviologens is an order of magnitude slower, again suggesting a strong diffusional component to these reactions. Current efforts are directed at distinguishing between alternative kinetic models by obtaining essential structural and thermodynamic data and by direct measurement of transverse diffusion rates using radioisotope methods. Also under investigation are a series of dimeric ruthenium  $\mu$ -oxo ions as potential water-oxidation catalysts.

Pennsylvania State University  
 University Park, PA 16802

Department of Chemistry

**166. The Gaseous Free-Radical and Ion Chemistry of Silanes, Germanes, and Phosphines**  
 Lampe, F.W. **\$83,500**

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-phosphine, and germane-phosphine 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 ( $\alpha$ -Si:H) produced by the low-intensity  $\gamma$ -ray irradiation of silane admixed with noble gases.

**167. Experimental and Computational Studies of Polar Solvation**

*Maroncelli, M.*

**\$96,000**

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.

**Princeton University**  
**Princeton, NJ 08544**

**Department of Chemistry**

**168. Surface Chemistry at Semiconductor-Electrolyte Interfaces**

*Bocarsly, A.B.*

**\$115,000**  
**(15 months)**

This study encompasses the role of surface chemistry in photodecomposition processes occurring at the cadmium chalconide-electrolyte interface as well as primary processes associated with water oxidation at stable semiconductor surfaces. Recent work has focused on the surface chemistry of  $n$ -CdX (X = S, Se, Te) photoelectrodes in a  $\text{Fe}(\text{CN})_6^{4-/3-}$  electrolyte. Illumination of such interfaces produces a layer of cadmium ferrocyanide on the electrode surface. This overlayer has alkali cation exchange properties. 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%. Substitution of ascorbate for the ferrocyanide 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. In a separate investigation of  $n$ -TiO<sub>2</sub> photoelectrolysis (water) cells using laser-induced optical transients, it has been found that the mechanism of water oxidation varies with the pH of the electrolyte. In base, the predominate reaction channel is inner sphere. This latter process is very efficient and involves the formation of a Ti-OH surface site. Similarly,  $p$ -GaP based cells, which reduce water to H<sub>2</sub> are found to be sensitive to chemisorption of alkali cations. The interfacial charge transfer process is found to be enhanced by the presence of cesium ions.

**169. Photochemistry of Metalloporphyrins**

*Spiro, T.G.*

**\$125,000**

The photochemistry of metalloporphyrins is being explored with a view toward developing new photoenergy transfer catalysts. Porphyrin cation radicals, the primary product 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. These will be applied to linked porphyrins which show optical evidence for electron transfer photochemistry. 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**

**170. Femtosecond Studies of Electron Transfer Processes at Semiconductor Interfaces**

*Miller, R.J.D.*

**\$85,000**

Interfacial electron transfer is one of the most fundamental steps in surface reaction processes and is the key step in many solar energy transduction schemes. Three new, surface-specific, optical spectroscopies have been developed for the direct study of the electron transfer event. Holographic gratings, written in the form of free electron hole carriers, have demonstrated that electron transfer at the  $n$ -TiO<sub>2</sub> (001)/H<sub>2</sub>O interface involves thermalized hole

carriers at the atomic surface. The hole carrier mass ( $m_h^*$ ,  $\geq 3$ ), thermalization dynamics, and interfacial electron transfer rate constants have been determined and are all consistent with a thermalized electron-transfer mechanism involving adsorbed hydroxide as the electron donor. Optical excitation of surface acoustic waves, using grating excitation, has given direct evidence for a phase change of the water layer to a solid phase at the  $\text{TiO}_2$  surface boundary. This new optical method is extremely sensitive. Light diffraction detection in the presence of an electron-hole pair phase grating for reference heterodyne detection enables a detection limit for surface displacements of  $10^{-3}$  Å. Studies of n-GaAs (100) have also been conducted. In this high mobility material, surface state trapping is found to occur in less than 30 psec. The non-linear optical properties of the initial trap indicate a highly delocalized site, i.e., a structural defect and not a molecular impurity. The other new optical method relies on the electro-optic effect to measure changes in electron density at the surface. A crystal distortion that occurs upon changes in trap occupation number makes this technique extremely sensitive to surface state dynamics. Both grating and electro-optic surface state studies indicate that shallow defect states are the initial intermediate in the overall interfacial electron-transfer mechanism at the GaAs (100) surface.

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

Whitten, D.G.

\$120,000

These investigations are focused on light-induced electron transfer reactions in solution which can lead to efficient and potentially useful net chemical reaction. Most of these processes involve single electron transfer quenching of an excited state and subsequent steps involving cooperative reactions between ion radicals formed in the quenching step. Recent efforts have been directed toward the use of 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 two heteroatom functionalities (amine, alcohol, thiol, thioether, ether); one of these 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. A number of aspects of these reactions is being investigated, including solvent effects, stereochemical requirements, the role of acceptor and donor structure, and reaction energetics. The key features of this investigation are the findings 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-days) timescales.

**University of South Florida  
Tampa, FL 33620**

**Department of Chemistry**

**172. Frontier Orbital Symmetry Control of Intermolecular Electron Transfer**

Stevens, B.

\$110,000  
(18 months)

Electron-donor-acceptor (EDA) frontier  $\pi$ -orbital correlations provide a basis for identifying adiabatic or nonadiabatic intermolecular electron-transfer processes involving intermediate EDA complexes or exciplexes, with the prediction that weak EDA complexes provide the highest yields of separated radical ions unless isomerization-induced correlation switching is significant. Rates of photoinduced electron transfer and of geminate charge neutralization are being measured for 1:1 EDA complexes that exhibit two absorption bands tentatively associated with strong and weak complexes, and in a series of terminally functionalized (DA) polyphenyls that have been synthesized. From the theoretical standpoint, the roles of promoting, accepting, and van der Waals vibrational mode symmetries in coupling locally excited and charge transfer configurations are being examined.

**Stanford University  
Stanford, CA 94305**

**Department of Chemistry**

**173. Energy Transfer Processes in Solar Energy Conversion**

Fayer, M.D.

\$127,000

Experiments and theory are being used to study photoinduced, intermolecular electron transfer processes and electronic excitation energy transport phenomena in complex molecular systems. Photoinduced electron transfer from an excited donor to an acceptor produces chemically reactive anion and cation radicals. The ability of these species to do useful chemistry is inhibited by electron back transfer. Recent experiments and statistical mechanical theory show that an understanding of this problem in solid solutions at intermediate (100 psec) to long times is now in hand. Additional important theoretical advances have been made. The influence of solvent relaxation on electron back transfer has been included in the theory to provide an accurate short time description. Brownian diffusive motion of the donors and acceptors can also be treated. This means that the theory can describe liquid solutions as well as solid solutions. Furthermore, experiments have been performed and theoretically analyzed that are the first excitation energy transfer experiments in polymeric solids in which the rate of excitation transfer among chromophores attached to a polymer chain has been increased by changing the thermodynamic interactions of the chain with the bulk polymeric material in a solid blend. The extent of chain collapse has also been calculated, with great accuracy, by using the excitation transport observables.

Syracuse University  
Syracuse, NY 13244-1200

Department of Chemistry

**174. Photochemical Solar Energy Conversion  
Utilizing Semiconductors Localized in  
Membrane Mimetic Systems**  
Fendler, J.H. **\$115,000**

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

Department of Chemistry

**175. Studies of Radiation-Produced Radicals  
and Radical Ions**  
Williams, T.F. **\$110,000**

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; and (4) the photogeneration of radical ions in solution and at colloidal semiconductor surfaces.

University of Texas  
Austin, TX 78712

Department of Chemistry

**176. Organic Redox Phototransformations at  
Chemically Modified Surfaces**  
Fox, M.A. **\$110,000**

This research project seeks to establish the mechanisms of organic redox reactions that occur upon photoexcitation of native and chemically modified semiconductor surfaces. New catalysts are being designed to act as relays for multiple electron transfer. Organometallic coordination polymers and N-alkylated nicotinamide derivatives are being tested as vehicles for catalytic reduction of solution phase substrates. New electrode materials prepared for electrocatalytic studies are being evaluated for high turnover catalytic sequences. Techniques for anchoring the specifically designed electrocatalysts include covalent binding, electrosorption, and chemisorption of redox active polymer layers. Polymers with pendent chromophores are being synthesized in order to produce materials capable of efficient light collection and vectorial energy migration.

**177. Studies of Photochemically and Electro-  
chemically Driven Electron Transport in  
Zeolites**  
Mallouk, T.E. **\$79,100**

This project involves the study of zeolites as templates for self-organizing molecular and semiconductor-based electron transport assemblies. Ion exchange and size exclusion effects can be used to cause molecules to line up into multicomponent chains that are well-organized at the molecular level. Both photochemically and electrochemically driven unidirectional electron transport has been achieved with these chains. The photochemistry and electrochemistry of zeolites L and Y ion-exchanged with viologens and covalently linked ruthenium(polypyridyl)—viologen complexes are being investigated. In this system attempts are being made to improve upon a previously demonstrated ca. 15% quantum efficiency for long-lived charge separation, by varying the separation distances and energetics of the redox-active components. Using internally platinized zeolites and electrochemically reversible anionic electron donors, the factors that influence the photochemical evolution of hydrogen from water are being studied. Quantum-size TiO<sub>2</sub> has been prepared in zeolites L and Y in an effort to create systems in which the TiO<sub>2</sub> mediates light-induced electron transfer between surface-bound sensitizers and electron acceptors within the zeolite cavities. This work also involves fundamental studies of electron transfer rates between molecules co-adsorbed on macroscopic oxide semiconductor particles. The role that tunneling and/or superexchange via delocalized semiconductor orbitals plays in facilitating intermolecular electron transfer is being investigated.

**178. Photoinduced Charge Separation by  
Polymer-Bound Chromophores**  
Webber, S.E. **\$42,500**

New work has emphasized polymethacrylic acid with various loadings of phenanthrene and naphthalene, which



are suitable chromophores for excimer laser 308 nm radiation that is currently being used for experimentation. With this particular combination of chromophores and wavelengths, it is possible to study only the electron quenching of the aromatic triplet state using a zwitterionic viologen (SPV = 4,4'-bipyridinium, 1'-bis(trimethylene sulfonate)). While many aspects of the observations have not been thoroughly quantified, the overall efficiency of reduction of SPV is quite high at all pHs. Unlike our observations for anthracene singlet-state quenching, the most efficient production of  $SPV^{\cdot-}$  seems to be at higher pH, where the polyacid is deprotonated. This observation is consistent with the idea that an S=1 geminant radical pair is slow to recombine to yield the S=0 ground state, such that the requirement for the polymer to provide hydrophobic protection (as is the case at low pH) is lifted. These systems exhibit the unexpected result that the efficiency of intersystem crossing ( $S_1 \rightarrow T_1$ ) is strongly dependent on aromatic loading. This result will strongly affect the strategy for using photon harvesting polymers, since it implies that use of singlet state energy transfer along the chain will be more productive than attempting to use the triplet state.

**Washington University  
St. Louis, MO 63130**

**Department of Chemistry**

**180. Reaction Studies of Hot Silicon, Germanium, and Carbon Atoms**

*Gaspar, P.P.*

**\$80,000**

The project goal is to determine: (1) the reactions of high-energy silicon, germanium, and carbon atoms; (2) how their reactions take place; and (3) how the reaction pathways are influenced by the energy and the electronic states of the free atoms and of the reactive intermediates that they produce. Silicon, germanium, and carbon atoms are formed with high kinetic energies and electronic excitation by nuclear transformations such as  $^{31}P(n,p)^{31}Si$ ,  $^{76}Ge(n,2n)^{75}Ge$ , and  $^{12}C(p, pn)^{11}C$ , and at thermal energies by evaporation of the pure elements. A nearly complete picture of the primary reactions of silicon atoms recoiling in phosphine-silane mixtures has been developed, with the finding that silyl and disilyl radicals,  $^{31}SiH_3$  and  $^{31}SiSiH_5$ , are formed as minor, but mechanistically revealing, reactive intermediates. The role of recoiling silicon ions  $^{31}Si^+$  has been quantitatively assessed via the yields of alkyl group abstraction products.

**Washington State University  
Pullman, WA 99164-4630**

**Department of Chemistry**

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

*Crosby, G.A.*

**\$90,000**

Complexes of Zn(II) and Cu(I) that display charge-transfer transitions in the visible region of the spectrum are under spectroscopic investigation. Both emission intensity and lifetime have been recorded for a series of Cu(I) complexes as a function of temperature in a rigid matrix. Arrhenius parameters have been determined for the thermal repopulation of the singlet state(s) from the lower-lying triplet state(s). Zn(II) complexes containing N-heterocyclic ligands and also coordinating sulfur ligands have been extensively studied. The species containing bidentate sulfur-coordinating ligands exhibited unexpected spectral differences from those observed from the analogous monodentate species. X-Ray structural determinations revealed that the former species form binuclear and trinuclear clusters—an entirely unexpected result, but one that explains the substantial differences between the spectra of the two classes of compounds. Synthetic, structural, and spectroscopic studies of Cu(I), Zn(II), Pt(II), and Cd(II) complexes containing both acceptor and donor ligands are under way. Thermal modulation measurements are also planned for those systems exhibiting sets of excited states spanning 20 to 500 wave numbers.

**Wayne State University  
Detroit, MI 48202**

**Department of Chemistry**

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

*Endicott, J.F.*

**\$90,000**

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). Very considerable electronic mixing of donor and acceptor seems to be an important characteristic of polynuclear transition metal complexes with  $CN^-$  bridging groups, with the effects of mixing being manifested in spectroscopic, photophysical, and even in ground state electrochemical behavior. Studies of the relaxation pathways of Cr(III) complexes are mapping out the factors controlling transition metal excited state lifetimes. The  $(^2E)Cr(III)$  relaxation rate can be represented by  $(\tau)^{-1} = k_r + k_{nr}^{lf} + k_{nr}^{hf} + k(T)$  where  $k_r$  is the radiative relaxation rate constant,  $k_{nr}^{lf}$  and  $k_{nr}^{hf}$  are the limiting low temperature nonradiative rate constants that depend on low frequency and high frequency vibration modes respectively, and  $k(T)$  represents thermally activated pathways. The variations of  $k_r$ , spanning about a 100-fold range, arise from  $^2E - ^4T_2$  spin-orbit coupling of

the excited states, and similar electronic factors are important in  $k_r$ ,  $k_{nr}^{lf}$ , and  $k_{nr}^{hf}$ . Several pathways have been shown to contribute to  $k(T)$ .

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## Chemical Physics

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### Aerospace Corporation Los Angeles, CA 90009

#### Aerophysics Laboratory

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

Bott, J.; Cohen, N.

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 will be 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<sub>2</sub>, CH<sub>4</sub>, i-C<sub>4</sub>H<sub>10</sub>, and c-C<sub>5</sub>H<sub>10</sub> have been analyzed and published. 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<sub>3</sub>) and to determine the reaction path.

### Arizona State University Tempe, AZ 85287

#### Department of Chemistry

#### 183. Electronic Structure and Reactivities of Clusters Containing Heavy Atoms

Balasubramanian, K.

\$83,860

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 provide important clues to our 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<sub>4</sub>, In<sub>3</sub>, Ag<sub>4</sub>, and Pd<sub>3</sub> 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<sub>2</sub>, Zr<sub>2</sub>, Au<sub>2</sub>, 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<sub>2</sub> and M<sub>2</sub> + H<sub>2</sub>. The potential energy surfaces of MOH<sub>2</sub>, NbH<sub>2</sub>, YH<sub>2</sub><sup>+</sup>, ZrH<sub>2</sub><sup>+</sup>, RuH<sub>2</sub>, and so forth, are being determined

with the objective of understanding the reactivities of these atoms with H<sub>2</sub>. The Pt<sub>2</sub> + H<sub>2</sub> system is 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

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

Lichtenberger, D.L.

\$94,000

Photoelectron spectroscopy is used to provide detailed and independent information regarding the electronic interactions of organic molecules with transition metals. A formal relationship between measured molecular ionization energies and thermodynamic bond dissociation energies has been established. The value of this relationship has been demonstrated in the study of the electronic factors that contribute to  $\beta$ -hydride addition to a metal center in niobocene and tantalocene complexes. In relation to the study of metallocenes, detailed electronic structure features of osmocene have been obtained from the vibrational fine structure and spin-orbit splitting in the high-resolution photoelectron spectrum of this complex. Important information has been obtained on metal—methylene, metal—alkylidyne, and metal—heteroatom multiple bonding interactions. For instance, the catalytic activity of the metal—alkylidyne complexes increases with increasing M—C  $\pi$  ionization energies. This has specific implications for the mechanism controlling the polymerization reaction. The electronic effects of intermolecular interactions are observed by comparing the ionizations of metal complexes in the gas phase with the ionizations of thin solid organometallic films. Further instrumentation developments for improved He(I)/He(II) UPS, XPS, and Auger capabilities are under way.

### Brown University Providence, RI 02912

#### Department of Chemistry

#### 185. Interactions of Molecules with Surfaces

Greene, E.F.

\$83,000

Helium diffraction has been used to study structural phase transitions on the (111) and (100) surfaces of silicon. Earlier evidence that the 7 x 7 to 1 x 1 phase transition at 1138  $\pm$  7 K on Si(111) is an order-disorder one has been confirmed. Scattering from Si(100) shows that the 2 x 1 reconstructed surface, stable at room temperature, undergoes a structural phase transition at 930  $\pm$  20 K. This had previously been deduced only from theoretical calculations and earlier experiments in this laboratory on the kinetics of desorption of alkali atoms

from this surface. Temperature rises observed when molecular beams from a nozzle at 300 K strike a small platinum surface also at 300 K can be as large as 100 K for argon seeded into an excess of helium. Interpretation of the results gives: (1) a way of measuring the temperature  $T_s$  a surface attains at steady state due to interactions of gas molecules but in the absence of heat conduction or radiation; (2) a simple determination of the average kinetic energy of an atomic beam without the need for measurement of the velocity distribution or the flux in the beam; and (3) a quantity like an accommodation coefficient that is useful for predicting the amount of energy transfer between gases and solids. Measurement of the dependence of the yields of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$  ions on the kinetic energy with which beams of the corresponding alkali atoms hit a Si(111) surface show an abrupt rise above a threshold energy of 0.5 to 1.0 eV. Fitting to a simple model leads to a determination of the rate of electron transfer from the atom to the silicon as this varies with their distance of separation. At 5 Å the rate for all three atoms is  $1 \times 10^{11 \pm 0.2} \text{ s}^{-1}$ .

**University of California  
Davis, CA 95616**

**Department of Chemistry**

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

*Jackson, W.M.*

**\$60,000**

Rate constants for the reactions of CN radicals with methane, ethane, and propane have been measured. The propane rate constants indicate that the activation energy is negative as suggested in earlier work. This has been interpreted in terms of a long range attractive potential model that suggests that weak attractive forces promote the chemical reaction. IR fluorescence studies have begun on the quenching of vibrationally excited radical species from the 193 nm photolysis of ketones, acids, alcohols, alkynes, and dienes using a transient IR spectrophotometer. The results thus far indicate that the S/N ratio is high enough to allow a spectral resolution on the order of a few wave numbers. Such studies are important for understanding the role of vibrational energy in flames. Studies have also begun on the quenching of  $\text{C}^1\pi_g$  state of the  $\text{C}_2$  radical, an important combustion intermediate. The quenching rate constant with rare gases and with reactive gases such as  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{O}_2$  will be measured.

**Catholic University of America  
Washington, DC 20064**

**Department of Chemistry**

**187. Studies of Combustion Kinetics and Mechanisms**

*Gutman, D.*

**\$150,000**

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 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.,  $\text{CH}_3 + \text{CH}_3$ ), reactions of free radicals with atomic oxygen (e.g.,  $\text{O} + \text{C}_2\text{H}_5$  and  $\text{O} + \text{C}_3\text{H}_5$ ), and reactions of these same free radicals with molecular oxygen (e.g.,  $\text{C}_2\text{H}_5 + \text{O}_2$ ). 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**

**188. Quantum Dynamics of Fast Chemical Reactions**

*Light, J.C.*

**\$83,000**

The current objectives of this research are the quantum formulation and accurate evaluation of cross sections and rate constants of fast gas phase reactions. These goals are now feasible to approach because an accurate  $L^2$  representation of three atom systems (in three dimensions) in the interaction region is now possible using discrete variable representations and the technique of sequential diagonalization and truncation. Thus one can solve explicitly for the eigenvectors of the Hamiltonian, the Green's function, and the flux operators. The thermal rate constants for the  $\text{H} + \text{H}_2$  reaction 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**

**Department of Chemistry and Biochemistry**

**189. Laser Photoelectron Spectroscopy of Ions**

*Ellison, G.B.*

**\$105,000**

This project involves the spectroscopic study of ions and radicals likely to be reactive intermediates in combustion processes. Mass-selected ion beams are prepared and crossed with the output of a CW ArII laser operating on a single line ( $\lambda_0 = 488 \text{ nm}$ ). The laser detaches electrons

from the negative ions ( $M^-$ ) and the kinetic energy (KE) of the scattered electrons are monitored using a pair of hemispherical analyzers:  $M^- + h\nu_0 \rightarrow M + e^-$  (KE). The borane ion,  $BH_3^-$ , is isoelectronic with the methyl radical,  $CH_3$ . The photoelectron spectra of  $BH_3^-$  and  $BD_3^-$  and have been measured from which the electron affinities of borane,  $EA(BH_3) = 0.039 \pm 0.015$  eV and  $EA(BD_3) = 0.027 \pm 0.014$  eV, have been determined. The peak splittings and intensities demonstrate that the  $BH_3^-$  ion and the  $BH_3$  neutral have very similar geometries and the spectra are consistent with a planar structure for both species. Variational calculations of a coupled oscillator basis over an *ab initio* potential give an excellent fit to the experimental frequencies and photodetachment Franck-Condon factors. This *ab initio* model leads to equilibrium geometries with both  $BH_3$  and  $BH_3^-$  as planar molecules with  $r_e(BH_3^-) = 1.207$  Å and  $r_e(BH_3) = 1.188$  Å. We find  $\Delta H_{f_0}^0(BH_3^-) = 23.1 \pm 3.8$  kcal mol $^{-1}$ . In a separate study, the photoelectron spectra of  $CH_3CO^-$  and  $CH_2DCO^-$  have been measured. The acetyl radical has been observed as an adduct of  $CH_3$  and CO and the electron affinities,  $EA(CH_3CO) = 0.423 \pm 0.037$  eV and  $EA(CH_2DCO) = 0.418 \pm 0.038$  eV, have been obtained. The photoelectron spectra show excitation in the C—C—O bending vibration of the radical and bending frequencies  $\nu_{11}(CH_3CO) = 490 \pm 30$  cm $^{-1}$ ,  $\nu_{11}(CH_2DCO) = 500 \pm 50$  cm $^{-1}$ , and  $\nu_{11}(CH_3CO^-) = 570 \pm 180$  cm $^{-1}$  have been measured. From a Franck-Condon analysis of the vibronic peak intensities the C—C—O bond angles have been estimated for the acetyl and radical:  $\alpha(CCO)[CH_3CO^-] = 110^\circ \pm 5^\circ$  and  $\alpha(CCO)[CH_3CO] = 133^\circ \pm 5^\circ$ . These angles are consistent with *ab initio* Hartree Fock geometry optimizations of both the ion and radical (in a triple zeta plus polarization basis set). Finally, the measured electron affinities can be used to determine the following thermodynamic parameters:  $\Delta H_{f_{298}}^0(CH_3CO) = -5.4 \pm 2.1$  kcal/mol,  $\Delta H_{f_{298}}^0(CH_3CO^-) = -14.9 \pm 2.3$  kcal/mol,  $DH_{298}(CH_3-CO) = 10.6 \pm 2.2$  kcal/mol and  $DH_{298}(-CH_3-CO) = 17.6 \pm 2.3$  kcal/mol.

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

Leone, S.R.

**\$85,000**

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 HF product from chloro-fluoro-ethylene, CCH from acetylene, and CO from acetone. The dynamics of these decomposition processes are also explored. A new version of the apparatus is operational and will obtain time resolutions of 10's of nanoseconds for the study of chain reaction systems.

**Columbia University  
New York, NY 10027**

**Department of Chemistry**

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

Bersohn, R.

**\$85,000**

Elementary gas-phase reactions, both bimolecular and unimolecular, are being studied by laser generation of reactants and laser-induced fluorescence detection of the reaction products. Recent experiments have focused on excited alcohol molecules, exchange of H atoms with D atoms in deuterated unsaturated hydrocarbons, and the thermalization of fast hydrogen atoms. Excited alcohol molecules have been prepared by electronic excitation and by chemical activation. Electronic excitation of methanol or ethanol at 193 nm causes a direct subpicosecond dissociation of a fast hydrogen atom. Vibrationally hot methanol and ethanol prepared by the insertion reaction of  $O(^1D)$  with methane and ethane decomposed into slower hydrogen atoms. Collisions of fast ( $\sim 1$  eV) H atoms with  $C_2D_2$  molecules produce fast D atoms with 60% of the initial H atom kinetic energy. A similar result is obtained with  $CH_3CCD$  showing that the exchange process at this energy is direct, not involving an intermediate internally equilibrated radical. H atoms with translational energies around 2.5 eV were prepared by photodissociating  $H_2S$  in a large excess of rare gas. By measuring the Doppler broadened fluorescence excitation spectrum as a function of rare gas pressure, the time evolution of the velocity distribution is measured.

**Cornell University  
Ithaca, NY 14853**

**Department of Applied and Engineering  
Physics**

**192. Mass Resolved Resonance Ionization Spectroscopy of Combustion Radicals**

Cool, T.A.

**\$85,000**

A better understanding of the reaction mechanisms by which soot and toxic aromatic compounds are formed in hydrocarbon combustion depends on the development of suitable methods for monitoring trace concentrations of several key radical intermediate species. The goal of this research is the application of a new laser-based technique to this task. Resonance-enhanced multiphoton ionization spectroscopy (REMPI) is capable of the detection of combustion radicals at the part-per-million level. Widespread application of REMPI for flame diagnostics is presently limited by a scarcity of spectroscopic data for Rydberg electronic states of several key combustion radicals. A systematic search for REMPI spectra for excitation of the  $3s^2\Pi$  and  $3p\sigma^2\Pi$  Rydberg states of the ethynyl radical,  $C_2H$ , has been completed. A weak, diffuse REMPI spectrum near 276 nm has been observed and tentatively assigned to the ethynyl radical. In the course of this work, a new electronic state in the  $C_2$  radical has been identified. Thirteen vibronic bands assigned to the two-photon  $1^1\Delta_u \leftarrow A^1\Pi_u$  transition have been observed by REMPI spectroscopy for laser wavelengths ranging from

370 to 480 nm. Accurate spectroscopic constants have been obtained for the previously unobserved  $1^1\Delta_u$  state. Work has been completed on the REMPI spectroscopy of the  $3p^2\Pi$  Rydberg state of the HCO radical which has resulted in the first laser-based *in situ* monitoring of HCO profiles in hydrocarbon flames.

#### Department of Chemistry

#### 193. State-Resolved Studies of the Methyl Radical

Houston, P.L.

\$85,000

The methyl radical is important in combustion, in atmospheric chemistry, and in the decomposition of energetic materials. This project will develop 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 will be 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  $\text{CH}_3\text{I}$ , acetone, and  $(\text{CH}_3)_2\text{M}$  ( $\text{M} = \text{Cd}, \text{Zn}, \text{Hg}$ ) at 266, 248, and 193 nm. Once characterized, the methyl fragments from these dissociations will be used to investigate the rates of two important combustion reactions. The  $\text{CH}_3 + \text{O}_2$  reaction will be investigated to learn how the rate depends on the reacting methyl distribution, while the  $\text{H} + \text{CH}_4$  reaction will be investigating what methyl distributions are produced.

#### Emory University Atlanta, GA 30322

#### Department of Chemistry

#### 194. Theoretical Studies of Combustion Dynamics

Bowman, J.M.

\$79,663

The objectives of this research project are to obtain 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  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  and  $\text{H}_2 + \text{CN} \rightarrow \text{HCN} + \text{H}$ . 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 under way, and results on the  $\text{OH} + \text{H}_2$  will be forthcoming. Detailed quantum studies of direct and resonant scattering are under way for the  $\text{H} + \text{CO}$  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 initiated using a new code developed in the past several months.

This code is being applied to the HCO system, as well as to resonances in IHI and ClHCl.

#### Georgia Institute of Technology Atlanta, GA 30332

#### School of Physics

#### 195. Reactive Collisions of High-Temperature Systems

Graff, M.M.

\$83,579

A neutral beam apparatus is being developed to study reaction dynamics of neutral systems whose endothermicities or activation barriers preclude study by molecular beam techniques. The experiment will investigate the dependence of reactivity on collision energy and on molecular internal energy. Systems to be studied initially include the basic oxygen-hydrogen combustion system  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$  and its isotopic analogs. The experiment is based on a double mass spectrometer design, modified for the study of neutral species. Production of a velocity- and mass-selected beam of radicals is effected by photodetachment of the corresponding negative ion with a large-frame argon ion laser in an intracavity multipass configuration. Neutrals are detected by ionization and mass analysis. The influence of  $\text{H}_2$  rotational energy will be studied by comparing results for para- and normal hydrogen at low temperature. The structure of the excitation function will be observed for the entire range of chemically interesting collision energies.

#### University of Georgia Athens, GA 30602

#### Center for Computational Quantum Chemistry

#### 196. Potential Energy Surfaces for Chemical Reactions

Schaefer, H.F.

\$95,000

In recent years theoretical chemistry has become a significant source of broad generalities and 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. Using *ab initio* quantum mechanics, reactions being studied include  $\text{CH}_3 + \text{O}_2$ ,  $\text{CH}_4 + \text{O}_2$ ,  $\text{C}_2\text{H}_5 + \text{O}_2$ , and  $\text{C}_2\text{H}_6 + \text{O}_2$ . Other problems of current interest include the reactions of triplet methylene with saturated hydrocarbons, the heats of formation of the  $\text{C}_2\text{H}$  and  $\text{C}_2\text{H}_3$  radicals, the infrared spectra of  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$ , quantitative theoretical predictions of infrared and Raman spectral intensities, the characterization of ketocarbenes, the understanding of the relationship between the two nearly degenerate isomers of the  $\text{HO}_2$  dimer, hydrocarbon rearrangements on small metal clusters, and the nature of hydrated hydronium clusters.

**Harvard University**  
**Cambridge, MA 02138**

**Division of Applied Sciences**

**197. Fundamental Studies of Carbenes and Hydrocarbon Radicals**

Thaddeus, P.; Gottlieb, C. **\$70,000**

This project emphasizes fundamental millimeter-wave spectroscopy of the carbenes, carbon chain radicals, and ring-chain hybrids, nearly all of which are involved in reactions of hydrocarbon combustion. The investigation is being made with a very sensitive free-space, double-pass millimeter-wave spectrometer. The reactive species are produced in a dc glow discharge through flowing mixtures of gases at a pressure of approximately 10 mTorr. Measurements of the rotational spectra of the deuterated carbon-chain radicals  $C_4D$  (in the ground and three vibrationally excited states) and  $C_5D$  show that the structures of long carbon-chain radicals can be predicted remarkably well from *ab initio* calculations. The rotational spectra of  $C_2H$  and  $C_4H$  in their lowest excited vibrational states have also been measured. Much spectroscopy remains to be done on vibrationally excited states of reactive hydrocarbons because all hydrocarbons have excited vibrational states and, as has been demonstrated, reactive hydrocarbons in low-lying vibrational states are readily detectable at millimeter wavelengths. A frequency survey in a discharge through  $C_2H_2$  and He has established that the density of unknown lines at the limit of our sensitivity is quite large, on average one every 50 MHz. The major effort during the next year will be the identification of the fairly large number of reactive hydrocarbon molecules (presumably radicals, isomers, and carbenes) now being found that are of importance in combustion processes. The molecules that will be sought in the next year are cyclopentadienylidene, vinylidene, methyl carbene, propargylene, vinylmethylene, and  $C_5H_2$ , a ring-chain hybrid whose structure was recently calculated *ab initio*. All of these molecules should be readily identifiable, given the excellent quality of the spectra, because all are predicted to have distinctive spectroscopic signatures.

**Howard University**  
**Washington, DC 20059**

**Department of Chemistry**

**198. Photolytic Processes for Measurement of Combustion Heats of Formation and Reaction Rates**

Halpern, J.; Okabe, H. **\$55,000**  
**(36 months)**

Alkoxy radicals, RO (R =  $CH_3O$ ,  $C_2H_5O$ ,  $i-C_3H_7O$ , and  $t-C_4H_9O$ ), are important species in the combustion of hydrocarbons. This project includes measurements of their kinetics, fluorescence spectra, and thermochemistry. RO radicals were produced by the laser photolysis of RONO at 355 nm or 193 nm. Following 355 nm photolysis RO\* emission was excited by a fixed frequency 337 nm nitrogen laser. Quenching rate constants have been measured against NO and  $O_2$ . Direct emission has been measured following 193 nm laser photolysis which produced excited

radicals. The collision-free lifetime of  $i-C_3H_7O$  is  $0.64 \pm 0.09$  microseconds and that of  $n-C_3H_7O$  is  $0.70 \pm 0.08$  microseconds. The fluorescence spectra of  $i-C_3H_7O$ ,  $n-C_3H_7O$ , and  $t-C_4H_9O$  were measured. To determine heats of formation of RO radicals, the threshold for production of excited RO from the photolysis of RONO is measured. Tunable light is produced by Raman shifting doubled Nd-YAG pumped dye laser light. The threshold for  $CH_3O$  production from  $CH_3ONO$  photolysis and  $C_2H_5O$  production from photolysis of  $C_2H_5ONO$  lie above 215 nm. A laser photolysis/ESR detection system is being tested for detection of complex gas-phase free radicals.

**University of Illinois**  
**Chicago, IL 60680**

**Department of Chemical Engineering**

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

Kiefer, J.H. **\$90,000**

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 gradient (net endothermic rate) and a 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 and mechanism for 1, 3-butadiene dissociation. A study of the dissociation of vinylacetylene has led to the proposal of a new carbene insertion 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 a study of allene/propyne pyrolysis and further development of the acetylene model.

**Department of Chemistry**

**200. Kinetics of Elementary Atom and Molecule Reactions**

Gordon, R.J. **\$90,000**

The project objective is to study the chemical reactions and vibrational energy transfer rates of small molecules. Recent efforts have dealt with the photodissociation of carbon dioxide and quenching of electronically excited carbon monoxide. When  $CO_2$  is irradiated 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 produced is 5%. This finding contradicts the expectation of spin conservation, which predicts only singlet products. The results can be understood if the energized molecule exists as a long-lived complex, which is able to undergo a nonadiabatic transition to the ground electronic potential energy surface. In the second study, CO was excited to the B state using a 115 nm vacuum ultraviolet laser. Fluorescence from this state was monitored in real time. The addition of various quenching gases accelerated the decay

rate of the fluorescence. Very rapid quenching rates have been measured so far for HCl, H<sub>2</sub>, D<sub>2</sub>, and N<sub>2</sub>, with no apparent effect of CO rotational state. These results are consistent with a direct, long-range interaction between CO and the quenching molecule, followed by radiationless dissociation of the acceptor.

**University of Iowa**  
**Iowa City, IA 52242**

**Department of Chemistry**

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

*Tardy, D.C.*

**\$84,642**

The understanding of intermolecular vibrational energy transfer (IVET) is important since it is involved in any mechanism in which internal energy is added or removed from molecules. The data base for the details of IVET for highly excited polyatomic molecules is inadequate and must be expanded. The overall objectives of this project are: (1) to determine the dependence of energy relaxation on excitation energy and on the molecular complexity of substrate and deactivator, (2) to assess the importance of intermolecular attractions on IVET, (3) to obtain more detailed information on the energy distribution after collision, and (4) to evaluate the importance of IVET on high temperature unimolecular reactions. The first three objectives are being met by experimentally measuring the time evolution of the average energy of the vibrationally excited species (hydro- and fluorocarbons excited by a pulsed CO<sub>2</sub> laser) and the average energy transferred into relative translation via time-resolved IR spectrometry, interferometry, and optoacoustic techniques. Trajectory calculations simulating IVET are being performed for model substrate/deactivator pairs to provide additional details and insight on the important parameters. Calculations for high temperature unimolecular reactions indicate that IVET effects are significant and must be correctly taken into account.

**Jackson State University**  
**Jackson, MS 39217**

**Department of Chemistry**

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

*Bhatnagar, R.*

**\$49,128**

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<sub>2</sub> laser while others are collisionally pumped by the CO<sub>2</sub> laser excited donor molecules such as SF<sub>6</sub> and CH<sub>3</sub>F. 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<sub>2</sub> 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**

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

*Clouthier, D.J.*

**\$60,000**

The spectroscopy and excited-state dynamics of sulfur-containing polyatomic transient species of importance in combustion chemistry are under investigation. Using pyrolysis jet spectroscopy, in which precursor molecules are pyrolyzed in the throat of a supersonic nozzle, the spectra of such transient species as H<sub>2</sub>CS, H<sub>2</sub>CCS, S<sub>2</sub>O, and C<sub>2</sub>S have been observed or are currently under investigation. Spectroscopic techniques for analysis include laser induced fluorescence, photoacoustic spectroscopy, and absorption spectroscopy.

**Massachusetts Institute of Technology**  
**Cambridge, MA 02139**

**Department of Chemical Engineering**

**204. Aromatics Oxidation and Soot Formation in Flames**

*Howard, J.B.*

**\$105,000**

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 electron microscope analysis of molecular-beam deposits. 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 1,000 amu and larger, containing alkyne, alkene, and alkane structures.

Department of Chemistry

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

Silbey, R.; Field, R.W. \$141,000

The spectra of highly excited ground electronic state acetylene have been studied using new spectroscopic methods in order to determine the energies of metastable isomeric forms of acetylene and the dissociation energy of acetylene. These new methods include spectral cross correlation and Fourier transform of the stimulated emission pumping (SEP) spectra. Using these, a resonance associated with the vinylidene structure ( $H_2CC$ ) has been found at an energy  $\sim 15600\text{ cm}^{-1}$  above the ground state with a lifetime of  $\sim 200$  femtoseconds. In addition, experiments at higher energy have provided evidence for the large amplitude motion of H orbiting the CCH core. Other experiments have been performed that give an upper bound for the dissociation energy of acetylene of 553.5 kJ/mole.

University of Massachusetts  
Amherst, MA 01003-0035

Department of Chemistry

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

Jackson, B.E. \$34,251

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

Department of Atmospheric, Oceanic, and Space Sciences

**207. Energy-Transfer Properties and Mechanisms**

Barker, J.R. \$96,999

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 leasing. 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. An offshoot of this effort has been the development of the Reactant States Model for calculating unimolecular rate constants  $[k(E,J)]$  from high order spectroscopic constants. Collisional/reaction master equation calculations are also being 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

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

Gentry, W.R.; Giese, C.F. \$105,000

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. Where excitation of ground-state molecules has been found to be highly mode-selective due to the effect of collision geometry on the coupling between vibrational and rotational degrees of freedom. 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.

## Department of Chemistry

### 209. Variational Transition State Theory

Truhlar, D.

\$86,000

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 polyatomic reactions in the gas phase and in solution. Another important aspect of this work is the determination or modeling, semiempirically and from electronic structure calculations, of potential energy surfaces. New flexible procedures for representing the potential surfaces of reactive systems by global and semiglobal analytic functions have been developed and implemented. Variational and tunneling effects are also being included in a thermochemical data base.

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

### Center for Atomic, Molecular, and Optical Physics

### 210. Laser Studies of Chemical Dynamics at the Gas-Solid Interface

Cavanagh, R.R.; King, D.S.

\$81,000

The focus of the present research is on laser diagnostics of molecular desorption from surface. 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). The kinetic energy distributions for individual rotational states showed a marked wavelength dependence, as did the vibrational level populations. These distributions and studies of the influence of angle of incidence on the desorption yield have shown that excited carriers are responsible for this desorption process. Internal state population measurements have revealed highly non-Boltzmann distributions and inverted spin-orbit populations that are essentially independent of the desorption laser wavelength. These experiments are sensitive to the details of the trajectories associated with the

optically excited states that are involved in the desorption process. Current work is directed at establishing the importance of such excited carriers for adsorbates such as CO, and for semiconductor adsorbates where the excited carriers should have substantially longer lifetimes.

## Center for Chemical Physics

### 211. Kinetics Data Base for Combustion Modeling

Herron, J.T.

\$95,000

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<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, 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 data base covering the literature from 1971-1987. Data for more than 2500 reactions are in this data base, 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

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

Kern, R.D., Jr.

\$73,500

A shock tube coupled to a time-of-flight (TOF) mass spectrometer, is used to investigate thermal decompositions of compounds that either undergo aromatic ring rupture (e.g., benzene, toluene, ethylbenzene, pyridine) or that involve the formation of aromatic rings from acyclic fuels (e.g., acetylene, 1,2- and 1,3-butadiene, allene, vinylacetylene). The technique features the acquisition of data on reactant decay, product formation, and intermediate(s) detection during the reaction at known time intervals and well-characterized pressures and temperatures. Mechanisms are proposed and tested using computer modeling. Results from other shock tube techniques such

as laser schlieren densitometry and atomic resonance absorption spectrometry are included in the modeling effort. The TOF technique is used also to detect chemi-ions in oxidative mixtures of aromatic and acyclic fuels. Deuterated compounds are tested to demonstrate the absence of chemi-ions in oxygen free mixtures. The information obtained from the thermal decomposition and chemi-ion experiments is applicable to understanding the soot formation process.

**State University of New York/Buffalo  
Buffalo, NY 14260**

**Department of Electrical and Computer Engineering**

**213. Picosecond CO<sub>2</sub> Laser Interactions with Polyatomic Molecules**

*Kwok, H.-S.*

**\$76,000**

Picosecond laser pulses are used to study energy relaxation and population dephasing in large molecules. In a previous experiment, rapid internal conversion in CrO<sub>2</sub>Cl<sub>2</sub> was measured as a function of vibrational excitation. Recently, the phenomenon of ultrafast dephasing in aromatic dye molecules such as the rhodamines has been studied. These molecules have fast energy relaxation times in the subpicosecond region. Using a four wave mixing transient grating technique, it was determined that population dephasing in these molecules occurs in about 10 fs. To obtain such high temporal resolution, a broadband picosecond incoherent light pulse was used. The ultimate resolution of the system is ~5 fs. In addition to normal dephasing, 30 fs oscillations in the signal, possibly caused by quantum beats have been observed. This is the first evidence of femtosecond quantum beats in these large molecules with incoherent laser pulses. Further experiments are planned to understand the incoherent transient grating process and the physics of the observed relaxation oscillations.

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

**Department of Chemistry**

**214. Multiphoton Ionization Spectroscopy and Photochemistry of Transient Species**

*Johnson, P.M.*

**\$78,000**

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 species are studied by preparing molecules in excited states, which act as initial levels for resonance ionization spectroscopy, using multiphoton transitions from ground electronic levels. Normally the species under study is entrained 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 or a pyrolysis region at the exit of a pulsed valve.

Current molecules being studied include carbon dioxide and metastable nitrogen. Multiphoton techniques, including mass spectroscopy and photoelectron spectroscopy, are used to provide a more detailed look into the electronic and vibrational structures, as well as the photochemistry of these important atmospheric molecules. A multiphoton ionization study of the iodine molecule has revealed several new excited states that have interesting dissociation dynamics in competition with the ionization. Studies of the ionization processes of argon atoms have given additional insight into the mechanisms of multiphoton ionization processes in gases.

**University of North Carolina  
Chapel Hill, NC 27514**

**Department of Chemistry**

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

*Baer, T.*

**\$80,000**

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. Fused ring 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 and ionization potentials of the parent ion and of the remaining fragments are determined from the photoionization energies, the energies of photodissociation fragments, and the ionization potentials and heats of formation of some of the fragments.

**University of Pennsylvania  
Philadelphia, PA 19104**

**Department of Chemistry**

**216. Unimolecular and Biomolecular Reactions Induced by State-Specific Vibrational Excitations**

*Dai, H.-L.*

**\$100,000**

A transient vibrational spectroscopic method, Flash Photolysis Stimulated Emission Pumping, for radical species has been developed. The vibration-rotation levels of a radical, generated by flash photolysis at a concentration  $\gtrsim 10^{-4}$  Torr, and with a lifetime of  $\gtrsim 10^{-8}$  sec, can be characterized with 0.04 cm<sup>-1</sup> resolution over a wide energy range (up to 10<sup>4</sup> cm<sup>-1</sup>). This method was first demonstrated on CH<sub>2</sub>. Vibrational levels as high as the 3rd overtone of the bending mode of the lowest singlet

state has been detected. 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  $\sim 9800 \text{ cm}^{-1}$  and the origin of the first excited singlet state  $\sim 8200 \text{ cm}^{-1}$ . Abnormally strong  $\Delta K_a = 3$  transitions in the  $\bar{a} \longleftrightarrow \bar{b}$  band were observed. Several singlet-triplet couplings in the singlet spectra were identified and can be used to characterize the triplet excited vibrational levels. Using Stark Level-Crossing Spectroscopy, we have shown that highly excited, single vibration-rotation quantum states of small polyatomics can be characterized with great detail. This can be done even though these levels are dissociative, have high densities, and are optically inaccessible. We have determined, for  $\text{H}_2\text{CO}$  at  $28,300 \text{ cm}^{-1}$ , that the isoenergetic vibration-rotation eigenstates have dissociative lifetimes fluctuating between 1 and  $>50$  nsec. The dissociation barrier of  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$  is deduced to be  $\sim 81$  to  $84$  kcal/mole. The vibrational level density at this high energy is measured to be  $75 \pm 25$  per  $\text{cm}^{-1}$  and the vibrational levels were found, even for  $J = 1$ , to interact with each other through the Coriolis coupling mechanism.

### 217. Half-Collision Studies of Inelastic Energy Transfer Processes

Lester, M.I.

**\$86,000**

Spectroscopic measurements and half-collision studies of weakly bound complexes are being pursued to probe the interaction potential between molecules in a state-specific manner. Complexes of the hydroxyl radical with argon are currently being investigated as OH-Ar represents a model case for examining the intermolecular potential in an open shell system. Spectroscopic studies show a dramatic change in the OH-Ar potential upon electronic excitation of the OH moiety from the  $X^2\Pi_{3/2}$  to the  $A^2\Sigma^+$  state. The OH (center-of-mass) to Ar distance is substantially reduced ( $\Delta r_e = 0.6 \text{ \AA}$ ) and the Ar becomes much more tightly bound to OH, presumably due to charge transfer interactions in the excited electronic state. The changes in the OH-Ar potential upon electronic excitation of the OH radical are also manifested in the half-collision dynamics occurring on these surfaces. The rate of vibrational predissociation is found to be at least three orders of magnitude faster in the excited electronic state than in the ground electronic state. The nascent rotational distribution of the OH product reveals details of the inelastic scattering process that occurs as the OH and Ar fragments separate.

## University of Pittsburgh Pittsburgh, PA 15260

### Department of Chemistry

### 218. Quantum State Resolved Desorption of CO from Solid Surfaces

Janda, K.C.

**\$84,000**

The goal of this research is to characterize precisely the dynamical pathways by which atoms and molecules stick to, and subsequently desorb from, solid surfaces. Although the general energetic constraints on such processes have been studied for many years, the actual time dependence of the motion of the atoms is unknown. In recent work hydrogen atoms were found to combine and

desorb from a silicon surface via a dynamical path much different from that previously supposed. A vacuum ultraviolet photoionization mass spectroscopy technique is currently being developed in order to measure the hydrogen atom motions in more precise detail. Laser spectroscopic techniques will be used to study the interaction of CO molecules with nickel surfaces, an important model surface science problem for which a dynamical analysis has yet to be performed.

## Princeton University Princeton, NJ 08544

### Department of Chemistry

### 219. Dynamics and Kinetics of Molecular Systems

Rabitz, H.A.

**\$136,031**

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.

### Department of Mechanical and Aerospace Engineering

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

Dryer, F.L.

**\$100,447**

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<sub>2</sub>/O<sub>2</sub> 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<sub>2</sub>/O<sub>2</sub> 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.

**221. Aromatic-Radical Oxidation Kinetics**  
*Glassman, I.; Brezinsky, K.* **\$80,301**

The primary goal of this research effort has been to evaluate the role of oxygen atom reactions in the oxidation process of aromatic fuel components. Altering the O, H, and OH radical concentrations through the addition of NO<sub>2</sub> to benzene oxidation experiments conducted in the turbulent flow reactor revealed that the predominant route to the formation of the important intermediate phenoxy radical is by the reaction of phenyl with O<sub>2</sub> and not by O atom addition to benzene to form phenol and then phenoxy. When the NO<sub>2</sub> was added to toluene oxidation systems the concentration of benzaldehyde, which is ordinarily formed by an O atom reaction with a benzyl radical, increased but its rate of change as function of the extent of reaction decreased. This interesting result suggests that though the benzaldehyde is an essential intermediate in the oxidation of toluene to small hydrocarbons, its reactions are not rate determining. The pyrolysis of phenol, another significant intermediate, also was studied in the flow reactor by analyzing concentration-time profiles of three major decomposition products: carbon monoxide, cyclopentadiene, and benzene. The concentrations and rates of formation of these species have been successfully modeled by a mechanism that incorporates both literature and approximate rate coefficient data.

**Purdue University**  
**West Lafayette, IN 47907**

**Department of Mechanical Engineering**

**222. Quenching-Independent Measurement of Species Concentrations in Flames by Laser-Induced Fluorescence**  
*Laurendeau, N.M.* **\$31,052**  
**(21 months)**

The primary objective of this research is the development of laser-induced fluorescence methods for measuring the concentrations of flame species, including monatomic and diatomic radicals and polycyclic aromatic hydrocarbons. Development of these methods will result in major advances in combustion diagnostics. An associated, long-term research goal is the development of diagnostic techniques that will provide new understanding of combustion kinetics, the interaction between kinetics and turbulent flow, and the influence of kinetics on the performance and emissions of practical combustion devices.

Recent accomplishments include: (1) demonstration of quantitative, laser-saturated fluorescence measurements of both OH and NH concentrations; (2) development of a linear-fluorescence method for analyzing mixtures of polycyclic aromatic hydrocarbons in a vapor cell; (3) demonstration of quantitative, two-photon measurements of atomic hydrogen using photoionization controlled-loss spectroscopy; and (4) development of a temperature measurement technique, using the anomalous fluorescence of pyrene. Current research involves the application of OH and H measurements to the kinetics of soot formation in premixed flames and extension of the laser-saturated fluorescence method to nitric oxide.

**Rensselaer Polytechnic Institute**  
**Troy, NY 12180-3590**

**Department of Chemical Engineering**

**223. Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges**  
*Fontijn, A.* **\$80,000**

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 the 300 to 1800 K range. Studies of a series of reactions of oxygen atoms with H<sub>2</sub>, D<sub>2</sub>, the C<sub>2</sub>-hydrocarbon molecules, and propylene have been completed. Quantum-mechanical tunneling is found to be an important contributing factor to the rate coefficients of several of these reactions. In the butadiene reaction a fraction of the oxygen atoms is regenerated and as a result, the rate coefficient values in the literature, based on oxygen atom consumption alone, are too low. Accurate determination of these latter values requires the shorter observation time domains available from laser photolysis. A facility to do HTP by such photolysis is being built. A study of benzene photolysis has shown that above 600 K the rate coefficients for H-atom consumption are pressure-dependent and are considerably larger than reported in literature. The O + HCl reaction is of interest to flame inhibition and incineration problems. Work in progress shows (over the 350 to 1400 K range), close agreement with the recommendations of the Leeds tables, contrary to the single other elevated temperature (950 to 1150 K) study of this reaction.

**Rice University**  
**Houston, TX 77005**

**Department of Chemistry**

**224. Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals**  
*Curl, R.F., Jr.; Glass, G.P.* **\$78,000**

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 mechanisms of two free-radical reactions have been investigated using free radicals produced by excimer laser flash photolysis and monitoring by infrared absorption spectroscopy. In one study, the  $C_2H + O_2$  reaction at room temperature was investigated. Infrared absorption lines of a variety of possible products of this reaction, HCO, OH,  $HO_2$ , CO, and  $CO_2$ , were monitored; the only products observed are CO and  $CO_2$  in a ratio of 5 to 1. This work established that CO is produced by two mechanisms, a direct channel producing  $H + 2CO$  in which the CO produced is vibrationally excited up to  $v = 6$  and an indirect channel producing (relatively) vibrationally cold CO. In the other study, the branching ratio for the reaction,  $NH_2 + NO$ , was investigated as a function of temperature. The products observed are OH and  $H_2O$ . The pathways represented by these products account for all the  $NH_2$  consumed at 300 K, but for only 3/4 of it at 1200 K. The pathway leading to OH increases from about 13% at room temperature to about 25% of the  $NH_2$  reactant at 1200 K.

**225. Supersonic Bare Metal Cluster Beams**  
Smalley, R.E. **\$95,000**

Continued research into the surface chemistry and physics of bare metal clusters has proceeded this year in two major areas. The first has been the extension of previous FT-ICR measures of the dissociative chemisorption behavior of niobium clusters to the other transition elements in the same group (vanadium and tantalum) as well as the group VIII elements cobalt, rhodium, and iridium. Large variations of reactivity as a function of cluster size are seen with these other elements, but it is clear that there is a strong group trend in the chemisorption patterns that should provide a major key in the ultimate understanding of these phenomena. In the case of iridium, these new FT-ICR experiments involved the first use of "SWIFT" technology to sweep out all but one isotopic form of the bare clusters prior to reaction with  $H_2$ . The second major extension has involved UPS probes of copper, silver, gold, and aluminum clusters using a much-improved cluster UPS apparatus. The results near the "fermi energy" of the cluster provide the best confirmation yet of the simple jellium, shell-like electronic structure model for clusters of simple metals. However, the UPS patterns for the more deeply bound electrons are found to deviate markedly from simple independent electron shell models. For the Group IB metals these deeper structures will reveal the evolution of the valence d band as a function of cluster size.

**University of Rochester**  
**Rochester, NY 14627**

**Department of Chemistry**

**226. Low-Energy Ion-Molecule Reactions and  
Chemi-ionization Kinetics**  
Farrar, J.M. **\$83,000**

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. Emphasis is on studies of proton transfer reactions occurring on double-minimum potential surfaces. 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 important combustion related reactions such as  $O^- + H_2$  and  $O^- + C_2H_4$ , as well as atmospheric reactions such as  $O^- + N_2O$ .

**227. Double Resonance Reactant Preparation  
for State-to-State Unimolecular Reaction  
Studies**  
Rizzo, T.R. **\$72,497**

The primary goal of this work is to investigate unimolecular dissociation reactions of small unstable molecules at a sufficiently detailed level to provide critical tests of statistical and dynamical models. The testing and refinement of these models is important for quantitative prediction of reaction rates and energy partitioning in combustion reactions. This project involves a new approach to state selective preparation of reactant molecules which when combined with state specific detection of reaction products provides a detailed picture of unimolecular dissociation. Infrared-optical double resonance, in which a fundamental vibrational transition is first excited with an infrared optical parametric oscillator and a vibrational overtone transition is then excited with a pulsed dye laser, prepares reactant molecules in specific (quasi-bound) states above the dissociation threshold on the ground potential surface. Individual quantum states of the reaction products are then probed by using laser-induced fluorescence. The initial application of this approach to the unimolecular decomposition of hydrogen peroxide has revealed a strong rotational dependence of the intramolecular dynamics which current theoretical models do not predict. The partitioning of the energy among the products of the selectively excited hydrogen peroxide has served to distinguish between competing statistical models.

**SRI International**  
**Menlo Park, CA 94025**

**Molecular Physics Laboratory**

**228. Flame Studies, Laser Diagnostics, and  
Chemical Kinetics**  
Crosley, D.R. **\$132,978**

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 data base 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  $A^3\Pi_i$  excited state of the NH radical has been found to depend on rotational level,  $N'$ . That of the  $A^2\Sigma^+$  of OH by  $H_2O$  depends on  $N'$  at room temperature but not in a low-pressure flame at 2300 K. Quenching by hydrogen atoms is important at 1200 K. Systematic investigations establishing quantitative determination of OH concentrations and rotational temperatures in the flame have been made. Quenching of the  $\tilde{A}^2 A_1$  state of  $NH_2$  also depends on  $N'$  but in a way varying with vibrational level, suggesting perturbations, not collision dynamics, are responsible.

**University of Southern California  
Los Angeles, CA 90089**

**Department of Chemistry**

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

*Reisler, H.*

**\$80,047**

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.

**230. Product Kinetic and Internal Energy Distributions via Velocity-Aligned Doppler Spectroscopy**

*Wittig, C.*

**\$95,000**

This research has focused on developing and applying velocity-aligned Doppler spectroscopy (VADS) to determine kinetic and internal energy distributions for photoproducts and reaction products. The technique utilizes only a slight modification on conventional Doppler spectroscopy, yet the results can be quite revealing when compared with what one observes in a typical Doppler

profile. Initial experiments have focused on the photodissociation of hydrides to produce hydrogen atoms. Examination of HBr (193 nm) and HI (193 and 248 nm) photodissociation has enabled spin-orbit populations and anisotropy parameters ( $\beta$  values) to be measured, and the results are interpretable within the context of spin-orbit coupling schemes. The 193 nm photodissociation of  $H_2S$  reveals the presence of significant vibrational excitation in the SH fragment. While in the photolysis of HBr, HI, or  $H_2S$ , most of the available energy is channeled into translational motion,  $NH_3$  photolyzed at 193 nm produces relatively little translational excitation. The majority of the available energy appears as  $NH_2$  vibrational and/or rotational energy. Efforts are under way to improve the resolution of the VADS method. Technological advances in the dye laser industry combined with sample cooling techniques can increase the energy resolution of the VADS technique markedly, and applying VADS to study molecules such as  $C_2H_2$  looks promising. In addition, a variety of applications for the VADS method are being explored, including the study of photoinitiated cluster reactions. By using van der Waals forces to orient the reactants HBr and  $D_2$  subsequent to HBr photodissociation, one can probe the  $H + D-D \rightarrow H-D + D$  reaction in an environment where the initial conditions have been constrained.

**Stanford University  
Stanford, CA 94305**

**Department of Mechanical Engineering**

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

*Hanson, R.K.; Bowman, C.T.*

**\$130,000**

This research focuses on two complementary activities: (1) development and application of cw ring dye laser absorption methods for sensitive detection of radical species and measurement of fundamental spectroscopic parameters; and (2) shock tube studies of radical-molecule and radical-radical reactions relevant to combustion. A novel aspect of the shock tube work is the use of excimer laser photolysis to produce controlled levels of radical species in shock-heated gases. Reactions involving NH,  $NH_2$ , NCO, O, H, and OH radicals are of particular interest, and candidate source compounds for radical production are  $H_2O$ ,  $NH_3$ , HNCO,  $N_2O$ , NO, and  $H_2O_2$ . The primary excimer wavelength used for photolysis thus far has been 193 nm (argon fluoride), although other wavelengths are also of interest. Species to be investigated in the spectroscopic portion of the research include OH, NH,  $NH_2$ , and NCO.

**University of Wisconsin  
Madison, WI 53706**

**Department of Chemistry**

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

*Crim, F.F.* **\$84,170**

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 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.

**Atomic Physics**

**Atlanta University  
Atlanta, GA 30314**

**Department of Physics**

**233. Theoretical Investigation of Electron—Ion Interaction**

*Msezane, A.Z.* **\$73,956**

Dominant physical mechanisms underlying the processes of electron impact excitation and ionization of ions and atoms of importance in astrophysical and laboratory fusion plasmas are identified and cross sections calculated, using the close-coupling and R-matrix methods. Both integral and differential cross sections are calculated and compared with measurements. In particular, detailed numerical studies are carried out to investigate (1) coupling and inner-shell effects in low Z boron-like ions; (2) the importance of correlations and coupling effects in K-like Cr and the relative size of the  $3p^5 3d^2$  type cross sections; (3) photoionization of K and Na 3d subshell using the R-matrix method to determine the importance of correlation of polarization effects upon the  $\ell \rightarrow \ell-1$  dipole zero; and (4) the importance of correlations as a function of Z for

the inner-shell transition  $2p^6 3s \rightarrow 2p^5 3s^2$  leading to autoionization in Na isoelectronic sequence. Extensive configuration interaction target wave functions are used. They are constructed such that the length and velocity dipole oscillator strengths are consistent and compatible with accepted values.

**California State University-Fullerton  
Fullerton, CA 92634**

**Department of Physics**

**234. Correlated Processes in Atomic Collisions**

*Feagin, J.M.* **\$41,988**

A diatomic molecular description of atoms is further developed to calculate simple cross sections for electron-pair excitations in heavy ion collisions. The description is based on a comparison of two-electron atoms with molecular  $H_2^+$ . In zeroth order, the model simply recognizes that the ions  $H^-$  and  $H_2^+$  have identical electrostatic energies. The interelectronic axis in the atom is given the role of the internuclear axis in the molecule. Two-electron potential energy curves as a function of the interelectronic separation R are obtained by a scaling of molecular  $H_2^+$  potential energy curves as a function of the internuclear separation. Thus, in first order, one classifies potential curves and two-electron states according to familiar molecular orbital symmetries and quantum numbers of  $H_2^+$ . The first-Born approximation for direct excitation of an electron pair has been analyzed, in particular, the inelastic form factor. Several interesting features emerge. In an independent-electron model the form factor vanishes identically, i.e., electron-pair excitations are forbidden in first-Born approximation. In molecular coordinates, however, one finds the inelastic form factor to be a nonvanishing product of a Franck-Condon integral and a molecular form factor. Thus, the language of molecular spectroscopy finds application in atomic spectroscopy. Related work includes the determination of Wannier threshold angular distributions for molecular dissociation, quantum diffusion (Monte Carlo) computations of two-electron excited states, and electron transfer and excitation in ion—atom collisions.

**University of Colorado  
Boulder, CO 80309-0440**

**Joint Institute for Laboratory Astrophysics**

**235. Spectroscopic Diagnostics of Electron—Atom Collisions**

*Gallagher, A.C.* **\$94,000**

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. Measurements of electron excitation of low-lying states of the alkaline earth elements are being made. These measurements also depend on laser detection of the excited atoms, and will yield differential cross sections for the excitation components.

**236. Near-Resonant Absorption by Atoms in Intense Fluctuating Fields**

*Smith, S.J.*

**\$100,000**

This research is an experimental investigation of the behavior of phased arrays 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 decorrelation of these phased dipole arrays is observed as the atomic phases evolve in time in the presence of 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. This provides a unique experimental environment in which to study the role of these controlled perturbations in the decorrelation process, in the absence of any other perturbations except spontaneous decay. Measurements on the Hanle effect in ytterbium (isotope 174) are complete. The results show strong effects on the bandwidth and amplitude of the spectrum fluctuations, and of the laser intensity, and clearly demonstrate the inadequacy of existing theoretical treatments. A new experimental study of phase noise decorrelation effects in the case of photon echoes in ytterbium is in progress. In addition, recently predicted correlations between fluctuations in resonance fluorescence of atoms and fluctuations in the driving field are being tested experimentally.

**Cornell University**  
**Ithaca, NY 14853**

**Nuclear Science and Engineering Program**

**237. Experimental Study of Interactions of Highly Charged Ions with Atoms at keV Energies**

*Kostroun, V.O.*

**\$293,446**

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. The very highly charged ions used in the experiments are produced by the Cornell Electron Beam Ion Sources CEBIS I and CEBIS II, which produce such species by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam. Ions available from these sources include bare nuclei of light ions, argon ions up to  $\text{Ar}^{16+}$  (helium-like), and xenon ions up to  $\text{Xe}^{30+}$ . CEBIS II, a superconducting solenoid, cryogenic EBIS, designed and constructed in this laboratory, has been rebuilt and improved to operate continuously with minimal cryogen consumption. A 60 keV electron gun has been installed that gives the source the potential capability of producing  $\text{U}^{90+}$  (helium-like uranium). The technique of resonance electron impact excitation/ionization has been applied to very highly charged argon ions trapped in the

electron beam of the source and preliminary results indicate that the EBIS is suitable for this type of spectroscopy. Small angle (milliradian) scattering of highly charged ions by atoms following single and multiple electron capture is used to investigate in detail the nature of highly charged ion-atom interactions at very low energies.

**Georgia Institute of Technology**  
**Atlanta, GA 30332**

**School of Physics**

**238. Statistical Fluctuations in Lasers**

*Roy, R.*

**\$61,208**

The phenomenon of stochastic resonance in bistable ring lasers has been studied carefully both experimentally and theoretically. The response of a bistable system to a periodic modulation can be enhanced by the injection of noise into the system. The experimental realization of this effect has been explained by analytic and numerical calculations, and a broad theoretical basis developed that indicates that this phenomenon should occur in a number of physical systems. It has also been shown that a Q-switched laser can be used as an extremely sensitive detector of radiation with a high bandwidth resolution. In this mode of operation, called super-regenerative detection, the initiation of laser radiation from a background of either spontaneous emission or an injected signal is measured. The difference in the time of growth of the radiation with and without the injected signal is used as an indicator of the strength of the signal. Initial experiments have shown that signals down to the level of approximately one photon on the average in the cavity mode of the receiver can be detected.

**239. Metastable Enhancement of  $\text{C}^+$  and  $\text{O}^+$  Capture Reactions**

*Thomas, E.W.*

**\$57,417**

Metastable ions exhibit collisional charge-transfer cross sections in gases that are up to an order of magnitude greater than for the ground state. This observation is related to the smaller energy defect for metastable collisions. The interpretation is not yet amenable to detailed theoretical treatment for complex species. This project studies charge transfer for 20 to 100 eV  $\text{C}^+$  and  $\text{O}^+$  ions in  $\text{H}$ ,  $\text{He}$ , and  $\text{H}_2$ , comparing ground and metastable excited-state cross sections. A low-energy (20 to 2000 volt) accelerator has been constructed with a well-controlled electron impact source that produces beams of ground state  $\text{C}^+$  and  $\text{O}^+$  ions or mixed metastable and ground state species in a determined ratio. Cross-section measurements in  $\text{H}_2$  and  $\text{He}$  targets will begin shortly. Simultaneous studies examine how metastable species influence ion-induced sputtering and electron ejection from surfaces; both processes may be related to electron-transfer mechanisms. It has been shown that ejection of atoms from a Si surface by  $\text{O}^+$  impact is identical for ground and metastable species. This is not surprising since ejection is primarily through physical sputtering. For ejection from carbon, findings suggest that metastable  $\text{O}^+$  ejects carbon more efficiently than ground state  $\text{O}^+$ . The enhanced ejection is through formation of  $\text{CO}$ , a volatile species, in the mechanism of chemical sputtering.



**Harvard University  
Cambridge, MA 02138**

**Harvard-Smithsonian Center For Astro-  
physics**

**240. Theoretical Studies of Highly Ionized  
Species**

*Dalgarno, A.* **\$137,000**

The stability of the multiply charged molecular ion  $AlH^{3+}$  is being studied and the lifetimes of its excited states toward radiative decay and predissociation in a Coulomb explosion are being calculated. Radiative and direct charge transfer of helium ions in collisions with neutral hydrogen atoms has been investigated. Calculations of the radiative association to form  $HeH^+$  are in progress. Analogues of the Berry phase in molecular processes are being explored. Calculations are in progress on the structure of the molecular ion  $HCl^+$ , its photodissociation channels, and the radiative emission that occurs during the collisions of protons and neutral chlorine atoms.

**Kansas State University  
Manhattan, KS 66506**

**Department of Physics**

**241. Atomic Physics of Strongly Correlated  
Systems**

*Lin, C.D.* **\$104,000**

This project is directed toward the study of one- and two-electron processes in ion-atom collisions in the low and intermediate energy region. Cross sections for single electron capture, single ionization, double electron capture, transfer excitation, and transfer single and double ionization are calculated. The close-coupling method with atomic orbitals as basis functions is used to make the calculations and the results are compared with experiments. The orientation and alignment of excited states are also studied. Investigations of bound and scattering states for Coulombic three-body systems with arbitrary masses are being conducted in hyperspherical coordinates to identify a single classification scheme from the atomic to the molecular limit. The variations of the rotation-vibrational normal modes with the relative mass of the charged particles are examined. The energies of doubly excited states of positive ions are determined to assist interpretation of observed electron spectra obtained from ion-atom collisions.

**Department of Physics, J.R. MacDonald Laboratory**

**242. Atomic Physics with Highly Charged Ions**

*Richard, P.* **\$1,480,000**

The cross section for transfer ionization (TI) has been measured for 0.5 MeV/u to 2.0 MeV/u  $C^{+6}$ ,  $N^{+7}$ ,  $O^{+8}$  and  $F^{+9}$  projectiles on He. Resonance transfer excitation (RTE) to Be-like states and excitation to Li-like states have been measured for  $F^{+7}$  on  $H_2$  and He. The first observation of electron-electron excitation in ion-atom collisions was observed in these experiments. Angular distributions

for single and multiple ionization of Ne and Ar targets by 3 and 6 MeV protons have been measured and analysis is directed toward separation of shakeoff and inner-shell-vacancy-generated ionization. Measurements of cross sections for two electron processes, including correlated ionization, excitation, and capture events, have been measured for 0.5 to 1.2 MeV/u oxygen nuclei on molecular deuterium targets. This project is now being directed toward determination of the dependence of these processes on the orientation of the molecular axis. Angular distributions of slow recoils from 1 MeV/u fluorine nuclei are being studied. A multidimensional coincidence experiment has been put into operation in which outgoing electrons, recoiling target ions, and projectile charge states and scattering angles are measured simultaneously to completely determine dynamical parameters of electron transfer and ionization. A high-efficiency low beam divergence recoil ion source has been built and tested. The source has an angular beam spread of  $\leq 5$  mrad and an extraction efficiency of  $\approx 30\%$ . Work has continued on the  $F^{9+} + Li$  collision system, and diode lasers have been added to the existing copper vapor and dye system (to be used in exciting the Li target). A projectile Rydberg analyzer has been constructed and used to monitor Rydberg production in collisions of  $F^{6+} + Ne$  (final  $n \sim 200$ ). The systematics of the Z-dependence of autoionization and radiation rates were investigated for selected states of two-electron ions. Calculations of many-body effects in atomic and molecular scattering have been performed and have supported experimental observations of single and multiple ionization with photons, protons, antiprotons, electrons, and positrons. Calculations of electron capture cross sections in ion-molecule collisions are being carried out with an orientation-dependent atomic model.

**University of Kansas  
Lawrence, KS 66045**

**Department of Chemistry**

**243. Theoretical Studies of Many-Body Processes in Atomic and Molecular Physics**

*Chu, S.-I.* **\$15,000**

The project objective is to develop new theoretical formalisms and practical computational methods for *ab initio* investigations of a number of atomic and molecular processes in intense laser fields as well as the structure and dynamics of many-body resonances of current significance in science and technology. The projects being pursued currently are: (1) development of a most probable path approach (Floquet theory + artificial intelligence algorithms) techniques for probing multiphoton dynamics and quantum diffusion phenomena in Rydberg atoms, (2) development of a non-Hermitian Floquet matrix method for the treatment of intensity-dependent threshold shift and above-threshold multiphoton ionization (MPI) of complex atoms, (3) development of Floquet-Liouville Supermatrix (FLSM) approaches for nonperturbative treatment of various time-dependent and intensity-dependent nonlinear optical processes, and (4) development of generalized density matrix formalism for probing geometric quantum phases in dissipative quantum systems undergoing multiphoton Rabi floppings.

**Louisiana State University**  
**Baton Rouge, LA 70803**

**Department of Physics and Astronomy**

**244. Electron Collisions with Positive Ions**  
*Henry, R.J.W.* **\$70,500**

The fundamental goal of this project is to delineate the important physical processes governing electron impact excitation processes for impurity ions in high-temperature plasmas of interest in thermonuclear reactors. The energy range considered is from the threshold to approximately four times the ionization energy. Calculations are based on a close-coupling expansion, which includes the important physical effects of electron exchange and resonances. Coupling effects among the channels for collisional excitation of  $2s^2 2p^4$ ,  $2s 2p^5$ , and  $2p^6$  configurations of oxygenlike krypton have been reinvestigated and found to be small. Density sensitive emission line ratios  $R_1 = I(338.27 \text{ \AA})/I(364.47 \text{ \AA})$  and  $R_2 = I(338.27 \text{ \AA})/I(352.10 \text{ \AA})$  for Fe XII have been determined using our calculated electron collision rates. Electron densities deduced from the observed values of  $R_1$  and  $R_2$  for solar active regions and flares are in excellent agreement with these calculations. Coupling effects in the carbon isoelectric sequence are being examined for low  $Z$  ions. Sensitivity for various types of transitions in the energy region beyond the resonance region is being investigated, in particular transitions for which  $\Delta n = 0$  ( $2 \rightarrow 2$ ),  $\Delta n \neq 0$  ( $2 \rightarrow 3$ ), E1 allowed, E1 forbidden, spin allowed, and spin forbidden.

**University of Louisville**  
**Louisville, KY 40292**

**Department of Physics**

**245. Spectroscopic Studies of Hydrogen Atom and Molecule Collisions**  
*Kielkopf, J.* **\$73,500**

The hydrogen atom and molecule offer simple systems for theoretical modeling and analysis, because, when isolated, their structure and optical spectra are well understood. In collision, either with each other or with more complex partners such as the rare gases or oxygen, new and unexplored phenomena appear. This is partly a consequence of the degeneracy of the atom and the exceptional symmetry of the molecule, but also because there are nearly resonant interactions that cannot occur in atoms or molecules that are more easily ionized than hydrogen. A new technique has been developed for producing high concentrations of atomic hydrogen in transient plasmas, and using time-resolved spectroscopy with lasers and conventional spectrometers to study the neutral interactions that follow recombination. A reliable method for computing simulated spectra of  $H_2$  in the vacuum ultraviolet, given a population of excited states, is combined with solutions of the rate equations, for the analysis of multiphoton excitation and collisional quenching in the molecule. Theoretical studies are being made of the spectral line shapes that result from radiative collisions of the hydrogen atom. Experiments are under way on radiative dissociation of  $H_2$ , spectral line shapes and satellites in H-H and H-rare gas collisions, collision excitation

transfer in the  $B^1\Sigma_u^+$ ,  $C^1\Pi_u$ , and  $E$ ,  $F^1\Sigma_g^+$  states of the molecule, and the dissociation of excited states of OH.

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

**Quantum Physics Division**

**246. Atomic and Molecular Collision Processes**  
*Norcross, D.W.* **\$30,000**

Theory is used to calculate cross sections for collisions of low-energy electrons with atoms and atomic ions. Results have been obtained for electron-impact excitation of sodium-like aluminum. These calculations are based on the highly sophisticated close-coupling approach. They employ both pseudostates to incorporate highly excited states and the continuum in the close-coupling expansion, and one-body and two-body terms in the potential to allow for polarization and correlation interactions between the outer electrons and the ionic core. The latter is a 10% effect in cross sections for the resonant  $3s$ - $3p$  excitation. As an additional check on these calculations, binding energies and oscillator strengths for bound states of the compound system ( $Al^+$ ) are also computed and compared with measurements and other calculations. In some cases these results provide data that are either new or more reliable than that previously available. Work was initiated on transitions to and between fine-structure substrates of excited states of sodium by low-energy electrons. Orientation of both atom and scattering electron will be taken into account in these studies.

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

**Radiation Physics Division**

**247. Electron-Atom Collision Studies Using Optically State Selected Beams**  
*Celotta, R.J.; Kelley, M.H.* **\$87,610**

Scattering experiments are performed with spin-polarized electrons and optically pumped, spin-polarized sodium atoms. Spin-polarization of both collision partners allows direct investigation of both exchange and the continuum spin-orbit interaction in elastic and inelastic low-energy electron scattering. Elastic scattering measurements at 54.4 eV incident energy show that the spin-orbit interaction and exchange effects both play a significant role in the scattering and must be included in theoretical calculations to achieve agreement with the experimental results. Measurements of inelastic scattering at incident energies of about 2 eV, 10 eV, 20 eV, and 54 eV have yielded benchmark results against which to compare state-of-the-art theoretical calculations of low-energy electron scattering. Work in progress is directed toward elastic scattering measurements at lower incident energies, between 2 eV and 50 eV. Future work will include energy analysis of the scattered electrons in order to study other atomic transitions, and spin analysis to complete the characterization of exchange in these collisions.

**University of Nebraska  
 Lincoln, NE 68588-0111**

**Department of Physics and Astronomy**

**248. Dynamics of Collision Process**

*Starace, A.F.*

**\$62,000**

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, for 0.5 MeV  $H^-$  detachment collisions with He targets resulting in excitation of  $H(n=2)$ , the low energy states of the  $H(n=2)-e^-$  three-body system have been shown to produce distinct "cusp," "shape resonance," and/or "shoulder" features in the laboratory frame doubly differential cross sections (DDCS's). Also for this detachment process, the first quantitative predictions of Gailitis-Damburg dipole-field-induced oscillations in the DDCS's above the  $H(n=2)$  threshold have been obtained and distinguished from effects of the  $1^1P^0$  shape resonance, which dominates the laboratory frame DDCS's for detached electron angles less than  $1^\circ$ . Second, the first three photon detachment cross sections for  $H^-$  have been calculated using a newly developed variational procedure within an adiabatic hyperspherical coordinate representation. Third, it has been shown that the final state wave function describing excitation of  $H_2^+$  in fast collisions can often be replaced by a simple scaled atomic orbital, indicating that the first term in a multipole expansion of the final state wave function dominated the scattering amplitude. Among additional processes being studied are DDCS's for detachment of fast  $H^-$  ions in collision with rare gas targets other than He, photoionization 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**

**249. Relativistic Atomic Beam Spectroscopy**

*Bryant, H.C.*

**\$90,000**

The structure of the  $H^-$  ion is being explored using laser probes and a beam with near luminal velocity. The photodetachment spectrum near the single electron threshold at 0.75 eV is studied under both  $\sigma$  and  $\pi$  polarized light in the presence of electrostatic fields ranging up to 60 kV/cm and in motional electric fields as high as 2 MV/cm. Using the same technique, cross sections for the production of high-lying doubly excited states in  $H^-$ , embedded in the  $1^1P$  continuum, will be measured, and the double detachment cross section will be determined with a precision adequate to distinguish between the Wannier and Temkin theories. The yields of excited hydrogen states resulting from the passage of  $H^-$  at relativistic velocities through thin foils will be determined. The dependence of yield on foil thickness, material, and principal quantum number will be observed. The kinematics of the interaction of a photon beam with a relativistic atomic beam will make possible the study of multiphoton processes in  $H^-$  as a function of wavelength and intensity, using a pulsed  $CO_2$  laser.

**University of Oregon  
 Eugene, OR 97403**

**Department of Physics**

**250. Nonlinear Dynamics of Broad-Band Lasers**

*Raymer, M.G.*

**\$104,000**

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. Coherent four-wave mixing in the gain medium continually couples energy from one mode into another; 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 a titanium-sapphire laser, a recently developed room-temperature, solid-state laser that is tunable in the visible. The absence of a flowing gain medium, as in a dye laser, should allow stable operation very near threshold. 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**

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

*Winter, T.G.*

**\$60,000**

Theory is used to calculate electron transfer, excitation, and ionization in ion-atom collision cross sections. Emphasis is placed on simple one- or two-electron systems to minimize the approximations and reveal clearly the basic collisional mechanisms. Attention is focused on the important kilo-electron-volt energy range in which the electron-transfer probability has its largest value. In this energy range, many electronic states are strongly coupled and perturbative approaches are inappropriate. As a result, coupled-state approach has been used. This approach has been applied recently to one-electron systems. It is being extended to two-electron systems. A large calculation for the proton-helium-atom collision is under way. Preliminary results indicate that the two-electron aspect of the collision (electron-electron correlation) is tractable provided the calculation is sufficiently large; for example, 90% of the ground-state-helium correlation can be included using 70 coupled Sturmian functions. The coupled-Sturmian-state method shows promise for systematically treating electron transfer and direct excitation to the lower lying states of hydrogen and helium, respectively, as well as single ionization of helium.

**University of Pittsburgh**  
**Pittsburgh, PA 15260**

**Department of Physics and Astronomy**

**252. New Infrared Photon Absorption Processes**  
*Bayfield, J.E.* **\$120,000**

The response of excited atomic electrons to intense picosecond mid-infrared laser pulses is being investigated to study rapid noncollisional breakdown of gases. Possible nonperturbative infrared multiphoton ionization cross sections are being measured for isolated laser state-selected hydrogen atoms with principal quantum number ranging from seven to ten. An infrared laser system capable of producing 150 picosecond, 1 gigawatt per square centimeter pulses is being used. The peak laser field exceeds the static field required for ionization by a factor of two or more. An apparatus for studying above threshold ionization (ATI) is being constructed. A longer term objective is to study the effect of 5 picosecond, 10 gigawatt per square centimeter pulses on hydrogen atoms with quantum numbers of four and five. Under these conditions the system may exhibit a rapid transient near-classical behavior that is chaotic in the classical limit.

**Purdue University**  
**West Lafayette, IN 47907**

**School of Electrical Engineering**

**253. Nonlinear Optical Interactions Involving the Real Gaussian Field**  
*Elliott, D.S.* **\$57,850**

The goal of this experimental project is to determine the effect of laser bandwidth on nonlinear optical interactions. In particular, a laser field known as the Real Gaussian Field is being synthesized in which the amplitude of the field is a randomly fluctuating (Gaussian) process. Principal efforts thus far have been directed toward developing a technique for the random amplitude modulation of the output of a stabilized cw dye laser source. By use of an acousto-optic modulator and a high-frequency circuit designed to produce a random-amplitude suppressed carrier drive signal, this optical field can now be generated. Further work is required to finish characterization of this field's statistical properties. The laser field will be used to study nonlinear optical processes such as two-photon absorption and intense field single-photon interactions. This experiment will provide a source of information for direct comparison with other theoretical works that have treated this effect. These results will aid the understanding of the effect of the bandwidth of broadband lasers routinely used for a variety of analytical, diagnostic, and spectroscopic applications.

**Rice University**  
**Houston, TX 77005**

**Department of Physics**

**254. Theoretical Atomic and Molecular Physics**  
*Lane, N.F.* **\$96,410**

Collision cross sections, rates, and other observable physical parameters for a variety of important atomic and molecular processes have been determined using theory. Recent progress includes results for: (1) differential direct and charge-transfer scattering of protons by He and Ar atoms; (2) alignment and orientation of Na(3p) resulting from collisions of ground-state Na and He atoms; (3) state changing between excited states of Rydberg Na in slow collisions with He and Ne atoms; (4) Penning electron energy distributions for slow collisions of metastable He with Na and K atoms; and (5) charge-transfer in collisions between highly stripped and neutral atoms:  $\text{Li}^{3+}$  and  $\text{Li}^{2+}$  collisions with Li atoms. Research is continuing on similar physical processes and systems and on the development of new theoretical methods.

**St. John Fisher College**  
**Rochester, NY 14618**

**Department of Physics**

**255. Multilevel Relaxation Phenomena and Population Trappings**  
*Hioe, F.T.* **\$74,000**

This theoretical research deals with the aspects of multiphoton absorptions by a multilevel quantum system in an intense laser field. Among the many analytic results obtained are those for coherent population trapping that are related to certain  $\text{SU}(N)$  symmetry. Conditions for multiple solitary pulse propagation through a multilevel atomic medium have also been derived. Analytic and numerical studies of above-threshold ionization through multiphoton absorption are now in progress.

**University of Tennessee**  
**Knoxville, TN 37996**

**Department of Physics and Astronomy**

**256. Production and Destruction of Metastable Negative Ions**  
*Pegg, D.J.* **\$48,000**

The destruction of negative ions by photoabsorption is being studied. The source of the negative ions is a fast-moving beam produced by charge changing a beam of positive ions in an alkali vapor cell. Photon-negative ion collisions are investigated in the interaction region where both ion and laser beams are crossed at right angles. Photoelectrons detached from the negative ions into the forward direction are collected, energy analyzed, and detected by an electrostatic electron spectrometer. The resulting photoelectron spectra are used to determine the structure of the negative ions. Angular distributions of

the ejected photoelectrons can also be mapped out by rotating the electric field vector of the linearly polarized laser beam. The structure of  $\text{Ca}^-$  has been determined. This ion is, contrary to earlier expectations, stably bound in the  $(4s^2 4p)^2 P$  state. The electron affinity of calcium has been measured to be 43 MeV. Photoelectron yields and angular distributions are presently being measured in order to determine the partial cross sections for photodetachment of the metastable ion,  $\text{He}^-(^4P)$  via the competing  $\text{He}(^3S)$  and  $\text{He}(^3P)$  exit channels. Preliminary results indicate a discrepancy between experiment and theory.

**Texas A and M University**  
**College Station, TX 77843**

**Cyclotron Institute**

**257. Excitation of Atoms and Molecules in Collisions With Fast, Highly Charged Ions**  
*Watson, R.L.* **\$82,710**

Time-of-flight (TOF) spectroscopy is being used to study the ionic species produced in collisions of 1 to 3 MeV/amu  $\text{Ar}^{13+}$  with a variety of simple molecular gases. In diatomic gases, such as  $\text{O}_2$ , ions from the dissociation of molecular ions having charges as high as 10+ are observed. The flight times of both fragments from binary dissociation events are recorded event by event, thereby retaining their correlation. Off-line sorting of the data provides TOF and time difference spectra containing well-resolved peaks associated with each of the fragmentation pairs. The total kinetic energy released in the dissociation is determined either from the  $0^\circ$  and  $180^\circ$  flight time differences of individual ions or from the flight time differences of fragment pairs. For symmetric charge divisions, the time difference spectra display a structure that appears to be associated with specific excited states of the parent molecular ion.

**University of Texas**  
**Austin, TX 78712**

**Department of Physics**

**258. Kinetic Studies Following State-Selective Laser Excitation**  
*Keto, J.W.* **\$96,000**

State-to-state rates for reactive energy transfer from excited rare gas atoms to halogen molecules are measured. The atoms are excited in two photon transitions using ultraviolet lasers. Accurate ( $\pm 2\%$ ) measurements of the bimolecular reaction rate from  $\text{Xe}^*$  to  $\text{Cl}_2$  have been extended to now include states in  $5p^5 5d$ ,  $5p^5 6p$ , and  $5p^5 7p$  configurations. This gives a range of ionization potentials for the excited states to compare with a multichannel curve crossing theory. States closer to the ionization limit are in poorer agreement with the model than states of  $5p^5 6p$ , but by modifying the form of the charge transfer matrix elements better agreement is obtained. An *ab initio* calculation of the coupling elements is desirable, and it is likely that a quantum defect model would be adequate. A large termolecular contribution has been observed for this reaction in xenon buffers but not in argon

buffers. Models of this reaction using collisions in the entrance channel with third bodies which cause inwardly spiraling orbits were attempted. While such a model has been successful for ion reactions, here it leads to rates that are too small to explain the experimental results, and it fails to predict the difference observed between xenon and argon buffer gases. A better 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. An experiment that tests this model using krypton buffer gases is under way. The  $\text{Xe}^+ - \text{Cl}_2$  reaction complex formed by exciting either collision pairs in a gas cell or bound pairs in a supersonic beam is continuing.

**University of Toledo**  
**Toledo, OH 43606**

*John Kunkle*

**Department of Physics and Astronomy**

**259. Semiempirical Studies of Atomic Structure**  
*Curtis, L.J.* **\$50,000**

The atomic structure and properties of highly-ionized many-electron systems are studied with 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. These data are combined with those available from laser- and tokamak-produced plasmas, astrophysical sources, and conventional light sources. The experimental studies are supported with large scale *ab initio* calculations using the MFE Cray X-MP computer. Large blocks of data are systematized and parameterized along isoelectronic, homologous, isoionic, Rydberg, and yrast series. Projects conducted during the past year include: (1) a theoretical study of lifetimes and transition wavelengths for highly ionized members of the Ne isoelectronic sequence; (2) a combined experimental and theoretical study of doubly excited levels in sodiumlike  $\text{Al}^{+2}$ ; (3) high precision coincidence measurements of the lifetimes of the two-photon decays of the metastable 2s levels in both heliumlike and hydrogenlike nickel; (4) combined use of semiempirical parameterizations and theoretical calculations to obtain precise predictions for the lifetimes of the lowest lying np and nd levels for all ions in both the Na and Cu isoelectronic sequences; and (5) studies of magnetic dipole decays in highly ionized members of the Be, Mg, and Zn isoelectronic sequences.

**Vanderbilt University**  
**Nashville, TN 37235**

**Department of Computer Science**

**260. Theoretical Studies of Atomic Transitions**  
*Fischer, C.F.* **\$115,000**

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 emphasized the electron affinities of the alkaline earths and the nsnp  $^3P$  states of  $Rb^-$  and  $Cs^-$ . Cray computer codes have been modified to allow for an order of magnitude in growth of the complexity in the calculations and are now being used. Further development is in progress. When completed, some highly accurate calculations will be performed for negative beryllium ions and results compared with those obtained by other methods. More stable algorithms have been developed for continuum states in the presence of resonances. These algorithms are being applied to the study of photoionization in both beryllium and magnesium.

**University of Virginia  
Charlottesville, VA 22901**

**Department of Physics**

**261. Studies of Autoionizing States Relevant to Dielectronic Recombination**  
*Gallagher, T.F.* **\$104,716**

An important atomic process that contributes to energy loss in fusion plasmas is dielectronic recombination, the recombinations of ions and electrons through autoionizing atomic states. To understand and correctly account for dielectronic recombination in plasmas it is necessary to know not only the recombination rates for isolated pairs of electrons and ions, but also the macroscopic effects of other ions and electrons in the plasma. To reach an understanding of dielectronic recombination we are measuring the rates of the inverse process, autoionization, using laser excitation of atoms in a beam. Specifically we have been measuring the autoionization rates of the  $Ba6pn\ell$  states in the presence of static and microwave electric fields that mimic the electric fields due to the ions in a plasma. Preliminary analyses of our measurements indicate that the accepted theory of ionic field effects, which strictly applies only to static fields, may in fact be applied to the time varying ionic fields in a plasma. In both static and microwave electric fields autoionization rates are found to scale not as  $n^{-3}$ , but as  $n^{-4}$ , where  $n$  is the principal quantum number of the outer electron. The origin of the new scaling is mixing of the angular momentum states. Extending this reasoning, it is apparent that in a real plasma the rates scale as  $n^{-5}$ , due to the temporally varying direction of the ionic fields.

**Western Michigan University  
Kalamazoo, MI 49008-5151**

**Department of Physics**

**262. Correlated Charge-Changing Ion-Atom Collisions**  
*Bernstein, E.M.; Tanis, J.A.* **\$78,000**

Experimental studies of fundamental atomic interactions are conducted for collisions of few-electron ions with neutral gas targets. A major emphasis of this research is the study of two-electron interactions, and particularly those in which electron correlation effects play a significant 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 involve ions with  $2 \leq Z \leq 92$  in charge states  $q \geq Z/2$  and energies ranging from 5 keV/u to 100 MeV/u. Accelerator facilities at Lawrence Berkeley Laboratory, Argonne National Laboratory, and Western Michigan University are used in this work. Specific recent studies include: (1) resonant transfer and excitation (RTE) for 1.7 to 4.0 MeV/u  $Nb^{(28-32)+} + H_2$  and 100 to 150 MeV/u  $U^{89+} + C$  collisions, (2) RTE for 5.6 to 6.7 MeV/u  $Ti^{19,20+}$  ions channeled in Au crystals, (3) transfer ionization in 0.1 to 3.0 MeV/u  $He^+$  and  $O^{9+} + He$  collisions, and (4) correlated continuum- and bound-state capture in 3.75 keV/u  $O^{6+} + He$  collisions. Additionally, a new project involving the study of dielectronic recombination for  $He^+$  ions using the Electron Cooler and Storage Facility at the Indiana Cyclotron has recently been initiated.

**The College of William and Mary  
Williamsburg, VA 23185**

**Department of Physics**

**263. Collisional Detachment of Negative Ions**  
*Champion, R.L.; Dover-spike, L.D.* **\$93,500**

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 formation on alkali surfaces is also under way. In this latter experiment, it is observed that some molecules that impinge upon alkali surfaces at room temperature can fragment and desorb from that surface as negative ions with a surprisingly high efficiency. The mechanism that drives this phenomenon is being examined.

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**Chemical Energy**

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**Brigham Young University  
Provo, UT 84602****Department of Chemical Engineering****264. Effects of Dispersion and Support on Adsorption, Catalytic, and Electronic Properties of Cobalt/Alumina CO Hydrogenation Catalysts***Bartholomew, C.H.***\$85,000**

An investigation of the effects of surface structure, dispersion, and support on the adsorption, catalytic, and electronic properties of cobalt/alumina is in progress. The project objectives are (1) to determine the effects of surface structure and metal dispersion on the adsorption and catalytic properties of cobalt and (2) to determine the effects of decorating support species on metal crystallites and of direct electronic interactions between metal clusters and support, on the adsorption, catalytic, and electronic properties of cobalt supported on alumina. Work has been conducted in three areas: (1) study of the effects of surface structure on the adsorption and catalytic properties of cobalt monolayers deposited on W(100) and W(110), using TPD, LEED, and AES spectroscopies, and CO hydrogenation reaction measurements; (2) study of the effects of dispersion and support decoration on the CO adsorption/desorption and catalytic properties of well-dispersed cobalt/alumina; and (3) Mossbauer study of the effects of metal-support interactions and decoration on the electronic properties of well-dispersed cobalt/alumina and iron/alumina. Results from these studies provide definitive evidence that CO hydrogenation on cobalt is structure-insensitive and that large activity variations in cobalt/alumina with metal loading are due to metal-support interactions.

**California Institute of Technology  
Pasadena, CA 91125****Department of Chemistry****265. Hydrocarbon Rearrangements Promoted by Highly Electrophilic Transition Metal Complexes***Bercaw, J.E.***\$135,000**

This project studies the scope, mechanism, and thermodynamics of olefin and alkyne insertion into metal-hydrogen and metal-carbon bonds for highly electrophilic scandium derivatives. The reversible olefin insertion/ $\beta$  H and  $\beta$  alkyl elimination for scandocene derivatives with varying degrees of steric crowding is being explored:  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc-R}$ ,  $[(\eta^5\text{-C}_5\text{Me}_4)_2\text{SiMe}_2]\text{Sc-R}$ , and  $[(\eta^5\text{-C}_5\text{H}_3\text{CMe}_3)_2\text{SiMe}_2]\text{Sc-R}$  (R = H, alkyl, and so forth). Clean oligomerization and polymerization of ethylene with specified polydispersities have been realized using well defined (one-component) scandocene alkyl catalysts, and under some conditions these meet all the

criteria for a "living" Ziegler-Natta ethylene polymerization system. With the latter two scandocene systems, developments include (1) catalytic dimerization of  $\alpha$  olefins to the "head-to-tail"; (2) *gem*-disubstituted olefins with remarkable selectives (>99% for >50 turnovers); (3) a related catalytic intramolecular cyclization of  $\alpha$ ,  $\omega$  diolefins selectively to *exo*-methylene cycloalkanes; and (4) catalytic branching of 1,4-pentadienes to substituted 1,3-dienes. With a new linked cyclopentadienyl-amide ligand system a hydride,  $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2\text{NCMe}_3]\text{Sc}(\mu_2\text{-H})(\text{PMe}_3)_2$ , and a dimeric propyl derivative,  $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2\text{NCMe}_3]\text{Sc}(\mu_2\text{-CH}_2\text{CH}_2\text{CH}_3)_2$ , were prepared and structurally characterized. Both of these effect oligomerization of  $\alpha$  olefins. The latter is being explored as a possible living Ziegler-Natta system for preparing monodispersed block polymers. The results of the studies have provided an understanding of some of the fundamental steps in olefin metathesis, dimerization, polymerization, hydroformylation and hydrogenation, hydrocarbon cracking, branching, and isomerization reactions.

**266. Catalytic Assembly of Hydrocarbons from Carbon Monoxide***Grubbs, R.H.***\$120,000**

Methylene fragments are key intermediates in the assembly of hydrocarbons on metal centers. Important classes of the species are those that bridge between an early and late transition metal. A family of such complexes has been synthesized by the reaction of a titanaethylene fragment with a late transition metal halide. During the last research period, emphasis has been placed on the reactions of the platinum and palladium analogs ( $\text{CP}_2\text{Ti-CH}_2\text{-MLnX}$ , M = Pt and Pd) and the role of the supporting ligand in their reactions with CO. It was found that the doubly bridged complexes reacted very slowly with CO to produce a ketene complex. However, the addition of one equivalent of a phosphine opened the bridge and increased the reactivity. These complexes result in the production of ketene complexes with no supporting bridges. A second important reaction studied is the reaction of the titanaethylene species with sulfur donors. This desulfurization reaction is mechanistically interesting and results in the production of thioformaldehyde complexes. Work is in progress to develop the reaction chemistry of the thioaldehydes and the corresponding aldehyde and ketone complexes.

**University of California  
Irvine, CA 92717****Department of Chemistry****267. Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes***Evans, W.J.***\$86,500**

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., is under investigation. Complexes of these metals containing bonds to carbon and to hydrogen can accomplish unusual and highly selective reactions. To be able to transform many types of substrates under a variety of reaction conditions, studies involve the synthesis of durable complexes of

these metals that contain these M—C and M—H bonds. Alkoxide ligands have been studied in this regard and are providing not only the desired complexes, but also some unexpected opportunities to develop other types of catalytic and reaction chemistry. The alkoxide complexes are typically polymetallic and the extended metal-oxygen (from the alkoxide) frameworks mimic metal oxides used as supports in heterogeneous catalysis. Hence, these molecules are being examined as models for oxide catalyst supports. In addition, these molecules are providing examples of how molecular alkoxides form extended oligomerized oxides. New research opportunities opened up by the fundamental studies on the alkoxides as well as the initial goals involving selective transformations are being pursued.

**University of California  
Santa Barbara, CA 93106**

**Department of Chemical and Nuclear Engineering**

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

Weinberg, W.H.

**\$127,000  
(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)-(1x2), 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**

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

Ford, P.C.

**\$116,000**

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<sub>1</sub> 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<sub>1</sub> 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**

**270. Chemically Modified Electrodes and Related Solution Chemistry**

Elliott, C.M.

**\$85,000**

The chemical and/or physical properties of electrode solution interfaces can be modified in useful ways by interposing thin polymer films at that interface. Such modifying films may contain bound electrochemically active catalyst molecules or they may simply serve to alter the chemical environment in which the electron transfer event takes place. Studies are being made of new schemes for incorporating electroactive systems of interest into polymers that can be used to modify electrode surfaces. Additionally, molecules that are of potential interest as catalysts that can subsequently be incorporated into electrode bound films are being developed and studied. Specific areas of interest include (1) the catalytic electrochemical oxidation of olefins employing polymer films of heteropolynuclear porphyrins and (2) electrocatalytic hydrogenation of unsaturated centers employing molybdenum-sulfur complexes and catalytic oxidation of water to form dioxygen. 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.

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

Norton, J.R.

**\$85,000**

This project has developed several efficient general syntheses of diosmacycloalkanes. These syntheses were used to prepare compounds that may serve as models for hydrocarbons and hydrocarbon fragments adsorbed to metal surfaces. The structures and the reactivity of several of these compounds were explored. It was shown that, in contrast to accepted theory, ethylene exchanges in and out of diosmacyclobutane occurred with retention of stereochemistry at carbon. Aromatic- and alkyl-substituted olefin adducts are in preparation (1) to explore any alternative olefin elimination pathways and



(2) to identify these compounds as models for metal surface-bound alkenes. Several larger ring diosmacycloalkanes were prepared that serve as models for methylene aggregation on the surface of Fischer-Tropsch catalysts. The properties of these dinucleardialkyl compounds will be compared to their mononuclear analogs to determine which (if any) steps in typical catalytic sequences require the presence of polynuclear systems.

**University of Colorado  
Boulder, CO 80309**

**Department of Chemistry and Biochemistry**

**272. Studies of Hydrogen—Hydrogen and Carbon—Heteroatom Bond Cleavage Reactions**

*DuBois, M.R.*

**\$65,000**

The objective of the project is to characterize hydrogenolysis reactions of dinuclear molybdenum complexes with bridging thiolate and sulfide ligands. Such reactions provide potential homogeneous models for the chemistry of the hydrodesulfurization catalysts. Certain cationic complexes of the type  $[(CpMo)_2(S_2CH_2)(\mu-S)(\mu-SR)]^+$  have been found to react with hydrogen to form RH,  $H^+$ , and  $(CpMo\mu-S)_2S_2CH_2$ . This reactivity shows a significant dependence on the nature of the thiolate substituent R. In general, thiolate substituents with electron withdrawing groups undergo facile hydrogenolysis, while those with electron donating character, such as alkyls, do not react with hydrogen. A mechanistic study of the hydrogenolysis of the cation  $[(CpMo)_2(S_2CH_2)(\mu-S)(\mu-SCH_2CO_2Me)]^+ Br^-$  revealed that the reaction was catalyzed by  $(CpMo\mu-S)_2S_2CH_2$ , which was formed in low yield when methylbromoacetate was eliminated from the cationic derivative. This observation was consistent with an observed induction period in the reaction with hydrogen. In contrast, the rate of the hydrogenolysis of the cation with  $R = CHMe(Ph)$  was not altered by the presence of the neutral dimer. This result and other data suggest that hydrogen activation by the cationic derivative is characteristic of the latter hydrogenolysis reaction. Attempts to identify an intermediate in the hydrogen activation process by low temperature NMR spectroscopy were unsuccessful.

**Cooperative Institute for Research of Environmental Sciences (CIRES)**

**273. Chemisorption and Reaction Studies on Well-Characterized Bimetallic and Alloy Surfaces**

*Koel, B.E.*

**\$124,000  
(19 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,  $\pi$ -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  $Pt(111)$ .

**University of Connecticut  
Storrs, CT 06268**

**Department of Chemistry**

**274. Structure Sensitivity of Iron and Cobalt Zeolite Catalysts**

*Suib, S.L.*

**\$79,000**

The structure sensitivity of iron and cobalt zeolite catalysts in cyclopropane ring opening, hydrogenation, hydrogenolysis, and oligomerization reactions has been the focus of our research program. Small cobalt particles ( $< 5$  angstroms) trapped in NaX zeolite catalyze ring opening reactions, larger (8 to 10 angstrom) particles catalyze hydrogenation reactions, and even larger ( $> 10$  angstrom) particles catalyze hydrogenolysis reactions. The smallest particles are 100% dispersed and have been characterized by a variety of methods including chemisorption, ferromagnetic resonance, and spin echo nuclear magnetic resonance methods. The unique aspects of this research include the preparation of extremely small particles via microwave discharge decomposition of organometallic precursors and the characterization of such particles with several complementary techniques. A variety of CoFe alloys with different chemical composition are being prepared in order to test their catalytic properties. Another emphasis of our research involves surface studies of catalysts. X-ray photoelectron spectroscopy and residual gas analysis have been used to distinguish  $O_2$  in the framework of zeolite Y, and oxygen from trapped water and molecular  $O_2$ . Elemental analyses of zeolite surfaces have been conducted with Rutherford backscattering via theoretical depth profiles and laser microprobe mass analysis. Morphological and surface studies of Raney Ni and doped Raney Ni hydrogen-deuterium exchange catalysts before and after ultrasonic treatment show that the particles are breaking up and exposing fresh metal surfaces for reaction. Photoreductions in ultrahigh vacuum of semiconductor surfaces have been used to prepare reduced metal particles. Similar electrocatalytic materials have been prepared by binding clays to semiconductor electrode surfaces. Sintering of ceramic fiber matrices in composites has been followed by surface characterization. Surface properties of lead iodide crystals grown in space have also been studied.





initiator the rate of reaction was approximately first order in tetralin and 1/2 order in tetramethylbutane. Liquid phase pyrolysis of tetralin gave mostly naphthalene at low conversions, but more 1-methylindan at longer reaction times. In an attempt to generate the 1,6-biradical that might be involved in the C<sub>2</sub> loss product, attempts were made to prepare 5-methylene-1, 3-cyclohexadiene-6,6-spiro cyclobutane by low temperature pyrolysis of the parent ketone. At 60 to 100° the ketone gave only tetralin and *o*-allyl toluene in a first order reaction. Work on a molecular program to calculate heats of formation and geometries of open shell conjugated systems and transition metal complexes continues.

## Indiana University-Purdue University Indianapolis, IN 46205

### Department of Chemistry

#### 284. *Studies of Metal—Ammonia Interactions with Aromatic Substrates*

Rabideau, P.W.

\$80,000

There is a considerable amount of interest in dissolving metal reduction and reductive alkylation reactions within the fuel science community, since these processes promote the solubilization of coal and related fossil fuels. Solubilization is important not only to coal liquefaction, but also to coal structure studies since the resulting soluble fractions can be studied by traditional spectroscopic methods. This research is directed toward a better understanding of the reduction pathways. Polynuclear aromatic compounds (PAs) are used as model compounds because of their presence in the coal structure (albeit not in monomeric form). Attention is also directed toward the structure and reactivity of hydroaromatics. These latter compounds are important because they may serve as hydrogen donors during coal liquefaction. The solubilization of coal during reduction is usually attributed to the cleavage of benzyl/benzyl C—O bonds, and ether C—O bonds. Recent results of this research, however, show that no bond cleavage occurs in the reduction of bis(methylnaphthyl)ethane in either THF or ammonia if the temperature is kept below -30°C (conditions which do in fact solubilize coal). Additional studies involve the reduction behavior of multiple PA sites connected by inert spacers and pi bond spacers.

## University of Iowa Iowa City, IA 52242

### Department of Chemistry

#### 285. *Synthesis and Chemistry of Cationic d<sup>0</sup> Metal Alkyl Complexes*

Jordan, R.F.

\$160,000  
(18 months)

The objective of this research is to understand the chemistry of new types of cationic, d<sup>0</sup> organometallic complexes of Group IV-VI metals that incorporate important features of heterogeneous catalysts, such as high steric and electronic unsaturation, terminal and bridging oxo ligands, and alkoxide groups. The scope and mechanisms of the olefin insertion and oxidation reactions, and the

H—H and C—H activation reactions of highly electrophilic metal complexes will be studied to increase understanding of (1) the generation, structures, and reactivity of olefin polymerization and oxidation catalysts and (2) the development of new catalysts and synthetic reagents for efficient hydrocarbon utilization. Efforts are focused on the chemistry of ZrR<sub>3</sub>L<sub>3</sub><sup>+</sup> and (C<sub>5</sub>R<sub>5</sub>)ZrR<sub>2</sub>L<sup>+</sup> systems, and related alkoxide derivatives.

## University of Kentucky Lexington, KY 40506-0055

### Department of Chemistry

#### 286. *Metallacumulenes and Carbide Complexes* Selegue, J.P.

\$109,000

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. Several "borderline cases" were discovered for the relative stability of alkyne ( $\eta^2$ -HC≡R) and vinylidene (C=CHR) ligands. Exposure of [Mo(HC≡CCMe<sub>3</sub>)L<sub>2</sub>(Cp)][BF<sub>4</sub>] (L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph) to CO effects conversion to *trans*-[Mo(C=CHCMe<sub>3</sub>)(CO)L<sub>2</sub>(Cp)][BF<sub>4</sub>]. Alkyne to vinylidene conversion does not occur with phosphite ancillary ligands, nor with cyanide ion, isocyanides, or PF<sub>3</sub> as incoming ligand. Reversible, one-electron, electrochemical reduction of [Mo(HC≡CR)L<sub>2</sub>(Cp)]<sup>+</sup> gives long-lived radicals [Mo(HC≡CR)L<sub>2</sub>(Cp)]. A second, one-electron reduction is quasi-reversible at fast scan rates, but irreversible at slower rates, suggesting that [Mo(HC≡CR)L<sub>2</sub>(Cp)]<sup>-</sup> rapidly tautomerizes to [Mo(C=CHR)L<sub>2</sub>(Cp)]<sup>-</sup> in solution. Reactions of acetylene with [MX{P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)] (MX = FeI, RuCl) lead to [M(HC≡CH){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)]<sup>+</sup>, which is stable for ruthenium, but gradually converts to the vinylidene form for iron. Also being studied are tungsten complexes bearing both alkyne and vinylidene ligands. For example, methylation of [W(C≡CCMe<sub>3</sub>)(PhC≡CPh)(CO)(Cp)] leads to [W(C=CHCMe<sub>3</sub>)(PhC≡CPh)(CO)(Cp)][PF<sub>6</sub>]; the alkyne ligands in this system may donate two, three, or four electrons. As a possible route to a mixed-metal bicarbide complex, [Ru(C≡CH)(PMe<sub>3</sub>)<sub>2</sub>(Cp)] was reacted with [WCl(CO)(PhC≡CPh)(Cp)] to give [(Cp)(PMe<sub>3</sub>)<sub>2</sub>Ru(μ-C≡CH)W(CO)(PhC≡CPh)(Cp)][BF<sub>4</sub>], which structurally resembles a tungsten-substituted ruthenium vinylidene complex. Deprotonation leads to [(Cp)(PMe<sub>3</sub>)<sub>2</sub>Ru—C≡C—W(CO)(PhC≡CPh)(Cp)], a novel heteronuclear ethynediyl complex.

**Lehigh University  
Bethlehem, PA 18015**

**Department of Chemistry**

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

*Eischens, R.P.*

**\$87,000**

The project objectives are (1) to determine the nature of carbon deposits on alumina-supported bimetallic catalysts and (2) to determine whether the species that produce infrared bands at 1585 and 1460  $\text{cm}^{-1}$  are caused by carbon-oxygen vibrations similar to the asymmetric and symmetric vibrations of carboxylate ions. This second objective has been accomplished. Studies with oxygen-eighteen labeled alumina unambiguously show that these bands are caused by carbon-oxygen vibrations rather than being attributable to aromatic carbon-carbons and carbon-hydrogens. The objective of relating the bands to catalyst performance requires a special apparatus in which a dedicated infrared spectrometer is equipped with a microbalance so that the weight of carbon deposits can be monitored simultaneously with observation of the infrared spectra. This apparatus has been constructed. The initial results show that in each case, the second metal constituent, Re, Ir, or Sn, in bimetallic platinum-alumina catalysts, lowers the amount of carbon oxygen species in the carbon deposit. Attempts will be made to determine whether these observations are significant in catalyst performance.

**288. Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane**  
*Klier, K.; Simmons, G.W.; Her-* **\$120,566**  
*man, R.G.*

The activation of methane on  $\text{O}/\text{CH}_2\text{Cl}_2/\text{Pd}(100)$  overlayers was studied by AES/LEED/TDS and HREELS. Dichloromethane, which is a compound used to control oxidation of methane to formaldehyde over real palladium catalysts, was found by HREELS to completely dissociate on Pd(100) with the formation of  $\text{Pd}_4\text{C}$ ,  $\text{Pd}_4\text{H}$ , and  $\text{Pd}_4\text{Cl}$  surface species with characteristic vibrational modes but no fragments with C—Cl or C—H vibrational modes. The surface structures formed from dichloromethane adsorption, as well as the residual Cl layers and their interactions with oxygen, have been modeled as a random arrangement of  $\text{CCl}_2$  units and oxygen atoms using a kinematic approach. Of the structures studied for fitting the  $\text{CH}_2\text{Cl}_2$  adsorption, the best features are obtained with Cl—C—Cl ensembles, having  $90^\circ$  Cl—C—Cl angles, that exclude nearest-neighbor adsorption and Cl—Cl next-nearest-neighbor adsorption. Upon oxidation of surface carbon species, CO was produced with increased selectivity compared to  $\text{CO}_2$  as the  $\text{CH}_2\text{Cl}_2$  preexposures increased. This selectivity can be explained by ensemble control of the oxygen supply to surface carbon species by strongly localized Cl atoms. With oxygen adsorbed on the surface, the previously observed disproportionation of the  $c(2 \times 2)\text{—O}$  structure into the mixture of a dense phase,  $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{—O}$ , and a rare phase,  $p(2 \times 2)\text{—O}$ , 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. This disproportionation of the  $c(2 \times 2)\text{—O}$  structure takes place before oxygen

desorption at ca 600 K. The activation energies and entropies for desorption from the  $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{—O}$  and  $p(2 \times 2)\text{—O}$  phases were determined to be  $168 \pm 8$  kJ/mol and 21 J/mol-K, and  $76 \pm 20$  kJ/mol and -143 J/mol-K, respectively. This reconstruction-assisted phase transformation indicates that the more reactive state of adsorbed oxygen phase, i.e.,  $p(2 \times 2)$ , may be produced thermochemically by carrying out the oxidation reaction near 600 K and at low oxygen partial pressures.

**University of Louisville  
Louisville, KY 40292**

**Department of Chemistry**

**289. Synthesis and Properties of Metallo-**  
**carboxylic Acids**

*Gibson, D.H.*

**\$80,000**

The synthesis and reaction characteristics of metallo-carboxylates ( $\text{M—COOR}$ ; M = transition metal, R = H, alkyl, triphenyltin, or alkali metal) are under investigation. The significance of these compounds is derived from their probable intermediacy in water gas shift reactions and in metal-catalyzed  $\text{CO}_2$  fixation processes. Reactions of the cations  $(\text{L})\text{Fe}(\text{CO})_2(\text{PPh}_3)^+\text{BF}_4^-$  (L = cyclopentadienyl or pentamethylcyclopentadienyl) with aqueous base have provided the acids and the corresponding metallo-carboxylate anions as their alkali metal salts. In each case, the potassium salt can be alkylated or converted to the triphenyltin derivative by reaction with appropriate electrophile. Reactions of arylphosphite-substituted iron cations,  $\text{CpFe}(\text{CO})_2[\text{P}(\text{OAr})_3]^+\text{BF}_4^-$  (Ar = phenyl or p-tolyl) and  $\text{C}_5\text{Me}_5\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]^+\text{BF}_4^-$ , with aqueous base provide good yields of the corresponding arylphosphonate complexes instead. The phosphonates are thought to arise by intramolecular oxide transfer from intermediate iron metallo-carboxylate anions. Probes of these and other arylphosphite-substituted metal carbonyl cations suggest the necessity of a significant lifetime for the metallo-carboxylate anion and a cis stereochemical relationship between the carboxylate and phosphite ligands in order for the phosphonate to be formed. Further examples of the nucleophilic behavior and oxygen transfer capacity of these anions are being studied.

**Massachusetts Institute of Technology  
Cambridge, MA 02139**

**Department of Chemistry**

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

*Ceyer, S.T.*

**\$200,000  
(18 months)**

The project objective is to carry out heterogeneous catalytic reactions that normally are observed only at high pressures of reactant gas in an ultrahigh vacuum environment. This is accomplished using molecular beam techniques to activate the reaction and high resolution electron energy loss spectroscopy (HREELS) as a sensitive and chemically specific detector of the reaction





products. In addition, for over half of the reactions, a rapid two electron change ( $\text{CO}^{2+}$  transfer) is observed that results in formation of a new cation and anion. This is a new type of reaction for metal carbonyl species. In reaction of metal carbonyl anions with dimeric complexes, a single electron transfer has been observed resulting in oxidation of the anion to a dimer and reduction of the first dimer to its anion. This reaction appears to occur by nucleophilic attack of the anion on a metal of the dimer followed by a single electron transfer. Reaction of metal carbonyl anions with coordination complexes such as  $\text{Co}(\text{o-phen})_3^{3+}$  results in oxidation of the anion to the dimer and reduction of the cobalt to  $\text{Co}(\text{o-phen})_3^{2+}$ . These reactions apparently occur by outer sphere electron transfer. Thus, reaction of metal carbonyl anions with three different types of oxidants results in three distinct mechanisms: (1) a two-electron ( $\text{CO}^{2+}$ ) transfer, (2) single electron transfer from attack of the anion on a metal, and (3) outer sphere electron transfer. Continuing research to define these mechanistic possibilities is under way.

## University of North Carolina Chapel Hill, NC 27514

### Department of Chemistry

#### **298. Reductive Coupling of Carbon Monoxide to $\text{C}_2$ Products** Templeton, J.L. **\$94,965**

Coupling reactions involving carbon monoxide and carbyne ligands are being explored. Formation of ketenyl ligands from coupling an arylcarbyne with an adjacent carbonyl ligand is a well-known reaction. One goal is to extend the reaction chemistry of the metal carbon triple bond to additional heteroatom carbynes. Preparation of a rare aryloxycarbyne has been achieved by nucleophilic attack on a phosphonium carbyne unit with a substituted phenoxide reagent. The properties of the resultant  $\text{W}\equiv\text{C}-\text{OAr}$  entity are under investigation. Electrophilic attack at the oxygen of a terminal carbonyl ligand to generate related alkoxy-carbyne species is a long term goal. Deprotonation of a methylcarbyne fragment forms an anionic vinylidene species that is nucleophilic at  $\text{C}_\beta$ . Alkylation and aldehyde condensation reactions have been accomplished with the vinylidene anion reagent.

## Northwestern University Evanston, IL 60201

### Department of Chemical Engineering

#### **299. Solid-State, Surface, and Catalytic Studies of Oxides** Kung, H.H. **\$109,500**

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 can be correlated to the presence of magnesium orthovanadate. It was then found that other vanadates of magnesium, magnesium pyrovanadate, and metavanadate were nonselective. The difference among these vanadates can be attributed to the absence of  $\text{V}-\text{O}-\text{V}$  bonds in the orthovanadate. Indeed, when the magnesium ions were replaced by neodymium or samarium ions in the orthovanadate structure, nearly equally selective catalysts were obtained. However, when magnesium was replaced by europium that was much more reducible than magnesium, the catalyst became much less selective. On the magnesium orthovanadate catalyst, it was found that some reactive reaction intermediates desorbed from the surface above  $550^\circ\text{C}$  that could initiate gas phase chain reactions involving alkane and oxygen. The extent of gas phase reaction in the presence of the catalyst could be more than double that in the absence of the catalyst. This desorbed intermediate was probably an alkyl radical or an OH species.

### Department of Chemistry

#### **300. Supported f-Element Organometallic Complexes: Surface Chemistry and Catalysis** Marks, T.J.; Burwell, R.L., Jr. **\$91,000**

The project objective is to understand the dramatic and technologically important changes in catalytic activity that occur when organometallic 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  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgCl}_2$ , and other supports. A parallel solution chemistry effort focuses on the synthesis and structural characterization of complexes that model the surface environment and test ideas about the chemistry. A kinetic/mechanistic study has been completed on hydrogenation of a variety of olefins by  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{Al}_2\text{O}_3$  ( $\text{Cp}' = (\text{CH}_3)_5\text{C}_5$ ). There are striking mechanistic similarities to f-element reaction patterns in solution. Furthermore, NMR studies reveal that unsaturated cationic complexes of the type  $\text{Cp}'_2\text{ThCH}_3^+$  and  $\text{Cp}_2\text{ZrCH}_3^+$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) are formed in large quantities on  $\text{Al}_2\text{O}_3$  surfaces. Rational synthetic routes to such f-element cations have now been developed in solution. Cationic organothorium species have also been identified on  $\text{MgCl}_2$ , and dosing with various reagents affords a detailed, *in situ* picture of the surface reaction chemistry.

#### **301. Chemical Interactions in Multimetal—Zeolite Catalysts** Sachtler, W.M.H. **\$95,560**

The chemistry and physics controlling the formation of metal particles in faujasite-type zeolites are studied and the results exploited for the preparation of catalysts with predetermined properties. Transition metals (TMs) are



introduced into the zeolite either by ion exchange, followed by calcination and reduction, or by decomposition of metal carbonyls. After losing their ligands, TM ions tend to migrate to smaller cages. Reduction then requires high temperature and is reversible: at high T and low  $p(\text{H}_2)$  the metal atoms are re-oxidized by protons and  $\text{H}_2$  is released, which is identified by a characteristic TPD peak. Cation migration to small cages can be suppressed and their reducibility dramatically increased by first occupying these cages with cations of a second, nonreducible TM. This auxiliary element can also serve as chemical anchor and catalyst promoter. Bimetallic catalysts are prepared by controlled ion exchange/calcination aimed at locating platinum ions in supercages, and nickel or copper ions in sodalite cages. TPR shows a profound effect of platinum on the reducibility of nickel or copper. Bimetallic particles are formed in supercages; their catalytic properties confirm predictions. Decomposing rhenium carbonyl on Pt/NaY results in PtRe particles, identified as selective catalysts for C-C fission. A Pd carbonyl cluster displaying a highly structured IR spectrum is formed in supercages of NaY.

**302. Organometallic Surface Chemistry**  
*Shriver, D.F.* \$102,000

The overall objective is to develop 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. Current focus is on the nature of the catalytically important ligands, C, O, CO, and CCR. Current research involves a study of the nature of the interaction of  $\text{ZnO}_x$  with rhodium catalyst and correlation of this interaction with selectivity for hydroformylation. The preparation and reactivity of d-metal clusters with light main group hetero-atoms is under investigation. For example, oxo-containing low-oxidation state clusters were prepared and are characterized. The mode of bonding of the oxygen atom to low-oxidation state molecular clusters has many analogies to metal surfaces, and both of these systems contrast with simple metal oxides. Finally, the metal cluster-assisted formation and cleavage of C—C bonds is being investigated.

**University of Oregon**  
**Eugene, OR 97403**

**Department of Chemistry**

**303. Polyoxoanion-Mediated Methane Activation and Functionalization: Molecular Design of New Homogeneous and New Solid-State/Heterogeneous Catalysts**  
*Finke, R.G.* \$86,589

The major goal of this research is to molecularly engineer polyoxoanions to produce new types of homogeneous and heterogeneous polyoxoanion-supported catalysts for  $\text{H}_2$ ,  $\text{O}_2$ , RH, and  $\text{CH}_4$  activations and functionalizations. One current goal is to prepare and characterize compounds such as  $(\text{Bu}_4\text{N})_5\text{Na}_3[(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  and  $(\text{Bu}_4\text{N})_4\text{Na}_2[(1,5\text{-COD})\text{Ir}\cdot\text{SiW}_9\text{Nb}_3\text{O}_{40}]$ , to explore their ability to act as homogeneous catalysts for  $\text{H}_2$  and  $\text{O}_2$  activations, and then to move on to more challenging

reactions such as RH and  $\text{CH}_4$  activation and their selective functionalization. Other efforts in progress will attempt to prepare analogs of the above catalyst precursors but where the  $\text{Bu}_4\text{N}^+$  organic counter cations are replaced by all inorganic cations such as  $\text{Na}^+$ . The resultant systems would be all inorganic, once the 1,5-COD ligand is removed, and hence would provide a more robust and oxidation inert type of ligand system than is typically available. Careful product studies, plus kinetic and mechanistic work to establish the catalytically active species, round out the experiments under examination.

**Pennsylvania State University**  
**University Park, PA 16802**

**Department of Chemical Engineering**

**304. Enhancement of Activity and Selectivity by Metal—Support Interactions**  
*Vannice, M.A.* \$300,000  
(18 months)

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 determined heats of adsorption and of  $\text{H}_2$ , CO, and  $\text{O}_2$  on Pt and Pd using a modified differential scanning calorimeter. Kinetic studies have been made on hydrogenation reactions involving aromatic hydrocarbons and the C—O bond in carbon monoxide, acetone, and crotonaldehyde. A greater than 100-fold enhancement was found for acetone hydrogenation over  $\text{TiO}_2$ -supported Pt, similar to that for CO hydrogenation. This latter catalyst preferentially activated the CO bond in crotonaldehyde to give selectivities of over 35% crotyl alcohol whereas typical Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts produced 100% butyraldehyde. A model invoking special metal—support interface sites has been proposed to explain this selective activation of carbonyl bonds. Studies of BTX's (benzene, toluene, and o-, m-, and p-xylene) have shown that turnover frequencies (TOF's) can be increased using acidic supports, with the greatest enhancements occurring with benzene. The addition of methyl groups to the ring decreases TOF values. The presence of additional acidic adsorption sites near the Pd crystallites has been proposed to explain this behavior. Emphasis is now on the characterization of these adsorbed molecules using infrared spectroscopy and solid-state MAS-NMR. The selectivity of aromatics containing a carbonyl bond (acetophenone) is being investigated over Pt. After arrival of an UHV system later this year, HREELS and XPS studies of adsorbed species on Pt and  $\text{TiO}_2$  single crystals and on Pt-covered  $\text{TiO}_2$  single crystals will begin.

Department of Chemistry

**305. Mechanistic Studies of Carbon Monoxide Insertion into Metal—Nitrene and Metal—Carbene Bonds**  
*Geoffroy, G.L.* **\$118,700**

The reactivity of nitrene, carbene, and ketene ligands on metal clusters and the cycloaddition reactions of metal carbyne complexes are 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 from these studies, and unique bimetallic Fe/Ru catalysts for nitroaromatic carbonylation have been discovered. Recent 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 in the current research. In other aspects of this work it has been demonstrated that the combination of an oxidation step with NO addition will induce the carbonylation of acyl ligands to form  $\alpha$ -ketoacyl ligands. The chemistry of these  $\alpha$ -ketoacyl complexes has been explored with a variety of electrophiles, nucleophiles, and alkynes. An important finding is that the  $\alpha$ -ketoacyl carbon—carbon bond is easily cleaved by oxidation or protonation. The  $\alpha$ -ketoacyl complexes react with alcohols and amines to give  $\alpha$ -ketoesters and  $\alpha$ -ketoamides, and these complexes react with alkynes to form metallacycles that result from coupling of the alkyne and the  $\alpha$ -ketoacyl ligand. The reaction of diiron methylene compounds with phosphinimines has been found to give rise to unprecedented transformations that lead to the formation of binuclear ferra-pyrrolinone and ferra-azetine complexes. Preliminary results indicate that these in turn react with alkynes to give pyrroles, and efforts are now being given to devising catalytic routes to these important organic chemicals.

**306. Transition Metal Mediated Transformations of Unsaturated Molecules**  
*Sen, A.* **\$83,000**

Transition metal mediated transformation of organic molecules in homogeneous solutions is of considerable scientific and practical importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The project objectives are: (1) to achieve a fundamental mechanistic understanding of a number of important systems of this type and (2) to use this knowledge to develop new and useful transition metal mediated organic transformations. The following systems are currently under study: (1) a novel palladium(II) mediated procedure for the selective oxidative functionalization of alkanes and arenes; (2) a palladium(II) catalyzed process for the alternating copolymerization of carbon monoxide and olefins that leads to the formation of highly functionalized polymers; (3) a procedure for the synthesis of complex organic molecules that involves the use of palladium(II) enolate species; and (4) a molybdenum(VI) system incorporating oxo and alkyl ligands that may serve as a model for the heterogeneous, molybdenum(VI) catalyzed oxidation of alkanes.

Department of Materials Science and Engineering

**307. Determination of the Distribution of Hydrogen in Coal by FTIR**  
*Painter, P.C.* **\$105,009**

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 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 at the level of both local composition and at the larger scale of the effect of the balance of intermolecular forces on solution and swelling behavior. At this time, more than fifty coal samples have been characterized by FTIR and proton NMR spectroscopies. The parameters obtained from these studies are being used to predict the solubility and swelling characteristics of these coals.

University of Pennsylvania  
Philadelphia, PA 19104

Department of Chemical Engineering

**308. Support Effects Studied on Model Supported Catalysts**  
*Gorte, R.J.* **\$85,500**

Model catalysts consisting of thin films of Group VIII metals deposited on alumina, silica, 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 ethane hydrogenolysis 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

**309. Synthesis and Properties of New Pre-ceramic Materials**  
*Sneddon, L.G.* **\$90,000**

This project is focused on the development of new high-yield, low-temperature routes to nonoxide ceramics, including silicon carbide, boron nitride, boron carbide, and metal borides and silicides, which have been shown to have important electronic and mechanical properties. Of particular interest is the development of new polymer precursor routes to these ceramics since the use of such polymers should facilitate the formation of thin film or

coated materials. Recent work has resulted in the development of new high yield routes to the new inorganic polymers, poly(vinylpentaborane), poly(vinylborazine), and poly(borazylene). Poly(vinylpentaborane) has now been shown to undergo high yield conversions to boron carbide, while poly(vinylborazine) and poly(borazylene) have proved to be efficient precursors to boron nitride. Studies are now ongoing concerning the chemical and physical properties of these new polymers and derived ceramic materials, as well as the development of new chemical precursors to a wider range of ceramics.

**310. Catalytic Hydrogenation of Carbon Monoxide**

Wayland, B.B.

**\$147,500  
(15 months)**

This project is focused on developing strategies to accomplish the hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. Approaches to this issue are based upon the recognition that rhodium macrocycles have unusually favorable thermodynamic values for producing a series of intermediates implicated in the catalytic hydrogenation of CO. Observations of metalloformyl complexes from reactions of H<sub>2</sub> and CO, and reductive coupling of CO to form metallo  $\alpha$ -diketone species have suggested a multiplicity of routes to organic oxygenates that utilize these species as intermediates. Thermodynamic and kinetic-mechanistic studies are used in constructing energy profiles for a variety of potential pathways, and these schemes are used in guiding the design of new metallospecies to improve the thermodynamic and kinetic factors for individual steps in the overall process. Variation of the electronic and steric effects associated with the ligand arrays along with the influences of the reaction medium provide the chemical tools for tuning these factors. Current 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.

**University of Pittsburgh  
Pittsburgh, PA 15260**

**Department of Chemistry**

**311. Studies of the Fundamental Nature of Catalytic Acidity, Sites, and Intermediates**  
Hall, W.K. **\$105,000**

The acidic and catalytic properties of various solid acids (particularly H-zeolites) are under investigation. <sup>13</sup>C-MASNMR studies of adsorbed alcohols and olefins have shown that carbenium ions are formed as transient metastable species, not stable intermediates as suggested recently. Ways of producing stronger (super) acid systems are being studied and ways of assaying the acid strength using Hammett and H<sub>R</sub> indicators, adsorbed alcohols, and heterocyclics are being developed. An objective is to determine just how strong the solid acid must be to stabilize a given ion. The reaction chemistry of isobutane and

neopentane over solid acids is being used as a tool to evaluate acidic properties. CH<sub>4</sub>, H<sub>2</sub>, and the corresponding carbenium ions (or olefins) are formed in the primary decomposition step; this is followed by secondary carbenium ion reactions of these products. Means were found to separate these processes so that their response to the surface acidity could be evaluated. The fraction of the overall reaction which occurred in the primary step varied from 100% to about 10%; it increased with temperature with a given catalyst, but also necessarily decreased with increasing conversion (increasing catalyst acidity). These effects were inseparable. Poisoning with NH<sub>3</sub> increased this fraction. Interestingly, the adsorption of an amount of NH<sub>3</sub> equivalent to less than 10% of the potential Brønsted sites was lethal. Thus, either only a few sites are effective in these reactions or else this chemisorption reduces the effectiveness of all the sites.

**312. Studies of Supported Metal Catalysts**

Hercules, D.M.

**\$94,500**

The adsorption of molybdate and tungstate on alumina was studied by comparison with the adsorption of perchlorate and permanganate. Two types of interactions between metal oxyanions and alumina have been observed. Permanganate and perchlorate ions appear to adsorb on alumina primarily through electrostatic interactions. The amount of permanganate or perchlorate adsorbed is directly proportional to the fraction of perchlorate or permanganate anions present in the solution. Molybdate and tungstate oxyanions appear to adsorb on the alumina surface by some other mechanism, such as acid-base or condensation reaction. Adsorption of molybdate and tungstate occurs on two types of sites to yield tightly and loosely bound surface species. The distribution of Mo oxidation states in reduced 5 wt % Mo/TiO<sub>2</sub> catalysts has been determined by ESCA. The results were consistent with the average oxidation state estimated from gravimetric analyses. Mo oxidation states varying from +6 to 0 can be produced by increasing the reduction temperature up to 650°C. The activity of the reduced Mo/TiO<sub>2</sub> catalyst for benzene hydrogenation was found to be strongly dependent on the extent of reduction. Comparison of the benzene hydrogenation activity with the distribution of Mo oxidation states determined by ESCA suggests that Mo centers with oxidation state +2 are the most active species.

**313. Infrared Studies of Influence of Alkali Metals on C—O Bond in Chemisorbed Carbon Monoxide**

Yates, J.T., Jr.

**\$144,000**

This research employs a state-of-the-art Fourier Transform infrared Spectrometer for examining the details of the interaction between chemisorbed species on single crystal transition metal surfaces. Projects under way are: (1) the study of the interaction of electronegative poisons with chemisorbed CO on Ni(III); (2) the coadsorption of chemically inert molecules with dipolar adsorbates yielding characteristic redshifts; (3) the observation of hydrogen bonding effects between adsorbates; and (4) the novel use of reflection infrared to investigate the behavior of specific surface species upon excitation by electron impact, and direct observation of dissociation by spectroscopic means. Comparisons of these results with infrared studies on technical catalytic surfaces will yield a deeper understanding of the

mechanism of catalytic chemistry. In addition to reflection ir spectroscopy, this project involves XPS, thermal desorption, work function, LEED, and electron stimulated desorption measurement techniques.

## Rensselaer Polytechnic Institute Troy, NY 12180

### Department of Chemistry

#### 314. Selective Transformations of Carbonyl Ligands to Organic Molecules

Cutler, A.R.

**\$142,500**  
**(14.5 months)**

Studies were completed on anionic phosphido alkyl and acetyl complexes, (1)  $\text{Cp}(\text{CO})(\text{PPh}_2)\text{Fe-R}^-$  and (2)  $\text{In}(\text{CO})(\text{PPh}_2)\text{Fe-R}^-$ , and their neutral phosphine derivatives, (3)  $\text{Cp}(\text{CO})(\text{PPh}_2\text{H})\text{Fe-R}$  and (4)  $\text{In}(\text{CO})(\text{PPh}_2\text{H})\text{Fe-R}$ , where  $\text{In} = \eta^5\text{-indenyl}$  and (a)  $\text{R} = \text{CH}_3$  or (b)  $\text{R} = \text{COCH}_3$ . Attempts to carbonylate 1a and 2a to 1b and 2b failed; also, 3a and 4a resist carbonylation. Reacting 1b with  $\text{MeI}$  affords a neutral  $\text{PPh}_2\text{Me}$  acetyl compound 5, whereas  $\text{MeOSO}_2\text{CF}_3$  gives the Fischer carbene complex (6)  $\text{Cp}(\text{PPh}_2)(\text{CO})\text{Fe}=\text{C}(\text{OMe})\text{CH}_3$ . Carbene 6 isomerizes to 5 at room temperature. Reaction conditions have been optimized for generating vinylidene compounds  $\text{In}_2(\text{CO})_3\text{Fe}_2\mu\text{-}$ (where  $\text{C} = \text{CHR}$ ) from  $\text{InFe}(\text{CO})_2^-$  and  $\text{In}(\text{CO})_2\text{Fe-CH}_2\text{R}$  (where  $\text{R} = \text{H, Me, OMe}$ ). The bimetallic carbonylation procedure for converting  $\text{Fp}^-(\text{Li}^+, \text{Na}^+, \text{PPN}^+)$  and  $\text{In}(\text{CO})_2\text{Fe-CH}_3$  to  $\text{InCp}(\text{CO})_3\text{Fe}_2(\text{COCH}_3^-)$  and then regioselectively to  $\text{FpCOCH}_3$  (1 atm. CO) has been optimized. Studies are finished on the diastereofacial selectivity observed during reduction of the alkoxy-carbenes  $\text{Cp}[\text{P}(\text{OR})_3](\text{CO})\text{Fe}=\text{C}(\text{OCH}_3)\text{CH}_3^+$  (where  $\text{R} = \text{Me, Ph}$ ) with borohydride reagents  $\text{R}_3\text{BH}^-$  ( $\text{Li}^+, \text{Na}^+, \text{K}^+$ ) and with  $(\text{PPh}_3\text{CuH})_6$ . A survey of the  $\text{Rh}(\text{I})$ -catalyzed hydrosilation of a variety of iron acyl complexes has been concluded.  $\text{FpCOR}$  thus adds  $\text{R}'_2\text{SiH}_2$  to give  $\alpha$ -siloxyalkyl complexes  $\text{FpCH}(\text{OSiHR}'_2)\text{R}$  (where  $\text{R} = \text{CH}_3, \text{Et, n-Pr, i-Pr, i-Bu, Ph}$ ; and  $\text{R}'_2 = \text{Et}_2, \text{Ph}_2, \text{PhMe}$ ). With  $\text{PhSiH}_3$ , catalytic hydrosilation produces fully reduced  $\text{FpCH}_2\text{R}$  (where  $\text{R} = \text{Me, Ph}$ ). Hydrosilation of  $\text{Mn}(\text{CO})_5\text{COR}$  gives  $(\text{CO})_5\text{Mn-CH}(\text{OSiR}'_2)\text{H}$  (where  $\text{R} = \text{Me, Ph}$ ) without a  $\text{Rh}$  catalyst. Thus,  $\text{Co}_2(\text{CO})_8$  and  $(\text{CO})_5\text{MnCOR}$  also act as efficient hydrosilation catalysts for  $\text{FpCOR}$ .

## University of Rochester Rochester, NY 14627

### Department of Chemistry

#### 315. Transition Metal Activation and Functionalization of Carbon—Hydrogen Bonds

Jones, W.D.

**\$98,199**

The investigation of homogeneous C—H bond activation by  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)$  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  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(2\text{-furyl})\text{H}$

over an  $\eta^2\text{-furan}$  complex indicates that the aromaticity of the group activated may play an important part in the strength of the carbon—metal bond. The phosphine also plays a role in the stability of the phenyl hydride complexes, with  $\text{PPh}_3$  being the least stable and  $\text{PMe}_3$  being the most stable. The steric and electronic effect of the phosphine contributes to the stability of the complex. In the presence of conjugated polyaromatics (naphthalene, anthracene, phenanthrene, and so forth), the  $\eta^2\text{-arene}$  complexes  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\eta^2\text{-arene})$  are formed upon heating a solution of  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{Ph})\text{H}$  with arene. These complexes are much more stable than the corresponding  $\eta^2\text{-benzene}$  or phenyl hydride complexes.  $\text{Fe}(\text{PMe}_3)_2(\text{CNR})_3$  can catalyze the insertion of isonitrile into aromatic C—H bonds. Visible light is used to dissociate an isonitrile ligand from the complex, and low concentrations of added isonitrile are used to increase efficiency. Indoles are catalytically produced by an intramolecular insertion reaction of ortho-methylarylisonitriles using  $\text{Ru}(\text{dmpe})_2\text{H}_2$  as catalyst. The complexes  $\text{RhCl}(\text{CNR})(\text{PMe}_3)_2$  also catalyze this type of isonitrile insertion reaction.

## Rutgers University Piscataway, NJ 08854

### Department of Physics and Astronomy

#### 316. Structure and Reactivity of Model Thin Film Catalysts

Madey, T.E.

**\$70,000**

The research is focused on characterizing the structure and reactivity of model bimetallic catalysts, i.e., ultrathin films of metals on metals. The overall objective is to search for unusual surface reactivity as a function of film thickness and composition, and substrate structure. Present studies are focused on the platinum on tungsten system, and involve a comparison between the atomically smooth  $\text{W}(110)$  surface and the atomically rough  $\text{W}(111)$  surface. One of the specific goals is to determine the growth characteristics and thermal stability of monolayer Pt films on  $\text{W}(111)$ . This surface reconstructs to form microscopic facets upon annealing and LEED and scanning tunneling microscopy to study surface morphology are used. Another specific goal is to characterize the adsorption behavior, catalytic activity, and the effect of adsorption on the stability of ultrathin Pt films on  $\text{W}$ . Future studies will focus on the growth and thermal stability of metal films on atomically rough surfaces of fcc and hcp metals.

## SRI International Menlo Park, CA 94025

### Materials Research Laboratory

#### 317. Interaction of Carbon and Sulfur on Metal Catalysts

McCarty, J.G.

**\$86,499**

Significant progress has been made in the development of a new analytical technique, surface analysis by laser ionization (SALI), for measurement of the thermochemical

properties of carbon coadsorbed with chemisorbed sulfur. SALI consists of the stimulated desorption of surface C atoms by a low current pulsed Ar<sup>+</sup> beam at 2 keV, followed by laser ionization at 193 nm wavelength of the desorbed neutral species and reflecting time-of-flight mass spectrometry of the resulting C<sup>+</sup> ions. The equilibrium surface carbon coverage was measured for fractional sulfur coverages of 0, 0.1, 0.16, and 0.26 monolayers over a temperature range between 600 and 1100 K. Surfaces containing fractional monolayers of sulfur were prepared by exposing the Ni(100) crystal at 500 K to 0.1% H<sub>2</sub>S in H<sub>2</sub> from a molecular beam doser. Absolute carbon and sulfur coverages were calibrated by Auger Electron Spectroscopy of saturated ordered overlayer structures. Identical carbon segregation coverages were obtained for both increasing and decreasing temperature profiles suggesting that the measured carbon coverages represented equilibrium values. The heat of formation of carbon on Ni(100) was determined by Langmuir-McLean segregation, and found to range from -20 to -30 kJ/mol and was essentially independent of the coadsorbed sulfur coverage. However, coadsorbed sulfur reduced the saturation carbon coverage from 0.5 to 0.12 monolayers for sulfur coverages from 0 to 0.26 monolayers, respectively. The effect of chemisorbed sulfur on hydrogasification of carbonaceous overlayers has been examined using temperature-programmed reaction with hydrogen (TPRH). Multilayers of bulk carbon deposited on fused iron by extended exposure to C<sub>2</sub>H<sub>4</sub> exhibited 50 to 100 K higher characteristic TPRH peak temperatures when partially (about 50% saturation) and fully sulfur poisoned. Future work will focus on TPRH experiments and isosteric heat of formation measurements for carbon chemisorbed on MgO- or silica-supported iron and alumina-supported platinum catalysts with fractional monolayers of chemisorbed sulfur.

**University of South Carolina  
Columbia, SC 29208**

**Department of Chemistry**

**318. Ligand Transformations and Catalysis by Transition Metal Cluster Compounds Containing Sulfur**

*Adams, R.D.*

**\$112,000**

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.

**Stanford University  
Stanford, CA 94305**

**Department of Chemical Engineering**

**319. Catalytic Steam Gasification of Carbon**

*Boudart, M.*

**\$90,000**

This work explores tungsten carbide as a new catalytic material. Recently, we have prepared three phases of tungsten carbide with high specific surface area, namely  $\alpha$ WC (35 m<sup>2</sup>g<sup>-1</sup>; hexagonal),  $\beta$ WC<sub>0.61</sub> (100 m<sup>2</sup>g<sup>-1</sup>; face centered cubic), and  $\beta$ W<sub>2</sub>C (15 m<sup>2</sup>g<sup>-1</sup>; hexagonal). Two catalytic reactions forming water were studied on tungsten carbides and platinum: the H<sub>2</sub>—O<sub>2</sub> reaction and the H<sub>2</sub>—N<sub>2</sub>O reaction. The H<sub>2</sub>—O<sub>2</sub> reaction was carried out in a flow recirculation reactor near atmospheric pressure between 273 and 600 K in excess H<sub>2</sub> or O<sub>2</sub>. The H<sub>2</sub>—N<sub>2</sub>O reaction was studied in a differential flow reactor at atmospheric pressure between 300 and 600 K either in excess H<sub>2</sub> or N<sub>2</sub>O. All rates were first order in the concentration of limiting reactant and zero order in the concentration of the excess reactant. For each tungsten carbide, a break in the Arrhenius diagram near 450 K is observed.

**320. Molecular Beam Studies of Activated Adsorption and Heterogeneous Kinetics on Transition Metal Surfaces**

*Madix, R.J.*

**\$132,416**

Initial trapping probabilities for CH<sub>4</sub> on Pt(111) were measured between 0.94 and 0.16 for incident total translational energies between 3.4 and 20.2 kJ/mole and angles of incidence  $\theta$ , between 0 and 45° at a surface temperature of T<sub>s</sub> of 100 K. The initial trapping probability decreases with increasing incident translational energy and decreasing angle of incidence and varies smoothly with incident normal energy. The dependence of the initial trapping probability on incident normal translational energy agrees quantitatively with existing theories at incident normal translational energies below 8 kJ/mole, but at higher incident normal kinetic energies the observed initial trapping probabilities are higher than the values predicted by both models. Energy loss mechanisms other than surface phonon excitations may partially account for this discrepancy. In accordance with these models, the measured in-plane angular distributions indicate that the trapping probability is relatively independent of surface temperature between 160 and 500 K. Comparing the initial trapping probability vs normal kinetic energy data to previous mean translational energy measurements of methane molecules desorbing from Pt(111) at the surface normal suggests that detailed balance applies for the nonequilibrium situation involving a collimated monoenergetic molecular beam of methane incident on a Pt(111) surface.

**Syracuse University**  
**Syracuse, NY 13244**

**Department of Chemical Engineering and Materials Science**

**321. Metal—Support Interactions: The Effect of Catalyst Preparation on Catalytic Activity**  
*Schwarz, J.A.* **\$85,000**

Research efforts have been focused on the effect of preparation variables on the performance of both monometallic and bimetallic catalysts. In the former case, previous research directed toward studies of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts has been extended to examine the impact of the properties of Al<sub>2</sub>O<sub>3</sub> carriers on the catalytic activity of the supported metal. Four types of  $\gamma$ -aluminas with varying surface area and porosity manufactured by Union Carbide, Degussa, Engelhard, and Kaiser Aluminum were used as supports. The amount of Ni adsorbed and the amount of Al dissolved in the Ni(NO<sub>3</sub>)<sub>2</sub> impregnation solution were found to vary. The Ni/Al<sub>2</sub>O<sub>3</sub> precursors have been characterized by temperature-programmed reduction and desorption (TPR/TPD) and the hydrogenolysis of ethane. The experimental results indicate variation in reduction profiles, crystallite size, and activation energy for the test reaction. These results correlate with the propensity of Al<sub>2</sub>O<sub>3</sub> dissolution in acidic impregnation solution and the degree of crystallinity of Al<sub>2</sub>O<sub>3</sub>. The structure and activity of composite oxide (Al<sub>2</sub>O<sub>3</sub> on TiO<sub>2</sub>, and TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) supported monometallic (Pt, Ir) and bimetallic (Pt-Ir) catalysts have also been studied. The surface charge behavior of the composite oxides are characterized in terms of their point of zero charge (pzc). A model has been developed to determine the dopant surface area. Catalyst precursors were prepared from H<sub>2</sub>PtCl<sub>6</sub> and H<sub>2</sub>IrCl<sub>6</sub>. These materials were characterized by TPR and TPD and by a structure sensitive reaction, the hydrogenolysis of ethane. The pure oxide supported monometallic catalysts were used as standards to compare the behavior of composite oxide supported catalysts. Bimetallic formation was observed on all supports. Varying degrees of H<sub>2</sub> chemisorption occurred on composite oxide supported catalysts. The effect of the SMSI carrier (TiO<sub>2</sub>) on H<sub>2</sub> chemisorption suppression is dependent on the composition of the composite oxide.

**Texas A and M University**  
**College Station, TX 77843**

**Department of Chemistry**

**322. Correlations Between Surface Structure and Catalytic Activity/Selectivity**  
*Goodman, D.W.* **\$230,000**  
**(16 months)**

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.

**323. Catalysts and Mechanisms in Synthesis Reactions**  
*Lunsford, J.H.* **\$104,000**

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 which emanate from a hot metal oxide surface during a catalytic reaction. It has been demonstrated that 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. Generally, those reactive oxides have metal ions with multiple oxidation states. The radicals presumably react by reductive addition to form methoxy ions. 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 X-ray photoelectron spectroscopy and ion scattering spectroscopy studies have shown that the sodium carbonate essentially covers the cerium oxide. 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**

**324. Study of Synthesis Gas Conversion over Metal Oxides**  
*Ekerdt, J.G.* **\$84,843**

The project objective is to develop an understanding of the causes for catalytic activity and selectivity and the effects of metal oxide structure and acidic and basic additives during hydrocarbon synthesis and oxidation over metal oxides. Research has focused on zirconium dioxide systems and has (1) identified the structure of adsorbed C<sub>1</sub> fragments, (2) established the reaction mechanisms for methanol, methane, and higher weight hydrocarbon synthesis, (3) identified lattice oxygen vacancies as the active surface site for CO adsorption and conversion, and

(4) indicated that acidic sites control the CO insertion reactions and that basic sites control the condensation reactions that are responsible for the synthesis of higher weight products. Current work on zirconium dioxide is focused on  $^{13}\text{C}$ -labeled studies to determine the structure of the reaction intermediates that are stabilized by acidic and basic sites. Current work is also directed toward the synthesis of MoMo, WW, and MoW organometallic complexes and the use of these complexes to prepare model systems of oxide catalysts for the study of how composition and structure influence catalytic properties. These model systems will consist of isolated MoMo, WW, and MoW cation pairs supported on inert oxide carriers.

## Department of Chemistry

### 325. Morphological Aspects of Surface Reactions

White, J.M.

**\$185,000**  
**(18 months)**

The chemical activities of metal single crystals, oxide-supported small metal particles derived from organometallic precursors, and metal thin films on oxide and metal substrates are under investigation. Novel photochemical and electron-stimulated methods of synthesizing hydrocarbon fragments on Ag(111) have been investigated. These methods allow preparation of large surface concentrations of normally reactive intermediates for study by spectroscopic and kinetic methods. Silica-bound molecular rhodium complexes have been examined as isolated species, as aggregates, and as metal particles derived therefrom. Novel tunneling microscopy and spectroscopy methods are being initiated so that individual small metal particles can be studied. The activation of hydrocarbon and carbon-oxide species by potassium-promoted metals is being studied at the molecular level. The long-range goal is to establish correlations between particle morphology and catalytic activity over a broad range of conditions.

University of Utah  
Salt Lake City, UT 84112

## Department of Chemistry

### 326. Ligand Intermediates in Metal-Catalyzed Reactions

Gladysz, J.A.

**\$110,400**

The project goal is the synthesis and study of homogeneous complexes containing ligand types (-CHO, =CHOH, -CH<sub>2</sub>OH,  $\equiv\text{C}$ , =CH<sub>2</sub>, H<sub>2</sub>C=O, -OCHO, CO<sub>2</sub>, and so forth) intermediate in C<sub>1</sub>/C<sub>2</sub> catalytic reactions. Mechanistic understanding of key steps and insight needed for the design of new catalysts is sought. The study has been extended that involves the chemical and electrochemical oxidation of methyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$  to trimethylphosphine analog  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PMe}_3)(\text{CH}_3)$ . A reasonably stable intermediate that is a dimer of the cation radical  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PMe}_3)(\text{CH}_3)]^+$  was observed. This species slowly converts at room temperature to 1 equivalent each of methylidene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PMe}_3)(=\text{CH}_2)]^+$ , acetonitrile complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PMe}_3)(\text{NCCH}_3)]^+$ , and CH<sub>4</sub>. This new methyl ligand activation might be

coupled with known reactions to achieve the catalytic conversion of methane to ethylene. Also studied is the chemistry of carbide complexes C<sub>x</sub>. The C<sub>2</sub>H complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CH})$  was prepared in high yield, and it is readily deprotonated by MeLi to give  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$ , which is believed to be the first well-defined lithiocarbon complex. Heterobimetallic C<sub>2</sub> complexes of the formula  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CM}'\text{L}_n)$ , where M' is a transition metal, are being studied. The reaction of CO<sub>2</sub> with chlorobenzene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{ClC}_6\text{H}_5)]^+ \text{BF}_4^-$  gives cationic CO<sub>2</sub> complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^2\text{-O=C=O})]^+ \text{BF}_4^-$ . Its properties are being compared to the analogous anionic complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{C}(\text{=O})\text{O}^{-1})$  previously reported.

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

Grant, D.M.; Pugmire, R.M.

**\$105,269**

This project objective is to develop new 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  $^{13}\text{C}$  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  $^{13}\text{C}$  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 nine  $^{13}\text{C}$  CSA tensors in 1,3,5-trimethoxybenzene (1,3, 5-TMB) were measured and compared with previous one-dimensional results. Chemical shift values of all carbons in 1,3,5-TMB, 1,2,3-TMB, and 1,4-DMB, and the orientation of their principle axes were determined *ab initio*, and calculations of the shielding tensors were performed. Results agreed with experimental substituent effects obtained from correlating values obtained in the polysubstituted compounds. Carbon-13 NMR shielding tensors were determined for two anthracite coals and a fusinite maceral, using powder pattern line-shapes; theoretical calculations on the model compound circumcoronene(I) supported these interpretations. Spectroscopic analysis of nonprotonated to protonated aromatic carbons agreed with elemental analysis and dipolar dephasing NMR techniques. The method is 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.

Wayne State University  
Detroit, MI 48202

Department of Chemistry

**328. Reactive Characterization as a Probe of  
the Nature of Catalytic Sites**  
Brenner, A. **\$98,500**

Hydrogen activation is an important step in many catalytic reactions and may be conveniently studied by measuring the rate of H<sub>2</sub>-D<sub>2</sub> exchange over a catalyst. Although this reaction has been extensively studied over metals, the process is much less understood over metal oxides. In very few cases has the site density for the exchange reaction been determined, which makes it difficult to compare the activity to that of other types of catalysts. Research during the past year has been concentrated on a study of the rates of H<sub>2</sub>-D<sub>2</sub> exchange over the oxides of Mg, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, and Mo. The rates have been determined as a function of the temperature of activation of the oxides. It is found that the rate of reaction usually strongly varies with the pretreatment. The number of active sites has been determined by two methods. (1) Exchange of surface OH groups with D<sub>2</sub>(g) gives a lower limit to the number of active sites, since any site that can undergo this stoichiometric reaction is also a site for catalytic exchange. (2) Selective poisoning by CO has been used to obtain an upper limit to the number of active sites. The site density is always very low. The general rate of exchange over a transition metal oxide was found to be less than the rate over the corresponding metal, but much higher than the rate over a homogeneous catalyst of the same metal.

University of Wisconsin  
Madison, WI 53706

Department of Chemical Engineering

**329. Experimental and Kinetic Modeling of  
Acid/Base and Redox Reactions Over Oxide Catalysts**  
Dumesic, J.A. **\$93,000**

Microcalorimetric measurements of heats of adsorption for selected basic molecules have been conducted to formulate a thermodynamic scale of acidity for metal oxide catalysts. Previous work showed that the heat of adsorption of pyridine on a number of silica-supported oxides could be correlated with the Sanderson electronegativity of the oxide, thereby providing a predictive means of preparing acid catalysts with desired strength. Recent studies have extended this concept by measuring the heats of adsorption of a series of bases (i.e., pyridine, ammonia, trimethyl amine, triethyl amine) on different acid sites. The heats of acid-base adduct formation in solution can be characterized for each of these bases by two parameters (one electrostatic and one covalent, the Drago-Wayland parameters); this allows heats of adsorption to be correlated in terms of two analogous parameters for the acid site. This approach was found to be applicable to the silica and silica/alumina acid sites that have been studied calorimetrically to date. The implication of these results is that it allows the heats of

adsorption to be predicted for basic molecules in terms of their known solution-phase properties. Studies of surface acidity are being complemented by solid-state NMR and Mössbauer spectroscopy studies of the acid site structure. Work during the past year has focused on <sup>27</sup>Al NMR characterization of silica/alumina and on the construction of a low-temperature Mössbauer spectrometer for <sup>121</sup>Sb studies.

Department of Chemistry

**330. Organometallic Chemistry of Bimetallic  
Compounds**  
Casey, C.P. **\$150,000**  
**(16 months)**

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 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.

Yale University  
New Haven, CT 06520

Section of Applied Physics

**331. Model Catalyst Studies of Active Sites and  
Metal-Support Interactions on Vanadia  
and Vanadia-Supported Catalysts**  
Henrich, V. **\$81,000**

This project is investigating the surface properties and the nature of active sites on vanadias that are important in catalytic applications. The electronic structure and chemisorption properties of vanadia surfaces are being studied using surface-sensitive electron spectroscopic techniques such as HREELS, XPS, UPS, LEED, Auger spectroscopy, and so forth. In order to separate the role of different valence states of the V ion on vanadia, well-characterized single-crystal surfaces are used, along with V metal that has been oxidized in different ways. Currently the properties of V<sub>2</sub>O<sub>5</sub> single crystal surfaces are being measured, along with the way in which reduction of V<sub>2</sub>O<sub>5</sub> surface changes its electronic structure and chemisorption properties. The interaction of V and vanadia with TiO<sub>2</sub> supports is being studied by depositing V on well-characterized, single-crystal TiO<sub>2</sub> (110) surfaces in UHV. The TiO<sub>2</sub> surfaces can be prepared either nearly perfect, in which all surface Ti cations are in a Ti<sup>4+</sup> valence state, or partially reduced by the removal of some lattice O<sup>2-</sup> ions; some of the cations on the latter surfaces



are in (roughly) a  $Ti^{3+}$  state, thus increasing the electronic interaction between the titania and the V. The oxidation and chemisorption properties of the surfaces are also being studied. The program will yield important basic information about active sites on vanadia-based catalysts and the interactions between vanadia and transition-metal oxide supports.

## Department of Chemical Engineering

### 332. *A Spectroscopic and Catalytic Investigation of Active Phase—Support Interactions*

Haller, G.L.

\$97,000

Metal-support interaction in Ag/TiO<sub>2</sub> catalysts has been investigated by chemisorption, catalytic reaction, X-ray absorption spectroscopy, and electron microscopy. Two Ag loadings of 1 and 10 wt % on TiO<sub>2</sub> were studied, and these were compared to similar SiO<sub>2</sub>-supported catalysts. The dispersion is always substantially greater on TiO<sub>2</sub> than on SiO<sub>2</sub> for a given pretreatment. Oxidation results in a pronounced increase in dispersion on SiO<sub>2</sub> but has a very modest effect on TiO<sub>2</sub>-supported Ag. All catalysts supported on SiO<sub>2</sub> have turnover frequencies for CO oxidation that are equivalent to unsupported Ag. However, the rates are suppressed when Ag is supported on TiO<sub>2</sub> and the degree of suppression is more pronounced on the catalyst of lower loading which has a higher dispersion. EXAFS and XANES analysis suggests that suppression of Ag activity is the result of Ag reacting with TiO<sub>2</sub> to form a surface compound. This strong interaction of Ag with TiO<sub>2</sub> relative to SiO<sub>2</sub> can act as a driving force for migration of Ag from SiO<sub>2</sub> to TiO<sub>2</sub> as demonstrated with physical mixtures.

## Department of Chemistry

### 333. *Alkane Photoreactions With Mercury Vapor*

Crabtree, R.H.

\$107,300

Substantial advances have been made in applying the Hg\* chemistry to new systems and in understanding the mechanism. Even fluorinated compounds can be dimerized. For example, previously unknown fluorinated glycols, potentially useful in polyester materials, have been prepared directly from the readily available fluorinated alcohols. Amines have been studied in greater detail and conditions found for the preparation of useful diamines, such as 2,2'-dipyridyl. Cross dimerization has been extended, e.g., to the preparation of 11 previously unobtainable carbinols and of a protected form of prolinol. Turning to the mechanism, it is now understood why alkenes do not build up in the system; H atoms add and return the alkene to the radical pool. This has important effects on the selectivity of the reaction. The selectivities observed, which result from differences in vapor pressure, in intrinsic reactivity, and from reactions subsequent to the photosensitization step are now understood.

### 334. *Energies of Organic Compounds*

Wiberg, K.B.

\$107,000

This research project is designed to provide information on the 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. A method has been developed for determining the heats of reduction of carbonyl compounds and has been tested with a variety of simple compounds. It will now be applied to a series of cyclic ketones and lactones in order to gain information on strain energies. The study of heats of hydration of alkenes will be continued with special emphasis on the formation of tertiary alcohols. Rotational barriers for hetero-substituted butadienes will be examined theoretically in order to gain information on the nature of conjugative interactions in pi-electron systems.

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## Separations and Analysis

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### Aerospace Corporation Los Angeles, CA 90009

#### Chemistry and Physics Laboratory

### 335. *Isotopically Selective, Two-Step, Laser Photodissociation of Triatomic Molecules in Cryogenic Solutions*

Zittel, P.F.

\$136,022

This research is directed toward understanding photo-physical, 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 infrared spectroscopy and two-step photodissociation of OCS dissolved in liquid rare gases. Oxygen isotopes have recently been enriched by a factor of four using this technique. The dependence of isotope enrichment on experimental variables is used to probe vibrational relaxation and chemical reaction processes in the cryogenic solution. The cryogenic solution work is complemented by gas phase experiments designed to measure cross sections for photodissociation of molecules in specific excited vibrational states. The separation of sulfur and oxygen isotopes by two-step photodissociation of OCS in the very low temperature gas phase is also being investigated. Of increasing interest are photodissociation cross sections and vibrational relaxation rates for highly excited vibrational states of small molecules in both the gas phase and in cryogenic solution.

**Auburn University**  
Auburn, AL 36849

Department of Chemical Engineering

**336. Interfacial Chemistry in Solvent Extraction Systems**

*Neuman, R.D.*

**\$106,000**

The interfacial chemistry of solvent extraction of metal ions in hydrometallurgical and nuclear industries is still incompletely understood. The present research emphasizes characterization of the structure and dynamics of the macroscopic liquid/liquid interface in organophosphorus solvent extraction systems associated with  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{UO}_2^{2+}$ . An interfacial film balance has been assembled to study long-chain model extractants at non-polar organic/aqueous interfaces. Monolayer studies, as such, can be of great value in understanding the interfacial behavior of extractant molecules and their interactions with metal ions because they offer the advantage of performing experiments on a well-defined and well-controlled interfacial system. In addition, two advanced laser techniques, surface laser light scattering (SLLS) and fluorescence recovery after photobleaching (FRAP), are to be applied to model extractant films to provide new fundamental information on the interfacial properties of these systems. The molecular aggregates or microstructures that form in the bulk organic phase of organophosphorus extractant systems are also being examined using various spectroscopic and scattering techniques to resolve questions concerning their physico-chemical nature.

**Brigham Young University**  
Provo, UT 84602

Department of Chemistry

**337. Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport**

*Lamb, J.D.*

**\$84,814**

The macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems is being investigated. Potential macrocyclic carriers are screened by measuring extraction equilibrium constants and partition coefficients. 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

**338. Photochemical Generation of the Photoacoustic Effect**

*Diebold, G.J.*

**\$82,000**

The application of the photoacoustic effect to chemical processes is being investigated. In the case of molecular photodissociation, the shape of the acoustic waveforms arising from thermalization of the recoil energy of the photofragments has been calculated. The release of thermal energy by a chemical reaction that follows molecular photodissociation also affects the temporal profile of the acoustic signal. The shape of the waveforms is being studied in order to determine kinetic and thermodynamic parameters of the reactions. It has been shown that the acoustic waveforms generated by laser irradiation of particles 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. Experiments to demonstrate a new technique of selective isotope ionization are also being performed. A two-photon interference effect dependent on laser polarization to determine the degree of suppression of the ionization signal from a major isotopic constituent relative to a minor one is under investigation. The interference effect can be used in conjunction with existing high-resolution spectroscopic techniques based on isotope shifts for selective ionization of isotopes.

**University of California**  
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

**339. Multiheteromacrocycles That Complex Metal Ions**

*Cram, D.J.*

**\$125,000**

The goals of this research are to design, synthesize, and test organic multiheteromacrocycles for their abilities to complex metal anions and inorganic cations. The ligating 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  $\text{Li}^+$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  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****340. Utilization of Magnetic Effects as a Means of Isotope Enrichment**  
Turro, N.J. **\$84,096**

The project objective is to provide a basic understanding of the mechanism of separation of magnetic isotopes from nonmagnetic isotopes. The knowledge provided by these investigations has allowed the design of some of the most efficient (nonlaser) isotope separation methods ever reported. In particular, systems have been constructed based on the photolysis of ketones which allow the separation of carbon-13 from carbon-12 with unprecedented efficiency. The working mechanism involves an interplay between electron and nuclear spin dynamics, molecular motions of fragments produced by photolysis, chemical reactions of the fragments produced by photolysis, and the reaction space available to the fragments. In addition to its impact on the science of isotope separation, these studies have employed the efficiency of isotope separation itself to provide an understanding of the geometry and chemical nature of reaction spaces provided by aqueous aggregates such as micelles and by porous solids such as zeolite molecular sieves. Recent investigations have stressed the use of a molecular chain to mimic the constraints of a reaction space. The efficiency of isotope separation has been found to be a function of chain length and chain dynamics. These results will allow the construction of "tailor-made" molecules whose structures can be systematically varied in order to test the ultimate limits of efficiency of isotope separation and to provide deeper insight to the details of the mechanism of magnetic isotope effects on chemical reactions.

**University of Delaware**  
Newark, DE 19716**Department of Chemistry****341. Studies of the Analyte—Carrier Interface in Multicomponent Flow Injection Analysis**  
Brown, S.D. **\$70,000**

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. Experimental profiles can then be compared to

theory. The goal is a better understanding of homogeneous and heterogeneous chemical reactions.

**Duke University**  
Durham, NC 27706**Department of Chemistry****342. Studies of Multifrequency Phase-Resolved Fluorescence Spectroscopy for Spectral Fingerprinting**  
McGown, L.B. **\$80,000**

Fluorescence lifetime selectivity in the frequency domain is being explored as a new dimension of information for spectral fingerprinting of complex samples. Recent developments in this project have been in the area of data analysis: phase-resolved fluorescence spectroscopy and total luminescence spectroscopy have been combined to yield three-way arrays of intensity as a function of emission wavelength, excitation wavelength, and modulation frequency. This new, tensorial format can be used to uniquely extract component spectra and lifetimes; this is in contrast to two-dimensional matrix analogs, which do not provide unique solutions without additional constraints and boundaries. The fundamental limits of resolution and detectability in the analysis of mixtures by the three-way array approach are currently being explored using both real and simulated data. Future research will then explore increasingly complex systems, through the integrated use of multiway data formats and sophisticated data analysis strategies. Of particular interest are dynamic interactions between analytes and matrix constituents that occur in complex samples, such as those of biological and environmental origin, which are germane to elucidation of transport, binding, and aggregation phenomena.

**University of Florida**  
Gainesville, FL 32611**Department of Chemistry****343. The Glow Discharge as an Atomization and Ionization Source**  
Harrison, W. **\$91,000**

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 laser ablation of material from a metal alloy into a glow discharge. The effect of buffer gas type and pressure is of interest in determining redeposition rates. The rf discharge is being studied in an attempt 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. Another active project deals with pulsed 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.

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

*Winefordner, J.D.*

**\$90,000**

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**

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

*Montaser, A.*

**\$142,000**

New high-temperature plasmas and new sample introduction systems are investigated for rapid elemental and isotopic analysis of gases, solutions, and solids using atomic emission spectrometry and mass spectrometry. These devices offer promise of solving analytical problems in the fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is on: (1) generation and fundamental investigation of annular helium plasmas that are suitable for the excitation of high-energy spectral lines, to enhance the detecting powers of a number of elements; (2) generation of plasmas that require low gas flows and low input power, to decrease the cost of analytical determination; (3) formation and investigation of tandem plasmas to separate and maximize atomization and excitation processes; and (4) development and characterization of new sample introduction systems that consume microliter or microgram quantities of samples and produce a minimal amount of solvent loading in plasma spectrometry. Investigations

are focused on 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**

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

*Browner, R.F.*

**\$89,999**

**(15 months)**

The investigation of a monodispersed aerosol generation interface for liquid chromatography/mass spectrometry (MAGIC-LC/MS) has continued. A number of instrumental developments to the interface have been accomplished, based on the need to improve chromatographic performance using the interface. The improved interface has been thoroughly characterized for the purpose of determining the quality of the chromatographic performance. This work has demonstrated that the interface is capable of producing separations that have comparable, or superior peak broadening to conventional ultraviolet detectors for liquid chromatography. The scope of the interface has been further studied for important classes of compounds, including high molecular weight polynuclear aromatic compounds. Searchable quality electron impact spectra for compounds with molecular weights in excess of 550 daltons (e.g. rubrene) have been readily produced. The transport properties of the interface have been thoroughly studied using a specially constructed test device, to correlate the signals observed in the mass spectrometer with the transport properties of the interface.

**Hampton University  
Hampton, VA 23668**

**Department of Chemistry**

**347. Use of Ion Chromatography-DC Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals**

*Urusa, I.T.*

**\$61,000**

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.

**University of Houston**  
Houston, TX 77004**Department of Chemical Engineering****348. Mechanisms of Thickening, Cake Filtration, Centrifugation, and Expression**  
Tiller, F.M. **\$103,000**

Fluid-particle separation is being studied both theoretically and experimentally. Of primary interest is the unification of the theory underlying sedimentation, thickening, filtration, centrifugation, deliquoring, and washing. Common to these operations is the compaction of particulate structures under loads derived from fluid friction, gravity, centrifugal forces, mechanically applied stresses, and diffusion. Generalized simultaneous differential equations governing fluid flow, deformation of particulate structures, and particle deposition form the foundation for attacking various classes of problems. An experimental correlation of permeability and compactibility in relation to colloidal and rheological properties is under way. Continuum laws involving sedimentation and flow through porous media are being examined from theoretical and experimental standpoints. Examination of data involving stress distribution in particulate matrices, local deviations in concentration of sedimenting suspensions using a computerized axial tomographic scanner (CATSCAN), and microscopic examination of beds of particles indicates that revision of some commonly accepted concepts may be required. Theoretical equations have been developed to describe both radial and planar deposition of ceramic suspensions in slip casting.

**University of Idaho**  
Moscow, ID 83843**Department of Chemical Engineering****349. Drop Oscillation and Mass Transfer in Alternating Electric Fields**  
Carleson, T.E. **\$48,000**  
(15 months)

An analytical solution was obtained for the flow field produced within and outside of 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 ratio of the amplitude of drop distortion to the wavelength of the electric field. 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 transfer rate would pass through a maximum as a function of the applied frequency, as observed experimentally. Work has been started on incorporating these results in a mass transfer relationship as well as comparing them quantitatively with velocities inside oscillating drops.

**University of Illinois**  
Urbana, IL 61801**Department of Chemistry****350. Thin Films Under Chemical Stress**  
Bohn, P.W. **\$130,000**  
(15 months)

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. Current research is examining the molecular level structural details important in Case II diffusion in aromatic polymers. The understanding gained will eventually allow processes involving differential solubility in a macromolecular matrix (e.g., photoresist removal in microlithography) to be operated more efficiently.

**351. Theta Pinch Discharges for Emission Spectrochemical Analysis**  
Scheeline, A. **\$74,000**

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. It has been shown in past years that any solid can be sufficiently vaporized and excited to reveal qualitatively the elemental composition of the solid. Efficiency of excitation has never been as great as desired, so modified discharge induction coils are being tested with the goal of increasing this efficiency, thus decreasing requirements for voltage. If this succeeds, safety and system reliability will be improved. Simultaneously, an echelle spectrometer and charge-coupled array detector to allow single shot multielement analysis is being completed. Work during the past year has indicated that it is essential to perform background subtraction, line selection, and internal standardization on each discharge, and this is most economically performed using array detector technology. Attempts to use conventional photomultiplier technology suffered from inaccurate background estimates and anomalies in line shapes to such an extent that the qualitative success of the theta pinch could not be used even to estimate concentrations of analytes within one order of magnitude. Photographic plates "quantitated" by eye proved to be more accurate than photoelectric detection. The array detector approach will circumvent this anomaly. At that point, studies of the evolution of sample uptake with repeated pinch firings will be resumed.

**Kansas State University**  
Manhattan, KS 66506**Department of Chemistry****352. Development of a Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry**  
Fateley, W.G. **\$82,000**

A Hadamard transform spectrometer (HTS) has been developed that can be used for Raman spectroscopy in the near-infrared (NIR). A 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 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<sup>+</sup> (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.

### Lehigh University Bethlehem, PA 18015

#### Department of Chemistry

##### 353. *Perforated Monolayers*

*Regen, S.L.*

**\$64,000**

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.

### University of Michigan Ann Arbor, MI 48109

#### Department of Chemistry

##### 354. *Hadamard Transform Imaging*

*Morris, M.D.*

**\$195,000  
(19 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<sup>2</sup> to 10<sup>5</sup> enabling use of high-power pulsed or 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

##### 355. *Continuous Reaction Chromatography*

*Aris, R.; Carr, R.W.*

**\$82,000**

Work continues on a systematic study of the benefits of performing chemical reaction under chromatographic conditions. The theoretical analysis of the countercurrent moving bed showed how thermodynamic limitations of a fixed bed could be overcome, and an experimental countercurrent reactor was successfully built and tested. This motivated work with the switched column in which countercurrency is simulated in a discontinuous fashion by switching the feed point between short fixed beds in a cyclic manner. It has been shown that this gives better performance than a single fixed bed and can emulate the countercurrent system. A small switched column has been built and tested on separations and is now running as a reactor. Simplified computational methods for difficult separations are also being investigated and the control problems that this system may generate are being formulated.

### University of Missouri Rolla, MO 65401

#### Department of Chemistry

##### 356. *Use of Functionalized Surfactants and Cyclodextrins in Chemical Analysis*

*Armstrong, D.W.*

**\$67,000**

Organizing media such as micelles, microemulsions, vesicles, cyclodextrins, and so forth are playing an increasingly important role in chemical analysis. New separation and spectroscopic detection methods have been developed using highly specific micelles, microemulsions, and cyclodextrins. For example, micelles composed of brominated Brij 96 surfactant allow resonance Raman spectra to be taken of low levels of many fluorescent molecules. This is possible because this micelle shifts absorption and luminescence bands, changes luminescence lifetimes and quantum yields, facilitates quenching effects, allows the use of aqueous rather than organic solutions, stabilizes transient species, alters fluorescence depolarization, and changes the apparent pK<sub>a</sub> of ionizable solutes. Good resonance Raman spectra were obtained for fluorescent metalloporphyrins using the micellar approach. A variety of fluorescent, heterocyclic-aromatic compounds were successfully analyzed using ultraviolet laser excitation. The potential use of this

technique as a detection method for micelles liquid chromatography is being investigated. A particularly novel use of micelles and microemulsions is in field flow fractionation (FFF). It has been demonstrated that the molecular weight range of FFF can be extended by several orders of magnitude by use of secondary equilibrium to these species. This allowed the first separation of small solutes by FFF. The theory, mechanism, and application of this technique are being explored in detail. It appears that FFF will be an effective method for characterizing the size and aggregation number of association colloids.

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

### Chemical Kinetics Division

#### 357. *Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation*

*Sieck, L.W.* **\$142,700**

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  $\Delta H$  and  $\Delta S$  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

#### 358. *Stable Isotope Studies*

*Ishida, T.* **\$82,000**

The general goal of this project is development of isotope separation processes, especially those for the effective fractionation of isotopes of hydrogen and other first-row elements, and basic studies in the related fields to correlate the isotope separative effects with the molecular structure and the forces acting on the molecules. The current efforts are being directed in the following two principal areas. The first area is development of *in situ* regenerable hydrophobic catalysts for hydrogen isotope

exchange reactions between gaseous hydrogen and liquid water. Platinum group metals dispersed on a conductive substrate such as pyrolytic carbon are rendered variable degrees of hydrophobicity needed for a desirable dihydrogen coverage of the catalyst metal surface by means of modifications of the substrate surfaces with (1) poly(biphenyl) and poly(terphenyl), (2) highly methylated saturated silyl compounds, and (3) perfluoroalkene derivatives. Surface derivatization is obtained through various electrochemical techniques. Characteristics of the surfaces are investigated as a function of choice of substrate material, the crystallographic orientations of the surfaces, the pre-derivatization preparation of substrates, and derivatization processes. The second area is correlation of inter- and intramolecular forces and the thermodynamic equilibrium isotope effects through theoretical interpretation of observed effects in vapor pressures and vibrational fundamentals. The theoretical tools used include normal coordinate analysis, orthogonal polynomial approximations, second-order perturbation methods, *ab initio* molecular orbital calculations, and molecular dynamics.

## University of North Carolina Chapel Hill, NC 27514

### Department of Chemistry

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

*Murray, R.W.* **\$72,000**

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

#### 360. *Unsegmented Continuous Flow Sample Processing and Electrochemical Detection and Determination of Gaseous Species*

*Mottola, H.A.* **\$69,000**

This work is a comprehensive study of chemically modified electrodes based on metal complex redox couples of

the 1,10-phenanthroline family and similar ligands for use in continuous-flow detection of oxidizing and reducing gaseous species. Three basic ways of producing modified surfaces are studied: (1) direct admixing of a relatively insoluble salt (in aqueous media) of a complex cation with carbon pastes, (2) covalent binding of the complex cation to chemically modified graphite and pasting liquids, and (3) oxidative electropolymerization of some derivative complex cation of the same family of ligands. Completed work has resulted in the development of a family of amperometric sensors offering selectivity and competitive limits of detection for  $\text{NO}_2(\text{g})$ . The presence of a catalytic cycle during the sensing period is responsible for considerable enhancement in sensor response. Glassy carbon coated with a polymeric film of tris[5-amino-1,10-phenanthroline]iron(II) perchlorate adds the advantage of protection to surface poisoning and results in a useful sensor for  $\text{SO}_2(\text{g})$ . Incorporation of these sensors to thin-layer electrochemical cells and operation under continuous flow results in "bathing" of the sensor surface with supporting electrolyte that ensures the presence of an unbroken film of ionic solution to support electrical migration and satisfies the electroneutrality requirement. Work is being extended to chemical modification utilizing enzymes adding selectivity (e.g. sulfite oxidase for  $\text{SO}_2(\text{g})$  detection) and to automation of the process of sample collection, injection, detection, and data acquisition and handling.

**University of Oklahoma**  
**Norman, OK 73019**

**Department of Chemical Engineering and Materials Science**

**361. A Study of Micellar-Enhanced Ultrafiltration**

Scamehorn, J.F.; Christian, S.D. **\$67,000**

Colloid-enhanced ultrafiltration methods are being developed to purify polluted wastewater or groundwater. In micellar-enhanced ultrafiltration (MEUF), surfactant is added to an aqueous stream containing dissolved organic and/or multivalent ions. The micelles (aggregates containing approximately 100 molecules) formed by the surfactants tend to solubilize the organics and bind the multivalent ions if the surfactant is of opposite charge to these ions. The solution is treated using ultrafiltration with membrane pore sizes small enough to block the passage of the micelles. Extremely pure permeate streams have been produced using MEUF from feed streams containing both organics and heavy metals (rejections of 99.8%). Removal of a wide range of organic solutes and metal cations has been demonstrated using MEUF. Spiral wound ultrafiltration units have been shown to result in approximately the same separation efficiencies as stirred cell units, which is important to scaleup of the technology. Two new technologies, polyelectrolyte-enhanced ultrafiltration and ion-expulsion ultrafiltration have been developed, which can effectively remove heavy metals from water without leaving any significant concentration of organics in the purified water.

**Purdue University**  
**West Lafayette, IN 47907**

**Department of Chemistry**

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

Freiser, B.S. **\$101,000**

Studies on the gas phase chemistry and photochemistry of bare atomic metal ions, metal ion complexes, and small metal cluster ions continue. These studies use a methodology involving laser desorption: Fourier transform mass spectrometry. Some of the highlights from this past year include: (1) developing a new FTMS method for measuring kinetic energy release in charge transfer reactions such as  $\text{Nb}^{2+} + \text{benzene} \rightarrow \text{Nb}^+ + \text{benzene}^+$ ; (2) observing the first examples of photo-induced reactions involving organometallic ions, in particular, observing photoisomerization of  $\text{Co}_2(\text{N})(\text{O})^+$  to  $\text{Co}_2\text{NO}^+$  by monitoring a change in reactivity, with the results holding implications for surface photocatalysis; (3) making photodissociation threshold measurements to determine the bond energies of  $\text{D}^0(\text{MFe}^+ - \text{benzene})$  and  $\text{D}^0(\text{benzene Fe}^+ - \text{benzene})$  yielding information on the effect of the second benzene on the  $\text{M}^+ - \text{Fe}$  bond energy and on the first  $\text{Fe}^+ - \text{benzene}$  bond energy, respectively; and (4) obtaining some of the first information on the chemistry and photochemistry of doubly charged metal ions. Of particular interest was the finding that  $\text{D}^0(\text{La}^+ - \text{propene}) > \text{D}^0(\text{La}^{2+} - \text{propene})$  despite the greater electrostatic attraction in the latter. This finding has been confirmed and explained by an intensive theoretical study done in collaboration with NASA-Ames.

**Rensselaer Polytechnic Institute**  
**Troy, NY 12180**

**Department of Chemistry**

**363. Macrocyclic Ligands for Uranium Complexation**

Potts, K.T. **\$95,000**

Representative macrocycles, designed for complexation of the uranyl ion by computer modeling studies and utilizing six ligating atoms in the equatorial plane of the uranyl ion, have been prepared and their ability to complex the uranyl ion will be evaluated. The ligating atoms, either oxygen or sulfur, are part of acylurea, biuret or thiobiuret subunits, and alkane chains or pyridine units complete the macrocyclic periphery. Refinement of the cavity diameter by variation of the peripheral functional groups is currently being studied to achieve an optimized cavity diameter of 4.7 to 5.2 Å. An acyclic ligand, essentially a precursor to the macrocycles and containing the same ligating atoms in equivalent functional entities, forms a crystalline 1:1 uranyl-ligand complex that undergoes a facile DMSO-induced rearrangement to a 2:1 uranyl-ligand complex. X-ray data for these two uranyl complexes show the cavity diameters to be 5.02 Å (1:1 complex) and 4.99 and 4.88 Å (2:1 complex), values which are in good agreement with those predicted on the basis of modeling studies. Synthetic plans call for the synthesis



of more highly preorganized macrocycles and the introduction of substituents likely to influence solubility of the macrocycles in a favorable manner.

**San Diego State University  
San Diego, CA 92182**

**Department of Chemistry**

**364. Synthesis and Characterization of Mesomorphic and Other Stationary Phases**  
*Laub, R.J.* **\$77,000**

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. Certain smectic MEPSILs are being synthesized for direct comparison of their physicochemical and chromatographic properties with the most useful of the nematic MEPSILs.

**Syracuse University  
Syracuse, NY 13244**

**Department of Chemical Engineering and Materials Science**

**365. Mechanisms of Gas Permeation Through Polymer Membranes**  
*Stern, S.A.* **\$126,000**  
**(18 months)**

Three different studies were completed during the past report period. Solubility coefficients (S) and diffusion coefficients (D) for Ar and CH<sub>4</sub> in poly(vinyl chloride) and for H<sub>2</sub> in poly(vinyl acetate) were determined over a range of temperatures and at pressures up to 20 atm. These data, in conjunction with earlier studies, show that the onset of "dual-mode sorption" (DMS) behavior as the temperature is decreased is accompanied by changes in the slopes of log S and log D versus 1/T plots, and vice versa; T is the absolute temperature. DMS behavior is characterized by a strongly nonlinear dependence of S and D on the gas pressure or concentration in a polymer. This behavior has been observed with a variety of gases in many glassy polymers. However, the present study has also shown that its onset may occur at temperatures considerably below the glass transition of a polymer if the "excess" free volume of the polymer is small. The DMS model of gas solution and transport in glassy polymers has been extended to cases where the polymers are plasticized by the penetrant gases. The case of "antiplasticization" has also been considered. The "in-plane" diffusion of a fluorescent dye in glassy poly(1-trimethylsilyl-1-propyne) membranes has been measured by a novel technique known as "laser

fluorescence photobleaching recovery." Evidence has been obtained for the existence of two dye populations with different mobilities, whose diffusion coefficients differ by two orders of magnitude.

**366. Particle Deposition in Granular Media**  
*Tien, C.* **\$145,000**  
**(18 months)**

This project is concerned with the analysis and examination of various phenomena arising from deposition of aerosol particles from gas suspensions flowing through granular media. In achieving this objective, both analytical and experimental studies will be conducted. The specific topics of investigation include: (1) the effect of deposition, particularly the change of media structure because of the presence of collected particles on both the rate of filtration and pressure drop increase; (2) establishment of correlations from experimental measurements with the guidance of theoretical analysis of general correlations on both collection efficiency and pressure drop increase as functions of the extent of deposition; (3) modification of porous media model as a basis for studying filtration; and (4) developing algorithms for estimating collection efficiencies of small particles when the effect of Brownian diffusion is significant.

**University of Tennessee  
Knoxville, TN 37996**

**Department of Chemistry**

**367. Dual Mechanism Bifunctional Polymers: Design, Synthesis, and Application of a New Category of Metal Ion Complexing Agents**  
*Alexandratos, S.D.* **\$80,392**

A new series of ionic polymers, termed dual mechanism bifunctional polymers (DMBPs), has been synthesized with unique applications to separations science. These polymers are prepared with two groups on a polystyrene support, each of which operates by a different mechanism. One mechanism is relatively aspecific, and its primary purpose is to allow the solution species access to the ligands responsible for the specific recognition reaction. The principal application of these polymers has been selective metal ion separations from aqueous solutions. The Class I DMBPs are the ion exchange/redox resins; the reduction of metal ions with a reduction potential greater than 0.3 volt to the free metal is responsible for the resin's specificity. The reduction of Hg(II) to mercury metal is particularly facile. The Class II DMBPs are the ion exchange/coordination resins; different coordinating ligands lead to different metal ion specificities. The penta(ethylene glycol) ligand, in particular, has been found to yield a resin with a high affinity for Group IIA ions. The Class III DMBPs are the ion exchange/precipitation resins; quaternary amine ligands electrostatically bind different anions and lead to the recovery of different metal ions through the precipitation of the metal salts. Bifunctional group cooperativeness is evident with the tributylammonium/phosphonic acid resin in the thiocyanate form wherein 40% of the Ag(I) ions in

solution are absorbed into the resin within 1h and precipitated as AgSCN, compared to an expected 26% based on the performance of the monofunctional resins.

**368. Study of the Surface Properties of Ceramic Materials by Chromatography**  
Guiochon, G. **\$82,000**

The aim of this research is a better understanding of 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.

**369. Capillary Liquid Chromatography Using Laser-Based and Mass Spectrometric Detection**  
Sepaniak, M.J. **\$95,000**  
(16 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, solutes are separated based on their differential distribution between an electro-osmotically pumped mobile phase and an electrophoretically retarded micellar phase. Efficiencies in excess of 500,000 theoretical plates/meter have been achieved with the technique. Factors that influence efficiency and factors that affect selectivity (e.g., micelle-type and mixed mobile phases) have been studied. Elution range has been extended through the addition of certain organic modifiers to the mobile phase, and procedures have been developed to perform gradient elution. Investigations of other capillary bioseparation techniques (i.e., capillary isoelectric focusing and affinity chromatography) have been initiated. Detection in MECC is complicated by the diminutive volumes of eluted bands (typically about 100 nL). Laser-based fluorescence detection is used extensively in our laboratory. However, fiber optics and a unique laser-etched, on-column flow cell have also been used in the development of absorbance detectors. These include a synchronous-type detector, a

modified commercial absorbance detector, and a photodiode array detector. The analytical characteristics of these detectors have been extensively investigated. A fast atom bombardment mass spectrometry interface for use with these capillary separation techniques has also been constructed and subjected to preliminary tests.

**Texas A and M University**  
**College Station, TX 77843**

**Department of Chemistry**

**370. Development of Laser-Ion Beam Photodissociation Methods**  
Russell, D.H. **\$83,000**

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. These studies are designed to evaluate the effects of the method of ion production and rates of dissociation of the photoexcited ion on the photofragment ion yield. In addition, the potential analytical utility of laser-ion beam photodissociation for the structural characterization of large biomolecules is being evaluated. These latter studies are being performed on ions formed by fast-atom bombardment (FAB) ionization and include molecules such as chlorophyll a, vitamin B<sub>12</sub>, small peptides, and glycopeptides (1500 to 4000). These studies are performed on modified analytical instruments (e.g., Kratos MS-50TA and MS-902 and a Fourier transform mass spectrometer (Nicolet FTMS-1000)).

**Texas Tech University**  
**Lubbock, TX 79409**

**Department of Chemistry and Biochemistry**

**371. Metal Ion Complexation by Ionizable Crown Ethers**  
Bartsch, R.A. **\$88,000**

Goals of this research are the synthesis of new metal ion complexing agents and their application in the solvent extraction and liquid membrane transport of metal ions. New crown ether carboxylic acids and phosphonic acid monoethyl esters 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. Solvent extraction and bulk liquid membrane transport of Co(II) and Ni(II) ammine cations by proton-ionizable crown ethers are being investigated. In addition, the ability of thiocrown ethers that do not possess ionizable groups to extract trace levels of toxic heavy metal cations is being explored.

**372. Novel Approaches to Ionic Chromatography**  
Dasgupta, P.K. \$80,000

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. Recent achievements include: the development of dc conductivity detection which allows the construction of extremely small volume detectors ( $\leq 50$  nL) with concentration sensitivity comparable to or better than the best of the commercial detectors for high resistivity backgrounds. Further, a stopped-flow technique has been developed that does not require stopping the chromatographic run and enables the eluting ions in a suppressed ion chromatography system to be identified by stopped-flow chronoamperometry in under one minute from their unique chronoamperometric profile. Other work includes: (1) the development of a unique, highly selective and sensitive optical detection mode for the detection of weak acids in the ion exclusion modes and (2) the fabrication of the first completely electrochemically operated membrane suppressor. This device does not use any acid regenerant; only water and electrical energy are used as consumables. Detection at trace levels is possible even with eluents containing several hundred millimolar NaOH. Ongoing research is focused on the use of electro-dialytic devices for the on-line generation of ultrahigh purity NaOH and schemes for positive identification of eluting ions via mobility measurements.

**University of Texas**  
Austin, TX 78712

**Department of Chemical Engineering**

**373. Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications**  
Koros, W.; Paul, D. \$77,998

The project focus is synthesis and characterization of a series of polymeric materials for advanced gas separation applications. The fundamental sorption and diffusion factors governing the permeability and permselectivity of the polymers are being measured at pressures up to 1000 psia with both pure and mixed gas feeds. Materials with extremely 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. For some of these materials, attractive permselectivities for gas pairs such as hydrogen/methane, carbon dioxide/methane, and oxygen/nitrogen have been found. 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. If this principle can be refined to a more quantitative form, it will provide a critically useful tool for identifying advanced materials for future generations of membranes.

**University of Utah**  
Salt Lake City, UT 84112

**Department of Chemistry**

**374. Pulsed Laser Photothermal Spectroscopy of Liquids and Solids**  
Eyring, E.M. \$75,000

Pulsed laser photothermal spectroscopies have intrinsic advantages over microphonic photoacoustic spectroscopy (PAS), such as the capacity for the time resolving faster chemical events and diminished background noise in the desired photothermal signals. A combination of pulsed photothermal beam deflection and pulsed thermal lens spectroscopies is being used to investigate the photophysical behavior of dyes dissolved in various solvents. Recent experiments have shown the utility of the thermal lens technique for making kinetic measurements in liquids on a nanosecond time scale. Dyes presently under investigation absorb in the red and have very short lifetimes, in some cases as short as a few picoseconds. Reliable determination of quantum yields necessitates the elimination of multiphoton effects in these experiments. Pulsed photothermal radiometry (PPTR) using a Q-switched, frequency doubled, neodymium:YAG laser permits the determination of physical properties of solids such as thermal diffusivities and physical thickness as well as their infrared emissive spectral properties. Materials under study include high-temperature superconductors and powdered dye samples diluted with KBr. The latter samples lend themselves to depth profiling investigations. Microphonic photoacoustic techniques are being used to investigate the properties of solids illuminated with synchrotron x-radiation.

**Department of Metallurgy and Metallurgical Engineering**

**375. Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species**  
Miller, J.D. \$160,000  
(18 months)

*In situ* FTIR/internal reflection spectroscopy (FTIR/IRS), microcalorimetry, and electrochemical methods have been used to investigate adsorption and reaction phenomena of olefinic collector monomers at nonsulfide mineral surfaces. Using these techniques, measurements have been made to establish important fundamental information about nonsulfide mineral flotation systems. For instance, the adsorption density of oleate on a fluorite internal reflection element has been calculated from theory using *in situ* FTIR/IRS spectral data. The adsorption isotherms found agree well with isotherms previously determined by conventional indirect methods. The use of microcalorimetric techniques allowed for the determination of heats of reaction in both the chemisorption and surface precipitation regions of the adsorption isotherm. The application of anodic potential biases to lanthanum fluoride electrodes in oleate solutions has shown that it is possible to significantly increase the hydrophobicity of the electrode surface. Research is continuing in the FTIR/IRS characterization of the fluorite/oleate system. Polarized ir

sources are being used to determine the orientation of adsorbed collector species at the fluorite IRE surface. Also, the oxidation/polymerization reaction that the adsorbed collector monomers undergo at the fluorite surface, found initially during FTIR transmission studies, is also being studied in real time by the innovative FTIR/IRS technique. The final characterization of the fluorite/oleate system being studied is the bonding characteristics of the carboxylate functionality at the fluorite surface. Future research activities include the extension of FTIR/IRS into the near-ir region of the electromagnetic spectrum. This will enable many more minerals to be studied since most minerals are opaque to mid-ir but transmit near-ir light. Also, FTIR/IRS will be used to examine collector adsorption at IREs cut from naturally occurring minerals crystals. Finally, spectroelectrochemical experiments will be conducted to determine by FTIR/IRS the processes responsible for the enhanced hydrophobicity of lanthanum fluorite electrodes in oleate solutions.

**Virginia Commonwealth University  
Richmond, VA 23284**

**Department of Chemistry**

**376. Compensation for Peak Shifts and  
Variable Background Responses in Fluorescence Spectroscopy**

*Rutan, S.C.*

**\$72,000**

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. In conjunction with this development, the effects on the spectra of polyaromatic hydrocarbons caused by changes in the mobile phase composition are investigated. Major shifts that occur for perylene in variable compositions of acetonitrile/water, methanol/water, and tetrahydrofuran/water mobile phases have been identified, and mathematical methods that can automatically detect and correct for these spectral distortions are being developed. In addition, the effect of changing the derivative order on the performance of a previously developed background subtraction routine for fluorescence detection in thin-layer chromatography is being studied.

**University of Wyoming  
Laramie, WY 82071**

**Department of Chemistry**

**377. Solid-Surface Luminescence Analysis**

*Hurtubise, R.J.*

**\$85,000**

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 infrared spectroscopy. Several experiments are performed in which the temperature is changed from room temperature to  $-180^{\circ}\text{C}$ . From the data obtained, quantum yields and rate constants related to the luminescence processes are calculated. The calculated parameters are correlated with adsorbed phosphor properties and solid-matrix properties. For example, with filter paper as a solid matrix the phosphorescence quantum yield values are related to the modulus of filter paper. In other experiments, the effects of humidity on adsorbed compounds are studied to determine the magnitude of moisture quenching. The resulting data are related to current theories on the disruption of hydrogen bonds in solid matrices and how the disruption affects the fluorescence and phosphorescence quantum yields of the adsorbed compounds. Other work includes the investigation of  $\beta$ -cyclodextrin as a solid matrix in trace organic analysis via luminescence. Also, the fluorescence detection of model compounds on chromatographic columns is being pursued to develop an understanding of solution-phase and solid-phase interactions in chromatography.

**Heavy Element Chemistry**

**Florida State University  
Tallahassee, FL 32306**

**Department of Chemistry**

**378. Research in Actinide Chemistry**

*Choppin, G.R.*

**\$109,000**

The reduction kinetics of  $\text{AnO}_2^{2+}$  by hydroxy compounds has been shown to involve interaction with the phenoxy anion via a 1-electron transfer. Studies at Argonne National Laboratory (ANL) of the reduction of  $\text{UO}_2^{+2}$  bound to humic acids and synthetic polyelectrolytes by viologen anion radical showed a reduction in rate. Conformational effects of the polyelectrolyte changed the reduction rate. Such conformational effects have been demonstrated in a study of the dissociation kinetics of actinides bound to humic acids wherein population of the various dissociation paths varied with the length of predissociative binding time. Uranyl and  $\text{H}_3\text{SiO}_4^-$  were measured to have a stability constant ca.  $10^5$ . Binding of  $\text{Th}^{4+}$  and  $\text{UO}_2^{+2}$  to silicotungstates and phosphotungstates gave constants  $\geq 10^6$  for  $\text{Th}^{4+}$  and  $10^3$  for  $\text{UO}_2^{+2}$ . The thermodynamics of the synergistic extraction of actinides by PMBP and TTA with crown ethers indicated no size effect

for the CE cavity, but were related to the number of oxygens involved in the actinide-crown ether interaction. Luminescent lifetime studies of Eu(III) gave information on the inner vs. outer sphere character of the haloacetate complexes which confirmed the earlier correlation from thermodynamics that outer sphere character increases as the  $pK_a$  of the ligand acid decreases. Luminescence spectroscopy and solvent extraction were used to study the interaction of Eu(III) and Am(III) with  $F^-$  in  $H_2O + CH_3OH$  solvent. The measured  $\log \beta_1$  correlated with the dielectric constant calculated from the relative numbers of  $H_2O$  and  $CH_3OH$  molecules in the primary coordination sphere of Eu(III).

## University of New Mexico Albuquerque, NM 87131

### Department of Chemistry

#### 379. Development of Surface Immobilized Ligands for Actinide Separations

Paine, R.T.

\$87,877

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. As part of the ligand design studies, appropriate model coordination chemistry is examined, and liquid-liquid extraction data are obtained by radiochemical methods. Further, syntheses are developed that result in the attachment of promising extractants to solid supports including organic polymers (e.g., polystyrene divinyl benzene and polyethyleneimine) and inorganic networks (e.g., zirconium phosphate and silica). The extraction capabilities of the supported ligands are characterized by chromatographic techniques employing Ln(III) and An(III) ions.

## Ohio State University Columbus, OH 43210

### Department of Chemistry

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

Bursten, B.E.

\$80,000

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 the past year in understanding the bonding in complexes that contain three Cp ligands coordinated to an actinide center. A detailed analysis of the bonding in  $(\eta^5-C_5H_5)_3U-X$  and  $(\eta^5-C_5H_5)_3U-L$  complexes has been reported. 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  $X\alpha$ -SW molecular orbital method continues to be the primary method of analysis, recent access to the Cray X-MP supercomputer at the Ohio Supercomputer Center has allowed the expansion of the theoretical methodology to include the DV- $X\alpha$  method and *ab initio* methods. 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). Collaborations between this group and experimental and theoretical groups at LANL have been established.

## SRI International Menlo Park, CA 94025

### Physical Sciences Division

#### 381. Chemistry of Gaseous Lower-Valent Actinide Halides

Hildenbrand, D.L.; Lau, K.H.

\$100,930

The project objective is to provide accurate thermochemical information for key actinide halide, oxyhalide, and related systems, starting with uranium 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 oxychlorides of uranium and thorium, the neptunium fluorides and oxyfluorides, and the equilibrium thermal ionization of uranium vapor. Bonding energy patterns in the uranium fluorides are substantially different from those of the chlorides and bromides, and also from those of the thorium halides, but the reasons are not yet clear. The entropy data indicate that the gaseous uranium tetrahalides most likely have distorted tetrahedral structures, while the thorium analogs are regular tetrahedra. These patterns will be useful in modeling the thermochemistry of the heavier actinide halides, which will be much more difficult to study.

## University of Tennessee Knoxville, TN 37996

### Department of Chemistry

#### 382. Physical-Chemical Studies of the Transuranium Elements

Peterson, J.R.

\$142,000

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

##### **383. *Magnetic Measurements of the Transuranium Elements***

*Nave, S.E.*

**\$102,000**

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. One such instrument under development is a device to measure susceptibility as a function of pressure.

## Chemical Engineering Sciences

### American University Washington, DC 20016

#### Department of Physics

##### **384. *Theory of Condensable Gases***

*White, J.A.*

**\$130,181  
(18 months)**

The project objective is to refine a new theory that calculates the thermodynamic gas, liquid, and supercritical properties and phase diagrams of condensable gases. The theory includes three-body intermolecular forces and takes into account especially the shortness of the range of attractive interactions found in real gases and the enhanced fluctuations at all wavelengths that result. The fluctuation enhancement contributes 10 to 30% or more of the total pressure at many temperatures and densities. This large contribution from fluctuations is currently estimated only crudely and unreliably using empirical formulas to amend mean field theories or to interpolate between laboratory values found in measurements. The new theory has been found, in tests against measurements performed for several gases, to make predictions with order of magnitude improvement in accuracy compared with predictions made using existing mean field theories. The theory also makes correct predictions at the critical point as well as elsewhere on the gas-liquid phase diagram. Further test of the theory will be made and computer programs will be developed that are capable of producing tabulations of thermodynamic properties of condensable gases for use where measurements are unavailable or insufficiently accurate.

### University of California Santa Barbara, CA 93106

#### Department of Chemical and Nuclear Engineering

##### **385. *Reaction Enhancement of Heterogeneously Catalyzed Reactions by Concentration Forcing***

*Rinker, R.G.*

**\$74,000**

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 5%. 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**

**386. Premixed Turbulent Combustion**  
*Libby, P.A.* \$58,440

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 with cylindrical geometry has been completed. A follow-on study of flamelets subject to swirl is presently under way. The configuration being considered involves counterflowing reactant streams with swirl about an axis of rotation. The analysis for low rates of swirl is reasonably straightforward and has been completed, but beyond a critical rate of rotation multiple stagnation planes appear, calling for careful study that is presently under way. The second area of research concerns counterflowing premixed turbulent flames. These flames are presently under experimental investigation at several institutions (UCB, Cambridge, Imperial College of Science and Technology, and University of Karlsruhe) 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 simple turbulent transport while a second uses the well known  $k-\epsilon$  model. 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 yet to be initiated. Predictions of extinction will be compared with data being obtained at Cambridge. A final area of research just getting under way relates to premixed combustion in a channel.

**Clarkson College of Technology**  
Potsdam, NY 13676

**Department of Chemical Engineering**

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

*Lucia, A.* \$59,000

Analysis can play an important role in the development of reliable computer tools for the simulation and design of separation processes. 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. Thus, the analysis clearly shows that homogeneity is a necessary condition for solution uniqueness for two-phase, multistage, multicomponent separation processes. The analysis has been used to study the convergence behavior of certain existing algorithms and develop new methods for multicomponent separation process simulation. As a consequence, new sum-rates 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. Current research includes the construction of simple examples that illustrate turning points and bifurcations in the two-phase solutions, and analysis of the number of three-phase solutions to multicomponent, multistage separation processes, and the study of the convergence behavior of Newton-like methods used to simulate these processes.

**Colorado State University**  
Fort Collins, CO 80523

**Department of Chemical Engineering**

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

*Lenz, T.G.; Vaughan, J.D.* \$82,000

Computational and experimental studies are being conducted to develop methods capable of accurately predicting condensed state chemical equilibria. During this period a modified Boyd MOLBD3 program was used to complete the study of a variety of acyclic and cyclic -enes and dienes. A detailed study of the thermodynamics of the dimerization of 1,3-cyclopentadiene was then conducted, by application of the Boyd force-field program to the reactant 1,3-cyclopentadiene and the endo- and exo-dicyclopentadiene products. These gas-phase force-field results were extended to the liquid phase through use of literature vapor pressure data for reactant and products. The force-field results agreed well with literature for both the gas-phase and liquid-phase dimerizations. This indicates that the proposed force-field technique is sufficiently accurate to permit calculations of chemical equilibrium constants for liquid phase reactions involving nontrivial molecules. Work has also been done with Allinger's MMP2 force-field program as well as Bugay and Leenstra's VAX

version of the Warshel-Levitt program, QCFF/PI, with the goal of assembling a single force-field program having very general chemical thermodynamic predictive capability. The experimental portion of this recent work has involved accurate determination of the heats of combustion for 4-methyl-cyclohex-1-ene, 4-vinyl-cyclohex-1-ene and the Diels-Alder adduct of anthracene and maleic anhydride. X-ray crystallographic structures have also been obtained for the Diels-Alder adducts of maleic anhydride/anthracene and maleic anhydride/9-phenylanthracene in support of developing the computational model.

**Cornell University**  
**Ithaca, NY 14853-5201**

**School of Chemical Engineering**

**389. Theory and Simulation of Fluids of Associating Chain Molecules**

*Gubbins, K.E.*

**\$225,000**  
**(18 months)**

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.

**390. Exact Calculations of Phase and Membrane Equilibria for Complex Fluids by Monte Carlo Simulation**

*Panagiotopoulos, A.Z.*

**\$146,528**  
**(19 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 two coexisting fluid phases from a single computer experiment, and is applicable to multicomponent systems with arbitrary equilibrium constraints imposed. The specific goals of this work are to investigate (1) highly asymmetric mixtures with large differences in size and potential energies of interaction, (2) chain molecules, and (3) ionic systems. A combination of techniques, including species identity interchange and gradual particle insertion, are being used to extend the scope of the original Gibbs methodology. Conventional vapor-liquid, liquid-liquid and fluid-fluid equilibria as well as partitioning in the presence of semipermeable membranes are currently under investigation. The results are being compared with theoretical models and engineering correlations in order to determine the range of applicability of existing techniques and provide the data required for systematic improvements. It is hoped that the end result from this project will be a general set of simulation tools for exact predictions of phase equilibria in a wide range of systems.

**391. Experimental and Theoretical Studies of Dense Fluid Mixtures**

*Streett, W.B.*

**\$121,000**  
**(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 which 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 which 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 which simultaneously describe PVT, speed-of-sound, and heat capacity data. A modification of the Liebenberg-Mills-Tait Equation, using a supercritical isobar instead of the saturation curve as reference state led to superior correlations of the thermodynamic properties of CFC1<sub>3</sub>. In representing speed-of-sound data alone as a function of temperature and pressure, a two-variable rational approximant gave results far superior to a double Taylor series expansion.

**University of Delaware**  
**Newark, DE 19716**

**Department of Chemical Engineering**

**392. The Generalized van der Waals Theory of Pure Fluids and Mixtures**

*Sandler, S.I.*

**\$66,230**

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 polydispersity 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

**393. Development of the Analytic Variational Inequality Minimization (VIM) Equation of State**  
Mansoori, G.A. **\$74,000**

The primary objective and scope of this research project is to use modern approaches of statistical mechanics to develop new phase equilibrium computational schemes and analytic equations of state for polar, quantum, and associated molecular fluids and fluid mixtures of practical interest. Topics studied include: (1) introduction of an analytic thermodynamic model for fluids with an intermolecular potential consisting of a hard core and an attractive Yukawa tail; (2) development of an analytic technique for calculation of the hard core molecular diameter of fluids, using experimental entropy data; (3) application of the conformal solution theory of polar fluids for the development of mixing rules applicable for equations of state; (4) development of computational schemes for phase equilibrium calculation of mixtures consisting of species with large molecular size and shape differences and highly polar and hydrogen bonding mixtures; (5) application of the statistical mechanical theory of monomer/polymer solutions for the development of a continuous mixture model for asphaltene and wax deposition from petroleum crude caused by the addition of a completely miscible solvent into the crude; and (6) investigation of the asphaltene deposition and its role in enhanced oil recovery miscible gas flooding processes.

**394. Evaluation of Mixing Rules for Viscosity and Thermal Conductivity Using Nonequilibrium Molecular Dynamics**  
Murad, S. **\$63,000**

A study to examine the various mixing rules for thermal conductivity, and to evaluate the n-fluid approximations for continuous mixtures (also referred to as polydisperse, or many component mixtures) has been completed. Results have shown that the simple Kay's mixing rules, are, overall, as accurate as the more sophisticated Enskog mixing rules. It was also found that the 2-fluid approximation is significantly better than the 1-fluid approximation, and going to higher order approximations (such as 4, 8, and so forth) improves results only marginally. A previous study on viscosity also yielded similar results, which means that these results should be valid for all transport properties. For thermodynamic properties it has been thought that the 1- and 2-fluid approximations are of comparable accuracy. These studies so far have been conducted for fluids modeled by the Lennard-Jones potential. These studies will be extended to nonspherical potential models.

Johns Hopkins University  
Baltimore, MD 21218

Department of Chemical Engineering

**395. Prediction of Thermodynamic Properties of Coal Derivatives**  
Donohue, M.D. **\$82,000**

An understanding of a variety of physical phenomena is necessary in order to predict the thermodynamic properties of chemicals found in coal processing. To this end, the Associated Perturbed Anisotropic Chain theory (APACT) has been developed which incorporates intermolecular forces such as Lennard-Jones, anisotropic interactions caused by dipoles and quadrupoles, and Lewis acid-base or other chemical association forces. The theory was tested by calculating the thermodynamic properties of many systems containing wide ranges of organic molecules. Treatment of various forces in APACT is being rigorously tested by appropriate computer simulations. Computer simulation results for nonpolar chain molecules verify the treatment of van der Waals forces in APACT at high densities. Simulations are under way for systems at low densities to study the effect of intramolecular forces on heats of vaporization. APACT has been reformulated into a group-group interaction theory. A number of group parameters have been determined. These will be compared with parameters determined through computer simulation for geometrically similar molecules. Since the mathematical form of APACT is complex and thus computationally intensive, efforts are under way to determine if the theory can be simplified without loss of accuracy.

Louisiana State University  
Baton Rouge, LA 70803-7303

Department of Chemical Engineering

**396. Molecular Dynamics Studies of Aromatic Hydrocarbon Liquids**  
McLaughlin, E.; Gupta, S. **\$81,745**

Methods based upon molecular theory can accurately predict thermophysical properties of dense liquids and computer simulation can be used to develop such methods and to study the relationship between the intermolecular forces and the behavior of bulk fluids. Focus is on molecular dynamics simulation of fluids containing nonspherical molecules, particularly aromatic hydrocarbons, which are important in synfuels and alternative feedstocks. So far, algorithms have been developed to utilize the vector and/or parallel processing capabilities of supercomputers; the effect of molecular shape and polar interactions on properties of pure fluids has been studied; and the data have been utilized to test methods such as perturbation theory and the spherulized potential method. This work is being extended and, at present, studies are being conducted to determine the effects of molecular shape and polar interactions on the attractive and repulsive force terms in an equation of state by simulating fluids of nonspherical molecules on supercomputers. Studies of fluid mixtures of nonspherical molecules, to test mixing rules for thermodynamic properties of mixing, are also being conducted.

**University of Maryland  
College Park, MD 20742**

**Institute for Physical Science and Technology**

**397. Thermophysical Properties of Supercritical Fluids and Fluid Mixtures**  
*Sengers, J.V.* **\$135,000**  
**(19 months)**

This research project is concerned with the development of scientifically based representative equations for the thermophysical properties of fluids and fluid mixtures, which incorporate the crossover of the singular behavior of these properties near the vapor-liquid critical point to the regular behavior of these properties far away from the critical point. Research to develop such equations for the thermodynamic and transport properties of one-component fluids is in an advantage stage. The equations are based on the renormalization-group theory and mode-coupling theory of critical phenomena. An extension of this approach to fluid mixtures has been initiated.

**Massachusetts Institute of Technology  
Cambridge, MA 02139**

**Department of Chemistry**

**398. Thermodynamics and Kinetics of Complex Organic Systems**  
*Alberty, R.A.* **\$86,000**

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, and matrix methods for writing thermodynamic and kinetic equations and making computations. Equilibrium calculations on the polymerization of alkenes on a zeolite catalyst have been followed up by numerical integrations of rate equations, which incorporate thermodynamics and permit use of various assumptions about either forward or backward rate constants. The use of isomer groups has its counterpart in statistical mechanics and the partition function  $\Delta(T, P, N)$  can be used to derive expressions for isomer group thermodynamic properties. The use of homologous series groups also has its counterpart in statistical mechanics and the semigrand partition function  $\Gamma(T, P, N_1, \mu_2)$  can be used to derive expressions for thermodynamic properties of homologous series groups. Calculations on the benzene series of polycyclic aromatic hydrocarbons in a near-sooting flame studied by Bittner and Howard provide information on the type of mechanism of polymerization. It has been shown that chemical thermodynamic tables for a whole homologous series over a range in temperature can be fit by functions of temperature and carbon number that are linear in twelve parameters.

**National Institute for Petroleum and  
Energy Research (NIPER)  
Bartlesville, OK 74003**

**Processing and Thermodynamics Division**

**399. Thermodynamic Properties by Noncalorimetric Methods**  
*Strube, M.M.* **\$210,000**

The goal of the project is the noncalorimetric determination of thermodynamic properties. This research includes the development or extension of correlational methodologies and the derivation of thermodynamic data from molecular spectroscopy via statistical mechanics. The focus is on methods applicable to polynuclear aromatic compounds, especially those with heteroatoms. The experimental results obtained in recent years at NIPER for the ARTD (Advanced Research for Technology Development) and AER (Advanced Exploratory Research) programs of the Department of Energy, as well as suitable results published by other research groups, are used in the extension of existing group-contribution methods for the reliable prediction of thermodynamic properties. Many processing reactions are performed at high temperatures. The measurement of thermodynamic properties of pure organic compounds at high temperatures (>600 K) by conventional calorimetry is limited by both compound stability and present equipment technology. Thermodynamic property data derived by statistical mechanics do not have these limitations, provided the molecular structure is known and the vibrational frequencies are correctly assigned by proper interpretation of the molecular spectra. Efforts are continuing in extending the capabilities of the molecular spectroscopy laboratory for the collection, interpretation, and assignment of infrared and Raman spectra of polynuclear aromatic hydrocarbons.

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

**Thermophysics Division**

**400. Integrated Theoretical and Experimental Study of the Thermophysical Properties of Fluid Mixtures**  
*Ely, J.F.* **\$270,000**

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**

**401. Thermophysical Properties of Fluids and Fluid Mixtures**  
*Stell, G.R.* **\$107,000**

A theoretical investigation of the transport properties of liquids and liquid mixtures continues. The latest results include a study of the shear and bulk viscosities of a system of hard-sphere solute with a polydisperse size distribution in a monodisperse solvent, obtained on the basis of the revised Enskog theory. Studies have been completed on (1) transport properties on the Boltzmann equation level for a binary fluid of hard-core square-well particles and (2) a Lorentz gas of particles with a hard-core square-well interaction between the scatterers and diffusing particles. The investigation of the transport coefficients of Lennard-Jones fluids has yielded predictions in good agreement with computer-simulation results for a variety of thermodynamics states and is continuing. A quantitative study has been completed of clustering in a fluid of hard-core particles with Yukawa attraction at equilibrium, with results relevant to condensation, gelation, and nucleation. Ongoing work includes an integral-equation approach to the structure and thermodynamics of liquids in pores and next to membranes, as well as free-energy transfer and partitioning of ionic species between two fluid phases.

**Department of Mechanical Engineering**

**402. Theoretical Studies of Multicomponent Mixtures: Phase Equilibrium and Transport**  
*Kincaid, J.M.* **\$78,000**

The purpose of this research is to develop methods for characterizing the thermodynamic and transport properties of multicomponent fluids. The fluids may consist of a finite number, a countable infinity, or a continuum of chemical species. Recent progress includes: (1) a new geometric representation of the dew/bubble conditions of polydisperse fluids that leads to simple algorithms for solving those conditions, as well as accurate analytic approximations for the dew/bubble curves; and (2) an extension of the Modified Enskog Theory to the case of multicomponent fluid mixtures.

**University of Pennsylvania**  
**Philadelphia, PA 19104**

**Department of Chemical Engineering**

**403. Thermodynamics of Systems of Very Many Components**  
*Glandt, E.D.* **\$88,000**

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**

**404. Anisotropy, Charge Distribution, and the Properties of Dense CO<sub>2</sub>: Molecular Dynamics Studies**  
*Debenedetti, P.G.* **\$49,779**

This project is aimed at studying, via molecular dynamics computer simulations, the influence of molecular elongation, mass distribution, and charge distribution on the equilibrium and time-dependent properties of dense fluids composed of linear, quadrupolar molecules, such as carbon dioxide. The systematic perturbation of elongation and quadrupole moment has allowed the quantification of individual contributions of geometric and electrostatic effects on shear viscosity, rotational and translational diffusivities and relaxation times, configurational energy, and pressure, at dilute gas, near-critical, and liquid densities. Quadrupolar interactions induce orientational order, which becomes significant at liquid-like densities and high elongations. Correlations between the orientational order and a reduction in the fluid's viscosity are currently being investigated.

**Purdue University Research Foundation**  
West Lafayette, IN 47907

**School of Chemical Engineering**

**405. Gas—Liquid—Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons**  
Chao, K.-C. **\$62,000**

An equation of state called the Augmented BACK equation has been developed to describe gas-liquid-liquid equilibria in mixtures of water, light gases, and hydrocarbons. The pressure of water is decoupled into a nonpolar pressure and a polar pressure according to the molecular model for water developed by Jorgensen and coworkers. The polar pressure thus obtained is embedded in the BACK equation to extend it to polar substances. Experimental data on the phase behavior of mixtures of water and paraffins from methane to n-decane are correlated with the equation. Light gases such as hydrogen, carbon monoxide, and nitrogen in aqueous mixtures are likewise correlated. Enthalpies of mixtures of steam + light gases and + hydrocarbons investigated by Wormald and coworkers are predicted with the new equation using interaction constants determined from volumetric or phase equilibrium data. Mixtures of polar + nonpolar components have offered great difficulty to previous theories and equations of state. The new equation explains the difficult behavior by allowing for interaction of poles only with poles, and dispersion only with dispersion. The hydrophobicity of hydrocarbons and nonpolar substances in general is obtained because of the absence of poles on their molecules which can interact with water only by means of dispersion mode which is very weak in the water molecule. A visual phase equilibrium cell with sapphire windows has been assembled. The cell is being installed in a high-pressure flow vapor-liquid equilibrium apparatus to observe near critical behavior of water + hydrocarbon mixtures and their critical states.

**Stanford University**  
Stanford, CA 94305

**Department of Chemical Engineering**

**406. Fundamental Studies of Fluid Mechanics and Stability in Porous Media**  
Homsy, G.M. **\$120,519**

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 description of instabilities that occur during displacements that are driven by differences between the properties of the displaced and displacing fluids. Either density differences (when coupled with gravity) or viscosity differences may drive such instabilities and the fluids may be either immiscible or miscible. Important results involving the secondary instabilities associated with tip splitting have been obtained through the use of large-scale simulations, leading to quantitative description of the growth of the mixing zone due to fingering. Other important results include the

description of the coupling between fingering and fluctuations in flow driven by permeability heterogeneity. Results indicate that mutual enhancement of the two mechanisms occurs when the length scales of fingering are commensurate with the correlation scale of the heterogeneities. Several research papers, as well as two major review articles have been published. Current research is focused on the description of miscible fingering in the presence of anisotropic dispersion.

**University of Virginia**  
Charlottesville, VA 22901

**Chemical Engineering Department**

**407. Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems**  
Cummings, P.T. **\$110,000**  
(18 months)

The objective of this research is to understand and develop predictive tools for the thermodynamic properties and phase equilibria of mixed solvent electrolytes. The approach is a fundamental study, incorporating theory, simulation, and approximate models to the practical problem of salting out in mixed solvents. Statistical mechanical modeling as well as development of analytic expressions for the thermodynamic properties are used to model the behavior of the electrolyte systems. Experimental work is included to enlarge the data base on which to found the models.

**University of Wisconsin**  
Madison, WI 53706

**Department of Chemical Engineering**

**408. Interphase Transport and Multistage Separations**  
Stewart, W.E. **\$92,000**

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. The recently published asymptotic analysis of laminar and turbulent mass transfer operations is now implemented for multi-component fractionation stages and is being tested with fractionation data collected from the literature. A study is in progress on variable-property transport calculations based on optimal reference states calculated from perturbation theory. New weighted-residual strategies are being investigated for robust reduced-order simulation and design of stagewise separations. A frequency-domain computation of mass transport in fully developed wall turbulence is under way, to test the asymptotic theory against available measurements of mass transfer power spectra.

**Yale University**  
New Haven, CT 06520

**Department of Mechanical Engineering**

**409. Computational and Experimental Study  
of Laminar Premixed and Diffusion  
Flames**

*Smooke, M.D.; Long, M.B.* **\$200,000**  
**(18 months)**

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 applies nonintrusive multidimensional imaging techniques in the measurement of the temperature and species concentrations in the flames with the goal of refining the experimental techniques and the accuracy with which such measurements are made. The research seeks to develop a more fundamental understanding of the important fluid dynamic and chemical interactions that occur in such systems.

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## **Small Business Innovation Research**

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The following projects were funded during FY 1989 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 6½ 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.

**Aerodyne Research, Inc.**  
Billerica, MA 01821

**410. Development of Concentration Modulated  
Absorption as a Combustion Diagnostic**

*Annen, K.D.* **\$49,980**  
**(6.5 months)**

This is a program to extend work in laser techniques for point measurements in complex combustion systems to the high sensitivity measurement of the concentrations of a wide variety of molecular species using the technique of concentration modulated spectroscopy. This technique, which uses a single laser to both perturb molecular level populations and detect this perturbation, has several features that make it attractive for the quantitative detection of transient species in combustion and other reactive systems. Among the most attractive is the property of allowing the measurement of an absolute species concentration without a prior knowledge of the molecular absorption coefficient, under conditions where an independent measurement of direct transmission provides a second equation by which the unknown absorption cross section may be eliminated. In the one application to a combustion system so far attempted, its sensitivity has been equal to the best of such methods as laser-induced fluorescence, without their difficulties in quantification. Since the effect is generated only in the small volume defined by the focusing of pump and probe laser beams, the technique provides a point measurement capability while having the ease of access associated with almost collinear laser beams.

**Bend Research, Inc.**  
Bend, OR 97701

**Bioprocess Division**

**411. High-Flux, High-Selectivity Cyclodextrin  
Membrane**

*van Eikeren, P.* **\$498,790**  
**(24 months)**

Membrane-based separations are important in a broad range of market areas and offer many advantages over conventional separation technologies, including greater energy efficiency. However, the full potential for membrane-based operations has not yet been realized. A principal reason is that current membrane materials exhibit poor selectivity for the separation of molecules of similar size or physical properties. This Phase II project is a continuation of a successful Phase I project aimed at developing a novel ultrathin membrane material that exhibits very high selectivity. The material consists of an array of ordered channels. During Phase I it was demonstrated that this membrane material is capable of separating isomeric solutes. During Phase II, the goals will be (1) to develop further techniques for the fabrication of the membrane, (2) to establish the fundamental relationships between the structure and composition of the novel membrane material and its separation properties, and (3) to develop techniques for the large-scale fabrication of membrane sheets and the incorporation of those sheets into modules.

## Separations Division

### 412. Novel High-Flux Antifouling Membrane Coatings

McCray, S.B.

**\$244,931**  
(24 months)

Membrane-based separations are important in a broad range of market areas and offer many advantages over conventional separation technologies, including greater energy efficiency. However, the full potential for membrane-based operations has not yet been realized. One reason is that membrane performance (flux) often declines with time as the result of membrane fouling. This decline dramatically increases the costs of membrane processes and puts severe limits on the number of separations to which membranes can be applied economically. The cost-effectiveness of many membrane processes could be significantly improved by the development of fouling-resistant membranes. This Phase II project continues a successful Phase I project that demonstrated the feasibility of a promising new approach for increasing the fouling resistance of membranes. During Phase II there will be continued (1) development and testing of fouling-resistant membrane coatings that were developed during Phase I and (2) exploration of other surface treatments. The most promising new membranes will be incorporated into fouling-resistant prototype membrane modules, and long-term tests will be conducted using fouling-prone feed streams. Once the utility of these novel membrane coatings has been demonstrated, the improved membranes will be commercialized.

## Bio-Metric Systems, Inc. Eden Prairie, MN 55337

### 413. Affinity Coupling of Receptors on Microchips: Capacitance Biosensor for Aromatic Hydrocarbons

Guire, P.E.

**\$50,000**  
(6.5 months)

The development of reagent and reaction procedures is planned for the affinity coupling of receptor molecules to the activated surface of immunoelectrodes used in capacitor affinity sensor devices under development. Proprietary tri-functional photoreactive reagents are being synthesized and coupled to the electrode surface for the specific covalent binding of monoclonal antibody (using one of the two antibody binding sites), leaving the remaining stabilized antibody binding site available for functional exchange between surface immobilized analyte and free analyte molecules, if present in the sample. A current version of this immunosensor has the detecting reagents enveloped in a semipermeable membrane. Achievement of these objectives will eliminate the need for this membrane and will demonstrate a sensor with improved performance (faster response and regeneration, as well as increased sensitivity, particularly when rapid analyses are required). The planned system will detect toluene and derivatives. Demonstrating sensor feasibility with this type of analyte will support the utility of this technology for sensitive, rapid, and selective sensing and monitoring of adverse agents. The sensor device will reversibly analyze and quantitate analyte content in batch

or continuous sampling situations and transduce the signal with electronic recording and transmission of data. Such a device will offer a broad range of applicability for periodic sample analysis and real-time, on-line monitoring of fluids (air, water, fuels), as well as dosimetry measurements in air and physiological fluids.

## Cape Cod Research, Inc. Buzzards Bay, MA 02532

### 414. Molecular Recognition Membrane

Dixon, B.G.

**\$50,000**  
(6.5 months)

A new type of composite membrane that will allow for significantly enhanced separations of complex mixtures of inorganic and/or organic chemicals is under development. Mature separation technologies, such as ion exchange and reverse osmosis, are very useful but, in general, cannot achieve the degree of selectivities necessary to be useful for the practical separations of such mixtures. The design of the proposed novel membrane combines the property of enhanced selectivity with other attractive features of state-of-the-art membranes.

## CeraMem Corporation Waltham, MA 02154

### 415. Low-Cost Ceramic Ultrafiltration Membrane Module

Goldsmith, R.L.

**\$49,984**  
(6.5 months)

Ceramic membranes are rapidly emerging as a new technology in membrane separations. However, commercially available devices have high costs relative to polymeric membranes, typically five to ten times higher. The technology being developed employs a unique approach to ceramic membrane module design. This design has a very high packing density (up to 450 sq ft membrane area per cubic ft) and will result in production of ceramic membranes with a cost less than those for any currently available polymeric product and at least ten-fold less than the cost for any ceramic membrane product. A membrane module production cost of \$1.50 to \$3.00/sq ft is projected. In Phase I, laboratory scale ceramic ultrafiltration membrane modules are being developed based on zirconia chemistry. Individual modules will have a diameter of 1 inch and a length of 1 foot with a membrane area of 1.5 sq ft. The membrane modules will be tested for water flux and retention properties with standard test markers. Membranes will be characterized also by scanning electron microscopy.

## Cortest Laboratories, Inc. Cypress, TX 77429

### 416. Photoelectrolysis of Liquid H<sub>2</sub>S

Wilhelm, S.M.

**\$48,350**  
(6.5 months)

The planned research will identify semiconductor photoanodes and photocathodes which optimize photoelectrolysis of liquid H<sub>2</sub>S. The quantum (photovoltaic)

efficiency of n-type and p-type electrodes will be measured in a high pressure photoelectrochemical cell with the goal of increasing the yield of hydrogen and sulfur over that recently obtained in work using p-Si and n-CdS. Phase I research is being directed at identifying those classes of semiconductors (n or p, arsenide, sulfide, selenide, phosphide) that have the most promise as photoelectrodes. Secondly, efficient electrodes are being screened for resistance to photocorrosion. The effort is expected to further the mechanistic understanding of photocleavage of H<sub>2</sub>S and the energetics of direct electrolysis.

**KSE, Inc.**  
**Amherst, MA 01004**

**417. Novel Chlorine-Resistant Reverse Osmosis Membrane**

*Singh, R.*

**\$49,896**  
**(6.5 months)**

Reverse osmosis (RO) membranes are needed that are not susceptible to degradation by chlorine attack. Currently available and widely used aromatic polyamide (PA) RO membranes have very low tolerance to strong oxidants, especially chlorine. Production of a chlorine resistant RO membrane is being explored by using a chemically modified polymer. The chemical modification involves the addition of nitro groups to an aromatic PA. Nitro substitution of electron rich aromatic rings deactivates the ring toward chlorine reaction while increasing the hydrophilic character of the polymer. Commercially available Aramid polymers are being nitrated and characterized for degree of nitration, nitration group functionality, and viscosity. Suitable solvents are being identified both for polymer dissolution and membrane casting. Nitrated PA membranes will be tested for chlorine resistance and flux-rejection characteristics. The skin layer will be examined for pore size and pinholes by scanning electron microscopy. This program will establish the technical feasibility of improving RO membrane chlorine resistance using a nitrated aromatic PA polymer.

**Mickley & Associates**  
**Boulder, CO 80303**

**418. A Novel Surface Modification Approach to Enhance Flux/Selectivity of Polymeric Membranes**

*Mickley, M.C.*

**\$49,999**  
**(6.5 months)**

The planned feasibility research involves the use of a novel grafting technique to modify membrane materials in such a way as to enhance their permeation properties. The work focuses on proving the technical feasibility of the grafting approach by conducting studies on both dense films and porous polymer membranes. Feasibility will be demonstrated by grafting charged monomers onto several materials including polysulfone, cellulose acetate, and polyamide. Successful membranes will exhibit enhanced rejection of multivalent ions at high flux and low operating pressure.

**Microsensor Systems, Inc.**  
**Springfield, VA 22150**

**419. SAW Chemical Microsensors for Monitoring and Control of Vapor Phase Industrial Processes and Waste Streams at High T and P**

*Jarvis, N.L.*

**\$49,839**  
**(6.5 months)**

The use of very small sensitive surface acoustic wave (SAW) microsensors is being investigated as highly localized, rapidly responding, *in situ* chemical vapor sensors capable of operation at high temperatures and pressures. SAW microelectronic devices currently under development are as small as a few square millimeters, have response times of only a few seconds, and are inherently stable at high temperatures. Multiple SAW sensor arrays, in which each sensor has a coating with different chemical selectivity, could be used with simple pattern recognition schemes to monitor the composition of manufacturing processes, detect chemical changes in waste streams, or simply identify specific chemical vapors. However, the current state-of-the-art chemical microsensors are essentially limited to analytical measurements at or near ambient temperature because of the use of chemically selective organic coatings for their specificity and sensitivity. The principal Phase I efforts are (1) to develop chemically selective coatings based on the use of thermally stable materials in order to extend the new SAW technology to high temperature and pressure applications and (2) to explore innovative SAW designs to further reduce device size and improve performance.

**Precision Analytics, Inc.**  
**Palouse, WA 99161**

**Research and Development Division**

**420. Continuous Ion Mobility Monitoring as a Liquid Stream Process Sensor**

*Shumate, C.B.*

**\$500,000**  
**(24 months)**

A novel universal chemical detector is under study. The detector, known as the ion mobility detector (IMD), is being adapted for continuous monitoring of liquid process streams. Such process streams are common in almost all industrial processes. A knowledge of the constituents of these often complex process streams is essential for process control, quality control, and process development activities. The research has indicated that the proposed detector is indeed capable of monitoring a wide variety of chemicals with high resolution. The presently established limits of detection are in the picogram to nanogram range for a variety of compounds. Current work is focusing on establishing the operational limits of the IMD and the optimization of its hardware and software systems. A sampling manifold is also being studied that will interface the IMD with the liquid process stream. The sampling manifold will be capable of basic sample pretreatment and automatic injection of microliters of process liquid into the IMD assembly. The optimized IMD process monitor is expected to find widespread use in chemical,

pharmaceutical, plastic, petrochemical, waste treatment, and numerous other industries that use liquid chemicals.

**Spectral Sciences, Inc.**  
**Burlington, MA 01803**

**421. Development of a Molecular Intracavity  
Diode Absorption Spectrometer (MIDAS)**  
Goldstein, N.M. **\$484,594**  
(24 months)

Molecular intracavity diode absorption spectroscopy (MIDAS) offers great potential to meet the need for laboratory and industrial chemical species monitors that are sensitive to parts-per-billion concentrations, species-selective, and compact. The MIDAS technique can be used for a wide variety of environmental conditions, including extremes of temperature, pressure, and high background luminosity. Intracavity absorption is accomplished with an external optical cavity that feeds back a portion of the light emitted by the diode, resulting in multiple traversals by the light in the cavity. By placing the sample within the cavity, absorption of light by the sample is enhanced many orders of magnitude compared to a single pass of the laser beam. Diode lasers have the advantages of being small, extremely stable, solid-state devices. When placed in an external cavity, they can be tuned accurately over a large frequency range, allowing identification and quantification of multiple species in a multicomponent sample. In Phase I, enhancement in a sample absorption line using MIDAS was demonstrated

without altering the spectral lineshape or line center location. In Phase II the development issues necessary to turn MIDAS into a sensitive and reliable analytical technique are being investigated. This will lead to the production of a laboratory breadboard instrument that will demonstrate the high sensitivity and selectivity that is possible with MIDAS.

**Spire Corporation**  
**Bedford, MA 01730**

**422. Novel Electrically Conductive Membranes  
for Enhanced Chemical Separation**  
Lu, P.-H. **\$500,000**  
(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 future Phase II work, the process optimization necessary to support the synthesis on a commercial scale will be evaluated, the principles of separation by electromembranes will be examined, and potential applications will be 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. 20545.

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	\$5,866,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	\$17,925,000
	Radiochemical Engineering Development Center	\$7,113,000
	Electromagnetic Isotope Separations (Calutron) Facility	\$1,752,000
Sandia National Laboratories, Livermore	Combustion Research Facility	\$3,475,000
Stanford University	Stanford Synchrotron Radiation Laboratory	\$8,281,000

## ATOMIC SPECTROSCOPY FACILITY (KC-03-01-02)

Chemistry Division  
Argonne National Laboratory  
Argonne, IL 60439

The Argonne 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 multiphoton excitation processes. In addition, Nd-YAG and excimer lasers are available to pump high-resolution dye oscillators and amplifiers. Nonlinear techniques such as sum frequency generation in nonlinear crystals and four-wave mixing in vapors are available to cover the wavelength range from 120 to 1000 nm.

### COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

### PERSON TO CONTACT FOR INFORMATION

Jan P. Hessler      Phone: Comm. (312) 972-3717  
Chemistry Division      or FTS 972-3717  
Argonne National  
Laboratory  
9700 South Cass      BITNET: HESSLER  
Avenue      @ ANL CHM  
Argonne, IL 60439      Facsimile: (312) 972-4470

### TECHNICAL DATA

Resolving power:  
Czerny-Turner spectrograph >10<sup>6</sup>  
Tunable dye oscillators >10<sup>6</sup>  
Wavelength range: (nm)  
Czerny-Turner spectrograph 120 to 500  
Dye oscillators/amplifiers 360 to 720  
Sum frequency generators 200 to 360  
Four-wave mixing systems 120 to 200  
Hydrogen Raman Shifter 720 to 1000

## 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 beams 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 nsec to several

msec at repetition rates variable up to 8 MHz. A VAX 11/750 computer system with direct links to Argonne's central computing facility is used for on-line data acquisition, analysis, and the control of experiments.

### COLLABORATIVE USE

Visiting scientists use the accelerator either in collaboration with Argonne investigators or as independent groups.

### PERSON TO CONTACT FOR INFORMATION

E. P. Kanter      Phone: Comm. (312) 972-4050  
Physics Division      or FTS 972-4050  
Argonne National  
Laboratory  
9700 South Cass Avenue  
Argonne, IL 60439



can be varied from 25 ps to 10  $\mu$ s. In addition, a 5-ps pulse with the same peak current has been developed. In liquids, transient concentrations up to 20  $\mu$ M can be generated with the 25-ps pulse, and concentrations in excess of 10 mM can be generated with the longest pulse. Instrumentation for measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. A 2-ps streak camera with custom software is available for fast emission measurements. 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      Phone: Comm. (312) 972-3471  
Chemistry Division      or FTS 972-3471  
Argonne National  
Laboratory  
9700 South Cass  
Avenue  
Argonne, IL 60439

#### TECHNICAL DATA

Energy		
Transient mode	21 MeV	
Steady-state mode	14 MeV	
Average current	200 $\mu$ A (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)	4 nC	
Pulse width	5 ps	} transient mode
	25 ps	
	4 to 100 ns	
	.15 to 10 $\mu$ s	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 solely 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 1989, 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, and Transverse Optical Klystron (TOK) experiments. Active experimental programs are under way on both insertion device lines on the VUV ring. The insertion devices and beam lines on the X-ray ring are in various stages of commissioning and operation. The first General User programs using insertion device beam lines are expected to begin in 1990.

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 December 1988, scientists from 162 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 70. 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.

### PERSON TO CONTACT FOR INFORMATION

Susan White-DePace Phone: Comm. (516) 282-7114  
 NSLS, Bldg. 725B or FTS 666-7114  
 Brookhaven National  
 Laboratory  
 Upton, NY 11973

### TECHNICAL DATA

Facilities	Key features	Operating characteristics
VUV electron storage ring	High brightness; continuous wavelength range ( $\lambda_c = 25 \text{ \AA}$ ); 17 ports	0.75-GeV electron energy
X-ray electron storage ring	High brightness; continuous wavelength range ( $\lambda_c = 2.5 \text{ \AA}$ ); 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	$2.5 \times 10^4$ to $1.2 \times 10^8$	2
Lithography/microscopy/ tomography/radiography	0.6 to 15	8
Medical research	0.37	3
Nuclear physics	$2.5 \times 10^{-6}$ to $2.5 \times 10^{-4}$	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

## NUCLEAR ANALYTICAL TECHNIQUES (KC-03-02-02)

Atomic and Applied Physics Division  
Department of Applied Science  
Brookhaven National Laboratory  
Upton, New York 11973

This program makes available facilities for the development and application of nuclear analytical techniques. A 3.5-MV electrostatic accelerator provides ion beams of various gaseous species such as  $^1\text{H}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ,  $^3\text{He}$ , and  $^4\text{He}$ . Notable features include a triton beam, medium resolution microprobe, rabbit system, and 200-kV ion implanter arranged for simultaneous implantation and analysis. Photon beams with energies from 3 to 20 keV are provided at the National Synchrotron Light Source (NSLS). After current beam line changes are finished, use of either white or monochromatic radiation will be possible. The high brightness of the NSLS X-ray source gives unique opportunities for analytical microprobe methods: deter-

minations of elemental composition using fluorescence techniques are possible with spatial resolutions of  $\sim 10 \mu\text{m}$  and detection sensitivities of about 100 parts per billion (mass fraction). Applications in the geochemical, biomedical, and materials sciences are actively supported.

### COLLABORATIVE USE

These facilities are open for use by qualified scientists. Arrangements can be made for collaboration with Brookhaven scientists or for independent experiments. Proprietary use is possible on a full-cost recovery

basis. In some cases a proposal for review by program advisory committees will be necessary.

### PERSON TO CONTACT FOR INFORMATION

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Division of Atomic            or FTS 666-4588  
and Applied Physics  
Department of Applied  
Science Building 815  
Brookhaven National  
Laboratory  
Upton, New York 11973

### TECHNICAL DATA

200-kV ion implanter	
Range of terminal voltages attainable	20 to 200 kV
Range of maximum ion beam currents available	1 to 20 $\mu$ A
Ion beams available	Many elements
3.5-MV electrostatic accelerator	
Range of terminal voltages attainable	.3 to 3.5 MV

Range of maximum ion beam currents available	10 to 50 $\mu$ A
Ion beams available	$^1\text{H}$ , $^2\text{H}$ , $^3\text{H}$ , $^3\text{He}$ , $^4\text{He}$ , and heavier gaseous elements
Repetition rate	DC only
MP-TANDEM accel-decel accelerators	
Range of terminal voltages available	1 to 18 MV
Output currents	Up to 1 $\mu$ A
Ion beams available	Most elements
Ion energy and charge state	Variable with accel-decel capability
Repetition rate	DC or pulsed with variable repetition rate
NSLS X-ray facility	
Photon energy range	White or monochromatic radiation
Photon flux at target	$\sim 10^9$ photons/ ( $\mu\text{m}^2 \cdot \text{s}$ ) (depends on experimental configuration)

## 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 LINAC and CRYEBIS facilities are in the final phases of construction and should become available during the next year. 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) 532-6782  
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 mA, 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, super- conducting Nb, operated at 97 MHz
Beam repetition rate	12 MHz with 75% of beam bunched
Mass limitation	$M < 80u$ 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	$\pm 0.00002$ absorbance
Conductivity	
pH range	3 to 11
Sensitivity	$\pm 5$ mhos/cm



## ELECTROMAGNETIC ISOTOPE SEPARATIONS (CALUTRON) FACILITY (KC-03-01-04)

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

The objective of this facility is to separate and provide multigram quantities of highly enriched separated stable and selected radioactive isotopes, including the actinides, to the research community. Important aspects of the program are process improvement, demonstration of cost-effective methods of isotope enrichment, and chemical recovery procedures. All isotopically enriched samples are distributed through a regular sales program or are circulated to the research community on a loan basis from the Research Materials Collection, administered under the direction of DOE. The program is responsible for the production, distribution, quality control, and reprocessing of the material in the Research Materials Collection. Applications for the loan of samples from this

collection for nondestructive research projects germane to DOE programmatic interests are received at any time.

### PERSON TO CONTACT FOR INFORMATION

J. G. Tracy                      Phone: Comm. (615) 574-0425  
Isotope Enrichment                      or FTS 624-0425  
Chemical Technology  
Division  
Oak Ridge National  
Laboratory  
P.O. Box 2009  
Oak Ridge, TN 37831-8044

## 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) a 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                      Phone: Comm. (615) 574-4789  
Bldg. 5500                                      or FTS 624-4789  
Oak Ridge National  
Laboratory  
P.O. Box 2008  
Oak Ridge, TN 37831-6377

### TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 7.0 MV
Source beam currents	Several hundred nA to several $\mu$ A
Output currents	Up to 2 $\mu$ A, depending on the ion species and charge state
Repetition rate	DC only
Magnet limitations	ME/q <sup>2</sup> $\leq$ 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  $3 \times 10^{15}$  neutrons/(cm<sup>2</sup> · 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 <sup>235</sup>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 beryl-

lium reflector contains numerous experiment facilities with thermal-neutron fluxes up to  $1 \times 10^{15}$  neutrons/(cm<sup>2</sup> · 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

B. L. Corbett                      Phone: Comm. (615) 574-7001  
Research Reactors                      or FTS 624-7001  
Division  
Oak Ridge National  
Laboratory  
P.O. Box 2008  
Oak Ridge, TN 37831

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

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

The objective of 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 <sup>257</sup>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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Chemical Technology                      or FTS 624-7071  
Division  
Oak Ridge National  
Laboratory  
P.O. Box 2008  
Oak Ridge, TN 37831-6384

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

Sandia National Laboratories, Livermore  
Livermore, CA 94551-0969

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, as well as research in fundamental chemistry in combustion. (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, DOE/Fossil supports programs in coal combustion and related diagnostics development, 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 14 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 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.

### PERSON TO CONTACT FOR INFORMATION

Peter L. Mattern,      Phone: Comm. (415) 294-2520  
Director                      or FTS 234-2520

Combustion and  
Applied Research  
Sandia National  
Laboratories  
Livermore, CA 94550  
or

J. Stephen Binkley,      Phone: Comm. (415) 294-2174  
Manager                      or FTS 234-2174

Combustion Sciences  
Department  
Sandia National  
Laboratories  
Livermore, CA 94550

**TECHNICAL DATA**

<b>Equipment</b>	<b>Key features</b>		
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2- $\mu$ s pulse length 5 J/pulse, 10 Hz Tunable 440 to 620 nm 0.03-nm bandwidth	Vertical turbulent diffusion flame	chamber: Pressures up to 20 atm Slot- or cylindrical-geometry burner 2-D axisymmetric laminar diffusion flame
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	Combustion bomb	Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow
Low-pressure flames	10 torr to 1 atm Mass spectrometer sampling probe LIF detection of radicals	Internal combustion research devices	Simulated constant-volume engine combustion Highly repeatable environment for homogeneous charge, diesel combustion, and pulse combustion studies
Atmospheric flames	Diffusion and premixed flames	Experimental diagnostics research facilities	Laser fluorescence laboratory
High-pressure flame	Combination of diffusion flame burner with high pressure flow	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 22 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 micros-



## CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS\*

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution $\Delta E/E$	Approximate spot size, hgt $\times$ width, mm	Dedicated instrumentation
<b>Insertion Devices Stations</b>							
Wiggler Lines-X-ray							
End stations							
4-2 (8-pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0 $\times$ 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 $\times$ 20.0	
6-2 (54 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 $\times$ 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 $\times$ 20.0	
7-2 (8 pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0 $\times$ 6.0	Six-circle diffractometer
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 $\times$ 20.0	
10-2 (31 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 $\times$ 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 $\times$ 20.0	
Side stations							
4-1	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	2.0 $\times$ 20.0	
4-3							Two-circle diffractometer vertically focussing mirror
Focused	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	.5 $\times$ 20	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 $\times$ 20.0	
7-1	1.0		Curved crystal	6,000 to 13,000	$\sim 8 \times 10^{-4}$	0.6 $\times$ 3.0	Rotation camera
7-3	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 $\times$ 20.0	
Undulator lines- VUV/soft X-ray							
5-2	1.5		Rowland circle- multiple grating	10 to 1,200	$\geq 7\%$ (raw undulator)	6.0 $\times$ 8.0	Angle integrated e- spectrometer
Undulator lines-X-ray							
PEP 1B							
Focused	1.7	22	Double crystal	12,000 to 22,000	$2 \times 10^{-5}$	.5 $\times$ 3	
Unfocused	Full		Double crystal	12,000 to 42,000	$\sim 10^{-5}$	0.6 $\times$ 6.0	Six-circle diffractometer
PEP 5B							
Focused	1.7	22	Double crystal	12,000 to 22,000	$2 \times 10^{-5}$	.5 $\times$ 3	
Unfocused	Full		Double crystal	12,000 to 20,000	$\sim 10^{-5}$	0.6 $\times$ 6.0	
<b>Bending Magnet Stations</b>							
X-ray							
1-4	2.0		Curved crystal	6,700 to 10,800	$0.3 \times 10^{-3}$	0.25 $\times$ 0.5	Small angle scattering detector

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution $\Delta E/E$	Approximate spot size, hgt $\times$ width, mm	Dedicated instrumentation
1-5	1.0		Double crystal	2,800 to 30,000	$\sim 10^{-4}$	3 $\times$ 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 $\times$ 4	
2-2	1.0		None	3,200 to 30,000		4 $\times$ 22	
2-3	1.0		Double crystal	2,800 to 30,000	$\sim 5 \times 10^{-4}$	3 $\times$ 20	
VUV/soft X-ray							
1-1	2.0		Grasshopper	64 to 1,000	$\Delta\lambda = 0.1$ to $0.2 \text{ \AA}$	1.0 $\times$ 1.0	
1-2	4.0		6m TGM	8 to 180	$\Delta\lambda = 0.06$ to $3 \text{ \AA}$	TBD	
3-1	2.0		Grasshopper	25 to 1,000	$\Delta\lambda = 0.05$ to $2 \text{ \AA}$	1.0 $\times$ 1.0	
3-2	4.0		Seya-Namioka	5 to 40	$\Delta\lambda = 0.2$ to $6 \text{ \AA}$	2 $\times$ 7	
3-3	8 to 10	4.5	UHV double crystal (jumbo)	800 to 4,500	0.35 to $7 \text{ eV \AA}$	2.0 $\times$ 4.0	
3-4	0.6		Multilayer	0 to 3,000	White or $\Delta\lambda/\lambda = 0.6\%$	2 $\times$ 8	Vacuum diffractometer/ lithography exposure station
8-1	12		6m TGM	8 to 180	$\Delta\lambda = 0.06$ to $3 \text{ \AA}$	1mm <sup>2</sup>	Angle resolved e- spectrometer
8-2	5		6m SGM	50 to 1,000	$E/\Delta E \leq 22,000$	1mm <sup>2</sup>	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 1989 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 1989 equipment funds for Chemical Sciences programs were assigned as follows:

	<b>Facility</b>	<b>Equipment funds</b>	<b>Equipment funds</b>
	Idaho National Engineering Laboratory		20,000
	Lawrence Berkeley Laboratory		860,000
	Los Alamos National Laboratory		50,000
	Notre Dame Radiation Laboratory		280,000
	Oak Ridge National Laboratory		2,340,000
	Pacific Northwest Laboratories		165,000
	Sandia National Laboratories, Albuquerque		15,000
	Sandia National Laboratories, Livermore		580,000
	Solar Energy Research Institute		185,000
	Stanford Synchrotron Radiation Laboratory		700,000
Ames Laboratory		\$ 460,000	
Argonne National Laboratory		4,200,000	
Brookhaven National Laboratory		1,860,000	



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