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Summaries of FY 1982 Research in the Chemical Sciences

September 1982

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

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September 1982

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences
Washington, D.C. 20545

PREFACE

The purpose of this booklet is to help those interested in 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 are intended to provide a rapid means for becoming acquainted with the Chemical Sciences program to members of the scientific and technological public and interested persons in the Legislative and Executive Branches of the Government. Areas of research supported by the Division are to be seen in the section headings, the index and the summaries themselves. Energy technologies which may be advanced by use of the basic knowledge discovered in this program can be seen in the index and again (by reference) in the summaries.

Chemists, physicists, chemical engineers and others who are considering the possibility of proposing research for support by this Division will find the booklet useful for gauging the scope of the program in basic research, and the relationship of their interests to the overall program. The research program summarized here is intended to add significantly to the knowledge base on which successful energy technologies can grow. For this purpose, scientific excellence is a major criterion applied in the selection of research supported by Chemical Sciences. Another important consideration is the emphasizing of chemical, physical and chemical engineering subdisciplines which are advancing in ways which produce new information related to energy, needed energy data, or new ideas.

The program is distributed among several different kinds of performing organizations. About half the projects take place at DOE laboratories, and half take place at universities and industrial laboratories. In DOE laboratories, most of the researchers are fully engaged in this work, while most university and industrial researchers necessarily divide their time among duties involving this research, other research, teaching responsibilities, etc. Thus, about 70% of the funding goes to Federal laboratories, 25% goes to the academic sector, and the remainder is at industrial and not-for-profit laboratories.

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 booklet). Other questions about the program may be directed to the undersigned.

Elliot S. Pierce, Director
Division of Chemical Sciences
Office of Basic Energy Sciences

Chemical Sciences Division
Office of Energy Research
Department of Energy
Washington, D.C. 20545

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*on leave from Brigham Young University

Each Branch of the Division of Chemical Sciences is divided into programs which cover various disciplines. The following is a description of each of those programs. The staff members responsible for each program are indicated on page iii.

FUNDAMENTAL INTERACTIONS BRANCH (01-)

Photochemical and Radiation Sciences (01-01)

This program consists of research into the interactions of radiation with matter in all forms, but particularly with gases and liquids. A large part deals with the effects of ionizing radiation and fast electrons. The photochemical research is largely devoted to studies with visible radiation aimed at the capture and conversion of solar energy. This encompasses such fields as artificial photosynthesis, photoinduced electron transfer reactions in homo- and heterogeneous media, photoelectrochemistry, photocatalysis, and the molecular storage of energy. 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 new and growing program of photochemistry, spectroscopy and related studies will be centered at the National Synchrotron Light Source at Brookhaven National Laboratory.

Chemical Physics (01-02)

Disciplines covered by this program include chemical dynamics, energy transfer, molecular structure and spectroscopy, theoretical quantum chemistry, and statistical mechanics.

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

Atomic Physics (01-03)

The Atomic Physics Program supports basic research on phenomena concerning atoms and their ions. Support is provided for experimental and theoretical studies of atom and ion structures, energy levels and energy state lifetimes, and of transport and exchange processes characterized by the rate at which transfer of energy, momentum or matter occurs. These studies strive to attain the best and most complete knowledge of the properties and interactions of photons, electrons, atoms, ions and simple molecules.

Recent emphasis of this research has been on the understanding of relatively high energy atomic physics that involves (1) ions stripped of all or most of their electrons, and (2) atoms and ions whose electrons are promoted in energy up to and including the energy continuum.

PROCESSES AND TECHNIQUES BRANCH (02-)

Chemical Energy (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 characterization and transformation of fossil resources - particularly coal, (3) the conversion of biomass and related cellulosic wastes and (4) hydrogen production and storage. The disciplines of organic, bio-, inorganic, physical, thermo- and electrochemistry, including the more chemically oriented chemical engineering, are central to this program. 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 (02-02)

The separations part of the program is directed at improving our basic understanding of methods for separating mixtures of gases, liquids, solids and their component molecules, cations, anions, and isotopes. A substantial part of the program involves research aimed at discovering the relationship between the structure of organic extractant molecules and their selectivity for cations, anions and their complexes as used in solvent extraction. The isotope separation program emphasizes isotopic properties and isotope effects and is quite basic.

The analysis part of the program is aimed at supporting research on analytical techniques where a better understanding of basics would enable other investigators to improve the sensitivity, reliability, ease of operation and/or lower the costs of analytical determinations. Entirely new analytical techniques are also investigated but this program is not an instrument development program. New techniques are quickly reported in the literature so that those interested in instrument development can build on work supported by this program. The program covers optical spectroscopy, mass spectroscopy, photoacoustic spectroscopy, particle spectroscopy, laser spectroscopy, activation analysis, and many other areas of analytical chemistry. In other words, this program is not geared to using existing techniques to unravel the composition of materials nor to develop techniques to analyze particular species, but is aimed at obtaining a thorough understanding of all of the various aspects of chemical analysis so that others may use this understanding to improve the uses of analysis.

Chemical Engineering Sciences (02-04)

This program addresses the more scientific and energy-related aspects of such engineering topics as fluid and particle dynamics, mass transport, thermodynamics and physical and chemical rate processes. Particular attention is given to turbulence research related to combustion; experimental and theoretical thermochemical and thermophysical properties, especially on mixtures, and phase equilibria, including supercritical extraction phenomena; research on gas-solid reaction modeling; and transport through porous media. Emphasis is given to improving and/or developing the scientific base for engineering generalizations and their unifying theories.

The following is a list of "persons in charge" of Chemical Sciences projects at DOE laboratories. These individuals are department/division, or laboratory administrators who can provide information about specific programs or refer inquiries to appropriate individuals.

AMES LABORATORY
Iowa State University
Ames, Iowa 50011

Chemical Sciences - Fundamental Interactions
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Chemical Sciences - Processes and Techniques
J. H. Espenson - Phone: (FTS) 865-5730 or (515) 294-5730

ARGONNE NATIONAL LABORATORY
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Chemical Engineering Division
F. A. Cafasso - Phone: (FTS) 972-4542 or (312) 972-4542

Physics Division
J. P. Schiffer - Phone: (FTS) 972-4066 or (312) 972-4066
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National Synchrotron Light Source
J. McTague - Phone: (FTS) 666-4966 or (516) 282-4966
A. van Steenbergen - Phone: (FTS) 666-4606 or (516) 282-4606

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A. Schwarzschild - Phone: (FTS) 666-4015 or (516) 282-4015
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IDAHO NATIONAL ENGINEERING LABORATORY
Idaho Falls, Idaho 83401

EG&G Idaho, Inc. P. O. Box 1625
R. L. Heath - Phone: (FTS) 583-1291 or (208) 526-1291

Exxon Nuclear Idaho Co., Inc. P. O. Box 2800
W. A. Emel - Phone: (FTS) 583-3031 or (208) 526-3031

LAWRENCE BERKELEY LABORATORY
University of California
Berkeley, California 94720

Chemical Biodynamics Division
G. C . Pimentel - Phone: (FTS) 451-4355 or (415) 486-4355

Energy and Environment Division
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LAWRENCE LIVERMORE NATIONAL LABORATORY
University of California
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LOS ALAMOS NATIONAL LABORATORY
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P Division
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MOUND LABORATORY
P. O. Box 32
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Nuclear Operations Department
R. E. Vallee - Phone: (FTS) 774-3318 or (513) 865-3318

NOTRE DAME RADIATION LABORATORY
University of Notre Dame
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R. H. Schuler - Phone: (FTS) 333-8222 or (219) 239-7502
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OAK RIDGE NATIONAL LABORATORY
P. O. Box X
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Analytical Chemistry Division
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Chemical Technology Division
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Chemistry Division
O. L. Keller - Phone: (FTS) 624-4987 or (615) 574-4987

Physics Division
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Radiological Sciences Department
N. E. Ballou - Phone: (FTS) 444-3061 or (509) 376-3061

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P. O. Box 10904
Pittsburgh, Pennsylvania 15236

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P. O. Box 5800
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Radiation and Surface Physics Research Department
R. L. Schwoebel - Phone: (FTS) 844-4309 or (505) 844-4309

SANDIA NATIONAL LABORATORIES/LIVERMORE
Livermore, California 94550

Combustion Sciences Directorate
D. L. Hartley - Phone: (FTS) 532-2747 or (415) 422-2747

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1617 Cole Boulevard
Golden, Colorado 80401

A. J. Nozik - Phone: (FTS) 327-1953 or (303) 231-1953

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DOE Laboratories

Photochemical and Radiation Sciences

Chemical Physics

Atomic Physics

Chemical Energy

Separations and Analysis

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Brookhaven National Laboratory

Lawrence Berkeley Laboratory

Oak Ridge National Laboratory

Offsite Contracts

Argonne National Laboratory

Brookhaven National Laboratory

Kansas State University

Notre Dame Radiation Laboratory

Oak Ridge National Laboratory

Sandia National Laboratories - Livermore

Laboratory Project Data

All the summaries of projects funded by a particular Chemical Sciences program (e.g., chemical physics) in a particular Laboratory's division or department are in a contiguous sequence in this book. Total dollars for each such sequence are given at its beginning.

There are two numbers above each summary, other than its entry number. The number immediately to the right of the project title indicates the scientific person years devoted to the project. The other number is the four digit code which identifies the Chemical Sciences program which funds the project, as defined previously.

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $350,000

1. PHOTOPHYSICS, PHOTOCHEMISTRY AND SPECTROSCOPY

G. J. Small

2.5 01-01

The interaction of light with individual molecules and their aggregates produces electronically and vibrationally excited states. It is important to probe such states with single- and multi-photon laser spectroscopies since the nature of the state and its relaxation processes determine light energy conversion. Research on polaritons (mixed electronic-photon states) focuses on excitation mechanisms and how coherent excitation of polaritons accelerates intermolecular electronic energy transfer by several orders of magnitude, of interest for light to electrical energy conversion. A second area is the development of new spectroscopies; e.g., solid state hole burning. Understanding their underlying principles leads to exciting applications for other programs, e.g., high selectivity analysis techniques for organic pollutants. Of current interest are the dependence of intramolecular photochemistry of isolated molecules (e.g., cyclic diones) on specific electronic-vibrational states and photoisomerization quantum reactions of amorphous solids. So too are intra- and intermolecular charge-transfer processes being studied by free jet laser spectroscopy.

2. PICOSECOND SPECTROSCOPY AND REACTION DYNAMICS

W. S. Struve

3.8 01-01

Molecular photochemistry and time-resolved photocurrents in liquid junction solar cells are probed using nanosecond and picosecond laser pulses. The studied dynamic phenomena include effects of molecular electronic and vibrational structure on mechanisms of photodissociation, isomerization, and charge transfer photoreactions of organic carbanions in solution, and the elementary processes involved in charge transfer between the semiconductor and electrolyte in liquid junction cells. Solvent effects in photochemistry are inferred from contrasts between fluorescence lifetimes in solution and the vapor phase. The primary goals of this research are an improved understanding of excited state processes potentially relevant to solar photochemistry, and insights into interfacial process kinetics contributing to the design of liquid junction cells which are free of semiconductor oxide layer formation.

Photochemical and Radiation Sciences

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total $3,665,000

3. RADIATION CHEMISTRY OF LIQUIDS, SOLUTIONS AND ORGANIC COMPOUNDS 5.3 01-01
G. Closs, C. Jonah, J. Miller,
M. Sauer, S. Gordon, A. Trifunac,
K. Schmidt

The objectives of this program are (1) to understand the mechanisms of energy deposition in polar and nonpolar liquids and the reactions that follow from this energy deposition, and (2) to use the reactive species formed by primary events as probes to study problems of fundamental chemical interest. Major questions in the study of nonpolar liquids focus on the nature of the initially observed transient species and their kinetics, the time-evolution of excited states, the importance of tracks and spurs as compared to homogeneous particle distributions and the evolution of electron spin functions to geminate ion pairs. Comparative photoionization studies in nonpolar media are also being conducted. The short time scale of events in nonpolar liquids requires the maximum time resolution in both pulse and detection equipment. The major tool used in these studies is the Argonne high-current picosecond electron linac. Questions on electron solvation are being answered by studying the solvation process in ice. Finally, pulse radiolysis and flash photolysis techniques are used to study the redox reactions of actinides and lanthanides.

4. PREPARATION OF ORGANISMS AND BIOLOGICAL MATERIALS OF UNUSUAL ISOTOPIC COMPOSITION 2.0 01-01
H. Crespi, J. J. Katz, J. Norris

This program has as its objective the production of photosynthetic and other organisms substituted with biologically important stable isotopes. It is important to have the ability to substitute rare, stable isotopes such as ^{2}H, ^{13}C, ^{15}N, ^{17}O and ^{18}O into the complex molecules associated with living systems in order to simplify their study. In addition to replacement by deuterium, the ANL Chemistry Division is able to grow organisms in which non-magnetic ^{12}C is replaced by magnetic ^{13}C, ^{14}N by ^{15}N, ^{16}O by ^{17}O or ^{18}O, and ^{24}Mg by ^{25}Mg. Large quantities of green algae, blue-green algae, bacteria, yeasts and molds are routinely available in unnatural isotopic composition involving either single or multiple substitution. These organisms, and the compounds obtainable from them, have important applications in magnetic resonance spectroscopies, small-angle neutron scattering, and resonance Raman spectroscopy. Of particular interest are applications in the study of chlorophyll, photosynthesis and biomimetic photochemistry.

5. GAS PHASE RADIATION CHEMISTRY RELEVANT TO COMBUSTION AND ATMOSPHERIC REACTIONS 1.3 01-01
S. Gordon, M. Sauer, C. Jonah, W. Mulac

The techniques of pulse radiolysis are being applied to the study of gas-phase reactions of importance in atmospheric and combustion chemistry. Simple radical and atom species are produced by radiolysis and their reaction kinetics are determined by absorption spectroscopy with the aim of determining reaction mechanisms. Hydroxy radical reactions are being studied at very high temperatures to obtain kinetic parameters relevant to combustion reactions. Pressure-dependence studies give information on the importance of third body effects.

6. CHLOROPHYLL AND PHOTOSYNTHESIS RESEARCH

5.0 01-01

J. J. Katz and J. C. Hindman

The principal objective of this research is to acquire sufficient knowledge of chlorophyll function in natural photosynthesis to make possible ultimately the replication of the natural primary light conversion event outside the living cell. Current research focuses on: (a) laser photochemistry and photophysics of chlorophyll, including the study of the anomalous optical properties of chlorophyll and synthetic linked chlorophyll pairs in methylene chloride, and of energy transfer from highly excited chlorophyll *a* states; (b) new methods for the synthesis of chlorophyll model systems, including oxidative coupling at the C-10 position of Ring V; and (c) applications of californium-252 plasma desorption mass spectroscopy to determine the composition of natural and synthetic chlorophyll species involved in photosynthesis.

7. ELECTRON TRANSFER PROCESSES STUDIED BY RADIATION CHEMISTRY AND PHOTOCHEMISTRY

5.8 01-01

J. Miller, G. Closs, D. Meisel, C. Jonah

Two aspects of electron transfer reactions are studied in this program: (1) electron transfer at fixed distances; and (2) energy conversion and storage. The approaches used in the study of electron transfer at fixed distances are as follows: (a) pulse radiolysis of solids which yields information on electron transfer rates and distances which, in turn, provide fundamental information on how electronic barriers control rates of electron transfer; (b) light-driven electron transfer reactions which provide information on transfer distances from photoexcited molecules; and (c) synthesis of molecules containing two electron accepting groups held close together (∿5 A) by an insulating bridge, the study of which provides information on electron exchange and rearrangement energies. The work on energy conversion and storage is concerned with investigations of charge separation in various microenvironments in order to enhance the efficiency of photoelectron transfer, increase yields of photoredox products and minimize rates of back reactions. Also under study are the mechanisms of the catalysis of water-splitting reactions.

8. PHOTOSYNTHESIS STUDIES: REACTION CENTER STRUCTURES, FUNCTIONS AND MECHANISMS

5.6 01-01

J. Norris, G. Closs, M. Wasielewski,
M. Thurnauer, M. Bowman

The goal of this research is to elucidate in detail the efficient utilization of light energy at the molecular level by natural photoreaction centers so that efficient artificial systems can be constructed. The structure of natural electron transfer systems is being investigated by very fast magnetic resonance techniques in order to measure distances and orientations among the participating electron transfer molecular components. The structural requirements for charge separation in the reaction centers of photosynthetic bacteria also are being studied, which assists in the design of artificial systems. Also, the kinetics and mechanisms of electron transport in green, oxygen-evolving systems are under study, with emphasis on the mechanisms of charge separation.

9. RADIATION AND PHOTOCHEMISTRY STUDIED BY MAGNETIC RESONANCE 4.0 01-01
A. Trifunac, G. Closs

The development at Argonne of novel magnetic resonance tools for the study of radiation chemistry and photochemistry has made it possible to observe and delineate a multitude of chemical and physical interactions found in radical reactions of importance in chemistry, biophysics and biology. The research presently focuses in two general directions. One is the study of reactions, kinetics and spin dynamics of transient radicals produced by pulse radiolysis or laser photolysis. The other is the study of processes whereby excited states are created, such as in radical ion recombination. This fundamental knowledge of radical reaction dynamics is used to influence and steer radical reactions into desired and beneficial directions. Much of the studies is vectored by the advantages and insights inherent in the development of new magnetic resonance techniques.

10. ARTIFICIAL PHOTOSYNTHESIS 2.3 01-01
M. Wasielewski

The goal of artificial photosynthesis research is the development of molecular systems in the laboratory that not only mimic but improve upon natural photosynthetic energy conversion. This work focuses on three interrelated facets of this problem. First, a molecular design program involves the synthesis of biomimetic models of natural energy conversion molecules. Second, the photophysics and photochemistry of these systems is being investigated with a primary emphasis on light-induced electron transfer reactions. Third, the primary photosynthetic processes in vivo are being investigated with a view toward integrating the knowledge obtained from the laboratory systems with new knowledge of the natural photosynthetic process.

Photochemical and Radiation Sciences

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $3,100,000

11. RADIATION CHEMISTRY — 5.1 — 01-01

B. H. J. Bielski, R. W. Dodson,
R. A. Holroyd, H. A. Schwarz

Energy production processes (direct solar conversion, combustion, etc.) often involve chemical reactions of transient species, such as ions, electrons, free radicals, and molecules in excited states. The aim of this program is to obtain basic information needed for the understanding and control of these important chemical reactions. The experimental approach uses radiolysis and photolysis techniques, emphasizing pulse methods. Some experiments will also be carried out using VUV radiation from the National Synchrotron Light Source. Principal areas under investigation are: electron transfer reactions in photosynthesis, reactions of singlet oxygen and superoxide radicals, properties and reactions of electrons in dielectric fluids, and redox reactions involving metal ion intermediates.

12. PHOTOCHEMICAL ENERGY CONVERSION AND SOLUTION KINETICS — 8.6 — 01-01

C. Creutz, T. L. Netzel, N. Sutin

Transition metal complexes show considerable promise as mediators in solar energy conversion and storage because they strongly absorb visible light and readily undergo electron-transfer reactions. This program involves photochemical investigations of such complexes and, in particular, the electron-transfer properties of charge-transfer excited states exemplified by their reactions with inorganic oxidants and reductants in solution. Particular attention is being paid to systems capable of effecting the decomposition of water into hydrogen or other useful chemicals and oxygen. A major objective of this program is the quantitative study of physical and chemical deactivation processes that compete with useful light conversion and energy storage reactions. The lifetimes and other physical properties of excited states are being measured and the rates of electron-transfer reactions of transition metal complexes are being determined. The long range goal of these efforts is the design of homogeneous catalysts for the photoproduction of valuable chemicals.

13. CHEMISTRY RESEARCH AT THE NSLS — 5.9 — 01-01

M. D. Newton (Coordinator)

In this program, the aim is to advance a number of areas of chemical research by utilization of photon beams from the National Synchrotron Light Source (NSLS), which is to begin first operations at Brookhaven in FY 1982. Crucial to the research are the experimental facilities to be available, and members of the Chemistry Department have been active in designing and building beam lines to be used by themselves, university researchers, scientists from industry, and colleagues from other National Laboratories. High intensity, pulsed, polarized photon beams ranging in energy from the ultraviolet to the x-ray region will be used for gas phase photoionization and chemical kinetics studies, fluorescence lifetime and photoconductivity measurements, photoelectron spectroscopy, and x-ray diffraction. Experiments are also being planned on the EXAFS and x-ray fluorescence facilities which will be available at the NSLS, and a new Departmental program in chemical catalysis will benefit greatly.

14. ENERGY TRANSFER IN CHEMICAL KINETICS 3.9 01-01
R. E. Weston

Chemical reaction rates depend strongly on the distribution of reactant energy among translational, rotational, vibrational, and electronic degrees of freedom. Conversely, the energy distribution in reaction products provides a sensitive probe of the reaction mechanism. Collisional energy transfer from excited atoms or molecules perturbs the energy distribution and plays an important role in the reaction mechanism. In this program, the transfer of translational, vibrational, or electronic energy is being studied. Atoms or molecules are produced in excited states by a pulse of ultraviolet, visible, or infrared radiation. The time-dependent disappearance of these excited species is monitored by the detection of radiation either from the parent species or from molecules that have been excited by collisional energy transfer. In a complementary part of this program, laser-induced reactions are being investigated, including detailed studies of the laser energy absorption process, energy flow within excited molecules, and energy transfer from excited species.

15. CHEMISTRY OF ENERGETIC ATOMS: BASIC RESEARCH AND APPLICATIONS 3.6 01-01
A. P. Wolf, R. A. Ferrieri,
R. A. Lambrecht

The chemistry of atomic and molecular species, either in energy-rich states or of exceptionally high chemical reactivity is being studied. Neutral or charged reactants in ground or electronically excited states, reactants with high kinetic energies, or species which react with high efficiency are being investigated. Included are reactive intermediates produced by nuclear processes, reactions of C, N, O, and halogen atoms, and studies of atom-atom and atom-molecule reactions in an energy range inaccessible by conventional methods. Atomic species are also produced in known electronic states and with a known temperature by use of a microwave discharge. New methods of generation will include the use of synchrotron "light" to produce high concentrations of molecular ions in reactive media and the development of a new type of ion accelerator to produce intense beams of singly-charged atoms and low molecular weight species. Cyclotron-generated radionuclides are also being used to investigate surface chemistry and heterogeneous catalysis.

Photochemical and Radiation Sciences

Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Total $1,110,000

16\. PORPHYRIN CHEMISTRY 7.3 01-01
J. Fajer

This program addresses the function of chlorophylls in the photosynthetic transduction of light into chemical energy, the catalytic role of porphyrins in bioenergetic enzymic reactions, and the application of these reactions to synthetic multi-electron photocatalysts for the fixation of carbon and nitrogen, and the decomposition of water. The work encompasses synthetic, structural, physical and theoretical chemistry, and presently includes oxygen evolution catalyzed by catalases and the storage of oxidizing equivalents in photosystem II; the six-electron reduction of nitrite to ammonia mediated by isobacteriochlorins; the identification of the primary electron acceptors in green bacteria; theoretical and experimental modeling of environmental effects on the properties of porphyrin and chlorophyll radicals; X-ray studies of Chlorobium chlorophylls as models for dimeric, cofacial primary donors; and picosecond electron transfers in covalently-linked arrays of porphyrins modeled on the mechanisms postulated for photosynthetic organisms.

17\. CONVERSION OF LIGHT BY SEMICONDUCTOR - ELECTROCHEMICAL SYSTEMS 2.2 01-01
S. Feldberg and T. Skotheim

Research in this program is being carried out in two major areas. 1. Research on photoelectrochemical cells: N-type silicon coated with a thin film of polypyrrole acts as a stable photoanode in contact with an aqueous redox system (e.g., I_2/KI). The film precludes the formation of a passivating SiO_2 layer. Replacing the aqueous phase with a polyethylene oxide film loaded with I_2 and KI, and using a transparent indium tin-oxide glass electrode gives a stable, solid state, photoelectrochemical device. The engineering efficiency of the cell is about 0.5%. Improvement to better than 5% is hoped for. 2. Theoretical studies of the behavior of systems involving Nernst-Planck transport, photoeffects, and kinetics (heterogeneous and homogeneous): A model for the analysis of the relaxation of photopotentials of semiconductor electrodes following pulsed light excitation has been developed. Electron-hole recombination in bulk and at the electrode surface are the controlling factors. Other problems involving steady state illumination of semiconductors and dielectric relaxation of a system containing dissociating ion pairs are also being investigated.

18\. CHEMICAL PROPERTIES AND REACTIONS OF MONO- AND DINUCLEAR FERROCENE DERIVATIVES 1.8 01-01
M. Hillman

This program is an investigation of the preparation and properties of unusual metallocenes and related compounds that are expected to have application in the energy program, especially towards the splitting of water. Particularly, for the oxidation of water a bridged ferrocene derivative was prepared and its reactions on a silicon electrode are being studied. The oxidized state of the compound has a potential high enough to oxidize water and is stable under the conditions required. For the reduction of water, a bridged bisfulvalenediiron derivative was prepared. This compound has tilted Cp rings and is expected to be protonated more easily than the parent non-bridged derivative and therefore to release hydrogen at a lower pH. The investigation of the kinetics of the reduction reaction is underway.

19. PHOTOLYSIS IN THE ADSORBED STATE J. W. Sutherland	1.1	01-01

The research program is directed towards understanding the modifying influence of the surface environment and the state of aggregation of a sorbate molecule on its photophysical and photochemical properties. The investigation into the photochemistry of polynuclear aromatic molecules adsorbed on porous glass continues; short-lived absorbing species, prompt and delayed fluorescence properties and absorption and excitation spectra are being studied as functions of surface coverage, light intensity and the presence of quenchers. Some significant findings are: molecular cations, identified by their characteristic spectra, are produced on flash photolysis of adsorbed anthracene and pyrene by a two photon process; triplet energy migration occurs readily in aggregates of adsorbed pyrene at surface coverages less than that of a monolayer; and evidence which suggests that excited states are interacting with specific sites on the surface to form transient excited surface complexes.

Photochemical and Radiation Sciences

National Synchrotron Light Source Brookhaven National Laboratory Upton, New York 11973	Total $2,300,000

19 A. NATIONAL SYNCHROTRON LIGHT SOURCE - OPERATIONS AND DEVELOPMENT J. McTague and A. van Steenbergen	30.0	01-01

The objective of this program is to support operations and development of the National Synchrotron Light Source (NSLS). The operations aspect covers operation and maintenance of the two NSLS electron storage rings and its associated injector combination of linear accelerator-booster synchrotron; operation and maintenance of the photon beam lines of the VUV and X-ray storage rings; and the technical support of experimental users. The development of the NSLS encompasses the further improvement of the storage rings to achieve maximum brightness photon sources and the further development of the photon lines of the facility by means of new developments in high resolution photon optics, state of the art monochromators, X-ray mirror systems, detectors, and so on.

Photochemical and Radiation Sciences

Chemical Biodynamics Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $825,000

20. ARTIFICIAL PHOTOSYNTHESIS M. Calvin, J. W. Otvos	4.5	01-01

This research is directed toward devising synthetic systems to accomplish the photoinduced transfer of electrons across phase boundaries, the way natural chloroplasts convert light into chemical energy. We have demonstrated the transfer of electrons across the lipid walls of vesicles and the production of oxidation and reduction on opposite sides of the wall. The use of ionophores and controlled electric fields across the membrane wall can greatly enhance the rate of the overall photochemical reaction. Other types of charged, single surfaces such as SiO_2 colloid have also been found to increase the reaction yield when a primary reaction product is electrostatically repelled from the surface and prevented from back-reacting. Thus the various steps in the oxidation-reduction system have been studied and their dependence on important parameters determined. Emphasis is shifting now to assembly of the entire system and the development of good catalysts, based on iron-sulfur complexes on the reduction side and manganese complexes on the oxidation side, to provide hydrogen and oxygen as end products in the photolysis of water.

21. PICOSECOND PHOTOCHEMISTRY J. H. Clark	1.5	01-01

Proton-transfer and electron-transfer reactions of electronically excited molecules form the basis for virtually all existing and proposed methods for the photochemical fixation of solar energy. In this research, the techniques of picosecond laser spectroscopy are used to directly monitor, in real time, the dynamics of these ultrafast processes. Such studies provide insight into the details of the mechanism and kinetics of these reactions at the molecular level. This work has shown that the naphthols and substituted naphthols provide prototypical systems in which the dynamics of excited-state proton transfer are exquisitely sensitive to subtle chemical changes. The effects of solvent environment, intermolecular and intramolecular hydrogen bonding, molecular conformation, and reactant geometry are being studied with the aim of quantifying their role in excited-state proton-transfer processes. The dynamics of the conversion of the free energy of chemical reaction into electronic excitation, and _vice versa_, are also being investigated through the study of the chemiluminescent reactions of solvated electrons.

22. PHOTON CONVERSION G. C. Pimentel	4.0	01-01

This research is directed toward the study of chemistry and energy movement as it occurs on electronic hypersurfaces as an aid in the design of systems that facilitate chemical storage of photon energy. Cryogenic solids furnish particularly favorable environments for the study of light-initiated and reaction-initiated movement between and on electronic hypersurfaces. Energy transfer among electronically excited states is studied through chemiluminescence at cryogenic temperatures. Temporal aspects of the behavior of gaseous transient intermediates in energy storage reactions (including electronically excited molecules) will also be studied on the 10 nanosecond time scale as we extend Stimulated Electronic Raman Spectroscopy to the 10 micron spectral range.

Photochemical and Radiation Sciences

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $410,000

23. PHOTOCHEMISTRY OF MATERIALS IN THE STRATOSPHERE

H. S. Johnston

5.5

01-01

This research is concerned with fundamental gas-phase photochemistry, emphasizing chemical species that occur in the stratosphere. Laboratory studies are carried out to obtain optical cross-sections, quantum yields, and rate coefficients for molecules and reactions currently important toward interpreting atmospheric observations. By use of laser flash photolysis and resonance fluorescence, the "negative activation energy" of the reaction $HO + HNO_3 \rightarrow H_2O + NO_3$ was confirmed, and a theoretical justification for this unusual effect was found. The rate constant for the fast resonant energy transfer between singlet delta oxygen and the HOO radical has been determined; and its unrecognized, possible role in various laboratory studies is being examined. A narrow tunable diode laser was used to obtain absolute intensities and line shapes for infrared vibrational-rotational absorption by the hydroxyl radical, which has potential use for spectroscopic analysis of hydroxyl radicals in the atmosphere.

24. PHOTON-ASSISTED SURFACE REACTIONS, MATERIALS, AND MECHANISMS

G. A. Somorjai

0.9

01-01

This project explores photocatalyzed chemical reactions that take place at the solid liquid and solid-vapor interfaces. These include the photodissociation of water (H_2O) to produce hydrogen and oxygen, and the photon-assisted reactions of carbon dioxide (CO_2) and water to produce simple hydrocarbons (photosynthesis). The purpose of these studies is to explore the mechanism of photon-assisted surface reactions and then to establish the optimum conditions (of surface structure, composition, temperature and reactant mixture) to maximize the rate of production of the desired chemicals (hydrogen and/or hydrocarbons). The materials that are being used include strontium titanate, iron oxides and iron silicates.

Photochemical and Radiation Sciences

Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, Indiana 46556
Total $2,450,000

25. THEORETICAL STUDIES ON REACTING SYSTEMS 7.0 01-01
D. M. Chipman, W. M. Huo, J. J. Kozak

Quantum and statistical mechanics methods are being developed to interpret phenomena in radiation chemistry and photochemistry, especially those involved in chemical-dynamic processes related to energy storage and transfer. New quantum mechanical methods to perform and analyze electronic structure calculations on molecules are being developed to study microscopic properties such as molecular structures, potential energy surfaces, reaction mechanisms, photochemical properties, intermolecular forces, electron-solvent interactions, spin density distributions and various spectroscopic parameters of molecules. Quantum dynamical aspects of the interaction of radiation with matter are being studied using new analytical techniques developed in this laboratory for solving the time-dependent Schrodinger equation. A comprehensive statistical mechanical theory of photo- and radiation-induced redox reactions in organized molecular assemblies is being developed. These latter studies have considerable relevance to our understanding of experiments in which organizates may be applied in photochemical processes to effect the storage of solar energy.

26. ORGANIC PHOTOCHEMICAL PROCESSES 4.8 01-01
P. K. Das, M. V. George, T. Kilp

Nanosecond laser flash photolysis experiments are being carried out to examine the role of intermediates (radicals, biradicals, singlet and triplet states, exciplexes and ion pairs) on the photochemical reactions of organic systems in solution. Included are studies of addition, fragmentation and hydrogen abstraction reactions, intermolecular energy transfer between quasi-isoenergetic triplets, intramolecular transfer in molecules containing two chromophores, energy hopping along a polymeric chain and energy trapping. Supplementary information is obtained from photophysical studies such as absorption, fluorescence and phosphorescence spectroscopy and measurements of fluorescence depolarization and nanosecond fluorescence lifetimes. Model systems being investigated include phenyl substituted polyenes and polyynes containing heteroatoms, aromatic hydrocarbons and carbonyl compounds, small ring heterocyclic systems, flavins and polymers containing carbonyl groups. The studies on energy migration in polymers are particularly relevant to photosynthesis and to possibilities for enhancing the properties of polymers toward photodegradation or photostabilization. Programmatic emphasis is on obtaining mechanistic details of photochemically induced reactions.

27. INORGANIC PHOTOCHEMICAL STUDIES 5.0 01-01
G. J. Ferraudi

The photochemical properties of coordination complexes of copper(II), rhodium(III) and ruthenium(II) with macrocyclic ligands are being investigated. Both conventional and laser flash photolysis methods are used and supplemented by product analysis studies. This research is carried out with compounds that exhibit either a direct or sensitized photochemical redox reactivity for excitation in the visible region in the spectrum and therefore are candidates for use in solar energy conversion. Two families are targets of these studies, the phthalocyanines and complexes with macrocyclic ligands possessing simple structures. It is sought to establish the general relationships between photoreactivity and the molecular structure of the macrocycles. Reference pulse radiolytic experiments are carried out to provide spectroscopic and rate information on the reactive intermediates. Photoinduced hydrogenation of aromatic compounds with structures similar to those found in coal is being investigated. These latter studies involve the use of rhenium hydrides which exhibit properties required for photogeneration of hydrogen.

28. MICROWAVE STUDIES ON RADIATION CHEMICALLY PRODUCED INTERMEDIATES

3.8 01-01

R. W. Fessenden

Electron spin resonance (ESR) spectroscopy is being used to study radical structures, radical reaction mechanisms and kinetics, and the nature of electron spin interactions in fluids. Continuous *in situ* radiolysis generates radicals for characterization of their geometric and electronic structures by means of the observed ESR hyperfine patterns. The identity of the radicals produced and any subsequent transformations observed provide information on reaction mechanisms. Time-resolved experiments on radicals produced by pulse radiolysis measure reaction rates for intramolecular rearrangements and bimolecular disappearance, as well as rates of bimolecular spin relaxation and the extent of signal enhancement by chemically induced dynamic electron spin polarization. The latter quantities taken together with reaction rates provide very detailed information on reaction mechanisms in liquids. Pulsed microwave experiments, including ones using saturation recovery and electron spin echo techniques, provide information on relaxation times in a more direct way. The spin echo method also allows improved time resolution for fast reaction rate measurements. Microwave methods are also used to study electron attachment processes in high pressure gases and liquids.

29. TIME RESOLVED STUDIES OF PHOTOLYTIC REACTIONS

2.6 01-01

R. W. Fessenden

Time-resolved microwave absorption methods are applied to characterize the charge distribution in intermediates produced by laser excitation. Particular attention is being given to measuring the dipole moments, i.e. the degree of charge separation, in various radicals, excited states and exciplexes that are intermediates in photochemical processes. Parallel optical experiments employing two lasers, one to form and the second to photolyse the intermediate states, are also being carried out. Applications are directed toward characterizing the various absorption bands of the intermediate in terms of their photochemical activity. Optical absorption spectroscopy is used for diagnosis. Where dissociation is observed studies of the recombination kinetics of the resultant fragments often provide rate data not directly available. These investigations are complimented by both steady state and time resolved ESR studies of photolytically produced radicals. Photochemical studies are also being carried out in liquid crystals to examine the effects of orientation on photochemical activity.

30. THEORETICAL ASPECTS OF RADIATION CHEMISTRY

2.0 01-01

K. Funabashi, A. Mozumder

Attention is focussed on the development of a unified theoretical framework capable of describing the various physico-chemical properties of solvated electrons such as their optical absorption spectra and transport properties, on problems associated with thermalization of radiation produced electrons in both gases and liquids and on the nature and properties of reactions at early times, especially as they apply to track effects. Contributions of secondary electrons to the reactions within heavy particle tracks are being examined. The thermalization studies are being extended to examination of the time evolution of the effective electron temperature in molecular gases based on experimentally available elastic and inelastic cross-sections. Conclusions from these various studies are important both to many aspects of radiation chemistry and to other areas where ions are important such as in considerations in the reactions of ions in the atmosphere or on the electrical properties of insulators.

31. SPECTROSCOPY OF REACTION INTERMEDIATES 4.0 01-01
J. Hardwick, J. J. Bentley, Y. Inel,
G.N.R. Tripathi, D. Winicur

High resolution spectroscopic studies of reactive species produced in radiolysis, photolysis and combustion processes are being carried out to identify those species, determine their molecular structure and the inter- and intramolecular pathways through which excess energy is redistributed and to examine their reaction kinetics. Laser excited fluorescence methods are used to determine rotational, vibrational and electronic energies of radicals present in flames and produced by the reactions of hydrocarbons with a flowing afterglow of metastable rare gas atoms. Absorption experiments are also being carried out that probe the high-lying vibrational states of stable molecules since these states have appreciable populations in typical flames. Radicals are also being studied in both the liquid and solid phase by resonance Raman techniques. Photoacoustic techniques are used to examine the collision-induced absorption of forbidden vibrational modes to provide information on the transient dipole moments and molecular distortions which result from molecular collisions.

32. ELECTRON TRANSFER REACTIONS 6.2 01-01
P. Neta, H. Levanon

Pulse radiolysis techniques are being used to characterize the kinetic properties of short lived transient species involved in electron transfer and redox reactions. Approaches developed in this laboratory provide methods for examining electron transfer equilibria and allow the determination of one-electron oxidation or reduction potentials for various types of organic radicals. Details of the oxidation and reduction of organic molecules by both organic and inorganic radicals are being examined. Additionally, time resolved studies are used to determine the reactivities of the intermediates following radiation initiated cleavage of both organic compounds and inorganic ions. Special attention is given to electron transfer reactions involving metalloporphyrins and chlorophylls, which are important in photosynthetic environments and also to intramolecular electron transfer within organic radicals and metal complexes. The ultimate aim of these various studies is to expand our understanding of reaction intermediates so as to be able to predict their role in radiation, photochemical and conventional chemical systems.

33. INFLUENCE OF ORDERED MOLECULAR ASSEMBLIES 5.8 01-01
ON CHEMICAL PROCESSES
L.K. Patterson

These studies are directed toward developing a better understanding of the relationships between structure in organized molecular assemblies and the influence these assemblies may exert on kinetic behavior. A variety of unique properties have been observed for systems in which such assemblies - micelles, vesicles, spread monolayers - are formed. Such properties include compartmentalization of reaction, non-homogeneous distribution of reactants, surface orientation of reactant molecules, surface charge effects and reduction in dimensionality of the reactant phase. Alterations in rates and reaction mechanisms that are observed when reactions are initiated in such assemblies strongly suggest the possibility for kinetic control over a variety of photochemical and radiation chemical processes not possible in homogeneous solution. An increasing proportion of effort is being directed toward studies in spread monolayers. Because these latter assemblies provide for far greater control in the degree of organization which may be imposed on a reaction system, it is to be expected that correlations may more readily be derived between extended assembly structure and kinetic behavior.

Notre Dame Radiation Laboratory, continued

34. RADIATION CHEMISTRY DATA CENTER 1.0 01-01

A. B. Ross, W. P. Helman, G. Hug,
I. Carmichael

The Radiation Chemistry Data Center (RCDC) maintains and continuously updates a bibliographic data base on radiation chemistry and photochemistry and provides a variety of information services to the scientific community. A current-awareness publication, <u>Biweekly List of Papers on Radiation Chemistry and Photochemistry</u> is produced from the data base and distributed to subscribers. Experimental data for reaction intermediates produced by light or ionizing radiation are compiled from the published literature. Data are included for photochemical and photophysical processes in solution. Critical reviews of these data are prepared for publication. A goal of this program is the development of a numeric data base of kinetic and spectroscopic properties of reaction intermediates which can be effectively used by many types of users. These bibliographic and numeric data bases are expected to be of increasing importance in the basic scientific study of chemical processes in irradiated systems and in technological applications such as solar energy utilization and photochemical effects on the environment.

35. RADIATION INDUCED REACTIONS 6.8 01-01

R. H. Schuler, L. K. Patterson,
G.N.R. Tripathi

A wide variety of chemical reactions induced by the absorption of ionizing radiation are being examined using the Laboratory's broad base of highly developed chemical and instrumental methods (absorption spectrophotometric, conductivity, ESR, laser Raman and chromatographic methods) for examining both intermediates in time resolved studies and for analysis of ultimate products. Attention is, to a large extent, focussed on competition between recombination processes that occur within the radiation produced track and scavenging by added solutes. Interpretation of the data is enhanced by improvements in dosimetry and time resolution at the LINAC facility which allow optical and conductometric pulse radiolytic studies to be carried out at nsec times. Studies are also being carried out at the Notre Dame Heavy Ion Facility to examine track effects in radiation chemical reactions induced by low Z ions having LET's of 1-100 ev/Angstrom. These track studies are complemented by studies at very high intensities using a Febetron as a radiation source.

36. ENERGY TRANSFER IN ATOMIC AND MOLECULAR SYSTEMS 1.0 01-01

D. H. Winicur

Molecular beam methods are being used to examine the mechanisms, cross sections and intermediate species involved in energy transfer in elementary processes. Interactions between metastable, excited rare-gas atom and various small molecules such CO_2, H_2O, $(CH_3)_2O$, H_2, and F_2 are determined from measurements of differential scattering cross sections using crossed-molecular beams. The results from these experiments provide detailed information on the nature of the interactions during the molecular collision, indicate the states present immediately after the initial energy transfer and allow a determination of the potential-energy curves for the interacting species and on translational-to-rotational and translational-to-vibrational energy exchange.

Photochemical and Radiation Sciences

Research Division
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

Total $440,000

37. PHOTOPHYSICS AND PHOTOCHEMISTRY OF CHLOROPHYLLS, POPHYRINS AND MODEL SYSTEMS FOR ARTIFICIAL PHOTOSYNTHESIS 0.75 01-01
J. S. Connolly

This program is concerned with fundamental studies of energy- and electron-transfer processes of excited states in a variety of porphyrin-related systems. The focus is on the detailed photophysical properties of chlorophylls and porphyrins and on light-induced electron transfer in synthetic models of natural photoreaction centers. The goal is to contribute to an improved understanding of the molecular properties required for efficient light-induced electron transfer in photosynthesis and photocatalysis. Patterns of subtle influences of molecular structure and the local molecular environment on the excited-state properties of the chlorophylls and porphyrins are beginning to emerge, and the results should have implications in terms of understanding the in vivo environments of these macrocycles. In the model-systems area, laser flash photolysis and fluorescence-lifetime studies are being carried out on covalently linked porphyrin-quinones to sort out the effects of photophysical properties, redox potentials, and molecular geometry on the kinetics and mechanisms of light-induced electron transfer and subsequent charge stabilization.

38. BASIC PHOTOELECTROCHEMISTRY RESEARCH 3.6 01-01
A. J. Nozik, J. A. Turner, A. J. Frank,
J. Cooper, B. A. Parkinson

Basic research in photoelectrochemistry is being conducted on the energetics of semiconductor-electrolyte interfaces; on hot-carrier effects in photoelectrochemical systems; on the properties and applications of electrically-conducting organic polymers; on colloidal and particulate semiconductor systems; and on doubly-illuminated p/n photoelectrolysis cells. The movement of semiconductor band-edges is being analyzed and characterized. Hot carrier effects are being experimentally verified with GaP and InP photoelectrodes. Electrically-conducting films of polypyrrole are being studied as stabilizing elements in photoelectrolysis cells. Microdispersions of semiconductors are being studied as novel photocatalytic systems, and the energetics of p/n photoelectrolysis cells is being established in detail.

Chemical Physics

Ames Laboratory Iowa State University Ames, Iowa 50011	Total $690,000

39. STATISTICAL MECHANICS OF GASEOUS SYSTEMS D. K. Hoffman	2.0	01-02

This work has two basic aspects. One is the development of mathematical models which predict the spatial correlation of events occurring irreversibly and cooperatively at sites on a lattice. In applications the "lattice" might be a polymer backbone or the (bulk or surface) sites of a solid at which "events" such as irreversible adsorption of atomic or molecular species, reaction, radiation damage, or structural transformations can occur. The aim is to show how the energetic or geometric features of the system determine the spatial distributions of such events. These distributions in turn affect bulk properties of the system. A second aspect of the work is to understand the kinetic theory of transport, relaxation and reactive processes in polyatomic gases. Such processes are not only of intrinsic importance but also provide a macroscopic probe of the collision dynamics. Current emphasis concerns collision models and dynamic approximation schemes from which phenomenological cross sections with sensitive dependence on inelastic and reactive collisions can be calculated with accuracy.

40. ATOMIC MOLECULAR AND FREE RADICAL CROSSED BEAM KINETICS C. Y. Ng	3.0	01-02

This program emphasizes obtaining accurate thermochemical data needed to characterize elementary chemical reactions of species related to combustion. A series of experiments, which involve photoionization studies of some simple molecules and their clusters are completed, underway, or are planned.

(i) Simple inorganic molecules: H_2S, H_2O, HCN, O_3, and NO_2.

(ii) Unsaturated hydrocarbons: C_2H_2, C_2H_4, C_3H_6, and cyclo-C_3H_6.

(iii) High temperature vapors: S, P, Hg, Cd, Zn, and Pb.

41.	MOLECULAR BONDING THEORY K. Ruedenberg, S. T. Elbert	3.0	01-02

This project concerns determinations of molecular properties and of energy changes during chemical reactions through quantum theoretical calculations of electronic structures. Its aim is the prediction of reaction and activation energies for elusive intermediates and transition states which are needed in energy-related research but difficult or impossible to obtain experimentally. For the reliable, yet practical calculation of such quantities new fundamental theoretical methods are developed which furnish unrestricted descriptions of electronic rearrangements along chemical reaction paths, predict reactive energy changes and elucidate reaction mechanisms. These methods also furnish quantitative models for intuitive reasoning in terms of interpretative concepts consistent with ab-initio calculations, so as to anticipate the consequences of reactive changes with minimal computation. The methods are applied to studies of oxidation-reduction and exchange reactions involving carbon, nitrogen, oxygen and hydrogen to elucidate reactions occurring during combustion, in the atmosphere, and during hydrogenations.

42.	ION CHEMISTRY - MASS SPECTROSCOPY H. J. Svec, G. D. Flesch	2.0	01-02

This program emphasizes studies of the production of gaseous ions and neutral products resulting when molecules and energetic electrons interact. The development of a double-ended, dual ionization chamber mass spectrometer facilitates this work. Studies of the tetramethyl derivatives of Si, Ge, Sn and Pb, and N_2, O_2, Ar, and He and mixtures thereof have elucidated excitation to high Rydberg states of the neutral species, far above their ionization energies. These states have lifetimes >10 μs and are very reactive. Autoionization, dissociative autoionization, molecule/molecule interactions and dissociation to neutral products have been observed. Ion and excited state chemistry, unavailable via optical spectroscopy is tractable. Results of interactions between excited N_2 and O_2 have implications for the chemistry occurring in the upper atmosphere and gas discharges. Results of studies of mixtures of O_2 and hydrocarbons are related to processes occurring during combustion.

Chemical Physics

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total $1,500,000

43. HIGH RESOLUTION SPECTROSCOPY 3.3 01-02
H. M. Crosswhite, F. S. Tomkins,
K. T. Lu

Large grating spectrographs and tunable, pulsed dye lasers are being used to investigate fundamental problems in atomic structure and atomic theory. Interest is concentrated on spectroscopic detail of diamagnetic effects immediately below and above the ionization limit of atomic vapors, including perturbational effects induced by collisions with rare-gas atoms. We have heretofore been confined to the spectroscopic region above 2000 Å, but several recent advances permit us to extend this work to shorter wavelength. Of particular interest is the recent development in the program of a four-wave nonlinear optical mixing technique in mercury vapor to efficiently generate tunable radiation down to 1175 Å with a bandwidth of about 0.02 cm^{-1} with high efficiency. This system is the basis for developing a convenient, reliable and dedicated source for various atomic and molecular spectroscopic experiments. The experimental program is reinforced by a theoretical one which includes treatment of collisions and quasi-molecular resonances, magneto-electric effects and Multichannel Quantum Defect Theory.

44. THEORETICAL CHEMISTRY 5.6 01-02
T. H. Dunning, Jr., L. B. Harding,
R. L. Shepard, A. F. Wagner

This program is concentrated in three major areas of research: A. Theoretical Studies of Chemical Reactions focus on theoretical characterization of the energetics and kinetics of chemical reactions, with emphasis on reactions of importance in the combustion of hydrogen and simple hydrocarbon fuels; B. Theoretical Studies of Metal Atom Clusters entail theoretical characterization of the structure, spectra, and energetics of clusters of metal atoms with and without adsorbates, particularly clusters relevant to catalytic processes; C. Method and Code Development for Chemical Computations. The basic thrust of the program is on the calculation of accurate atomic and molecular interaction potentials, the study of the chemical dynamics on the computed, or other realistic potential energy surfaces, and on the accurate calculation of the structure, spectra, and energetics of relevant molecular species.

45. MOLECULAR BEAM AND METAL CLUSTER CHEMISTRY RESEARCH 4.8 01-02
S. Wexler, E. K. Parks,
S. J. Riley, T. H. Dunning, Jr.

In a program designed to study heterogeneous catalysis on a molecular level, beams of catalytically active naked metal (Ni, Ag, Al, Fe) atom clusters (2-20 atoms) are generated and their physical and chemical properties are characterized by in-flight techniques. Electronic and spectral properties are determined and experimental results are correlated with theoretical calculations. The goal of this work is the determination of the mechanisms and dynamics of adsorption and catalytic processes on surfaces of clusters of known size. A second program involves investigation by a crossed-molecular beam method of ion-pair formation from dissociation of molecules by collision with hyperthermal atoms and molecules. Absolute cross-sections, energetics, dynamics and reaction mechanisms are being determined, from which are derived factors important in translation to internal energy transfer. A new direction in this area is the study, by crossed beam techniques, of reactions of fast refractory atoms, as Fe, of importance in corrosion.

Chemical Physics

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $3,565,000

46. LASER PHOTOCHEMISTRY AND PHOTOPHYSICS 2.1 01-02
D. M. Brenner

The research program in laser photochemistry has been concerned with the phenomenon of infrared multiphoton excitation (IRMPE) in small molecules. Experiments have been carried out to understand the photophysics of absorption in the ladder where absorption is "mode selective." They involve infrared-visible double resonance under molecular beam conditions and photoacoustic studies in bulbs. Other studies have been undertaken to understand the effect of IRMPE on the branching ratio in dissociation where two reaction pathways exist.

47. NEUTRON SCATTERING 3.2 01-02
L. M. Corliss, J. M. Hastings,
R. Thomas

Neutron scattering is used in this program to study the statistical mechanics of phase transitions, the dynamical properties of solids, properties and spin configurations of magnetic materials, and also crystal structures where relevant to the general program.

The strong interaction of neutrons with vibrational, rotational, and diffusive modes in crystals makes inelastic neutron scattering an excellent probe of atomic motion in solids and particularly well adapted to studies of phonons and hydrogen motion. In the case of magnetic systems one can measure the spatial distribution of magnetization and the behavior of spontaneous fluctuations, both of which are essential to understanding magnetic phase diagrams and their associated first- and second-order transitions. Because of the universal nature of critical phenomena, information gained from magnetic systems can be readily transferred to the study of other systems exhibiting second-order phase transformations, such as simple and multicomponent liquids, alloy systems, and superfluids.

48. THEORETICAL CHEMISTRY 5.1 01-02
S. Ehrenson, J. T. Muckerman,
M. D. Newton

Theoretical methods are applied to the study of energy flow in chemical reactions and to the elucidation of molecular interactions involved in the storage and interconversion of energy in the gas phase and in condensed phases, including phenomena associated with charged species. The methods principally used are *ab initio* and semiempirical calculations of the energies and structures of molecules in specific electronic states, and classical and semiclassical treatments of the nuclear motion in kinetic processes involving these systems. Specific chemical problems of interest are: *ab initio* models for aqueous charge-transfer processes and related electronic structure properties of transition metal complexes; hydrogen bonding in hydroxylic systems; the nature of chemical bonding in silicates; dielectric effects of solvents surrounding cavities of various shapes; application of statistics for free energy correlation methods to chemical and physical properties of large molecules; dynamics and energetics of elementary combustion reactions; and dynamics of reactions involving excited states of atoms and molecules.

49. ION-MOLECULE REACTIONS WITH APPLICATIONS TO FUSION ENERGY SYSTEMS 2.6 01-02

L. Friedman, R. J. Beuhler

High molecular weight mass spectrometric techniques are used to investigate nucleation processes responsible for the formation of cluster ions and neutral microclusters. Immediate goals are the development of cluster-ion sources and their exploitation as a basic research tool. The present capability of mass analysis of molecular species with m/e values up to approximately 200,000 will be expanded to higher m/e values using high voltage ion post-acceleration and time of flight mass analytical techniques. Ion source facilities capable of generation of plasmas from gases cooled to temperatures as low as 10 K will be used to study cluster ion generation from inert gases and diatomic molecular species. The generation of cluster ions from hydrogen isotopes is considered a major task objective because of the potential role these cluster ions may have in the study of controlled thermonuclear reactions. Studies on energy transfer processes with cluster ions in gas phase collision processes and on impact with solid surfaces will provide basic new knowledge on the properties of these very interesting and potentially important molecular species.

50. MOLECULAR BEAM STUDIES OF CHEMICAL DYNAMICS USING SHORT-LIVED RADIOACTIVITY AND SYNCHROTRON LIGHT 0.5 01-02

J. R. Grover
M. White

A user-oriented windowless experimental facility for gas phase studies at the NSLS, using photons of wavelengths 300 Å to 2000 Å, has been constructed. The monochromator delivers the most intense photon beams possible from an NSLS port, and suppresses diffracted beams of second and higher orders. The BNL Chemistry Department use of this facility features a nozzle molecular beam apparatus in which atoms, and strongly cooled molecules, radicals, and clusters are studied by photoionization mass spectrometry and electron spectrometry. Thermochemical, spectroscopic, and structural information is thereby made accessible for a wide variety of species, especially those that cannot be prepared in bulk. Detailed studies of the dynamics of single-photon induced processes are also made possible, e.g. energy and angular distributions of photofragments and photoelectrons, dissociation pathways as a function of photoexcitation energy, and double ionization. Cross section measurements from crossed molecular beams using 0.032-sec ^{217}At have led to new insight into halogen-hydrogen-halogen' reactions.

51. CHEMICAL CRYSTALLOGRAPHY 2.0 01-02

T. F. Koetzle, Å. Kvick, R. K. McMullan

Neutron and x-ray diffraction methods are used to solve significant problems in crystal and molecular structure. This program emphasizes structures where hydrogen atoms are important, and disordered or partially-ordered structures, since in these areas neutron diffraction, alone, or in combination with x-ray diffraction, has unique advantages for determining molecular structure and investigating chemical bonding. Examples of systems studied include organometallic compounds, transition-metal hydrides, ferroelectric and pyroelectric materials, and ionic conductors. Highly precise structures determined for simple molecules are compared to geometries derived from *ab initio* quantum mechanical calculations. Studies combining x-ray and neutron diffraction are also undertaken to examine molecular electronic charge-density distributions.

52. ELECTRONIC STRUCTURES OF SOLIDS AND THEIR SURFACES: STRUCTURE AND BONDING IN IONS IN SOLUTION 1.4 01-02

M. L. Perlman, T. K. Sham

The main object of this effort is to improve the understanding of the electronic interactions among atoms in metals, alloys, and compounds, some of which are technological materials. It is especially important to learn about differences between the interactions in the bulk of such solids and interactions at the surfaces, where heterogenous physico-chemical phenomena occur. These studies are being carried out mainly through photoelectron spectroscopy with conventional photon sources and will soon be greatly aided by use of installations at the NSLS. Development of the theory used to analyze the electron spectroscopic data is itself one of the objectives of this work. Studies are also being made of the geometrical and electronic structures of ions and metal complexes in solution. This work, an application of extended x-ray absorption fine structure (EXAFS), has been carried on during visits at the Stanford SSRL and will be pursued further at the NSLS. The results are directly related to certain aspects of the chemical behavior of the ions, and to electron transfer in solution.

53. HIGH FLUX BEAM REACTOR OPERATIONS --- 01-02

G. C. Kinne

Several research programs at Brookhaven are centered at the High Flux Beam Reactor (HFBR), which was specifically designed for neutron beam research. There are nine ports from which neutron beams can be extracted, and seven vertical thimbles which provide a variety of neutron energy spectra for sample irradiations. The thermal neutron beams are as free as possible of contamination by γ rays and high energy neutrons. At its original power level of 40 megawatts, the HFBR provides a total flux of 1.6×10^{15} neutrons/cm^2-sec (peak thermal flux 7×10^{14} neutrons/cm^2-sec). A construction project to raise the power level to 60 megawatts has been completed, and as soon as DOE safety review is completed and operating approval received, the power level will be increased to 60 megawatts. This will result in a 50% increase in these fluxes, making the HFBR at least equal to the best in the world in these categories.

Chemical Physics

Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Total $330,000

54. KINETICS AND MECHANSIMS OF ALTERNATIVE FUELS COMBUSTION 3.1 01-02
R. B. Klemm and J. V. Michael

The objectives of this task are to investigate the detailed chemical kinetic and mechansistic factors involved in gas phase combustion and pollutant formation processes. Emphasis is placed on alternative fuels that comprise a wide range of fuel types, including alcohols and hydrocarbon synfuels. The complementary techniques of discharge flow and flash photolysis are used to determine specific rates for combustion related, elementary atom- and radical-molecule reactions. Combined, these methods provide a wide temperature span, ∿300-1100K, over which direct kinetic studies of combustion initiation reactions and oxidation reactions of combustion intermediates are made. High temperature, absolute rate data for these reactions are important for the further development of kinetic theories as well as for modelling combustion systems. A shock tube experiment with atomic absorption detection (under construction) will extend rate constant measurement capabilities to the combustion temperature regime. In addition, a photo-ionization mass spectrometer experiment that utilizes the National Synchrotron Light Source is being developed jointly with the Chemistry Department.

Chemical Physics

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $90,000

55. UNIMOLECULAR KINETICS 1.2 01-02
N. J. Brown

This research is concerned with the application of theoretical kinetics to study reactions important in combustion processes. Emphasis has been placed upon investigating the dynamics of reactions using classical trajectories. Unimolecular reactions at the high and low pressure limits and in the fall-off regime are investigated with realistic potential energy surfaces. Special emphasis has been placed upon elucidating the role of molecular angular momentum on the intramolecular and intermolecular energy transfer processes. The role of reactant rotational angular momentum in a four-center reaction is also under investigation. Rate coefficients for dissociation reactions of molecules important in combustion were determined with statistical theories. Results of statistical and dynamical theories will be compared.

Chemical Physics

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $2,000,000

56. ENERGY TRANSFER AND STRUCTURAL STUDIES OF MOLECULES ON SURFACES 4.0 01-02
C. B. Harris

This project is directed toward an understanding in a fundamental manner the way electronic excitation associated with the excited states of molecules and atoms is transferred to metal surfaces. The research utilizes short laser pulses to excite a molecule which is placed above an inert spacer gas at a specified distance above a metal crystal. The lifetime of the excited states is monitored by measuring the influence the metal surface has on the molecular emission (phosphorescence or fluorescence). Utilizing this technique, it is possible to understand and confirm the theoretical basis for the processes down to a point where the molecule is only 10Å above a surface. Another part of this research is directed towards understanding in a fundamental way, chemiabsorption induced perturbations in the electronic spectrum of metals. In these experiments, the influence of the chemisorption process is monitored optically and interpreted in terms of the effect surface bond formation has on metal interband transitions. From the data it is possible to infer which bands are most important in the formation of chemisorbed bond on various metal surfaces.

57. CROSSED MOLECULAR BEAMS 6.9 01-02
Yuan T. Lee

This research is directed toward the understanding of elementary chemical reactions and primary photochemical processes. Various molecular beams methods are used for obtaining information on energetics and dynamics of elmentary chemical reactions from the measurements of product angular and velocity distributions. The elucidation of complex reaction mechanisms of reactions involved in combustion, such as reactions of oxygen atoms with unsaturated hydrocarbons, and the investigations of quantum mechanical dynamic resonance phenomena in the reactive scattering of $F + H_2 \rightarrow HF(v=2) + H$, etc. have been among our major programs. In the area of laser chemistry, the possibility of bond selective dissociation through electronic transition has been under extensive investigation for halogen containing organic molecules. For the understanding of the intramolecular dynamics of highly excited molecules in the continuum, the interaction of an IR laser with chemically activated complexes is now under investigation using stimulated emission stabilization techniques.

58. MOLECULAR INTERACTIONS 2.0 01-02
W. A. Lester, Jr.

This program is directed at extending fundamental knowledge of combustion processes by the study of the dynamics of energy transfer, reactive, and photodissociative molecular processes. The approach is based on the reliable description of the inter- and intra-molecular interactions - potential energy surfaces and coupling matrix elements - needed in theoretical approaches for the evaluation of cross sections and rates. Emphasis is placed on the use of state-of-the-art Hartree-Fock(HF), multi-configuration self-consistent field(MCSCF), and configuration interaction(CI) *ab initio* methods for molecular interactions, and selected methods for collision dynamics. The electronic structure studies emphasize the determination of the critical geometries and energetics that govern reaction pathways. The dynamics studies are directed towards rotational and vibrational energy transfer in molecules by atom impact, and photodissociation of tri- and tetraatomic molecules. An adiabatic approach to the latter area has recently been developed that is yielding significant physical insight into the underlying mechanism.

Materials and Molecular Research Division, LBL, continued

59. CHEMICAL DYNAMICS STUDIES

0.7 01-02

B. Mahan and Y. T. Lee

Derivation of fundamental and practical information about chemical dynamics from the study of collision processes which involve ions, molecules, and photons in the gas phase. Methods of predicting the rates of chemical reactions, energy transfer processes, collisional dissociations, collisional ionizations and charge transfer processes, using as primary information the electronic energy states of the reactants, products, and intermediates. Prediction of the kinetic behavior of complex systems; reactive and non-reactive scattering of hydrogen of a number of ions that appear prominently as contaminants in hydrogen plasmas. Rapid and economical estimation of the energy distributions of the products of some classes of reactions. Reactions and charge transfers of vibrational state selected H_2^+, HD^+ and D_2^+ with rare gas atoms and diatomic molecules have been under intensive investigation using photoionization and ion trapping techniques.

60. THEORY OF ATOMIC AND MOLECULAR COLLISION PROCESSES

3.8 01-02

W. H. Miller

This research is primarily involved with the development of theoretical methods and models for describing atomic and molecular collision processes. The overall goal is to understand the dynamics of chemical phenomena at a molecular level and may thus be described as "molecular level chemical kinetics." Specific topics of interest include the theory of inelastic and reactive scattering, collision processes involving electronically excited atoms or molecules, collisional ionization phenomena, statistical theories of chemical reactions, scattering of atoms and molecules from surfaces, and the interactions of molecular systems with high power laser radiation. Much of this research is involved with the development and application of a general semiclassical mechanics that allows one to combine classical mechanics and quantum mechanics in a correct and useful manner. Certain research topics are more amenable to a completely quantum mechanical approach, and these sorts of theoretical techniques are also used.

61. SELECTIVE PHOTOCHEMISTRY

2.8 01-02

C. B. Moore

Lasers are used to produce molecules in specific excited states. The ensuing chemical reaction and energy transfer processes are studied by spectroscopy and chemical analysis. Highly vibrationally excited molecules are produced by excitation of high overtones of single chemical bonds using visible lasers. The possibility of bond selective reaction is being studied in the gas-phase for cyclobutene and methyl cyclopentadiene. Vibrationally specific photoionization of liquid water is being studied as a function of temperature. High overtone spectral structure is measured with a laser optoacoustic spectrometer to obtain information on transfer of vibrational energy among the modes of a molecule. The relative rates of chemical reaction and energy transfer determine the possibility of bond selective chemistry.

Chemical reaction rates of free radicals important in combustion are measured. A pulsed uv laser produces radicals and a cw dye laser monitors radical concentration as a function of time to give chemical reaction and energy transfer rates. CH_2 and CHO are now being studied.

62. PHYSICAL CHEMISTRY WITH EMPHASIS ON THERMODYNAMIC PROPERTIES 2.3 01-02

K. S. Pitzer

One important set of objectives includes the development of a quantum chemistry for heavy atoms where relativistic effects are important and the prediction of numerous properties of molecules containing such heavy atoms. The major relativistic effects, which arise for electrons near the nucleus, are incorporated into effective potentials which then reflect these indirect effects on the valence electrons and their capacity to form chemical bonds. Calculations for Pb_2 show major relativistic effects, enable several spectral bands to be assigned, and predict several previously unknown electronic states. Another area of research concerns the statistical thermodynamics of ionic systems including aqueous electrolytes over wide ranges of temperature and pressure as well as plasmas. Emphasis is given to conditions of practical application including those for synthetic fuels and for geothermal energy. Equations have been developed which successfully predict the properties of mixed electrolytes (brines). This work is being extended to wider ranges of temperature and pressure.

63. POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS 5.0 01-02

H. F. Schaefer, III.

This research program has two purposes, related yet distinct. The first goal is the development of new theoretical and/or computational methods for the description of molecular electronic structure. Specifically, the single outstanding problem in the field is the correlation problem, that of formulating models for going beyond the single-particle or Hartree-Fock approximation. The second goal of this research is to apply these theoretical methods to significant problems of broad chemical interest. Currently, two areas of special interest are: (a) model theoretical studies of organometallic compounds, chemisorption, metal clusters and catalysis, and (b) the potential energy surfaces which govern gas-phase chemical reactions. Research in the former area is aimed at a truly molecular understanding of catalysis, a subject critical to future energy requirements, but sometimes approached by brute force trial and error methods. In the latter area, the present research involves molecules potentially important in interstellar space, atmospheric chemistry, and the development of high power laser systems.

64. PHOTOELECTRON SPECTROSCOPY 10.2 01-02
D. A. Shirley

Electron spectroscopy: electronic structure of matter, as determined by photoelectron spectroscopy and related techniques. The electronic structure of gas-phase species, including high-temperature species, as determined by the use of pulsed synchrotron radiation, including absorption, fluorescence, and time-of-flight photoelectron spectroscopy. Photoelectron angular distributions and correlation-state studies. Electronic structure of solids from angle-resolved, variable-energy photoemission. Atomic and electronic structure of surface-adsorbate systems. Photoelectron spectroscopy of Van der Waals' molecules and other exotic species. Exploration and development of new experimental methods based on synchrotron radiation in the energy range 10-4000 eV, such as photoelectron diffraction and surface EXAFS.

65. MOLECULAR BEAM SPECTROSCOPY 2.0 01-02
J. S. Winn

This research program derives fundamental spectroscopic information on molecular states of importance to several practical techniques. A molecular beam electric resonance spectrometer is being used to generate HF and DF in high vibrational states and to measure the dipole moment and other spectroscopic constants in these states. Similar data on other molecules and radicals of importance to combustion processes will be sought. Various visible and UV spectroscopies are being used to study metal carbonyl dissociation mechanisms, thin film formation from such dissociations, and the chemical reactivity of such films. The dissociation of $Fe(CO)_5$ to $Fe + 5CO$ has been characterized under VUV photolysis, electron bombardment, metastable rare gas collisional dissocation, and multiphoton photolysis conditions.

Chemical Physics

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Total $600,000

66. MOLECULAR RESEARCH WITH ELECTRON SPECTROSCOPY 2.0 01-02

T. A. Carlson, M. O. Krause

Electron spectroscopy at synchrotron sources is now providing the best and most comprehensive basis for evaluating molecular orbital theory and photoelectron dynamics. Basic processes of ionization and the electronic structure are delineated as a function of photon energy and photoelectron emission angle. The systems studied range from metalic vapors to diatomic molecules to complex gaseous organic molecules. Measurements are made on partial cross sections, angular distribution parameters, autoionization, shape resonances, Cooper minimum and correlation satellites. Interpretation is by multiple scattering $X\alpha$ calculations. In addition to the study of valence orbitals, experiments on the core shells of bromine and silicon near ionization threshold are underway that hold promise for a new, sensitive approach to the study of chemical bonding.

67. ATOMIC AND MOLECULAR COLLISION DYNAMICS 1.0 01-02

H. F. Krause

The goal of this program is to contribute to the fundamental understanding of atomic and molecular processes under high temperature molecular beam conditions. The species of primary interest are C, C_2, and C_3. The carbon beam is produced by a graphite evaporation source operating up to 3800°K. The velocity selected carbon beam collides with reagent gas in a reaction cell operating under single collision conditions. Product molecules formed by chemical reaction in the ground electronic state are detected and vibronic state analyzed by the laser induced fluorescence technique. Chemical reaction products formed in electronically excited states are analyzed by dispersing the luminescence created as the excited state(s) decay radiatively. Carbon atom reactions in each category involving the reagents NO, SO_2, and OCS have been studied most recently. These energy transfer studies at thermal and epithermal energies are relevant to the understanding of combustion and detonation phenomena.

68. PHOTOCHEMICAL, PYROLYTIC AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE 1.0 01-02

R. Livingston

ESR equipment is utilized in which a pressurized fluid is circulated and heated as it passes through the spectrometer. Temperatures to 700°C and pressures to 3000 psi are used. Short lived chemical free radicals are observed at high temperature while being formed by pyrolysis. In appropriate systems free radicals can now also be formed at high pressures and high temperatures photolytically. Work to date has centered largely on aromatic compounds that are constituents of fuel and are of interest in combustion processes and coal conversion processes. A recent measurement has been made on the dissociation constant of bibenzyl: $C_6H_5CH_2CH_2C_6H_5 \rightleftarrows 2\ C_6H_5\dot{C}H_2$. In the course of this study a new ESR technique was developed for assaying radical concentration when signals are weak and consist of closely spaced hyperfine components. A study is nearing completion on the pyrolysis of benzyl ether where the benzyl radical is observed at high temperature and a chain process takes place. One of the reactions of the chain, $C_6H_5\dot{C}HOCH_2C_6H_5 \rightarrow C_6H_5CHO + C_6H_5\dot{C}H_2$, has been separately studied using photolytic methods and the activation energy measured.

Chemical Physics

Combustion Sciences Department
Sandia National Laboratories/Livermore
Livermore, California 94550

Total $4,270,000

69. TURBULENT REACTING FLOW RESEARCH 4.0 01-02
R. Dibble, R. Schefer, B. Sanders

This research is directed toward an increased understanding of turbulent reacting flows by application of laser diagnostic systems in the Sandia Turbulent Diffusion Flame Facility. Laser Doppler velocimetry and laser Rayleigh scattering have been combined to produce the first joint velocity-density correlations in a high Reynolds number nonpremixed flame. Turbulent axial and radial mass fluxes $\overline{\rho'u'}$ and $\overline{\rho'v'}$ have been measured by this combined technique, as well as probability distributions of density and velocity, from which the means, higher moments, and spatial gradients were generated. Results show that the gradient diffusion assumption commonly used to model $\overline{\rho'u'}$ in first-order closure theories results in nonphysical prediction of turbulent mass transport for portions of the flowfield.

70. CRF DIAGNOSTICS RESEARCH-NONLINEAR PROCESSES 3.0 01-02
R. Farrow, L. Rahn

This research effort is directed toward developing optical diagnostic techniques based on nonlinear processes in support of Combustion Research Facility programs. New normalization techniques have been demonstrated for Coherent Anti-Stokes Raman Spectroscopy (CARS), a leading technique for time-resolved measurements of major species concentrations and temperatures. This new in situ normalization scheme was shown to provide accurate corrections to fluctuating CARS signals in high pressure environments and was subsequently implemented in a CRF internal combustion engine experiment. A new anisotropic Stark effect was discovered and quantitatively characterized using high resolution inverse Raman spectroscopy. The vibrational Stark effect discovered last year was applied in a crossed-beam infrared absorption experiment to provide spatially-precise CO spectra from a laboratory flame.

71. SOOT CHEMISTRY 3.5 01-02
W. Flower, R. Schmieder, R. Perry,
M. Gusinow

This research is aimed at understanding the roles of chemical precursors in soot formation. Hydrocarbon-oxygen reactions are studied in flat flames and in flow reactors, where special diagnostics provide unique information. Laser photolysis is used on a slow-flow reactor to produce radicals, and a cw, laser-induced fluorescence system has been implemented to probe the subsequent radical-molecule reactions. Radiolysis techniques are being employed to study hydrocarbon particulate formation and its relevance to soot formation. Light scattering techniques are used to observe soot formation in a flame, to measure particle diameter and number density, and to relate that information to a variety of experimental conditions. The origin of chemi-ionization in hydrocarbon flames and the role ions play in precursor chemistry is being studied spectroscopically.

72. CRF DIAGNOSTICS RESEARCH - ADVANCED METHODS 3.5 01-02
J. Goldsmith, M. Koszykowski,
F. Tully

This program supports three broad areas of diagnostics research: development of new techniques for detecting trace species in combustion environments, research on advanced methods for kinetics studies, and theoretical studies in support of CRF projects. In the first area, atomic hydrogen has been observed in a flame using multiphoton optogalvanic spectroscopy, representing the first direct in situ optical detection of this extremely important radical in a combustion environment. Atomic oxygen and NO are also being studied with this technique. Spatially-resolved absorption methods are being developed for measuring other radicals in flames. Kinetic studies using a pulsed laser photolysis - cw ultraviolet laser induced fluorescence experimental configuration are in progress. Polyatomic free radical spectroscopy is concurrently being pursued. Theoretical techniques involving electronic structure and quantum scattering calculations, as well as approximate chemical kinetic theories, are being applied to a variety of CRF projects, including high resolution spectroscopy, modeling, and kinetic studies.

73. CRF CENTRAL LASER SYSTEMS 4.0 01-02
C. Layne, R. Farrow, L. Rahn,
M. Gusinow

This project includes the continued development of existing CRF central lasers and research in support of future major laser systems. The tunable dye laser, Diana, is operational, with performance levels which meet or exceed design specifications in all significant characteristics. Beam delivery and control throughout the Facility have been demonstrated. SNLL and visiting scientist experiments are now routinely using Diana. Possible system improvements include frequency doubling to obtain radiation from 240 to 370 nm and mode-locking to obtain sub-nanosecond pulses. A new multipurpose laser system is being designed for installation in the Facility during FY83.

74. COMBUSTION RESEARCH FACILITY OPERATIONS AND VISITING SCIENTIST SUPPORT 11.0 01-02
J. Marion, C. Wright, D. Benthusen
M. Libkind, R. Johnsen

This task supports all phases of Combustion Research Facility operations, including operation of the central facility lasers, operation and maintenance of the Facility VAX computer and networked minicomputers, operation of the computer terminals to the Sandia CRAY, staffing of the users shop and chemistry laboratory, and maintenance of the safety and control system. This task also provides support for visiting scientists, and for the transfer of technology developed and implemented at the Facility to other users in the combustion community. Visitor support includes technician and engineering staff dedicated to the visitor's project, computer time, shop work, and purchases used directly by visitors or in support of them. The transfer of technology activity provides technical information to industry and university scientists through workshops on relevant topics, short courses in specialized areas, and combustion-related meetings and seminars.

75. FLAME CHEMISTRY - MODELING AND EXPERIMENT 6.0 01-02
J. Miller, R. Cattolica, W. McLean,
R. Mitchell, M. Smooke

The principal objective of this research is the development of comprehensive models for the chemical processes which govern flames. New numerical techniques have been implemented to provide fast and accurate methods for solving the one- and two-dimensional laminar flame equations, thereby facilitating comparisons with a wide range of experimental results. Laboratory studies emphasize the use of laser probes for measurement of radical and stable species concentration profiles in flames. Other techniques, including molecular beam-mass spectrometry, are also employed. In the past year a comprehensive model for acetylene oxidation was developed. Results provide generally favorable comparisons with a very large body of experimental data. Further experiments on lean and rich acetylene flames are now underway, as are measurements and chemical kinetic analyses of hydrogen-nitrous oxide flames.

Physics Division
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Argonne, Illinois 60439

Total $1,605,000

76. PHOTOIONIZATION-PHOTOELECTRON RESEARCH 3.9 01-03
J. Berkowitz

This research aims at understanding the electronic structures of atoms and molecules and their ions, by observing and interpreting the interaction of vacuum ultraviolet (VUV) radiation with complementary techniques of photoelectron spectroscopy (PES) and photoionization mass spectrometry (PIMS). The PES experiment on atomic tellurium yielded an intensity distribution of fine structure ion states in good agreement with the previously developed irreducible tensor angular momentum coupling scheme. A series of PES experiments and calculations has been initiated on the rare earth halides, aimed at elucidating the involvement of 4f electrons in chemical bonding. Two PIMS studies are essentially completed. The photodissociative ionization of NH_2OH established the heats of formation of HNO^+ and NOH^+ quantitatively, and thereby distinguished between two ab initio calculations with opposite conclusions. A similar study of CH_3SH, CH_3SD and CD_3SH showed that HCS^+ was more stable than CSH^+. A new effort permits the direct study of molecular-ion properties using an ultraviolet laser. The masses and recoil velocities of fragments are determined mass spectrometrically.

77. BEAM-FOIL RESEARCH AND COLLISION DYNAMICS OF HEAVY IONS 2.8 01-03
H. G. Berry

The work in atomic structure using fast-ion beams is aimed principally at improving the understanding of relativistic and quantum-electrodynamic effects in heavy ions. Studies are being done on systems with only a few (1 - 4) electrons to test precise ab initio calculations and many-electron systems to test more general relativistic calculations (e.g., relativistic Hartree-Fock). In atomic collision studies, analyses of the alignment and orientation production of excited states in fast ion-solid interactions are being carried out. Total excitation probabilities are also measured and studied in terms of secondary-electron production and molecular coherence effects. Optical techniques are used to study the dynamics of fast molecular and atomic ions in solids.

78. THEORETICAL ATOMIC PHYSICS 1.0 01-03
K. T. Cheng

The objective of this program is to investigate the role of relativity and many-electron correlation effects in atomic processes, using advanced theoretical techniques such as the relativistic random-phase approximation. The emphasis is on photoexcitation and photoionization processes where one can gain important insights into the dynamics of many-electron interactions. Current efforts include studies of the spectra of highly stripped ions, where accurate theoretical data are needed for plasma diagnostics in astrophysics and in fusion energy research. Studies are also being done on the autoionization resonances between the first two ^2P thresholds of Ar-, Kr- and Xe-like ions, using the multichannel quantum defect theory. The effects of channel interactions on the positions and profiles of these resonances, as well as those on the absorption spectra of interacting Rydberg series in the bound state region are of particular interest.

79. HIGH-RESOLUTION LASER-rf SPECTROSCOPY WITH ATOMIC AND MOLECULAR BEAMS 3.3 01-03

W. J. Childs, L. S. Goodman

The aim of this program is to enhance the understanding of the structure of atoms and small molecules through high-resolution laser and radiofrequency spectroscopy. In the past year, great progress has been made toward obtaining the data necessary for a basic understanding of the alkaline-earth monohalide radicals, a family of diatomic molecules characterized by a single electron outside closed shells. In parallel with this ongoing work, a corresponding apparatus for the study of slow beams of atomic and molecular ions is being prepared. When this system is operational, it will be possible to extend the ultrahigh resolution laser-rf double-resonance methods for the first time to molecular ions, thereby opening this completely unexplored field to high resolution study. Because many of the most interesting molecules are difficult to produce in a beam, work is concurrently being done to develop a system for studying them at high resolution with sub-Doppler, nonlinear laser spectroscopy in a cell. A new method, like intermodulated fluorescence spectroscopy but with digital methods, is being developed: it has potentially significant advantages over even the newest conventional methods for the high-resolution spectroscopy of vapors in cells.

80. DISSOCIATION AND OTHER INTERACTIONS OF ENERGETIC MOLECULAR IONS IN SOLID AND GASEOUS TARGETS 4.9 01-03

D. S. Gemmell and E. P. Kanter

Argonne's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) molecular ions with matter. A unique feature of the apparatus is the exceptionally high resolution ($\sim$0.005° and $\sim$300 eV) in angle and energy obtained in measuring dissociation fragments. The apparatus also permits the coincident detection of up to three dissociation fragments. The work has two main objectives:

(a) a general study of the interactions of fast charged particles with matter, but with the emphasis on those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., the feature that each molecular ion incident upon a solid target forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target) and

(b) a study of the structures of the molecular ions that constitute the incident beams. Precise measurements on the energies and angles of the breakup fragments produced when fast molecular ions dissociate in foils and gases show promise of providing new information on the structures of the molecular ions themselves.

Physics Division, ANL, continued

81. ELECTRON SPECTROSCOPY WITH FAST ATOMIC AND MOLECULAR-ION BEAMS --- 01-03
D. Schneider

Argonne's 4.5-MV Dynamitron accelerator is used to carry out high-resolution electron spectroscopy on excited ions produced as a result of the bombardment of gases and foils by fast (MeV) atomic and molecular-ion beams. The work constitutes a new program that complements existing atomic physics research in the Physics Division. A 45° parallel plate electrostatic electron analyzer (PPA) has been incorporated into an existing scattering chamber. Electrons with energies of up to about 10 keV can be analyzed and the energy resolution of the spectrometer is variable and has an optimum resolution better than 0.1% (FWHM). The first goal of the research is to investigate further the interactions of fast molecular ions with matter by studying details of the electronic states that are involved. Measurements with high energy resolution ($\Delta E/E < 0.1\%$) on single-electron spectra yield information on the formation of specific electronic states and the way that excited atomic states are affected by the proximity of partner fragments.

Atomic Physics

Physics Department
Brookhaven National Laboratory
Upton, New York 11973

Total $210,000

82. ATOMIC PHYSICS RESEARCH 2.7 01-03
K. W. Jones and B. M. Johnson

Beams from the Brookhaven Double Tandem Van de Graaff Facility are used to study various aspects of ion-atom and ion-electron collisions. The decays of outer-shell excited states produced by foil or gas excitation are studied for elements such as Ti, Fe, and Mo which are important in laboratory and astrophysical plasmas. Charge transfer and equilibrium values in ion-gas collisions are studied with negative ions and with positive ions produced by the tandem accel-decel method. The energies for the negative ions cover the range from about 1 to 9 MeV. Beams of almost fully stripped elements up to iron can be produced with energies from several MeV to several hundred MeV when the tandems are operated in the accel-decel and 3-stage configurations. A lesser degree of ionization is obtained for heavier elements. Inner-shell vacancy processes are also studied with these beams. Equipment for study of ion-electron and ion-plasma collisions is now under test. Equipment to study the excitation and ionization of atoms and ions by photons from the National Synchrotron Light Source is now being assembled.

Atomic Physics

Materials and Molecular Research Division
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Berkeley, California 94720

Total $455,000

83. ATOMIC PHYSICS 5.0 01-03
R. Marrus

The primary concern of this project is the atomic physics of highly stripped heavy ions. Spectroscopic measurements in the VUV and X-ray regions are designed to test theories of relativistic effects and quantum electrodynamic effects and to provide data useful in the study of laboratory and astrophysical plasmas. Scattering measurements are concerned with electron capture and loss to continuum states. These measurements will test a theory based on the second Born approximation to explain a strong asymmetry in the cusp observed when the electron velocity and the ion velocity are equal. An ion trapping technique is being applied to measurements of charge-capture cross-sections of highly ionized, low energy (20 ev) ions. Measurements in this regime of high ionization state and low energy have heretofore not been possible with existing techniques. In a separate experiment, measurement of the parity-violating electron-nuclear interaction in atomic thallium is being pursued using ultraviolet lasers.

Atomic Physics

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Total $95,000

84. RADIATION FROM A HIGH TEMPERATURE PLASMA SEEDED WITH HIGH-Z ELEMENTS 0.8 01-03
L. A. Jones

The goal of this experiment is to study the atomic physics and photon flux transport which occurs in a hot, dense plasma. This study requires the development of a hot, dense plasma source, and diagnostic techniques to investigate this source. In this experiment, a large axial current is passed through a hollow cylindrical jet of gas causing it to collapse due to its self-magnetic field. The large kinetic energy of collapse is converted to thermal energy when the plasma reaches the axis. The resulting pinched plasma will reach unusually high densities and temperatures. A 2.5cm diameter Argon gas shell has been collapsed with a velocity exceeding 3×10^7 cm/sec. Quantitative schlieren measurements show that the shell thickness, which initially is ~1 mm, decreases as the shell is accelerated inwardly. Curved crystal x-ray spectroscopy has shown that the pinched plasma emits H, He and Li -- like Argon lines. Analysis of imaged VUV spectra indicate that Ar X and XI lines are also emitted at the time of pinch. An x-ray diode detector has been used to show that the x-ray pulse emitted when the shell strikes the axis has a duration of ~ 12ns.

Atomic Physics

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Total $1,054,000

85. THEORY OF COLLISIONS OF IONS WITH ATOMS 1.0 01-03
R. L. Becker and C. Bottcher

This project has the goal of predicting outcomes of atomic collision processes, particularly those of fusion energy and heavy-ion-accelerator research programs, and of interpreting results of experimental studies. Recent calculations include the following: Collisions of bare nuclei with atomic hydrogen are treated 1) below 250 eV/amu by a molecular coupled-channels (CC) method with a fully quantal description of the nuclear motion and 2) at low to intermediate energies, for the first time by direct numerical integration in terms of finite elements. At intermediate to high energies 3) the "One and a half center" atomic CC expansion method, introduced for collisions in which a unified treatment of electron transfer and ionization are needed, has been applied with success to processes involving H, He, and Li; 4) the single-center expansion method for large target atoms, used previously for K-shell vacancy production, has been extended to L-shell vacancies; and 5) a dynamical theory of multiple vacancy production, based on the independent Fermi particle model and CC collision theory, has been developed and applied to x-ray satellite data.

86. ACCELERATOR ATOMIC PHYSICS 4.9 01-03
S. Datz, P. F. Dittner, P. D. Miller,
and C. D. Moak

The objective of this project is a detailed understanding of interactions of high energy particles with gas, solid and electron targets. The primary facility used is the EN tandem accelerator. Collaborative experiments using electron and positron accelerator facilities are also carried out. Examples of subjects receiving particular attention are: (1) Dielectronic recombination of multiply charged ions using a merged electron-ion beam technique, e.g., B^{2+} $(1s^2 2s)$ + e^- $[B^{1+}(1s^2 2p,n\ell)]$ → $B^{1+}(1s^2 2s,n\ell)$ + $h\nu$ using 18 MeV B^{2+} and ~ 1 keV electrons at relative energies of 3-6 eV. (2) Development of a positron beam facility to produce high intensities of positrons at 1 eV to 6 MeV using the EN tandem. (3) Studies of radiation from bound state transitions of channeled electrons and positrons, e.g., radiation from electrons bound in one dimensional and two dimensional "atomic" potentials as well as two dimensional "molecular" potentials has been observed. (4) Collisional- and photo-detachment to resonances of He^- using lasers in conjunction with EN tandem ion source.

87. EN TANDEM OPERATION 1.3 01-03
P. D. Miller and G. F. Wells

The EN-tandem Van de Graaff is operated for Atomic Physics Research. Terminal voltages up to 6.2 MV are achieved and ions of elements from Z=1 through 9 and heavier ions such as Si, P, S, Cl, Ti, Fe, Ni, Cu, Br, I, and Au are available. Ion beams are used by personnel from the Physics Division for Accelerator Atomic Physics. Frequently, this work is collaborative with members of the Chemistry, Analytical Chemistry, Health and Safety Research, Metals and Ceramics, and Solid State Divisions. There is also a strong group of users from universities and industry. Last year, the single largest user of available EN-tandem beam-time was the merged electron heavy ion beams experiment. Other large users have been in-house accelerator atomic physics experiments, University of Tennessee atomic physics experiments, hydrogen depth profiling, and beam-time for the development of a gas jet target for the Holifield Heavy Ion Research Facility (HHIRF). Final Title I and II design for the modifications to and installation of the Elbek magnetic spectrograph have been substantially completed. Installation should start this summer and be completed by year's end.

Physics Division, ORNL, continued

88. COLLISIONS OF LOW ENERGY MULTIPLY CHARGED IONS 1.1 01-03
R. A. Phaneuf and D. H. Crandall

This experimental program is aimed at improving our understanding of inelastic collision processes involving multiply charged ions at the lowest attainable collision energies. The current emphasis is on measurement of total cross sections for electron capture by highly stripped ions from hydrogen atoms at energies below 1 keV/amu. Toward this end, two different experimental approaches are being pursued. A pulsed-laser-produced plasma is utilized as a unique source of low-energy, highly-stripped ions which are directed through a calibrated thermal-dissociation atomic hydrogen gas target. Charge and energy analysis is effected by a time-of-flight technique. Total electron-capture cross sections have been measured for C^{+q} and O^{+q} ions ($3 \leq q \leq 6$) colliding with H and H_2 at energies in the range 50-200 eV/amu, and provide data for direct tests of emerging coupled-molecular state calculations. An ion-atom merged-beams apparatus is also being developed for studying such collisions at center-of-mass energies as low as 1 eV/amu, where theoretical predictions of increasing cross sections with decreasing energy remain untested.

Atomic Physics

Laser Research and Development Department
Sandia Laboratories/Albuquerque
P. O. Box 5800
Albuquerque, New Mexico 87115

Total $140,000

89. ATOMIC PROCESSES 1.5 01-03
A. Owyoung, J. P. Hohimer, A. V. Smith

This research is directed toward the study of collisional interaction and energy relaxation processes in atomic and molecular systems. Current studies are concentrating on the measurement of Stark broadening and shift parameters for potassium Rydberg transitions using a multi-step state-selective laser excitation technique which was developed in an earlier phase of this program. Unique to these studies is the development of a low-pressure potassium-seeded wall-stabilized argon source which provides a precisely controlled reservoir of electrons whose density may be determined by means of a far-infrared Michelson interferometer. As an extension of these studies, multi-step laser excitation techniques are being applied to the measurement of collisional processes in simple molecular systems. In particular, collisional relaxation processes are being examined in NO, a simple molecular analog of the alkali atoms.

Chemical Energy

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $725,000

90. ORGANOMETALLIC COMPLEXES IN HOMOGENEOUS CATALYSIS

R. J. Angelici

2.7 02-01

Transition metal carbene complexes are implicated in several homogeneously catalyzed reactions, including the Fischer-Tropsch reaction. This program includes developing methods of synthesizing carbene complexes and exploring their reactivities. Iron, tungsten, and ruthenium complexes with terminal carbene ligands, $=C(X)(Y)$, where X and/or Y is SR, OR, NR_2, SeR, and H, are prepared from metal carbonyl and thiocarbonyl precursors. Synthetic and kinetic studies of reactions of some of these complexes with nucleophiles such as phosphines, phosphites, and amines are leading to new organometallic complexes and a better understanding of carbene ligand reactivity.

91. CHEMICAL KINETICS AND REACTIVITY OF TRANSITION METAL COMPLEXES

J. H. Espenson

5.1 02-01

Organometallic complexes such as $(H_2O)_5Cr\text{-}R^{2+}$, $R\text{-}Co(dmgH)_2L$, and $R\text{-}Rh(dmgH)_2L$ are under active investigation, as are dinuclear compounds having a metal-metal bond. The research concerns the reactions which occur, and their kinetics and mechanisms, especially reactions in which the metal-carbon bond is formed or broken, or in which rearrangements or transformations of the organic group, R, occur. Novel displacement processes by attacking free radicals are being investigated using techniques such as stopped-flow kinetics, product competition ratios, stereochemical labeling, and flash photolysis. Included are classes of compounds important in Fischer-Tropsch reactions, such as α-hydroxyalkyls. Studies of spontaneous metal-carbon bond homolysis permit: (a) evaluation of thermodynamic bond energies, (b) study of the mechanism of homolytic cleavage in contrast with competing heterolytic pathways, (c) examination of novel free radical displacement reactions, and (d) evaluation of the kinetic reactivity of aliphatic radicals under conditions where pulse radiolysis is not feasible.

92. NUCLEAR MAGNETIC RESONANCE (NMR) STUDIES OF COALS AND CATALYSTS

B. C. Gerstein

3.8 02-01

Solid state NMR is being used to study environments of hydrogen, aluminum, and silicon in synthetic zeolites, which form part of bifunctional catalytic systems used to convert coal synthesis gas to selected hydrocarbons. Recently developed high resolution techniques are used to infer hydrogen mobilities, to identify and quantify different Brønsted acid sites, and average silicon and aluminum coordinations. These results are correlated with catalytic activity toward F-T reactions such as methanation and conversion of methanol to olefins. Theories of domain morphology in polymers as related to diffusion of spin information have been developed, and are used to infer the nature of proton clustering in synthetic zeolites. High resolution proton and carbon NMR is used to infer chemical functionality in coals.

93. SPECTROSCOPIC AND KINETIC CHARACTERIZATION OF METAL OXIDE AND SULFIDE CATALYSTS

0.8 02-01

G. L. Schrader

The goal of this research is to develop a fundamental understanding of the solid state and surface chemistry of heterogeneous catalysts and the mechanism of catalytic reactions. Metal oxide and sulfide catalysts which can be used industrially to produce synthetic fuels or to hydrotreat coal-derived liquids are being investigated. Spectroscopic techniques such as laser Raman spectroscopy and Fourier transform infrared spectroscopy provide characterization of catalysts and adsorbed species. *In situ* experiments are being performed involving functioning catalysts; simultaneous spectroscopic and kinetic measurements can be performed at temperatures and pressures typical of industrial operating conditions. These techniques provide a direct method for relating structure and composition to catalytic activity, selectivity, and stability: the effects of defect structures, structural disorder, and nonstoichiometry are particularly important for the metal oxide and sulfide catalysts being examined. In addition, adsorption studies using pulsed microreactors are being performed.

94. HIGH-TEMPERATURE GAS-PHASE PYROLYSIS OF ORGANIC COMPOUNDS

2.0 02-01

W. S. Trahanovsky

This research is directed toward an understanding of the fundamental thermal reactions of coal and coal-derived products. The general approach is to identify and to characterize these reactions by studying the pyrolysis of model compounds using primarily the Flash Vacuum Pyrolysis technique. Most of the experimental work consists of separating and identifying the pyrolysis products. Many of the model compounds are tetralins and substituted tetralins and progress is being made toward understanding the thermal reactions of tetralin in detail, one of our major goals. We are also studying the chemistry of 2,3-dimethylene-2,3-dihydrofurans, the furan analogs of *ortho*-quinodimethanes, compounds which are thought to be reactive intermediates in thermal reactions.

95. STUDY OF SOLID-GAS REACTIONS WHICH INVOLVE STRUCTURAL CHANGES IN THE SOLID 1.5 02-01
D.L. Ulrichson, A.H. Pulsifer

The objective of this work is to understand and describe the behavior of solid-gas reactions which have solid products with much larger volume than the solid reactant. The increased volume of the solid product closes diffusion paths for the gaseous reactant and stops the reaction at less than total conversion. The reaction of sulfur dioxide with calcium oxide (used for removal of sulfur dioxide from boiler flue gas) is an example in which only about thirty percent of the calcium oxide reacts before solid expansion halts the reaction. Previous models have concentrated on the effect of the reduced porosity which results from product expansion. Data from this project indicate that diffusion of reactant through the solid product layer is as important as pore reduction. Inconsistencies in published results for some solid-gas reactions can be explained by inclusion of this term. Further work is aimed at relating solid expansion to parameters used to predict diffusion in porous solids.

Chemical Energy

Chemical Engineering Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total $400,000

96. FLUID CATALYSIS 4.2 02-01
J. W. Rathke, M. J. Chen,
R. J. Klingler, J. J. Heiberger

This research attempts to determine the mechanisms whereby molecular complexes catalyze the conversion of small molecules (e.g., carbon monoxide) to form specific desired products. Currently under study are a new series of organometallic catalysts for the reaction of carbon monoxide with water to form methanol and a new catalytic method for the selective conversion of methanol to ethanol. The methanol conversion reaction has been found to be promoted by a wide variety of organotransition metal catalysts and thus to be general in nature. The mechanistic details of both the methanol synthesis and the methanol homologation reactions are being investigated using a combination of high pressure kinetic, tracer, spectroscopic (including multinuclear FT-NMR), thermochemical, and theoretical (molecular orbital) methods.

Chemical Energy

Total $970,000

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

97. INORGANIC AND FLUORINE CHEMISTRY 3.0 02-01
E. H. Appelman, L. J. Basile, L. Stein

This program undertakes the preparation and characterization of new and novel inorganic oxidants and fluorinating agents. In addition to the physical and chemical characterization of these compounds, this program is especially interested in finding and exploiting applications of these exotic materials to other areas of chemistry. Examples of such applications are the use of HOF as a model for biological oxidants, the use of KrF_2 to aid the characterization of noble gas matrices by EXAFS spectroscopy, the effect of perbromate as the counterion on the structures of salts in inorganic complexes, and the application of fluoroxysulfate, SO_4F^-, as an inorganic analytical reagent, as a reagent for organic synthesis, and as a reagent for probing the structure of coal.

98. FUNDAMENTAL CHEMISTRY OF COALS AND OTHER FOSSIL FUELS 5.5 02-01
R. E. Winans, R. Hayatsu,
R. E. Botto

This program's major objective is to provide an understanding of the molecular structures of coals and their relationship to the chemical reactivity of coals. Whole coals, separated macerals and oil shale kerogens are characterized by a variety of methods such as selective oxidations, mass spectrometric analysis and a novel high field solid ^{13}C nuclear magnetic resonance technique. Variations in aliphatic macromolecular structures are particularly important in understanding reactivity. Future research directions include (1) a comprehensive evaluation of the relationship between chemical structures, density and chemical reactivity in macerals; (2) a thorough statistical analysis of the complex structural data being obtained; and (3) an emphasis on the characterization of high molecular weight species derived from mild chemical reactions. All of these areas are important in the search for new fossil fuel conversion processes.

Chemical Energy

Bartlesville Energy Technology Center
P. O. Box 1398
Bartlesville, Oklahoma 74003

Total $160,000

99. THERMODYNAMIC CHARACTERIZATION OF CONDENSED-RING COMPOUNDS 3.0 02-01
William D. Good

Research continues on synthesis, purification and measurement of thermodynamic properties of polynuclear aromatic hydrocarbons and their hydrogenation products and for similar compounds with nitrogen in their ring structures. These substances are important in processing of coal, oil shale, and heavy petroleum to produce liquid fuels and chemical feedstocks. Preparation of manuscripts is in progress reporting thermodynamic properties of tolylphenylmethane, isoquinoline and 1,2,3,4,5,6,7,8-octahydroanthracene. Measurements are in progress on 2,2'-dimethylbiphenyl, 4-methylphenanthrene and quinoline, and several other compounds are purified awaiting measurements. Synthesis and purification of others are in progress. Gibbs energies of formation derived from these studies facilitate understanding of hydrocracking and denitrogenation. The data obtained also form the base for improved correlations based on molecular structure. The comprehensive experimental program involves enthalpy of combustion, low-temperature adiabatic calorimetry (third-law entropy determinations), PVT relations including vapor pressure, Raman and infrared spectroscopy and molecular statistical mechanics.

Chemical Energy

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $390,000

100. ORGANOMETALLICS IN HOMOGENEOUS CATALYSIS 3.0 02-01
M. A. Andrews

Research is being carried out to understand the role of soluble transition metal complexes in the homogeneous catalytic oxidation of organic substrates, with primary emphasis on the scope, selectivity, and function of recently developed transition metal catalysts exemplified by the nitro complex $Pd(CH_3CN)_2ClNO_2$. This compound converts terminal olefins to the corresponding methylketone with concurrent formation of the nitrosyl complex $[Pd(NO)Cl]_n$. The nitrosyl group is air oxidizable back to a nitro functionality completing a catalytic cycle. A mechanism involving sequential formation of an olefin pi complex and a heterometallacycle has been developed based on spectroscopically detectable intermediates. Work in progress with cyclic olefins has resulted in the isolation of a heterometallacycle and the formation of expoxides as a major product. This latter finding is significant since olefin epoxidation is one of the more technologically difficult chemical processes. The detailed mechanisms of these reactions will be investigated in order to develop new and more selective oxidation catalysts.

Chemistry Department, BNL, continued

101. MECHANISMS OF PHOTO-, ENZYME-, AND CHEMICALLY CATALYZED CIS-TRANS ISOMERIZATION 1.9 02-01

S. Seltzer

Cis-trans isomerization can be brought about by the application of heat, light or by catalysts. Because the physical and chemical properties of the two isomers differ, relaxation of a nonthermodynamic mixture of isomers (achieved by irradiation) to the thermodynamic mixture can result in the release of thermal or electrical energy. This cis-trans energy producing effect is utilized in biological processes such as the light-driven proton pump of Halobacteria and vision in animals. The proton pump can be utilized in a photogalvanic cell.

Studies at BNL are concerned with the mechanisms of enzymically and chemically catalyzed and photosensitized cis-trans isomerizations and their application to the mechanisms of the proton pump.

Chemical Energy

Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Total $625,000

102. HIGH TEMPERATURE CHEMISTRY 2.4 02-01

J. J. Egan

This is a study of the thermodynamic and transport properties of inorganic substances at high temperatures and attempts to explain the results in terms of appropriate atomic models. The substances include solid and liquid compound semiconductors, solid electrolytes, and molten salts. Electrochemical techniques are used to investigate the effect of composition on the concentration, mobility, and diffusion of electrons and electron holes in these substances. Cells employing solid electrolytes at high temperatures as well as molten salt electrolytes prove especially useful for characterizing these systems. High temperature calorimetry is being used to study liquid semiconductors and other liquid alloy systems. Molten salts are studied since they are important for the development of high energy-density batteries and fuel cells. The electronic conductivity of these melts in particular is examined by special techniques. Solid compound semiconductors of potential use as solar cells are studied by high temperature electrochemical techniques.

103. METAL HYDRIDES J. J. Reilly	4.4	02-01

The overall concern of this program is the determination of the thermodynamic properties and structural parameters of metal alloy-hydrogen systems. Particular goals are to relate the hydriding properties of metal alloys to their structure and composition, to elucidate the role of defect and surface properties in system behavior, the determination of alloy-hydrogen phase diagrams, the determination and systematization of crystal structure and, finally, to relate all pertinent data and observations to develop a predictive capability regarding the behavior of a given alloy-hydrogen system. Current topics of interest are the causes of the observed deviations fom ideal behavior of certain intermetallic-hydrogen systems, surface segregation effects in alloy-hydrogen systems, the partial molar volume of hydrogen in intermetallic compounds, the influence of defects upon system behavior and hydrogen isotope effects. The major experimental tools and/or techniques consist of X-ray and neutron diffraction, equilibrium pressure-temperature-composition measurements and magnetic susceptibility measurements.

Chemical Energy

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $115,000

104. BIOCONVERSION OF CELLULOSE AND PRODUCTION OF ETHANOL C. Wilke, H. Blanch	2.0	02-01

The conversion of biomass feedstocks to sugars requires basic information on the mechanism and rates of depolymerization of the hemicellulose components. This hydrolysis can be accomplished either enzymatically or using a range of acids. In addition, this basic information yields insights into the hydrolysis of other insoluble polymeric materials. Further kinetic and "nutritional" studies on high rates fermentation processes are examined to provide information to be used in the development of the ethanol fermentation and other related chemical feedstock production.

Chemical Energy

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $1,140,000

105. HIGH ENERGY OXIDIZERS AND DELOCALIZED-ELECTRON SOLIDS 4.8 02-01
N. Bartlett

The central concern of this program is in synthesis of new materials. The synthetic work exploits and tests theoretical models developed to account for the dependence of observed properties (such as electrical conductivity) upon chemical composition and structure. 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 salt formation) generates durable and conductive materials (some better than aluminum). Chemical, stoichiometric and structural requirements for the best conductivity are being defined. Some may have application as electrodes in electrochemical generation of potent new oxidizers. It may be possible electrochemically, to add or take away protons reversibly from oxy-acid salts. This may also be possible for fluorine, incorporated as F^- ion, into salts such as $C_{12n}AsF_6$ ($n \geqslant 2$) and graphite itself. Salts which are either proton or fluoride ion conductors, but not metallic, and which are resistant to oxidation, are being sought as solid electrolytes for use with the metallic layer-material salts.

106. TRANSITION METAL CATALYZED CONVERSION OF CO, NO, H_2, AND ORGANIC MOLECULES TO FUELS AND PETROCHEMICALS 2.5 02-01
R. G. Bergman

The goal of this project is the discovery of new chemical reactions in which transition metals interact with organic materials, and the understanding of how these reactions work. The approach begins with the synthesis and structural characterization of new types of stable organotransition metal complexes. Following that the self-reactions of these materials (induced, for example, by heat or light) are investigated, as well as their reactions with small gaseous molecules such as carbon monoxide, nitric oxide, and hydrogen, and larger organic compounds such as hydrocarbons, alcohols and alkenes. Attention is focused on transformations which break and form carbon-hydrogen, carbon-carbon, carbon-oxygen and carbon-nitrogen bonds, which are the most fundamental processes involved in organic transformations. Studies of the mechanisms of these reactions involve spectroscopy, kinetics, isotope labeling, and stereochemistry.

107. FORMATION OF OXYACIDS OF SULFUR FROM SO_2 0.9 02-01
R. E. Connick

Sulfur dioxide is an atmospheric pollutant produced primarily from the burning of coal. The present research is aimed at a fundamental investigation of its chemistry and that of species formed from it so that processes for its abatement will be understood better and can be improved. The lability of the oxygens of HSO_3^- in aqueous solution is under study using the nuclear magnetic resonance of oxygen -17 as a probe. The results of the research should clarify the mechanism and rate of exchange of oxygen atoms between HSO_3^-, $S_2O_5^{2-}$ and H_2O. The rate of oxidation of HSO_3^- by oxygen is being investigated by following the reaction in the liquid phase with an oxygen meter. Because the reaction occurs by a chain mechanism, it is highly sensitive to impurities. The approach used is to add deliberately species that will control the initiation, propagation and termination steps of the chain so as to overwhelm impurity effects.

108. CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION * 1.5 02-01
H. Heinemann

Coal liquefaction proceeds either by direct hydrogenation of dissolved coal or by gasification of coal to synthesis gas (CO + H_2), which is then catalytically converted to hydrocarbons. Present processes are largely based on empirical information and major improvements seem possible by a better understanding of the basic chemistry and engineering principles underlying the technology. This project involves six tasks studying mechanisms, conditions, and new catalysts for the reactions of carbon and steam, hydrocarbon synthesis from syn-gas, carbon-carbon splitting in aromatic rings and selective hydrogenation of heteroatoms in polynuclear hydrocarbons.

*Joint program funded by Chemical Sciences and the Office of Fossil Energy.

109. SYNTHETIC AND PHYSICAL CHEMISTRY 1.8 02-01
W. L. Jolly

The main objective of this project is to elucidate the nature of the chemical bonding in organometallic compounds related to catalysts. The experimental tool is gas-phase x-ray photoelectron spectroscopy, which provides atomic core electron binding energies. The binding energies give information about nucleophilicity, atomic charge, bonding and antibonding character of orbitals, and heats of formation. Hence it is possible to make predictions regarding molecular reactivity, structure, and energetics. The method has been used to study the back-bonding abilities of various ligands, to test the "isolobal" formalism of organometallic chemistry, and to quantify the bonding and antibonding character of molecular orbitals.

110. SURFACE CHEMISTRY - APPLICATION OF COORDINATION PRINCIPLES 2.3 02-01
E. L. Muetterties

The characterization of hydrocarbon chemistry on metal surfaces is the objective of this research. Major focus has been on carbon-hydrogen bond breaking and making reactions as a function of surface topography and composition. All results to date indicate that the stereochemistry of the initial hydrocarbon chemisorption state is the major factor that affects the facility of C-H bond breaking; if C-H hydrogen atoms closely approach the surface they tend to be cleaved. Conversion of cyclohexene, cycloheptatriene and cyclooctene to C_6H_6, C_7H_7 and C_8H_8, respectively illustrate the apparent principle.

111. ELECTROCHEMICAL SYSTEMS 1.3 02-01
J. Newman

This program includes investigation of fluid flow and electrochemical transport, measurement of transport properties in concentrated electrolytic solutions, analysis of mass-transfer rates and current distribution, design of practical electrochemical systems, and investigation of corrosion processes. Coupled kinetic, mass transfer, and fluid flow phenomena are investigated in semiconductor electrode systems, with emphasis on the optimization of configurational and operating parameters of liquid-junction photovoltaic cells.

112. CATALYTIC HYDROGENATION OF CO: 5.7 02-01
Catalysis on Well-Characterized Surfaces
G. A. Somorjai
Catalysis by Supported Metals
A. T. Bell

The purpose of this program is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors which limit catalyst activity, selectivity, and resistance in poisoning, and the relationship between catalyst composition/structure and performance. To meet these objectives, a variety of surface diagnostic techniques (LEED, AES, XPS, EELS, IRS, TPD) are used to characterize supported and unsupported catalysts before, during, and after reaction. The information thus obtained is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon-monoxide hydrogenation.

113. ORGANOMETALLIC CHEMISTRY OF COAL CONVERSION 1.9 02-01
K. P. C. Vollhardt

The basic program objective is to apply organometallic processes and techniques to the solution of problems concerned with the conversion of coal to liquid and gaseous fuels. A detailed study is being undertaken of the mechanistic details involved in the extrusion of sulfur from thiophene and thiophene oxide complexes of transition metals. This reaction has been observed for the first time cleanly in a cobalt complex and has allowed the design and execution of specific labeling experiments. Soluble transition metal complexes are being synthesized containing novel ligands aimed at bringing together and holding transition metal nuclei at defined distances in an effort to observe bimetallic catalysis. A new method of constructing fulvalene complexes in high yield has allowed the synthesis of cobalt, ruthenium, and molybdenum complexes. These are being tested as potential activators of hydrogen, hydrocarbons, carbon monoxide, and carbon dioxide. Work is being continued in the area of metal biscarbyne cobalt clusters as potential models in heterogeneous Fischer-Tropsch polymerization and C-H activation chemistry.

Chemical Energy

Chemical Engineering Division
Lawrence Livermore National Laboratory
University of California
P. O. Box 808
Livermore, California 94550

Total $170,000

114. EFFECTS OF METAL SURFACES ON KINETICS OF HYDRIDE FORMATION 2.4 02-01
R. M. Alire and S. A. Steward

The objective of this study is to elucidate the surface chemistry of metals, alloys, and especially intermetallic compounds that react extensively with hydrogen. Many of these compounds are potential hydrogenation catalysts as well as hydrogen storage media. Important compounds, such as FeTi and $LaNi_5$, are being examined with a variety of modern surface techniques, such as Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), Secondary Ion Mass Spectrometry (SIMS), and Electron Stimulated Desorption (ESD). Our emphasis is now on single crystals of intermetallics, which should provide valuable insight into the gas adsorption mechanisms that affect hydrogen reactivity in the technologically important polycrystalline materials. A recently completed surface structure determination of FeTi with LEED is the first part of this new direction.

Chemical Energy

Metals and Ceramics Division
Lawrence Livermore National Laboratory
University of California
P. O. Box 808
Livermore, California 94550

Total $70,000

115. THERMOCHEMICAL PRODUCTION OF HYDROGEN 0.6 02-01
O. H. Krikorian, P. K. Shell

Thermochemical cycles for hydrogen production from water have been studied with objectives to (1) find new cycles that are both scientifically and economically viable, (2) improve known cycles by innovative chemical approaches, and (3) advance the knowledge on mechanisms of reactions associated with thermochemical cycles. Our study searching for possible electrolytes to be used in the high temperature electrolysis of water identified a potential electrolyte based on partially neutralized phosphoric acid. These phosphate-based melts undergo condensation reactions at elevated temperatures to produce long chain polymers with abnormally high electrical conductivity, probably due to a proton-switch mode of conduction. Our studies of these compounds indicate that the cation used in neutralization significantly affects the electrolyte's behavior during electrolysis by determining the formation or absence of solid phases at the temperature of interest ($\sim$673 K). We have also found the resistance of these melts is strongly dependent on their water content. This study will be completed in FY82.

Chemical Energy

CMB Division
Los Alamos National Laboratory
University of California
P. O. Box 1663
Los Alamos, New Mexico 87545

Total $390,000

116. SYNTHESIS OF THERMOCHEMICAL CYCLES 3.6 02-01
T. Wallace, W. Jones, C. Mason,
E. Onstott, M. Bowman(Consultant)

This research is directed to an understanding of the basic chemistry and engineering principles required to synthesize efficient thermochemical cycles for the production of hydrogen from water by the use of heat sources such as solar, nuclear fission and nuclear fusion reactors. A general objective is to establish the criteria required for development of this new technology and for evaluation of worldwide programs concerned with such processes. The program consists of the identification, initial evaluation, and preliminary development of different cycles. The cycles are first identified by the application of thermochemical principles and then tested by determinations of reaction rates, reaction yields, and thermochemical properties. Current studies include: 1) thermochemical and hybrid thermochemical-electrochemical cycles based on solid sulfate decomposition reactions, 2) mixed metal sulfate-metal iodide cycles, 3) low temperature reactions in cycles based on oxide decompositions, and 4) evaluation of key reactions in methanol-based cycles.

Chemical Energy

CNC Division
Los Alamos National Laboratory
University of California
P. O. Box 1663
Los Alamos, New Mexico 87545

Total $210,000

117. LABILE SO_2 COMPLEXES 2.0 02-01
G. J. Kubas, G. D. Jarvinen, R. R. Ryan

The basic knowledge of sulfur dioxide chemistry is being expanded with the goal of developing new SO_2 removal processes. Current emphasis is being placed on the reactivity of SO_2 coordinated to metal complexes in order to promote catalytic reactions of SO_2 with other abundant small molecules. A successful process could convert both SO_2 and NOx into less harmful or useful by-products (e.g. hydrogen reduction to sulfur, nitrogen, and water). Reactions of SO_2 and SO_2/H_2 mixtures at elevated temperatures and pressures with metal cluster complexes and hydride complexes are being investigated in order to develop homogeneous catalytic methods. Reduction of SO_2 by Mo and Os hydride complexes to water and sulfur or sulfur-containing products is observed at ambient temperatures, and intermediates are being studied. "Side-on" bonding of SO_2 and coordinatively-unsaturated SO_2 complexes (e.g. three-coordinate Pt(0)-SO_2 species) are also very much of interest in terms of activating SO_2. The η^2 form of the SO_2 ligand contains the longest and weakest S-O bonds, and the terminal oxygen can bind to other metal centers or Lewis acids.

Chemical Energy

Mound Facility
P. O. Box 32
Miamisburg, Ohio 45342

Total $216,000

118. FUNDAMENTAL INVESTIGATIONS OF METAL HYDRIDES 2.6 02-01

G. C. Abell, R. C. Bowman, Jr.,
M. P. Guse

The program objectives are to identify and evaluate the electronic and structural properties of transition metals as they are influenced by the addition of interstitial hydrogen. Both the crystal structure of the host metal and the interstitial sites occupied by the hydrogen must be considered. Experimental techniques such as NMR, XRD and thermal analysis are used to determine: 1) the roles of crystal structure, phase transformations, and alloy composition on hydrogen solubility and transport mechanisms, and 2) the modification in the electronic structure surrounding a protium atom dissolved in a metal matrix. Current experimental studies involve hydrides formed with the intermetallic compounds of the types A_2B, AB_2 and AB_5, amorphous transition metal alloys and vanadium. Additionally, advanced density functional theory is being developed to elucidate the electronic structure of clusters of metal atoms containing hydrogen in the highly non-stoichiometric transition metal hydrides. A model system for hydrogen chemisorption on a metal surface is also being developed. This model focuses upon the energetics of the hydrogen molecule bond-breaking step.

Chemical Energy

Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total $230,000

119. KINETICS OF ENZYME CATALYZED REACTIONS 2.6 02-01

E. Greenbaum, J. Woodward

This research is focused on the understanding of the fundamental chemical and physical mechanisms of photosynthesis. The specific system under investigation is the *in vitro* photosynthetic system composed of isolated chloroplasts, ferredoxin, and hydrogenase (CFH). The CFH system is capable of the simultaneous photoproduction of hydrogen and oxygen when irradiated with visible light, a photoreaction which is of special significance due to its endothermic nature. Recently, experimental studies of this system were made using repetitive flash illumination which measured, for the first time, the steady-state turnover times of photosynthetic hydrogen and oxygen production. These results are encouraging because they indicate the turnover times for the CFH system are comparable to that of normal intact photosynthesis. Further work is planned in this area by measuring the light saturation curves of simultaneous photoproduction of hydrogen and oxygen. Research is also being performed on the stabilization and immobilization of cellulase, chloroplasts, and hydrogenase with the aim of improving the yields and stability of isolated organelles and enzymes.

Chemical Energy

Chemistry Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total $1,960,000

120. BASIC AQUEOUS CHEMISTRY TO HIGH TEMPERATURES AND PRESSURES

5.3 02-01

R. H. Busey, W. L. Marshall
H. F. Holmes, R. E. Mesmer
D. A. Palmer

The safe and efficient operation of energy production, reprocessing, and waste disposal facilities depends on a broad and detailed understanding of the chemical processes occurring in aqueous systems to high temperatures and pressures. This program is directed toward this goal through the development and application of specialized physical-chemical apparatus and techniques to selected chemical systems and processes to acquire understanding of the basic principles controlling reactions under P-V-T conditions of interest in aqueous media. The principal methods developed and used in this program are calorimetry, conductance, potentiometry, spectrophotometry, and isopiestic and phase equilibrium studies. Studies are made to about 300°C except for the calorimetry and conductance studies which extend into the supercritical region. The most significant scientific and practical contributions have been made with respect to: ionization, association, and hydrolysis reactions; the phase behavior of oxides, sulfates and phosphates; excess thermodynamic quantities for chlorides and sulfates; and models for the P and T dependencies of chemical equilibria.

121. HETEROGENEOUS CATALYSIS RELATED TO ENERGY SYSTEM

2.2 02-01

S. H. Overbury, P. A. Agron

A fundamental understanding of surface catalyzed reactions requires the determination of the structure and bonding geometry of atoms and molecules adsorbed on the catalytic surface. The goal of this project is to develop and apply angle and energy resolved low energy ion scattering as a probe of substrate and adsorbate geometry on model catalytic systems. The use of alkali ions as scattering probes is being explored and it is found that scattering from the second and third layers must be considered in order to explain the angle dependence of the scattered intensity. Computer simulation techniques have been improved to allow quantitative interpretation of the experimental results, as was proven in the case of Li^+ scattering from clean Mo(001) where good agreement between computed and experimental energy distributions was obtained. Such comparisons allow scattering mechanisms to be assigned to the features observed in the energy distributions. The effect of an adsorbate on these features provides an indication of its location. Using these methods, the interaction of O_2 and CO with single crystal Mo has been studied using K^+, Li^+ and He^+ scattering.

122. ORGANIC CHEMISTRY AND THE CHEMISTRY OF FOSSIL FUELS

7.0 02-01

M. L. Poutsma, E. W. Hagaman
R. R. Chambers, L. L. Brown

The objective of this project is improved understanding of the structure and reactivity of coal. Solid-state ^{13}C NMR is a key structural tool being applied to native, chemically modified, and thermally altered coals. Double-labelling (^{13}C,^{14}C) experiments have shown that the standard CP/MAS experiment does not give unit response for all carbons in coal; particular emphasis is being placed on specifying and circumventing the factors responsible. Selective methods to cleave C-C bonds in coal and to introduce functional groups which will perturb ^{13}C chemical shifts are being developed as structural diagnostic tools. Reactions of radical anions and carbanions are being emphasized. Mechanistic description of the pathways for thermal decomposition of key structural features in coal, particularly aliphatic bridges and phenolic functionality, has been advanced by use of model compounds. Unravelling the perturbations introduced by the diffusional restraints and the potential for mineral matter catalysis imposed by coal itself is the current aim of these studies.

123. MOLTEN SALT CATALYSTS FOR CLEAN FUEL SYNTHESIS	4.7	02-01
G. P. Smith, A. S. Dworkin,
A. C. Buchanan, III, S. P. Zingg

The mechanisms by which coal is hydrocracked to form gasoline reforming stock are investigated with compounds that model key features of coal structure. Two new reaction types have been discovered, by in situ NMR and by quench and separation procedures, which occur only if $SbCl_3$ is the solvent and not a solute. These are the novel, selective transfer hydrogenation of polycyclic arenes by tetralin which proceeds rapidly at 100°C, and the selective transalkylation for α,ω-diphenylalkanes. Investigations of $SbCl_3$-rich catalysts by low-shift Raman spectroscopy and electrical conductivity show that $SbCl_3$ molecules are linked to each other and to chloro complex ions by chloride-bridge bonds that act like hydrogen bonds in aqueous media. Recent initiatives include the discovery that molten gallium trichloride is a redox catalyst as well as a super-acid catalyst, and the development of an $SbCl_3$-rich redox catalyst which is liquid at room temperature. In the room temperature $SbCl_3$ melt, optical spectroscopy plus ESR shows that the more oxidizable arenes form radical cations which are slowly converted into photochemically active arenium ions (plus other products).

Chemical Energy

Chemical Technology Department
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Total $365,000

124. MECHANISMS OF HYDROGENATION OF COAL	1.6	02-01
J. A. Franz, R. D. Barrows

The objectives of this research are to determine relative and absolute rates and related thermochemical values for organic free radical rearrangements and to utilize these data in determining mechanisms of thermal dissolution of coal in hydrogen donor media. Relative rates of free radical isomerization, fragmentation and hydrogen abstraction are studied by competition of the desired radical reaction with bimolecular hydrogen abstraction from a suitable donor. Absolute rates of hydrogen abstraction are being determined by kinetic laserflash spectroscopy. Thermal rearrangements of organic structure under coal dissolution conditions can then be described by Arrhenius expressions resulting from this work in combination with thermochemical parameters for the various radicals. The kinetics and product studies of deuterium transfer from deuterated donor solvents to coal are also under examination, as well as unique radical initiation mechanisms.

Chemical Technology Department, PNL, continued

125. THERMOCHEMICAL CONVERSION OF SOLID WASTES INTO LIQUID FUELS 2.2 02-01
P.M. Molton, D.A. Nelson, J.A. Russell,
S.D. Landsman

The purpose of this research is to determine the reaction mechanisms involved in biomass liquefaction in aqueous media at elevated temperatures. Because of the complexity and variability of composition of biomass the liquefaction of pure cellulose and lignin is now being studied. The compounds present in cellulose and lignin oils are being identified. Mechanisms of formation for some of the identified ketones, alcohols, and furans have previously been determined. Formation of aromatic compounds from cellulose liquefaction are being vigorously examined since reduction-oxidation mechanisms appear to be involved in some of these components. Various analytical techniques, including liquid chromatography, gas chromatography, mass spectrometry, and nuclear magnetic resonance spectroscopy are used to identify compounds in the cellulose and lignin oils. Postulated intermediates (small aldehydes and ketones) are used as models to aid the determination of reaction mechanisms. The end result of this research will be detailed knowledge of the chemical processes involved in thermochemical biomass-liquefaction.

Chemical Energy

Chemical and Instrumental Analysis Division
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, Pennsylvania 15236

Total $75,000

126. VIBRATIONAL SPECTROSCOPIC STUDIES OF COAL CONVERSION CATALYSTS 1.0 02-01
John M. Stencel

Research during the current year has concentrated on the understanding of molybdenum-support interactions in Mo/TiO$_2$, Mo/ZrO$_2$, and Mo/SiO$_2$ catalysts, and on the influence of these interactions in the hydrodesulfurization of coal. Raman spectroscopy is the primary tool used to define molecular speciation for different Mo concentrations, catalyst preparation procedures, and support surface areas, and to follow molecular speciation during catalyst reduction and sulfidation. Other bulk and surface sensitive techniques, such as x-ray diffraction and x-ray photoelectron spectroscopy, are also used to supplement Raman experimentation. The importance of catalyst structure on the conversion of coal to preasphaltenes, asphaltenes, and oil, and on desulfurization of the coal, is investigated by correlation of catalytic reaction data with catalyst structural information.

Chemical Energy

Radiation and Surface Physics Research Department — Total $100,000
Sandia National Laboratories/Albuquerque
P. O. Box 5800
Albuquerque, New Mexico 87115

127. REACTION KINETICS OVER SINGLE CRYSTAL CATALYSTS — 1.0 — 02-01
D. Wayne Goodman

The goal of this research is to develop an understanding of surface catalyzed reactions at the molecular level using the full complement of modern surface probes. Of primary importance are those reactions relating to the synthesis of hydrocarbons from H_2 and CO. The experimental work includes the determination of reaction kinetics of hydrocarbon formation and rearrangement over single crystal catalysts. The work is carried out in a specially built ultra-high vacuum apparatus allowing both kinetic measurements and surface analysis. Several reactions representative of important categories of catalytic systems have now been studied on well-defined, single crystal nickel surfaces. These reactions include methanation, hydrogenolysis, and hydrogenation. Clear evidence is seen for the "structure sensitivity" of the hydrogenolysis of ethane and butane over Ni(100) and (111) surfaces. Poisoning studies of the above reactions by sulfur indicate that the dominant influential effect is an electronic one and one that extends over distances larger than the atomic radius of sulfur.

Chemical Energy

Research Division — Total $100,000
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

128. BASIC RESEARCH IN SYNTHESIS AND CATALYSIS — 1.25 — 02-01
J. C. Smart, D. L. DuBois and C. J. Curtis

This basic research program involves the synthesis, characterization and reaction studies of transition metal coordination complexes and organometallic compounds for the photoconversion of N_2, CO, CO_2, H_2O and related substrates to fuels and chemicals. It includes structural, spectroscopic and mechanistic studies with the goal of understanding the interrelationship of molecular geometry, electronic structure and catalytic reactivity in photochemical and photoelectrochemical transformations. Designed organometallic synthesis of new dinuclear complexes of the early transition metals with the bridging fulvalene, *s*- and *as*-indacene ligands is underway. Spectroscopic and photochemical studies of the Group VIII metallofulvalene complexes is contributing to an understanding of their electronic structures and the potential utility of their low-lying excited states in photocatalysis. Photoelectrochemical N_2-fixation studies involve the synthesis and characterization of surface bound phosphine molybdenum(0) dinitrogen complexes. These include the preparation of new pendant tridentatephosphine polymethacrylamide polymers, together with electrochemical and FT-infrared studies.

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $900,000

129. HYDROMETALLURGICAL PROCESSING — 2.5 — 02-02
Renato G. Bautista

The development and understanding of hydrometallurgical methods of recovering metals to include dissolution (leaching), separation and concentration (ion exchange, solvent extraction, and membrane separation) and metal reduction from solutions (cementation, precipitation, and electrolysis) based on the equilibria, mechanisms, kinetics, and transport properties of the chemical reaction system are the related activities which are the principal objectives of this research program. The research projects presently being completed include: the kinetics of the dissolution of pyrite and uranium dioxide by ferric sulfate and sulfuric acid and the prediction of the concentration changes of the various species in solution during the dissolution process using the partial equilibrium model; the separation and concentration of ppm europium chloride solution using a supported liquid membrane impregnated with di-2-ethylhexyl phosphoric acid as a mobile carrier and the elucidation of its mass transfer mechanism for permeation through the membrane; and the electrowinning of dilute copper sulfate solution using a fluidized bed electrochemical reactor.

130. ANALYTICAL SPECTROSCOPY — 5.0 — 02-02
V. A. Fassel, A. P. D'Silva,
R. N. Kniseley, J. F. McClelland

This effort is devoted to the systematic observation of spectroscopic phenomena with the ultimate goal of utilizing these observations for devising new spectroscopic analytical concepts that offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, the conversion of coal to liquid and gaseous fuels, solid state materials research and in environmental pollution. Emphasis is being placed on: (a) novel applications of electrical plasmas as vaporization-atomization-excitation-ionization sources for analytical atomic emission and fluorescence spectroscopy; (b) analytical applications of highly selective energy transfer processes from x-ray and laser beams to trace constituents in solid materials, leading to optical emission, e.g., x-ray or laser excited optical luminescence; (c) selective energy transfer from gaseous metastable species to trace level gaseous organic or inorganic constituents, with the intent to devise new analytical concepts; and (d) photoacoustic spectroscopy and detection analytical techniques.

131. ANALYTICAL SEPARATIONS AND CHEMICAL ANALYSIS — 2.1 — 02-02
J. S. Fritz

A major effort is underway to improve and exploit our new chromatographic method for the rapid analysis of anions and certain metal and organic cations (U.S. Patent # 4,272,246, June 9, 1981). We hope to improve this method to the extent that complex mixtures of inorganic ions can be separated and analyzed with the same facility that currently is possible in organic chromatography. Research is underway to provide improved analytical procedures for concentrating and separating trace organic pollutants in water. A new furoyl hydroxamic acid is proving to be particularly effective for concentrating metal ions prior to chemical analysis by emission spectroscopy. An improved plate theory of chromatography is being developed which should correct many of the inadequacies of existing theory and provide a better foundation for chromatographic work.

132. ANALYTICAL MASS SPECTROSCOPY 1.5 02-02
H. J. Svec, R. J. Conzemius

This project involves the application of mass spectrometry to analytical problems involving organic, conducting, semiconducting and insulating solids and the organic constituents in complex mixtures. The basic science is emphasized. A most successful recent study concerned development of a scheme to separate complex mixtures into compounds of various chemical classes as an adjunct to GC/MS analyses. Publication of this scheme, based on a liquid-liquid extraction, has elicited worldwide requests for reprints. A second study completed during the past year concerns improvements in the spark source mass spectrographic analysis of coal and its residues for elemental impurities. The analytical coverage involves 65 elements and the absolute results, when applied to two kinds of coal and their by-products entering and leaving a power plant, were good enough to establish a meaningful materials balance. A third continuing study involves further refinement of a laser/MS probe now tested for assaying phases (10-20 μm diameter) for trace impurities. Prospects that this instrumental analytical technique will not require reference standards is excellent.

133. LASERS IN ANALYTICAL CHEMISTRY 4.6 02-02
E. S. Yeung

This program is aimed towards the development of new analytical techniques relevant to pollution monitoring, combustion diagnosis, and material evaluation in energy production. New spectroscopic concepts and instrumentation, particularly those involving lasers, are studied so that analytical methods can gain in sensitivity, selectivity, accuracy, and speed. Specific areas of concern include (1) the development of the laser microprobe for atomic spectroscopy on surfaces; (2) new optical detectors for liquid chromatography suitable for complex samples; (3) Raman methods and two-photon methods applied to analytical problems; (4) photoacoustic and interferometric concepts for improved absorption measurements; and (5) laser-induced chemiluminescence for specific gas analysis. Investigations include the fundamental principles behind the measurements, the evaluation of the analytical potentials, and the demonstration of the analytical method in representative samples.

Separations and Analysis

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total $1,160,000

134. SEPARATION SCIENCE RELATED TO FOSSIL FUEL TECHNOLOGIES   3.3   02-02
E. P. Horwitz, G. R. Dyrkacz,
C. A. A. Bloomquist

The major emphasis in this program lies in the area of separation and characterization of the maceral constituents of coal. An efficient laboratory-scale method for separating maceral constituents from coal in a relatively pure form has been developed. The properties of macerals from coals of varying rank are being studied. Surface properties of macerals are studied with regard to developing new and improved separations methods. Density profiles and chemical structure are also being studied to gain a fundamental understanding of the properties, origins and geochemistry of these macerals, and of the behavior of coal during gasification and liquifaction. Research on oil shale is directed toward use of surfactant dispersion and selective wetting as methods for enriching the organic constituents (kerogen and bitumen) from the inorganic constituents. Both Green River and Devonian shales are being studied.

135. CHEMICAL SEPARATION SCIENCE RELATED TO NUCLEAR AND HYDROMETALLURGICAL TECHNOLOGY   6.0   02-02
E. P. Horwitz, D. Kalina, L. Kaplan,
G. Mason, P. Danesi, P. G. Rickert

This program has as its objectives the investigation of the complexation of metal ions by organic extractants and the investigation of the principles of mass transfer of solutes between an aqueous and an organic environment. Knowledge gained is applied to the development of new and improved separation methods of importance in nuclear fuel reprocessing, nuclear waste processing, and the recovery of strategic metals. Liquid extractant systems in separation modes which require small amounts of energy or perform high efficiency separations are also being studied. The major areas of work are: (1) The synthesis and characterization of new extractants tailored for actinide extractions, actinide(III) - lanthanide(III) separation, and the recovery of valuable metals by hydrometallurgical processing; (2) Kinetics and mechanisms of interfacial mass transfer to elucidate mechanisms by which metal ions are transferred from an aqueous to an organic environment; (3) New separation techniques, based on liquid-liquid extraction systems, which require small amounts of energy and/or perform large scale high-efficiency high-resolution separations.

136. STUDY OF ATMOSPHERIC TRACE GASES BY MASS SPECTROSCOPY 1.3 02-02
C. M. Stevens

This program is engaged in studies of the atmospheric trace gases CH_4 and CO, primarily from the standpoint of understanding the sources of these gases and their fate in the atmosphere. The stable isotopic composition of these gases, of carbon in the case of CH_4 and of both carbon and oxygen in the case of CO, is precisely measured by mass spectrometry in order to determine the relative distribution of various sources of the gases, both natural and anthropogenic. These data can be used to deduce global fluxes of CH_4 and CO. Another aim of this program is to measure the global average concentration of atmospheric OH radicals, a very important measurement as OH radical is the main atmospheric scavenging agent for pollutants.

Separations and Analysis

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $200,000

137. APPLICATIONS OF NUCLEAR METHODS TO ANALYSIS 2.0 02-02
G. Harbottle, E. V. Sayre,
R. W. Stoenner

This program is concerned with the extension and improvement of nuclear methods of elemental analysis, particularly methods that permit the determination of many components (including trace impurities) quickly and efficiently, and with the development of computer-based multivariate statistical analysis for large assemblages of such analytical data. These methods are being applied to a wide variety of materials for which geographic origins are of significant interest. The effects of geochemical processes on trace element patterns are being investigated in several natural materials and artifacts made from them. Neutron activation analysis is also used in an innovative method for tracing the redistribution of pollen during flower fertilization. Studies of the accuracy and precision of standardization in activation analysis are an important part of the program. The improved proportional counter method for carbon-14 measurement in samples as small as 10 mg is being applied to the dating of marine sediments in an attempt to account for the carbon dioxide inventory of the world.

Separations and Analysis

Department of Energy and Environment — Total $350,000
Brookhaven National Laboratory
Upton, New York 11973

138. SPECIFIC MOLECULAR PROPERTY DETECTORS FOR CHROMATOGRAPHIC ANALYSIS — 0.9 — 02-02

J. Gaffney and E. Premuzic

This research effort is focused on the development of novel specific molecular property detectors for use in gas and liquid chromatography. The approach is to devise detection schemes which simplify the separation analyses by increasing the detector response for the specific molecules of interest while reducing the background noise from potential interferences. Areas of application range from process monitoring to trace analysis in environmental and biomedical investigations. The program is currently developing monitors for specific hydrocarbons and hydrocarbon classes. Far-ultra violet (130-300nm) circular dichroism is under investigation as a means of monitoring optically active hydrocarbons. This device will use the National Synchrotron Light Source (NSLS). The spectral and thermal properties of ozone-chemiluminescence as a means of monitoring hydrocarbon classes as well as photothermal laser spectroscopies are also being investigated as selective and sensitive devices for chromatographic detection.

139. TRACE ELEMENT ANALYSIS USING SYNCHROTRON RADIATION — 0.7 — 02-02

B. Gordon

This program is concerned with the application of synchrotron radiation from the National Synchrotron Light Source (NSLS) to multielemental trace analysis by x-ray fluorescence. The effort is directed in part toward the design and construction of an x-ray microprobe with one micrometer spatial resolution and 1 ppm sensitivity and in part toward the trace elemental analysis of bulk samples. A ray tracing program used in the design of the microprobe optical system is being improved to provide a more useful description of the photon distribution at any point on the beam axis. A theoretical study of multielemental trace analysis in bulk samples indicates the use of newly developed wide bandwidth monochromators and the NSLS photon source can result in quantitation limits of 10-100 ppb in thin biomedical samples and 30-300 ppb in thin geological samples for one minute irradiations. Bulk sample analysis experimentation is to begin with the initiation of the NSLS x-ray program.

140. CYCLIC SEPARATIONS PROCESS RESEARCH — 1.7 — 02-02

F. B. Hill

The purposes of this program are to obtain an understanding of the characteristics and basis of operation of cyclic separation processes as a class, and to explore the feasibility of using these processes to perform specific separations important in the energy field. The cyclic processes of interest include pressure and temperature swing adsorption, parametric pumping, cycling zone adsorption and various forms of preparative chromatography. Applications presently under study involve hydrogen isotope separations of concern in fusion reactor fuel processing and in heavy water reactor technology, and helium extraction from natural gas. Future work will include applications such as hydrogen recovery and purification, and ion exchange separations useful in nuclear waste management. Elements of the program include development of the theory of cyclic processes, measurements of equilibrium and kinetic properties of selected fluid-solid separation systems, measurement of the characteristics of cyclic separation processes employing these systems, and process design and evaluations studies.

Department of Energy and Environment, BNL, continued

141. DETERMINING FRAGILE MOLECULES IN THE ENVIRONMENT R. L. Tanner	1.0	02-02

The program goal is analytical methods development for trace amounts of potentially reactive constituents of environmental samples, emphasizing derivatization-chromatographic techniques which show promise in solving basic analytical problems involving by-products of energy production technologies. Research is being conducted in the use of capillary-column GC with an electron capture detector (ECD) for determination of polynuclear aromatic hydrocarbons (PAH) which may be nitratable (to form even more toxic by-products) by reaction with NO_2 or nitric acid in the ambient atmosphere. Preliminary results show that certain PAHs can be analyzed by nitration + GC-ECD determination and work is underway using GC with mass spectrometry and other N-sensitive detectors to confirm the apparent linkage between parent PAHs (pyrene and benzo(a)pyrene) and nitro-derivatives in ambient aerosol samples. A second area of focus is the use of liquid chromatography with pre-column derivatization for trace determination of aldehydes as their 2,4-dinitrophenylhydrazone derivatives.

Separations and Analysis

Physics Department
Brookhaven National Laboratory
Upton, New York 11973

Total $155,000

142. DEVELOPMENT AND APPLICATIONS OF NUCLEAR PARTICLE MICROSCOPY K. W. Jones and H. W. Kraner	2.1	02-02

The methods of nuclear and atomic physics are used to develop and apply techniques for the quantitative measurement and precise spatial localization of stable isotopes. Beams from a 3.5-MV Van de Graaff, MP Tandem Van de Graaff Facility, high flux reactor are used to identify isotopes through production of unique atomic and nuclear signatures. The use of proton and x-ray induced x-ray fluorescence, Rutherford backscattering, and nuclear reactions makes possible the determination of multi-element concentrations with excellent sensitivity. Spatial distributions are determined by use of particle microbeams with a resolution of about 10 μm and depth distributions by nuclear reaction analysis or Rutherford backscattering with resolutions of .01 μm. The use of synchrotron radiation for trace element measurements has been considered and equipment for use in a program at the National Synchrotron Light Source is being assembled. Collaborative projects in a variety of disciplines are in progress and include in-vivo lead determinations, hydrogen profiling, and transport of heavy metals in graphite at high temperatures.

Separations and Analysis

EG&G Idaho, Inc.
Idaho National Engineering Laboratory
P. O. Box 1625
Idaho Falls, Idaho 83415

Total $60,000

143. SELECTED ELEMENTAL SEPARATION STUDY 1.0 02-02
J. D. Baker

The purpose of this program is to study selective elemental extractants which could be used to partition valuable metals from fission-product waste. This year, the extraction behavior of Zr from aqueous HNO_3 was studied using dihexyl N, N-diethylcarbamoylmethylphosphonate (DHDECMP). Distribution ratios were examined as a function of contact time, concentration of solute, acid and extractant and extractant temperature. It was found that the extractant dependency for Zr is second power. Temperature dependency studies were hindered by an apparent Zr specie change above $30^{\circ}C$. Extraction of Zr is strongly NO_3^- dependent.

Separations and Analysis

Exxon Nuclear Idaho Co., Inc.
Idaho National Engineering Laboratory
P. O. Box 2800
Idaho Falls, Idaho 83401

Total $60,000

144. NEGATIVE THERMAL IONIZATION MASS SPECTROMETRY 1.0 02-02
J. E. Delmore

This research involves the application of negative surface ionization (NSI) to the isotopic analysis of electronegative elements, and of electronegative molecules that are suitable for measurement of the isotopic composition of one of the constituent atoms. Initial studies demonstrated that a straight forward use of NSI limited application to only a few cases (Cl^-, Br^-) due to the constraint of excessive electron emission. This was circumvented by using ionizers of low work function refractory powders that chemisorb the species to be ionized as an anion. The anion is then thermally desorbed, with a greatly increased probability of ionization. This technique improves the ion to electron ratio by orders of magnitude for the systems studied to date. A magnetron type ion source is presently being tested, which prevents electrons from entering the focusing lens. Preliminary results indicate that this raises the permissible electron current substantially. One or both of these approaches will be applied to a number of ion/ionizer systems for performing isotopic analyses.

Separations and Analysis

Energy and Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $50,000

145. CHEMICAL ANALYSIS R. Giauque	0.4	02-02

The research and development of X-ray fluorescence (XRF) analytical techniques is the basis of this program. Emphasis is placed on improving the sensitivity capability of XRF and establishing accurate methods which compensate for matrix effects. A method for the determination of sulfur in crude oil and petroleum products is being established. The use of AgL excitation radiation and a closely coupled excitation-specimen-detector geometry permits high sensitivity to be realized. Scattered AgL excitation radiation is to serve as an internal standard. X-ray fluorescence techniques applicable for multielement analysis of small quantities (<10 mg) of geochemical specimens is being developed. Emphasis is being placed on establishing procedures for the preparation of deposits of uniform mass thickness. Several mathematical methods using coherent and incoherent scattered excitation radiation to determine matrix absorption effects is being studied.

Separations and Analysis

P Division Los Alamos National Laboratory University of California P. O. Box 1663 Los Alamos, New Mexico 87545	Total $160,000

146. THE FORMATION AND PROPERTIES OF COMPLEXES OF HELIUM AND HYDROGEN ISOTOPES R. D. Taylor	1.0	02-02

Under certain conditions tritium forms a metastable bound-state with helium-3. T_2 decays with a half life of 12.3 years ultimately producing a pair of free ^{3}He atoms. However, the ^{3}He formed in liquid T_2 is retained in the liquid in an amount far exceeding the ordinary solubility, suggesting that a complex of ^{3}HeT is formed. This complex is virtually stable in liquid and solid tritium and is definitely unstable in the gaseous state. The formation of the complex appears to be inhibited in liquid T_2 subjected to a modest electric field gradient. Experiments are underway to verify this observation and to quantify the conditions that prevent formation of the complex. Other time-temperature measurements made to characterize the complex include magnetic susceptibility, electrical conductivity, vapor pressure, and compositional studies.

Separations and Analysis

Mound Facility
P. O. Box 32
Miamisburg, Ohio 45342

Total $700,000

147. ISOTOPIC EXCHANGE RATES IN H-T AND D-T MIXTURES 0.8 02-02
G. T. McConville and W. L. Taylor

The purpose of this study is to obtain a more complete understanding of gaseous mixtures of hydrogen isotopes, in particular, the mechanism for isotopic exchange in such mixtures. Such information is necessary to support design criteria for fuel handling systems in the controlled thermonuclear power program. Measurements have been made at room temperature of the D_2+T_2 reaction rate as a function of T_2 concentration and pressure. The beta particle given off in the decay of T_2 serves as a catalyst for the reaction. It was shown that the reaction is a gas phase reaction as opposed to a catalytic surface reaction in the stainless steel container. It was also found that very small amounts of tritiated methane (CT_4), ~0.02%, in the gas sample acts as a very strong inhibitor for the reaction, whereas ~0.01% T_2O does not inhibit the reaction. The reaction rate increases exponentially with increasing T_2 concentration when no inhibitor is present.

148. ISOTOPE SEPARATION RESEARCH AND DEVELOPMENT 3.0 02-02
W. M. Rutherford, B. E. Jepson,
E. D. Michaels, W. R. Wilkes

This program is concerned with the investigation of chemical exchange and liquid phase thermal diffusion as techniques for stable isotope separation. The chemical exchange work is directed toward finding significant equilibrium isotope effects in metal isotope exchange reactions with an emphasis on macrocyclic complexants, and towards the development of two-phase isotope exchange systems which can serve as the basis for practical countercurrent exchange separation processes. The liquid thermal diffusion work is directed, in part, toward developing a basic understanding of the behavior of liquid phase thermal diffusion columns and, in part, toward gaining experimental information about the isotopic thermal diffusion factor in the liquid phase.

149. MOLECULAR SCIENCE RESEARCH 3.4 02-02
W. L. Taylor, G. T. McConville,
R. W. York

The objective of this project is to investigate the physical properties of stable isotopes and their mixtures. A new detector system was installed on the molecular beam chamber so that differential scattering cross sections can be measured. Total cross sections for the He-Ar system were completed and experimental precision showed a marked improvement over previous results. Mass diffusion measurements for the He-Ne and He-Xe systems were conducted from 350 to 1400 K. A new Ta/W diffusion cell has been constructed and is being installed in a vacuum furnace to extend diffusion measurements up to ~2800 K. An apparatus to study the thermodynamics of the thermal diffusion process has been constructed and instrumented to provide "in situ" analysis of the separation process. The quadrupole moment of deuterium in the solid and liquid phase was determined from vapor pressure measurements and characterization of the molecular interaction of the hydrogen isotopes is in progress.

Analytical Chemistry Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total $1,135,000

150. ION MICROPROBE MASS ANALYSIS R&D: SURFACE CHARACTERIZATION 1.4 02-02
W. H. Christie, R. E. Eby

The overall objectives of this program are: 1) develop state-of-the-art methods for acquiring, processing, and quantifying SIMS data; 2) develop methods for applying SIMS to the solution of surface analytical problems in ongoing DOE research programs; and 3) develop methodology to investigate the suitability of SIMS in new analytical areas such as the characterization of non-volatile organic material and the analysis of difficult sample types produced in various nuclear related processes. Ion implanted materials are being investigated as standards for quantifying sputtered ion yields. These materials are of special significance to SIMS as accurate standards can be prepared to calibrate the sputtering response in chemical systems. The effect of laser annealing, using excimer lasers with high spatial homogeneity of the energy density, on the redistribution of dopants in photovoltaic devices is being investigated via SIMS depth profiling. SIMS profile shapes may offer a precise technique for the determination of melt depth in these systems.

151. MASS SPECTROMETRY R & D ORGANIC ANALYSES 2.4 02-02
G. L. Glish, P. J. Todd, E. H. McBay

This research is directed toward the development of new techniques and analytical applications involving mass spectrometry. In particular, emphasis is being placed on mass spectrometry/mass spectrometry (MS/MS) as a method to determine ion structure via metastable and collision activated decompositions. Also, new scanning modes are being investigated as well as the collision process. The use of secondary ion mass spectrometry for involatile organic compounds in conjunction with MS/MS is also being investigated. Ion structure work is being performed on the high resolution instrument using high resolution measurements to confirm elemental composition and various scanning modes to elucidate fragmentation pathways. Pyrolysis gas chromatography/mass spectrometry of labeled coal is continuing in an effort to determine hydrogen transport mechanisms. A new investigation into the potential of thermal desorption/ionization of involatile organics has been initiated.

152. ADVANCED SPECTROSCOPIC METHODS FOR CHEMICAL ANALYSIS 2.0 02-02
L. Hulett, J. Dale, T. Rosseel

The goal of this work is to explore new physical phenomena for possible innovations as spectroscopic methods and to upgrade applications of older principles. The more recent approaches of this program use monoenergetic positron and heavy ion sources, which are facilities unique to ORNL; the high risk aspects of these efforts are counterbalanced by other studies that use the more proven electron and x-ray methods. Positron spectroscopy is being studied for use in surface and bulk materials analysis. X-ray fluorescence and Auger electron emission, stimulated by heavy ion bombardment, will be studied as tools for analyzing solids and gases. A miniature electron spectrometer will be interfaced to a scanning electron microscope for surface analysis of individual particles. Auger electron spectroscopy for the metering of gas chromatograph effluents will be evaluated. An inexpensive miniature electron spectrometer, disposable in case of contamination, is being built for nuclear waste analysis. This work involves collaboration with the ORNL Physics, Chemical Technology, and Instrument and Controls Divisions, and with the State University of New York.

Analytical Chemistry Division, ORNL, continued

153. RESEARCH DEVELOPMENT & DEMONSTRATION OF ADVANCED CHEMICAL MEASUREMENT TECHNIQUES

3.3 02-02

H. Ross, M. Ramsey, R. Shaw,
W. Whitten, J. Young

New spectroscopic techniques for chemical analysis are being developed that have the potential of meeting critical measurement needs in research, industry, and the environment. Some techniques, such as delayed lasing, can yield new analytical information quickly and at low cost. Also unusual, is a new approach to Fourier transform microwave spectroscopy. Time-resolved spectroscopy, using fluorescence or fiber-optic waveguides, is being developed for a broad range of existing critical monitoring problems. The technique of laser excited fluorescence of actinide-lanthanide fluorides is being applied to the determination of ultra-trace concentrations of actinide ions. Work is also continuing on the piezoelectric detection of optoacoustic signals from matrix isolated organic materials. This technique will permit the rapid qualitation of some complex organic mixtures. Other techniques under investigation include optogalvanic spectroscopy, laser ablation for solid sampling, and the general problem of new laser applications for chemical analyses.

154. ORGANIC SECONDARY ION MASS SPECTROMETRY

0.6 02-02

P. J. Todd, W. H. Christie

This research is directed toward the development of the methodology of sputtering secondary ions from involatile organic sample targets. The in-house developed SIMS source described previously functions as it was designed, working well with both single sector and triple sector (MS/MS) mass spectrometers. The ion optics of this source were tailored to the known physical characteristics of secondary ion emission. Sufficient sensitivity is obtained that analog rather than pulse counting detection is used. In particular, tetraalkyl ammonium halides show a substantial secondary ion signal, with a fragmentation pattern indicating minimal surface damage per unit area. These results indicate that secondary organic ions are best emitted from species which exist as ionic salts on the target. Thus, present work is directed toward derivitization reactions to convert organic analytes to salts. Ultimately, the goal of this work is to perform the derivitization reaction in situ so that organic adherents may be ionized by primary ion bombardment and so analyzed.

155. MASS SPECTROMETRIC R & D FOR INORGANIC AND ACTINIDE ANALYSIS

2.0 02-02

R. L. Walker, D. H. Smith
D. L. Donohue, H. S. McKown

This work is directed toward improving analysis of samples of inorganic origin by thermal emission (TEMS) mass spectrometry. In TEMS, internal standards (double spikes of ^{233}U and ^{236}U) have been developed and will be applied routinely to isotope abundance and isotope dilution measurements. Isotope dilution methods have been developed to measure ppm amounts of Th in Ir-W alloys used in the Space Power Program, and to measure sub-ppm amounts of Th and U in zircaloy cladding. A laser technique involving resonance ionization spectroscopy has been developed and applied to mixtures of Nd, Sm, and Ce, selectively ionizing each element from the mixture. Expanded applications of this technique will be developed and the measuring procedure improved. In SSMS, further applications of a hot-cell mounted instrument will be developed and refined. Areas of investigation which will be continued are identification of dissolver solution residues and verification of the ORIGEN code.

Separations and Analysis

Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total $1,910,000

156. RESEARCH IN CHEMICAL ENGINEERING SEPARATIONS 4.6 02-02
J. M. Begovich, C. H. Byers, J. S. Watson

Fundamental chemical engineering separations studies include new concepts and improved basic understanding of separations techniques. Continuous separation of several components by a rotating annular chromatograph is being explored. A solution of the transport equations for a multicomponent interactive system was completed and is being extended to include dispersion effects. High temperature slagging studies explored distribution of copper between sodium sulfide and iron and short-term diffusion effects which could be important in recycling of currently unusable scrap iron. Expanded beds, stabilized by electric fields, exhibit many characteristics of fixed bed sorption but with low pressure drop. Studies of electric field effects which restrict solids movement and flow and sorption characteristics continue. A study of the mass transfer to oscillating droplets in forcing fields is in its initial stages. Significant transport enhancement is anticipated.

157. FUNDAMENTAL CONCEPTS FOR RESOURCE RECOVERY 4.3 02-02
R. M. Canon, A. D. Kelmers

This research program investigates fundamental variables of importance in separations methods important for various forms of resource recovery. These separations include liberation of components from waste materials or low-grade ores, ion exchange, solvent extraction, and crystallization. Investigations recently have concentrated on separations in hydrochloric acid systems. These studies identify the most promising methods and define the solution chemistry as it relates to the separation of materials. Liberation methods studied include use of nonaqueous (aprotic) leaching agents. Extremely high chloride activities can be obtained in such systems, and the present studies are aimed at determining phase equilibria for several groups of potentially useful systems. These data will make it possible to select aprotic solvent systems for use in extraction testing based upon fundamental data and understanding.

158. SEPARATIONS SYSTEMS RESEARCH 4.5 02-02
C. F. Coleman, W. J. McDowell

This research is directed toward innovation and improvement in, and understanding of the scientific basis for, chemical and physical separations methods related to the production of energy. The scope includes applications to hydrometallurgy, fossil fuel conversion, nuclear fuel reprocessing, and waste treatments. Present studies include the use of macroheterocycles (crown ethers and others) as size-selective coordinating synergistic agents in liquid-liquid extraction; the chemical and physical factors controlling liquid-liquid dispersion and coalescence rates and the formation of interfacial intrusives; effects of molecular size and structure of extractants on extraction power and physical performance; equilibria, kinetics, mechanisms, and solute species in selected systems. The work also includes the use of separations procedures in conjunction with PERALS (photon-electron rejecting alpha liquid scintillation) Spectrometry for alpha assay, and assembly and maintenance of the Separations Science Data Base.

Chemical Technology Division, ORNL, continued

159. BASIC TRITIUM SEPARATION SCIENCE 1.6 02-02
P. W. Fisher, S. D. Clinton

This research is directed toward an understanding of tritium separation methods for fusion and fission reactor systems. Since liquid lithium is the most promising breeding material for fusion reactors, experimental investigations have focused on the removal of tritium from molten lithium. Experiments indicate that yttrium can remove tritium from lithium and maintain a low inventory of residual tritium in the fusion blanket. Tritium mass transfer rates are controlled by diffusion within the yttrium sorbent and can be correlated with the yttrium porosity. Effects of yttrium impurities and surface conditions appear to be less important than anticipated. Experiments designed to enhance tritium diffusion within the metal sorbent and to recover tritium from the yttrium have been initiated. Studies to measure gas phase tritium sorption on selected surfaces with controlled conditions are being initiated.

160. FUEL CYCLE CHEMISTRY 3.0 02-02
L. M. Toth, D. J. Pruett, R. L. Fellows

Fundamental aspects of nuclear fuel cycle chemistry are investigated with emphasis on the discovery and optimization of chemical separations and on the control and minimization of wastes. The effort concentrates on the solution chemistries of actinides and fission products, and on low temperature photochemistry of uranium and plutonium salts. Studies include: (1) solids formation in reprocessing solutions; (2) actinide and fission product ion complexation with solvent degradation products; (3) plutonium polymer formation; (4) solvent extraction kinetics; (5) chemistry of specific fission products; ruthenium, technetium, and tellurium; and (6) photo- and associated chemistry of the actinides and fission products. Both the concentration and the nature of species in question are determined in order to describe the basic physical chemistry of the system. Standard analytical techniques of spectrophotometry, electrochemistry, chromatography, and tracer analysis are combined with α-, β-, and γ-containment techniques to study realistic fuel recycle systems over a wide range of experimental conditions.

Separations and Analysis

Chemistry Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total $460,000

161. FUNDAMENTALS OF SEPARATION CHEMISTRY 1.5 02-02
J. H. Burns, C. F. Baes, Jr.

The purpose of this program is to obtain basic information about solvent-extraction systems that may lead to improved methods of recovering important metals. Known successful processes are being investigated with the goal of understanding, on a molecular level, the mechanism by which they operate and establishing which variables of chemical reactivity and structure are important to their success. Extraction complexes from typical systems for extraction of uranium by organophosphorous ligands are being analyzed by x-ray and neutron diffraction and Raman spectroscopy of solids and liquids. The structural information so obtained is being combined with energy calculations in a molecular modeling effort to design even more effective solvent-extraction reagents.

162. FLOW THROUGH POROUS BODIES 1.5 02-02
J. S. Johnson, Jr.,
C. G. Westmoreland

Processes involving fluid flow through porous media which have been of interest include column chromatography; mixing of fluids of different density and viscosity in passage through porous solids; filtration; membrane transport; and reactions in suspensions and fluidized beds. Recent emphasis is on the preparation in forms suitable for column operation of adsorbents stable in difficult environments — radiation, chemical, or temperatures. Efforts are concentrated on evaluation of separation properties of activated charcoals whose ion-exchange properties have been increased by controlled exposure to HNO_3 and of charcoals whose pores have been filled with hydrous Zr(IV) oxide and with mixed hydrous Zr(IV)-P(V) oxides.

Chemistry Division, ORNL, continued

163. MOLTEN SALT PROCESSES FOR HIGH LEVEL RADIOACTIVE WASTE 1.0 02-02
F. J. Smith

This research is directed toward developing the basic chemistry that relates to high-temperature non-aqueous methods of nuclear waste management. Separation processes utilizing liquid-liquid partitioning between immiscible liquid metals/and or molten salts are being developed for the recovery of valuable fission products and to provide methods for safer storage techniques. Distribution measurements demonstrate the feasibility of the molten magnesium — molten uranium-iron eutectic in isolating significant quantities of nonradioactive palladium and rhodium from short cooled fuel. Other studies involve the liquid aluminum-molten chloroaluminate systems and immiscible chloroaluminate salt pair systems. In addition to distribution measurements, thermodynamic and spectral studies of fission products and actinide elements in the molten salt and liquid metal media are emphasized.

Separations and Analysis

Chemical Technology Department
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Total $80,000

164. PYROCHEMICAL SEPARATIONS 0.4 02-02
L. L. Burger, L. G. Morgan

This research develops pyrochemical methods for chemical separations in the nuclear fuel cycle. Separation of constituents into chemical families where the forms and behavior are unique benefits nuclear fuel reprocessing and treatment of nuclear wastes. Pyrochemical processes remove the complication of the water molecule which largely determines conventional chemical behavior. Laboratory studies emphasize molten alkali metal nitrate systems and glass slag reductions. We have previously demonstrated uranium-plutonium-fission product separations using molten alkali metal nitrate systems. The chemical behavior of the thorium-protactinium-uranium system in molten alkali metal nitrates is currently being determined. Recovery of noble metals, including silver, has been demonstrated using a glass slag reduction technique. The source materials for the noble metals include simulated nuclear wastes and inorganic substrates or matrices such as zeolites. Optimum fluxes and reductants are being determined.

Separations and Analysis

Physical Sciences Department
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Total $655,000

165. ULTRASENSITIVE LASER-BASED SPECTROMETRIC ANALYTICAL TECHNIQUES

R. C. Fukuda

1.6

02-02

The objective of this program is to develop ultrasensitive analytical techniques whose basis is laser-induced atomic and molecular beam spectroscopy. Currently, the photon burst and intracavity excited state absorption methods are being investigated. The photon burst method is based on the occurrence of resonant scatter of many photons by a single atom as it passes through a laser beam. Measurement of such time-correlated photons is being investigated as a method of isotopically specific single atom detection. Initial measurements are with sodium, rubidium, and potassium atoms and their available isotopes. Design and construction of an intracavity excited state absorption spectrometer is being initiated. This device uses a pulsed dye laser to generate the excited states and cw intracavity absorption is used to detect them.

166. ANALYTICAL MASS SPECTROMETRIC RESEARCH

R. L. Gordon, D. M. Robertson, J. M. Kelley, J. J. Stoffels

3.3

02-02

This task develops new knowledge and techniques to extend the application of mass spectrometry to problems in chemical and isotopic analyses. The task elucidates physicochemical mechanisms responsible for efficient ion production in isotopic analysis by surface ionization mass spectrometry, develops new materials for surface ionization techniques, and develops techniques for application of mass spectrometry to real-time analysis. Surface-sensitive techniques are used to investigate the structure and composition of surface ionization sources, the dependence of the surface work function on composition and temperature history, the kinetics of ion production, and the dependence of chemical pathways for ion production on sample preparation. Development of real-time mass spectrometry focuses on the direct-inlet technique and encompasses work on ion sources, mass separators and ion detectors.

167. ULTRASENSITIVE RADIOACTIVITY SPECTROMETRIC ANALYTICAL TECHNIQUES

J. H. Kaye and F. P. Brauer

1.0

02-02

The objective of this program is to develop new and improved ultrasensitive and selective radioactivity spectrometric techniques for analysis of radionuclides. Current studies include an evaluation of time-of-event counting, a method wherein the time at which each counting event occurs is recorded as well as the pulse height. At very low counting rates the detector efficiency cannot be considered a simple constant, but rather must be represented by a statistical function. Computer simulation methods will allow us to see how this function affects the precision and detection limit attainable by this method. Another study involves evaluation of a special type of phoswich detector for beta-gamma coincidence counting. A low-background counting system employing a silicon surface-barrier detector is being evaluated for measurement of beta radiation and internal-conversion electrons. Advanced data reduction and manipulation methods recently developed at PNL will be adapted to and evaluated for the handling and interpreting of large data sets generated by multiparameter coincidence counting measurements.

Physical Sciences Department, PNL, continued

168. *COMBINED ATOMIC ABSORPTION-MASS SPECTROMETRIC ANALYTICAL TECHNIQUES* 1.2 02-02
D. L. Styris and J. H. Kaye

This program elucidates experimentally the mechanisms that control sample vaporization in furnace atomic absorption spectrometry. Models that are developed from these results are needed in order to predict the vaporization behavior of a particular analyte in a given matrix/furnace material combination. The neutral atoms, ions and molecular species that appear in vapor phases during the temperature rise of the furnace are monitored simultaneously by atomic absorption and mass spectrometric techniques. Correlation of results from these experiments with furnace temperature and application of chemical thermodynamic and kinetic data help to identify and characterize the controlling chemical and physical processes. Vitreous carbon, tantalum, and graphite furnace materials are being used presently in the investigation of mechanisms that control the vaporization of barium compounds. Chemical treatment (matrix) effects studies for the Group IVA elements are being initiated.

Separations and Analysis

Laser Research and Development Department
Sandia National Laboratories/Albuquerque
P. O. Box 5800
Albuquerque, New Mexico 87115

Total $70,000

169. LASER-BASED ANALYTICAL TECHNIQUES 0.7 02-02
A. Owyoung, A. V. Smith

The purpose of this research is the development of new, highly sensitive, species-specific laser-based analytical techniques which provide capabilities beyond the reach of conventional analytical methods. Emphasis is placed on multi-step laser excitation techniques which can, in themselves, be developed as sensitive tools for trace analysis and which can also be used to enhance the sensitivity and selectivity of certain conventional analytical methods, e.g., mass spectrometry. To this end, the development of a coherent tunable VUV source is currently being completed for incorporation into the laser ionization mass spectrometer developed for this program. In addition, a pulsed molecular free-expansion jet is being designed for incorporation into the apparatus, thus providing added capabilities for cooling and concentrating the sample species. New approaches to state- and species-specific measurements, based on selective excitation of IR- and Raman-active modes using tunable narrowband laser sources, are also being investigated.

Chemical Engineering Sciences

Nuclear Energy Department
Brookhaven National Laboratory
Upton, New York 11973

Total $75,000

170. TWO PHASE FLOW STUDIES 1.0 02-04
N. K. Tutu

This investigation is directed towards the goals of developing a simple, low cost, and objective method of flow pattern recognition in two phase gas-liquid flows, and studying the flow regime transitions. It has been demonstrated that the probability density function and a few moments of the pressure drop signal provide a simple and objective method of flow pattern recognition. Presently, an extensive set of measurements under varying flow conditions is being made to throw light on the flow regime transitions. This should help in developing flow regime prediction models.

Chemical Engineering Sciences

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $215,000

171. TURBULENT COMBUSTION 3.0 02-04
F. Robben, R.K. Cheng, L. Talbot

A fuller understanding of the effects of turbulence on combustion is being sought through experimental measurements in two idealized turbulent combustion configurations. These consist of premixed combustion in a turbulent boundary layer with a strongly heated wall, and the propagation of a flame in a premixed turbulent flow. The principal diagnostics are laser Rayleigh scattering and laser Doppler velocimetry, used to obtain the density and velocity. Detailed measurements of turbulent densities and velocities are being used to determine the statistical stresses, moments, probability density functions and spectra. In the analyses, emphasis has been placed on understanding the properties of the fluid-mechanical flowfield and the physical structure of the combustion zone.

Chemical Engineering Sciences

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $105,000

172. HIGH-PRESSURE PHASE EQUILIBRIA IN HYDROCARBON-WATER (BRINE) SYSTEMS
J. M. Prausnitz

1.6 02-04

The goal of this research is to construct a molecular-thermodynamic model for vapor-liquid equilibria in aquifer reservoirs where natural gas (mostly methane) is in contact with water (or brine) at advanced temperatures (50-250°C) and high pressures (to about 1.5 kilobars). Toward that end, a high-pressure cell has been built for obtaining experimental data; both phases are sampled and analyzed. Further, a generalized van der Waals model for fluids has been established. Instead of the usual one-fluid mixing rules (appropriate for simple mixtures), extension to mixtures is accomplished through the concept of local compositions applied to two-fluid theory. Since aquifer deposits in the Gulf-of-Mexico region contain very large amounts of natural gas, this research may be useful toward establishing engineering procedures for efficient production of that gas.

Chemical Engineering Sciences

Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total $75,000

173. FUNDAMENTAL PROCESSES IN SORPTION PUMPING AND TRANSFER OPERATIONS USING DEEP BEDS OF SORBENTS
C. H. Byers, J. J. Perona

0.7 02-04

Processes involving pumping, storage, and transfer of materials by sorption on deep beds of sorbents are being utilized in several energy production and energy storage areas. This research seeks a fundamental understanding and analysis of the chemical engineering of these operations. Deep-bed sorption processes are studied experimentally to determine the relative importance of heat transfer, mass transfer, pressure drop, equilibrium, and reaction kinetics. In the current phase, sorption processes controlled by mass transfer in the molecular flow regime are being studied experimentally in deep beds and simultaneously are being modeled mathematically using analytical and computer techniques. A fundamental framework for predicting the performance of deep-bed sorption systems will result.

Chemical Engineering Sciences

Combustion Sciences Department
Sandia National Laboratories/Livermore
Livermore, California 94550

Total $175,000

174. ANALYSIS OF REACTING, TURBULENT FLOWS 1.5 02-04
W. Ashurst, B. Sanders

This research consists of the development and application of an unsteady turbulence computational procedure to practical combustion situations of high Reynolds number and large heat release. The fluid mechanics of turbulent mixing is computed by a discrete vortex method, known as vortex dynamics. A one-step kinetic reaction system has been incorporated into the time-dependent computations in two space dimensions. Both premixed and nonpremixed turbulent reacting cases have been computed, and the dependence of turbulence intensity and length scale on the disappearance of fuel has been calculated in the limit of small heat release. Full variable-density formulation is currently being evaluated to study the effects of volumetric expansion on turbulence parameters.

OFFSITE CONTRACTS

Photochemical and Radiation Sciences

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

175. MOTION OF ELECTRONS INJECTED IN NON POLAR LIQUIDS G. Ascarelli Department of Physics	\$60,000	01-01

We measured the Hall mobility of injected electrons in tetramethyl silane (TMS) and obtained $\mu_H = (124 \pm 12)$ cm^2/Vs at room temperature. This value is ~ 25% larger than the corresponding time of flight mobility μ_D. Preliminary measurements appear to indicate that the ratio μ_H/μ_D does not vary much below room temperature. The measurement was done using the technique developed by A. G. Redfield for both diamond and the alkali halides. The observed μ_H/μ_D is only compatible with deformation potential acoustic scattering. Its confirmation will depend on the measurement of μ_H/μ_D between the triple and the critical point. Theoretical work has also been carried on to calculate the disorder generated density of states below the conduction band edge of liquid Ar and/or other liquids or amorphous materials. The energy dependence observed experimentally is predicted from first principles. We also were able to explain the increase of the magnitude of the trapping cross section of N_2O in liquid Ar and liquid Xe as a function of the external electric field.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

176. STUDIES IN CHEMICAL REACTIVITY Robert W. Carr, Jr. Department of Chemical Engineering and Materials Science	\$70,696	01-01

Research is being done on fundamental processes occurring in gas phase chemical kinetics and photochemistry. Effort is currently being placed on the kinetics and mechanism of the oxidation of halomethyl radicals, the chemistry of methylene, collisional deactivation of highly vibrationally excited polyatomic molecules, and sensitivity analysis of kinetic mechanisms. Flash spectroscopy is being used to study the rate of ClO formation in the flash photolysis of 1,3-dichlorotetrafluoroacetone. An improved apparatus for flash photolysis with time resolved mass spectrometry currently being constructed will be used for future studies of halomethyl radical oxidation, as well as other reactions. An attempt is being made to produce $CH_2(^1B_1)$ (to be detected by observation of the $CH_2(^1B_1) \rightarrow CH_2(^1A_1)$ emission bands) from dye laser photolysis of diazomethane. Experiments are being done to determine whether highly vibrationally excited molecules can be selectively photoionized in the presence of unexcited bath gas molecules. The variational method of sensitivity analysis is being applied to a photochemical smog mechanism.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

177. INVESTIGATIONS OF THE TRIPLET STATES OF CHLOROPHYLLS Richard H. Clarke Department of Chemistry	\$163,000 24 mo. FY 81-82	01-01

The characterization of the structures assumed by chlorophyll molecules upon aggregation in photosynthetic systems is important for an understanding of the mechanisms of energy conversion in photosynthesis. Since the properties of the excited triplet state of the pigment molecules such as the electron distribution and excited state dynamics are sensitive to the surrounding interactions and to the state of aggregation, triplet state properties serve as a convenient and nondestructive probe into the makeup of photosynthetic systems. Our present research program utilizes optical detection of magnetic resonance spectroscopy to investigate the triplet state properties of the chlorophyll molecule in lipid bilayers, in protein matrices, and as films deposited on surfaces. These measurements allow an evaluation of in vitro chlorophyll systems for structural features proposed as models for the antenna and reaction center of naturally occuring photosynthetic systems and for their general applicability as model systems for photosynthesis.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

178. SENSITIZATION AND QUENCHING IN THE CONVERSION OF LIGHT ENERGY INTO CHEMICAL ENERGY
Stanley J. Cristol
Department of Chemistry

$105,000
24 mo.
FY 81-82

01-01

Studies of sensitized and unsensitized reactions are being carried out to attempt to define the factors which affect the efficiencies (chemical and quantum yields) in such processes. A novel relay mechanism in the "sensitized" conversion of dibenzobarrelene to dibenzosemibullvalene has been identified. Acetone can quench the singlet of the reactant, which would otherwise give dibenzocyclooctatetraene, intersystem cross and then triplet sensitize the reactant to give triplet product. Singlet lifetimes have been measured for two compounds. Preliminary work on photosolvolysis of benzylic fluorides has been carried out in the hope of obtaining structure-reactivity data for the triplet-state reactions. Geometric and regiochemical constraints for intramolecular excitation and electron transfer in bichromophoric molecules are being investigated. The effects of varying substituents upon such transfers are being studied in several systems with rigid structures.

THE OHIO STATE UNIVERSITY
Columbus, Ohio 43210

179. PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS
Leon M. Dorfman
Department of Chemistry

$153,786
24 mo.
FY 81-82

01-01

The main program objective is an understanding of the rates and mechanisms of chemical reactions induced by high energy electrons. The method used is the direct observation, in real time, of the short-lived intermediates and their elementary reactions. Electron pulse radiolysis, with fast optical detection (time resolution 5 nanoseconds) is the technique used. The observations also provide the optical absorption spectra of the reactive transients. Current activities are: (a) investigation of the reactivities of organic molecular ionic species (carbocations and carbanions as well as ion-radicals) in solution. These ionic species, important in radiation-induced reactions, also play a major role in catalytic reactions of hydrocarbons and in cationic polymerization. (b) optical absorption spectra of transition metal carbonyl radicals in solution, specifically $Mn(CO)_5^\bullet$ and $Re(CO)_5^\bullet$, have been obtained and their reactivities are under investigation. The properties of these free radicals are relevant in homogeneous catalysis. Since all the reactions we are studying are initiated by high energy electrons, the results inherently relate to radiation chemistry.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

180. TIME-RESOLVED LASER STUDIES ON THE ENERGY TRANSFER AND THE CONFIGURATIONAL CHANGES IN BACTERIORHODOPSIN
M. A. El-Sayed
Department of Chemistry

$150,000

01-01

The objective of this study is to understand the mechanism by which the simplest naturally occurring photosynthetic system, bacteriorhodopsin (bR), stores solar energy. Our emphasis is to study the primary processes, the absorption act and the formation of the photochemically and thermally formed transients in the millisecond to picosecond time scale. Time resolved resonance Raman techniques have been developed to examine the vibration spectra of the chromophore (retinal) and to obtain structural information on these transients. These studies show that retinal isomerization is one of the early steps in the photosynthesis of this system. Time resolved polarized-photochemical techniques are developed for detecting whether energy migration processes take place prior to the photochemical change in this system as in the principal photosynthetic system in nature, i.e., chlorophyll (in green plants). The results suggest that unlike chlorophyll, no energy transfer takes place prior to photochemistry in the bR system. These results might be understood in the light of the detailed mechanisms involved in the energy storage within the two systems.

Photochemical and Radiation Sciences, continued

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

181. PHOTOCHEMICAL ACTIVATION AND REACTIVITY OF POLYNUCLEAR TRANSITION METAL COMPLEX MOLECULES — $60,000 — 01-01
John F. Endicott and Richard L. Lintvedt
Department of Chemistry

This research program is concerned with the preparation and characterization of molecular metal complexes capable of photoinduced, multielectron transfer. To this end, several new binuclear and trinuclear complexes (including homo- and heterometal complexes) have been prepared from β-polyketone-type ligands and fully characterized. The multielectron transfer capabilities of several complexes have been confirmed by electrochemical measurements which constitute the major portion of our thermal multielectron transfer studies. Photophysical studies on both bi- and trinuclear uranyl complexes are being pursued. The bulk of these studies are being done with mixed metal -UO_2^{2+} and transition metal ion - complexes in order to investigate intramolecular energy and electron transfer in these complexes that exhibit strong absorption in the visible region due to LMCT transitions involving UO_2^{2+}. Intramolecular quenching measurements and excited state life-time measurements are being carried out.

STANFORD UNIVERSITY
Stanford, California 94305

182. ENERGY TRANSFER PROCESSES IN SOLAR ENERGY CONVERSION — $130,786 24 mo. FY 82-83 — 01-01
Michael D. Fayer
Department of Chemistry

The thrust of this research is the efficient utilization of radiationless excitation transport and trapping to overcome reabsorption problems in solar energy collection. Fundamental to this goal is a detailed understanding of excited-state dynamics in donor/trap systems. Experiments on solution systems confirm the general applicability of a diagrammatic energy transport theory developed here. The theory and experiments are being extended to locally nonrandom polymeric systems. These utilize donors and traps [or excimer-forming (self-trapping) chromophores] attached to polymer backbones. Donors are clustered around traps by controlling polymer morphology. This allows very efficient trapping with low trap concentrations, hence minimizing reabsorption.

CLARKSON COLLEGE OF TECHNOLOGY
Potsdam, New York 13676

183. PHOTOCHEMICAL SOLAR ENERGY CONVERSION IN SURFACTANT VESICLES — $60,000 — 01-01
Janos H. Fendler
Department of Chemistry

This research program utilizes surfactant vesicles in photochemical solar energy conversion and hydrogen generation. Attention is focussed on obtaining mechanistic insight into artificial photosynthesis, and on developing improved vesicles, sensitizers, electron donors and acceptors. Lack of long term stabilities prompted the development of polymeric surfactant vesicles. Depending on the position of the double bond, vesicles can be polymerized either across their headgroups or bilayers. Formation of chemically dissymmetrical vesicles are particularly promising. Polymeric dissymmetrical vesicles, containing covalently linked methylviologens on their inner surfaces and carboxylate groups on their outer surfaces, are stable and possess transbilayer potentials which are favorable to electron transfer. Photosensitized electron transfer from tris(2,2'-bipyridine)ruthenium cation, placed on the outer surface of the polymeric dissymmetrical vesicles, to the redox active viologen moiety, located at the inner surface of the vesicles, and subsequent charge separations are being examined by fluorescence spectroscopy, steady state and nanosecond time resolved laser flash photolysis.

THE OHIO STATE UNIVERSITY
Columbus, Ohio 43210

184. KINETICS OF FAST REACTIONS OF EXCITED SPECIES — $62,000 — 01-01
Richard F. Firestone
Department of Chemistry

Goals include identification of mechanisms for growth and decay of excited rare gas atoms (Paschen 1s and 2p) in pure rare gas samples and in mixtures with molecular quenching agents subjected to a pulsed high energy electron beam. Identities and relative contributions of excited atom precursors of bound excimer states are sought by analysis of effects of T, P and quenching agents on the temporal behavior of excited species. Monitoring is performed by emission spectrometry and fast absorption spectrophotometry using tunable cw dye laser probing beams for excited atoms and continuum source methods for excimer species. Excited atoms of the 2p manifold are monitored by recording pulsed dye laser induced fluorescence. Kinetic parameters of selected 1s-2p state pairs are to be sorted out by cw pumping coupled with absorption measurements at low power densities and at power densities sufficiently great to induce bleaching of the 1s population.

COLUMBIA UNIVERSITY
New York, New York 10027

185. LASER ENHANCED CHEMICAL REACTION STUDIES — $155,000, 24 mo., FY 82-83 — 01-01
George W. Flynn
Department of Chemistry

This project is aimed at the study of chemical reactions of laser pumped molecules with particular emphasis on the role of vibrational energy transfer processes in chemical dynamics. SF_6 is being excited by a relatively low power, continuous wave CO_2 laser in the throat of a supersonic molecular beam nozzle expansion. Chemical reactions of the internally excited SF_6 with potassium atoms are being investigated in a crossed beam apparatus. The relaxation dynamics and spectroscopy of the B, A, and A' states of bromine molecules trapped in rare gas matrices are being studied by photodissociating the bromine with a dye laser and observing fluorescence emission after atom recombination. Fast hydrogen, chlorine, and deuterium atoms are being produced by excimer laser photolysis of gaseous diatomic molecules. These medium hot atoms cause vibrational excitation of stable molecules during collisions. Infrared fluorescence and absorption techniques are being used to probe the population of the vibrational and rotational states produced in these fast atom-molecule encounters.

UNIVERSITY OF TEXAS/AUSTIN
Austin, Texas 78712

186. SOLAR-INDUCED ORGANIC PHOTOCHEMISTRY AT SEMICONDUCTOR SURFACES — $120,000, 24 mo., FY 82-83 — 01-01
Marye Anne Fox
Department of Chemistry

A comprehensive program is continuing for the photoelectrochemical investigation of organic redox reactions occurring at the surface of semiconductors. Two approaches to the primary photoexcitation are employed: (1) direct excitation of single crystalline or polycrystalline semiconductor electrodes or powders or (2) sensitization by highly absorptive carbanions, radical ions or polycyclic aromatic compounds. Upon photolysis, such species exchange electrodes, producing photocurrents or redox products. These techniques are being used to investigate mechanistic details for novel functional group transformations: oxidative cleavage of olefins, oxidative couplings of phenols, and reductive cleavages of arenes. Surface modifications by covalent or adsorptive attachment of photo- or electroactive molecules are being evaluated as methods for controlling electron transfer rates.

Photochemical and Radiation Sciences, continued

WASHINGTON UNIVERSITY
Saint Louis, Missouri 63130

187. *REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS* \$85,000 01-01
Peter P. Gaspar
Department of Chemistry

The goals of this research program are to discover what are the reactions of high energy Si and Ge atoms, how do the reactions take place, and how are the pathways for reaction influenced by the energy and electronic state of the free atoms and the reactive intermediates that they produce. Silicon and germanium atoms are formed at high energies by nuclear transformations such as $^{31}P(n,p)^{31}Si$ and $^{76}Ge(n,2n)^{75}Ge$, and at low energies by thermal evaporation. Intermediates such as SiH_2 and $GeMe_2$ are generated in pyrolysis and photolysis experiments. In the past year the completely relaxed ground electronic singlet state of SiH_2 was identified as the major product-forming species in reactions of recoiling silicon with molecules containing Si-H bonds. New rearrangements of substituted silylenes have been found, and kinetic spectroscopic studies of silylene reactions by laser flash photolysis are underway.

TEMPLE UNIVERSITY
Philadelphia, Pennsylvania 19122

188. DYNAMIC ASPECTS OF THE DYE-SENSITIZED PHOTOCONDUCTIVITY OF SEMICONDUCTORS \$130,000 24 mo. FY 81-82 01-01
Antonio M. P. Goncalves
Department of Chemistry

This research program is designed to probe the dynamics of the elementary processes (injection, recombination, and escape) which determine the efficiency of dye-sensitized semiconductor/electrolyte solar cells. The general experimental approach relies on the use of subnanosecond time-resolved spectroscopic techniques: fluorescence and transient absorption. Injection rate constants are being explored by measuring the fluorescence lifetime of dyes adsorbed on semiconductor surfaces, which can be as much as 40 times shorter than in solution. Processes which follow injection and destroy the oxidized dye are being probed by transient absorption experiments using a novel high sensitivity laser spectrometer with 175 ps time resolution. A study of the relevant processes is being made with dyes of varying excited state energies, both above and below the semiconductor conduction band. Competing surface processes such as energy transfer are being probed by adsorbing the same dyes on insulator surfaces.

UNIVERSITY OF FLORIDA
Gainesville, Florida 32611

189. RADIATION CHEMISTRY OF HYDROCARBON AND ALKYL HALIDE SYSTEMS \$60,000 01-01
Robert J. Hanrahan
Department of Chemistry

Current work is directed towards understanding the mechanism of product formation in the gamma and pulsed electron radiolysis of simple chemical systems. Studies of the radiolysis of H_2-CO mixtures on alumina surfaces include effects of temperature, pressure, and addition of finely divided nickel. An investigation of the radiolytic oxidation of propane indicates many similarities to thermal auto-oxidation, in both products and reaction pathways. Data are being taken on effects of temperature, radiation dose, and O_2 concentration. Studies of the pulse radiolysis of alkyl and perfluoroalkyl iodides include measurement of the rates of deactivation of excited iodine atoms, as well as excited state/ground state formation ratios. The results support the feasibility of constructing an electron-beam activated atomic iodine laser. Measurements are also being made of the rate constants for attack of OH radicals on hydrocarbon and halocarbon gases, using the pulse radiolysis method. Studies of photolysis and mass spectrometry of CH_3I-CF_3I mixtures show both similarities and differences when compared to the pure compounds; the tendency of CF_3 to attack CH_3I is evident.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

190. STUDY OF INTERMEDIATES FROM TRANSITION METAL EXCITED-STATE ELECTRON-TRANSFER REACTIONS — $125,088 — 24 mo. — FY 81-82 — 01-01
Morton Z. Hoffman
Department of Chemistry

This research is concerned with the kinetic and mechanistic behavior of intermediates that result from excited-state electron-transfer reactions involving transition metal coordination complexes and quenchers in solution. These species are generated photochemically or from the interaction of substrates with radiation-generated radicals using continuous and pulse radiolysis techniques. Emphasis is being placed on polypyridyl complexes of Ru(II) and Rh(III), and on viologens in aqueous solution. The yields of reduced species and the uncatalyzed and Pt-catalyzed formation of H_2 are being investigated as a function of pH, ionic strength, and other solution medium parameters. The goal is to understand the structure-reactivity relationships governing the generation of energy-rich charge-separated species and potentially useful fuels.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

191. FORMATION OF FUEL VIA PHOTOCHEMICAL ELECTRON TRANSFER — $88,000 — 01-01
Guilford Jones, II
Department of Chemistry

This study involves photochemical electron transfer reactions which are induced by quenching the excited states of dyes or by irradiation of organic charge-transfer complexes. Appropriately selected reactions may be employed in the photoformation of hydrogen after absorption of visible light and catalyzed reaction of water with charge carriers. CT complexes of viologen and pyridinium ions and electron donors such as aromatic amines are under investigation, including measurement of visible absorption properties, efficiencies of ionic photodissociation, and yields of evolved hydrogen. Pyridinium ions are also being deployed as quenchers of excited ruthenium tris-bipyridyl complexes for comparison with viologen electron relays. Electron transfer processes include reaction of an organic dye, eosin, with electron donor phenols. For this system, rates of excited state quenching and yields of electron transfer determined by flash photolysis are of interest, with particular attention to steric factors which stabilize the products of phenol oxidation.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

192. PHOTOELECTROCHEMISTRY AT IRON OXIDE ELECTRODES — $48,000 — 01-01
John H. Kennedy
Department of Chemistry

The object of the research program is to extend the knowledge of semiconductor photoelectrochemistry for the decomposition of water into hydrogen fuel and oxygen. In particular, a study of iron oxide electrodes in various electrolytes is being investigated. Semiconductor n-Fe_2O_3 is produced by chemical doping, especially with the addition of group IV elements such as Si, Ge, and Ti. Iron oxide doped with Cr_2O_3 is also under investigation because chromium oxide has a lower bandgap than iron oxide and may, therefore, extend the photoresponse to longer wavelength. Photopotentials as a function of redox potential in the electrolyte have been measured. Iron oxide electrodes have also been shown to exhibit high photocurrents in acid solution while still maintaining good stability. Competition between solute species for photogenerated electron holes at the electrode surface is a major objective of the program. Competition between halide and hydroxide ions has been studied and is being extended to various organic solutes using Rotating Ring Disc Electrode techniques.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

193. THEORETICAL STUDIES OF EXCESS ELECTRONS IN FLUIDS: STRUCTURE AND ELECTRON TRANSFER $27,524 01-01
Neil R. Kestner
Department of Chemistry

This research involves the calculation of electron transfer processes, especially those taking place in polar media. We are completing work on small negatively charged water clusters which provide detailed tests of electron trapping processes. Most of the current research involves the study of electron transfer reactions and especially their temperature dependence using multiphonon theory and better liquid models. Accurate calculations of the interactions between electron transfer species in water, especially the ferrous-ferric system, are underway. As a side product of this research, very accurate studies of water-water interactions, have been made. They show clearly the role of many body interactions in condensed phases. Finally, we are studying the complex dependence of electron transfer reactions in frozen media when trap depth variations are considered.

UNIVERSITY OF HOUSTON
Houston, Texas 77004

194. CHARGE SEPARATION IN PHOTOREDOX REACTIONS $160,000 01-01
Larry Kevan 24 mo.
Department of Chemistry FY 82-83

The objective of this research is to probe the molecular mechanistic and structural aspects of charge separation in photoredox reactions in micellar systems in order to eventually couple this charge separation to chemical energy storage. Tetramethylbenzidine has been photoionized to produce the cation radical in liquid and frozen micellar solutions of anionic, cationic and nonionic surfactants. The cation is observed by electron spin resonance and electron spin echo (ESE) spectrometry. Cation-water interactions have been detected by electron spin echo modulation analysis and are found to increase with decreasing alkyl chain length in anionic micelles. It is concluded that the photo produced cation is located asymmetrically within the micellar structure. Stearic acid nitroxide probes have also been used to determine structural aspects of the location of the neutral tetramethylbenzidine molecule in anionicmicelles. Direct electron spin echo detection of laser photogenerated tetramethylbenzidine cation has been achieved in liquid micellar solutions and the phase memory time has been related to structural information.

THE UNIVERSITY OF ALABAMA
Tuscaloosa, Alabama 35486

195. ELDOR INVESTIGATIONS OF RADIATION PROCESSES $57,800 01-01
Lowell D. Kispert
Department of Chemistry

The objective of this research is to determine how a crystalline lattice affects energy transfer and primary radiation and photochemical processes in irradiated organic crystals. Such information is vital to understanding photoinduced solid-state polymerization and stereospecific reactions in solids. Electron spin resonance, electron-nuclear double resonance and electron-electron double resonance spectroscopy are being used to identify the molecular fragments formed and to detect the energy transfer processes that occur. In particular, selected model low molecular weight halogenated carboxylic acid and acetamide crystals are being studied to determine the effect of hydrogen bonding on radical formation and stability as a function of temperature in crystals containing a) varying number of waters of crystallization, b) rotational disorder, c) chirality, d) impurities, and e) varying crystallographic forms. Electron attachment and oxidation processes for model systems containing fluorine, chlorine and bromine as substituents are being determined as a function of excitation source and reaction coordinate.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

196. STUDIES IN SPECTROSCOPY AND CHEMICAL DYNAMICS — $88,000 — 01-01
Aron Kuppermann
Division of Chemistry and
Chemical Engineering

Studies are being conducted using variable angle electron impact spectroscopy to investigate spin-forbidden electronic transitions. A new apparatus with a molecular beam target is being employed that permits the study of systems of low vapor pressure as well as of free radicals. The technique of pulsed ultraviolet laser photoacoustic spectroscopy (PULPS), which has very high sensitivity, is also being utilized to study very weak transitions: spin-forbidden electronic transitions and high-overtone vibrational transitions. The spin-forbidden PULPS studies are aimed both at an understanding of the electronic structure of the excited state and of the dynamics of its relaxation. The dynamic studies involve using a second laser time-delayed with respect to the first one. The system being currently investigated is SO_2. The overtone PULPS studies involve the investigation of highly excited vibrational states. The objective of these studies is to search for vibrationally excited states whose lifetime is sufficiently long for mode-specific chemical reactions to occur.

THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

197. THE FREE-RADICAL AND ION CHEMISTRY OF VOLATILE SILANES, GERMANES AND PHOSPHINES — $91,000 — 01-01
F. W. Lampe
Department of Chemistry

This research program consists of studies of the elementary chemical reactions and reaction mechanisms that play important roles when gaseous silanes, germanes and phosphines and mixtures thereof are irradiated with infrared, vacuum-ultraviolet and ionizing radiation. The photodecomposition, which involves free-radical reaction mechanisms, are studied using intense pulses of infrared radiation from a CO_2-TEA laser and continuous vacuum ultraviolet radiation from rare-gas resonance lamps. Ionic species, $Si_xH_y^+$, $Ge_xH_y^+$ and PH_x^+, are formed in an electric discharge and are then allowed to react with silane, germane, phosphine and other substances under conditions that permit direct study of the elementary reactions. Presently under study are the lifetimes and collisional stabilization dynamics of energy-rich collision complexes and the dynamics of large negative group abstractions from alkyl silanes and germanes.

BROWN UNIVERSITY
Providence, Rhode Island 02912

198. A UNIFIED APPROACH TO CHARACTERIZATION OF COLLISIONS BETWEEN REACTIVE RADICAL PAIRS IN SOLUTION — $50,000 — 01-01
Ronald G. Lawler
Department of Chemistry

A program has been initiated to systematically characterize the interactions between members of a representative class of organic free radicals, having the general structure $\cdot CH_2X$, in aqueous and organic solvents. Four recently developed experimental techniques or phenomena are being employed: (A) Kinetic Electron Spin Resonance, (B) Heisenberg exchange rate measurements using the Electron Spin Echo and Free Induction Decay methods, (C) Chemically Induced Dynamic Electron Polarization, and (D) Chemically Induced Dynamic Nuclear Polarization. Measurements are being carried out on radicals produced by 3 Mev electron radiolysis and laser photolysis using equipment available at Argonne National Laboratory. Standardized methods are being developed for dosimetry using ESR and NMR detection. A simplified unified theory is being developed to relate (A) - (D) to molecular properties.

BRANDEIS UNIVERSITY
Waltham, Massachusetts 02254

199. PHOTOCHEMICAL REACTIONS OF COMPLEX MOLECULES IN CONDENSED PHASE
Henry Linschitz
Department of Chemistry
$96,000
14 mo.
01-01

Electron-transfer reactions of excited molecules lead to high-energy products (radicals) and offer a means of energy conversion and storage. However, such initial interactions may also lead to quenching and energy dissipation. This program is aimed at elucidating the factors which govern the efficiency of primary radical formation. These include excited state redox potential, spin multiplicity, solvent polarity, associated proton displacements and imposed fields. The main test reactions are porphyrin photo-oxidations and ketone photoreductions, in which rates and quantum yields are being studied by laser flash photolysis. In connection with this, triplet and radical extinction coefficients are being obtained by direct energy absorption measurements, providing generally useful actinometric systems. Interactions of singlet and triplet excited states of ketones with simple anions are being studied to clarify spin effects in quenching processes.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

200. THE CONTRIBUTION OF ELECTRONICALLY EXCITED STATES TO THE RADIATION CHEMISTRY OF ORGANIC SYSTEMS
Sanford Lipsky
Department of Chemistry
$180,000
24 mo.
FY 82-83
01-01

A general study is being made of those photophysical properties of organic molecules that have relevance in determining their radiation-chemical behavior. Projects currently in progress include (a) study of the photoionization of TMPD in organic solvents and the effect of perfluorocarbons to quench the photocurrent and the recombination fluorescence and (b) study of the effect of perfluorocarbons to perturb the absorption and emission properties of saturated hydrocarbon liquids by charge transfer interactions and to search for possible photocurrent by virtue of these interactions. Both projects (a) and (b) are designed to better characterize the nature of electronic states in fluids that lie close to the photoionization threshold. In addition we are systematically surveying (c) the effects of temperature and deuteration on emission quantum yields of saturated hydrocarbons and (d) the effects of electron impact energy and scattering angle on the electron energy-loss spectra of saturated hydrocarbons in order to probe further into the nature of their electronic states.

DREXEL UNIVERSITY
Philadelphia, Pennsylvania 19104

201. A STUDY OF PHOTOSENSITIZED REDOX REACTIONS IN MICROEMULSIONS
Raymond A. Mackay
Department of Chemistry
$110,000
24 mo.
FY 81-82
01-01

The objective of this research program is to probe the utility of microemulsions in solar energy conversion systems. Microemulsions are stable fluids consisting here of an oil dispersed in water stabilized by a surfactant and a cosurfactant. The photoreduction of an absorbed dye (principally methyl red) by a reducing agent (principally ascorbate) has been used to examine the effect of microemulsion type, pH, reaction product(s) and sensitizers (type and location) on the quantum yield. The sensitizers employed are chlorophyll a, other chlorins and a number of synthetic surfactant porphyrin derivatives of tetra (pyridyl and carboxy)phenylporphine. The effect of the number and length of the alkyl chains and ring charge on the quantum yield and photostability are being examined. An investigation of the use of microemulsions as photogalvanic cell fluids is in progress, initially utilizing a surfactant thionine-iron (II) system.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

202. ENERGETICS OF THE FORMATION AND REACTIONS OF GASEOUS IONS — $85,000 — 01-01
G. G. Meisels
Department of Chemistry

We work in two areas. In the first, we establish the energetics of the formation, isomerization, fragmentation, and collision reactions of gaseous ions derived from small organic molecules. We investigate ions whose internal energies are well defined by detecting only photoions coincident with near-zero energy electrons. We also use collision induced and high pressure mass spectrometry. Energetics, kinetic energy release, and reaction rates indicate that some molecular ions of methylnitrite, nitromethane and anisol exist in long-lived excited electronic states which do not readily interconvert to the ground state, contrary to a common assumption. In the second area we assess the ionization characteristics of 100 to 1000 eV electrons in order to better model chemistry in tracks of heavy ions such as fission recoils. Linear ionization rates, and the ranges derived from them, are inferred from ion residence time distributions since ion drift is much slower than electron penetration. An ion source with coaxial electron entrance and ion exit apertures is used for this purpose. Range is linear with energy from 100 to 600 eV for N_2,CH_4 and i-C_4H_{10}.

UNIVERSITY OF NORTH CAROLINA/CHAPEL HILL
Chapel Hill, North Carolina 27514

203. ENERGY CONVERSION PROCESSES BASED ON METAL COMPLEX EXCITED STATES — $92,357 — 01-01
Thomas J. Meyer
Department of Chemistry

The basis for the current research effort is in the characterization and exploitation of a series of charge transfer excited states based on metal complexes containing polypyridyl ligands. Detailed photochemical and photophysical measurements are being undertaken in order to understand the origins of excited state lifetimes and reactivity. Attempts are being made to extend the work both to a series of new excited states and to the development of new photochemical pathways based on multiple electron steps. The work with new excited states includes an investigation of the photochemical and photophysical properties of charge transfer chromophores bound to polymers. The one-electron transfer properties of charge transfer excited states are being applied to the photochemical and photoelectrochemical generation and storage of chemical energy.

CLEMSON UNIVERSITY
Clemson, South Carolina 29631

204. INTRAMOLECULAR ENERGY TRANSFER REACTIONS AS A METHOD FOR METAL COMPLEX ASSISTED PRODUCTION OF HYDROGEN — $110,000, 24 mo., FY 82-83 — 01-01
John D. Petersen
Department of Chemistry

This program is designed to study and develop an understanding of excited-state, energy-transfer reactions in mixed-metal, bimetallic complexes. Current studies involve the coupling of highly absorbing, but nonreactive, metal centers to photoreactive metal centers such as metal dihydrides. Recent developments have shown that 2,2'-bipyrimidine bound to metal centers such as $Ru(NH_3)_4^{2+}$, $Fe(CN)_4^{2-}$, $W(CO)_4$ and $Ru(bpy)_2^{2+}$ generate highly absorbing, photosubstitutionally inert metal fragments which are strongly coupled to other metal fragment bound to the remote side of the bipyrimidine bridge. Ground state spectroscopy, stability, and properties are studied by electronic, magnetic resonance, and Mössbauer spectroscopies and cyclic voltammetry.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

205. HIGH ENERGY HALOGEN REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS — $112,700 — 01-01
24 mo.
FY 81-82
Edward P. Rack
Department of Chemistry

The fundamental goal of this project is to understand better the chemical reactivity of high energy monovalent species. High energy reactions of halogen atoms or ions activated by nuclear transformations are studied in gaseous, high pressure and condensed phase saturated and unsaturated hydrocarbons, halomethanes and liquid and solid aqueous solutions of biological molecules. Specifically, the stereochemistry of single chiral center molecules, systematics, mechanisms and halogen reactivity in a collapsing molecular environment and caging of halogen hot atoms in an ice lattice are under investigation. Practical applications of recoil atom chemistry to activation analysis for trace elements or molecules in biological or environmental systems, to radiopharmacy involving synthesis and radioprotection, and to the study of solute-solute and solute-solvent interactions of dilute aqueous solutions of biological molecules are being carried out.

CARNEGIE-MELLON UNIVERSITY
Pittsburgh, Pennsylvania 15213

206. PHOTODECOMPOSITION OF WATER IN HOMOGENEOUS SOLUTION — $60,367 — 01-01
13 mo.
Robert M. Richman
Department of Chemistry

The goal of this project is to study the chemical, photochemical, and electrochemical behavior of compounds that are likely to be useful in solar energy conversion. Mechanisms of energy storage other than redox quenching of long-lived excited states are sought. One line of inquiry follows the photochemistry of dioxomolybdenum compounds, which have the cis-MoO_2^{2+} moiety. Absorption changes are computer simulated to deduce mechanistic pathways following irradiation of the dithiocarbamate, benzacac, and porphyrin compounds. The goal here is to find conditions under which oxygen will be liberated or to characterize whatever photochemistry is observed. A second line of inquiry seeks examples of photodisproportionation reactions. Dimers which, upon irradiation, yield strong oxidants and/or reductants could be used in energy storage schemes. Iron, chromium, and ruthenium dimers are being pursued for their potential to do this photochemistry. For example, irradiation of μ-oxo-bis(tetraphenylporphinato iron (III)) yields the ferryl ion, TPPFeO, which can epoxidize olefins.

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

207. NUCLEAR METHODS IN CHEMICAL KINETICS — $60,000 — 01-01
John W. Root
Department of Chemistry

This research program is designed to probe the fundamental nature of very energetic chemical reactions. The reactions presently under study are initiated by recoiling radioactive fluorine-18 and chlorine-39 halogen atoms, which have been produced using cyclotron induced nuclear reactions. Product analysis is accomplished using conventional radiochemical separations as well as radio gas chromatography. The measured results include the distributions and the relative rates of formation of the labeled organic and inorganic reaction products at sample pressures ranging from 0.1 to 200 atmospheres. The derived results include the mechanisms of product formation, the internal excitation energy distributions, and the unimolecular decomposition and collisional energy transfer behavior of the nascent species formed in hot halogen-for-hydrogen and halogen-for-halogen atomic exchange reactions. With simple fluorocarbon reagents these reactions probe center-of-mass collision energies in the range from ca. 2 to more than 25 eV. The 11th International Hot Atom Chemistry Symposium is being hosted at U.C. Davis during the present contract period.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

208. RESEARCH IN CHEMICAL KINETICS — $160,000 — 01-01
F. Sherwood Rowland
Department of Chemistry

Radioactive halogen atoms (^{18}F, ^{38}Cl) are produced by nuclear reactions, thermalized by multiple collision with an inert parent molecule (SF_6, $CClF_3$), and reacted with various substrate molecules present in low mole fraction in the gas phase. Rapid substitution reactions are observed for many organometallic substances, with the displacement of the metal at the C-M bond ($X + R_nM \rightarrow RX + R_{n-1}M$, with X=F,Cl; M = Pb, Hg, Sn, Ge; R = CH_3, vinyl, etc.). Addition reactions at multiple bonds (e.g., $F + CH_2{=}CHCl$) provide information about the selectivity of such additions and the lifetimes of the resulting radicals. Addition to the C-2 position of $(allyl)_4Sn$ leads to radical decomposition to $CH_2{=}CHF$ on a time scale (10^{-9} sec) indicating non-participation of the other three allyl groups in the energy pool (i.e., non-RRKM behavior). The rates of solar photodecomposition in the upper stratosphere are being calculated for NaOH, NaCl, KCl, and other molecules. Absolute calibration programs continue for trace atmospheric gases, including CH_4, CCl_4, CCl_3F, and CCl_2F_2. Photolysis studies are being carried out with $^{14}CS_2$ and $O^{14}CS$ in the presence of N_2 and O_2.

WORCESTER POLYTECHNIC INSTITUTE
Worcester, Massachusetts 01609

209. THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS — $78,483, 24 mo., FY 81-82 — 01-01
Alfred A. Scala
Department of Chemistry

This research is designed to provide basic information concerning the interactions between high energy radiation and heterocyclic organic compounds. Both vacuum ultraviolet photons and ^{60}Co γ-rays are used as energy sources and reactions of both neutral and ionic species are examined. A series of thermodynamic generalizations have been developed which allow the prediction of major reaction channels for new molecules. The nature of the excited states involved in these reactions is also under investigation. In addition a photoionization mass spectrometer is being used to study the physical organic aspects of gas phase ion-molecule reactions. The ultimate objective of these studies is to compare gas phase ion-molecule reactions with their counterparts in solution. This information will enable a test of some of the basic assumptions of organic chemistry and permit an assessment of the role and importance of the often forgotten solvent.

CHARLES F. KETTERING RESEARCH LABORATORY
Yellow Springs, Ohio 45387

210. PARTICULATE MODELS OF PHOTOSYNTHESIS — $57,000 — 01-01
Gilbert R. Seely

The program consists of the investigation of photophysical and photochemical properties of chlorophyll, absorbed together with other amphiphilic molecules to particles of polyethylene swollen with low molecular weight hydrocarbon diluents. When suspended in aqueous media, the particles are intended to provide a viscous medium for anchorage of the hydrophobic parts of amphiphilic molecules. In general, chlorophyll is maintained in monomeric form in the presence of amphiphiles that interact with it, such as alkylamides, or as fluorescent dimers or higher aggregates at greater concentration. Specific aspects under investigation include absorption, fluorescence, and CD spectroscopy, resolution of the spectra into their components as a function of temperature and concentration, and energy transfer among chlorophyll species and to traps. The photochemistry of chlorophyll in these systems is of interest particularly in regard to the distribution of oxidants and reductants between the aqueous and particle phases.

UNIVERSITY OF PUERTO RICO/MAYAGUEZ
Mayaguez, Puerto Rico 00708

211. PHOTOELECTROCHEMICAL KINETIC CHARACTERIZATION OF PHENOTHIAZINE DYE DERIVATIVES — $45,000 — 01-01
Fernando A. Souto
Department of Chemistry

This research program is designed to assess the potential of new thiazine dye derivatives for the study of solar energy conversion with photoelectrochemical systems in homogeneous solution. Emphasis is being placed on the photoelectrochemistry of hydrophilic derivatives of thionine and methylene blue, compounds that are being produced now with higher chemical selectivity and efficiency than previous reports indicate. Conventional techniques are being employed to study the rates and mechanisms of the electron transfer processes involved in the photoreduction with ferrous ions of the excited states of the new dyes. Particular attention is given to the kinetics and efficiency of photoreduction of the dyes with respect to ground state quenching of the excited states and to thermal reoxidation of photogenerated species. The effects of suitable micellar assemblies and ferric ion chelating agents are being investigated. These studies are expected to provide valuable structural and kinetic information on the photochemistry of the reduction of thiazine dye derivatives so that other new dye derivatives may be designed that are more efficient in an energy conversion arrangement.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

212. DYNAMICS AND MECHANISMS OF CATALYTIC PROCESSES AND HOT CHEMISTRY — $87,106 — 01-01
Leonard D. Spicer
Department of Chemistry

This research is designed to explore reaction kinetics and mechanisms, collision dynamics, and energy transfer in thermal, photochemical, and hot reactions. Photo-assistance of homogeneous catalytic reactions as a mechanistic probe and photochemical modification of catalyst species are of particular interest. Results with Wilkinson's Catalyst show that distinct action spectra can be obtained for hydrogenation and isomerization of 1-hexene. Isomerization occurs with high quantum yield indicating the formation of a new, efficient catalyst species. Hot and thermal reactions of recoil chlorine atoms are also being studied, and the dynamics of nascent chlorinated products are under investigation. A method of forming chlorocarbonium ions from recoil chlorine in SF_6 moderator has been developed and characterized. The vapor phase components in equilibrium with the new solid ammonium trimethylsilylsulfite reported from this laboratory have been identified by FT-IR to be ammonia, sulfur dioxide and silanol. Nucleation phenomena in the presence of laser irradiation at 337 nm have also been studied for gas phase systems containing sulfur dioxide.

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

213. PHOTOELECTROCHEMISTRY WITH CHEMICALLY MODIFIED ELECTRODES — $130,000 24 mo. FY 81-82 — 01-01
Thomas G. Spiro
Department of Chemistry

This research program is designed to investigate the possibility of catalyzing oxidation-reduction reactions at photoelectrodes, with a view toward producing useful products, including fuels, and of protecting electrodes from photocorrosion. Photo- and electro-active molecules are being attached to electrode surfaces in a variety of ways. These include heterocyclic transition metal complexes and metalloporphyrins. Conditions for forming stable electro-active films of these materials are being defined. The films are under investigation for their electron transfer chemistry, and for their potential in stabilizing reactive intermediates, and catalyzing fundamental oxidation-reduction processes. Surface Raman spectroscopy is being used to provide structural information on the films.

MOUNT HOLYOKE COLLEGE
South Hadley, Massachusetts 01075

214. PHOTOELECTROCHEMISTRY OF ORGANIC DYES Mark T. Spitler Department of Chemistry	$114,480 24 mo. FY 82-83	01-01

This project seeks to determine the role of electron transfer in the quenching of the excited states of organic dyes adsorbed at electrode surfaces. An attenuated total reflection technique is used to enable in situ determinations of the quantum efficiency of current producing photoreactions at both metal and semiconductor surfaces. Photooxidation of dyes at ZnO and TiO_2 surfaces is being studied with series of cyanine, merocyanine, and oxanine dyes varied to demonstrate the effect of redox potential, excitation energy, molecular structure, and charge on the electron transfer from the excited state of the dye to the conduction band of the semiconductor. Photoassisted oxidation of dyes at Pt electrodes is also being investigated with these dyes. Estimation of the degree of excitation quenching caused by this oxidation is allowed through concomitant measurements of the fluorescence intensity of the adsorbed dye.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

215. HOT ATOM REACTIONS INVOLVING MULTIVALENT AND UNIVALENT SPECIES Yi-Noo Tang Department of Chemistry	$56,683	01-01

The purpose of this research is to study the reactions of various types of energetic atoms (such as Si-31, C-11, and H-3), and the mechanism of catalytic hydrogenation. For the energetic atoms, the emphasis is on the reactions of Si-31 formed by the nuclear recoil method. The studies include the abstraction, addition and insertion reactions of the hot Si-31 atoms and the derived silylenes and radicals in organic systems such as C_2H_4 and 1,3-butadiene. For the catalytic hydrogenation studies, temperature programmed desorption of T_2 from various types of surfaces are being carried out to reveal the nature of active sites. Hydrogen isotopes such as H_2, D_2 and T_2 are being used to label different kinds of active sites to study the mechanism of hydrogenation and hydrogenolysis processes.

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

216. ELECTRON PHOTOEJECTION IN CARBANIONS Laren M. Tolbert Department of Chemistry	$48,000 15 mo.	01-01

Carbanions eject electrons at very high potentials when irradiated with visible light. The ways in which this potential can be varied as a consequence of the structure of the carbanion is being investigated. 2-Aryl-1,3-diphenylpropenyl anions, for instance, exhibit nearly identical ground state behavior but decidedly different excited state behavior as a consequence of the reduction potential of the central aryl moiety. Conventional physical models—i.e., using electron-donor properties of substituents—are not predictive for excited state behavior, and new models are being sought. A consequence of the high reactivity of photoexcited carbanions is the production of unusual intermediates, e.g., reactive carbenes, in the photochemistry of halogenated carbanions. Such intermediates provide novel synthetic routes to other potential carbanions for photophysical studies.

UNIVERSITY OF ARIZONA/TUCSON
Tucson, Arizona 85721

217. MECHANISMS OF PHOTOCHEMICAL ENERGY CONVERSION BY CHLOROPHYLL Gordon Tollin Department of Biochemistry	$68,000	01-01

Laser photolysis techniques are used to investigate the kinetics and mechanism of light-induced electron transfer reactions between chlorophyll and various donors and acceptors such as EDTA, quinones and viologens. Both homogeneous solutions and heterogeneous matrices (polymer films, lipid bilayers) are studied. Special emphasis is given to vectorial electron transport across the walls of lipid bilayer vesicles. We wish to develop a body of fundamental information which can be used to devise strategies for increasing the yields of the high energy products of such reactions, to physically separate these products and to decrease the probability of recombination (i.e. back reaction), and to facilitate secondary electron transfer to external donors and acceptors. Such information should prove useful in the development of biomimetic systems for practical solar energy conversion based on green plant photosynthesis.

UNIVERSITY OF MASSACHUSETTS AT BOSTON
Boston, Massachusetts 02125

218. INVESTIGATION OF THE STRUCTURE OF PHOTOSYNTHETIC REACTION CENTERS Hans van Willigen Department of Chemistry	$115,525 24 mo. FY 81-82	01-01

The research program involves the study of the structure of photosynthetic reaction centers with the aid of magnetic resonance techniques. Structural information is obtained by probing the unpaired-electron distribution in the photoexcited triplet state of these systems with the aid of Electron Spin Resonance (ESR), Electron Nuclear Double Resonance (ENDOR), and Electron Nuclear Nuclear Triple Resonance (TRIPLE). Research has focused on the development of the methodology of the acquisition and interpretation of ENDOR spectra of photoexcited triplets randomly oriented in solid solution. Using a number of model systems (both ground state triplets as well as photoexcited triplets) it is found that the measurements have to be performed near 4 K. Instrumentation for such measurements has been improved. Currently measurements are performed on a series of (metal) porphyrins in various host matrices to investigate the effects of solvation and aggregation on the (electronic) structure. This information will provide a data base that will be of aid in the interpretation of spectra from reaction centers.

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE
Chicago, Illinois 60680

219. EVALUATION OF THE ESE ENVELOPE MODULATION TECHNIQUE FOR STUDIES OF FREE RADICALS Robert I. Walter Department of Chemistry	$70,624 24 mo. FY 81-82	01-01

Analysis of the electron spin echo envelope modulation (ESEEM) can give precise information on the hyperfine parameters for dilute crystals of paramagnetic species. The objective of this work is to determine whether the method can also yield useful data on free radicals in random glassy solution, the only state in which some important biological systems can be prepared and observed. A series of nitroxide radicals which differ in deuterium labelling of magnetically equivalent sites, or in structural constraints on geometry or internal motion have been prepared and characterized by standard magnetic resonance techniques (EPR, NMR contact shifts, or ENDOR). The same radicals are then examined in a random glassy matrix by the three-pulse electron spin echo technique; these studies are carried out at the Argonne National Laboratory under the supervision of James Norris. The results are expected to indicate the range and precision of data which can be extracted from the ESEEM by adjusting parameters to optimize fit to the modulation, or by Fourier transform methods.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

220. ENERGY TRANSFORMATIONS IN TRANSITION METAL COMPLEXES — $72,532 — 01-01
Richard J. Watts
Department of Chemistry

The structure, photochemical activity, optical spectroscopy and photophysics of solvated transtion metal complexes are being studied. Included in the study are 2,2'-bipyridine complexes of Ir(III) and Rh(III) in which the ligand now appears to participate in both N- and C- bonding to the metal center. These complexes appear to be formed in intramolecular metalation reactions. Techniques of ^{1}H and ^{13}C NMR are being applied to determine the solvated ground state structure of these complexes. Laser flash photolysis techniques are used to establish their excited state and photoredox product absorption characteristics. These techniques also facilitate determination of the decay kinetics of excited states and photoredox products. Photoredox via excited state-ground state disproportionation is also under investigation. An effort to study photochemical and spectroscopic properties of metallofulvalene complexes has been undertaken. Initial activity in this area incoporate high pressure absorption spectroscopy and solvent-induced photoredox reactions.

UNIVERSITY OF NORTH CAROLINA/CHAPEL HILL
Chapel Hill, North Carolina 27514

221. APPLICATIONS OF PHOTOINDUCED ELECTRON TRANSFER AND HYDROGEN ABSTRACTION PROCESSES TO CHEMICAL AND ELECTROCHEMICAL CONVERSION PROCESSES — $130,000 24 mo. FY 81-82 — 01-01
David G. Whitten
Department of Chemistry

The research program involves studies of photochemical redox reactions occurring via electron transfer and hydrogen atom abstraction processes initiated by the excitation of chromophores absorbing visible and near ultraviolet light. Both the direct photochemical reactions are being investigated as well as combined photochemical and electrochemical processes. An example of the latter involves studies of the light-indiced oxidation of various alcohols to produce ketyl radicals which are then oxidized electrochemically concurrent with the production of molecular hydrogen in the photocurrent. This general reaction has been investigated with a variety of light absorbing substrates and a number of different types of electrode material. Direct photoreduction reactions of a number of dyes, particularly thioindigo and various acelated indigo derivatives are also being investigated. Very recent results suggest that, depending upon redox potentials and reducing agents available, several of the indigo dyes can undergo net one or two electron reduction processes under single photon activation. The effect of the substrate structure on photoredox reaction efficiency is being widely investigated.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

222. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY — $21,019 — 01-01
J. E. Willard
Department of Chemistry

The objectives of this continuing project are to obtain a better understanding of the production, migration, trapping, reactions and spectra of free radicals, hydrogen atoms, electrons, and ions formed in solid organic matrices at 4 K - 200 K. The species studied are formed by irradiation with γ-rays, X-rays, and ultraviolet radiation. Electron spin resonance, ultraviolet, visible and infrared spectrometry are used for analysis. Current emphasis is on the investigation of hydrogen atoms, free radicals and mercury adducts formed by mercury photosensitized decomposition of CH_4 in CH_4 and rare gas matrices; reactions of CH_2 formed by the photolysis of radiation-produced radicals;and the role of neutralization processes in radical production in radiolyzed hydrocarbons.

THE UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37996

223. STUDIES OF RADIATION-PRODUCED RADICALS AND RADICAL IONS $85,000 01-01
T. Ffrancon Williams
Department of Chemistry

The major objective of this program is to identify and characterize free radical and radical ion intermediates generated by irradiation of molecular systems. Current emphasis is being placed on the radical ions produced in the primary chemical processes resulting from the absorption of high energy radiation. Novel radical ions derived from saturated molecules are being generated and stabilized in suitable solid matrices, examples being fluorocarbon radical anions in hydrocarbon matrices and the radical cations of alkanes and ethers in fluorocarbon matrices. Electron spin resonance (ESR) spectroscopy is used to detect these paramagnetic species. Measurements of hyperfine coupling constants, including those of ^{13}C-labeled radicals, are being made on each radical species to provide information about its geometrical structure and spin density distribution. The chemical reactivity of these species is also being investigated. Studies are also underway on the generation and characterization of organometallic radicals and radical ions in systems which are relevant to solar energy conversion.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

224. PHOTOCHEMICAL ENERGY STORAGE: STUDIES OF INORGANIC PHOTOASSISTANCE AGENTS $220,000 01-01
Mark S. Wrighton
Department of Chemistry

Research in this program is aimed at understanding and characterizing photosensitive solids that can be used to effect the conversion of light to electricity or fuel. Semiconductor or photoconductor materials can be used as photoelectrodes in electrochemical cells where the optical to electrical or chemical energy conversion efficiency is governed by the energetics and kinetics at the photoelectrode/liquid electrolyte interface. Photoelectrode materials such as n- and p-Si, InP, GaAs, WS_2 and intrinsic a-Si:H are under study for use in electricity or fuel-forming reactions such as H_2 evolution from H_2O. Experimentation to characterize interface energetics and to manipulate the interface states for these materials is being carried out for photoelectrodes in contact with aqueous or non-aqueous electrolytes. A variety of photoelectrode surface modification procedures, including molecular derivatization, are being explored to alter the kinetics for O_2 and H_2 evolution from H_2O. New solvent/electrolyte/redox couple combinations are also under study to elaborate basic principles and to find new, efficient, durable photoelectrochemical devices.

Chemical Physics

CORNELL UNIVERSITY
Ithaca, New York 14853

225. STUDIES OF THE COMBUSTION OF MODEL FUELS WITH LOW HYDROGEN CONTENT $49,937 01-02
Simon H. Bauer
Department of Chemistry

Our objective is to compare the sooting characteristics of several structurally distinctive hydrocarbons with low H/C ratios, when pyrolyzed at temperatures 1500 to 2500°K, and when burned at low O_2/fuel levels. Our investigations are performed in a single-pulse shock-tube which is heated to approximately 425°K, so that compounds in the molecular weight range 130-150 (AU) can be manipulated in the vapor phase. We analyze the residual gases chromatographically, both of the gas phase and of solutions of those low vapor pressure products which are carried by the argon diluent from the shock tube into the heated sample containers. The onset of sooting, and the relative amounts developed during the initial stages of condensation is determined by the percent of absorbed He/Ne laser light, which is directed along the axis of the 1" I.D. shock tube. Thus far we have shock heated 1% (in Ar) of C_6H_6 and $C_6H_5CH_3$, to develop and test the essential operational procedures, and we have initiated investigations of the pyrolysis of napthalene.

THE UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

226. TOPICS IN FINITE-TIME THERMODYNAMICS $65,000 01-02
R. Stephen Berry
Department of Chemistry

This program continues the extension of thermodynamic analyses to processes subject to constraints on their rates or times of operation. The span of the work extends from the demonstration of newly discovered principles to finding new devices and new ways to optimize the performance of existing devices and processes. The concept of available work (also called availability and exergy) is being extended to provide a measure of the maximum work extractable from a system allowed to relax for a fixed, finite interval from an initial state toward equilibrium with its surroundings. The evaluation of this extended, finite-time available work appears to be associated with lengths computed with the so-called Weinhold metric. Of a more concrete nature, the methods of finding extremal work for processes operating at nonzero rates are being extended from the earlier work largely devoted to mechanical systems to systems involving chemical work, particularly to separation processes. A new type of solar-driven engine is being developed theoretically, based on a working fluid that operates between two chemical forms, in which the system is continuously in contact with both the hot and cold reservoirs at all times.

COLUMBIA UNIVERSITY
New York, New York 10027

227. ENERGY PARTITIONING IN ELEMENTARY GAS PHASE REACTIONS $65,000 01-02
Richard Bersohn
Department of Chemistry

The mode of energy release of elementary reactions of atoms with di- and triatomic molecules is being studied by means of laser induced fluorescence (LIF). Incident to these studies LIF was observed in nitrogen molecules and in sulfur atoms in their ground (^3P) and excited (^1D) states. When irradiated at 248 nm, OCS was found to dissociate primarily into $S(^1D)$ atoms but that the rate constant for conversion of $S(^1D)$ into $S(^3P)$ is very high. Reactions of S atoms in both of those states with OCS molecules have been studied by LIF of the reactant S atoms and the product $S_2(^3\Sigma)$ molecules. The spin forbidden reaction with $S(^1D)$ produces vibrationally and rotationally cold S_2 whereas the less exothermic spin allowed reaction with $S(^3P)$ paradoxically produces hot S_2 molecules. A possible explanation is that the spin forbidden reaction takes place via a "long lived" complex COS_2 which undergoes intersystem crossing and subsequent symmetric dissociation.

Chemical Physics, continued

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

228. THEORETICAL STUDIES OF COMBUSTION DYNAMICS \$56,000 01-02
Joel M. Bowman
Department of Chemistry

The objective of this research is to develop and apply approximate but accurate quantum methods to important reactions in gas phase combustion. A theory in which a reduced number of degrees of freedom are treated dynamically and the remaining degrees of freedom are treated by transition state theory has been developed. Recently the theory has been extended by a rigorous derivation beginning with the exact Schroedinger equation. Rate constants, integral and differential cross sections have been or are being calculated using this theory for the $O + H_2$, $O + D_2$, and $O + HD$ reactions using a fit to an accurate ab initio potential energy surface. In addition, differential cross sections have been calculated for the reactions $F + H_2(v=0) \rightarrow HF(v'=2), HF(v'=3) + H$, $F + D_2(v=0) \rightarrow DF(v'=3), DF(v'=4) + D$, $F + HD(v=0) \rightarrow HF(v'=3), DF(v'=2)$, and compared to the experimental results of the Y.T. Lee group. The major experimental findings are reproduced. The interpretation of certain pronounced features in the experimental differential cross sections to form specific product vibrational states as being due to resonances has been directly confirmed by the calculations.

Yale University
New Haven, Connecticut 06520

229. SIMULTANEOUS MULTIPOINT MEASUREMENTS OF DENSITY GRADIENTS AND TEMPERATURE IN A FLAME \$63,000 01-02
R. K. Chang, Dept. of Applied Physics
B. T. Chu and M. B. Long, Dept. of Applied Mechanics

New nonintrusive, in situ optical techniques are being developed which are capable of providing quantitative measurements of temperature and gas species concentration in turbulent reacting flows. Several different light scattering processes are being used for these studies with special emphasis being placed on scattering mechanisms which have potential for providing measurements at many points simultaneously. Rayleigh scattering has been used to determine the instantaneous gas concentration field at 10,000 points within a plane intersecting a nonreacting flow. Raman scattering is also being pursued as a means for making two-dimensional gas concentration measurements in reacting flows. These "Ramanography" experiments are being conducted at the Combustion Research Facility at Sandia National Laboratories in Livermore, California. The unique characteristics of the facility's Diana dye laser make this experiment feasible. Another group of experiments is seeking to evaluate the applicability of broadband rotational CARS to making single-shot, spatially resolved measurements of flame temperature.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

230. UNIMOLECULAR DECAY DYNAMICS OF INTERNAL ENERGY SELECTED MOLECULES \$100,320 01-02
24 mo.
FY 81-82
F. Fleming Crim
Department of Chemistry

This program is an experimental study of the unimolecular decay dynamics of internal energy selected molecules using direct production of highly vibrationally excited molecules by dye laser excitation of overtone vibrations combined with time resolved spectroscopic detection. Previous measurements detecting product chemiluminescence have been extended to other overtone vibration excitations in order to test the role of mode identity in the decay dynamics and to provide more extensive comparisons with statistical theory. An even more detailed view of unimolecular decay dynamics is coming from recent experiments in which laser induced fluorescence probes the OH produced in the overtone vibration induced decomposition of hydroperoxides (t-BuOOH and HOOH). These experiments provide overtone excitation spectra, state-selected unimolecular decay rates, and product quantum state distributions.

SRI INTERNATIONAL
Menlo Park, California 94025

231.	COMBUSTION RESEARCH PROGRAM: FLAME STUDIES, LASER DIAGNOSTICS AND CHEMICAL KINETICS David R. Crosley Molecular Physics Laboratory	$100,000	01-02

This research program involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the chemistry of combustion processes. The research comprises several related parts: LIF probing of flat flames, the development of an LIF spectroscopic and collisional data base, computer modeling of combustion chemical networks, development and application of rate constant estimation methods, and a laser pyrolysis (LP)/LIF experiment. The systems under study are NH_3/O_2, CH_3NH_2/O_2, $CH_4/NH_3/O_2$, and $C_3H_8/NH_3/O_2$, whose chemistry is important in NO_x formation in combustion systems. The LP/LIF technique has been developed within the last year. In it, reactants are rapidly heated through absorption (by SF_6 seeded in the mixture) of pulsed CO_2 laser radiation, with LIF measurements of radical concentrations and temperature made as a function of time. The LP heating processes and the test reaction OH + CH_4 have been investigated thus far, in the range 800-1400 K. Extensions to other radical reactions and high-temperature collision processes important for LIF diagnostics are under way.

WILLIAM MARSH RICE UNIVERSITY
Houston, Texas 77001

232.	INFRARED ABSORPTION SPECTROSCOPY WITH COLOR CENTER LASERS Robert F. Curl Department of Chemistry	$57,000	01-02

This research program is directed at the development of high sensitivity, high resolution methods for detecting and monitoring small free radical species which are thought to be important intermediates in combustion by means of infrared absorption spectroscopy using color center laser sources. The lowest electronic transition of C_2H near 3800 cm^{-1} has been observed for the first time using a sensitivity enhancing absorption spectroscopy method developed in this program which utilizes the magnetic rotation effect to balance out source noise from the laser. Another method being developed is aimed at situations where Zeeman modulation is not possible and uses frequency modulation of the source with the molecular absorption acting as a discriminator. The source frequency modulation is introduced by means of phase modulation using an electro-optic crystal. This tone modulation scheme has been tested and does work, although there is an unexpected rolling background which is now understood and can be eliminated. Future work will focus on obtaining the spectra of new species such as CH_2OH and HCCN.

UNIVERSITY OF COLORADO
Boulder, CO 80309

233.	LASER PHOTOELECTRON SPECTROSCOPY OF IONS G. Barney Ellison Department of Chemistry	$53,000	01-02

Laser photoelectron spectroscopy has been used to study a number of negative ions. During the last year our spectrometer has reached its ultimate resolution of 20 meV (FWHM). A careful study has been completed of the nitroxide ion, HNO^-. Studies are well underway with HOO^-, C_2O^-, and $HCCO^-$ as well. During the next year studies will be completed on a wide variety of C_3 ions. The experiment provides direct, reliable thermodynamic information such as electron affinities, and dissociation energies for ions and radicals. These are crucial data required for an understanding of many combustion processes and atmospheric chemistry.

UNIVERSITY OF OREGON
Eugene, Oregon 97402

234. LASER SPECTROSCOPY OF COMBUSTION INTERMEDIATES --- 01-02
Paul C. Engelking
Department of Chemistry

Laser induced fluorescence measurements of the electronic spectra of molecular radicals found in combustion systems are being made. Radicals are prepared for study in either a fast flow reactor, or in a cold molecular nozzle expansion; the latter makes the study of the complex rotations of the radicals simpler. Dispersion of the laser induced fluorescence gives spectroscopic information about the structure and the internal dynamics of both the upper and lower states involved in the observed electronic transitions. Several alkoxy radical spectra have been observed and vibrationally analyzed, but await rotational analysis. Several open-shell cyano cations (XCN^+) have been examined at high resolution under cold conditions, and the forbidden CF a–X transition has been rotationally analyzed on both the 1,0 and 0,0 bands. The analogous transition in CH is now being sought.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

235. INFRARED LASER INDUCED ORGANIC REACTIONS $50,300 01-02
William E. Farneth
Department of Chemistry

This project is an investigation of the potential and present utility of high power, infrared lasers for initiating and directing chemical reactions of organic molecules. Laser-induced chemical reactions in both homogeneous gas phase systems and in heterogeneous gas/solid mixtures are being examined. Particular emphasis is placed on characterizing systems that show several competitive reaction pathways, and understanding the variation in yield and product ratios with experimental parameters in terms of simple mechanistic models. Completed work on vinylcyclopropane, bicyclopropyl-d_4 and diethylcarbonate-d_5 suggests that changing pressure, laser fluence or frequency can produce only modest alterations in product ratios. Heterogeneous gas/solid laser chemistry promises to be more responsive because of the existence of at least two other important variables, the nature of the surface, and the beam/solid geometry. The laser-induced decomposition of 2-propanol over CuO yields acetone and propene in a ratio that can be varied by over two orders of magnitude by simple changes in reaction conditions.

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

236. LOW ENERGY ION-MOLECULE REACTIONS AND CHEMIIONIZATION KINETICS $60,000 01-02
James M. Farrar
Department of Chemistry

This research program is devoted to an understanding of the dynamics of important reactions of gas phase cations as related to combustion processes. Molecular beam scattering is employed, and measurements of product energy and angular distributions as a function of reagent translational energy provide insights into reaction dynamics of proton transfer reactions, with special emphasis on the formyl cation HCO^+. Proton transfers from HCO^+ to H_2O, CH_3OH, and C_2H_5OH are all exothermic and proceed in a direct stripping reaction. In the latter two cases, the protonated alcohol may undergo two unimolecular decay channels: C-O bond cleavage to a carbonium ion plus H_2O; and elimination of molecular hydrogen across the C-O bond, yielding protonated aldehydes. Recoil distributions and isotope effect measurements indicate the importance of tunnelling through the exit channel barrier in the latter reaction. Current work involves further studies of proton transfer reactions of HCO^+ and initiating studies of H_3O^+ proton transfer chemistry and reactions of CH_3^+.

AEROCHEM RESEARCH LABORATORIES, INC.
Princeton, New Jersey 08540

237. EXPERIMENTAL DETERMINATION OF RATE COEFFICIENTS FOR IMPORTANT COMBUSTION/ FUEL CONVERSION REACTIONS BY A NOVEL HIGH TEMPERATURE PHOTOLYSIS TECHNIQUE — $85,000 — 01-02
William Felder

The aim of this project is to measure the rate coefficients and their temperature dependences of isolated, elementary free radical reactions which are of key importance in combustion and pollutant formation (or destruction) processes of fossil fuels. Flash photolysis of parent compounds forms the free radicals and resonance fluorescence or absorption is used to monitor their concentrations for rate coefficient measurements. The range of this technique was extended in this work to permit measurements from room temperature to practical combustion temperatures (ca. 1500°C). Work on production and measurement of CH_3 for kinetic studies with O_2 and O using optical absorption techniques shows that such studies require a different apparatus geometry from the current one. Insufficient column densities of CH_3 are produced from the flash photolysis of acetone or methyl iodide to allow absorption kinetic measurements; a longer path length is required. A new apparatus for CH_3 studies is being designed. Measurements on OH reactions above 700°C resumed after improving flash lamp performance, apparatus geometry, and the signal processing system.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

238. REACTIONS OF IONS WITH ATOMIC AND MOLECULAR FREE RADICALS — $33,000, 7 mo. — 01-02
W. Ronald Gentry
Department of Chemistry

In the reactions between two atomic or molecular species in which both species have open-shell electronic configurations, there will usually be several closely-spaced electronic potential energy surfaces for the system. Transitions among these surfaces may play an important role in the reaction dynamics. The University of Minnesota merged molecular beam facility is unique in its capability for measuring microscopic reaction cross-sections for such systems, over the range of relative kinetic energy from 0.001 eV to 30 eV. Recently completed work includes investigations of the reactions $H_2^+ + X \rightarrow XH^+ + H$, where X = C, N, O, F. The influence of the atomic quadrupole moment at very low kinetic energies permits the reaction probability to be determined as a function of angular momentum projection quantum numbers. Systems presently being studied include the reactions $X^+(XH^+) + YH(Y) \rightarrow XY^+ + H$, where X,Y = C, N, O, F.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

239. REACTION MECHANISMS IN COMBUSTION: FORMATION OF SOOT AND POLYCYCLIC AROMATIC HYDROCARBONS — $64,000 — 01-02
William A. Goddard III
Department of Chemistry

We are studying the microscopic mechanisms of the gas phase and heterogeneous processes involved in the formation of soot and polycyclic aromatic hydrocarbons (PCAH). The initial emphasis is on the mechanisms of formation of precursors to the soot nuclei. Later we will examine the homogeneous and heterogeneous processes (polymerization, chemisorption onto the soot nucleus, and dehydrogenation) involved in the growth of the soot nuclei and the formation of PCAH. In carrying out these studies, we use ab initio theoretical methods including electron correlation (generalized valence bond, configuration interaction) to calculate detailed potential surfaces for the various reaction pathways. We have also examined the reaction mechanism for

$$NH_2 + NO \rightarrow\rightarrow N_2 + H_2O ,$$

presumed to be the critical step in the thermal $DeNO_X$ process for converting NO to N_2 in stationary power plants.

UNIVERSITY OF ILLINOIS/CHICAGO
Chicago, Illinois 60680

240. KINETICS OF ELEMENTARY ATOM AND RADICAL REACTIONS $100,000 01-02
Robert J. Gordon
Department of Chemistry

The objectives of this research are to measure the reaction rates and to study the dynamics of elementary gas phase reactions. One reaction being investigated is D+HCl, which yields either abstraction (DH+Cl) or exchange (H+DCl) products. Previous determinations of the abstraction to exchange ratio differed by as much as four orders of magnitude. Using the real time method of laser photolysis with resonance fluorescence detection, it was found that the rate of the exchange process is less than 0.2% of the abstraction rate at 325 K. This finding supports the theoretical prediction of a large barrier inhibiting the exchange reaction. Another reaction being studied is O+HD, which is important for understanding combustion processes. Resonance fluorescence detection of O atom decay is being used to measure the total reaction rate, while laser induced fluorescence of OH and OD is employed for determining the branching ratio.

BROWN UNIVERSITY
Providence, Rhode Island 02912

241. INTERACTIONS OF MOLECULES WITH SURFACES $62,000 02-01
E.F. Greene
Department of Chemistry

Surfaces of Si, SiO_2, SiC, and graphite are studied by measuring the rate of formation and yield of ions produced when the surfaces are hit by beams of Cs, K, Na, Li, and Tl atoms. Interpretation of the results over a range of surface temperature yields information about the work function of the surface, phase changes occurring in the surface, the energies of adsorption of the atoms, their diffusion on and into the surface, and their interactions as they move. In a second experiment, highly expanded nozzle beams of He and Ar are scattered from the basal plane of graphite, velocity analyzed, and detected over a range of scattering angles to probe the nature of the surface. In a third experiment molecules such as $W(CO)_6$, trioxane, paraldehyde, 3-sulfolene, and tetramethyl dioxetane are accelerated to high speeds in a seeded nozzle beam and suddenly brought to rest when they hit a stationary surface. In some cases the sudden transfer of kinetic to internal energy leads to decomposition when the kinetic energy exceeds a threshold value.

UNIVERSITY OF UTAH/SALT LAKE CITY
Salt Lake City, Utah 84112

242. INFRARED LASER-INDUCED PHOTOCHEMISTRY $66,000 01-02
William A. Guillory
Department of Chemistry

The objective of this research program is to use the phenomenon of infrared multiple-photon absorption (MPA) to study elementary photochemical and photophysical processes occurring in flame and combustion systems. Emphasis is being placed on state-to-state energy transfer processes in medium-sized molecules and state-selective chemical reactions. We are presently studying the energy flow dynamics in propynal, glyoxal, and methylglyoxal by the use of laser stimulated pumping of CH_3F and SF_6 to efficiently transfer energy into aldehyde molecules. Rotational and vibrational state selective reaction of CH(J,v) + CO + OH is presently being studied using nanosecond time-resolved spectroscopy.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

243.	STUDIES OF COMBUSTION KINETICS AND MECHANICS David Gutman Department of Chemistry	$80,000	01-02

The purpose of this research is to gain a more thorough and more basic understanding of hydrocarbon combustion mechanisms through obtaining an increased knowledge of the reactivity and role of polyatomic free radicals which are involved in combustion. A new versatile technique to generate polyatomic free radicals has been coupled with a sensitive method of monitoring their concentrations. Radicals are generated by the infrared multi-photon-induced decomposition of suitable precursors, and photoionization mass spectrometry is used to monitor their concentrations during the reaction with other molecules present in the system. The facility is now being used to identify suitable precursors which have the general formula C_6F_5R, where R is the free-radical of interest. New procedures are being used to study recombination reactions quantitatively including the self reactions of acetyl and phenyl radicals. Absolute rate constants are being measured, product channels are being identified, and branching constants for each of the reactive route is being determined.

STANFORD UNIVERSITY
Stanford, California 94305

244.	COMBUSTION GAS SPECTROSCOPY USING TUNABLE LASERS R. K. Hanson Department of Mechanical Engineering	$62,000	01-02

Objectives of this research are: (1) the measurement of fundamental spectroscopic parameters (band strengths and collision widths) for critical combustion species, particularly pollutants and radicals; and (2) the development of tunable laser absorption techniques for species measurements in studies of chemical kinetics. Laser sources include a tunable CW infrared diode laser, a tunable CW ring dye laser, and discretely tunable CO and CO_2 lasers. Species currently under study include HCN, CO, OH, C_2H_2,H_2O and CH_3 . Measurements are made over a range of conditions in a controlled-temperature absorption cell, in the post-flame region of a flat flame burner and in a shock tube.

STANFORD UNIVERSITY
Stanford, California 94305

245.	THE KINETICS OF SOME REACTIONS OF HCN AT HIGH TEMPERATURES R. K. Hanson and C. T. Bowman Department of Mechanical Engineering	$32,000 6 mo.	01-02

The objective of this research program is the determination of the mechanisms and rate parameters of HCN reactions at high temperatures. A shock tube is used to heat various gas mixtures containing HCN, and spectroscopic diagnostics are employed to monitor time-histories of important species during reaction. Reactions of particular interest include the thermal decomposition of HCN and the reactions of HCN with CN, H, O and OH.

HOWARD UNIVERSITY
Washington, District of Columbia 20059

246. LASER STUDIES OF THE DYNAMICS OF ATOM-MOLECULE REACTIONS William M. Jackson Department of Chemistry	$47,000	01-02

This program has been designed to use tunable dye lasers to measure the quantum state distributions of free radicals formed as a result of atom molecule reactions. A secondary objective is to probe free radicals in individual quantum states to determine how these free radicals react with stable and unstable molecules. In addition to using tunable dye lasers to monitor these free radicals, other lasers such as excimer lasers have been used to produce free radicals in unstable molecules. The dynamical process associated with photodissociation has been characterized for various systems to ensure that we understand the way in which we produce these free radicals before we try to obtain detail kinetic information. The reaction of CN radicals with NO has been reinvestigated and a discrepancy between our rate constants and the rate constant reported in the literature is about a factor of two. We are currently investigating the nature of this discrepancy.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

247. HIGH RESOLUTION INFRARED SPECTROSCOPY: DISCRETE STATES IN THE QUASICONTINUUM Kenneth C. Janda Department of Chemistry	$60,000	01-02

Molecular beam laser photodissociation spectroscopy is being used to characterize the rate of intramolecular energy redistribution in highly excited vibrational states of molecules. van der Waals molecules are used as prototypes for this effect because energy redistribution results in breaking of a weak bond--a process which is easy to observe. Results have been obtained for clusters containing C_2H_4, C_2F_4, C_6H_6, BCl_3, CO_2, CF_3I, CF_3Br and CF_2Cl_2. All of the clusters dissociate with excited state lifetimes shorter than 10^{-9} sec. Ethylene containing clusters, irradiated at 950 cm^{-1}, dissociate in less than 10^{-12} sec. Current efforts are concentrated on two types of experiment. First, survey spectra for a variety of molecules are being recorded to create a catalog of rate versus molecular structure data. Second, attempts to record high resolution spectra of ArHF and $ArCO_2$ are being made to help understand the dynamics of these molecules in detail.

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

248. MULTIPHOTON DISSOCIATION SPECTROSCOPY AND PHOTOCHEMISTRY Philip M. Johnson Department of Chemistry	$52,000	01-02

The detection and characterization of radicals and other intermediates of gas phase reactions is necessary for understanding the basic processes occurring in combustion and atmospheric chemistry. This research is developing techniques for the production and spectral investigation of these species. In order to produce intermediates of combustion processes, clusters of hydrocarbon and oxygen are produced in a supersonic expansion and irradiated with an excimer laser. Reaction products are detected and spectrally investigated using multiphoton ionization-mass spectroscopy. The characterization of these species is providing evidence of reaction mechanisms and enables their detection in more complex environments. Reactions between benzene and oxygen in clusters have been shown to produce a wide range of reaction products which include up to four oxygen atoms. More complex mixed clusters will provide an insight into solid state photochemical reactions in systems of managable size, and produce reaction intermediates for spectral analysis which are otherwise diffult to obtain in an environment suitable for detailed study.

UNIVERSITY OF NEW ORLEANS
New Orleans, Louisiana 70148

249.	IDENTIFICATION AND TEMPORAL BEHAVIOR OF RADICAL INTERMEDIATES FORMED DURING THE COMBUSTION AND PYROLYSIS OF GASEOUS FUELS Ralph D. Kern, Jr. Department of Chemistry	$47,000 10 mo.	01-02

The formation of soot from the pyrolysis and combustion of aromatic fuels is a process of importance in the design of energy efficient and environmentally acceptable engines and furnaces. The chemical kinetic pathways which precede soot formation are being investigated by recording the product profiles generated during the thermal decompositions of toluene, benzene, butadiene, and acetylene. The reaction zone is created by the passage of a reflected shock wave and the gas is analyzed dynamically by a time-of-flight mass spectrometer. The major products detected in the pyrolyses of toluene and benzene were acetylene and polyacetylenes up to C_8H_2 which were shown to be relatively stable under these reaction conditions. Carbon atom balances derived from the observed products accounted for 70-100% of the total carbon atom input. The major finding of this work is that the reaction routes utilized mostly in the pyrolyses of aromatics are those involving ring fragmentation steps as opposed to ring condensations which occur to a much lesser extent over the temperature (1400-2300 K) and pressure (0.21-0.57 atm) range investigated.

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE
Chicago, Illinois 60680

250.	LASER SCHLIEREN, SHOCK TUBE STUDIES OF HIGH TEMPERATURE HYDROCARBON PYROLYSIS RATES John H. Kiefer Department of Energy Engineering	$57,000	01-02

The purpose of this project is the determination of rates and mechanisms for fuel hydrocarbon pyrolysis at high temperatures. The experiment uses the laser-schlieren, shock tube technique which provides accurate rates for initiation and other secondary reactions to previously unattainable temperatures. Rates and mechanisms for the pyrolysis of propane, propene, ethane, ethylene, acetylene, and the butenes are being determined. The ethane study probes the high temperature reactions of methyl radicals, both radical dissociation and bimolecular reaction. The ethylene/acetylene study suggests alterations in mechanism of the pyrolysis of acetylene leading to the formation of solid carbon.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

251.	DEPOPULATION RATES FOR COMBUSTION-RELATED SPECIES IN LONG-LIVED VIBRATIONALLY OR ELECTRONICALLY EXCITED LEVELS James L. Kinsey and Robert W. Field Department of Chemistry	$100,000	01-02

In this research program a new technique, Stimulated Emission Pumping (SEP), is being used to investigate the properties of vibrationally hot electronic ground state and electronic metastable levels of a number of small molecules such as HCCH, H_2CO, and CO. The initial phases of this work have concentrated on the demonstration of SEP for preparing molecules in such states with complete rovibronic selectivity but without the usual limitations imposed by vibrational and electronic selection rules. Having demonstrated the power of SEP to prepare chemically significant populations in single levels with in excess of 25,000 cm^{-1} of vibrational excitation, the focus has shifted to an attempt to identify levels which exhibit structural features unlike those of the majority of nearby levels. The collisional and chemical properties of these structurally unusual levels will be examined by the combination of SEP preparation with time-resolved LIF probing.

Chemical Physics, continued

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

252. IONIC ASPECTS OF SOOT FORMATION — $60,000 16 mo. — 01-02
Walter S. Koski
Department of Chemistry

A number of studies of hydrocarbon flames indicate that ions play an important part in the process leading to soot formation. Much of this information cannot be adequately interpreted because of the dearth of knowledge of the thermodynamic properties of the ions and of the pertinent ion chemistry. Using ion beam techniques and tandem mass spectrometers the cross sections of pertinent ion molecule reactions are being measured as a function of projectile ion kinetic energy. Threshold measurements are being used to obtain information on the heats of formation of ions. In view of the proposed importance of charge transfer and proton transfer to aromatic molecules we have measured the cross sections for such reactions between H_3O^+ and benzene and napthalene and will measure the corresponding reactions using CHO^+ as the projectile ion. Ion molecule reactions of $C_3H_3^+$ with acetylene, ethylene etc. are also being studied.

STATE UNIVERSITY OF NEW YORK AT BUFFALO
Amherst, New York 14226

253. MULTIPHOTON INTERACTIONS IN MOLECULES WITH PICOSECOND LASER PULSES — $57,000 — 01-02
Hoi-Sing Kwok
Dept. of Electrical and Chemical Engineering

Picosecond CO_2 laser pulses are employed in this research program to study the process of infrared laser-induced photochemistry in polyatomic molecules with the goal of achieving mode-selectivity. During the reporting period, a picosecond CO_2 laser system has been successfully constructed using the OFID scheme. The system has been thoroughly characterized in terms of pulse duration, absorption saturation in the hot CO_2 resonant medium and peak power efficiency. 30 picosecond pulses of 1.5 MW peak power are now routinely available. Preliminary measurements on multiphoton absorption behavior of CF_3Br were performed. A Varian model 3700 gas chromatograph has been installed and characterized. This system will be connected to the laser system for on-line diagnostics. Experiment is now underway to analyze the products of multiphoton induced dissociation in CF_3Br using picosecond pulses with various ambient molecules such as H_2 and He.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

254. MEASUREMENT OF RADICAL SPECIES CONCENTRATIONS AND POLYCYCLIC AROMATIC HYDROCARBONS IN FLAMES BY FLUORESCENCE AND ABSORPTION USING A TUNABLE DYE LASER — $81,854 — 01-02
N.M. Laurendeau and D.W. Sweeney
School of Mechanical Engineering

The goal of this research program is the development of quantitative laser fluorescence techniques for the measurement of flame radical and polycyclic aromatic hydrocarbon (PAH) concentrations. During the past year we have demonstrated accurate laser-saturated fluorescence techniques for measuring OH concentration and rotational temperature. The laser-saturated fluorescence measurements have been shown to be insensitive to collisional transfer rates by comparing fluorescence and absorption measurements in $H_2/O_2/N_2$ flat flames at pressures ranging from 30 to 240 torr. Single pulse laser-saturated OH fluorescence measurements have been demonstrated in 350 torr flames. Current research includes (1) laser-saturated NH fluorescence measurements, (2) laser fluorescence studies of PAH compounds in a vapor cell at room and elevated temperatures and (3) laser-saturated OH fluorescence measurements in sooting $CH_4/O_2/N_2$ flames.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

255. THEORETICAL STUDIES ON HETEROGENEOUS COMBUSTION $48,000 01-02
Chung K. Law
Department of Mechanical and Nuclear Engineering

This program aims at gaining fundamental understanding on the basic physical and chemical mechanisms governing the vaporization, ignition, combustion, and extinction of fuel droplets and sprays in environments simulating those within practical combustors. During the reporting period we have investigated the importance of gas-phase transient diffusion on droplet combustion by suppressing all other unsteady processes. Results show that this transient diffusion increases the burning rate, reduces the flame size and increases the flame temperature. These modifications, however, are generally quite small even when the system pressure is close to the fuel's critical point. Therefore it is quite adequate to assume gas-phase quasi-steadiness in modeling droplet combustion. We have also formulated a theory describing droplet combustion under the combined influence of forced and natural convection. The states of gasification, ignition, steady burning, and extinction have all been analyzed. Explicit expressions for the gasification and burning rates, and criteria governing ignition and extinction, have also been derived.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

256. INTERMOLECULAR ENERGY TRANSFER PROCESSES $40,000 01-02
Edward K.C. Lee
Department of Chemistry

This research program is designed to probe dynamics of energy flow in simple excited molecules through collisions and in chemical reactions. Selective excitation with ultraviolet lasers and subsequent monitoring of fluorescence decay provides information on radiative decay, intramolecular energy redistribution and collisional energy transfer involving specified electronic, vibrational and rotational states. Relaxation rates of sulfur dioxide and formaldehyde are being measured. Free radical reactions involving molecular oxygen important to hydrocarbon combustion are studied by infrared spectroscopy, after photooxidation of aldehydes in solid oxygen at cryogenic temperature. Dihydroperoxyl, $(HO_2)_2$, and formylperoxy radical have been trapped and their infrared spectra studied. $(HO_2)_2$ is a cyclic dimer of HO_2 bonded by two O-H···O bonds, and it decomposes to H_2O_2 (and O_2) at 25-35 K. The O_2 matrix is an ideal medium to study photooxidation processes.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

257. TIME-RESOLVED STUDIES OF FREE RADICALS AND LASER-INITIATED CHAIN REACTIONS $60,000 01-02
Stephen R. Leone
Department of Chemistry and Joint Institute for Laboratory Astrophysics

Time and wavelength-resolved infrared fluorescence techniques are used to study free radical reactions initiated by pulsed laser photolysis. Recently photofragmentation dynamics studies of CH_3I and $Hg(CH_3)_2$ have been completed. Detailed population distributions in the CH_3 out-of-plane bending vibration and antisymmetric stretch excitation were obtained. The methyl iodide precursor is being used to study the reaction of both translationally "hot" and thermal methyl radicals with chlorine. Emission is observed from the CH stretches of the methyl chloride product. Reaction of the "hot" radicals is tremendously enhanced and detailed rate coefficients are being obtained. A fundamental analysis of chain reaction kinetics has been explored. It is found that the translational temperature in a complex combustion system lags well behind the vibrational temperatures, even hundreds of chain cycles after initiation.

KANSAS STATE UNIVERSITY
Manhattan, KS 66506

258. DIFFUSION FLAME STUDIES OF THE CHEMICAL AND PHYSICAL MECHANISMS OF SOOT FORMATION FROM AROMATIC FUELS — $53,000 — 01-02
T. W. Lester, J. F. Merklin and C. Sorensen
Departments of Nuclear Eng. and Physics

Diffusion flames, doped with combinations of aromatic, substituted aromatic, and aliphatic hydrocarbons, are being used to explore the mechanisms of soot particle inception and growth over a range of temperatures. Emphasis continues to be primarily on the development of photon correlation spectroscopy, a dynamic light scattering technique that is not dependent on the index of refraction of the particles, and which has the potential of yielding the second moment of the particle size distribution. Resolution of the uncertainty in the proper relationship between the particle's diameter and its diffusion coefficient continues to be of utmost importance. The determination of large molecular weight hydrocarbons has been commenced, using physical probing of the flame with quartz micro-probes, trapping of the large species on XAD-2, and subsequently analyzing with GC-MS.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

259. EXPERIMENTAL STUDIES OF THE IONIZATIONS AND BONDING OF SMALL MOLECULES ATTACHED TO TRANSITION METALS — $63,000 — 01-02
Dennis L. Lichtenberger
Department of Chemistry

The purpose of this research program is to obtain experimental information on the ways metals bond and activate small organic molecules. The experimental techniques being developed are high-resolution HeI/HeII valence and high-precision X-ray core photoelectron spectroscopy of organometallic molecules in the gas phase. The organometallic complexes contain metal-molecule interactions that are significant to organometallic synthesis, surface chemistry, and catalysis. This year's work has included metals with bound carbonyls, olefins, alkyls, methylenes, and vinylidenes. Our previously demonstrated ability to observe metal-ligand vibrational fine structure in valence ionizations has been extended to observation of metal-metal vibrational fine structure for several dinuclear complexes. This structure provides a direct measure of the contribution of particular orbital electrons to the bonds with metals. The gas-phase core ionization studies are providing a highly useful experimental separation of charge distribution effects from bonding effects in the valence metal-molecule interactions.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

260. LASER-INDUCED CHEMICAL REACTIONS AND LASER-COLLISION PROCESSES — $60,000 — 01-02
John C. Light
James Franck Institute and
Department of Chemistry

Our research program is directed toward the development of a better theoretical understanding and predictive ability for a variety of photochemical and electron impact collision processes. To this end exact quantum theoretical scattering theory has been developed to apply to these processes, new numerical means of solving these equations have been developed, and applications have been made to several relatively simple systems. Four specific types of processes, each requiring different methods, have been studied. These are the single photon photodissociation of symmetric triatomic molecules which have been studied in the collinear geometry (e.g., CO_2); the photodissociation of asymmetric triatomic molecules studied in full three dimensional space (e.g., ICN, HCN); a study of intense laser induced multiphoton photodissociation of diatomic molecules by time independent means (e.g., HF); and, in a more recent project, a study of dissociative attachment in diatomic and triatomic molecules (e.g., $e^- + CO_2 \rightarrow CO + O^-$). In general the variation of the cross sections (or probabilities) with energy and the internal energy states of the product fragments have been determined.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

261. ELECTRONIC RELAXATION PROCESSES IN POLYATOMIC MOLECULES $65,000 01-02
Edward C. Lim
Department of Chemistry

The objective of this research continues to be the elucidation of electronic relaxation processes in polyatomic molecules. During the past year, the emphasis has been on the systematic study of the factors which influence radiationless transitions of composite molecules. Electron donor-acceptor complexes as well as diarylalkanes of various chain length are being investigated using nanosecond and picosecond fluorescence spectroscopy. Our results indicate that there may be a selection rule for singlet → triplet intersystem crossing in the charge-transfer complexes, and that the singlet → triplet intersystem crossing rate in dinaphthylalkanes is almost directly proportional to the corresponding radiative decay rate. Theoretical models are being developed for the observed behavior.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

262. STEREOELECTRONIC PROPERTIES OF AGGREGATED CHLOROPHYLL SYSTEMS $75,000 01-02
Gerald M. Maggiora
Departments of Chemistry and Biochemistry

This project seeks to elucidate theoretically the electronic and geometric structural factors which contribute to solar energy conversion in plants. Earlier studies characterized electronic structural features such as transition energies, oscillator strengths, and polarizations in chlorophyll and related photosynthetic pigments. Current studies are directed towards more complex dimer and trimer systems and recently, empirical potential function calculations have provided a number of insights into the geometric structure of "stacked" porphyrin and "special-pair" chlorophyll dimers. Electronic structure studies are being extended to these systems in an effort to gain insights into the nature of their excited electronic states. In addition, a quadratic valence force field is being developed to characterize the electronic ground and excited state vibrational properties of these molecules. This information will be used to interpret the IR and Resonance Raman spectra of these pigments and, coupled with electronic structural information, to characterize their photodynamic properties.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

263. MOLECULAR BEAM STUDIES OF METASTABLE RARE GAS CHEMILUMINSCENT REACTIONS $60,000 01-02
Richard M. Martin
Department of Chemistry

Metastable rare gas chemiluminescent reactions are being studied using a crossed molecular beam optical spectrometer to obtain emission spectra and a crossed molecular beam time-of-flight spectrometer to obtain cross sections as a function of collision energy. The major objectives of this research program are to determine reaction cross sections and product state distributions as a function of collision energy, and to compare these results with theoretical reaction models in order to elucidate the reaction mechanisms. The collisional processes under study include neutral excitation reactions, fluorescent chemiionization reactions, and atom transfer reactions giving excited rare gas halide and oxide molecules. The information to be obtained in this work is of current interest in furthering knowledge of excited state chemistry, and is also of practical importance for understanding the fundamental dynamic processes which occur in excited rare gas reaction systems such as rare gas excimer and excitation transfer lasers.

PRINCETON UNIVERSITY
Princeton, NJ 08544

264. DYNAMICAL STUDIES OF MOLECULAR SYSTEMS $78,000 01-02

Herschel Rabitz
Department of Chemistry

Research during the past year was carried out in the general areas of (a) sensitivity analysis and (b) collision dynamics. In part (a), work continued on the development of a transportable efficient numerical code for performing first and second order sensitivity analysis on time dependent kinetic or other transient problems. This work has been pursued with Dr. R. Kee at Sandia Livermore and the resultant code is based on analytically integrated Magnus type approximation to achieve its efficiency. In conjunction with this work, we have also been developing a set of feature sensitivity analysis tools which aim to provide a bridge between the mathematical modelling of kinetic systems and the analysis of physically identifiable features in laboratory concentration profiles. The second aspect of the research in the area of collision dynamics is primarily focused on the use of various singular perturbation techniques to develop a solution to the scattering equations starting from the sudden approximation wavefunctions. These collision studies aim to utilize sudden scattering dynamics to produce practical results away from this limiting regime.

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

265. A KINETIC STUDY OF RADICAL-AROMATIC HYDROCARBON REACTIONS $55,400 01-02

A. R. Ravishankara
Engineering Experiment Station

Improvements in the fundamental understanding of chemical reaction rates and pathways in radical-aromatic hydrocarbon reactions is the principal objective of this program. Using the technique of (laser/flash) photolysis - (resonance/laser induced) fluorescence, the absolute rate constant measurements for reactions of H, O, OH + aromatic hydrocarbon reactions are being carried out as functions of temperature, pressure, and where necessary, addition of scavengers. By judicious interpretations of observed kinetic isotope effects, the yield and identity of certain products, the temporal profiles of reactant concentrations, and the effect of pressure and scavenger concentrations on the rate coefficients, the reaction mechanisms for all the above reactions in the temperature range of 250-1100 K has been elucidated. Furthermore, the next important step in aromatic hydrocarbon oxidation has been identified. Information gained from these studies is expected to help better utilization of aromatic hydrocarbons both as combustibles and as feedstocks for synthetic fuel production, as well as increasing our understanding of aromatic hydrocarbon combustion.

STANFORD UNIVERSITY
Stanford, California 94305

266. KINETICS, MECHANISM, AND EFFICIENCY OF OSCILLATORY REACTIONS $52,000 01-02

John Ross
Department of Chemistry

This research is concerned with the kinetics, mechanism and efficiency of oscillatory chemical reactions. Externally perturbed oscillatory reactions are analyzed in regard to entrainment, resonance response and identification of chemical intermediates essential for oscillations. These techniques are useful in determining the mechanism of complex reactions. The theory is being applied to the study of the efficiency of energy transduction in glycolysis.

UNIVERSITY OF CALIFORNIA/BERKELEY
Berkeley, California 94720

267. ELECTRONIC SPECTROSCOPY OF TRAPPED MOLECULAR IONS $88,000 01-02
R. J. Saykally
Department of Chemistry

The goal of this project is to learn about the electronic structures of chemically important molecular ions and in some cases to obtain information about dynamical processes in ion-molecule systems, such as charge transfer. Experimentally, molecular ions are generated by electron impact of a suitable gas, mass-selected and confined for periods of milliseconds in a radiofrequency ion trap, and excited with a pulsed laser system. The resulting fluorescence emission provides a wealth of information on the molecular ion geometry and electronic properties. Recent efforts have focussed on the vibrational dependence of charge transfer processes of N_2^+ with Ar and N_2 and on studying the radiative lifetime of HBr^+. Both experiments involve excitation with coherent ultraviolet radiation. Future plans are directed toward the study of OH^+ and C_2^+, about which little is currently known.

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45433

268. THE DIRECT DETERMINATION OF ATOM AND RADICAL CONCENTRATIONS IN THERMAL REACTIONS OF HYDROCARBONS AND OTHER GASES $52,800 01-02
G.B. Skinner
Department of Chemistry

The general goal of this research is to study the kinetics of the atom and free radical reactions that are important in combustion reactions, by following the appearance and disappearance of H, O, OH and other such combustion intermediates. H, D and O atoms are currently being measured using resonance absorption measurements in the vacuum ultraviolet. Measurements made recently include H atom determinations in the pyrolysis of 2,2-dimethyl propane (neopentane) and D atom determinations in the pyrolysis of benzene-d_6. Computer modelling of propane oxidation, based on experimental measurements of H and O concentrations made last year, is also being carried out.

RICE UNIVERSITY
Houston, Texas 77251

269. HYPERSONIC BEAM LASER PHOTOLYSIS $66,000 01-02
R. E. Smalley
Department of Chemistry

This research focuses on the development and application of laser techniques using hypersonic molecular beams to study exotic radicals of importance to combustion and/or catalysis. The central, key idea is to use a rapid laser pulse to generate the radical of interest directly in the near-sonic entrance flow of a hypersonic nozzle. Radicals thus produced are found to be cooled to less than 2 K in the expanding hypersonic jet. Specific examples under study this year include CH_3O, CH_3OAr, Cu_2, Cu_3, Fe_2, Ni_2, and the silver clusters Ag_x, where $x = 1$ to 20. Research results now indicate this pulsed laser/hypersonic beam method is quite readily extended to a wide range of organic and metallic radical species.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

270. LASER FLUORESCENCE STUDIES OF THE DETAILED COMBUSTION OF NITROGEN AND SULFUR BEARING FUELS — $60,000 — 01-02
Martin Steinberg and Keith Schofield
Quantum Institute

This program is designed to identify the chemistry involved in NO formation in fuel rich flames, detail the chemistry of the NO_x/SO_x interaction in these flames, examine the interactions of C_2 and CH with the NO_x and SO_x cycles, and extend the application of the diagnostic methods developed in the program to examine the chemistry in fuel lean flames. Quantitative laser induced fluorescence is used to monitor the time varying concentrations of OH, NO, NO_2, CN, HCN, NH, NH_2, C_2 and CH in rich $H_2/O_2/N_2$ and $C_2H_2/O_2/N_2$ flames of widely varying composition and temperature to which traces of NH_3, CH_3NH_2, SO_2 and H_2S are added. The measured profiles are used along with previous measurements for S_2, SH, SO, and SO_2 to develop detailed models for the coupled chemistry in these systems. A two-photon fluorescence measurement is being developed for O-atom in fuel lean flames to be used with OH measurements to examine the partial equilibrium existing between the major products H_2O and O_2 and the trace species O, OH, H, and H_2.

UNIVERSITY OF CALIFORNIA/SAN DIEGO
La Jolla, California 92093

271. SHOCK-TUBE STUDIES OF IMPORTANT COMBUSTION-REACTION STEPS INVOLVING RADICALS — $55,000 — 01-02
Klaus G. P. Sulzmann
Energy Center

This research program is designed to unravel the fate and the detailed kinetics of the methyl radical as an important intermediate during the combustion of hydrocarbons by studying its pyrolysis and its chemical interactions with O_2 and intermediates like O, H, OH, etc. in a shock-tube. The methyl radicals are produced by the decomposition of $(CH_3)_2CO_2$ as a donor in argon-diluted mixtures behind reflected shock-waves at temperatures between 1500 and 2500^{o}K and at total pressures between 1 and 2 atm. This approach serves also to develop techniques for the rapid introduction of particular radicals and intermediates into a shock-heated environment. Atomic oxygen is generated by employing N_2O as a donor, and absolute intensity-time histories are obtained by emission and absorption spectroscopy in the infrared, visible and/or ultraviolet regimes and by infrared absorption of a HeXe-laser at 3.508μ. Analytical and computer analyses are applied to construct reaction models and to determine rate coefficients in order to model the observed concentration-time histories and to identify dominant reaction steps which are important to hydrocarbon combustion systems.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

272. VARIATIONAL TRANSITION STATE THEORY — $105,000, 24 mo., FY 81-82 — 01-02
Donald G. Truhlar
Department of Chemistry

The objective of this program is the development of variational transition state theory as a reliable method for calculating the rates of chemical reactions in the gas phase. Currently, special emphasis is placed on bimolecular reactions important for combustion. Improved methods are being developed for treating tunneling contributions, anharmonicity effects in polyatomics, and effects due to trajectories recrossing the best dividing surface. Unified statistical and unified dynamical theories are under investigation, as in a statistic-diabatic extension of the theory that predicts rate constants for state-selected reactions. The non-constancy of the activation energy over extended temperature intervals is also being studied.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

273. KINETIC DATA BASE FOR COMBUSTION MODELING Wing Tsang and Robert F. Hampson Chemical Kinetics Division	\$95,000 14 mo.	01-02

This research program has as its aim the compilation, evaluation and production of a data base of rate constants of elementary chemical kinetic processes of pertinence to the combustion of organic fuels in the gas phase. Initial evaluation efforts are in the area of methane combustion. This involves a basic set of about 270 reactions and 25 species. Evaluation is carried out by comparison of replicate measurements (if available), examination of reaction mechanisms, and within the constraint set by analogous processes and thermodynamics or other theoretical constructs. Where experiments do not exist estimates or extrapolated results are given. The data will be presented in the form of individual data sheets. The first publication should be available at the end of this fiscal year. Subsequent publications will involve data sheets on the pollution forming (NO_x) processes and extension to more complex hydrocarbon systems.

DYNAMICS TECHNOLOGY, INC.
Torrance, California 90505

274. COMPUTATION OF TURBULENT REACTING FLOWS: COMPARISON OF VARIOUS MIXING/CHEMISTRY INTERACTION MODELS John J. Wormeck	\$80,000	01-02

This research program is an analytical and computational study to compare various mixing/chemistry interaction models for turbulent combustion. Both equilibrium and finite-rate chemistry are utilized. Emphasis is directed towards a probability density function (PDF) approach. A novel technique has been developed in which the turbulent-chemistry correlations are modeled by PDF and then solved by a finite-difference procedure. Such a technique has the potential of describing both micro- and macro-mixing required in turbulent combustion. In all of these combustion simulations, a detailed fully coupled two-dimensional fluid flow scheme is employed. All of the results are being compared to experiment.

SURFACE ANALYTIC RESEARCH, INC.
Mountain View, California 94043

275. ELECTRONIC STRUCTURE OF HEAVY TRANSITION METAL CARBONYLS Cary Y. Yang	\$62,497	01-02

The program objective is to expand the existing fully relativistic self-consistent-field-Xα-Dirac-scattered-wave (SCF-Xα-DSW) method to calculate the continuum as well as bound electronic states and the corresponding photoelectron spectra of molecular clusters containing heavy transition metal (TM) atoms. The third-row transition metal carbonyl (TMC) complexes $W(CO)_6$, $Re_2(CO)_{10}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$ will be studied with the developed methodology. The geometry of the TMC is generally well characterized so that no geometrical optimization is required. The fully relativistic DSW formalism and computer codes for the continuum states of the molecular clusters are first developed. This formulation is parallel to the nonrelativistic photoionization scheme of Dehmer and Dill. The resulting codes will be used to calculate the energy-dependent photoionization cross sections and to investigate the role of relativistic effects on the bonding among the TM atoms as well as between the metal and its ligands.

NEW YORK UNIVERSITY
New York, New York 10003

276.	ENERGY-RELATED ATOMIC AND MOLECULAR STRUCTURE AND SCATTERING STUDIES Benjamin Bederson Department of Physics	\$80,000 18 mo. FY 81-82	01-03

Further measurements of the electric dipole polarizabilities of alkali halide dimers have been performed. These have been used in a combined ionic-bond model to infer values for the monomer polarizabilities of KCl (6.3); RbCl(7.2); CsCl(8.7) and CsF(5.6), in units of 10^{-24} cm^3. These are the first values of these important parameters derived from experiment. Work is in progress on determination of polarizabilities of selected heavy atomic systems, of interest since they serve as experimental checks on wave-function computations for heavy atoms. In our electron collision work we have observed our first scattering signals, using atomic sodium as a test system. We are at present engaged in performing measurements of small-angle differential and total collision cross sections for alkali dimers, and alkali halide monomers and dimers. These probe the very long-range contribution to electron scattering and electron transport in partially ionized plasmas, via the polarizability interaction ($\sim r^{-4}$), and the polar interaction ($\sim r^{-2}-r^{-4}$). The effect of dimer (and high order clusters) concentrations on earlier electron-alkali halide scattering is being studied.

THE UNIVERSITY OF NEW MEXICO
Albuquerque, New Mexico 87131

277.	ATOMIC PHYSICS WITH RELATIVISTIC BEAMS Howard C. Bryant Department of Physics and Astronomy	\$97,041	01-03

Doubly-excited resonance structures in the H$^-$ ion which are accessible by photoabsorption from its only bond state are under investigation. Our technique exploits the relativistic kinematics of the 800 MeV H$^-$ beam at LAMPF (Los Alamos National Laboratory) and high power, pulsed laser beams. The effects of extremely large motional electric fields on the resonances produced by near-luminal motion of the H ions through a set of pulsed Helmholz coils producing up to 10 KG are being observed for the first time. A multibeam laser spectrometer is designed to give a precise energy scale based on the H$^\circ$ Lyman series. The relative cross section measurement for photo-double detachment in which a single photon knocks both electrons from the ion near threshold (photon energies ranging from 14.35 eV to 15.8 eV with 7 meV resolution) is approaching completion. An experimental technique to measure the lifetime of the very narrow ^{1}P Feshbach resonance near n=2 is being developed based upon the "extended source" method which has been used in the determination of the lifetimes of short-lived elementary particles.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

278.	ELECTRON-ATOM COLLISION STUDIES USING OPTICALLY STATE SELECTED BEAMS Robert J. Celotta and Daniel T. Pierce Radiation Physics Division	\$111,200 24 mo. FY 82-83	01-03

The use of coherence and correlation techniques holds great promise for deepening our understanding of the electron-atom collision process. In particular, the recent rapid advancement in the technologies necessary to produce and detect spin polarization in free electron beams as well as the availability of optical pumping methods which can be used to orient atomic beams make possible electron-atom collision studies where both partners are in optically selected quantum states. In our research project we plan to apply such techniques to the electron-alkali system to study: the exchange interaction, the spin-orbit interaction, electron correlation in near threshold ionization, resonance effects, inelastic excitation, and super-elastic scattering. A crossed-beam apparatus, with both polarized atom and polarized electron beams, had been constructed for this purpose. The initial experiments will study the scattering of polarized electrons from polarized sodium atoms, leading to a sodium ion plus two free electrons in spin selected states. The spin dependence of threshold ionization process will be investigated for the sodium target atom in both the ground state and first excited states.

COLLEGE OF WILLIAM AND MARY
Williamsburg, Virginia 23185

279. COLLISIONAL DETACHMENT OF NEGATIVE IONS $72,000 01-03
R. L. Champion and L. D. Doverspike
Department of Physics

The purpose of this research program is to investigate the collisional dynamics for systems which involve negative ions. The energy range of the experiments, which involve both absolute and differential cross section measurements, is from a few electron volts up to several hundred eV. The processes being studied include collisional detachment, collisional excitation by negative ions, charge transfer and reactive scattering. Reactants such as $H^-(D^-)$ + N_2,O_2,H_2,D_2,HD,CO,CO_2 and CH_4 are being investigated with a particular emphasis placed upon a delineation of the various collisional processes that may occur for these reactants. Absolute total cross sections for electron detachment and for charge transfer or reactive scattering are coupled with doubly-differential cross section measurements to give a reasonably clear picture of the collisional dynamics. When possible, the experimental results are interpreted with the aid of various theoretical models. The results provide a basis for an understanding of the role of negative ions in various environments.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

280. MANY-BODY PROCESSES IN ATOMIC AND MOLECULAR PHYSICS $55,000 01-03
Shih-I Chu
Department of Chemistry

The fundamental goals of this project are to develop nonperturbative methods for comprehensive study of intense field atomic and molecular multiphoton processes as well as predissociation and intramolecular energetics in van der Waals molecules. (1) A quasi-vibration-rotation-energy method has been developed for the treatment of the quantum dynamics of high-order multiphoton excitation of molecules in intense laser and static electric fields. (2) Completion of a new methodology for extending the scope of the method of complex scaling to numerical potentials. (3) Completion of a high-precision rotational predissociation lifetime determination of Ar...H_2 van der Waals molecule. (4) A body-fixed complex-coordinate coupled-channel formalism appropriate for the treatment of the rotational predissociation of strong-coupled van der Waals molecules has been developed.

UNIVERSITY OF TOLEDO
Toledo, Ohio 43606

281. SEMIEMPIRICAL STUDIES OF ATOMIC STRUCTURE $20,500 01-03
L. J. Curtis
Department of Physics and Astronomy

The goal of this project is to combine experimental measurements by fast ion beam excitation with semiempirical data parametrizations to identify and exploit regularities in the properties of very heavy and very highly ionized atoms. The increasing use of spectroscopic line intensities as diagnostics for determining thermonuclear plasma temperatures and densities requires laboratory observation and analysis of such spectra, often to accuracies that exceed the capabilities of ab initio theoretical methods for these highly relativistic many electron systems. Through the acquisition and systematization of empirical data, remarkably precise methods for predicting excitation energies, transition wavelengths, transition probabilities, level lifetimes, ionization potentials, core polarizabilities, and core penetrabilities are being developed and applied. Although the data base for heavy, highly ionized atoms is still sparse, parametrized extrapolations and interpolations along isolectronic, homologous, and Rydberg sequences are providing predictions for large classes of quantities, with a precision that is sharpened by subsequent measurements.

Atomic Physics, continued

HARVARD-SMITHSONIAN CENTER FOR ASTROPHYSICS
Cambridge, Massachusetts 02138

282. THEORETICAL STUDIES OF HIGHLY IONIZED SPECIES $90,000 01-03
A. Dalgarno
Department of Astronomy

The composition of an ionized plasma can be modified by the presence of a small neutral component through processes of charge transfer recombination. Calculations have been performed to extend earlier results to the higher kinetic energies used in beam injection. In selected cases, the reverse process of charge transfer ionization may be a much more efficient source of impurity ionization than direct impact. Explicit results have been obtained for the charge transfer ionization of singly-ionized carbon. The radiation emitted during charge transfer may have interesting consequences and is a possible diagnostic probe of the plasma environment. An exploratory study has been carried out. A study has also been made of the sources of ionization in shock-heated plasmas. Chemi-ionization is often the initiating source. Estimates of its efficiency have been made.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

283. BASIC STUDIES OF ATOMIC DYNAMICS $90,000 01-03
U. Fano
Department of Physics

This project aims at describing and predicting the correlations and the energy transfers among the variables of atomic and molecular systems. The main result this year has been the analytical reproduction in great detail of the observed spectrum of sodium in an electric field across the ionization threshold. This work developed a new variant of the quantum defect procedures developed here earlier, which should have extended application. A comprehensive study of two-electron correlations has been prepared. A renewed analysis of the four-electron absorption spectrum of silicon has been initiated revealing the need for new procedures to take into account the combination of different types of electron excitation.

VANDERBILT UNIVERSITY
Nashville, Tennessee 37235

284. THEORETICAL STUDIES OF ATOMIC TRANSITIONS $72,000 01-03
Charlotte Froese Fischer
Computer Science Department

The present research is part of an ongoing project in atomic structure calculations using the MCHF method. The primary emphasis is on correlation effects. Relativistic effects are estimated using an intermediate coupling calculation based on a Breit-Pauli approximation. The program for computing allowed transition probabilities has been extended to include forbidden transitions of interest in plasma diagnostics. Non-orthogonal orbitals are permitted. An integrated set of programs, capable of executing interactively on minicomputers, is being developed. Several transitions of current interest are being investigated. These include the E2 and M1 transitions 2p $^2P_{3/2}$ - 2p $^2P_{1/2}$ of the Boron isoelectronic sequence. As a further test of the MCHF-BP method, calculations are being performed for Fe^{13+}. Energy levels and transition rates will be determined. Allowed transitions between doubly excited states of Be II and Be I are also under investigation.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

285.	FREE CHARGED PARTICLE BEHAVIOR IN INTENSE LASER FIELDS David M. Fradkin Department of Physics and Astronomy	$17,000 18 mo. FY 82-83	01-03

The objective of this project is to perform a theoretical analysis of the effects that intense laser pulses, possibly in conjunction with auxiliary electromagnetic field configurations, have on the dynamics of free charged particles. Various models of interaction between particles and fields are being investigated, with particular attention focussed on the amount of momentum-energy transfer to the particle. The effect of radiation reaction, laser polarization, special field configurations, and the nature of asymptotic spin direction change, and magnetic moment behavior are also being investigated. A classical treatment through third order in the radiation reaction parameter gives the asymptotic energy/momentum transfer in terms of pulse energy/unit area, laser polarization, and frequency. Asymptotic particle changes for interaction with an intense laser pulse and also an auxiliary uniform magnetic field along the pulse direction gives a stringent resonance condition for appreciable transfer. The general nature of the local active Lorentz transformation, as a function of earlier and later state specifications, that changes a particle state is under investigation.

SRI INTERNATIONAL
Menlo Park, California 94025

286.	STUDIES OF AUTOIONIZING STATES RELEVANT TO DIELECTRONIC RECOMBINATION Thomas F. Gallagher Molecular Physics Laboratory	$64,000	01-03

This program is directed towards the study of doubly excited atomic states of alkaline earth atoms which lie above the lowest ionization limit and thus autoionize. Both the intrinsic properties of the atoms and the effects of external fields are investigated. The approach employed is multistep laser excitation of atoms in a thermal beam followed by subsequent detection of the ions and electrons produced by autoionization. The high resolution of the laser affords an excellent spectral probe of the autoionizing levels, and energy analysis of the ejected electrons allows the final state to be unambiguously determined. The results, which are far more complete than those previously available, should afford a stringent test of theoretical models.

UNIVERSITY OF OKLAHOMA
Norman, Oklahoma 73019

287.	EXPERIMENTAL AND THEORETICAL STUDY OF VERY LOW INELASTIC PROCESSES IN ELECTRON-MOLECULE COLLISIONS David E. Golden and Michael A. Morrison Department of Physics and Astronomy	$86,000	01-03

The research program involves a comprehensive theoretical and experimental study of very-low-energy electron-impact excitation of molecules. This research is directed at determining reliable cross sections for molecules of basic scientific interest and of relevance to technological applications such as advanced energy programs. The program seeks to resolve significant discrepancies that exist among the results of various experimental and theoretical investigations of near threshold excitation of molecules by low-energy electrons and to develop a deeper understanding of the physics of this important collision process. In the experimental part of the program absolute differential cross sections for low-energy, electron-impact excitation of these molecules shall be measured using a crossed-beam time-of-flight (TOF) apparatus which is especially suited to low-energy collision studies. The theoretical program entails carrying out accurate ab-initio calculations of cross sections for vibrational and rotational excitation and developing new methodologies for handling collisions with large complex molecular targets in the near-threshold energy regime.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

288. ELECTRON COLLISIONS WITH POSITIVE IONS — $92,500 — 01-03
Ronald J. W. Henry — 24 mo.
Department of Physics & Astronomy — FY 81-82

The fundamental goals of this project are to delineate the important physical processes which govern electron impact excitation processes for highly stripped 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. Calculations are made for inner-shell excitation-autoionization contributions to total ionization for Na-like ions M_g^{+}, $A\ell^{2+}$, Si^{3+}, and S^{5+}. For $A\ell^{2+}$, the contributions of resonant-excitation-double-autoionization are estimated and shown to explain the absence of the largest predicted excitation-autoionization step in the measurements of Crandall et al.

ST. JOHN FISHER COLLEGE
Rochester, New York 14618

289. MULTILEVEL RELAXATION PHENOMENA AND POPULATION TRAPPINGS — $109,000 — 01-03
F. T. Hioe — 24 mo.
Department of Physics — FY 82-83

This research program employs a new approach to probe and to understand multiphoton relaxation phenomena and population trappings in laser-induced excitation of multilevel atomic and molecular systems. The framework of this new approach is provided by a set of previously unexpected conservation laws that restrict the evolution of coherences. The theoretical understandings and predictions are used to suggest experiments for measurements of multiphoton relaxation times, and to suggest experiments for achieving trapped excited electron population.

THE UNIVERSITY OF TEXAS AT AUSTIN
Austin, Texas 78712

290. KINETIC STUDIES FOLLOWING STATE SELECTIVE LASER EXCITATION — $125,000 — 01-03
John W. Keto — 24 mo.
Department of Physics — FY 81-82

Electronic energy transfer from xenon atoms and excimers is studied following selective excitation by multiphoton laser excitation. Reactions at higher pressures where termoleculor processes are observed are being emphasized. Initial experiments are studying radiative lifetimes and quenching of $5p^{5}6p$ xenon atoms in collisions with xenon and other rare gases. High-resolution two-photon excitation spectra are being used to obtain accurate potential curves for xenon excimers. Comparisons with line broadening theories are being made. Reaction rates with other molecules will be measured in a flowing cell by measuring the time decay of their fluorescence. Energy disposal into product states will be analysed by their fluorescence or by probing their populations with laser induced fluorescence. These experiments are initially emphasizing chlorides.

OREGON STATE UNIVERSITY
Corvallis, Oregon 97331

291. THERMAL-ENERGY SCATTERING OF ATOMS IN HIGH RYDBERG STATES — $45,000 — 01-03
Carl A. Kocher
Department of Physics

In this study of thermal-energy collisions, a beam containing long-lived highly excited Rydberg states is passed through a gaseous target. Previous measurements in our laboratory have demonstrated that Rydberg atoms are deflected in collisions with atomic and molecular targets. Excited states in an atomic beam are detected by field ionization, with velocities resolved by a time-of-flight technique using an on-line computer. The scattered Rydberg atoms are recorded as a function of scattering angle after the primary beam has passed through a localized target region. Because of the large average radius for the Rydberg valence electron, the electron and the core ion tend to scatter independently. The valence electron provides a charge-neutralizing sheath surrounding the core ion, rendering its trajectory virtually unaffected by non-ionizing external fields. Since ion-beam scattering experiments have proven difficult at thermal energies, this research program seeks to develop and exploit a new method for the determination of velocity-resolved cross sections for free ions.

SMITHSONIAN ASTROPHYSICAL OBSERVATORY
Cambridge, Massachusetts 02138

292. MEASUREMENTS OF IONIZATION BALANCE PARAMETERS IN ATOMIC IONS — $88,000 — 01-03
John L. Kohl
Atomic and Molecular Physics Division

The purpose of this research program is to measure parameters which govern the charge distribution of atomic ions in high temperature plasmas. Measurements have been initiated to determine the absolute cross section for dielectronic recombination in C^{3+} involving the 2s-2p stabilizing transition. Dielectronic recombination cross sections have never been determined experimentally and so the present measurements are expected to test the theoretical formulation of the process. The measurements utilize inclined electron and ion beams and in the experiments, ion-photon pairs of recombined C^{2+} ions and stabilizing photons from individual dielectronic recombination events are measured in coincidence to ensure the correct identification of the detected process. Future work will use field ionization techniques to determine the final state distribution of recombined C^{2+}, will include measurements of dielectronic recombination in other ions, and the measurement of cross sections for ionic species where radiative cascades into autoionization states of the recombined ion may affect the cross sections.

CORNELL UNIVERSITY
Ithaca, New York 14853

293. EXPERIMENTAL STUDY OF INTERACTIONS OF HIGHLY CHARGED IONS WITH ATOMS AT keV ENERGIES — $155,000, 24 mo., FY 81-82 — 01-03
Vaclav O. Kostroun
Nuclear Science & Engineering Program

This research program is designed to investigate experimentally interactions of highly charged ions with atoms at keV energies ($v/c < e^2/\hbar c$). Low energy multiply charged ion beams are to be provided by an electron beam ion source (EBIS), which generates multiply charged ions by successive ionization of ions trapped in an intense, magnetically confined electron beam. An EBIS has been constructed and all aspects of the source tested. Several areas have been pinpointed for modification, further development and optimization. Because of the simple and novel design of the source, any changes can be easily incorporated. Thus far, a 1.5 kV, 25 mA electron beam has been routinely propagated through the 16 stainless steel mesh, tubular, axial trapping electrodes concentric with the beam. At pressures below 5×10^{-8} torr in the interaction region of the source, the beam is free of oscillations and traps ions. Time-of-flight spectra of trapped background gas ions have been recorded at kinetic energies as low as 250 eV. Studies of the properties of the source and optimization of charge state yields of multiply ionized nitrogen and oxygen are in progress.

UNIVERSITY OF MISSOURI-ST. LOUIS
St. Louis, Missouri 63121

294. LOW ENERGY ION-NEUTRAL COLLISIONS $68,000 01-03
Jacob J. Leventhal
Department of Physics

The experiments performed in this program are designed to yield detailed information on energy disposal in atomic and molecular interactions. The emphasis in this work is on the precise determination of the final quantum states of the interaction products. This is usually accomplished by combining molecular beam techniques with those of emission spectroscopy. The most recent work has been concentrated on energy exchanging interactions involving state-selected excited reactants; the excitation is accomplished using one or more lasers. The data are providing valuable insights into the nature of ionization and energy conversion mechanisms at the atomic level.

UNIVERSITY OF ARKANSAS
Fayetteville, Arkansas 72701

295. A THEORETICAL STUDY OF ELECTRON CAPTURE IN ION-ION AND ION-ATOM COLLISIONS $40,000 01-03
M. Lieber and F. T. Chan
Department of Physics

Retype this one as is

Electron capture processes in ion-atom and ion-ion collisions, e.g. $A^+ + B \rightarrow A + B^+$, are of great intrinsic interest as well as importance to several areas of research, such as the controlled fusion energy program, astrophysics, and atmospheric phenomena. As a prototype of a rearrangement collision which is experimentally accessible, charge exchange has been studied since the earliest days of quantum mechanics, but the difficulty of calculation has limited theoretical progress. Recent work has shown that eikonal techniques can be successfully applied to problems of this type, and have surprising power and simplicity. Calculations are being performed on: (A) Simultaneous capture of two electrons in He^{++} collisions with neutral atoms; (B) The connection between the eikonal approximation and asymptotic behavior of the wave function; (C) The effect of Stark-mixing of energy levels on electron capture cross sections for capture into a subshell.

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

296. ATOMIC PHYSICS OF STRONGLY CORRELATED SYSTEMS $78,100 01-03
Chii-Dong Lin
Department of Physics

This program is directed toward identifying the dynamical correlations of atomic particles as well as developing practical methods of calculating inelastic atomic transition cross sections. Correlation patterns of two excited electrons are examined in hyperspherical coordinates and compared with the conventional configuration-interaction wave functions. Mechanisms of exciting two electrons to high principal quantum numbers are identified and the connection with the Wannier theory of threshold impact ionization has been established. A modified atomic expansion method (AO+) for calculating inelastic transitions in ion-atom collisions in the intermediate- and low-velocity regions has been developed. Accurate charge transfer cross sections for $H^+ + H$, $H^+ + He^+$, $He^{++} + H$, $Li^{3+} + H$ and $C^{6+} + H$ have been obtained over a broad energy range. Current investigation is to incorporate the effect of ionization channels to extend the model to high energies.

UNIVERSITY OF NEBRASKA/LINCOLN
Lincoln, Nebraska 68588-0111

297. HYPERSPHERICAL COORDINATE THEORY OF TWO-ELECTRON ATOMIC PROCESSES $55,000 01-03
Joseph Macek and Anthony F. Starace
Department of Physics and Astronomy

A new hyperspherical coordinate framework for treating two electron atomic processes is proposed. The Fock expansion for a two electron wavefunction near R = 0 is matched at a finite radius R_0 to a linear combination of separable hyperspherical channel wavefunctions. This procedure is proposed to solve the problem introduced by the too repulsive effective potentials in most previous hyperspherical treatments and thus to put the hyperspherical coordinate method on a fully quantitative basis. Numerical calculations will be performed for photoabsorption by He and for H^-, particularly in the region of the doubly excited resonances below and above the n = 2 excitation threshold of the ion.

NATIONAL BUREAU OF STANDARDS
Boulder, Colorado 80303

298. ATOMIC AND MOLECULAR COLLISION PROCESSES $103,000 01-03
David W. Norcross 14 mo.
Quantum Physics Division - 525

The focus of this program is the physics of low-energy collisions of electrons with atoms and molecules, with an emphasis on detailed computational studies. High precision calculations for elastic scattering by neutral helium are being extended to near-threshold excitation. A detailed study of computational and collisional algorithms is being carried out for the prototypical He-like ion Li(II), as an anchor to extensive earlier work on the helium isoelectronic sequence. A very efficient new computer program for differential cross sections is under development, based on a powerful extension of adiabatic-nuclei theory. New techniques are being developed for carrying out complex molecular scattering calculations, and for incorporating essential physics (e.g. exchange and polarization-correlation) more rigorously. These are being applied to rotational excitation of several molecules, e.g. HCl. Extension to vibrational excitation is in progress.

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

299. NONLINEAR OPTICS WITH BROAD-BAND LASERS $56,445 01-03
Michael G. Raymer
The Institute of Optics

Experiments are being carried out to observe the presence of, and the effects of, intensity cross-correlations and phase (or field) cross-correlations in several nonlinear optical processes induced by broad-band fluctuating laser pulses. A pulsed dye laser, which may be operated either multi-mode or "superradiant" is being used to pump stimulated Raman amplification and coherent anti-Stokes Raman scattering in hydrogen gas. The statistical properties of the laser are being partially characterized using a nonlinear intensity auto-correlator, and intensity and field cross-correlations which develop between pump and probe beams are being observed using a type of nonlinear interferometer, based on the interference of beams produced at the sum-frequency of the two beams of interest.

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

300.	ATOMIC PHYSICS WITH HIGHLY CHARGED IONS Patrick Richard Department of Physics	\$503,000 13 mo.	01-03

This research program is directed toward the study of the interaction of highly-charged ions with neutral atoms. Excitation cross sections and deexcitation rates are being studied for several atomic systems using high velocity, highly-charged ions from the KSU tandem accelerator and using very low velocity, highly-charged ions resulting from the recoil of high-velocity collisions. At the very low velocities (∿5 - 30 eV per charge per amu) electron capture is being investigated. Energy loss spectra of low velocity, highly-charged ions are being obtained using a double spectrometer system. A H oven is being used to measure the important atomic hydrogen cross sections such as $Ne^{+q} + H \rightarrow Ne^{+(q-1)} + H^{+}$. At high velocity the total and differential cross sections for K-shell to K-shell charge transfer, K-shell ionization and excitation are being investigated for nearly symmetric collision systems. The impact parameter dependence of F^{9+}(bare ions) + Ne is being measured by observing the prompt and delayed Auger electrons emitted in the collision. The primary mechanism for forming doubly excited atomic states in ion-atom collisions is being investigated.

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37996

301.	EXPERIMENTS ON CONTINUUM ELECTRON CAPTURE IN ATOMIC HYDROGEN AND COLLISIONAL INTERACTION OF TRAPPED IONS I. A. Sellin and S. B. Elston Department of Physics	\$50,000	01-03

An electron impact-heated atomic hydrogen target is being used to study velocity spectra and yields of electrons captured to the continuum by bare nuclei traversing atomic hydrogen. Steady operation at temperatures >2500°K has been achieved. An electron spectrometer has been successfully operated with the hot oven located at the object focus. Electron spectra from both hot and cold gas data are routinely acquired. Emphasis is now on dissociation fraction measurements with the spectrometer operating. We have also undertaken charge transfer and energy distribution measurements for stored, higly charged ions, created by highly ionized projectile impact, in collaboration with D.A. Church et al. of Texas A&M. Recently we have studied recoil neon ions with charged $e \leq q \leq e$ produced by a pulsed 35 MeV Cl ion beam stripped to a mean charge state near 10e. The ions are stored in a Penning trap, identified by cyclotron resonance, and detected by resonant axial excitation. Single exponential decays of the stored ion numbers with charged $e \leq q \leq 5e$ are observed with mean storage time constants ≥40 msec at total pressures near 10^{-8} Torr. The ion loss is due to electron capture. Preliminary estimates of the stored ion mean energy indicate that it is∿ 1-2 qeV for $2 \leq q \leq 4$ and somewhat larger for higher q values.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

302.	EXPERIMENTAL STUDIES OF ATOMIC INNER SHELL IONIZATION PHENOMENA S. M. Shafroth Department of Physics and Astronomy	\$60,000	01-03

This program is designed to study inner shell vacancy production. Its primary research tool is the TUNL FN tandem Van de Graaff, cyclotron and sputter ion source. We are concentrating primarily on experiments which relate to dielectronic recombination, i.e., RESONANT TRANSFER AND EXCITATION (**RTE**). One signature is that a Si^{q+} ion captures a weakly bound electron from He or Ar and simultaneously develops a K hole, which is followed by a Si-K x-ray and a Si^{q-1} ion. Thus we are measuring charge capture and loss as well as target and projectile x-ray cross sections. We are testing a high-efficiency, good resolution, position-sensitive, parallel-plate electron spectrometer so that we can search for RTE in the Auger channel. Coincidence measurements are in progress. Calculations relating RTE and dielectronic recombination as well as electron capture cross sections are underway. Radiative Electron Capture (REC) in solid targets is being studied as an indicator of the K-vacancy state of highly ionized projectiles in solids with application to stopping power.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

303. NEAR-RESONANT ABSORPTION BY ATOMS IN INTENSE FLUCTUATING FIELDS — $67,000 — 01-03

Stephen J. Smith
Joint Institute for Laboratory Astrophysics

This research is directed to the measurement of photon absorption by atoms immersed in very intense laser radiation fields, near an atomic resonance. A primary objective is the accurate comparison of atomic absorption in a strong monochromatic field with the absorption in a strong field on which statistically well-characterized frequency fluctuations are superimposed. Electro-optic and acousto-optic modulators, driven by frequency-modulated radio-frequency signals, are used to control the bandwidth and bandshape of the external beam from a highly stabilized single-mode ring laser. Synthesized laser lineshapes ranging from Gaussian to Lorentzian are obtained by controlling the time scale of the fluctuations. The role of fluctuations in nonlinear atomic absorption is measured in the two-photon 3^2S-4^2D transition in sodium, in a Doppler-free configuration; and also in the saturated $3S_{1/2}(F=2, M_F=2) \rightarrow 3P_{3/2}(F=3,M_F=3)$ transition in a highly collimated atomic beam using an optical double resonance technique to study broadening, shifting and splitting of the upper level as a function of laser intensity, detuning, and fluctuation parameters (linewidth and lineshape).

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45435

304. INVESTIGATION OF THE DYNAMICS AND THRESHOLD BEHAVIOR OF ENDOTHERMIC NEGATIVE ION-NEUTRAL REACTIONS — $85,000 — 01-03

Thomas O. Tiernan and Richard L.C. Wu
Dept. of Chemistry and Brehm Lab.

The objectives of this research program are to measure excitation functions and energy thresholds for certain charge-transfer and collision-induced dissociation (CID) reactions of selected negative ions, including various metal oxide species which may be important in various high-temperature environments. These data yield bond dissociation energies and heats of formation of these ions, as well as electron affinities of the corresponding neutral molecules. A tandem mass spectrometer is being utilized to study endothermic charge transfer of $M_oO_2^-$, $M_oO_3^-$, BO^-, BO_2^-, WO_2^- and WO_3^-. Further studies aimed at the development of improved techniques for generating more intense currents of metal oxide negative ions using specialized ion sources are in progress. The techniques under investigation include microwave and electrical discharges of selected organometallic compounds, Knudsen effusion vaporization of metal oxides, and sputtering of metal targets. Concurrent with the tandem studies, differential scattering experiments are being accomplished using a crossed ion-molecular beam apparatus. Kinematic studies of several negative ion reactions are underway.

RICE UNIVERSITY
Houston, Texas 77251

305. ENERGETICS OF ATOMIC AND MOLECULAR INTERACTIONS $175,000 01-03
G. K. Walters and N. F. Lane
Department of Physics

This program emphasizes studies of structure and interactions of excited atoms, molecules, electrons and ions. Research areas include reactions and radiative lifetimes in atomic and molecular systems of high-efficiency laser promise, spin dependence in electron-atom scattering and understanding of spectra and collisional effects of interest in plasma physics and controlled thermonuclear reaction technology. Specifically, time resolved spectroscopy of alkali-halide excimers excited by synchrotron radiation in yielding stimulated emission cross-sections, formation and quenching rates for excimer laser transitions. Experiments in a flowing afterglow apparatus are directed toward studies of electron cooling rates, electron exchange in polarized electron-atom/molecule collisions, and new approaches to electron spin polarimetry. New theoretical results include cross sections for: differential and radiative charge-transfer collisions between He^{++} ions and H atoms; inelastic electron-ion collisions in a dense, hot plasma; energy transfer in collisions of highly excited atoms with molecules; and near-threshold vibrational excitation of CO_2 by electron impact.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

306. X-RAY EMISSION IN HEAVY-ION COLLISIONS $60,866 01-03
R. L. Watson
Cyclotron Institute and Department of Chemistry

The distributions of inner-shell vacancy states produced in projectile and target systems as a result of high energy heavy-ion collisions are being investigated by means of high resolution x-ray spectroscopy. Particular emphasis is being directed toward the elucidation of rapid electron transfer processes in solid or gaseous media following single or double K- plus multiple L-shell ionization. Recently, a resonant electron transfer mechanism associated with the formation of a molecule-ion between adjacent cation and anion sites in ionic fluorine compounds was observed. Other topics of current interest include x-ray line shifts arising from static and dynamic screening in solids, collision broadening, and polarized x-ray emission from H- and He-like heavy ions.

Chemical Energy

YALE UNIVERSITY
New Haven, Connecticut 06511

307. STUDIES OF THE HYDROGENATION OF SMALL UNSATURATED MOLECULES USING ORGANOMETALLIC CLUSTER COMPOUNDS AS CATALYSTS — $125,000 — 24 mo. — FY 81-82 — 02-01
Richard D. Adams
Department of Chemistry

The nature of the activation and reactivity of small heteronuclear unsaturated molecules, such as CO and CO_2, and hydrogen by transition metal carbonyl cluster compounds is being actively investigated. Studies include syntheses of new clusters, characterizations of the nature of the coordination of the substrates and hydrogen to the clusters, and determination of the mechanisms of hydrogen transfer from the metal atoms to the substrates. Single crystal x-ray diffraction methods are extensively used in the determination of the molecular structures of the various products and isolable intermediates. These studies are supplemented by infrared, nuclear magnetic resonance and mass spectral analyses.

UNIVERSITY OF NORTH CAROLINA/CHAPEL HILL
Chapel Hill, North Carolina 27514

308. THE HEATS OF FORMATION OF GAS PHASE ORGANOSULFUR MOLECULES, RADICALS, AND IONS MEASURED BY PIPECO — $60,000 — 02-01
Tomas Baer and Slayton A. Evans, Jr.
Department of Chemistry

This research program is designed to determine accurately the heats of formation of simple organosulfur ions and fragments and to determine their structures by calculation using the Gaussian 80 ab inito molecular orbital program. Emphasis is currently being placed on the study of simple cyclic and acyclic sulfides and disulfides and their S-oxide derivatives. Useful comparisons are being made between the reactivities and structures of oxyhydrocarbons and their sulfur analogues. Selected α-halosulfides are primary targets for study based on the observation that during an ionic dissociation, the charge tends to remain with the organosulfur fragment. Successful competition for the charge by the halogen atom during ionic dissociation provides access to neutral sulfur containing fragments. Oxygen-17 and sulfur-33 NMR experiments are also providing new and useful insights into the bonding characteristics of sulfoxides and sulfones as well as thiolsulfinates and thiolsulfonates.

Brigham Young University
Provo, Utah 84602

309. METAL SUPPORT INTERACTIONS: THEIR EFFECTS ON CATALYTIC PROPERTIES OF COBALT — $136,311 — 27 mo. — FY 81-82 — 02-01
Calvin H. Bartholomew
Department of Chemical Engineering

Metal-support interactions and their effects upon adsorption and activity/selectivity properties of cobalt are being investigated. The objectives of this research are to (i) determine the effects of cobalt-support interactions on dispersion, oxidation state and adsorption properties of cobalt; (ii) correlate the catalytic properties for hydrocarbon synthesis on cobalt with dispersion, oxidation state and behavior of adsorption of CO and H_2 and (iii) measure directly the extent of interaction of various supports with iron and cobalt using Moessbauer Spectroscopy. The proposed work features a comprehensive, quantitative experimental investigation of Co on Al_2O_3, SiO_2, TiO_2, MgO, and carbon supports with careful characterization of the physical and chemical, bulk and surface properties of each catalysts with BET, H_2 and CO chemisorption, XRD, TEM, ESCA, TPD, and TPR measurements. Recent results provide evidence that supports and preparation methods can significantly influence adsorption and activity/selectivity properties of cobalt.

Chemical Energy, continued

WEBER STATE COLLEGE
Ogden, Utah 84408

310. THE ROLE OF THE HYDROGEN-DONOR SOLVENT IN COAL HYDROLIQUEFACTION $45,378 02-01
Robert R. Beishline
Department of Chemistry

The objective of this study is to evaluate a proposed method for obtaining the relative rates of H· addition to, and the relative rates of hydrogen abstraction by H· from tetralin (Tet), 1,2-dihydronaphthalene (1,2-DHN), naphthalene (Nap) and other polycyclic aromatic hydrocarbons. The expressions used in the calculations are derived from the newly proposed mechanism for the thermal disproportionation of 1,2-DHN, which, through recent work on this project, has been shown to be free radical in nature. Concentration vs time data for the disappearance of 1,2-DHN and the appearance of H_2, Nap, Tet and dimers are required to obtain the relative rates. Work is in progress to improve the accuracy and precision of the procedure for measuring H_2. Methods of data analysis are being studied to learn what approach will best minimize error propagation and to determine what degree of precision is required in the experimental data.

PURDUE UNIVERSITY
W. Lafayette, Indiana 47907

311. REDUCTION OF AROMATIC COMPOUNDS DERIVED FROM COAL BY CALCIUM $65,000 02-01
Robert A. Benkeser 16 mo.
Department of Chemistry FY 81-82

Calcium metal dissolved in a mixture of methylamine and ethylenediamine constitutes a new reducing system for aromatic rings. This research program is designed to test the utility of the new reducing system on aromatic compounds derived from coal. The following examples are representative results.
Naphthalene can be reduced by the calcium system to an 80-20 mixture of $\Delta^{9,10}$ and $\Delta^{1,9}$ octalin (98% yield). A new separation procedure has been developed which yields $\Delta^{9,10}$ octalin in 100% purity. The method constitutes the best preparative procedure now available for this useful alkene. Durene can be reduced to highly pure 3,6-dihydrodurene (98% yield). This also is the best method now available for synthesizing this unconjugated diene.
Anthracene is reduced to 1,2,3,4,5,6,7,8,9,10-decahydroanthracene in excellent yield and purity. The literature procedure for preparing this compound is tedious and cumbersome.
Other hydrocarbons under investigation are *o*- and *p*-xylene and norbornadiene.

STANFORD UNIVERSITY
Stanford, California 94305

312. CATALYZED GASIFICATION OF CARBON $152,407 02-01
Michel Boudart 24 mo.
Department of Chemical Engineering FY 82-83

This work was prompted by the perceived need for an improved catalytic process for the steam gasification of coal. It was decided to study the kinetics of gasification of a pure graphitized carbon black containing small particles (~4 nm) of platinum in the pores between approximately spherical (~30 nm) particles of carbon. During the past three years, William Holstein has conducted a thorough kinetic study of the uncatalyzed and platinum catalyzed gasification of carbon by H_2, H_2O and CO_2. As a result of this work, the action of the catalyst is viewed as a rupture of carbon-carbon bonds to form carbon metal bonds. The carbon at the surface of the metal is in a "carbidic" active state and reacts much more rapidly with the gasification reactants than the original carbon. This hypothesis explains all the kinetic data.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

313. AN INTEGRATED APPROACH TO THE SYSTEMATIC SYNTHESIS, CHARACTERIZATION, AND CATALYTIC ACTIVITY OF NOVEL HETEROGENEOUS CATALYSTS Alan Brenner Department of Chemistry	\$65,000	02-01

The surface chemistry and catalytic activity of a new class of heterogeneous catalysts consisting of carbonyl complexes directly deposited on high surface area supports is being investigated. Temperature programmed decomposition and chemisorption measurements provide information on stoichiometry, oxidation state, and dispersion. An automated reaction system is used to provide extensive data for the model reactions of ethylene hydrogenation, ethane hydrogenolysis, and methanation. Every element which forms a stable carbonyl complex has been studied, including a variety of cluster and mixed-metal complexes. A structure-activity relationship allows the prediction of the preferred method of catalyst activation and if the product catalyst is likely to be similar or higher in activity than a traditional (reduced salt) catalyst. A number of carbonyl derived catalysts have higher dispersions and activities than their traditional analogs, in some cases the increase in activity being as much as 1000-fold. However, neither cluster nor mixed-metal complexes show activity significantly different from mononuclear complexes.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

314. THE PROPERTIES OF SUPPORTED METAL CATALYSTS John B. Butt, Robert L. Burwell, Jr. and Jerome B. Cohen Ipatieff Laboratory	\$180,000 22 mo. FY 81-82	02-01

This research program is aimed at enlarging our understanding of the physical and catalytic characteristics of supported metal catalysts consisting of highly dispersed (1-10 nm) particles of metal on a high area, porous oxide support. Effort during the last year was concentrated on examination of Pd/SiO_2 and preparation of SiO_2-supported Co, Rh, and Co-Rh alloys via impregnation with the carbonyl complexes followed by decomposition of these carbonyls. The work on Pd/SiO_2 has included a study of propene hydrogenation and x-ray examination of Pd particle sizes for metal per cent exposed from 13.8 - 65%. An EXAFS study was completed on Pt/SiO_2 with special attention to the nature of the the interaction of the catalyst with O_2. Current work pursues the goal of obtaining homogeneous Co-Rh alloys with corresponding chemisorption and chemical reactivity characterization.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

315. MECHANISTIC STUDIES RELATED TO THE METAL CATALYZED HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS Charles P. Casey Department of Chemistry	\$169,000 24 mo. FY 82-83	02-01

The synthesis of organometallic compounds which contain functional groups similar to those proposed in homogeneous and heterogeneous catalyzed carbon monoxide reduction is being carried out so that the properties and reactions of these species can be studied. This basic information should contribute to the understanding and eventual design of catalysts for the reduction of carbon monoxide. Detailed comparisons of metal formyl compounds (M-CO-H) with the better known metal acetyl compounds ($M-CO-CH_3$) are being carried out to determine the unique properties of metal formyl compounds. Hydroxymethyl metal compounds (MCH_2OH) have also been prepared as models for intermediates in CO reduction. A series of compounds containing CH_3, CH_2, and CH groups bridging between two iron atoms have been synthesized and their reactions with CO, H_2O, and alkenes are being studied. Several heterobimetallic compounds linked by a heterodifunctional ligand have been synthesized. Their reaction with hydrogen is being studied as a possible route to heterobimetallic dihydrides that might serve as catalysts for CO reduction.

INDIANA UNIVERSITY
Bloomington, Indiana 47405

316. METAL-ALKOXIDES - MODELS FOR METAL OXIDES
Malcolm H. Chisholm
Department of Chemistry

$115,000
24 mo.
FY 81-82

02-01

Metal oxides provide the most versatile class of catalysts used in the petrochemical industry. Our research program is aimed at making homogeneous metal alkoxide/oxide catalysts which will mimic heterogeneous systems. Structural analogies between discrete cluster metal alkoxide-oxide compounds and macromolecular mixed metal oxides have been established. In searching for new organometallic chemistry of metal alkoxides we have studied reactions involving small unsaturated molecules such as CO, olefins and acetylenes with dinuclear and/or polynuclear alkoxides of Mo and W which contain M-M bonds. The tungsten alkoxide $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$ serves as an olefin isomerization catalyst at ambient temperatures in hydrocarbon solvents. Carbon monoxide binds to $M_2(OR)_6$ ($M{\equiv}M$) compounds to give μ_2-CO adducts with unusual spectroscopic properties, e.g. $\nu(CO) = 1550\ cm^{-1}$, M = W; there is some evidence that tungsten carbide clusters are formed. Alkyne polymerization by $M_2(OR)_6$ compounds is extremely efficient and $\mu_2\text{-}C_2R_2$ and $\mu_2\text{-}C_4R_4$ compounds have been characterized.

WESLEYAN UNIVERSITY
Middletown, Connecticut 06457

317. HOMOGENEOUS CARBON MONOXIDE FIXATION
Alan R. Cutler
Department of Chemistry

$115,000
24 mo.
FY 81-82

02-01

Coordinated ligand reactions by which ligated CO undergoes reduction and subsequent synthesis reactions (i.e., chain growth of C_1 alkoxymethyl ligand), before eliminating C_2 and C_3 organic products are being examined. Fully characterized $(\eta^5\text{-}C_5H_5)Fe(CO)L$ alkyl and acyl complexes (L=CO, PR_3, etc.) are involved in the stoichiometric conversion of CO ligands on $CpFe(CO)_3^+$ selectively to the C_2 organic molecules $CH_2{=}CH_2$, CH_3CO_2R, and CH_3CHO. Alkoxyacetyl complexes $CpFe(CO)L(COCH_2OR)$ thus serve as C_2-templates during the sequence of coordinated ligand reactions involving carbocation acyl activation and borohydride reduction. The resulting ethyl and formylmethyl complexes then afford $CH_2{=}CH_2$ and CH_3CHO, respectively. Carboalkoxymethyl complexes $CpFe(CO)L(CH_2CO_2R)$, which are generated by protic isomerization of $CpFe(CO)L(COCH_2OR)$, also serve as convenient C_2-templates. Excess acid degrades these complexes and releases CH_3CO_2R; in addition, the aforementioned sequence of ligand reactions (but in the β-position) selectively affords ethyl or formyl methyl complexes, depending on the reaction conditions.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

318. STUDIES OF NEW ELIMINATION REACTIONS OF METAL COMPLEXES
Mary Rakowski DuBois
Department of Chemistry

$89,657
24 mo.
FY 82-83

02-01

This research program is investigating new elimination reactions which occur at organosulfur ligands in reduced derivatives of the type $[C_5H_5Mo(S)SR]_2^{-n}$ (R = H or alkyl, n = 1 or 2). The work may be important in understanding the reactions catalyzed by metal sulfide surfaces. The reduction products of the complex $[C_5H_5Mo(S)SH]_2$ are being generated by chemical reagents and by electrochemical techniques. The reactions are of interest because hydrogen is eliminated from the hydrosulfido ligands during the reduction. The reduced products are being characterized and the reactions with protic sources are being investigated to determine whether the hydrosulfido complex can be regenerated. Electrochemical studies establish that $[C_5H_5Mo(S)SC_6H_5]_2$ is reduced at -1.1 V vs SCE, a less cathodic potential than that observed for the hydrosulfido complex. The ability of the reduced complex to react with protic solvents to produce hydrogen is being investigated. Thermally induced elimination reactions of alkenes and alkanes from complexes of the type $[C_5H_5Mo(SR)_2]_2$ are being studied. Intermediates are being characterized by cyclic voltammetry and NMR.

Chemical Energy, continued

UNIVERSITY OF TEXAS/AUSTIN
Austin, Texas 78712

319. STUDY OF FISCHER-TROPSCH SYNTHESIS THROUGH THE USE OF SURFACE INTERMEDIATE SCAVENGERS — $117,100, 36 mo., FY 81-83 — 02-01
John G. Ekerdt
Department of Chemical Engineering

The goal of this program is to develop a more complete understanding of the reaction intermediates involved in CO hydrogenation over two catalyst systems. Studies are being carried out over an oxide supported group VIII metal, iron, and over a refractory oxide, zirconium dioxide. Fischer-Tropsch synthesis generated fragments over iron, most likely alkyl fragments, are scavenged from the reacting surface by injecting pyridine into the reactant gas mixture. The resulting distribution of alkyl-substituted pyridines is dependent upon the synthesis conditions. Relationships between Fischer-Tropsch synthesis product and scavenged product distributions are used to develop reaction mechanisms, kinetic expressions, and explain reaction selectivity. Direct carbon monoxide hydrogenation to highly branched alkanes and aromatics, isosynthesis, is being studied over zirconium dioxide. A differential reactor is used to investigate reaction initiation and to determine the primary products. Oligomerization, isomerization, and dehydrocyclization to isosynthesis products is studied at high CO conversion in a Berty reactor.

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

320. CHEMICALLY MODIFIED CARBON, PLATINUM, AND NICKEL ELECTRODES — $62,000 — 02-01
C. Michael Elliott
Department of Chemistry

The goal of this project is to alter the kinetics of various solution electrode reactions by developing new chemically modified electrode surfaces. Of primary interest is the catalysis of various kinetically inert small molecules that are of economic interest; in particular, the respective four electron and six electron reductions of dioxygen and dinitrogen. Different synthetic procedures appropriate for each of the materials under study are being investigated in order to chemically bind the potential catalyst to the surfaces of bulk electrode materials. Our primary emphasis is the development of polymer coated electrodes containing the potential catalyst and/or other electroactive materials. Several such electrodes have been prepared and are under active investigation. A number of novel metalloporphyrin compounds have been prepared and their catalytic activity is presently under investigation both in solution and polymer bound. The primary methods of investigation of these surfaces are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry and the rotated disk electrode technique.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

321. SYNTHESIS, CHEMISTRY AND CATALYTIC ACTIVITY OF LANTHANIDE METALS IN UNUSUAL OXIDATION STATES AND COORDINATION ENVIRONMENTS — $60,000 — 02-01
William J. Evans
Department of Chemistry

The objective of this investigation is to identify the special chemical properties of the lanthanide metals (a series of 14 heavy metals which are mined in California) which distinguish them from other metallic elements and to exploit this unique chemistry to develop new stoichiometric and catalytic reactions which presently are not achievable with conventional catalysts. The basic chemistry of the lanthanide metal carbon bond is being studied and has led to the synthesis of the first molecular lanthanides containing lanthanide metal hydrogen bonds. Bimetallic complexes, $[(C_5H_5)_2LnH(solvent)]_2$ can be obtained as well as trimetallic polyhydridic species, $\{[(C_5H_5)_2LnH]_3H\}^-$, which are structurally unique in organometallic chemistry. The hydrides can now be synthesized in high yield allowing a determination of the basic chemistry of the Ln-H bond. The hydrides react with a wide variety of unsaturated hydrocarbons to form new classes of organolanthanides. The utility of these reactions and these new complexes in catalytic schemes is being investigated.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

322.	PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY John L. Falconer Department of Chemical Engineering	$145,000 24 mo. FY 82-83	02-01

The influence of alkali promoters on the hydrogenation of CO to methane and higher hydrocarbons is being investigated for supported nickel, ruthenium and iron catalysts. The purpose of this work is to understand how alkalis change catalytic activity and selectivity and how these changes depend on the oxide support and the method of preparation. Temperature-programmed desorption (TPD) and reaction (TPR) are being used with mass spectrometric detection to determine how promoters affect binding energies, individual reaction steps, reaction mechanism and activity. Differential reactor studies with gas chromatographic detection are investigating selectivity and poisoning changes with promoters and x-ray photoelectron spectroscopy is being carried out to determine the chemical state of the promoters.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

323.	STUDIES RELATED TO THE HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT REACTION Peter C. Ford Department of Chemistry	$60,000	02-01

The objective of these studies is to elucidate the fundamental chemical mechanisms related to the homogeneous catalysis of the water gas shift reaction by metal carbonyl complexes. Current emphasis is on the catalysis under a variety of conditions by metal carbonyls of the iron triad and by iridium carbonyl. The methodology employed in these studies involves both reaction kinetics via spectroscopic techniques and in situ spectral characterization of working catalysts. Recent studies of model systems have demonstrated dramatic differences in the reactivities of certain metal carbonyls toward nucleophilic reagents and provide a logical rational for differences noted in catalyst reactivities. The elucidation of such fundamental information will provide the basis for the molecular engineering of new, more active catalysts for this reaction and others important to the production of synthetic hydrocarbon fuels.

CORNELL UNIVERSITY
Ithaca, New York 14853

324.	ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS UNDER ULTRA-HIGH VACUUM CONDITIONS Jack H. Freed Department of Chemistry	$70,000	02-01

The objective of this project is the development of a new approach for the study of surface adsorption and catalysis on clean metallic and oxide surfaces by ESR spectroscopy. In the experiments performed in this project, the microwave cavity is itself part of the ultra-high vacuum (UHV) system, so that clean metallic surfaces are prepared by vacuum evaporation onto the interior of the cavity walls. Various clean gases are then directly adsorbed onto the surface and in situ ESR spectra are obtained which permit the study of paramagnetic adsorbates and surface reaction kinetics. These studies are complemented by simultaneous studies of the new phenomenon: CREMSEE (cyclotron resonance from microwave-induced secondary electron emission), which is also observed in the UHV-ESR microwave cavity and is found to be very sensitive to bonding of adsorbates to the metallic surface. By means of the Photo-CREMSEE technique, in situ work function measurements are also made to characterize the surface. New time-resolved ESR techniques will permit the study of fast surface reaction kinetics.

INDIANA UNIVERSITY
Bloomington, Indiana 47405

325. RADICAL CHAIN AND REARRANGEMENT REACTIONS IN COAL LIQUEFACTION — $115,000 — 24 mo. — FY 81-82 — 02-01
Joseph J. Gajewski and Kevin E. Gilbert
Department of Chemistry

This research focuses on providing fundamental data for the thermal reactions of aromatic hydrocarbons that will serve as a basis for understanding the chemistry of coal liquefaction. The thermal decomposition of 1,3-diphenylpropane, dibenzylether and phenethylphenylether have been found to proceed by free radical chain processes that can be initiated by benzylphenylether, but not by bibenzyl. These reactions are not inhibited by substituted phenols, but research on inhibition continues in order to understand why inhibitors work at low temperature but not at higher temperatures. Hydrocarbon transfer between hydroaromatics and alkenes, the products of the free radical processes given above, is of interest to understand how alkenes are stabilized and to determine the ultimate fate of hydrogen donating solvents. Finally, concerted retro-Diels-Alder reactions are being studied as a means of cleaving the saturated ring in a substituted tetralin.

THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

326. MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION — $50,000 — 02-01
Gregory L. Geoffroy
Department of Chemistry

The long-range objective of this research program is to contribute to the understanding of the mechanisms by which CO is reduced by H_2 on the surface of metal particles and in homogeneous solution, using polynuclear organometallic complexes as models. The conversion of $[Os_3(CO)_{11}(CHO)]^-$ into $Os_3(CO)_{11}(\mu\text{-}CH_2)$ has been demonstrated and treatment of the latter compound with H_2 leads to CH_4. These reactions show the feasibility of the transformations carbonyl-hydride→formyl→hydroxycarbene→hydroxymethyl→methylene for the non-dissociative path for CO reduction on a metal surface. Current extension of these studies is directed toward the preparation of polynuclear formyl, acyl, and hydroxycarbene complexes.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

327. THE NATURE OF THE CONTRIBUTION OF CELL WALLS OF THE HIGHER PLANTS TO COAL FORMATION — $61,600 — 16 mo. — FY 81-82 — 02-01
Peter H. Given
Coal Research Section

The purpose of the project is to identify with much more certainty than heretofore the role of cellulose and lignin as part of the input to coal formation. This will greatly aid the study of coal chemistry. Efforts will be made to determine how those plant polymers that escape complete depolymerization are chemically altered in surface litter or peat. Sample cores of peat from two locations in the Florida Everglades have been obtained, together with specimens of material from the plants that are now growing at the surface and whose organs were the source of the peat. Similar samples from two other contrasting sites will be obtained. Progress has been made with isolating the principal polymers from the woody tissue of the plants so far collected. The plants and plant organs that contributed to the peat are being identified by microscopic examination of thin sections. Recognizable fragments of plant tissue are separated from the peats by wet-sieving for study by chemical methods. Samples from peat will be compared with the polymers from the plants, using FTIR, Raman and ^{13}C nmr spectroscopy, and a selective oxidation reaction with GC/MS product analysis.

Chemical Energy, continued

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

328. LIGAND INTERMEDIATES IN METAL CATALYZED CO REDUCTION — $163,604 — 24 mo. — FY 82-83 — 02-01
John A. Gladysz
Department of Chemistry

This research program has as its basic goal the synthesis and study of homogeneous complexes containing ligand types (-CHO, =CHOH, $-CH_2OH$, ≡C, ≡CH, $=CH_2$, $H_2C{=}O$, etc.) believed to be intermediate in the metal catalyzed conversion of CO/H_2 gas mixtures to organic molecules. Mechanistic understanding of the steps involved in catalytic CO reduction, and insight needed for the design of new catalysts, is sought. Recent results include: the optical resolution of the methylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+ PF_6^-$ (1) and the mechanism of the thermal coupling of 1 to the ethylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+ PF_6^-$; the crystal structure of methylidene $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]^+ PF_6^-$; the conversion of 1 to a formaldehyde complex, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}O)]^+ PF_6^-$, and a thioformaldehyde complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}S)]^+ PF_6^-$, and the X-ray crystal structures of these species; the synthesis of $Re\overset{+}{=}CHR$ and $Re\overset{+}{=}C{=}CHR$ homologs of 1, which exist as photointerconvertible geometric isomers; the synthesis and study of stable cyclic α-hydroxyalkyl complexes such as $(CO)_4MnP(C_6H_5)_2(o\text{-}C_6H_4CHOH)$.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

329. CARBON-13 MAGNETIC RESONANCE OF HYDROCARBONS AND SPECIFIC COAL MACERALS — $83,260 — 02-01
David M. Grant and Ronald J. Pugmire
Departments of Chemistry
and Fuels Engineering

Use is made of both solid and liquid carbon-13 NMR spectroscopy for characterizing the structure of hydrocarbons and their derivatives. Focus is on molecules important in either the processing of or in the conversion of fossil fuels. Model systems have been used to calibrate the instrumentation and develop acceptable analytical procedures for structural characterizations. Both solid and liqud Fourier transform (FT) methods are sensitive to transient nuclear spin behavior and as such are sensitive to timing sequences used in the FT method. Typical relaxation parameters are determined so that the various methods can be optimized. We are also engaged in the synthesis and spectroscopic determination of the conformational structures important in hydroaromatics such as tetralins, di- and tetrahydroanthracenes, di- and tetrahydrophenanthrenes. Work on coal macerals extends the above methods developed on model organic systems to these homogeneous components of coal. In this manner the techniques established for model systems are tested on more applied materials.

California Institute of Technology
Pasadena, California 91125

330. ORGANOMETALLIC CATALYSTS AND ANALOGS FOR CARBON-CARBON BOND CLEAVAGE REACTIONS IN HYDROCARBONS AND FOR CO REDUCTION — $188,000 — 24 mo. — FY 82-83 — 02-01
Robert H. Grubbs
Department of Chemistry

Investigations into the catalysis of the reduction of carbon monoxide (CO) by hydrogen (H_2) to organic products via nucleophilic attack at transition metal bound CO are continuing. A move from $LiNMe_2$ to weaker nucleophiles, in order to avoid incorporation of the activating nucleophile in the organic products, has dictated the intramolecular delivery of the nucleophile. Stoichiometric reactions of functionalized arene chromium tricarbonyl complexes, while unsuccessful at reducing CO, have clarified the requirements for successful design of the desired bifunctional catalysts. The preparation of functionalized cyclopentadienyl metal carbonyl cations is in progress. The reaction of a novel class of bifunctional, phosphine oxide based nucleophiles with transition metal carbonyl complexes is being explored. Proposed intermediates in CO reduction, such as ketene complexes have been prepared and are under investigation.

YALE UNIVERSITY
New Haven, Connecticut 06520

331. SELECTIVITY ACTIVITY AND METAL-SUPPORT INTERACTIONS OF Rh BIMETALLIC CATALYSTS

$57,492

02-01

Gary L. Haller
Department of Chemical Engineering

This research program is designed to investigate the effects of a modifying second metal on the selectivity and activity of Rh supported catalysts. Because the kind of metal-metal interaction is greatly influenced by the support on which the Rh bimetallic catalyst is prepared, the project has as one of its objectives the physical characterization of metal-support interactions. Physical characterization involves X-ray photoelectron spectroscopy, infrared spectroscopy of chemisorbed probe molecules and extended X-ray absorption fine structure. Chemical characterization involves H_2 and CO volumetric chemisorption and the determination of kinetic parameters of catalyzed reactions. The principal bimetallic systems under investigation include Rh-Ag and Rh-Au supported on SiO_2, Al_2O_3, and TiO_2. Our goal is to analyze the nature of the metal-metal interaction, to determine the influence of the kind of support on the metal-metal interaction, and to understand how the kind of interaction is reflected in activity and selectivity of catalyzed reactions. The test reactions used are butane and neopentane hydrogenolysis/isomerization and reactions of H_2-CO.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

332. METALLOCARBORANES STRUCTURALLY ENGINEERED FOR THE REDUCTION OF CARBON MONOXIDE

$65,000

02-01

M. Frederick Hawthorne
Department of Chemistry

Our objective is to develop metallocarboranes which activate carbon monoxide toward reduction, oxidation and carbon-carbon bond formation. Those processes generally involve nucleophilic attack on coordinated carbon monoxide; therefore, the rational design of reagents which optimize this type of reactivity is being pursued. $3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}RuC_2B_9H_{11}$ (I) is prepared in moderate yield from $[Ru(CO)_3Cl_2]_2$ and $Tl_2C_2B_9H_{11}$. This compound is found to be very reactive with a variety of nucleophiles, including OH^-, OR^- and H^-, to yield anionic metallocarboxylic acid derivatives and the formyl complex, respectively. Research in the near future will elaborate the described work: The synthesis of $3,3\text{-}(CO)_2\text{-}3\text{-}(PPh_3)\text{-}3,1,2\text{-}RuC_2B_9H_{11}$ (II) as well as compounds analogous to I and II containing isomeric and carbon substituted carborane ligands should result in chemistry relevant to carbon monoxide reduction and derivatization as well as water-gas shift catalysis.

YALE UNIVERSITY
New Haven, Connecticut 06520

333. THE ROLE OF d-ELECTRONS IN CHEMISORPTION AND METAL/SUPPORT INTERACTIONS STUDIED BY ELECTRON SPECTROSCOPY

$68,503
24 mo.
FY 82-83

02-01

Victor E. Henrich
Applied Physics

This research program is an investigation of the origin of strong metal/support interactions (SMSI) between noble metal catalysts and transition-metal-oxide supports by using a model catalyst system consisting of small noble metal particles (from single atoms to small clusters) supported on single-crystal TiO_2 (rutile) supports. X-ray photoelectron spectroscopy and <u>in situ</u> metal evaporation are used to characterize the valence state of both the TiO_2 substrate ions and the catalyst atoms as a function of substrate surface electronic structure [i.e., whether the surface has been reduced to create $Ti^{3+}(3d^1)$ cations or whether all surface cations are $Ti^{4+}(3d^0)$], size of metal particles, reduction procedure, and nature of adsorbed molecular species. Ultraviolet photoemission spectroscopy (UPS) is also used to characterize the catalyst valence band electronic structure and the molecular orbitals of chemisorbed species. This information is used to deduce the extent of charge transfer between catalyst and support.

UNIVERSITY OF PITTSBURGH
Pittsburgh, Pennsylvania 15260

334. STUDIES OF SUPPORTED METAL CATALYSTS David M. Hercules Department of Chemistry	\$125,000 20 mo. FY 81-82	02-01

Work is continuing on surface characterization of calcined catalysts to understand the influence of surface species on catalytic behavior. Spectroscopic techniques (ESCA, AES, SIMS, ISS, Raman, FTIR) are combined with chemical treatment for these studies. The nature of submonolayer species on Mo/Al_2O_3 catalysts affect sulfiding behavior. Treatment with H_2/H_2S sulfided only Mo in octahedral sites (Mo-o); under similar conditions Mo in tetrahedral sites (Mo-t) was reduced to Mo^{+5} but not sulfided. Above monolayer coverage both $Al_2(MoO_4)_3$ and MoO_3 were sulfided. $Co/Mo/Al_2O_3$ oxidic catalysts were studied; Mo was held constant at 15% MoO_3 (submonolayer) as cobalt was varied from 1-9% CoO. The presence of cobalt had no effect on the behavior of molybdenum. However, molybdenum significantly affected the cobalt behavior. The tetrahedral cobalt interaction species (Co-t) was dominant for catalysts of low cobalt loading. As the cobalt concentration increased a new phase is formed by interaction between Co and Mo (Co-m) (not $CoMoO_4$). Co-m is produced up to 7% CoO concentration above which bulk Co_3O_4 is formed.

SRI INTERNATIONAL
Menlo Park, California 94025

335. HIGH TEMPERATURE CHEMISTRY OF COMPLEX VAPORIZATION/DECOMPOSITION PROCESSES Donald L. Hildenbrand Physical Sciences Division	\$53,240	02-01

The objective of this program is to obtain fundamental thermodynamic data for a variety of high temperature vaporization/decomposition processes that are relevant to current and emerging energy technologies such as stack gas cleanup, coal gasification, hydrogen generation, and MHD. These processes are being studied by high temperature mass spectrometry and by the torsion-effusion method so that both vapor composition and absolute pressures are determined. For substances that simultaneously undergo both decomposition and direct vaporization, particular emphasis is on quantitative determination of the relative contributions from each process, and on thermochemical characterization of the complex vapor species. Current studies are concerned primarily with metal sulfate processes, with recent work on the sulfates of Cu, Rb, Fe, and Ni. The effects of certain additives that catalyze sulfate decomposition are also being studied, since kinetic and mechanistic features have a crucial bearing on the interpretation of the dynamic effusion measurements as well as on the technological applications of these processes.

UNIVERSITY OF DELAWARE
Newark, Delaware 19711

336. AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND REGENERATION OF METAL SYNTHESIS GAS CATALYSTS J. R. Katzer and W. F. Howard, Jr. Center for Catalytic Science and Tech.	\$200,000 24 mo. FY 81-82	02-01

The poisoning of Ni and Co catalysts is being analyzed by Auger electron/X-ray photoelectron (AES/XPS), FTIR, and extended x-ray absorption fine structure (EXAFS) spectroscopies. CO is being adsorbed on Al_2O_3-supported Ni and Co catalysts, and the carbonyl vibrational bands are being monitored during sulfur poisoning by H_2S. The CO frequency shift to higher energy implies a weakening of the metal-carbon bond, as predicted from the loss of catalytic activity. AES and XPS are being used to study the extent and nature of carbonaceous residues deposited from CO on Co and Ni foils. Results indicate that Ni has a graphitic deposit only, while Co has both graphite and carbide formation. The carbide layer is also being examined by EXAFS to better define the carbon deactivation mechanism of the catalysts.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

337. SOLID STATE, SURFACE AND CATALYTIC STUDIES OF OXIDES Harold H. Kung Department of Chemical Engineering	\$145,000 24 mo. FY 82-83	02-01

This research program aims at elucidating the relationship among surface, solid state and catalytic properties of transition metal oxides. Current emphasis is on the study of properties of different crystallographic planes of ZnO, and on the modelling of oxides as ionic compounds. Three types of surface planes of ZnO are studied: flat nonpolar, stepped nonpolar, and polar Zn surfaces. The flat nonpolar surface adsorbs CO and desorbs it as CO_2. The stepped and the polar surfaces adsorb and desorb CO. CO_2 adsorbs and desorbs molecularly on all surfaces. Methanol decomposes on the flat and the stepped surfaces to CH_4, CO_2, CO and H_2. The fraction decomposed increases with the density of surface defect. The polar surface is very active in decomposing methanol to formaldehyde, CO, CO_2, H_2, and H_2O. In the modelling of oxides as ionic compound, it is found by calculation that when a cation is introduced into the matrix of another more ionic oxide, this cation becomes more electropositive and vice versa. This prediction explains some of the catalytic behavior of mixed oxides in reactions involving charge transfer rate limiting steps.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

338. SUPPORT OF CRITICAL DATA COMPILATIONS David R. Lide, Jr. Office of Standard Reference Data	\$200,000	02-01

The Office of Standard Reference Data of the National Bureau of Standards administers a collaborative interagency program for preparation of compilations of physical and chemical reference data. Current projects fall in the following areas: alloy phase diagrams, physical and thermodynamic properties of fluids, electrolyte properties, atomic data relevant to fusion, thermodynamics and kinetics of high-temperature systems, optical properties of solids, and surface properties. The approach is to review critically all relevant data from the literature, compare with theory, and select the most reliable values. Whenever possible, correlations are developed which allow prediction of unmeasured properties. Each project will lead to a publishable data compilation containing recommended values and accuracy estimates. In many cases, these data sets will also be merged with appropriate data from other sources to produce computerized data bases for access by the technical community.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

339. CATALYSTS AND MECHANISMS IN SYNTHESIS REACTIONS Jack H. Lunsford Department of Chemistry	\$130,000 24 mo. FY 81-82	02-01

Palladium supported on certain oxides is an active and selective methanol synthesis catalyst which rivals currently used commercial catalysts. The catalytic properties of supported palladium vary from one type of oxide to another. Moreover, palladium on different grades of silica exhibits remarkably different characteristics for methanol synthesis. A major part of this research program is devoted to understanding the structural and electronic factors which determine the catalytic properties of supported metals for the formation of alcohols. Variations in activity for methanol formation are observed following controlled modifications of the support; for example, by the addition of alkali metal salts. The physical and chemical properties of the supported palladium are also monitored by chemisorption, infrared, x-ray emission and other techniques. One is able to establish the importance of such factors as bonding of CO to the surface and the size and shape of the supported metal particles. Another aspect of the research involves a study of matrix-isolated gas phase radicals which are produced on surfaces of catalytic importance.

NATIONAL BUREAU OF STANDARDS
Washington, DC 20234

340. STRUCTURES AND REACTIVITY OF CHEMISORBED SPECIES AND REACTION INTERMEDIATES Theodore E. Madey and Richard D. Kelley Surface Science Division	$140,000	02-01

This program consists of a multiprobe study of the structure and reactivity of adsorbed molecules on both single crystal catalysts and high area catalysts. It involves four areas of research which have a common theme -- the investigation of surface processes related to catalytic chemistry. 1) The role of catalyst promoters and poisons in inducing new surface structures in adsorbed molecular complexes is being studied using the electron stimulated desorption ion angular distribution (ESDIAD) method; 2) Vibrational spectroscopy of the adsorption, decomposition, and reaction kinetics of CH_3NC, H_2O and $H_2 + O_2$ on single crystal metal surfaces is being studied using high resolution electron energy loss spectroscopy (EELS); 3) Neutron inelastic scattering (NIS) is being used to characterize the vibrations of surface species on Raney Ni and Pt-black catalysts. The first use of NIS as an in situ probe of CO hydrogenation under reaction conditions has been accomplished; 4) The influence of adsorbed metallic and inorganic impurities as promoters and/or poisons in CO hydrogenation reactions over single crystal Ni are under investigation.

STANFORD UNIVERSITY
Stanford, California 94305

341. MOLECULAR BEAM STUDIES OF THE DYNAMICS OF ACTIVATED ADSORPTION AND HETEROGENEOUS KINETICS ON SINGLE CRYSTAL SURFACES Robert J. Madix	$145,000 24 mo. FY 81-82	02-01

The research in this program is directed toward the understanding of the kinetics of fast surface reactions, including the dynamics of activated adsorption. For this purpose molecular beam techniques are employed. We have completed work on (1) the adsorption and desorption of CO from a stepped platinum surface with varying amounts of adsorbed sulfur, (2) the kinetics and mechanism of the hydrogen, oxygen reaction on stepped platinum, and (3) the decomposition of H_2CO, CH_3OH and HCOOH on platinum single crystals. CO desorption kinetics are affected by blocking step sites with sulfur. Though the rate constant for desorption changes slowly with sulfur coverage, the preëxponential factor and activation energy change appreciably, showing a pronounced compensation effect. The heat of adsorption of CO at the (100) steps is about ten kcal/gmol greater than on the (111) terraces. There is a decrease in entropy of the adsorbed species at the step sites. The H_2, O_2 reaction proceeds via dissociation of H_2 and O_2 with rapid equilibration to form adsorbed OH. Addition of a second hydrogen to form water is slow and rate-determining.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

342. SUPPORTED f-ELEMENT ORGANOMETALLIC COMPLEXES: SURFACE CHEMISTRY AND CATALYSIS Tobin J. Marks, Robert L. Burwell, Jr. Department of Chemistry	$125,000 24 mo. FY 82-83	02-01

The goal of this project is to elucidate the surface chemistry and catalytic properties of highly reactive f-element organometallic compounds supported on metal oxides. The nature of the supported species is probed by a battery of chemical and physical techniques, to understand the nature of the adsorption process as well as how it varies with metal and ligand identity as well as support preparation. The catalytic properties of the supported organometallics and how these can be "tuned" are also under investigation. In the past year we have conducted on extensive study of $M[(CH_3)_5C_5]_2(CH_3)_2$, $M[(CH_3)_5C_5]_2(CD_3)_2$, and $M(C_5H_5)_3CH_3$ complexes (M=Th,U) on partially and completely dehydroxylated alumina. A number of informative new surface species and reaction pathways have been identified.

STANFORD UNIVERSITY
Stanford, California 94305

343. MECHANISM OF ELECTROCATALYTIC OXIDATION OF HYDROCARBONS ON SOLID-OXIDE IONIC ELECTROLYTES $41,000 02-01
David M. Mason, Department of Chemical Engineering and Chemistry

Investigation of electrocatalytic oxidation of selected hydrocarbons on solid oxygen-ion, zirconia-type electrolyte anodes is of both scientific and engineering interest. Surface rate-processes mechanisms are a basis for the design of such devices as fuel cells and oxygen sensors. The general electrochemical reactivity of common fuel species: H_2, CH_3OH, CO, C_2H_5OH and CH_4 has been measured as a background for detailed mechanistic studies. In all cases electro-oxidation occurs primarily on active sites on the oxide-electrolyte and not on the porous electrode--be it Pt or Au. The catalytic sites are hypothesized to be colored-centers --electrons trapped in the electrolyte. Radiation experiments in which trapped electrons are formed non - electrochemically are underway to test this hypothesis. Partial electrolysis of the electrolyte causes a black sub-oxide or zirconia to form, markedly increasing the catalytic activity of the electrolyte. To elucidate mechanisms further, electrochemical measurements at various temperatures (giving activation energies), concentrations, and surface morphology are currently being made with two selected species: CO and CH_3OH.

SRI INTERNATIONAL
Menlo Park, California 94025

344. DETERMINATION OF FUNDAMENTAL THERMOCHEMICAL AND KINETIC DATA FOR RADICALS IMPORTANT IN COAL COMBUSTION AND CONVERSION $69,931 02-01
Donald F. McMillen
Department of Chemical Kinetics

The objective of this research is to obtain certain kinetic and equilibrium data necessary for a more complete understanding of the chemical reactions of coal and other alkyl-aromatic structures under conditions encountered in coal conversion and other thermal hydrocarbon processing. This objective is being accomplished by: (1) measurement of the rates at which critical bonds in important fossil fuel structures undergo homolysis to form the stabilized radicals that are important species in the thermal reactions of these substrates, and (2) incorporation of results for certain key species in group additivity and other estimation procedures so that the availability of readily applied, reliable techniques for estimating thermochemical and kinetic values eliminates the need for making individual measurements on each structure of importance in these materials. Very low-pressure pyrolysis is being used to measure the rates of initial bond cleavage reactions with minimum complication by rapid secondary reactions. Primary focus is on bond cleavages that result in formation of benzylic and cyclohexadienyl radicals in polycyclic aromatic systems.

UNIVERSITY OF SOUTHERN CALIFORNIA
Los Angeles, California 90007

345. SUPERACID CATALYZED DEPOLYMERIZATION AND CONVERSION OF COALS $60,000 02-01
George A. Olah
Department of Chemistry

Superacids possess acidities up to a billion times stronger than conventional strong mineral acids, such as sulfuric acid. Novel, superacid catalyzed conversions of bituminous coals and lignites are being studied in order to increase the H/C ratio of coals. Reactions being studied include depolymerization reactions, alkylation and transalkylation reactions, acylation, nitration and reductive coupling reactions. Reactions with both liquid and solid superacidic catalyst systems are being investigated. Liquid superacidic systems are also being used for structural studies (using ^{13}C NMR spectroscopy) of the solubilized carbocationic components of coals. In order to obtain a better understanding of the basic chemistry of the superacid catalyzed conversion reactions, model systems, such as diphenylmethane, dinaphthylmethane and dianthracylmethane are also being studied under comparable reaction conditions.

Chemical Energy, continued

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

346. REACTIONS OF IRON ATOMS WITH MOLECULES IN LOW TEMPERATURE MATRICES — $52,281 — 02-01
Ralph G. Pearson and Paul H. Barrett
Departments of Chemistry and Physics

This project's goal is to study the reactivity of metal atoms and clusters in low temperature matrices containing reactive molecules. Mössbauer, infrared, and UV spectroscopies are used to identify the reaction products. Reactions between Fe, Fe_2, and iron clusters and low temperature matrix isolated molecules of N_2, CO, HI, HCℓ, CH_4, C_2H_4, CH_2N_2 and other small molecules are under investigation. The reactions of other transition metals that are of importance to catalysis will also be studied.

THE UNIVERSITY OF TEXAS AT AUSTIN
Austin, Texas 78712

347. DEVELOPMENT OF CATALYSTS FOR THE UTILIZATION OF CARBON MONOXIDE — $125,000, 24 mo., FY 81-82 — 02-01
R. Pettit (Evan P. Kyba)
Department of Chemistry

The hydrogenolysis of linear alkanes and α-olefins in the presence of hydrogen over heterogeneous Co, Ru, and Ni catalysts produces product distributions consistent with a mechanism in which C-C bond cleavage occurs via the rearrangement of a surface-bound n-alkyl group to surface-bound methylene and the next lower alkyl species. A number of mixed metal catalysts have been evaluated in search of greater selectivity in the Fischer-Tropsch production of oxygenates *vs.* hydrocarbons. The key step is the reverse of the Fischer-Tropsch polymerization process. A number of bridged diiron species have been synthesized which have been aimed at investigating a homogeneous counterpart of a key moiety in important heterogeneously catalyzed reactions such as the Fischer-Tropsch reaction. Thus, a number of methylene-, methylidyne-, and vinylidene-bridged diiron species have been prepared and their chemistry investigated. For example, the reaction of $CpFe(CO)(PPh_3)^+BF_4^-$ with $KCpFe(CO)_2^-$ leads to the formation of a mixture of geometrical isomers of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$.

INDIANA UNIVERSITY-PURDUE UNIVERSITY
Indianapolis, Indiana 46205

348. STUDIES OF METAL-AMMONIA INTERACTIONS WITH AROMATIC SUBSTRATES — $44,000 — 02-01
Peter W. Rabideau
Department of Chemistry

An important method for the depolymerization of coal involves reduction effected by electron addition procedures. Important processes include ring reductions, functional group reductions, carbon-carbon and carbon-oxygen bond fission and reductive alkylations. In order to better understand these processes, this research is aimed at studies involving electron addition, via alkali metals, to aromatic and polynuclear aromatic substrates in liquid ammonia. Particular attention is directed towards the nature of the intermediates which are carbanions, radical anions and dianions. One approach involves deprotonation/alkylation studies, while another involves direct observation by proton and carbon NMR. Attention is also directed to the conformational analysis of the reduced products, and this is being approached on theoretical (force-field calculations) as well as experimental grounds (proton-proton and proton-carbon coupling constants).

MARQUETTE UNIVERSITY
Milwaukee, Wisconsin 53233

349. POLYMER-BASED CATALYSTS Steven L. Regen Department of Chemistry	$105,000 24 mo. FY 82-83	02-01

This research program is aimed at developing highly active and stable resin-based catalysts for use in aqueous/resin/liquid-organic three phase reactions. Current effort is focusing on the synthesis and evaluation of cross-linked polystyrene bearing pendant poly(ethylene glycol) groups for reactions involving aqueous base; e.g., elimination and alkylation processes. Operational comparisons are being made between triphase catalysts and conventional phase-transfer agents with regard to activity and stability in order to determine their viability for practical organic synthesis.

UNIVERSITY OF NEBRASKA/LINCOLN
Lincoln, Nebraska 68588

350. STUDIES ON UNUSUALLY REACTIVE METAL POWDERS. PREPARATION OF NEW ORGANO-METALLIC COMPOUNDS. Reuben D. Rieke Department of Chemistry	$90,000 18 mo. FY 82-83	02-01

This research program is involved with the preparation and study of highly reactive metal powders prepared by the reduction of metal salts with alkali metals. Current studies are concentrating on nickel, cadmium, palladium, and platinum. The nickel powders have been found to react rapidly with iodo- and bromobenzene derivatives to yield the corresponding biphenyl compounds in high yields. Nickel also reacts rapidly with benzylic halides to yield the corresponding bibenzyl compounds. Cadmium powders react with benzyl halides to yield the corresponding organocadmium compounds which can be added to acid chlorides to produce ketones. Reactions of platinum and palladium with alkyl and arylhalides are being investigated.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

351. CATALYTIC BEHAVIORS OF MULTI-VALENT LANTHANIDE OXIDES Michael P. Rosynek Department of Chemistry	$90,661 20 mo. FY 81-82	02-01

This research program is aimed at elucidating the catalytic and surface properties of selected lanthanide oxides, principally those of La, Ce, Pr, Nd, and Eu. In one segment of the investigation, olefin hydrogenation/isomerization and the dual-pathway (dehydrogenation/dehydration) decomposition reactions of alcohols are being used as diagnostic probes, in conjunction with infrared spectroscopic and thermal analysis methods, to characterize the multi-site nature of these rare earth oxide catalyst surfaces. The second portion of this project involves a study of the comparative behaviors of these oxides when used as supports for transition metal catalysts, particularly Fe, Co, and Ni, with a view toward identifying evidence for significant metal-support interactions. Appropriate test reactions, including CO hydrogenation and paraffin hydrogenolysis/dehydrocyclization, coupled with infrared and photoelectron spectroscopic studies, are being used to probe the nature and extent of these effects.

WASHINGTON STATE UNIVERSITY
Pullman, Washington 99164

352. TRANSITION METAL CATALYZED OXIDATIONS OF ORGANIC COMPOUNDS D.M. Roundhill Deparment of Chemistry	$60,000	02-01

This research program is aimed toward the discovery of new compounds for the catalytic oxidation of organic compounds such as alkenes. In particular emphasis is being placed on the reactivity of transition metal carbonyl cluster compounds for such oxidations. Reactions are being carried out under both thermal and photochemical conditions. In particular the metal carbonyls of interest are those of rhodium(0) and rhenium (0). Product analysis is by gas liquid chromatography, and isotopic labeling experiments, in conjunction with isotope ratio mass spectroscopy are being used to probe mechanism. Synthetic studies on new materials are directed at preparing complexes which can be used as oxygen atom transfer reagents. Much of this work is directed at the synthesis of new oxygen containing d^8 transition metal complexes for oxygen atom transfer to carbon.

RUTGERS UNIVERSITY
New Brunswick, New Jersey 08903

353. ROLE OF ODD-ELECTRON INTERMEDIATES IN SELECTED ORGANOMETALLIC REACTIONS Joseph SanFilippo Department of Chemistry	$62,514	02-01

This research effort is aimed at elucidating the role of odd-electron species in selected main group and transition metal organometallic processes. Chemical and physical techniques are being employed to identify such processes and characterize the reactive odd-electron intermediates. Processes which exemplify such reactivity are the reaction of organolithium reagents with transition metal dichalcogenides (a reaction employed in the preparation of electrodes used in lithium batteries), and the alkylation of several transition and main group metallate ions by alkyl halides.

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

354. FUNDAMENTAL STUDY OF CATALYSTS USING LASER RAMAN, INFRARED, AUGER ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION G. Sargent and E. Bradley College of Engineering	$140,000 23 mo. FY 81-82	02-01

The fundamental goal of this project is to develop an understanding of catalytic activity and selectivity with the long-range goal of producing better catalysts. The techniques of LEED, Auger spectroscopy, and laser Raman and infrared spectroscopies are being used to study the surface structure and bonding of CO, CH_4, H_2 and O_2 adsorbed on Ni(111) and Ni(100) single crystal surfaces. The surface coverage is controlled by varying the gas pressure and exposure time. Surface dipoles (magnitude and orientation) are being measured for each gas adsorbed on the surface by a combination of work function change measurements and spectroscopic techniques. Laser Raman and infrared spectroscopy are used to determine vibrational modes of surface structures of the adsorbed molecules and the polarization of Raman bands and changes in band intensities are used to determine electric dipole orientation and thermal desorption characteristics.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

355. REDUCTION OF CARBON MONOXIDE $93,003 02-01
Richard R. Schrock
Department of Chemistry

The ultimate goal of this project is to reduce carbon monoxide catalytically with hydrogen gas to an organic molecule containing two or more carbon atoms such as ethylene, ethylene glycol, etc. The immediate goal is to understand how to reduce carbon monoxide step-wise in model systems employing early transition metals. The project involves preparing and characterizing new hydride and carbonyl complexes and studying how they react with carbon monoxide and hydrogen, respectively. So far we have found that a dimeric tantalum hydride complex will reduce carbon monoxide to give a dimeric formyl hydride complex. This is the first well-characterized example of formation of a formyl ligand using a transition metal hydride and also cooperation between metals in doing so.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

356. ORGANOMETALLIC CHEMISTRY OF WEAKLY SOLVATED TRANSITION METAL CATIONS $115,000 24 mo. FY 82-83 02-01
Ayusman Sen
Department of Chemistry

The present research is concerned with the rational design of transition metal compounds which may be used as homogeneous catalysts for organic and polymer synthesis. The approach that we have developed is to synthesize transition metal cations incorporating weakly coordinating solvent molecules which dissociate readily, thus allowing substrates to enter and react within the coordination sphere of the metal. Thus far, using this approach, we have successfully synthesized an entirely new class of metal complexes which are versatile catalysts for the polymerization, linear and cyclic oligomerization and rearrangement of a wide range of olefinic substrates, as well as the linear polymerization of acetylenic substrates containing both electron-withdrawing and electron-donating substituents. Furthermore, by substituting some of the coordinated solvent molecules by other more strongly binding ligands, we are able to modify the activity of these compounds in a predictable way. In addition, we have discovered the first catalysts for the room temperature copolymerization of carbon monoxide with olefins to yield polyketones.

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

357. REACTIONS OF ALKYL PALLADIUM AND PLATINUM DIMERS. MECHANISMS OF DINUCLEAR ELIMINATION $51,893 02-01
J. K. Stille
Department of Chemistry

Metal Clusters can serve as models for metal surfaces in catalysis, and because the cluster is well defined and amenable to study by the methods and techniques available to homogeneous systems, the reactions on clusters can be studied in detail. Thus, a knowledge of the mechanisms of reactions that occur on clusters can provide a better understanding of heterogeneously catalyzed reactions and help in developing new heterogeneous catalysts. The synthesis of dinuclear platinum and palladium complexes containing alkyl groups on adjacent bonded metals, and the reactions of these complexes, particularly the 1,2-reductive elimination reactions are being carried out. The synthesis of certain other homo- and hetero-dinuclear transition metal complexes containing organic groups on the adjacent metal sites also is being accomplished. Elucidation of the mechanism(s) of these reactions should provide a better understanding of how coupling, oligomerization and isomerization reactions of hydrocarbons take place on metal surfaces.

THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

358. STRONG METAL-SUPPORT INTERACTIONS IN HETEROGENEOUS CATALYSTS — $93,415 — 02-01
M. A. Vannice
Department of Chemical Engineering

This program is directed toward a better understanding of the effect of metal-support interactions upon the adsorption and catalytic properties of dispersed metals. Chemisorption, kinetic, infrared and calorimetric studies are being used to examine CO hydrogenation and H_2, CO, and O_2 adsorption on supported Ni, Pd, and Pt. Studies of Pt/TiO_2 and Ni/TiO_2 have shown that only one model explains the higher activity observed, that adsorbed oxygen correlates with activity, and that $PtNi/TiO_2$ bimetallic catalysts are superior. Transient IR studies on Pt/Al_2O_3 are being used to test several mechanisms for methanation. Results to date have already allowed the rejection of one model. A calorimeter (DSC) has been modified and connected to a gas handling system so that isothermal heats of adsorption of H_2, CO, and O_2 on supported Pt can be measured directly. TPD experiments are also being conducted by following the endotherm produced by the desorption process. These studies are a direct probe of changes in the metal-adsorbate bond.

THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

359. CHARACTERIZATION OF ACTIVE SITES AND THEIR ROLE IN GAS-CARBON REACTIONS — $140,000, 24 mo., FY 81-82 — 02-01
Philip L. Walker, Jr., R. G. Jenkins, and F. J. Vastola
Dept. of Materials Science & Engr.

This research is concerned with measuring the concentration of active sites on carbons varying in crystallite size and orientation (all the way from microporous carbons of poor crystallinity to natural graphite flakes of high crystallinity) and relating this concentration to gasification rates. Gasification rates for the $C\text{-}O_2$ reaction are being measured over the pressure range from 1 Pa to 6 MPa. Concentrations of active sites are measured by dissociative chemisorption of oxygen in the absence of gasification and by differences in physisorption behavior of Kr on basal and prismatic (active) surfaces. Companion studies are being conducted in the presence of a 1% loading of platinum. Rate constants are being determined per unit of platinum surface area, using small angle x-ray scattering and electron microscopy to characterize platinum dispersion. The utility of measuring exchange rates between CO_2^{16-16} and CO_2^{18-18} to produce CO_2^{16-18} to characterize activities of carbon and catalyst active sites is being explored.

YALE UNIVERSITY
New Haven, Connecticut 06511

360. ENERGIES OF ORGANIC COMPOUNDS — $77,219 — 02-01
Kenneth B. Wiberg
Department of Chemistry

This project is concerned with factors which control the energies of organic compounds. As part of our study of steric effects, a series of methyl substituted 2,2-dimethoxynorbornanes have been prepared, and their enthalpies of hydrolysis to the corresponding norbornanones has been measured. Large effects have been observed showing that this is a useful system for quantitatively exploring steric effects. Enthalpies of hydration for a series of n-heptenes have been measured and have been compared with our data for the n-hexenes. Bis(dimethylphenylphosphine)iridium-cycloocta-1,5-diene hexafluorophosphate has been found to be a potentially useful homogeneous hydrogenation catalyst for calorimetric studies. Its use is being explored using a newly designed calorimeter head. Reduction of ketones is being studied using lithium selectride to see if this can be made into a calorimetrically useful reaction. Molecular mechanics calculations on these systems are continuing.

Chemical Energy, continued

SRI INTERNATIONAL
Menlo Park, California 94025

361. ADSORPTION THERMODYNAMICS ON METAL CATALYST SURFACES
Henry Wise and Jon G. McCarty
Materials Research Laboratory

$110,000
18 mo.
FY 81-82

02-01

Reversible chemisorption thermodynamics of strong adsorbate-metal surface interactions are measured in this research program. Emphasis is placed on those metal-adsorbate systems of great interest to catalysis of energy-related processes. They include sulfur poisoning of metal catalysts, surface diffusion of adsorbed sulfur, and poisoning of metal catalysts by chlorine. Sulfur chemisorption isosteres are measured on metal and supported metal catalyst in a closed recirculating stream of a dilute mixture of H_2S in 1 atm H_2. At equilibrium, the thermodynamic chemical potential of sulfur in the H_2S/H_2 stream equals that of chemisorbed sulfur. Metals examined or under examination include: Ni, Co, Fe, Ru, Cu, Pt, and Ir. In addition AES/LEED measurements of sulfur coverage on single crystal metal surfaces are in progress. Metals under study include: Ru(001), Ni(100), Ni(111), Cu(100), and Pt(100). Surface diffusion coefficients of chemisorbed sulfur on single-crystal surfaces are being studied by depositing sulfur to a specified coverage in a circular spot and observing the rate of spreading. Current studies involve sulfur diffusion measurements on Ni(111).

ROCKWELL INTERNATIONAL
Canoga Park, California 91304

362. MOLTEN SALT INTERACTIONS IN COAL PROCESSING
S. J. Yosim and G. B. Dunks
Energy Systems Group

$154,914

02-01

This research program is designed to develop an understanding of the fundamental chemical and physical processes involved in the oxidation of carbon in molten salt media. Electrochemical techniques are being employed to determine the effects of melt temperature and sparge gas composition on the *in situ* concentrations of the chemical species (potential oxidants) which exist in beds of pure sodium carbonate sparged with mixtures of oxygen, carbon dioxide and nitrogen between 900-1000°C. Changes which occur in the concentrations of the melt species and in the composition of the exhaust gas as a function of time after the addition of graphite to the melt together with subsequent changes which occur as oxidation of the graphite proceeds to completion are being evaluated. The results of these studies are providing information concerning the identity of transient melt species, the mechanisms through which they are formed and the mechanisms through which they are consumed during graphite oxidation.

Separations and Analysis

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

363. CONTINUOUS CHEMICAL REACTION CHROMATOGRAPHY — $48,000 — 02-02
Rutherford Aris and Robert W. Carr, Jr.
Department of Chemical Engineering
and Materials Science

In this research the behavior of novel chemical reactors for carrying out chemical reaction chromatography by continuous, as opposed to pulsed, operation is being investigated. Effort is currently being placed on countercurrent moving bed reactors. Mathematical models are being devised which, after numerical solution, give guidance for the sizing and selection of operating conditions for a laboratory scale reactor. Such a reactor is currently under construction. Conventional pulsed column reaction chromatography experiments are being done to obtain kinetic parameters for candidate chemical reactions to be used in the continuous reactor. Also, some aspects of the mathematical theory of countercurrent moving bed reactors are being investigated.

BEND RESEARCH, INC.
64550 Research Road, Bend, Oregon 97701-8599

364. FUNDAMENTALS OF COUPLED-TRANSPORT MEMBRANES — $73,892 — 02-02
Walter C. Babcock

The objective of this program is to study the fundamentals of coupled-transport membranes as applied to uranium separations. Coupled-transport membranes consist of a water-immiscible, liquid complexing agent held by capillary forces within the pores of a microporous polymeric support. This membrane separates two aqueous solutions of unequal concentrations. The complexing agent can pick up the ions on one side of the membrane and carry them across the membrane by diffusion in the form of a neutral complex. Metal ions can be transported from a dilute to a concentrated solution by coupling their flow to that of another ionic species. The membranes are also selective due to the selectivity of the complexing agent toward uranium over other metals. Thus, coupled transport is of potentially practical value in hydrometallurgy and in the treatment of radioactive wastes. Current program efforts are focused on studying the long-term performance of the membranes. The goal is to overcome problems of limited lifetime that are common with these membranes.

UNIVERSITY OF MASSACHUSETTS/AMHERST
Amherst, Massachusetts 01003-0035

365. **DYNAMICS OF, AND HEAT AND MASS TRANSFER IN, AN INDUCTION PLASMA** — $70,000, 15 mo. — 02-02
Ramon M. Barnes
Department of Chemistry

This project involves the computer modeling of the flow, temperature, concentration, and spectral radiation fields in an inductively coupled plasma discharge operated at atmospheric pressure in argon and in the presence of nitrogen under conditions popular in commercial configurations employed as a spectral excitation source or atom resevoir. In one computer model local plasma cooling is included in gas-particle interactions during solid vaporization, and a second computer model is being solved in terms of velocity and pressure formulations. Experimental verification of computer predicted plasma properties is being made using emission spectroscopy, laser Doppler anemometry, cine photography, and other physical probe diagnostics. Discharges have been generated at moderate power levels (0.8 - 5 kW) in air, argon, nitrogen, and oxygen at 27.12 and 40.68 MHz with popular plasma torch arrangements. Rotational, excitational, and electron temperature values measured in molecular gas induction plasma exhibit similaries within experimental error for the former two, and maximum temperatures follow the order oxygen > air > nitrogen. Computer models of argon and nitrogen discharges also include non-local thermodynamic equilibrium effects.

TEXAS TECH UNIVERSITY
Lubbock, Texas 79409

366. METAL ION COMPLEXATION BY IONIC CROWN ETHERS $43,178 02-02
Richard A. Bartsch
Department of Chemistry

The goals of this research are the preparation of crown ethers with ionizable functional groups and the utilization of these compounds in selective metal ion complexation. A variety of crown ether carboxylic acids are being prepared in which the following structural features are systematically varied: a) the size of the crown ether cavity; b) the number and type of ethereal oxygen atoms in the ring; c) the length of the hydrocarbon chain which connects the carboxylic acid group to the crown ether ring; and d) the attachment site(s) for lipophilic alkyl groups. The efficiency and selectivity of these crown ether carboxylic acids in solvent and emulsion extractions of alkali and alkaline earth cations from aqueous media are being assessed. The capacity of these novel complexing agents for active transport of alkali metal cations across liquid membranes is also being examined.

AMHERST COLLEGE
Amherst, Massachusetts 01002

367 ISOTOPE EFFECTS IN THE SOLUTION OF GASES IN LIQUIDS $47,080 02-02
Bruce B. Benson, Daniel Krause, Jr.
Department of Physics

Isotope effects associated with both solvent and solute are being used to study interactions of gases with liquids. Very precise manometric methods are making it possible for the first time to determine accurately the changes in the thermodynamic properties of gaseous solutions which accompany substitution of deuterium for hydrogen in water. With neon, for example, the solubility in D_2O is greater than that in H_2O by from approximately 13% at 5°C to about 7% at 50°C. Analysis of the data suggests that the minimum difference occurs at approximately 97°C. The precision is 0.05%. Interpretation of the measurements of isotopic fractionation of gases during solution in terms of an harmonic potential model indicates that the internal diameters for "clusters" in water are consistent with diameters in Structure I clathrate hydrates. Experiments are being carried out to examine possible isotopic fractionation of guest molecules during enclathration. Isotopic effects associated with thermal transport complicate the interpretation of the initial results, but fractionation apparently does occur, and improved experimental methods are being developed.

STATE UNIVERSITY OF NEW YORK, STONY BROOK
Stony Brook, New York 11794

368. FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY $113,784 02-02
Jacob Bigeleisen
Department of Chemistry

Experimental and theoretical investigations are being made of isotope effects in chemical and physical processes. When appropriate, applications are made to isotope separation processes and nuclear fuel cycles. A systematic study of the isotope chemistry of nitrogen is being made by the WIMPER(2) expansion. Compounds under investigation include NO, NO_2, HNO_3, NH_3, NOX (X = F, Cl, Br), etc. Further evaluation of feed cycles for the industrial production of heavy water is being carried out under this program. Particular attention is being given to hydrogen, ammonia and water as feed materials in a process in which fluoroform is isotopically selectively dissociated by multiphoton absorption of infra-red radiation from a CO_2 laser. The combination of a hydrogen feed cycle with fluoroform as a working medium appears to be the optimum laser process for annual D_2O production rates under 100 tons.

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

369. SEPARATION OF ALKALI, ALKALINE EARTH AND RARE EARTH CATIONS BY LIQUID MEMBRANES CONTAINING MACROCYCLIC CARRIERS — $72,500 — 15 mo. — FY 81-82 — 02-02
James J. Christensen
Thermochemical Institute

This research program studies the use of macrocyclic ligands such as crown ethers and cryptands as carriers of cations through hydrophobic liquid membranes. These ligands are noted for their high degree of selectivity among cations, and this selectivity may be exploited in liquid membrane systems to effect cation separations. Stirred, bulk chloroform membranes are being used to screen the macrocycles for cation selectivity and to study the characteristics of cation transport of this type using either single cations or mixtures of cations. A mathematical model has been developed to describe this membrane transport and is being tested against experimental transport data. In other experiments, macrocyclic carriers are incorporated into liquid surfactant or 'emulsion' membrane systems. These membranes offer high surface area and short diffusion paths necessary to allow large cation fluxes for efficient separations. Rapid transport and high cation selectivity have been observed with emulsion membranes. A model is being developed to describe these results.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

370. MULTIHETEROMACROCYCLES THAT COMPLEX METAL IONS — $118,139 — 02-02
Donald J. Cram
Department of Chemistry

This research involves the design, synthesis and evaluation of cyclic and multicyclic organic compounds that selectively complex metal salts and solubilize them in organic solvents. Spherands are synthetic ligand systems that in the uncomplexed state contain enforced cavities lined with electron pairs. They are composed of rigid cyclic frameworks that place heteroatoms in spherical arrangements around enforced cavities. Spherands are being studied that are composed of six or eight anisyl units attached to one another in a ring through aryl-aryl bonding in their 2,6-positions. They are highly cation selective in forming metallospherium salt complexes of unusual stability. Hemispherands are hybrids of spherands and chorands (crowns). Spherands and hemispherands are being prepared and examined which contain anisyl, methoxycyclohexyl, urea, pyridine, pyridine oxide and amide units. Metal ion and isotope-specific complexing agents are sought.

BROWN UNIVERSITY
Providence, Rhode Island 02912

371. PHOTOCHEMICAL GENERATION OF THE OPTOACOUSTIC EFFECT — $55,338 — 02-02
Gerald J. Diebold
Department of Chemistry

The purpose of this research is to study the optoacoustic effect produced in systems obeying second-order kinetics. When a diatomic gas is photodissociated the radicals recombine to generate an acoustic wave. The nonlinear rate equations describing the release of energy into translational motion have unique dependencies upon the radiation intensity and the modulation frequency, as a result of the second-order kinetics. These effects are being investigated with Br_2 and $C\ell_2$ in a high pressure acoustic cell over a wide range of conditions. If H_2 is added, two-center chain reactions are initiated by the radiation. Since they often are highly exothermic and have long chains, the propagation steps dominate the energy release and a large gain in the amplitude of the optoacoustic signal is observed. The reaction of $C\ell_2$ with H_2 is now being examined to verify this prediction.

NAVAL RESEARCH LABORATORY
Washington, DC 20375

372. XENON/KRYPTON ELEMENTAL PHOTOCHEMICAL SEPARATION — $69,000 — 02-02
Terence Donohue
Laser Physics Branch
Optical Sciences Division

The noble gases xenon and krypton have been separated by a photochemical technique in both static and flowing systems. Ultraviolet light is used to photolyze fluorine molecules to form atoms which selectively react with only the xenon in the gas mixture, forming solid xenon difluoride. The best results obtained give enrichments for xenon of 6850 (purity of 99.988%), where virtually all of the xenon has been removed, and the remaining krypton has a purity of 99.8%. The photolysis sources used include a medium-pressure mercury lamp at 366 nm, a XeF excimer laser at 351 nm and a high-power (up to 1 kW) low-pressure Hg lamp (254 nm) arranged in coaxial fashion around a quartz reaction vessel through which the gas mixture is flowed at various rates. Separation factors are satisfactory in the flowing system but yields are lower than expected, indicating possible photolysis of the product by the shorter wavelength light employed. Studies are being made of continuous separations using longer wavelength photolysis sources.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

373. FOURIER TRANSFORM PHOTOACOUSTIC SPECTROSCOPY — $65,000 — 02-02
Edward M. Eyring
Department of Chemistry

A combination of dispersive ultraviolet-visible and Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS) and X-ray photoelectron spectroscopy (XPS) is being used to elucidate the species adsorbed on heterogeneous catalysts, corrosion products on metals, and the surface chemistry of semiconducting polymers. Specific applications include the detection of infrared radiation induced disproportionation of carbon monoxide on a Ni/SiO_2 catalyst, the determination that Lewis acid sites that bind pyridine on a Mo-Co-alumina hydrodesulfurization catalyst are on the support rather than on a separate MoS_2 phase as previously hypothesized, and the identification of a mixed ferro(ferrocyanide) complex with some ammonium counterion as the corrosion product formed on iron metal in a commercial HCN production process. Work continues on the preparation of metal carbonyls such as $Re_2(CO)_{10}$ on SiO_2 by photolysis and the synthesis of n- and p-doped organic polymers such as polyacetylene and polypyrole. These materials have challenging spectroscopic properties that suggest useful improvements in the photoacoustic techniques.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

374. REACTIONS OF METAL IONS AND THEIR CLUSTERS IN THE GAS PHASE USING LASER IONIZATION-ION CYCLOTRON RESONANCE SPECTROSCOPY — $75,000 — 02-02
Ben S. Freiser
Department of Chemistry

The development of a combined pulsed laser source-ion cyclotron resonance spectrometer has proven to be a convenient and powerful method for generating and studying metal ions in the gas phase. In addition, this past year we put into operation a state-of-the-art Fourier transform mass spectrometer (FTMS) and found it to be particularly suited to this work. The capability of FTMS to obtain a complete spectrum from one laser shot at extraordinarily high resolution, for example, together with its extended mass range and capability for performing collision induced dissociation (CID), enhances our previous capabilities and opens new avenues which we are pursuing including: (I) the study of metal ions as chemical ionization reagents and (II) characterization and application of FTMS-CID techniques for the study of metal ion chemistry. These two major areas are the essence of our current research program and encompass a wide range of fundamental and applied studies.

University of Arizona
Tucson, Arizona 85721

375. CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY Henry Freiser Department of Chemistry	$71,000	02-02

This research is designed to develop chelating extractants of improved selectivity for separating individual lanthanide and actinide ions. Emphasis is being placed on uncovering molecular structural parameters of importance in the design of such extractants. Use of pattern recognition techniques represent one approach to the elucidation of molecular parameters. Study of the extraction equilibria for representative tervalent lanthanides with selected members of chelating extractants of the N-acylphenylhydroxylamine, 8-quinolinol, and acylpyrazolone families is being used both because they include some likely candidate extractants and because present gaps in fundamental data required to apply pattern recognition is thereby being acquired.

THE AEROSPACE CORPORATION
PO Box 92957, Los Angeles, California 90009

376. GAS PHASE ENERGY TRANSFER IN ALKALINE EARTH METAL IONS Jerry Gelbwachs Chemistry and Physics Laboratory	$95,000 18 mo. FY 82-83	02-02

Laser-induced nonresonant fluorescence spectroscopy has recently provided single-atom detection limits and volumetric detection ratios of 1 part in 10^{17}. The method has also provided a powerful means for the study of energy transfer processes that involve excited state atoms and various collision partners. The proposed work seeks to extend these studies to include the monovalent alkaline earth cations in an effort to better understand the energy transfer processes that control atomic/ionic fluorescence detection limits. A systematic study of the population redistribution that occurs in collisions between electronically excited ions and various collision partners will be undertaken. Besides the value to improved trace detection limits, the collisional cross sections will provide data to assist in the understanding of the range and nature of the ion-neutral interaction potentials important to our understanding of the plasma state.

UNIVERSITY OF MARYLAND/COLLEGE PARK
College Park, Maryland 20742

377. NON-DESTRUCTIVE DETERMINATION OF TRACE-ELEMENT CONCENTRATIONS Glen E. Gordon, William B. Walters, William H. Zoller and David L. Anderson Department of Chemistry	$108,300	02-02

An instrumental nuclear method of analysis, neutron-capture prompt γ-ray activation analysis (PGAA), has been developed. A neutron-beam facility was constructed at the National Bureau of Standards reactor. Samples are placed in the beam and prompt γ rays emitted following neutron capture by nuclei in the sample are observed between 0.1 and 11 MeV with a Ge(Li) detector system. Concentrations of most of the following elements can be measured in coal, fly ash, rocks and volcanic debris: H, B, C, N, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Cd, Sm and Gd. PGAA is an excellent tool for geochemical studies, as concentrations of all major species normally measured in rocks except P can be measured in 2-hr runs. The use of PGAA for energy-related materials has been studied: coal, oil, oil shale, fly and cores from bore holes. Analyses in progress include construction materials (concrete, cement, steels), special nuclear waters, burnable fuel element poisons (B, Gd), and biological samples, especially human liver samples. The use of ^{252}Cf as a neutron source is under study.

UNIVERSITY OF VIRGINIA/CHARLOTTESVILLE
Charlottesville, Virginia 22901

378. THE GLOW DISCHARGE AS AN ATOMIZATION AND IONIZATION SOURCE $63,000 02-02
W.W. Harrison
Department of Chemistry

This project is a study of the glow discharge as an atomization and ionization source. Of interest is the development of the discharge as a source for the trace element analysis of solids by mass spectrometry. By coupling the glow discharge to a quadrupole mass filter, a relatively simple mass spectrometer is obtained. Both atomic absorption and mass spectrometric studies are made with the present source, allowing information to be obtained concerning both ground state atoms and discharge generated ions. A disc electrode configuration has been developed for solution samples. Vitreous carbon has proven to be the best matrix for the disc cathode. Particular application is being made to the lanthanide elements. Reactive sputtering gases, such as oxygen, are under study for comparison to the inert gases normally used.

THE UNIVERSITY OF WYOMING
Laramie, Wyoming 82071

379. SOLID SURFACE LUMINESCENCE ANALYSIS $66,800 02-02
Robert J. Hurtubise
Chemistry Department

The primary goal of this project is to develop an understanding of the physical and chemical interactions needed for strong fluorescence and phosphorescence signals from organic compounds adsorbed on particular surfaces. Basic and nonbasic nitrogen heterocycles and hydroxyl aromatic compounds are being adsorbed on polyacrylic acid-NaBr mixtures, filter paper, and silica gel chromatoplates to induce fluorescence and room-temperature phosphorescence signals. Reflectance, infrared, nuclear magnetic resonance, and luminescence spectroscopy are being used to clarify the interactions. Luminescence polarization and phosphorescent lifetime experiments are also being performed. Solvent effects on adsorbing the samples, and the effects salts mixed with polyacrylic acid are being considered for their ability to enhance luminescence. In addition, total luminescence derivative spectroscopy is being developed as a new approach in organic trace analysis.

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

380. STABLE ISOTOPE STUDIES $119,574 02-02
Takanobu Ishida
Department of Chemistry

This program consists of basic and developmental studies of various methods for fractionating stable isotopes and exploration of theoretical basis to further our understanding of the differences in isotopic properties that make efficient separations possible. Fractionation of nitrogen-15 by an exchange between nitric oxide and dinitrogen trioxide is studied using a packed exchange column and a refluxer column at temperatures between -15°C and 20°C under pressures between 1 atm. and 15 atm. Two product refluxer systems for the Nitrox process for separating nitrogen-15 are investigated, in which no chemical feeds are required and no chemical wastes are produced. Catalytic isotope exchange reactions between ammonia, hydrogen, and nitrogen are studied. Relative volatilities of $^{12}CH_2F_2$, $^{13}CH_2F_2$, and $^{12}CD_2F_2$ and those of $^{14}NH_3$, $^{15}NH_3$, and $^{14}ND_3$ are measured using precision differential manometry, and ab initio molecular orbital calculations are carried out on clusters of CH_3F of various sizes. A new mathematical method is being developed to correlate the zero-point energy with molecular forces and structures.

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

381. DEVELOPMENT AND OPTIMIZATION OF METHODOLOGIES FOR ANALYSIS OF COMPLEX HYDROCARBON MIXTURES R. J. Laub Department of Chemistry	$72,200	02-02

The goals of this project comprise exploration and further clarification of optimization methodologies for gas- and liquid-chromatographic separations of complex hydrocarbon mixtures. Emphasis is being placed at present on temperature effects and mobile-phase composition in microbore-, conventional-bore, and rotating-disk thin-layer liquid-chromatographic techniques with silica, reversed-phase silica, and alumina adsorbents. Cartesian-coordinate graphical methods of data reduction are being developed for optimization of interdependent system variables in terms of maximal resolution of all solutes in a given mixture. Computer data acquisition and reduction with these and with triangular and prismatic coordinate systems are also being implemented. Fractions from the LC separations are being examined by ultra-high efficiency open-tubular column gas chromatography, where binary stationary phases and blended carriers are used simultaneously for resolution of literally thousands of components in each. A new class of mesogenic polysiloxane solvents has also been synthesized, characterization and evaluation of the practical utility of which are now under way.

University of Georgia
Athens, Georgia 30602

382. A Study of Mechanisms of Hydrogen Diffusion in Separation Devices M. Howard Lee Department of Physics and Astronomy	$101,521 18 mo. FY 82-83	02-02

The diffusion of hydrogen isotopes in transition metals is highly selective and does not follow the classical Arrhenius theory at low temperatures. The hydrogen diffusion properties can be a basis for isotope separation devices in heavy-water enrichment, hydrogen purification and nuclear fusion reactors. To explore these possible applications, a study of hydrogen diffusion mechanisms in Pd has been carried out by constructing a quantum statistical mechanical model of the lattice hydrogen. The PdH system shows well-defined phase transitions and mean-field critical behavior. For high temperatures our model for the cooperative hydrogen diffusion is found to be isomorphic to mean-field-like models of magnetism for biquadratic spin exchange interaction. For low temperatures, lattice hydrogen atoms appear to exist in clusters which can nucleate and grow like droplets in the metastable phase. Our study suggests that the low temperature phase of the PdH system has a striking similarity to the phase of ^{3}He/^{4}He mixtures below the tricritical temperature.

KENT STATE UNIVERSITY
Kent, Ohio 44242

383. ADSORPTION AND DESORPTION OF HYDROCARBONS AT LOW CONCENTRATIONS Richard Madey Department of Physics	$60,000	02-02

This research program is designed to examine experimental and theoretical aspects of the adsorption of single gases and gas mixtures on several adsorbents, and to study the dynamics of adsorption and desorption of adsorbates in adsorber beds. Experimental techniques involve measurements of the transmission (or normalized output concentration) of single gases and gas mixtures at various concentrations and temperatures flowing through selected adsorbents. Emphasis is placed on correlating data based on the potential theory approach and on relating the theoretical parameters to molecular properties. Theoretical studies are made on the kinetic parameters of adsorber beds such as the intraparticle diffusion coefficient and the longitudinal diffusion coefficient. Available analytical solutions are compared with experimental results.

TEXAS SOUTHERN UNIVERSITY
Houston, Texas 77004

384. SOLVENT EXTRACTION STUDIES USING HIGH-MOLECULAR-WEIGHT AMINES $27,210 02-02
Curtis W. McDonald
Department of Chemistry

The primary objective of this research is to develop efficient, simple and economic methods to remove trace quantities of metal ions, especially toxic metal ions such as mercury, lead, cadmium, chromium and nickel from aqueous solutions via high-molecular-weight amine liquid-liquid extraction and/or surfactant-foam separation. Of utmost concern is developing methods which require a minimum of energy and are amenable to scale-up for removal of metal ions from industrial wastewater. There is also concern for developing the chemistry associated with these separation techniques. High-molecular-weight tertiary amines proved to be excellent reagents for liquid-liquid extraction whereas certain high-molecular-weight quaternary ammonium salts are excellent reagents for surfactant foam separation techniques.

UNIVERSITY OF MINNESOTA
St. Paul, Minnesota 55108

385. INTERFACIAL CHEMISTRY IN SOLVENT EXTRACTION SYSTEMS $70,000 02-02
Ronald D. Neuman
Department of Forest Products

The objective of this study is to further our understanding of the complex chemistry involved in the solvent extraction of metal ions from an aqueous phase to a nonpolar organic phase. The behavior of extractant molecules and their interactions with metal ions at liquid/vapor and liquid/liquid interfaces are to be investigated using recently developed laser light-scattering techniques in conjunction with soluble and insoluble monomolecular film studies. The effects of HNO_3 and HCl on the interfacial properties of HDEHP/n-hexane/aqueous systems presently are being investigated. Model long-chain alkyl phosphates are being synthesized to examine the influence of specific molecular interactions on the interfacial properties. Their study requires the development of an interfacial film balance suitable for use in the optical cell for laser light-scattering measurements. In addition, electron microscopic techniques are being further developed to examine structural changes occurring in interfacial films.

UNIVERSITY OF GEORGIA RESEARCH FOUNDATION, INC.
Athens, Georgia 30602

386. FUNDAMENTAL STUDIES OF SEPARATION PROCESSES $77,000 02-02
L. B. Rogers
Department of Chemistry

This research has three major goals. First, vanadium non-porphyrins from Venezuelan crude oil will be used to examine solvent/column-packing interactions in liquid chromatography. Similar studies of nickel porphyrins and non-porphyrins will be started later. Assuming that successful separations of pure species can be obtained, spectroscopic identifications of the ligands will be attempted. Second, samples of monodispersed polystyrene will be used to explore solute/column-packing interactions. Studies will be directed toward minimizing the destructive effect of steric exclusion during an adsorptive fractionation of oligomers. Finally, basic studies of a chromatographic column-switching technique will be made using the recycle mode in gas chromatography and, possibly, a three-oven chromatograph.

NATIONAL BUREAU OF STANDARDS
Washington, District of Columbia 20234

387. COMPETITIVE REACTION KINETICS APPLIED TO FUEL TECHNOLOGY $117,000 02-02
L. Wayne Sieck
Center for Chemical Physics.

This effort focusses on the application of competitive ion-molecule reaction kinetics to the development of rapid, discriminatory, and accurate new mass spectrometric methods for the screening and characterization of fossil fuels and industrial petroproducts. The research encompasses two general areas, one dealing with the measurement of fundamental properties of ions, including enthalpies of ionization, reaction rates, and mechanisms, and the other involving application of the fundamental measurements to the quantification of classes of components in liquid fuels and other petroproducts for use in analysis, process control, energy content determination, forensic science and so forth. The experimental program utilizes the NBS high pressure mass spectrometer, which is capable of pulsed operation using either electron impact or photoionization, as well as the NBS pulsed ion cyclotron resonance mass spectrometer. In addition to the analytical developmental program, effort is also directed towards understanding the ionic role of soot formation in fuel-rich flames.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

388. MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES $75,836 02-02
15 mo.
FY 81-82

S. A. Stern, S. S. Kulkarni, and G.R. Mauze
Department of Chemical Engineering and
Materials Science

The main objective of this study is to assess the validity of a "free-volume" model of gas transport in and through polymer membranes. The model is applicable at temperatures above the glass-transition temperature of polymers. Studies performed up to now show that permeability and diffusion coefficients for simple gases in polyethylene, as well as the pressure and temperature dependence of these coefficients, are satisfactorily predicted by the free-volume model. The penetrant gases studied include He, N_2, Ar, CO_2, CH_4, C_2H_4, C_3H_8, and SF_6. Permeability and diffusivity measurements are being made between 5° and 50°C and at pressures up to 50 atm. Simple correlations of characteristic free-volume parameters have been developed. These correlations permit the prediction of diffusion and permeability coefficients for many other gases and vapors in polyethylene; solubility coefficients are also required for this purpose. The studies are being extended to other polymers [poly(vinyl acetate) and poly(n-butyl methacrylate)]. An extension of the model to glassy polymers is also being investigated. The ability to predict permeability coefficient will greatly facilitate the development of energy-efficient membrane processes for the separation of industrial gas mixtures.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

389. SELECTIVE METAL ION EXTRACTION FOR MULTIPLE ION LIQUID-LIQUID EXCHANGE REACTIONS $70,103 02-02
Lawrence L. Tavlarides
Department of Chemical Engineering and
Materials Science

This research in hydrometallurgical solvent extraction is to develop a fundamental means to predict selectivity during simultaneous solvent extraction of multiple metal ions when kinetic rates and thermodynamic equilibria do not favor the desired metal. The chemical kinetics and thermodynamic chemical equilibria models for the system copper-iron-acid sulfate solutions extracted by β-alkenyl-8-hydroxy quinoline in xylene are being determined. Chemical equilibria studies are in progress for the iron-acid-sulfate-β-alkenyl-8-hydroxy quinoline-xylene system. An aqueous phase ionic equilibrium model is available to calculate concentrations of various iron species present. Iron extraction data are obtained using both the AKUFVE, a high intensity stirrer with an in line centrifugal separator and a shaker bath apparatus. Analysis of the data with a thermodynamic equilibrium model is in progress. Kinetic experiments are conducted employing the novel liquid jet recycle reactor for the iron system. Chemical analysis includes in line spectrophotometry and atomic absorption photometry.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

390. PARTICLE DEPOSITION IN GRANULAR MEDIA — $94,495 — 02-02
Chi Tien
Department of Chemical Engineering
and Materials Science

This research is intended to obtain fundamental understanding of various phenomena arising from the flow of aerosol suspensions through and the deposition of aerosols in granular media. The study is focused on the following areas: (1) Experimental study of the transient state behavior of aerosol filtration in experimental filters; (2) The study of aerosol collection in magnetically stabilized fluidized filters and its modelling; and (3) The application of a specially designed two dimensional filter for in-situ observation of the change of media structure due to the retention of aerosol particles.

UNIVERSITY OF HOUSTON/Houston, Texas 77004
MARTIN-MARIETTA LABS/Baltimore, Maryland 21227

391. MECHANISMS OF CAKE FILTRATION — $160,108 — 02-02
Frank M. Tiller
Chemical Engineering-Univ. of Houston
Maher Tadros
Martin-Marietta Laboratories

This project is aimed at developing the theory of particulate separation involving compressible, porous beds or sediments as found in filtration, centrifugation, and sedimentation. A key feature of the investigation involves close collaboration between the University of Houston and Martin-Marietta Laboratories. Generation of reliable data under well-defined conditions and integrating the areas of pretreatment, thickening, and separation are objectives of the research. Particle characteristics are being related to suspension behavior and cake structure. Sedimentation rates and cake structure are being correlated. The initial structure of deposits as affected by surface charge, suspension concentration, and agitation is being studied in relation to resistance to flow. Included in the program are internal flow mechanisms involving porosity and pressure distribution. Fine particle migration is being related to cake and medium blinding. Rheological and electrophoretic properties of suspensions are being correlated with separation behavior.

Columbia University
New York, New York 10027

392. UTILIZATION OF MAGNETIC EFFECTS AS A MEANS
OF ISOTOPE ENRICHMENT — $60,000 — 02-02
Nicholas J. Turro
Department of Chemistry

This research program is directed toward the development of novel methods for the separation of isotopes based on exploitation of differences in magnetic properties of isotopes. Emphasis has been placed on discovering reactions and conditions which allow the separation of isotopes which possess a finite magnetic moment from those which do not possess a magnetic moment. Successful systems have been designed for separation of ^{13}C (a magnetic isotope) from ^{12}C (a non-magnetic isotope) and for the separation of ^{17}O (a magnetic isotope) from ^{16}O and ^{18}O (non-magnetic isotopes). The efficiency of ^{13}C enrichment via the photolysis of dibenzyl ketone (DBK) in micellar solution has been found to occur in other media, such as polymer films and porous solid surfaces. The ^{13}C enrichments in the products of DBK photolysis were shown to be dependent on the ^{13}C micellar-electronic hyperfine coupling of the ^{13}C atoms in the $C_6H_5CH_2CO$ $CH_2C_6H_5$ geminate radical pair produced by photolysis of DBK.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

393. STUDIES OF ISOTOPIC MASS EFFECTS IN CHEMISTRY Max Wolfsberg Department of Chemistry	$74,994	02-02

This project deals with theoretical studies of isotopic mass effects on the physical and chemical properties of molecules. While such theoretical work is usually carried out within the framework of the Born-Oppenheimer approximation, corrections to this approximation are now being explored. Theoretical calculations of the rotational-vibrational energy levels of diatomic molecules, of linear and non-linear triatomic molecules, and of four-atomic molecules are being carried out by quantum mechanical variational methods. These energy levels are employed in the very precise statistical mechanical evaluation of equilibrium constants for isotopic exchange reactions. Methods for doing such evaluations without explicitly calculating the energy levels are also being explored and are being used to obtain an insight into the origins of isotope effects. Molecular dynamics calculations are being employed to study the microscopic behavior of liquids in order to gain a better understanding of isotope effects involving the liquid phase such as isotope effects on vapor pressures.

THE AEROSPACE CORPORATION
El Segundo, California 90245

394. ISOTOPICALLY SELECTIVE, TWO-STEP, LASER PHOTODISSOCIATION OF MOLECULES P. F. Zittel Chemistry and Physics Laboratory	$102,275	02-02

This research is directed toward understanding the photophysical and chemical processes which underly the separation of isotopes by two-step, laser photodissociation of small molecules. The two-step technique involves the vibrational excitation of molecules containing a chosen atomic isotope with a pulsed infrared laser, followed by photodissociation of the excited molecules with a pulsed ultraviolet laser and chemical scavenging of the photodissociation fragments. Two-step photodissociation of carbonyl sulfide (OCS) is found to separate various isotopes of carbon, oxygen, and sulfur, including the "middle" isotope ^{33}S which is difficult and expensive to separate by conventional techniques. The study focusses on measuring the absorption of intense IR laser radiation by OCS, characterizing the effect of vibrational excitation on the UV photodissociation cross section of OCS, and determining a rate constant for collisional transfer of vibrational energy among OCS isotopes. A computer model aids in evaluating competing energy transfer and chemical reaction processes. Similar photophysical and isotope separation studies have been completed for HBr, O_3, and CH_3Br, and are being extended to a variety of other small molecules.

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

398. STATISTICAL MODELLING AND ANALYSIS OF CHEMICALLY REACTING TURBULENT FLOWS — $145,000 — 02-04
H. A. Dwyer, W. Kollmann — 24 mo.
Department of Chemical Engineering — FY 82-83

The research program is directed towards the goal of improving the modeling of turbulence flows with combustion. To accomplish this goal, three approaches are currently being used which are: (1) New closure models of statistical correlations; (2) Probability density function models; and (3) Sensitivity analysis of turbulence models. The closure of the equations for the density-velocity correlation and the kinetic energy of turbulence has been developed further to account for the influence of chemical heat release and velocity divergence. The closure model for the probability density function for passive scalars has been extended to include the prediction of the intermittency factor. This model is currently developed for turbulent diffusion flames and preliminary solutions have been obtained. Sensitivity analysis has been completed for the incompressible round jet, and preliminary solutions with mass averaged equations have been completed for the compressible jet.

NATIONAL BUREAU OF STANDARDS/BOULDER
Boulder, Colorado 80303

399. EXPERIMENTAL AND THEORETICAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF FLUID MIXTURES — $215,000 — 02-04
15 mo.
Howard J. M. Hanley — FY 82-83
Division 773

The program is a coordinated task of experiment, theory, and correlation to study the properties and behavior of fluids. Specific objectives are to produce PVT and thermodynamic data on hydrocarbon fluids and their mixtures at high temperatures (to 900 K) and pressures (to 35 Mpa, possibly to 100 Mpa), to develop the theory of liquids and to develop models to predict the properties based on the theory and optimized by the data. A high temperature high pressure PVT apparatus has been completed and the PVT properties of H_2S are being measured. A VLE/LLE phase equilibria apparatus is under construction. Phase equilibria VLE measurements of the system CO_2/i-butane are underway. Theoretical studies include computer simulation of fluids under shear. A computer package to predict the transport properties of hydrocarbons and their mixtures to C_{20} has been completed and will be extended to include polar species.

STANFORD UNIVERSITY
Stanford, California 94305

400. FUNDAMENTAL STUDIES OF FLOW AND INSTABILITIES IN POROUS MEDIA — $135,000 — 02-04
George M. Homsy — 24 mo.
Department of Chemical Engineering — FY 81-82

Research under this contract is focused on understanding the flow of non-Newtonian fluids through porous media and the stability of processes which seek to produce oil by displacement with dilute polymer solutions. Recent work has been focused on two aspects polymer flooding. The first is to understand the observed increase in flow resistance of polymers by considering constricted tube models of porous media, and by solving the relevant non-Newtonian flow equations. We find the flow resistance can either increase due to the extensional nature of the flow or decrease due to shear-thinning, and criteria are being developed to determine the conditions for which one of these situations will prevail. The second is to experimentally verify our recently-developed theory of optimal graded-mobility processes, by measurement of the growth constants for the viscous fingering instability in Hele-Shaw cells.

Chemical Engineering Sciences

STANFORD UNIVERSITY
Stanford, California 94305

395. TRANSPORT CHARACTERISTICS OF SLURRIES IN PIPELINES: FLOW REGIMES AND PRESSURE DROP Andreas Acrivos Department of Chemical Engineering	$150,000 36 mo. FY 81-83	02-04

This research aims to study the flow of slurries in pipelines from a fundamental point of view. Primary emphasis is placed on developing methods, based on sound scientific principles, for predicting the pressure drop and for delineating the various flow regimes that can occur in such systems. The theoretical framework is based on the equations of continuum mechanics and is being developed in close conjunction with a parallel experimental study. A theoretical model is currently being developed whose purpose is to explain quantitatively the curious and surprising phenomenon whereby a settled suspension was observed to resuspend in the presence of a laminar shear flow even under conditions of very small Reynolds numbers.

STATE UNIVERSITY OF NEW YORK/STONY BROOK*
Stony Brook, New York 11794

396. CHEMICAL REACTIONS AND TURBULENCE Rene Chevray Department of Mechanical Engineering	$103,785 15 mo. FY 82-83	02-04

The interactions of turbulence and chemical reactions are investigated for a well defined flow configuration in which we have chemical reaction. The reaction chosen ($NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu + O_2$) has a known simple kinetic scheme. To avoid the influence of finite heat release, we use small concentrations while investigaging large Reynolds numbers, small dilution numbers, large Damkhöler numbers and several concentration ratios. Measurements being made are conditional (based on the presence of one species) as well as conventional and include mean as well as fluctuating quantities. The velocity field is investigated by laser doppler velocimetry while the concentrations are measured by absorption spectroscopy. These results are being compared to the model established from the equations describing the evolution of the probability density functions of the species concentrations in this flow.

*This research will continue at Columbia University in FY 1983.

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

397. PREDICTION OF THERMODYNAMIC PROPERTIES FOR COAL DERIVATIVES Marc D. Donohue Department of Chemical Engineering	$56,000	02-04

The purpose of this project is to develop an engineering correlation to predict the thermodynamic properties of coal derivatives. The correlation is based on perturbed-hard-chain theory but includes additional terms for multi-pole interactions. The correlation allows prediction of vapor pressures, densities, enthalpies, heats of vaporization, and solubilities for a wide range of organic molecules including multiringed aromatics. Pure component and mixture parameters are determined from experimental data when available; a group-contribution correlation is being developed to allow prediction of parameters for systems where no experimental data are presently available. Experiments have been made to measure Henry's law constants for numerous alkane-alkane, alkane-aromatic and aromatic-aromatic pairs. A new experimental apparatus is being built to study such mixtures over wider ranges of temperature, pressure and composition.

NATIONAL BUREAU OF STANDARDS
Washington, D. C. 20234

401. TRANSPORT AND PHASE EQUILIBRIA IN MULTICOMPONENT FLUIDS — $70,000 — 02-04
John M. Kincaid
Thermophysics Division

The purpose of this project is to develop and implement simple, accurate techniques to treat the transport and phase transition properties of multicomponent systems. There are three basic aspects to the project: (1) the development of new techniques to study multicomponent systems; (2) the "translation" and adaptation of recent theoretical advances in transport and phase transition phenomena to forms usable to the energy technologies; (3) approximation assessment and implementation. All three of these areas can be expected to advance our understanding of multicomponent fluids at high temperatures. Recent progress includes: the development of a kinetic perturbation theory (1); the solution of several phase equilibria problems for polydisperse fluids (1); and molecular dynamics studies of diffusion in binary hard-sphere mixtures are being used to calibrate the Revised Enskog Theory (3).

NORTH CAROLINA STATE UNIVERSITY
RALEIGH, NORTH CAROLINA 27650

402. DYNAMIC MEASUREMENTS OF TWO-PHASE FLOW PHENOMENA USING NMR TECHNIQUES — --- — 02-04
R. F. Saxe
Nuclear Engineering Department

The objectives of this project are to develop equipment which can measure the characteristics of two-phase flow as a function of time and of space within a reasonably large volume and to analyze the resulting characteristics as fluctuation phenomena. The measurement technique will utilize NMR imaging techniques to measure void volume as a function of space. Repetitive scanning and Fourier transform techniques will allow the spatial distribution to be studied as a function of time, the signals being stored on magnetic tape and subsequently analyzed by computer. The investigation of two-phase phenomena as fluctuation phenomena is important if transients are to be understood and computer calculations are to be verified.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

403. FUNDAMENTAL HEAT TRANSFER PROCESSES RELATED TO PHASE CHANGE THERMAL STORAGE MEDIA — $58,840 — 02-04
E. M. Sparrow
Department of Mechanical Engineering

Research on the fundamental heat transfer processes which occur during freezing and melting is being performed in connection with the storage of thermal energy by phase change. Emphasis is being given to freezing and melting in closed circular tubes in order to obtain information on encapsulated thermal storage. In the melting studies, the solid is initially either at the phase-change temperature or subcooled, while in the freezing studies both superheated and non-superheated liquids are employed. For freezing (or melting), measurements are made of the energy extracted (or added) as a function of time. The separate contributions of latent heat and sensible heat to the extracted (or added) energy are being determined. Natural convection in the liquid melt plays an important role in the heat transfer during melting, but there is little effect of natural convection in the unfrozen liquid on the heat transfer during freezing. Direct measurements of the freezing (melting) fronts are being made.

Chemical Engineering Sciences, continued

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

404. TRANSPORT PROPERTIES OF MULTIPHASE SYSTEMS — $145,000 — 02-04
George Stell — 24 mo.
Department of Mechanical Engineering — FY 81-82

Ongoing research on the microscopic theory of transport in two-phase random media continues, as does a study of multicomponent mixtures of particles with pair attraction treated in a mean-field approximation. A microscopic theory of intrinsic viscosities based on velocity chaos has been completed, and a kinetic perturbation theory (carried out to high order) for transport coefficients on the Boltzmann-equation level nears completion. New work on model Boltzmann equations, on a kinetic theory of polymerization and coagulation, and on percolation theory is in progress.

CORNELL UNIVERSITY
Ithaca, New York

405. EXPERIMENTAL AND THEORETICAL STUDIES OF DENSE FLUID MIXTURES — $180,000 — 02-04
W.B. Streett and K.E. Gubbins — 24 mo.
School of Chemical Engineering — FY 82-83

The two principal goals of this research are: (1) carry out wide-ranging equation of state (PVT) measurements for pure fluids and mixtures; and (2) to develop improved methods for correlating, extrapolating and predicting dense fluid properties using statistical mechanics and intermolecular potential theory. Experimental research completed includes: PVT measurements for H_2/CH_4 mixtures at 120, 140 and 160 K and pressures to 1100 atm; PVT measurements for C_2H_4 from 110 to 280 K and pressures to 1300 atm; and PVT studies of methanol (CH_3OH) from 289 to 489 K and pressures to 1000 atm. These results have been fitted to several equations of state and have been used to test the predictions of theories based in statistical mechanics. Theoretical work includes the extension of perturbation theories for molecular liquids to include fluids of nonaxial molecules (ethylene, hydrogen sulfide, etc) and quantum effects (hydrogen).

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

406. DYNAMICS OF VAPOR EXPLOSIONS — $71,223 — 02-04
B. Sturtevant — 20 mo.
Graduate Aeronautical Laboratories — FY 81-82

An experimental program is underway to study an evaporative instability which in previous experiments under this grant was discovered on the liquid-vapor interface of a vapor-exploding liquid. It had previously been shown that the interfacial instability can cause the effective rate of vaporization of the rapidly boiling liquid to be as many as two orders of magnitude greater than would be predicted by the classical diffusion-limited theory of the growth of spherical bubbles. Subsequent calculations, under the hypothesis that the instability is driven by the Landau mechanism, have shown that the instability is marginal for butane, the fluid previously studied, but that for other technically important fluids, such as water and liquid sodium, it can be very much stronger. The apparatus has been redesigned to operate with other hydrocarbons in which the stability should be both weaker and stronger.

Basic Energy Sciences outlay funds 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.) Chemical Sciences FY 1982 Equipment Funds were assigned as follows.

	Equipment Funds (K$)
Ames Laboratory	263
Argonne National Laboratory	880
Bartlesville Energy Technology Center	10
Brookhaven National Laboratory	1,122
Idaho National Engineering Laboratory	10
Lawrence Berkeley Laboratory	470
Lawrence Livermore National Laboratory	15
Los Alamos National Laboratory	60
Mound Facility	60
Notre Dame Radiation Laboratory	290
Oak Ridge National Laboratory	510
Pacific Northwest Laboratory	75
Pittsburgh Energy Technology Center	5
Sandia National Laboratories/Albuquerque	20
Sandia National Laboratories/Livermore	975
Solar Energy Research Institute	35

SPECIAL FACILITIES

The special facilities described on the following thirteen pages are supported wholly, or in part, 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 rsearch 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 which can be carried out through commercially available laboratories is not appropriate for these DOE supported facilites.

The process by which an off-site scientist can utilize a facility is discussed in each facility summary under the section "User Mode" for the National Synchrotron Light Source and the Combustion Research Facility or "Collaborative Use" for the remaining facilities. The latter are characterized as being dependent upon 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 also a list of technical data on the primary available instrumentation.

There are other facilities supported by the Office of Basic Energy Sciences (BES) which are not summarized here. Information concerning these can be obtained by contacting Dr. Louis C. Ianniello, Director of Materials Sciences, ER-13, U. S. Department of Energy, Washington, D.C. 20545.

Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

ATOMIC SPECTOSCOPY FACILITY

The Argonne spectroscopic facility is designed for high-resolution investigations of atomic and molecular optical spectra, using a unique combination of large-scale dispersive instruments with state-of-the-art holographic gratings and pulsed, sharply-tunable coherent light sources for excitation energies of up to 11 eV. Photographic, Reticon array and resonance-ionization detectors, with associated data-processing equipment are available for a wide variety of experiments. Peripheral equipment includes a 50 KG superconducting magnet with a 24-inch room-temperature bore, high -temperature furnances for metal-vapor absorption tubes and an automatic plate-measuring comparator. YAG-laser-driven dye lasers are used with doublers and H_2-Raman scattering to cover the 2500-8500A range and to produce coherent radiation between 1180 and 1250 A by four-wave mixing in mercury vapor at photon fluxes ranging from 10^{10} to 10^{16}/sec. for resolving powers of several million. The experimental work is reinforced by extensive computational programs for interpreting line broadening, diamagnetic and hyperfine structure data in terms of fundamental atomic theories.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Henry M. Crosswhite
Chemistry Division, Room K-117 (312) 972-3637
Argonne National Laboratory FTS 972-3737
9700 South Cass Avenue
Argonne, Illinois 60439

TECHNICAL DATA

Resolving power

30-foot Paschen-Runge spectrograph	$>5 \times 10^5$
5-meter Czerny-Turner spectrograph	$>10^6$
Tunable dye lasers	$>10^6$
Vacuum-ultraviolet coherent source	$>10^7$

Wavelength range

30-foot Paschen-Runge spectrograph	2000-9000 A
5-meter Czerny-Turner Spectrograph	1200-9000 A
Tunable Dye lasers	2500-8500 A
Vacuum-ultraviolet coherent source	1180-1250 A

Physics Division
Argonne National Laboratory
Agronne, Illinois 60439

4.5-MV DYNAMITRON ACCELERATOR

The ANL 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 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 spectroscopy set-up with associated high-resolution photon (optical and X-ray) spectrometers, (3) a 28-inch diameter general-purpose scattering chamber, (4) a simultaneous irradiation system by which ion beams from the Dynamitron and from a 2-MV Van de Graaff accelerator are focussed onto the same target, (5) a variety of electron spectrometers including a high-resolution, large solid-angle McPherson spherical analyzer, and (6) a post-acceleration 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 PDP-11/45 computer system with a direct link 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 ANL investigators or as independent groups.

PERSON TO CONTACT FOR INFORMATION

D. S. Gemmell (312) 972-4053
Physics Division FTS 972-4004
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

TECHNICAL DATA

Range of terminal voltages attainable	0.3 - 4.5 MV
Range of ion beam currents attainable	0.1 nA - 100 A
Monatomic singly-charged ion beams available	most elements
Monatomic multiply-charged ion beams available	rare gases, transition metals
Typical molecular-ion beams available	H_2^+, H_3^+, HeH^+, CH_n^+ (n=1,4), OH_n^+ (n=1,3), CO^+, O_2^+, etc.
Pulse mode (post-chopper)	
Pulse width	1 nsec - 10 msec
Repetition rate	1 MHz - 8 MHz

National Synchrotron Light Source
Brookhaven National Laboratory
Upton, N.Y. 11973

NATIONAL SYNCHROTRON LIGHT SOURCE

The National Synchrotron Light Source (NSLS) facility consists of 700 MeV (9 electron bunch) storage ring for VUV and IR research and a 2.5 GeV (30 electron bunch) storage ring for X-ray research. Attractive features of the synchrotron radiation include high brightness and intensity, its broad and continuous spectral range, high polarization and pulsed time structure (subnanosecond pulses). With each of the 28 X-ray and 16 VUV beam ports being further split into from 2 to 4 beam lines, it will be possible to have as many as 100 experiments running simultaneously at the NSLS.

The NSLS is a facility where a wide range of research techniques will be utilized by biologists, chemists, solid state physicists, metallurgists, and engineers for basic and applied studies. Among the techniques are EXAFS (extended X-ray absorption fine structure), scattering, diffraction, topography, fluorescence, interferometry, gas phase spectroscopy, photoemission, lithography, microscopy, dichroism, and infrared vibrational spectroscopy.

USER MODE

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in the design and fabrication of experimental apparatus, in addition to the beam lines constructed by the NSLS staff for general usage, a large number of beam lines are being designed and instrumented by "Participating Research Teams" (PRTs). The PRTs are given priority for up to 75% of their beam line(s) operational time for a three-year term.

General Users will be able to perform experiments on an NSLS facility beam line or on a PRT beam line which will be available for use by non-PRT members for at least 25% of its total operational time. In the latter case, PRTs will provide liaison and utilization support to General Users. After an initial commissioning period, NSLS and PRT beam lines will become available for use by General Users.

Proprietary research can be performed at the NSLS. A full-cost recovery fee will be charged for the amount of beam time utilized. The DOE has granted the NSLS a Class Waiver, under the terms of which Proprietary Users of the NSLS will have the option to retain title to inventions that result from research performed at the Light Source.

A limited amount of funding will be available to scientists from U.S. institutions of higher education under the NSLS-HFBR Faculty/Student Support Program. The program is designed to defray expenses incurred by faculty/student research groups performing experiments at the NSLS or at the HFBR. It is aimed at university users having only limited grant support for their research, and will be used to support only the most deserving cases.

Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

PULSE RADIOLYSIS FACILITY

The Argonne linear electron accelerator was designed for chemical research. The moderate energy of the electron accelerator (21 MeV transient mode, 14 MeV steady state) allows the use of the electron beam for the generation of transient species without nuclear activation. The pulse width can be varied from 30 picoseconds to 10 microseconds. In liquids, transient concentrations up to 20 micromolar may be generated with the 30 picosecond pulse and concentrations in excess of 10 millimolar may be generated with the longest pulse. Instrumentation for measurement of the chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. Simultaneous multiwavelength kinetic spectrophotometric measurements are possible and very high time resolution measurements which utilize the short pulse capability of the linac can also be made both in absorption and emission. Other detection techniques such as resonance Raman spectroscopy are under development. 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 may be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah (312) 972-3471
Chemistry Division FTS 972-3471
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

TECHNICAL DATA

Energy	
Transient Mode	21 MeV
Steady State Mode	14 MeV
Pulse Repetition Rate	single pulse - 800 pps (800 pps not possible for all pulses)
Current/pulse	
Transient Mode	20 amps
Steady State Mode	1.5 amps
Picosecond Pulse	25 nanocoulombs/pulse
Pulse Width	30 ps 4 - 100ns .25 - 10 microseconds

National Synchrotron Light Source, BNL, continued

PERSON TO CONTACT FOR INFORMATION

R. Klaffky
NSLS - Bldg. 725B
Brookhaven National Laboratory
Upton, New York 11973

(516) 282-4974
FTS 666-4974

TECHNICAL DATA

Facilities	Key Features	Operating Characterisitics
VUV electron storage ring	high brightness, continuous wavelength ($\lambda > 12\ \mathring{A}$) 16 beam lines	0.7 GeV electron energy
X-ray electron storage ring	high brightness, continuous wavelength range ($\lambda > .5\ \mathring{A}$) 28 beam lines	2.5 GeV electron energy

Instruments

Monochromators:	
plane grating	$12\ \mathring{A} < \lambda < 1500\ \mathring{A}$ high resolution
toroidal grating	$10\ \mathring{A} < \lambda < 80\ \mathring{A}$ high intensity, moderate resolution
Wadsworth	$300\ \mathring{A} < \lambda < 3000\ \mathring{A}$ high intensity, moderate resolution
Seya & Czerny Turner	$1200\mathring{A} < \lambda < 12000\ \mathring{A}$ high intensity, moderate resolution
two crystal	$.04\ \mathring{A} < \lambda < 10\ \mathring{A}$ high resolution, fixed exit beam
two crystal/two grating	$2.5\ \mathring{A} < \lambda < 2500\ \mathring{A}$ high resolution, fixed exit beam
Six circle spectrometer/diffractometers	high positional and rotational accuracy
Experimental stations	photoemission, magnetic circular dichroism, fluorescence, gas phase spectroscopy, microscopy, EXAFS, scattering, crystallography, topography
Superconducting wiggler	$\lambda > .1\ \mathring{A}$ high intensity

Department of Physics
Kansas State University
Manhattan, Kansas 66506

JAMES R. MCDONALD LABORATORY

Three accelerators are operated primarily for atomic physics research. These accelerators are: a 6MV EN-tandem accelerator, a 3 MV Van de Graaff, and a 100 kV accelerator. Either foil or gas post-stripping between the 90° and switching magnet is possible for tandem beams. Available experimental facilities include: a) a 4.5 meter flight tube for impact parameter measurements, b) curve crystal x-ray spectrometer, c) spherical sector and cylindrical electron spectrometers, d) hydrogen atom and metal vapor oven targets, e) low-energy high-charge recoil ion sources, and f) Si(Li), proportional counter, avalanche, and channel-plate detectors. The laboratory is available to users who require the unique facilities of the laboratory for experiments pertinent to DOE program goals.

COLLABORATIVE USE

Users are encouraged to seek a collaborator on the staff or can submit a brief proposal.

PERSONS TO CONTACT FOR INFORMATION:

Patrick Richard, Principal Investigator (913) 532-6783
or James C. Legg, Director (913) 532-6786
James R. Macdonald Laboratory
Department of Physics
Kansas State University
Manhattan Kansas 66506

TECHNICAL DATA

EN tandem:

Beams: Most Elements

Terminal Voltages: 0.3 - 6 MV

Output Currents: Up to 10 μA depending on the ion species and charge state

Repetition Rate: DC or 3 nsec pulses at rates up to 4 MHz

Magnet Limitations: $ME/q^2 \leq 150$

J. R. Macdonald Laboratory, KSU, continued

3 MV Van de Graaff:

Beams: ^{1}H or ^{4}He

Terminal Voltages; 0.3 - 3 MV

Output Currents: Up to 100 μA

Repetition Rate: DC only

Magnet Limitations: None

100 kV Accelerator:

Beams: Most elements

Terminal Voltages: 20 - 100 KV

Output Currents: Up to 10 μA depending on the ion species

Magnet Limitations: None

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

PULSE RADIOLYSIS FACILITY

The Notre Dame pulse radiolysis facility is based on a 5 ns electron pulse from a 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. 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

R. H. Schuler, Director	(219) 239-7502
Notre Dame Radiation Laboratory	FTS 333-8222
Note Dame, Indiana 46556	

TECHNICAL DATA

Electron source	8 MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	PDP 8
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	210-750 nm
Sensitivity	±0.00002 absorbance
Conductivity	
pH range	3-11
Sensitivity	± 5mhos/cm

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

RADIOLYSIS-ESR FACILITY

The Notre Dame Radiolysis-ESR Facility is a unique facility for carrying out electron spin resonance studies directly in the microwave cavity during continuous or pulse electron radiolysis. The electron source is a 3 MeV Van de Graaff capable of irradiating continuously with currents up to 10 µA or in pulsed mode up to 1 A. The recording of spectra during irradiation allows species with lifetimes in the microsecond or longer range to be examined by steady state methods. Most radicals in solution have well resolved narrow lines so that hyperfine constants can be measured to ±0.02 G and g-factors to ±0.00002. The reaction kinetics of many small radicals can be followed directly by time resolved methods. This facility is used for both quantitative identification of radiation produced intermediates and for measurement of their electronic and kinetic properties.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a research proposal to the laboratory director.

PERSON TO CONTACT FOR INFORMATION

R. H. Schuler, Director (219) 239-7502
Notre Dame Radiation Laboratory FTS 333-8222
Notre Dame, Indiana 46556

TECHNICAL DATA

Electron source	3 MeV Van de Graaff
ESR spectrometer	X BAND
Operating mode	Computer controlled field scan
Current - cw	10 µA
pulsed	0.1 A
Pulse width	0.1 µs to d.c.
Repetition rate	up to 100 kHz
Duty cycle	as needed
Field/frequency measurement	± 0.02 G

Physics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

EN-TANDEM

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 6.5 MV. The widest possible variety of ion species are available from a selection of ion sources. Two 90^{o} 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: a) A merged-electron-heavy ion beam apparatus with a merged region ∿1 meter in length; b) a ∿14 meter flight tube with the capability of doing very small angle scattering and detecting individual charge states; c) a Penning ion trap apparatus; d) an Elbeck magnetic spectrograph with position sensitive detectors; e) Si(Li) detectors and a curved crystal spectrometer; f) both low- (eV to keV) and high- (MeV) monoenergetic position sources are being developed.

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. D. Miller	(615) 574-4781
Bldg. 5500	FTS 624-4781

Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

TECHNICAL DATA

Beams: Most elements

Terminal Voltages: 0.3 - 6.5 MV

Source Beam Currents: Several hundred nA to several μA

Output Currents: Up to 1μA depending on the ion species, and charge state

Repetition Rate: DC only, at present

Magnet Limitations: $ME/q^2 \leq 80$

Combustion Sciences Directorate
Sandia National Laboratories/Livermore
Livermore, California 94550

COMBUSTION RESEARCH FACILITY

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and application of new diagnostic techniques to the study of basic flame processes, as well as research in fundamental chemistry important in combustion. (These programs are individually described elsewhere in this Summary Book.) In addition, DOE/Conservation sponsors programs at the CRF in combustion technologies, and DOE/Fossil supports programs in coal combustion and related diagnostics development.

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 laser systems, a dedicated VAX computer, and access to a Cray computer.

The facility is located in the San Francisco Bay area, near major universities and other U.S. Government-supported laboratories.

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 utilized, 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 to set up experiments. Visitors pay for their own salary, travel, housing, meals, and other local expenses. Facility lasers, apparatus, technicians, instrumentation, computers, and the services of support groups are provided at no cost for research which is not proprietary. Research results from non-proprietary projects are expected to be published and disseminated.

For scientsts with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are limited opportunities for faculty, post-doctoral scientsts, and graduate students to obtain Sandia support for combustion-related research at CRF.

Combustion Sciences Directorate, Sandia-L, continued
Combustion Research Facility

In specific instances, proprietary research can be carried out at 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

Danny L. Hartley	(415) 422-2747
Director	FTS 532-2747
Combustion Research Facility	
Sandia National Laboratories	
Livermore, California 94550	

-- or --

Peter L. Mattern	(415) 422-2520
Manager	FTS 532-2520
Combustion Sciences Department	
Sandia National Laboratories	
Livermore, California 94550	

TECHNICAL DATA

Equipment	Key Features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2 microsecond pulse length 5 Joules per pulse, 10 Hz tunable 440 to 620 nm 0.03 nm bandwidth
Multi-purpose pulsed laser system (under construction)	High peak power, high resolution doubled YAG and tunable dye lasers single mode capability 10-500 mJ per pulse 10-20 nanosecond pulse
Low pressure flames	10 microns to 1 atm. Mass spectrometer sampling probe
Atmospheric flames	Diffusion and premixed flames

Combustion Sciences Directorate, Sandia-L, continued
Combustion Research Facility

High pressure flame (Under construction)	Combination of diffusion flame burner with high pressure flow chamber: pressures up to 20 atm. slot-geometry burner 2-0 laminar diffusion
Vertical turbulent diffusion flame	Open-circuit, induced draft wind tunnel with co-flowing axisymmetric fuel jet 30 x 180 cm viewing section to 6000 scfm flow
Atmospheric Combustion Exhaust Simulator (ACES)	Atmospheric pressure combustion exhaust chamber to 1200 degrees C 0.5 - 100 m/s flow speed trace species and particulates Optical and physical probes Materials test section
Combustion bomb	Simulates constant-volume engine combustion
Internal combustion research engines	Highly repeatable environment for homogeneous charge and diesel combustion studies
Experimental diagnostics research facilities	Laser fluorescence laboratory Coherent Raman spectroscopy laboratories Laboratory for laser ionization, saturation, optogalvanic detection of trace species Kinetics laboratories with tunable quasi-cw uv and ring dye lasers for analysis, excimer lasers for photolysis
Computing facilities	Minicomputers in laboratories Access to CRF VAX 11/780 Access to SNLL CRAY via in-house staff

Topical Index

Index of Offsite Institutions

Universities

Universities (continued)

Universities (continued)

Industrial and Other Laboratories

INVESTIGATOR INDEX

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