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Summaries of FY 1983 Research in the Chemical Sciences

September 1983

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

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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 inform 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 provide to members of the scientific and technical public and interested persons in the Legislative and Executive Branches of the Government a means for becoming acquainted, either generally or in some depth, with the Chemical Sciences program. 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 generated 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 present program in basic research, and the relationship of their interests to the overall program. Proposals that expand this scope will also be considered or directed to more appropriate offices. 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 50% of 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 the 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 Lehigh University
**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 ii.

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, photocatalysi[, 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 experimental and theoretical efforts associated with the study of atom and ion structures, energy levels and lifetimes of quantum states, and of transport and exchange processes characterizing transfer of energy, momentum and matter. These studies strive to attain the best and most complete basic knowledge of the properties and interactions of photons, electrons, atoms, ions and simple molecules. Continued emphasis of this research has been on the understanding of relatively high energy atomic physics that involves atoms stripped of all or most all electrons and of atoms and ions in which electrons are located at upper energy levels. Recent emphasis has been on the study of processes that lead to the production of coherent radiation and on the statistical properties of this radiation as they modify elementary atomic physics processes.

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 chemistry of fossil resources - particularly coal, including characterization and transformation, and (3) the conversion of biomass and related cellulosic wastes. 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. The program covers a broad spectrum of separations concepts, including membrane processes, extraction at both standard and supercritical conditions, adsorption, chromatography, photodissociation, complexation, etc. The program is technique-oriented rather than species-oriented: i.e., the research involves elucidation of fundamental chemical phenomena for improved separations rather than developing specific processes for the separation of a particular species from particular matrices. The isotope separation program emphasizes isotopic properties and isotope effects and is very basic in nature.

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

Chemical Engineering Sciences (02-04)

This program addresses the more scientific and energy-related aspects of chemically related engineering topics, including momentum and transport phenomena, 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 of mixtures, and phase equilibria, including supercritical extraction phenomena. 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 Science 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
D. Hoffman - Phone: (FTS) 865-2113 or (515) 294-2113

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

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

Chemistry Division
E. Steinberg - Phone: (FTS) 972-3570 or (312) 972-3570

Chemical Technology Division
F. A. Cafasso - Phone: (FTS) 972-4542 or (312) 972-4542

Physics Division
D. S. Gemmell - Phone: (FTS) 972-4053 or (312) 972-4053

BARTLESVILLE ENERGY TECHNOLOGY CENTER
P. O. Box 1398
Bartlesville, Oklahoma 74003

W. D. Good - Phone: (FTS) 735-4210 or (918) 336-2400, Ext. 210

BROOKHAVEN NATIONAL LABORATORY
Upton, Long Island, New York 11973

Chemistry Department
A. P. Wolf - Phone: (FTS) 666-4301 or (516) 282-4301

Department of Applied Sciences
B. Manowitz - Phone: (FTS) 666-3037 or (516) 282-3037
D. J. Metz - Phone: (FTS) 666-3054 or (516) 282-3054

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

Physics Department
A. Schwarzschild - Phone: (FTS) 666-4015 or (516) 282-4015

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

Applied Sciences Division
E. J. Cairns - Phone: (FTS) 451-5001 or (415) 486-5001

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

Materials and Molecular Research Division
A. W. Searcy - Phone: (FTS) 451-6062 or (415) 486-6062

LAWRENCE LIVERMORE NATIONAL LABORATORY
University of California
P. O. Box 808
Livermore, California 94550

C. F. Bender - Phone: (FTS) 532-6340 or (415) 422-6340

LOS ALAMOS NATIONAL LABORATORY
University of California
P. O. Box 1663
Los Alamos, New Mexico 87545

CHM Division
G. M. Rosenblatt - Phone: (FTS) 843-6250 or (505) 667-6250

INC Division
D. C. Hoffman - Phone: (FTS) 843-4457 or (505) 667-4457

P Division
John C. Browne - Phone: (FTS) 843-6162 or (505) 667-6162

T Division
G. I. Bell - Phone: (FTS) 843-4401 or (505) 667-4401

MOUND LABORATORY
P. O. Box 32
Miamisburg, Ohio 45342

Nuclear Operations Department
R. E. Vallee - Phone: (FTS) 774-3318 or (513) 865-3318

NOTRE DAME RADIATION LABORATORY
University of Notre Dame
Notre Dame, Indiana 46556

R. H. Schuler - Phone: (FTS) 333-8222 or (219) 239-7502
R. W. Fessenden - Phone: (FTS) 333-8221 or (219) 239-5354
L. K. Patterson - Phone: (FTS) 333-8220 or (219) 239-5403

OAK RIDGE NATIONAL LABORATORY
P. O. Box X
Oak Ridge, Tennessee 37830

Analytical Chemistry Division
W. D. Shults - Phone: (FTS) 624-4881 or (615) 574-4881

Chemical Technology Division
R. G. Wymer - Phone: (FTS) 624-6275 or (615) 574-6275

Chemistry Division
O. L. Keller - Phone: (FTS) 624-4987 or (615) 574-4987

Physics Division
S. Datz - Phone: (FTS) 624-4984 or (615) 574-4984

PACIFIC NORTHWEST LABORATORY
P. O. Box 999
Richland, Washington 99352

Chemical Technology Department
R. E. Nightingale - Phone: (509) 375-2597
P. C. Walkup - Phone: (509) 375-2432

Radiological Sciences Department
W. A. Glass - Phone: (FTS) 444-3061 or (509) 376-3061

Biology and Chemistry Department
H. Drucker - Phone: (FTS) 444-5662 or (509) 376-5662

PITTSBURGH ENERGY TECHNOLOGY CENTER
P. O. Box 10904
Pittsburgh, Pennsylvania 15236

Chemical and Instrumental Analysis Division
H. L. Retcofsky - Phone: (FTS) 723-5786 or (412) 675-5786

SANDIA NATIONAL LABORATORIES/ALBUQUERQUE
P. O. Box 5800
Albuquerque, New Mexico 87115

Laser Research and Development Department
J. B. Gerardo - Phone: (FTS) 844-3871 or (505) 844-3871

Radiation and Surface Physics Research Department
F. L. Vook - Phone: (FTS) 844-9304 or (505) 844-9304

SANDIA NATIONAL LABORATORIES/LIVERMORE
Livermore, California 94550

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

SOLAR ENERGY RESEARCH INSTITUTE
1617 Cole Boulevard
Golden, Colorado 80401

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

Table of Contents

DOE Laboratories

Photochemical and Radiation Sciences

Chemical Physics

Atomic Physics

Chemical Energy

Separations and Analysis

Chemical Engineering Sciences
Lawrence Berkeley Laboratory

Los Alamos National 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 $290,000

1. PHOTOPHYSICS, PHOTOCHEMISTRY AND SPECTROSCOPY — 2.7 — 01-01
G. J. Small

This project seeks an understanding of dressed exciton states (polaritons) and ultra-fast coherent electronic energy transfer in molecular solids. It also considers photochemical, photoisomerization and photophysical processes of molecules in ordered and disordered solids utilizing coherent nonlinear laser spectroscopies to probe relaxation phenomena. Supersonic jet spectroscopy applied to charge-transfer excited states and vibronic interactions in molecules is also studied.

2. PICOSECOND SPECTROSCOPY AND REACTION DYNAMICS — 3.5 — 01-01
W. S. Struve

This work concerns kinetic studies of organic redox photoreactions of species attached to semiconductor surfaces using picosecond fluorescence, absorption, and photocurrent transients. Measurements of excited state processes of organic carbanions in solution are contrasted to their behavior on surfaces. Mechanisms of vibrational energy transfer of large molecules in solution and gas phase are determined as well as photodissociation processes.

Photochemical and Radiation Sciences

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

Total $3,900,000

3. PREPARATION OF ORGANISMS, PHOTOSYNTHETIC PIGMENTS, AND BIOLOGICAL MATERIALS OF UNUSUAL ISOTOPIC COMPOSITION

0.7 01-01

H.L. Crespi, J.J. Katz, J.R. Norris, M. Wasielewski

This program has as its objective the production of photosynthetic microorganisms substituted with biologically important stable isotopes. The major effort is in the production of fully deuterated organisms, but in addition 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, and photosynthetic bacteria 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, biomimetic photochemistry, and bacteriorhodopsin.

4. GAS PHASE RADIATION CHEMISTRY RELEVANT TO COMBUSTION AND ATMOSPHERIC REACTIONS

2.0 01-01

C. D. Jonah, W. A. Mulac

In this program, rate constants for simple free radical reactions are being measured, many of which are of great importance in atmospheric and combustion chemistry. The pulse radiolysis technique makes it possible to measure the kinetics at pressures of one atmosphere and above and over the temperature range of 50° to 1000°C, a range no other single experimental technique can easily span. The reaction rates of OH and OD radicals with CO and simple organic compounds are under investigation. In addition to the practical importance of these reactions to combustion, the data serve as an excellent test for reaction theories because of the rigorous restrictions provided by the wide temperature range and the use of two hydrogen isotopes.

5. CHLOROPHYLL AND PHOTOSYNTHESIS RESEARCH

4.5 01-01

J. J. Katz, 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, with particular attention to new model systems; (b) energy transfer from highly excited chlorophyll a states; (c) new methods for the synthesis of chlorophyll model systems, including oxidative coupling at the C-10 position of Ring V; (d) applications of californium-252 plasma desorption mass spectroscopy to chlorophyll systems; and (e) structural studies by small angle neutron scattering of chlorophyll aggregates and natural photoreaction centers.

6.	ELECTRON TRANSFER PROCESSES AND ENERGY CONVERSION AND STORAGE STUDIED BY RADIATION AND PHOTOCHEMICAL TOOLS J.R. Miller, D. Meisel, C.D. Jonah, K.H. Schmidt, M.C. Thurnauer, W.A. Mulac	7.4	01-01

This program is directed at the fundamental understanding of electron transfer between molecules held apart at fixed distances and the study of chemical mechanisms involved in the conversion and storage of light energy. Electron transfer rates are measured by pulse radiolysis of solids or compounds containing two functional groups separated by rigid molecular spacers to determine the effects of distance, energy, and molecular structure. The work on energy conversion and storage utilizes various microenvironments (1) to enhance charge separation and thus the efficiency of photoelectron transfer, and (2) to increase the yield of photo-redox products while minimizing the rates of back reactions. Particular attention is given to mechanistic studies of catalytic water-splitting in colloidal systems and in microenvironments such as micelles, polyelectrolytes, and membranes.

7.	PHOTOSYNTHESIS STUDIES: NATURAL AND ARTIFICIAL REACTION CENTER STRUCTURES AND MECHANISMS J. Norris, M. Wasielewski, M. Thurnauer, M. Bowman	6.5	01-01

The goal of this research is to elucidate in detail the utilization of light energy at the molecular level by natural photoreaction centers so that efficient artificial systems can be constructed. Emphasis is placed on the determination of the structural arrangement during the natural photosynthetic charge separation process for duplication in artificial photosynthesis. Very fast magnetic resonance techniques are used to measure distances, orientations and dynamics among the molecular components which participate in the transfer of electrons. Charge separation in single crystals of the reaction centers of photosynthetic bacteria also is being studied with magnetic and optical spectroscopy as well as x-ray and neutron diffraction.

8. RADIATION CHEMISTRY AND PHOTOCHEMISTRY OF LIQUIDS AND SOLUTIONS 14.6 01-01
A. D. Trifunac, C. D. Jonah, M.C. Sauer, Jr., S. Gordon, K. H. Schmidt, D. Meisel

The objective of this program is the study of chemical and physical processes that follow ionization (or photoionization) in both polar and nonpolar liquids. This is relevant to radiation chemistry, for the understanding of breakdown in dielectric liquids, and for the understanding of charge separation, recombination, and transfer, phenomena which are the basis of chemical and biological processes of energy storage and utilization. Various methods of radiation chemistry and photochemistry are used to provide details of the nature and dynamics of the early transient species and their chemical fates. This includes the study of electrons and positive ions, radical ions and excited states, and the subsequent fragmentation of the excited species into radicals and molecular species. Spin dynamics in radicals and radical ions is being used to provide better understanding of reaction kinetics. Essential tools used in this program are the Argonne high-current picosecond electron linac, the pulsed Van de Graaff accelerator, and innovative, time-resolved, magnetic resonance and laser techniques which are being developed and applied to these problems.

9. ARTIFICIAL PHOTOSYNTHESIS 4.3 01-01
M. Wasielewski, J. R. Norris

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 several interrelated facets of this problem. First, a molecular design program involves the synthesis of molecular models of the natural energy conversion system. These models, through their mimicry of features of natural photosynthesis, aid in the structural and mechanistic understanding of the natural process. Second, the photophysics and photochemistry of these systems are studied with emphasis on light-induced electron transfer reactions. Advanced spectroscopic techniques such as picosecond spectroscopy and time-domain magnetic resonance are used to study these ultrafast processes. Third, the primary photosynthetic processes themselves are being investigated with a view toward integrating the information obtained from the laboratory systems with new knowledge of natural photosynthesis.

Photochemical and Radiation Sciences

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $2,665,000

10. RADIATION CHEMISTRY

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

11.2 01-01

This program uses radiolysis and photolysis, emphasizing pulse methods, to study the behavior and reactions of transient chemical species (ions, electrons, free radicals, and excited states of molecules). Some experiments also involve the use of VUV radiation at the National Synchrotron Light Source. Principal areas of investigation are: properties and reactions of electrons in dielectric fluids, reactions of superoxide radicals and singlet oxygen, reactive metal ion intermediates in redox reactions, and electron transfer reactions in photosynthesis. The aims of the program are to provide the basic knowledge needed for the understanding and control of chemical reactions involving transient species, many of which are components of energy production processes (direct solar conversion, combustion, etc.) or are harmful consequences of these same processes (corrosion, environmental pollution, etc).

11. PHOTOCHEMICAL ENERGY CONVERSION AND SOLUTION KINETICS

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

11.7 01-01

Transition metal complexes strongly absorb visible light and readily undergo electron-transfer reactions. They are excellent mediators of outer-sphere light-induced redox reactions, many of which effect net storage of the light energy, and can also provide homogeneous catalytic routes for the thermal and photochemical formation of H_2 or the activation of CO. This program encompasses fundamental studies of the reactions of both excited-state and ground-state complexes. Since efficient light conversion and storage require the diversion of a significant fraction of the electronically excited molecules into "useful reactions" which must be driven in competition with rapid physical deactivation processes (luminescence and radiationless decay) and chemical "back-reactions", a major objective of this program is the quantitative study of these physical and chemical deactivation processes. In addition, because the overall efficiency of the conversion sequence may be limited by the rate of the subsequent "chemical" steps, mechanistic studies of the reactions of transition metal ions in high and low oxidation states are being conducted.

12. ENERGY TRANSFER IN CHEMICAL KINETICS 6.1 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 dynamics. Collisional energy transfer plays an important role in the reaction mechanism as a process by which energetic species are produced or removed. 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, including detailed studies of the laser energy absorption process, energy flow within excited molecules, and energy transfer from excited species, are being studied.

13. CHEMISTRY OF ENERGETIC AND UNSTABLE SPECIES: BASIC RESEARCH AND APPLICATIONS TO CHEMICAL CATALYSIS 4.6 01-01

A. P. Wolf, R. A. Ferrieri

In part, this program investigates the basic chemistry of atomic and molecular species in neutral or charged states possessing electronic and translational excitation. Included are studies of the reactive intermediates produced by nuclear processes in the gas-phase and of the reaction pathways available to C, N, O and halogen atoms during atom-molecule encounters. New methods of atomic species generation will use synchrotron "light" to produce concentrations of molecular ions high enough to allow standard instrumental analysis of the final products. The development of a new type of electrostatic ion accelerator to produce intense beams of charged atoms and low molecular weight species will also be approached. A second effort of this program uses cyclotron-generated radionuclides in catalyst research, permitting studies to be performed at femtomol concentrations.

Photochemical and Radiation Sciences

Department of Applied Sciences
Brookhaven National Laboratory
Upton, New York 11973

Total $1,180,000

14. PORPHYRIN CHEMISTRY 6.7 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 the storage and transfer pathways of oxidizing equivalents in peroxidases and photosystem II; the six-electron reduction of nitrite to ammonia mediated by isobacteriochlorins; theoretical and experimental modeling of environmental effects (ligands, charges, Schiff bases, conformations) on the properties of porphyrin and chlorophyll radicals; X-ray and neutron studies of Chlorobium chlorophylls as models for primary acceptors, and self-assembled aggregates of these chlorophylls as models of the light harvesting antenna of green and brown photosynthetic bacteria.

15. CONVERSION OF LIGHT BY SEMICONDUCTOR - ELECTROCHEMICAL SYSTEMS 3.1 01-01
S. Feldberg and T. Skotheim

Two general areas of electrochemical research are being pursued: 1) Investigation of new materials which may be applicable to photoelectrochemical or electrochemical studies (e.g., electronically and ionically conducting polymers) and 2) Development of theory to analyze various photophenomena in semiconductors. Electronically conducting polymers (pyrroles, n-substituted pyrroles) are being examined using electrochemical and optical (FTIR, ESCA, EXAFS) techniques. A high vacuum electrochemical technique for the x-ray spectroscopy (ESCA and EXAFS) is being developed using a solvent-free solid polymer electrolyte (polyethylene oxide - PEO). PEO is also being investigated for use as electrolyte in a photoelectrochemical cell. Slow electron transfer between an electrode and a polymer-bound redox system appears to be a critical limitation. Computer modeling is providing a theoretical basis for the analysis of fluorescence decay in semiconductors following high intensity picosecond irradiation. Fluorescence quenching caused by surface modification (e.g., adsorbed benzoquinone or hydroquinone) can be characterized.

16. CHEMICAL PROPERTIES AND REACTIONS OF MONO- AND DINUCLEAR FERROCENE DERIVATIVES 3.2 01-01
M. Hillman

This program is an investigation of the preparation and properties of 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 was prepared and its reactions on a silicon electrode were studied. The oxidized state of the compound has a potential high enough to oxidize water and is stable under the alkaline conditions required; however, the electrode was not stable under these conditions. Compounds with higher oxidation potentials are required. For the reduction of water, the mechanism of the generation of hydrogen from [1.1]ferrocenophanes with strong acids is under study. Early results indicate that the release of hydrogen is the slow step. An understanding of this reaction will enable modifications of the compound so that hydrogen may be obtainable from weak acids, perhaps even water. Bridged ferrocenophanes were prepared. These compounds have tilted Cp rings and are expected to be protonated more easily than the parent non-bridged derivative and therefore to release hydrogen at a lower pH.

Department of Applied Sciences, BNL, continued

17. PHOTOLYSIS IN THE ADSORBED STATE 1.2 01-01
J. W. Sutherland

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. Detailed studies have confirmed that molecular cations, but not carbonium ions, are readily produced at high light intensities by a two-photon process. The observation of a broad excimer-exciplex-like emission at very low surface coverages (e.g., 1 molecule of anthracene for 400,000 Å^2 of surface) implies that excited molecules are interacting strongly with specific sites on the surface or that the sorbate molecules are arranged in highly-ordered micro-aggregates.

National Synchrotron Light Source
Brookhaven National Laboratory
Upton, New York 11973

Total $3,800,000

18. NATIONAL SYNCHROTRON LIGHT SOURCE - OPERATIONS AND DEVELOPMENT 40.4 01.01
J. McTague and A. van Steenbergen

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 by means of new developments in high resolution photon optics, state-of-the-art monochromators, X-ray mirror systems, detectors, and so on. The NSLS storage rings will provide extremely bright photon sources, several orders of magnitude more intense in the VUV and X-ray regions than conventional sources. An extensive R&D program is necessary in order to optimize performance characteristics and also to develop new beam line instrumentation which will permit users to take full advantage of the unique research capabilities to be offered by this important new facility.

Photochemical and Radiation Sciences

Chemical Biodynamics Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $870,000

19. ARTIFICIAL PHOTOSYNTHESIS 4.1 01-01
Melvin Calvin, J. W. Otvos

We are seeking to devise a synthetic system to accomplish a photoinduced electron transfer 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. Other types of charged, single surfaces such as SiO_2 colloid have been found to increase the reaction yield when a primary reaction product is electrostatically repelled from the surface and prevented from back-reacting. We have shown that polymeric sulfonates can also produce this result. Presently we are focussed on the natural catalysts which will be required at both the oxidation and reduction ends. An iron-sulfur cluster has produced hydrogen electrochemically but not yet photochemically. A cobalt complex can be photochemically reduced to Co(I) and produce hydrogen. On the oxidation side the natural catalyst is a manganese compound of unknown structure. We have shown that a manganese porphyrin in a suitable microenvironment can be oxidized to Mn(IV) by a photosensitizer with the concomitant production of an intermediate reductant. Mn(IV) can be used to produce molecular oxygen, if desired.

20. PICOSECOND PHOTOCHEMISTRY 1.8 01-01
J. H. Clark

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. Picosecond time-resolved resonance Raman spectroscopy is being carried out on a number of electronically excited organometallic complexes to establish the changes in both geometrical and electronic structure which occur upon photoexcitation.

21. PHOTON CONVERSION 4.1 01-01
G. C. Pimentel

This research investigates the chemistry and energy movement as it occurs on electronically excited hypersurfaces. Since both natural and artificial photosynthetic processes depend upon the chemistry of electronically excited molecules, these studies aid in the design of systems for 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. Reactants under study include $O_2(^1\Delta_g)$, Hg ($^3P_1$ and $^1P_1$), and NH ($^1\Delta$ and $X^3\Sigma^-$) with various unsaturated compounds. Energy storage using near infrared light, photochromism, and hypersurface mapping are goals. Temporal aspects of electronically excited transient intermediates are examined using nanosecond infrared spectroscopy.

Photochemical and Radiation Sciences

Materials and Molecular Research Division
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Berkeley, California 94720

Total $420,000

22. PHOTOCHEMISTRY OF MATERIALS IN THE STRATOSPHERE — 5.0 — 01-01
H. S. Johnston

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. Studies using laser flash photolysis and laser resonance absorption show that the primary products of N_2O_5 photolysis are $NO_2 + NO_3$, not $2NO_2 + O$ as had been previously reported. Chlorine atoms react slowly with nitric acid vapor and, surprisingly, do not form NO_3 + HCl as reaction products. Measurements of this ultraviolet cross section of molecular oxygen in the Herzberg continuum show it to be a function of temperature and about 30 percent lower at stratospheric temperature than at room temperature, which has been used in atmospheric models. This effect may turn out to explain the anomalously high intensity of ultraviolet radiation recently observed in sites in the middle stratosphere.

23. PHOTON-ASSISTED SURFACE REACTIONS, MATERIALS AND MECHANISMS — 2.4 — 01-01
G. A. Somorjai

This project explores photocatalyzed chemical reactions that take place at the solid-vapor interface. These reactions 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 iron oxides, silicates, and sulfides of rhenium and molybdenum.

Photochemical and Radiation Sciences

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

Total $2,650,000

24. THEORETICAL STUDIES ON REACTING SYSTEMS 8.5 01-01
D.M. Chipman, 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. A comprehensive statistical mechanical theory of photo- and radiation-induced redox reactions in organized molecular assemblies such as monolayers and micelles 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. New quantum mechanical methods to perform and analyze electronic structure calculations on molecules and transient free radicals are being developed and used in conjunction with existing methods 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, specifically the temporal decay of excited states of two- and three-level atomic and molecular systems, are being studied using new analytical techniques.

25. ORGANIC PHOTOCHEMICAL PROCESSES 8.0 01-01
P.K. Das,

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, hydrogen abstraction and electron transfer reactions, intermolecular energy transfer between quasi-isoenergetic triplets, intramolecular transfer in molecules containing two chromophores, electron exchange interactions with stable radicals, energy hopping along a polymeric chain and energy trapping in copolymers containing several types of chromophores. Model systems being investigated include phenyl substituted polyenes and polyynes containing heteroatoms, aromatic hydrocarbons and carbonyl compounds, small ring heterocyclic systems, stilbene analogues 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.

26. INORGANIC PHOTOCHEMICAL STUDIES 10.0 01-01
G. Ferraudi

The photochemical properties of coordination complexes of copper(II), rhodium(II) and rutherium(II) with macrocyclic ligands are being investigated. Conventional laser flash photolysis methods are used and supplemented by product analysis. A sequential biphotonic excitation technique is also being used for probing the time and energy relationships between long-lived excited states. In addition, pulse radiolytic experiments are used to provide spectroscopic and rate information on active intermediates, such as coordination complexes in unusual oxidation states. This research is carried out with compounds that exhibit either a direct or sensitized photochemical redox reactivity for excitation in the visible region of the spectrum and are, therefore, candidates for use in solar energy conversion. Two families of compounds are the main targets of these studies: the phthalocyanines and complexes with macrocyclic ligands possessing simple structures. Elucidation of general relationships between photoreactivity and the molecular structure of macrocycles is an essential goal of this project. Some of the mechanisms under study may be seen to exhibit potential application to photocatalytic systems.

27. MICROWAVE STUDIES ON RADIATION CHEMICALLY PRODUCED INTERMEDIATES 7.5 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.

28. TIME RESOLVED STUDIES OF PHOTOLYTIC REACTIONS 5.5 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 intermediates 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. Two-pulse experiments involving laser photolysis and pulse radiolysis are also used to investigate photochemical activity of radiation chemical intermediates and reactivity of photoexcited states with radicals. These investigations are complimented by both steady-state and time-resolved ESR studies of photolytically produced radicals.

29. THEORETICAL ASPECTS OF RADIATION CHEMISTRY 3.0 01-01

K. Funabashi, A. Mozumder

These studies relate to the physical and chemical behavior of the electron in its various aspects and in different phases. Attention is focused 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. Problems associated with thermalization of radiation produced electrons in both gases and liquids are addressed to elucidate 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 applications where ions are important in, for example, fluorescence detectors and solid-state devices.

Notre Dame Radiation Laboratory, continued

30. SPECTROSCOPY OF REACTION INTERMEDIATES 7.5 01-01
J. Hardwick, G.N.R. Tripathi

Laser-excited fluorescence, long path absorption, and chemical luminescence spectroscopy are being used to conduct high resolution spectroscopic studies of small molecules, radicals and ions in the gas phase. High-lying rotational and vibrational levels of small molecules in their ground and excited electronic states are being studied through their infrared, visible, and ultraviolet spectra. Collisional transfer of energy in excited electronic states is being studied with rotational resolution in order to investigate in detail the important processes by which relaxation occurs during single collisions. Transfer of electronic energy from metastable rare gas atoms is being used to dissociate hydrocarbons in the gas phase, producing intense emission from excited electronic states of radicals and ions.

31. ELECTRON TRANSFER REACTIONS 6.0 01-01
P. Neta,

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.

32. INFLUENCE OF ORDERED MOLECULAR ASSEMBLIES OF CHEMICAL PROCESSES 8.0 01-01
L. K. Patterson

These studies are directed toward developing a better understanding of the relationships between structure in rganized molecular assemblies and the influence these assemblies may exert on kinetic behavior in bulk phase, assembly pseudophase, or at interfacial boundaries. A variety of unique properties has been observed for systems in which such assemblies - micelles, vesicles, spread monolayers and liquid crystals - are formed. Such properties under study include compartmentalization of reaction into microregions with well defined boundaries, 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 in such assemblies strongly suggest the possibility for kinetic control over a variety of photochemical and radiation chemical processes not possible in homogeneous solution. Principal attention is now directed toward studies in spread monolayers because these latter assemblies provide for significant control in the degree of organization which may be imposed on a reaction system. Preliminary investigations are now being carried out in liquid crystals which exhibit phases of varying organization.

33.	RADIATION CHEMISTRY DATA CENTER A.B. Ross, W.P. Helman, G. Hug, I. Carmichael	2.0	01-01

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. Retrospective searches are carried out and bibliographies on specific topics are prepared and made widely available. A current-awareness publication, Biweekly List of Papers on Radiation Chemistry and Photochemistry 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. The data are stored in computer-readable files and are readily available for correlation and reformatting in various ways. 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.

34.	RADIATION INDUCED REACTIONS R.H. Schuler, L.K. Patterson, G.N.R. Tripathi	13.0	01-01

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 for examining intermediates both in time resolved studies and by analysis of ultimate products. Improvements in dosimetry and time resolution at the LINAC pulse radiolysis facility allow detailed optical and conductometric pulse radiolytic studies to be carried out at nsec and longer times. Recent introduction of laser resonance Raman techniques allow parallel studies of time resolved vibrational spectra of intermediates. Currently focus is on the molecular and electronic structure of oxygenated radicals present in electron transport processes. Radiation chemical 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 studies are aimed at providing information on the importance of track structure in radiation chemical processes. These track studies are complemented by studies at very high intensities using a Febetron as a radiation source.

Photochemical and Radiation Sciences

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Total $450,000

35. PHOTOPHYSICS AND PHOTOCHEMISTRY OF PORPYHRINS AND MODEL SYSTEMS FOR ARTIFICIAL PHOTOSYNTHESIS 0.7 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 porphyrins and on light-induced electron transfer in synthetic models of photoreaction centers. The goal is to contribute to an improved understanding of the molecular properties required for efficient light-induced electron transfer in artificial photosynthesis. Laser flash photolysis and fluorescence studies are being carried out on covalently linked porphyrin-quinones and on their unlinked constituents to sort out the effects of photophysical properties, redox potentials, molecular geometry, temperature and solvent properties (dielectric constant, viscosity) on the kinetics and mechanisms of light-induced electron transfer and subsequent charge stabilization.

36. BASIC PHOTOELECTROCHEMISTRY RESEARCH 3.5 01-01
A. J. Nozik, J. A. Turner, A. J. Frank,
B. A. Parkinson, J. Cooper

Basic research is being conducted in the following areas: hot carrier effects in photoelectrochemical systems; energetics, kinetics, and characterization studies of semiconductor-electrolyte interfaces; colloidal and particulate semiconductors; and conducting polymers on semiconductor materials. Hot carrier injection is being verified via both supra-band-edge redox chemistry and dye sensitization experiments. The kinetics of minority carrier transfer across the semiconductor interface is being established by means of transient photocurrent experiments. New techniques for characterizing photoelectrochemical systems, such as chromocoulometry and photocapacitance, are being developed. The utility of Mossbauer spectroscopy for studying semiconductor particles and colloidals is being demonstrated; kinetic data are being obtained for several particulate systems. The nature of catalytic deposits on both naked and polymer-coated semiconductor electrodes is being studied. New polymers and catalyst combinations are being investigated as approaches to the stabilization of semiconductor electrodes against photocorrosion.

Chemical Physics

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $640,000

37. STATISTICAL MECHANICS OF GASEOUS SYSTEMS
D. K. Hoffman

01-02

Statistical mechanics are used to develop a kinetic theory of polyatomic and reactive gases, transport, relaxation, and reaction processes in polyatomic fluids. It utilizes classical and quantum mechanical scattering theory in the development of collision models for molecules with internal structure which bear on gas phase chemical reaction rates, the interaction of gas molecules with solid surfaces and surface distributions established under nonequilibrium conditions. The project includes an investigation of the effect of surface coverage on the nature of binding sites, an exploration of interactions between adsorbed surface species, a study of surface migration and cluster formation, and adsorbate effects on the catalytic properties of surfaces. These models for irreversible lattice processes can be tested with polymer and other (nonsurface) systems for which extensive empirical data is available.

38. ATOMIC, MOLECULAR AND FREE RADICALS:
CROSSED BEAM KINETICS
C. Y. Ng

01-02

This project involves crossed molecular beam studies bearing on the kinetics of fundamental processes in combustion and low pressure pyrolysis of hydrocarbons. It also includes the molecular dynamics of excited atoms and molecules, ion/molecule reactions, and high resolution photoionization of molecules, clusters, and transient radicals. An important aspect of the work is to understand the role played by stable molecules, intermediate radicals, and ions in flames.

39. MOLECULAR THEORY BONDING 01-02
K. Ruedenberg

This research concerns a theoretical determination of molecular properties, geometric, electromagnetic and spectral, and in particular of energy changes during chemical reactions through quantum chemical calculations of molecular electronic structures. It includes predictions of reaction energies and activation energies for elusive intermediates and transition states. Analyses are made of electronic rearrangements along reaction paths and their energetic and kinetic implications. Fundamental developments in many-electron quantum mechanics including electron correlation are made in order to achieve chemical accuracy by practical methods for predicting reaction mechanisms. Development of quantitative interpretative concepts are emphasized which can be used by nontheorists to analyze reliably and anticipate intuitively ab initio predictions. Studies of oxidation-reduction and exchange reactions involving carbon, nitrogen, oxygen, hydrogen and silicon, in particular reactions occurring during combustion, in the atmosphere and during hydrogenations are used as a test of the basic concepts.

40. ION CHEMISTRY - MASS SPECTROMETRY 01-02
H. J. Svec, G. D. Flesch

This research involves the ion chemistry of inorganic, organometallic and organic compounds and ions and complementary neutral fragments produced by electron bombardment. The latter leads directly into the chemistry of highly excited molecules and free radicals. The results bear directly on the origin of aromatic heterocyclic hydrocarbons produced in the combustion of natural gas, oil, wood and coal under fuel rich conditions.

Chemical Physics

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

Total $1,680,000

41. HIGH RESOLUTION SPECTROSCOPY AND EXCITED-STATE DYNAMIC PROCESSES 3.3 01-02
H.M. Crosswhite, F.S. Tomkins, K.T. Lu

The vacuum ultraviolet coherent-radiation facility, which makes use of nonlinear optical mixing in mercury vapor, is now available for use as a flexible excitation source for a variety of spectroscopic experiments. This is the most efficient upconversion process known, providing five-nanosecond pulses of the order of 10^{11} photons/pulse in the range 1150-1230 Å, with a resolving power of several million. Present experiments include energy-level structural and lifetime studies of simple molecular systems and fundamental diamagnetic experiments on atomic hydrogen. This facility is reinforced by two large spectrographs, both with resolving powers near one million, covering the wavelength range 1200-9000 Å, which are being used primarily as survey instruments for more detailed laser-based experiments.

42. THEORETICAL CHEMISTRY 6.5 01-02
T. H. Dunning, Jr., M. J. Davis, L. B. Harding, R. L. Shepard, A. F. Wagner

This program is concentrated on theoretical studies of the energetics and kinetics of chemical reactions, with an emphasis on reactions of importance in the oxidation of hydrogen and simple hydrocarbon fuels. The basic thrust of the program is on the calculation of accurate molecular interaction potentials, the study of the chemical dynamics on the computed (or other realistic) potential energy surfaces, and the characterization of the molecular species (including ephemeral species) involved. In addition, there is a continuing effort devoted to the development of the theoretical and computational methodology needed to provide a realistic description of these fundamental chemical processes.

43. MOLECULAR BEAM AND METAL CLUSTER CHEMISTRY RESEARCH 5.3 01-02
S. Wexler, E. K. Parks, S. J. Riley

The study of heterogeneous catalysis on a molecular level is being pursued. Beams of catalytically active naked metal (Ni, Cr, Ag, Cu, Al, Fe) atom clusters containing 2 to 20 atoms are generated either continuously or in pulses and their physical and chemical properties are characterized by laser based, in-flight diagnostic techniques. Spectral and electronic properties are determined and experimental results are correlated with theoretical calculations. Mechanisms and kinetics of adsorption and catalytic processes on surfaces of clusters are determined by the flow tube technique. The transient products are identified by laser ionization mass spectrometry.

Chemical Physics

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $2,480,000

44. THEORETICAL CHEMISTRY — 7.2 — 01-02
S. Ehrenson, J. T. Muckerman,
M. D. Newton

The goals of this program are to apply theoretical methods 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 (i.e., solvation and charge-transfer processes). 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. Many of the techniques currently being developed and applied in this program play an important role in analyzing and interpreting experimental data obtained in experimental programs in the Department.

45. ION-MOLECULE REACTIONS WITH APPLICATIONS TO FUSION ENERGY SYSTEMS — 5.8 — 01-02
L. Friedman, R. J. Beuhler

The development of high molecular weight mass spectrometric techniques has provided a facility for the investigation of 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. A high molecular weight mass spectrometer which has the capability of mass analysis of molecular species with m/e values up to approximately 200,000 is now in use. Efforts to extend this mass range to higher m/e values are being pursued using high voltage ion post-acceleration, and with the development of 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.

46. GAS-PHASE PHOTOIONIZATION AND PHOTOELECTRON SPECTROSCOPY OF MOLECULES AND CLUSTERS — 3.9 — 01-02
J. R. Grover, M. White

Fundamental data necessary to understand fast, exothermic gas phase reactions are being measured via photoionization of molecular beams. This work utilizes tunable, monochromatic radiation from the recently completed gas-phase beamline on the VUV storage ring at the NSLS. Excitation function measurements on mass-selected ions are being carried out for van der Waals and hydrogen-bonded dimers and clusters, free radicals, and molecules. From these data heats of formation and binding energies are determined for both neutral and ionized product species, and studies are made of the Rydberg structure and dissociative ionization pathways of molecules and weakly-bound dimers from which an inner-valence electron has been excited or ejected. New experiments involving the use of electron energy analysis following the resonant, multiphoton excitation and ionization of small molecules, are also being performed. From the observed electronic and vibrational state distribution of the ion, it is possible to investigate in detail the electronic structure and ionization dynamics of electronically excited states of neutral molecules.

Chemistry Department, BNL, continued

47. CHEMICAL CRYSTALLOGRAPHY 5.5 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. Emphasis is placed on structures where hydrogen and other light atoms are important and on 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. Completion of the chemical crystallography beamline at the National Synchrotron Light Source will open up new areas for x-ray diffraction studies. Examples of systems investigated under the crystallography program include organometallic compounds, transition-metal hydrides, zeolites, and pyroelectric and ferroelectric materials. 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 electron charge-density distributions.

48. ELECTRONIC STRUCTURES OF SOLIDS AND THEIR SURFACES: STRUCTURE AND BONDING IN IONS IN SOLUTION 4.5 01-02
T. K. Sham, R. Carr

The main objective of this effort is to improve the understanding of the electronic interactions among atoms in metals, alloys, metal oxides, and certain other compounds. It is especially important to learn about differences between the interactions in the bulk of such solids and interactions at the surfaces, and interaction of surfaces with adsorbates in order to study the heterogeneous physico-chemical phenomena at the interface. These studies are being carried out through photoelectron spectroscopy with conventional photon sources and synchrotron radiation at the NSLS. Studies are also being made of the geometrical and electronic structure of condensed matter, with emphasis on the systematics of the density of unoccupied states and the structure and dynamic behavior of metal complexes in solution. This work, an application of x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS), has been carried out during visits at the Stanford SSRL and will be pursued further at the NSLS. The results are directly related to certain kinetic and mechanistic aspects of chemical reactivity.

Chemical Physics

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Upton, New York 11973

Total $420,000

49. KINETICS AND MECHANSIMS OF ALTERNATIVE FUELS COMBUSTION
R. B. Klemm and J. V. Michael

5.2

01-02

The aims of this task are to make measurements of absolute rate constants for elementary combustion related reactions, and to investigate the mechanistic factors involved in gas phase combustion and pollutant formation processes. Emphasis is placed on alternative fuels that comprise a range of fuel types, including alcohols and hydrocarbon synfuels. To accomplish the aims of this task, a facility has been developed that features a wide variety of experimental techniques, including: flash photolysis-resonance fluorescence (FP-RF); discharge flow-resonance fluorescence (DF-RF); shock tube-atomic absorption (ST-AA); and discharge flow-photoionization mass spectrometry (DF-PIMS). The FP-RF and DF-RF methods are utilized in determining specific rates of elementary atom-molecule and radical-molecule reactions over a wide temperature span, ~200-1100K. The high temperature capabilities of this task have been extended to a considerable extent, up to ~2500K, by the recent addition of the shock tube apparatus. The DF-PIMS method is employed in this task to make direct observations of reactants and products for elementary reactions in an effort to investigate the relevant reaction mechanisms. This DF-PIMS experiment utilizes the National Synchrotron Light Source (NSLS).

Chemical Physics

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Total $96,000

50. UNIMOLECULAR KINETICS
N. Brown

1.25

01-02

Combustion chemistry consists of complex, multi-step chain mechanisms involving reactive radicals which are present in small concentrations. The complexity of the mechanisms, the inherent difficulties of working in high temperature environments, and the large number of species involved with the oxidation of an fuel make the study of combustion chemistry quite difficult. Our current research is concerned with the application of theoretical chemical kinetics to study unimolecular and bimolecular reactions important in combustion processes. The dynamics of reactions are investigated using classical trajectories with realistic potential energy surfaces. Special emphasis is placed upon elucidating the role of molecular angular momentum on intramolecular and intermolecular energy transfer and reactivity. Intermolecular energy transfer important in low pressure limit unimolecular kinetics has been investigated recently for prototype systems and compared with conventional models used to describe weak collision effects. Energy coupling effects have been elucidated. Research continues on microcanonical statistical theories and on diatom/diatom reaction dynamics.

Chemical Physics

Materials and Molecular Research Division
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Total $2,157,000

51. ENERGY TRANSFER AND STRUCTURAL STUDIES OF MOLECULES ON SURFACES — 2.6 — 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 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. 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, the observation of surface enhanced photochemistry on noble metal surfaces. The photochemistry on silver shows a non-linear dependence on incident intensity, decreases sharply as the surface plasmon energy is approached, and is interpreted as enhanced multiphoton absorption due to enhanced surface electromagnetic fields at the silver surface, followed by fragmentation of the excited molecules out of photoionized states.

52. CROSSED MOLECULAR BEAMS — 8.0 — 01-02
Y. T. Lee

This research is directed toward the understanding of elementary atomic and molecular processes and primary photochemical processes using various molecular beam methods and laser facilities. In the area of dynamics of chemical reactions, the investigation of dynamic resonance phenomena in F + H_2, HD, and D_2 have been very successful. The crossed molecular beam studies of electronically excited Na atoms with HCl using a single frequency dye laser have also yielded some very interesting results. The reaction of $O(^3P)$ with acetylene was further investigated. It appears that the intersystem crossing from triplet to singlet plays an important role in the formation of CH_2 + CO products. In the investigation of the primary photochemical processes of glyoxal, the prediction by Schaefer et al. of a concerted reaction forming 2CO + H_2 was verified. In addition to the major channel producing H_2CO + CO, the formation of hydroxymethylene (CHOH) and CO was also observed. Other systems investigated include the $HD^+(v) + He \rightarrow HeH^+ + D$ and $HeD^+ + H_2$ as a function of vibrational and translational energies.

53. MOLECULAR INTERACTIONS — 3.8 — 01-02
W. A. Lester, Jr.

This program is directed at extending fundamental knowledge of the dynamics of energy transfer, reactive, and photodissociative molecular processes. The approach is based on the reliable description of the 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, multi-configuration self-consistent field and configuration interaction _ab initio_ methods for molecular interactions, and various methods for collision dynamics. The electronic structure studies emphasize the determination of the critical geometries and energetics that govern reaction pathways and include the computation of global potential energy surfaces where appropriate. The dynamics studies involve ro-vibrational energy transfer in molecules by collision, and an adiabatic approach to chemical reaction and to single-photon photodissociation of small polyatomic molecules. A novel method that solves the Schroedinger equation stochastically is also being pursued to ascertain its usefulness for determining the energy and other properties of molecules.

54.	THEORY OF ATOMIC AND MOLECULR COLLISION PROCESSES W. H. Miller	3.8	01-02

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.

55.	SELECTIVE PHOTOCHEMISTRY C. B. Moore	3.0	01-02

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 cyclopropylcyclobutene. 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.

56.	PHYSICAL CHEMISTRY WITH EMPHASIS ON THERMDYNAMIC PROPERTIES K. S. Pitzer	2.5	01-02

The primary purpose of this program is the development of methods of prediction of thermodynamic properties of important and frequently complex systems. The relativistic quantum mechanical program for the calculation of dissociation energies and other properties of molecules containing very heavy atoms, recently developed in this project, is being applied to PtH, PtH^+, PbO, and PbH with calculations on SnO for comparison. Calculations are also in progress for UF_6, NpF_6, and PuF_6 in collaboration with LLNL. The methods are being modified and extended for calculations on larger clusters of atoms to investigate surface and catalytic properties.

Earlier work on the statistical thermodynamics of ionic systems is extended to the heat of unsymmetrical mixing. Good agreement is found with heat of mixing measurements on the aqueous systems $NaCl-BaCl_2$ and $NaCl-Na_2SO_4$. Statistical thermodynamic equations are being explored for the treatment of aqueous NaCl to 900 K and several kbar with the hope of prediction at even more extreme conditions.

57. SPECTROSCOPY AND STRUCTURES OF REACTIVE INTERMEDIATES 2.5 01-02
R. J. Saykally

A variety of spectroscopic techniques are being developed for the purpose of detecting and characterizing reactive intermediates of importance in combustion processes. Far-infrared laser magnetic resonsance (LMR) is being employed to measure rotational spectra of reactive intermediates with unpaired electrons. A new technique, called molecular beam laser electric resonance (MBLER), is being developed for the study of rotational spectra of polar species produced and cooled to extremely low temperatures in a supersonic expansion. Most recently, we have begun construction of a tunable far-infrared laser spectrometer which will compliment the preceding two experiments, carried out with fixed-frequency lasers, albeit with a somewhat reduced sensitivity.

58. POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS 5.5 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 pertinent to future energy requirements, but sometimes approached by brute force trial and error methods.

59. PHOTOELECTRON SPECTROSCOPY
D. A. Shirley

This program addresses both experimental and theoretical aspects of electron spectroscopy for the investigation of electronic structure of matter in the gas and condensed phase. Research is conducted using both laboratory sources at LBL and synchrotron radiation in the energy range 5-5000 eV available at the Stanford Synchrotron Radiation Laboratory where there is participation in developing the spectroscopy of this newly-accessible range of the electromagnetic spectrum. Time-of-flight measurements with synchrotron radiation are used to measure angular distributions of photoelectrons and resonant photoemission phenomena in gas phase. Ultrahigh resolution photoelectron spectroscopy based on molecular beams is yielding new information about small molecules and about the transition from single metal atoms to behavior characteristic of a three-dimensional solid. Employing angle-resolved, variable energy photoemission and electron energy loss spectroscopy, this program examines the electronic structure of solids as well as geometric and electronic structure of surface-adsorbate systems with photoelectron diffraction, ARPEFS, and surface EXAFS.

Chemical Physics

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

Total $510,000

60. MOLECULAR RESEARCH WITH ELECTRON SPECTROSCOPY 2.5 01-02
T. A. Carlson, M. O. Krause, A. Fahlman

A basic study of the photoelectron dynamics of molecules and metal vapors is being undertaken through the use of angle-resolved photoelectron spectroscopy and synchrotron radiation. Phenomena receiving particular attention include: the Cooper minimum, shape resonances, autoionization, correlation satellites, and interchannel coupling. Systematic studies are being pursued on halogen acids, halomethanes, metallic halides, and various metal vapors including Ag, Ga, Pb and some 3d transition metal elements. Supportive calculations using the multiple scattering $X\alpha$ method are being performed and correlated with observed minima and maxima in the cross sections and angular distribution parameters. Improved computer handling of the experiment has allowed the introduction of constant-ionic-state techniques.

61. PHOTOCHEMICAL, PYROLYTIC AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE 1.1 01-02
R. Livingston

Labile free radicals are observed at steady state concentration by ESR in circulating fluids at pressures up to 200 atm and temperatures to 700°C. Radicals are formed pyrolytically and photolytically with and without the use of added radical initiators such as peroxides. Work has centered largely on substances that are constituents of fuels and that are related to the production and combustion of organic fuels. A study has recently been completed on a chain reaction that occurs during the pyrolysis of benzyl ether. ESR observations have permitted measurement of kinetic parameters for important steps in the process. Chemical product assays have given additional information that correlates well with the kinetic parameters. New studies have been started on properties of allyl radical and radicals derived from iso-octane.

Chemical Physics

Combustion Sciences Department Sandia National Laboratories/Livermore Livermore, California 94550	Total $4,790,000

62.	TURBULENT REACTING FLOW RESEARCH R. Dibble, R. Schefer, S. Johnston	4.0	01-02

This research is directed towards an increased understanding of the coupling between the chemical kinetic and turbulent transport processes occurring in chemically reacting flows. The long-term goal is to use this understanding to improve predictive capabilities for turbulent combustion. Multi-species Raman concentration and temperature measurements, combined with simultaneous velocity determinations, have been compared with model predictions to estimate the influence of chemical nonequilibrium on mean turbulent flame quantities. A new laboratory incorporating a vertical flame tunnel (and making use of the CRF facility dye laser) was assembled and made operational. A chemically reacting turbulent flow cooperative group comprised of participants from private industry, universities, and Sandia has been formed.

63.	SOOT CHEMISTRY W. Flower, R. Schmieder, R. Perry, M. Gusinow, S. Johnston, W. McLean	4.0	01-02

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 critical information. Laser photolysis is used in 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 and radiocarbon tracer 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.

64.	CRF DIAGNOSTICS RESEARCH - ADVANCED METHODS J. Goldsmith, M. Koszykowski, F. Tully	3.0	01-02

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. Kinetics studies based on pulsed laser photolysis/quasi-cw ultraviolet laser induced fluorescence are in progress, and polyatomic free radical spectroscopy is concurrently being pursued. Theoretical techniques involving electronic structure and scattering calculations, as well as approximate chemical kinetic theories, are being applied to a variety of CRF projects, including high-resolution spectroscopy, modeling, and kinetics studies.

65. COMBUSTION RESEARCH FACILITY OPERATIONS AND VISITING SCIENTIST SUPPORT 12.0 01-02
M. Gusinow, D. Benthusen, R. Johnsen

This task supports all phases of Combustion Research Facility operations: 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 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 others 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 topic short courses in specialized areas, and combustion-related meetings and seminars.

66. CRF CENTRAL LASER SYSTEMS 3.0 01-02
C. Layne, R. Farrow, 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, Sirius, has been installed and remote CARS demonstrated. This new Facility laser system, when fully completed, will provide several sources of high peak power, ultra-high resolution radiation, thereby adding CARS (and other non-linear spectroscopic) capabilities to all of the CRF laboratories.

Combustion Sciences Department, Sandia/L, continued

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

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 comprehensive models for acetylene oxidation and ammonia oxidation were developed. Results provide favorable comparisons with a very large body of experimental data. Further experiments on lean and rich acetylene flames and on cyano-containing flames are now underway.

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

This research effort is directed toward developing nonlinear optical diagnostic techniques in support of Combustion Research Facility programs. New normalization techniques are being refined for coherent anti-Stokes Raman spectroscopy (CARS), a leading technique for time-resolved measurements of major species concentrations and temperatures. These new in-situ normalization schemes provide accurate corrections to fluctuating CARS signals in high-pressure environments, and have been implemented in a CRF internal combustion engine experiment. They are also being implemented in a laminar flat flame for use as a reference standard. High-resolution inverse Raman spectroscopic measurements are providing precise high-temperature N_2 and CO lineshape data. The vibrational Stark effect discovered earlier is being quantified in a crossed-beam infrared absorption experiment to provide spatially precise CO spectra from a laboratory flame.

Atomic Physics

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

Total $1,800.00

69. PHOTOIONIZATION MASS SPECTROMETRY, PHOTOELECTRON SPECTROSCOPY AND PHOTODISSOCIATION 4.5 01-03
J. Berkowitz, B. Ruščić, R. Pandolfi,
J. P. Greene

Fundamental processes in the photoionization of atoms and small molecules are studied at high photon resolution. For molecules, alternative decomposition modes are investigated, providing important thermochemical values, structural and dynamical information. Photoelectron spectroscopy is focussed on the more difficult high-temperature vapor species, and reveals their detailed electronic structure. A recently completed apparatus is intended for the direct study of the spectroscopy and dynamics of molecular-ion decomposition, by analyzing the decomposition products from interaction of UV-laser radiation with selected molecular ions.

70. ATOMIC SPECTROSCOPY WITH FAST BEAMS AT ANL 4.4 01-03
H. G. Berry

Measurements of $2s\,^3P_1-2p\,^3P_{0,2}$ transition wavelengths in highly-stripped two-electron atoms are continuing at the Argonne Tandem-Linac with ions of titanium. A new linear position-sensitive detector is being developed to replace the grating exit slit. A program of experiments utilizing laser excitation of fast ion beams has begun. Na and Na^+ autoionization electron spectra following collisions of 1-MeV He^+ ions on selectively-excited NaI, $3p\,^2P_{3/2}$ target atoms have been observed. This atomic state was populated by a cw dye laser at 50° to the incident ion beam axis. Several experiments involving ion beam resonant excitation by collinear laser beams are under construction. Optical polarization measurements have been made of the light emitted from excited states of hydrogen and hydrogen-like helium following perpendicular carbon-foil excitation of protons, H_2^+ and He^+, at energies of 50-100 keV and 0.7 to 1.7 MeV. Alignments of 100% for highly excited states have been observed.

71. THEORETICAL ATOMIC PHYSICS 1.1 01-03
K. T. Cheng

The main objective of this program is to improve the understanding of the effect of relativity and electron correlations on atomic processes such as photoexcitations and photoionizations. The emphasis is to develop and apply advanced relativistic many-body techniques to the studies of these processes where both relativity and correlation effects are important. Current efforts include studies of the systematic trend of autoionization spectra for Ar-, Kr-, and Xe-like ions. In particular, there is interest in the dynamics of Rydberg series interactions which determine the change in resonance profiles along isoelectronic sequences. Studies are also being done on the absorption spectra of Pd- and Xe-like ions in the region of $4d \rightarrow nf$, εf transitions with a combination of the relativistic random-phase approximation and the term-dependent Hartree-Fock techniques. The purpose of this study is to gain better understanding of the 4f orbital-collapse phenomenon and its effect on the absorption spectra of rare-earth elements.

72. HIGH-RESOLUTION LASER-rf SPECTROSCOPY WITH ATOMIC AND MOLECULAR BEAMS

W.J. Childs, L. S. Goodman, V. Pfeufer

3.1 01-03

This program is directed toward a detailed understanding of interactions in atoms and small molecules. In the recent past the spin-rotation and hyperfine interactions of alkaline-earth monohalide radicals have been systematically studied and their dependence on vibrational, rotational, and isotopic effects elucidated. Efforts are now underway to extend the high-precision techniques to determine the electric dipole moments of these molecules. A similar program aimed at a systematic understanding of the hyperfine interaction throughout the 4f-shell of the rare-earth atoms is underway concurrently.

73. DISSOCIATION AND OTHER INTERACTIONS OF ENERGETIC MOLECULAR IONS IN SOLID AND GASEOUS TARGETS

D. S. Gemmell, E. P. Kanter

4.9 01-03

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 (0.005° and 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 study of the interactions of fast charged particles with matter with emphasis on those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., the feature that each incident molecular ion 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. Current attention is being focussed on the production of highly-excited Rydberg atoms formed in foil-excited ion beams.

74. ELECTRON SPECTROSCOPY WITH FAST MOLECULAR AND ATOMIC ION BEAMS

D. Schneider, E. P. Kanter, H. Kudo, P. Arcuni, W. Stöffler

4.0 01-03

This research project is directed toward the understanding of interaction of fast (meV) ion beams with solids and gases. Spectroscopy of secondary electrons is used to study dynamic excitation processes and to study highly-excited states in projectile and target atoms. Cross-section measurements, spectroscopic investigation with high energy resolution, and coincidence measurements are performed. Using field ionization techniques, the yield of Rydberg states formed in fast atomic (H^+,He^+) and molecular (H_2^+,HeH^+) ion beams is measured when merging from thin foil targets. The electronic deexcitation of excited fragment ions from molecular-ion impact is investigated and compared to the case of atomic-ion impact. Yield measurements are performed using solid targets (Si, Au) and H^+ and He^+ as projectiles. Additional measurements, under channeling conditions, should yield information regarding surface analysis. First experiments on a Na vapor target using fast ion beams in combination with laser excitation are performed.

Atomic Physics

Physics Department
Brookhaven National Laboratory
Upton, New York 11973

Total $240,000

75. ATOMIC PHYSICS RESEARCH
K. W. Jones and B. M. Johnson

3.1 01-03

Beams from the Brookhaven Double Tandem Van de Graaff Facility are used to study various aspects of ion-atom and ion-electron collisions. Energies for 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. Charge transfer and equilibrium charge states in ion-gas collisions are studied with negative ions and with positive ions produced by the tandem accel-decel method. Inner-shell vacancy processes are also studied with these beams. An effort to measure electron ionization and excitation cross sections in an electron-heavy ion crossed-beam experiment is now in progress. Work to study the excitation and ionization of atoms and ions by photons from the National Synchrotron Light Source has been started.

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

Total $473,000

76. ATOMIC PHYSICS
R. Marrus

6.0 01-03

This research studies collision and spectroscopic properties of multi-charged ions. Measurements are made of cross-sections for electron capture by multi-charged neon ions on several rare gases. Using a novel trapping technique results are obtained at lower collision energies (Ne^{10+} at 1-10 ev) than have heretofore been possible. In another area, an experiment is being done to perfect observations of parity violation in atomic thallium. This effect represents a fundamental test of the new unified theories of electromagnetic and weak interactions. Using the highly stripped iron beam from the super-HILAC precision measurements are made on X-rays from hydrogenic and helium-like ions. These measurements exhibit effects due to quantum electrodynamics and relativistic effects. Dielectronic satellites associated with capture of an electron into a high-n state are also observed. These satellites are observed in fusion reactors where their intensities are used as a diagnostic tool.

Atomic Physics

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

Total $1,130.00

77. THEORETICAL ATOMIC PHYSICS — 1.0 — 01-03
R. L. Becker and C. Bottcher

Theoretical predictions, interpretations of experimental results, and detailed calculations are made for atomic collision, radiation, and structure phenomena. Emphasis is placed on reactions of highly stripped ions and of electrons with atoms, particularly those reactions of importance in fusion energy devices and those studied in atomic high-energy accelerator physics laboratories. Recent activities include calcuations of dielectronic recombination (being studied experimentally with merged beams at the ORNL EN-tandem Van de Graaff), multiple L-shell vacancy production by ions (being detected in x-ray satellites at the ORNL Holifield heavy ion accelerator), and ion-Rydberg atom collisions (for which the first experimental results, from the University of Kentucky, are appearing). New theoretical approaches include the "one and a half center" version of coupled-channels theory and the use of finite elements in the numerical integration of the time-dependent Schröedinger equation.

78. ACCELERATOR ATOMIC PHYSICS — 5.9 — 01-03
S. Datz, P. F. Dittner, P. D. Miller
and C. D. Moak

The objective of this task is to achieve a detailed understanding of the interactions of high-energy, multiply-charged, heavy ions with gas, solid, and electron targets. The primary facility used is the EN-tandem accelerator. Ion-Ion collisions at low energies are also being investigated, and two experimental programs have been started on the Holifield accelerators. Examples of subjects which have received particular attention during the past year are: 1) Cross section measurements of dielectronic recombination of B^{2+} and C^{3+} using a merged multiply charged ion beam concentric with an electron beam have been completed; 2) photodetachment and collisional detachment cross sections of He^- ions have been measured; 3) the study of radiation from channeled electrons and positrons has been continued; and 4) a program using positrons generated by the EN-tandem at all energies up to 6 MeV has been started. Results in these areas impinge directly on fusion research, solar corona studies, and material sciences, as well as improving our fundamental understanding of ion-atom, ion-solid, ion-ion, and ion-electron interactions.

79. EN TANDEM OPERATIONS — 1.6 — 01-03
P. D. Miller and G. F. Wells

The EN-tandem Van de Graaf is operated for atomic physics research. Terminal voltage up to 6.0 MV are achieved, and ions of all elements from Z=1 through 9 and many heavier ions are available for users. The user group includes members of the physics division, other divisions of ORNL, and faculty and students from various universities. During 1982 the design work for the installation of the Elbek Spectrometer was completed. The magnet was refurbished and long lead-time items were ordered. Sixty percent of the installation was completed. The major beam usage was for the merged electron heavy ion beams experiments, positron source development, and channeling studies. A small (<20%) portion of the available beam time was devoted to University of Tennessee and other university users.

Physics Division, ORNL, continued

80. COLLISIONS OF LOW ENERGY MULTIPLY CHARGED IONS 1.4 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 recently for Al^{+q} ions ($2 < q < 10$) and Fe^{+q} ions ($3 < q < 14$) colliding with H and H_2 at energies in the range 10-100 eV/amu, and provide data for testing predicted ionic charge scalings at low energies. 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.

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

Total$150,000

81. 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 using laser-based excitation schemes. Using resonant miltistep laser ionization techniques, we have measured rates of transfer between rotational states of NO due to collisions with rare gas atoms and NO molecules. These studies are being extended to other systems. In addition, similar methods are being applied to study electronic energy transfer between colliding molecules and orientational relaxation. By using appropriately polarized light, NO molecules in one rotational level can be oriented so their average angular momentum lies along one axis. The decay of the orientation or its transfer to other rotational states by collision processes are then probed by other polarized lasers. Other processes which may be investigated include collision induced vibration and electronic state changes and autoionization of NO.

Chemical Energy

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $892,000

82. ORGANOMETALLIC COMPLEXES IN HOMOGENEOUS CATALYSIS 2.2 02-01
R. J. Angelici

The major thrusts of this research are to understand the role of organometallic ligands in transition-metal-catalyzed reactions and to seek new catalytic reactions which provide energy-efficient routes to useful chemicals. Of particular interest are reactions of ethylene oxide with CO ligands of metal carbonyl complexes. It has been demonstrated that CO ligands in complexes of Fe, Ru, Mn, and Re react with ethylene oxide to form dioxo-carbene complexes of those metals. This type of reaction is being examined for possible catalytic applications. Studies of thiophene complexes of transition metals have been initiated for the purpose of providing some understanding of the hydrodesulfurization of organic sulfur-containing compounds.

83. CHEMICAL KINETICS AND REACTIVITY OF TRANSITION METAL COMPLEXES 4.5 02-01
J. H. Espenson

Organometallic complexes such as $(H_2O)_5Cr-R^{2+}$, $R-Co(dmgH)_2L$, and $R-Rh(dmgH)_2L$ 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 the organic group, R, reacts further. Novel displacements by 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 metal-carbon bond homolysis permit: (a) evaluation of thermodynamic bond dissociation energies, (b) resolution of the mechanism of homolytic cleavage vs. competing heterolysis, (c) examination of novel free radical displacement reactions, and (d) evaluation of the kinetic reactivity of aliphatic radicals. Conditions are being developed for the use of metal complexes to generate aliphatic radicals in solution in a controlled manner.

84. NUCLEAR MAGNETIC RESONANCE (NMR) STUDIES OF COALS, CATALYSTS, AND AMORPHOUS SEMICONDUCTORS 4.0 02-01
B. C. Gerstein

Solid state NMR is used to infer chemical functionality in coals and products of coal conversion, e.g. solid asphaltenes, and probe hydrogen, silicon and aluminum in zeolites used for conversion of methanol to ethylene. In addition, the morphology of proton containing regions in amorphous silicon-hydrogen alloys, and the types of SiH_x groups present in these materials are studied by solid state proton and silicon NMR utilizing a variety of experiments involving the proton and silicon spin dynamics.

Ames Laboratory, continued

85. SPECTROSCOPIC AND KINETIC CHARACTERIZATION OF METAL OXIDE AND SULFIDE CATALYSTS   1.9   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 mechanisms of catalytic reactions. Metal oxide and sulfide catalysts for producing synthetic fuels or for hydrotreating coal-derived liquids are being investigated; catalysts for energy-efficient routes to chemicals are also important in this research. Spectroscopic techniques such as laser Raman spectroscopy and Fourier transform infrared spectroscopy provide characterization of the 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. Adsorption and reaction studies are being performed using pulsed or steady-state fixed bed reactors.

86. HIGH-TEMPERATURE GAS-PHASE PYROLYSIS OF ORGANIC COMPOUNDS   1.9   02-01

W. S. Trahanovsky

This research is directed toward an understanding of the fundamental thermal reactions of organic compounds, especially those that could be important in the pyrolysis of coal and coal-derived liquids. The work can be divided into three main categories: 1) determination of the major pyrolysis reactions of model compounds; 2) preparation and study of the physical and chemical properties of reactive compounds thought to be intermediates in pyrolysis reactions; 3) determination of the importance of surface-catalyzed reactions under various pyrolysis conditions. Most pyrolyses are carried out using the Flash Vacuum Pyrolysis technique. Much of the work concentrates on the study of pyrolysis reactions that are thought to involve quinodimethanes as intermediates, on the preparation and characterization of these and related species, and on the thermal reactions of these species and products derived from them. Specific compounds under study include tetralins, 2,3-dimethylene-2,3-dihydrofurans, the furan analogs of *ortho*-quinodimethanes, and benzocyclobutenes, the closed forms of *ortho*-quinodimethanes.

87. STUDY OF SOLID-GAS REACTIONS WHICH INVOLVE STRUCTURAL CHANGES IN THE SOLID   1.0   02-01

D. L. Ulrichson, A. H. Pulsifer

The objective of this work is to understand and describe the behavior of the class of solid-gas reactions which exhibit either expansion or contraction of the solid during reaction. In the case of solid expansion, 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 the reaction stops. 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 several solid-gas reactions can be explained by inclusion of this term. Current work emphasizes measurement of diffusion rates through the pores and through the solid product layer.

Chemical Energy

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

Total $450,000

88. FLUID CATALYSIS 4.4 02-01
J. W. Rathke, M. J. Chen,
R. J. Klingler, J. J. Heiberger

This research attempts to determine reaction mechanisms and to find new catalysts for the conversion of small molecules (e.g., CO and CO_2) to specific desired products. Currently under investigation is a series of organometallic complexes which catalyze the reaction of CO with H_2O to form alcohols. This reaction occurs by a new mechanism which does not involve a prior water-gas shift pathway. Also studied are a general catalytic method for homologation of methanol to ethanol and a new catalytic pathway for hydrogen reduction of carbonate ion; the latter reaction being relevant to the utilization of inorganic carbon resources (e.g., CO_2). The mechanisms of these reactions are being investigated using a combination of high-pressure kinetic, tracer, spectroscopic (including multinuclear FT-NMR), thermochemical, synthetic, and theoretical (molecular orbital) methods.

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

Total $1,458,000

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

This program undertakes the preparation and characterization of novel inorganic oxidants and fluorinating agents. In addition to the physical and chemical characterization of these compounds, the program is devoted to the identification and exploitation of applications of these exotic materials to other areas of chemistry. A major current thrust is the application of hypofluorites, particularly the recently discovered fluoroxysulfate ion, SO_4F^-, as reagents in organic chemistry, with especial emphasis on their use as selective fluorinating agents for biologically important steroids. Other current efforts involve elucidation of the mechanism of interaction of F_2 with aqueous solutions and the use of powerful fluorinating agents to prepare unusual, highly oxidized compounds of the actinide elements.

Chemistry Division, ANL, continued

90. THE PREMIUM COAL SAMPLE PROGRAM 2.9 02-01

K. S. Vorres

The objective of this program is to provide the U. S. basic coal science research community with long-term supplies of a small number of premium coal samples. The premium coal samples produced and distributed by this program are to be as chemically and physically identical as possible, have well-characterized chemical and physical properties, and be stable over long periods of time. Coals are to be mined, transported, processed into desired particle and sample sizes, and packaged in environments which are as free of oxygen as possible and which maintain the natural moisture content to insure that the coals are kept in as pristine and stable condition as possible. These premium samples are to be distributed to researchers upon request. It is anticipated a computer data base will be included in this program to provide researchers with easy access to detailed information on sample availability, the physical and chemical properties of the coals, and references to the results of research obtained using these samples.

91. FUNDAMENTAL CHEMISTRY OF COALS AND OTHER FOSSIL FUELS 6.5 02-01

R. E. Winans, R. Hayatsu, R. E. Botto, R. G. Scott, R. M. McBeth

The major objective of this program is to provide a fundamental understanding of the macromolecular structure of coals and coal macerals and to relate these structures to the chemical and thermal reactivity of these materials. Information gained in this study is important for improving current conversion processes and for designing new, novel processes. The approach taken in this study is to solublize selectively the macromolecules and to characterize the products by mass spectrometry, both solution and solid C-13 nuclear magnetic resonance, Fourier transform infra-red spectroscopy, and with a large variety of separation techniques. A chemically realistic model and new insight into the formation of coal macerals are resulting from these studies on artificial coalification. The characterization and reactivity studies of separated macerals are being emphasized. Correlations of these data by statistical analysis are providing additional insight into the structure-reactivity relationship of coal macerals.

Chemical Energy

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

Total $170,000

92. THERMODYNAMIC CHARACTERIZATION OF CONDENSED-RING COMPOUNDS 3.0 02-01

B. E. Gammon

Research continues on synthesis, purification and measurement of thermodynamic properties of polycyclic aromatic hydrocarbons and their hydrogenation products and for similar polycyclic, organic, nitrogen compounds. 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 2,2'-dimethylbiphenyl, 3-methylpyrrolidine and isoquinoline. Measurements are nearing completion on quinoline, 4-methylphenanthrene and 2,6-dimethylpyridine; several other compounds are purified awaiting measurements. Synthesis and purification of others are in progress. Derived Gibbs energies of formation facilitate an understanding of hydrocracking and denitrogenation. The data 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.

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $400,000

93. ORGANOMETALLICS IN HOMOGENEOUS CATALYSIS 2.9 02-01
M. A. Andrews

The efficient production of chemicals from coal and petroleum-derived feed stocks is increasingly dependent on homogeneous catalysts. Basic research in this area provides a foundation for rational catalyst design and improvement. Work in this laboratory is devoted to understanding the role of soluble transition metal complexes in the homogeneous catalytic oxidation of organic substrates. The long range goal of this work is the development of a more efficient, selective alkene epoxidation catalyst. A new approach to this problem employs transition metal nitro-nitrosyl redox catalysts to oxidize a wide variety of alkenes, with concurrent formation of the nitrosyl complex. The nitrosyl group is air oxidizable back to a nitro functionality, completing a catalytic cycle. The oxidized organic products produced and the selectivities obtained are strongly dependent on the type of alkene. A mechanistic understanding of these distributions has been obtained, and future studies will utilize the insights obtained to understand related existing catalyst systems and to develop new and more selective epoxidation catalysts.

94. MECHANISMS OF PHOTO-, ENZYME-, AND CHEMICALLY CATALYZED CIS-TRANS ISOMERIZATION 2.9 02-01
S. Seltzer

Cis-trans isomerization can be brought about by the application of heat or 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 vision in animals and the light-driven proton pump of Halobacteria, which can be utilized in a photogalvanic cell. Studies at BNL are concerned with the mechanisms of enzymatically and chemically catalyzed and photosensitized cis-trans isomerizations and their application to the mechanisms of the proton pump.

Chemical Energy

Department of Applied Sciences
Brookhaven National Laboratory
Upton, New York 11973

Total $565,000

95. HIGH TEMPERATURE CHEMISTRY J. J. Egan	2.2	02-01

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.

96. METAL HYDRIDES J. J. Reilly	4.6	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, 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 from ideal behavior of certain intermetallic-hydrogen systems, surface and near surface properties of metal-hydrogen systems, the partial molar volume of hydrogen in intermetallic compounds, the influence of defects upon system behavior and reaction kinetics of metal hydride suspensions. The major experimental tools and/or techniques consist of X-ray and neutron diffraction, equilibrium pressure-temperature-composition measurements, ion beam analysis and magnetic susceptibility measurements.

Applied Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $120,000

97. BIOCONVERSION OF CELLULOSE C. R. Wilke and H. W. Blanch	2.0	02-01

This project investigates primarily the enzymatic hydrolysis of biomass to hexose and pentose sugars. Basic information on the kinetics and mechanism of enzymatic hydrolysis is to be obtained. This information can then be used to develop low-cost processing schemes for sugar production. High productivity fermentations to convert these sugars to ethanol or other chemical feedstocks are being developed. Fundamental studies on yeast metabolism in high cell density cultures will be obtained. This will be combined with basic studies on ethanol separation from the fermentation broth, using novel, low-energy solvent extraction schemes.

Chemical Energy

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

Total $1,250,000

98. HIGH-ENERGY OXIDIZERS AND DELOCALIZED-ELECTRON SOLIDS. 5.0 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. Recent findings indicate that fluorine can be intercalated, reversibly, into graphite by electrochemical means to a composition $\approx C_{2.5}F$. 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.

99. TRANSITION METAL CATALYZED CONVERSION OF CO, NO, H_2 AND ORGANIC MOLECULES TO FUELS AND PETROCHEMICALS 2.6 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 molecules and organic compounds. A recent discovery on this project was the finding that a certain class of iridium complexes undergo oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons. This is the first example of this long-sought reaction, and work on this project is now directed at examining the scope, selectivity, and mechanism of this reaction. Efforts are also being directed at converting the alkyl(hydrido)iridium products of the oxidative addition into functionalized organic molecules.

100. FORMATION OF OXYACIDS OF SULFUR FROM SO_2 2.3 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.

Materials and Molecular Research Division, LBL, continued

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

This research is concerned with a better understanding of technologically important reactions, and potentially leads to new process applications. It has been found that hydrocarbons as high as C_6 can be produced directly from graphite and water at temperatures as low as 500^{o}C and in the presence of alkali catalysts. Gasification and synthesis steps may thus be combined in a single operation. Mechanisms have been investigated. A selective hydrogenation of polynuclear aromatics containing nitrogen has been demonstrated with total selectivity for the nitrogen containing ring only.

102. SYNTHETIC AND PHYSICAL CHEMISTRY 1.7 02-01
W. L. Jolly

In this research, ionization potentials from core and valence photoelectron spectroscopy are used to characterize the bonding in organometallic compounds related to catalytic systems. Most of this work involves the study of molecular compounds in the gas phase using x-ray photoelectron spectroscopy. Studies of the interactions of olefins and isocyanides with transition metals in complexes such as $LFe(CO)_4$ and $LCr(CO)_5$ yield detailed information about the σ- and π-bonding in such systems. The heats of formation of gaseous ions are obtained from the core binding energies. It is planned to use a high-temperature sample cell on the spectrometer to allow the study of compounds which have too low a vapor pressure at room temperature.

103. SURFACE CHEMISTRY - APPLICATION OF COORDINATION PRINCIPLES 2.1 02-01
E. L. Muetterties

Establishment of the coordination chemistry of nickel and platinum surfaces represents the major thrust of this research. Definition of chemisorption states for important representative molecules from major classes of organic molecules and examination of catalytic reactions will comprise the major research objectives. Key organic molecules under investigation include thiophene, pyrrole, furan and aromatic hydrocarbons. In addition, these surface states will be modeled with molecular cluster complexes. Isotopically labeled cluster molecules such as $^{101}Ru_3(CO)_{12}$ and $^{104}Ru_3(CO)_{12}$ have been prepared for tests of metal-metal bond scission reactions.

104. ELECTROCHEMICAL SYSTEMS 0.7 02-01
J. Newman

This program includes investigation of fluid flow and electrochemical transport, 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.

105. CATALYTIC HYDROGENATION OF CO: 6.5 02-01
Catalysis on Well-Characterized Surfaces
G. A. Somorjai
Catalysis by Supported Metals
A. T. Bell

This research is aimed at developing a fundamental understanding of the chemical processes occurring during the hydrogenation of CO to hydrocarbons and oxygenated products. The experimental work involves measurements of reaction kinetics, elucidation of reaction pathways, and characterization of the catalyst surface using a variety of spectroscopic techniques. The influence of promoting Fe and Re with alkali metals, on the C_2^+ selectivity of these catalysts is being explored. High surface area thoria catalysts are being investigated for the synthesis of methanol. A study is being carried out of the structure and reactivity of different forms of carbon deposited on the surface of Ru during hydrocarbon synthesis. Attempts are being made to identify the physical and chemical interactions between Pd and metal oxide supports, which influence the performance of the Pd for methanol synthesis.

106. ORGANOMETALLIC CHEMISTRY OF COAL CONVERSION 2.4 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. Specific ligands to transition metal organometallic complexes are being constructed, the steric and electronic features of which have lead to the uncovery of novel processes in the coordination sphere of metals. Several of these constitute novel organometallic photochemical energy storage cycles. The use of light in the activation of complexed small ligands, such as carbon monoxide and carbon dioxide, is being explored. Morever, investigations are being carried out concerned with the activation of carbon-hydrogen and carbon-carbon bonds in coal model systems. Several novel molybdenum clusters have been prepared and their chemistry with respect to hydrodesulfurization is being studied. The reaction of sulfur with homogeneous transition metal clusters is being scrutinized as a potential analog to reactions occurring on catalytic surfaces poisoned by sulfur.

Chemical Energy

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

Total $184,000

107. EFFECTS OF METAL SURFACES ON KINETICS OF HYDRIDE FORMATION 1.9 02-01
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.

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

Total $250,000

108. SYNTHESIS OF THERMOCHEMICAL CYCLES 1.4 02-01
W. Jones, 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 the development of this new technology and for the evaluation of worldwide programs. The research consists of the identification, initial evaluation, and preliminary development of different cycles through measurements 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) low temperature reactions in cycles based on oxide decompositions, and 3) evaluation of key reactions in methanol-based cycles.

Chemical Energy

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

Total $225,000

109. LABILE SO_2 COMPLEXES 1.25 02-01
G. J. Kubas, G. D. Jarvinen,
R. R. Ryan

The basic chemistry of sulfur dioxide is being expanded with regard to its binding to transition metal complexes, enhancing its reactivity, and promoting catalytic reactions. The ultimate goal is development of new methods for scavenging SO_2 from flue-gases. Work includes synthesis and structural characterization of new SO_2 complexes and catalytic reactions of SO_2 with other small molecules. For example, SO_2 and NO_x have been converted to sulfur, nitrogen, and water by hydrogen reduction over a Ru/alumina catalyst and methods of catalyzing such reactions homogeneously are being investigated. Reactions of SO_2 with transition metal hydride complexes are being studied in order to identify intermediates and mechanisms involved in hydrogen transfer to SO_2, and insertion of SO_2 into a metal-hydride bond, a possible key step in hydrogenation, has been observed for the first time. As a spinoff of the above work, the first example of a molecular hydrogen complex, $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, has been discovered, and its possible role in catalytic hydrogenation is under investigation.

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

Total $233,000

110. FUNDAMENTAL INVESTIGATIONS OF METAL HYDRIDES 2.5 02-01
R. C. Bowman, Jr., G. C. Abell,
M. P. Guse

The program objective is to obtain a fundamental understanding of the role of the interstitial hydrogen on the electronic and structural properties of the host metal. Experimental techniques such as NMR, variable temperature x-ray diffraction and thermal analysis are being used: 1) to evaluate specific properties of the electronic structure; 2) to determine the effect of host metal structure, hydrogen site occupancy, and alloy substitution on hydrogen diffusion; 3) to study the ramification of phase transitions on the electronic structure of the metal hydrides. Among the hydrides under current investigation are the AB_5 compounds, zirconium and titanium based alloys both crystalline and amorphous, and the Laves alloys. Monte Carlo type calculations are used to correlate NMR lineshapes with hydrogen site occupancy. Quantum-mechanical calculations of the electronic properties of clusters of metal atoms with hydrogen interstitials are being used to describe additional experimental results. Short range electronic structures are being explained using a localized electronics states model.

Chemical Energy

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

Total $250,000

111. KINETICS OF ENZYME-CATALYZED REACTIONS 3.1 02-01
E. Greenbaum, J. Woodward

This research is focused on understanding the fundamental chemical and physical mechanisms of enzyme-catalyzed reactions. The specific systems under investigation are the in vitro photosynthetic system composed of isolated chloroplasts, ferredoxin, and hydrogenase (CFH) and the enzyme-catalyzed conversion of cellulose to glucose. The CFH system is capable of the simultaneous photoproduction of hydrogen and oxygen when irradiated with visible light. Experimental progress includes the first measurements of the light saturation curves of biophotolysis of water and the first demonstration of the simultaneous photoproduction of hydrogen and oxygen by immobilized chloroplasts, ferredoxin, and hydrogenase. The key result is that the analytical shapes of the light saturation curves are not the same. A higher light intensity is required to saturate the hydrogen curve. These results challenge the Z-scheme concept of photosynthesis. A cellulase enzyme system is being investigated for the conversion of cellulose. An immobilized enzyme has been shown to maintain long-term stability and high activity for this application.

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

Total $2,110,000

112. BASIC AQUEOUS CHEMISTRY TO HIGH TEMPERATURES AND PRESSURES 5.3 02-01
R. H. Busey R. E. Mesmer
H. F. Holmes D. A. Palmer
W. L. Marshall

This program is directed toward the goal of a broad and detailed understanding of chemical processes occurring in aqueous systems to high temperatures and pressures. Such information relates to the safe and efficient operation of energy production, steam generation, fuel reprocessing, and waste disposal facilities as well as to the extraction of heat and materials from natural resources. Specialized techniques are employed in calorimetry, conductance, potentiometry, spectrophotometry, isopiestic and phase equilibrium studies at temperatures generally to 300°C and at modest pressures and sometimes to 800°C and 4000 bars. Species identification, thermodynamic properties and equilibrium stability information are obtained but some new emphasis will be placed on structural and detailed quantitative information from neutron and Raman scattering. The most significant scientific and practical contributions have been made with respect to the following: the ionization reactions of water and weak acids and bases; the association of 1:1 chlorides; the hydrolysis of metal ions; the phase behavior of oxides, sulfates and phosphates; excess thermodynamic quantities for chlorides and sulfates; and models for the pressure and temperature dependencies of chemical equilibria.

113. HETEROGENEOUS CATALYSIS RELATED TO ENERGY SYSTEMS 2.2 02-01
S. H. Overbury, M. L. Poutsma

The technique of low energy ion scattering as a surface specific structural tool is being developed and applied to the study of clean and adsorbate covered single crystal surfaces of catalytic interest. Comparison of the experimentally observed energy and angle dependencies of the scattered ions with computer simulations allows for quantitative descriptions of surface structure. The information content from alkali metal ions (Li^+,K^+) exceeds that from inert gas ions because of their lower neutralization probability. These methods are being applied especially to adatoms such as O and C on clean Mo(100). These adatoms have been shown to occupy the four-fold sites at a perpendicular height of 0.3 Å above the surface.

114. ORGANIC CHEMISTRY AND THE CHEMISTRY OF FOSSIL FUELS 7.1 02-01
M. L. Poutsma, E. W. Hagaman,
B. M. Benjamin, R. R. Chambers,
L. L. Brown

This experimental program is designed to determine the structure and reactivity of coal. The key spectroscopic technique being used for native and chemically modified coals is solid-state CP/MAS ^{13}C NMR with particular emphasis on developing the technique for use in a quantitative reliable manner. Diagnostic reactions for structural features being used include C-C bond cleavage induced by electron donors, C-H deprotonation induced by carbanions, and excision of aliphatic connecting groups by acid-catalyzed transalkylation. Mechanistic description of the thermal decomposition pathways of key structural units in coal has been advanced by use of appropriate model compounds; the role of diffusional restraints is being probed by use of surface-attached model compounds.

115. MOLTEN SALT CATALYSTS FOR CLEAN FUEL SYNTHESIS 4.6 02-01
G. P. Smith, A. S. Dworkin,
A. C. Buchanan, III, S. P. Zingg

This research elucidates the respective roles of redox and acid/base functionality in the catalytic reactions of arene hydrocarbons. Liquid metal halides at 25-150°C serve as catalysts. For the purpose of basic investigations these liquid catalysts have the advantage over solid catalysts that key catalytic properties, such as redox potential and Lewis acidity, can be varied over wide ranges in an accurate and reproducible way. Current experimental work includes an investigation of the formation reactions of selected arene radical cations (reactive intermediates in redox catalysis) and the kinetics of their decay reactions in $SbCl_3$-rich melts as functions of concentration, temperature, and the redox potential of the melt. These reactions are studied by fast optical spectroscopy and electrokinetic methods. In another investigation the activity and selectivity of Ga(III)/Ga(I) halide mixtures with respect to arene H-transfer reactions are being studied by *in situ* NMR spectroscopy and byproduct analysis following quench and separation.

Chemical Energy

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

Total $450,000

116. HYDROGENATION MECHANISMS OF COAL 2.1 02-01
James A. Franz and Russell D. Barrows

This program is a basic research program directed at determining the energetics and mechanisms of free radical reactions related to thermal dissolution of coal in hydrogen donor media. Relative rates of radical rearrangements, atom transfer reactions, fragmentation reactions and change transfer reactions are being determined, with absolute rates determined by kinetic laserflash spectroscopy for key atom transfer reactions. The cyclization of ortho-allylbenzyl radical to 2-indanylmethyl radical, for example, is used as an intramolecular free radical "clock" to compare atom transfer rates to benzylic radicals, thereby determining the relative donor strength of a wide variety of coal-related donors. Thermochemical values of select radicals are being determined using ESR of equilibrating radical mixtures, allowing estimates of difficultey observed radical rearrangements.

117. THERMOCHEMICAL CONVERSION OF SOLID WASTES INTO LIQUID FUELS 1.8 02-01
D. A. Nelson, J. A. Russell, S. D. Landsman, P. M. Molton

The purpose of this research is to determine the reaction mechanisms involved in biomass liquefaction in aqueous media at elevated temperatures. Due to the complexity and variability of composition of biomass, the liquefaction of pure cellulose is now being studied. More than 90 components of the cellulose liquefaction product can be identified by gas chromatography-mass spectroscopy. Particular emphasis is now directed toward the aromatic products of the liquefaction product. The identification of alkyl substituted benzoquinones and benzenediols is quite interesting since their formation involves aldol condensation followed by a reduction-oxidation mechanism. Reactions occurring after formation of the cellulose liquefaction product apparently include oligomerization by auto-oxidation. The cellulose product oil shows rapid viscosity increases not associated with water or solvent loss; differential scanning calorimetry is consistent with nonlinear, branched oligomer formation.

Chemical Energy

Chemical and Instrumental Analysis Division — Total \$80,000
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, Pennsylvania 15236

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

Research during the current year has concentrated on understanding molybdenum-support and tungsten-support interactions in Mo/Al_2O_3, W/Al_2O_3, $Ni\text{-}Mo/Al_2O_3$, and $Ni\text{-}W/Al_2O_3$ catalysts. Raman spectroscopy is the primary tool used to define molecular speciation for catalysts in which Mo, W, and Ni concentrations have been varied systematically. Additional information concerning the influence of concentration of metals on the vibrational frequencies of molecular species is obtained by chemical modification of the catalyst surface structure and by low temperature experiments. Raman experimentation is supplemented by data from other bulk and surface sensitive techniques, such as X-ray diffraction, X-ray photoelectron spectroscopy, and ion scattering spectroscopy. Correlations are made with catalytic reaction data to provide insight into structural and chemical factors that influence catalytic activity.

Radiation and Surface Physics Research Department — Total \$160,000
Sandia National Laboratories/Albuquerque
P. O. box 5800
Albuquerque, New Mexico 87115

119. REACTION KINETICS OVER SINGLE CRYSTAL CATALYSTS — 1.6 — 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. Recent studies have addressed the role of potassium promoters in nickel catalysts for methanation. High-pressure kinetic measurements of this reaction over a Ni(100) catalyst containing submonolayer quantities of potassium adatoms have been combined with detailed surface analysis before and after reaction. Potassium decreases the rate of methane formation and increases the rate of higher hydrocarbons relative to the clean Ni(100) catalyst. Similar results have been reported for supported nickel catalysts suggesting that support effects play a small role in catalytic promotion by potassium.

Research Division — Total \$150,000
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

120. BASIC RESEARCH IN SYNTHESIS AND CATALYSIS — 1.5 — 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 has yielded new bi- and trimetallic complexes with bridging fulvalene, *s*- and *as*-indacene, and trindene ligands of Ti, Zr, Ta, Mo, and Mn. Spectroscopic and photochemical studies of Co and Ni 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 polymer-pendant phosphine molybdenum(0) dinitrogen complexes using combined FT-IR and electrochemical techniques.

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $990,000

121. HYDROMETALLURGICAL PROCESSING — 1.6 — 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 pyrrhotite and pentlandite 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 platinum chloride solution using a supported liquid membrane impregnated with trioctylamine as a mobile carrier and the elucidation of its mass transfer mechanism for permeation through the membrane; and the modeling of the electrowinning of dilute copper sulfate solution using a fluidized bed electrochemical reactor.

122. ANALYTICAL MASS SPECTROMETRY — 0.9 — 02-02
R. J. Conzemius, H. J. Svec

The objective of this project is to develop viable analytical techniques for a wide range of analytical requirements based on mass spectrometry of solids. The general approach involves the direct excitation of specimens to the ionic state using high energy processes such as a high frequency spark, a focused laser beam, and other plasma ion sources. The advantage of this approach is that it provides analytical characterization including speciation of surface contaminants as well as elemental analysis without requiring specimen dissolution or chemical treatment and with minimum sample preparation. The ultimate goal of the work is to realize an analytical system which is an absolute detector for all elements in the periodic table providing quantitative accuracies without the need for standards for major elements as well as those at ultratrace levels. Studies are also guided by the necessity to avoid excessive instrumentation costs.

123. ANALYTICAL SPECTROSCOPY — 4.7 — 02-02
V. A. Fassel, A. P. D'Silva,
R. N. Kniseley, J. F. McClelland
E. DeKalb

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 analytical techniques.

124.	ANALYTICAL SEPARATIONS AND CHEMICAL ANALYSIS J. S. Fritz	1.9	02-02

A major effort is underway to improve our new method of Ion Chromatography so that complex mixtures of inorganic anions and cations can be separated and analyzed with the same facility that is possible in organic chromatography. Research on ion-exchange resins is designed to provide better resins for chromatography and to give a better understanding of the important scientific problem of resin selectivity. New methods are being developed for the selective concentration of various organic compounds prior to chromatographic analysis. Work is progressing on an improved statistical theory of chromatography which should correct some inadequacies of prevailing theories and provide a better foundation for chromatography.

125.	MASS SPECTROMETRY OF PLASMAS R. S. Houk	1.5	02-02

The general objective of this research is to develop, evaluate, and characterize ionization techniques with potential value for analytical mass spectrometry (MS). Current efforts concentrate on improving techniques for extracting and mass analyzing ions from inductively coupled plasmas (ICPs). The value of this ion source for elemental and isotopic analysis of solutions on a rapid, direct basis is being demonstrated. Various alternate techniques for introducing samples are being studied with the ICP-MS device as an element-selective, isotopically-sensitive detector. These sample introduction methods include electrothermal furnaces or arc discharges for direct vaporization of solids and liquid chromatographic separations for determining elemental speciation via isotopic tracing experiments. Mass spectra of amino acids and other polar, nonvolatile organic compounds can be obtained directly from aqueous solutions provided ICP conditions are properly "cooled". Temperatures, ion and electron densities, and energy transfer processes in ICP are also being modeled and studied experimentally by mass spectrometric measurements.

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

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 $1,300,000

127. SEPARATION SCIENCE RELATED TO NUCLEAR AND HYDROMETALLURGICAL TECHNOLOGY — 7.7 — 02-02
E. P. Horwitz, P. R. Danesi, H. Diamond, D. Kalina, L. Kaplan, P. G. Rickert, G.W. Mason

This program has as its objectives the development of new organic extractants for the separation of metal ions and the study of the underlying principles involved in the transfer of metal ions from an aqueous to an organic environment. Knowledge gained from these basic studies 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 from low grade domestic sources. Major areas of investigation are: (1) The synthesis and characterization of new extractants for metal ions. This involves equilibrium studies, rate and mechanism studies of interfacial mass transfer, and elucidation of solution structures of metal extractant complexes. (2) The basic physical chemistry of supported liquid membranes. Systems are studied with respect to the hydrodynamic, diffusional, and equilibrium parameters which influence the permeability rates of metal ions. Major subdivisions are modeling of flat sheet and hollow fiber systems, multielement separations, and development of energy-efficient recovery systems for metal ions.

128. STUDY OF ATMOSPHERIC TRACE GASES BY MASS SPECTROMETRY — 1.3 — 02-02
C. Stevens

The carbon isotopic composition of atmospheric methane and its natural and anthropogenic sources is being measured to establish the relative distribution of these sources. In addition we are collaborating with Dr. R. Rasmussen of the Oregon Graduate Center in analyzing the isotopic composition of methane in old air samples collected in both hemispheres since 1978. Changes in the composition reflect changes in the fluxes of enriched or depleted ^{13}C-methane. The purpose of these measurements is to provide clues for causes of an increasing concentration of atmospheric methane; whether it is produced by increasing source fluxes or a decreasing rate of removal from the atmosphere. The results of this study bear on the extent of the methane contribution to the so-called "greenhouse effect" and its effect on future climate changes.

129. SEPARATIONS OF COAL MACERALS AND OTHER FOSSIL FUELS — 2.0 — 02-02
R. E. Winans, G. R. Dyrkacz, C. A. A. Bloomquist

The major objectives of this program are to separate and characterize coal macerals and to develop new separation techniques to achieve this end. A major problem in coal science is the complexity of the substance. However, we have made an important step in reducing this problem by separating coals into their maceral constituents by density gradient centrifugation. Significant differences in chemical structure and reactivity have been discovered among the various maceral groups and also within maceral groups. These findings are important in that they provide insight into the behavior of macerals in coal processes. Surface properties of coal macerals are being studied in a search for new and more efficient methods of separation and identification.

Separations and Analysis

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $215,000

130. APPLICATIONS OF NUCLEAR METHODS TO ANALYSIS
G. Harbottle, E. V. Sayre,
R. W. Stoenner

2.5 02-02

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 which will permit the efficient and effective analysis of 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. 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 marine sediments in an attempt to account for the carbon dioxide inventory of the world.

Separations and Analysis

Department of Applied Sciences
Brookhaven National Laboratory
Upton, New York 11973

Total $280,000

131. SPECIFIC MOLECULAR PROPERTY DETECTORS FOR CHROMATOGRAPHIC ANALYSIS
J. Gaffney, E. Premuzic

1.7 02-02

This research effort is developing novel specific molecular property detectors for use in gas and liquid chromatography. Detection schemes are being devised 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 eluting from a gas chromatograph. 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 (e.g., reduced sulfur compounds, olefins, etc.) as well as photothermal laser spectroscopies are also being investigated as selective and sensitive devices for chromatographic detection.

Department of Applied Sciences, BNL, continued

132. CYCLIC SEPARATIONS PROCESS RESEARCH 1.6 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 radwaste applications. 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.

Physics Department
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Upton, New York 11973

Total $310,000

133. ANALYTICAL TECHNIQUES WITH SYNCHROTRON RADIATION AND ION BEAMS 4.0 02-02
K. W. Jones, H. W. Kraner, B. M. Gordon

This program develops new analytical techniques for elemental analysis using synchrotron radiation from the National Synchrotron Light Source. Equipment is being designed and fabricated to produce a focussed x-ray beam with a spatial resolution around 10 μm. Techniques for precise trace element measurements with minimum detectable limits down to 10^{-9} g/g are being developed concurrently for both bulk and microanalysis. A searching test of the new methods is made by comparison of the results obtained with synchrotron radiation with those obtained by other methods. These tests require the application of the techniques to samples obtained from a variety of energy-related fields. The use of synchrotron radiation for elemental identification is supported by the use of nuclear ion-beam analysis which makes available complementary analytical techniques that are used to corroborate and extend the synchrotron radiation results.

Separations and Analysis

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

Total $65,000

134. SELECTED ELEMENTAL SEPARATION STUDY 1.0 02-02
J.D. Baker and J.S. Jessup

The focus of this research is studying selective elemental extractants which show promise in partitioning valuable metals from aqueous solutions. This year, the extraction behavior of Mo from HNO_3 was studied using dihexyl-N, N-diethylcarbamoylmethylphosphonate. Distribution coefficients were measured as a function of contact time, concentration of Mo, HNO_3, NO_3^- and extractant, and extraction temperature. There appears to be a Mo species change above ~6M HNO_3 which was an extractable moiety. Thus far, our research has been limited to organophosphorus extractants. Recently we extended these studies to include analogous organosulfur compounds.

Separations and Analysis

Exxon Nuclear Idaho Co., Inc.
Idaho National Engineering Laboratory
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Idaho Falls, Idaho 83401

Total $100,000

135. NEGATIVE ION MASS SPECTROMETRY 1.0 02-02
J.E. Delmore

This program is studying two ionization processes for application to negative ion mass spectrometry: negative surface ionization and electron capture. Surface ionization studies are focused on systems where the species of interest is chemisorped on a low work function surface, followed by thermal desorption. To date, ions studied by this method include Cl^-, Br^-, I^-, BO_2^-, CN^-, CNO^- and H^-. Ionization efficiency has been increased by several orders of magnitude using this technique. A unique electron capture ion source using crossed electric/magnetic fields has been theoretically modeled, designed, constructed and tested. This ion source forces electrons into a cycloidal orbit to reduce the kinetic energy to thermal values. The thermalized electrons are readily captured by gas molecules to form negative ions without the high pressure system otherwise required for electron capture mass spectrometry. Refinement of both the experimental model and instrumentation is the major thrust of the program for the next year.

Separations and Analysis

P Division
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Total $170,000

136. THE FORMATION AND PROPERTIES OF COMPLEXES OF HELIUM AND HYDROGEN ISOTOPES 1.5 02-02
R. D. Taylor

The conditions for formation and the properties of a metastable, bound-state complex of ^3He and tritium are under study. T_2 decays with a half life of 12.3 years ultimately producing a pair of ^3He atoms. However, vapor pressure-time measurements show that the ^3He formed in liquid T_2 is retained in the liquid in an amount far exceeding the ordinary solubility. This complex, once formed, is found to be unstable in the gas phase, but it is virtually stable in liquid or in solid tritium. Preliminary data for solid T_2 at 20.0 K suggest that the newly formed ^3He is also bound. The electrical conductivity of solid T_2 containing the complex shows an initial decline of about a factor of three from the conductivity of the liquid. After a few days, this conductivity is about 100 times less. A new cell is under development that will allow pressure buildup measurements of liquid or solid T_2 without the complication of gas phase corrections. Other time-temperature measurements to characterize the complex include magnetic susceptibility and compositional studies of successive portions of gas removed from the cold cell.

Separations and Analysis

Mound Facility
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Miamisburg, Ohio 45342

Total $745,000

137.	ISOTOPE SEPARATION RESEARCH AND DEVELOPMENT W. M. Rutherford, B. E. Jepson, E. D. Michaels, W. R. Wilkes	3.75	02-02

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 processes for practical separations. 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.

138.	MOLECULAR SCIENCE RESEARCH W. L. Taylor, G. T. McConville, R. W. York	4.8	02-02

The objective of this research is to investigate the physical properties of isotopes and their mixtures. To obtain a more complete understanding of gaseous mixtures of hydrogen isotopes, in particular, the mechanisms for isotopic exchange in such mixtures, measurements of the formation of DT in mixtures of D_2+T_2 are being made as a function of pressure, initial T_2 concentration, and temperature. The interaction with D_2 is very complex and the presence of excited state molecules plays a definite part in the reaction. Such information will be useful in design criteria for fuel handling systems in the controlled-thermonuclear power program. Total and differential cross sections are being measured for the permanent gases with supersonic molecular beams. The data are analyzed to yield the fundamental interactions of the colliding species. The temperature range of diffusion measurements in binary gas mixtures is being extended to ~2500°C by means of a Ta/W diffusion cell operating in a vacuum furnace. The thermodynamics of the thermal diffusion process is under study in a "swing separator" instrumented with thermistors for "in situ" and real time analysis of the separation process. Ortho- and para-deuterium are being separated in a cryogenic adsorption column and will be made available to the Stable Isotope Inventory Program.

Separations and Analysis

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Total $1,300,000

139. R&D IN SECONDARY ION MASS SPECTROMETRY

W. H. Christie, R. E. Eby, P. J. Todd

2.1 02-02

Sputtering has become one of the most intensely investigated methods for producing ions for mass spectrometric analysis. This technique, secondary ion mass spectrometry (SIMS), provides a unique capability in areas of surface analysis, diffusion studies, depth profiling, nonvolatile organic materials analysis, as well as providing isotopic and elemental information. The overall objectives of this program are: 1) developing state-of-the-art methods for acquiring, processing, and quantifying SIMS data; 2) applying this new technique to the solution of surface analytical problems in on-going DOE research programs; and 3) the development of instrumentation and methodology to investigate the suitability of SIMS in new analytical areas such as the characterization of non-volatile organic materials. A secondary ion source developed for work with organic species will be used in conjunction with an MS/MS mass spectrometer to investigate the chemistry and physics of secondary ion emission from involatile organic species.

140. MASS SPECTROMETRY R & D FOR ORGANIC ANALYSES

G. L. Glish, P. J. Todd,
E. H. McBay

2.4 02-02

This research is aimed at improving and extending the application of organic mass spectrometry to analytical problems. Included are development of instrumental techniques to advance the study of the chemistry and physics of gas phase ions; the study of the processes involved in desorption ionization; and study of the chemistry and physics of gas phase ions to arrive at a better understanding of the fundamental processes involved. Heavy emphasis is currently placed on the technique of mass spectrometry/mass spectrometry (MS/MS), both as an analytical tool and in developing instrumentation for new applications. Ionization of involatile organic compounds is being investigated, often in conjunction with MS/MS. By selecting an ion of interest and injecting it into a collision cell filled with a suitable gas, fragmentation characteristic of the compound in question is induced. This, the MS/MS technique, offers a powerful tool both for study of gas phase interactions and for unambiguous identification of compounds from isomeric or other mixtures.

141. ADVANCED SPECTROSCOPIC METHODS FOR CHEMICAL ANALYSIS

L. Hulett, J. Dale, T. Rosseel

2.5 02-02

The objective of this research is to explore new physical effects and to utilize facilities unique to ORNL as spectroscopic tools; also, methods involving more conventional principles are upgraded as improvements in the older technologies become available. Monoenergetic positron spectroscopy is being evaluated for its ability to determine surface and bulk properties of materials. X-ray fluorescence spectra, generated in heavy ion bombardment experiments, have been found to be sensitive to chemical properties of metals and alloys. Development of improved techniques for such problems as determining specimen thicknesses, sizes, and composition, using the transmission electron microscope, will be initiated. X-ray photoelectron spectroscopy will be combined with scanning electron microscopy. Fast turnaround methods for asbestos assay, using x-ray diffraction, will be investigated. Collaboration involves the ORNL Physics, Chemical Technology, and Metals and Ceramics Division.

142. RESEARCH DEVELOPMENT & DEMONSTRATION OF ADVANCED CHEMICAL MEASUREMENT TECHNIQUES 3.6 02-02

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

Advanced technology from a variety of disciplines is being brought together to develop unique analytical measurement systems. These systems have a generic application to analytical problems in research, industry, and energy technology. The major area of study is spectroscopy. Fourier transform microwave spectroscopy is a new, high resolution technique that has broad application potential. A technique that will allow the rapid qualitation and quantitation of complex mixtures, optoacoustic spectroscopy, is being applied to matrix isolated materials. A novel piezoelectric detector is under development for this work. The application of fiber-optic waveguides to analytical chemistry is also being studied. This work is concerned with spectral resolution in both the time and space domains. Ongoing studies of laser excited optogalvanic spectroscopy indicate several practical advantages with this method. Time-resolved laser-excited fluorescence, delayed lasing, and laser ablation for solid sampling are also under investigation. A project to examine the analytical utility of molecular beams in spectroscopy has been initiated.

143. MASS SPECTROMETRIC RESEARCH AND DEVELOPMENT FOR INORGANIC ANALYSES 2.6 02-02

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

The aim of this research is to improve the analytical precision and accuracy of isotope ratio measurements by mass spectrometry. Studies have been performed to improve the precision of conventional thermal ionization measurements by using an internal standard, or "double spike" method for uranium and plutonium analyses. Successful implementation has increased the measurement precision by a factor of 3-5, to below 0.1% RSD for uranium isotopes. The shortage of high purity spike material such as ^{236}U and ^{244}Pu is the only limitation on widespread use of this technique. Laser-induced resonance ionization techniques have been studied as a way to improve the accuracy of isotopic analyses for elements with overlapping isotopes. Useful information has been obtained with the rare-earth elements Nd, Sm, and Eu, and preliminary results for the system U:Pu:Am are very encouraging. An ion optical bench facility has been constructed and used to characterize and optimize ion detectors for pulse counting applications.

Separations and Analysis

Chemical Technology Division
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Total $2,000,000

144. CHEMICAL SEPARATIONS FOR LOW GRADE SOURCES — 3.9 — 02-02
R. M. Canon, S. D. Clinton, D. J. Pruett

Fundamental investigations are carried out on chemical separations important to the recovery of metal values from low grade domestic sources, including waste streams. These include the study of mechanisms of ion exchange, crystallization and solvent extraction systems, as well as extraction of metals from the source materials. Recent investigations have concentrated on separations and extractions utilizing chloride chemistry in both aqueous and nonaqueous (aprotic) systems. Studies in aqueous systems include multicomponent metal solubility determinations at various hydrogen chloride activities and the use of HCl gas sparging for crystallization from multicomponent systems. The high chloride activities possible in aprotic solvents make these systems attractive as extractants and as separation tools. Tests have concentrated on the determination of phase diagrams for selected ternary systems of solvent-metal chloride-water.

145. CHEMICAL SEPARATIONS BY COMPLEXATION PHENOMENA — 5.0 — 02-02
C. F. Coleman, W. J. McDowell

Basic scientific understanding of methods for separating mixed elements, compounds, or aggregate materials is being obtained by systematic and fundamental studies of equilibria and mechanisms and of the properties of the components in selected separations systems. The present emphasis is on solvent extraction and ion exchange systems, which are well defined and of wide-spread concern. A major aim is understanding of the relationship between reagent structure and selectivity for particular ions or molecules, so that agents can be designed for improved selectivity, kinetics, and phase behavior. Multidentate extractants, including chelating and macrocyclic compounds, are emphasized because their known complex-forming behavior gives basis for designing specificity into reagents. Detailed studies include: the effects on a range of functional groups when they are attached to carrier molecules or resin skeletons; synergistic combinations of different functions; and elucidation of the structures of adducts of metals with ligands that are known to be selective.

146. CHEMICAL SEPARATIONS FOR TRITIUM — 1.8 — 02-02
P. W. Fisher, S. D. Clinton

This program seeks to understand the fundamental physical and chemical aspects of tritium separation ultimately useful for fusion and fission energy systems. The major current efforts include the separation of tritium from molten lithium, separation of tritium from solid materials, and measurement of equilibrium and transport properties for tritium in solid materials. In earlier phases of this program it was found that sorption of tritium from molten lithium could be achieved through use of yttrium sorbers. These materials are able to reduce the tritium level to below 1 ppm. Fundamental physical properties, like diffusivities and solubilities, are obtained for yttrium-containing materials through a combination of experimentation and mathematical modeling. New classes of yttrium-bearing materials are being analyzed and tested to evaluate these findings.

147. CHEMISTRY OF ACTINIDES AND FISSION PRODUCTS 3.1 02-02
L. M. Toth, D. J. Pruett

The chemistry of actinides and of fission products are investigated with emphasis on the properties that affect separation and partitioning in the nuclear fuel cycle. The broad scope of subjects includes photochemical studies, the structures and properties of polymer materials, solvent extraction and co-extractions, and the induction times and precipitation in pseudo stable process and waste streams. Recent studies have concentrated on the solvent extraction of heptavalent technetium and rhenium in nitric acid systems with and without uranium, and on the photochemical reduction of heptavalent technetium to the V and IV states in nitric and hydrochloric acids. New research will include the photochemistry of low temperature uranium and plutonium frozen solutions or salts, and the catalytic effects of Pu(IV) on actinide redox reactions.

148. CHEMICAL AND PHYSICAL PRINCIPLES IN MULTIPHASE SEPARATIONS 5.3 02-02
R. M. Wham, C. H. Byers,
J. S. Watson

Fundamental chemical engineering investigations include new concepts and basic understanding of multiphase separation methods. Fluidized and expanded beds are stabilized by the imposition of an electric field, thus exhibiting the desirable sorption characteristics of fixed beds, while the pressure drop is approximately half the fixed bed. The applicability of this principle to a novel method for moving bed sorption is under study. Mass transfer enhancement in dispersed-phase systems by forcing the oscillation of small droplets in a continuous medium is being investigated. Preliminary results show that droplet motion can be forced by an oscillating electric field. A study to investigate separation phenomena associated with the distribution of a solute between a liquid and solidified (frozen) solvent has been initiated. Preliminary results indicate that a chromatographic separation of selected solutes is possible.

Separations and Analysis

Chemistry Division
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Oak Ridge, Tennessee 37830

Total $330,000

149. FUNDAMENTALS OF SEPARATIONS CHEMISTRY — 2.1 — 02-02
J. H. Burns, C. F. Baes, Jr.

The purpose of this research is to obtain basic information about solvent-extraction systems that may lead to improved processes for recovery of strategic materials for national energy needs. The approach is to investigate known successful processes with the aim of understanding on a molecular level the mechanism by which they operate and to determine which variables of reactivity and structure are important to their success. Typical systems for the extraction of uranium by organophosphorus ligands are being analyzed by X-ray diffraction of solids and liquids, and the structural information obtained is being used to develop structural criteria for solvent extraction which will have a general applicability. These criteria are being used in the design of more effective extraction reagents for uranium and could provide a guide for the development of new techniques for the separation of other metals.

150. MOLTEN SALT PROCESSES FOR HIGH LEVEL RADIOACTIVE WASTE — 1.1 — 02-02
F. J. Smith

The basic chemistry that relates to high-temperature non-aqueous methods for extracting useful products from spent nuclear fuel is being developed. A major accomplishment of this program is the demonstration of the chemical feasibility of isolating significant quantities of non-radioactive palladium and rhodium as by-products from conventional processing of LWR or LMFBR fuel. Separation processes which utilize liquid metal and molten salt systems are chosen because of their inherent radiation and proliferation resistance. Partitioning of palladium, rhodium, and ruthenium between liquid magnesium and molten uranium-iron eutectic at 750°C provides excellent separations (separation factors greater than 10^6) and forms the basis for the recovery process. Currently being determined is the distribution behavior of palladium, rhodium and ruthenium bromides between the two immiscible liquid phases in the $AlBr_3$-KBr system. Other studies involve molten alkali-metal cyanide/liquid metal (Zn, Bi, Sn) systems.

Biology and Chemistry Department
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Richland, Washington 99352

Total $70,000

151. FUNDAMENTAL PHASE PARTITIONING IN SUPERCRITICAL FLUID CHROMATOGRAPHY — 0.6 — 02-02
R. D. Smith, B. W. Wright,
H. R. Udseth

The goal of this program is a fundamental understanding of the kinetic and thermodynamic constraints upon partitioning of a solute between a supercritical fluid and a supported phase. The program involves investigation of fluid phase solubilities and phase partitioning kinetics relevant to supercritical fluid chromatography and extraction phenomena. Phase partitioning is being studied using direct fluid injection-mass spectrometry and various optical techniques. The program is directed at gaining an understanding of polar supercritical fluids and solute systems and the kinetic and thermodynamic limitations upon separations in supercritical media. These systems include supercritical ammonia, sulfur dioxide, and mixed fluid systems with solutes covering a wide range of polarity. Results of these studies will be compared with both theoretical methods for prediction of fluid phase solubilities and actual chromatographic separations for model systems.

Separations and Analysis

Chemical Technology Department
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Richland, Washington 99352

Total $80,000

152. PYROCHEMICAL SEPARATIONS — 1.1 — 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 & treatment of nuclear wastes. Pyrochemical processes remove the complication of the water molecule which largely determines conventional chemical behavior. Studies using molten alkali metal nitrate systems & glass slag reductions have been emphasized. Molten alkali metal nitrates are both an oxidizing and a complexing media. Distribution of actinides and fission products between the molten nitrates and the solid phases present have been determined for uranium-plutonium oxide fuels. Thorium-uranium oxide fuels were also studied. Recovery of noble metals, including silver, from a variety of source metals, including simulated nuclear wastes and various inorganic substrates or matrices, has been demonstrated using a glass slag reduction technique. Distribution of the noble metals between the source material, the molten flux, and the molten metal phase has been studied and the overall efficiency of recovery determined.

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Total $700,000

153. LASER-BASED ANALYTICAL TECHNIQUES 1.4 02-02
B. A. Bushaw, J. H. Kaye and
R. A. Warner

The objective of this program is to develop and evaluate ultrasensitive and highly selective laser-based analytical techniques. Current experimental work involves evaluating the potential of the photon burst technique for analytical applications. In this method, an atomic beam orthogonally intersects a CW dye laser beam which is tuned to the proper frequency to induce resonant absorption and fluorescence. As each individual atom passes through the laser beam a sudden burst of photons is emitted in a very short time interval. An innovative detection method based on the distribution of time intervals between detected photons allows the density of atoms of individual isotopes in the atomic beam to be determined, independent of minor fluctuations in the laser power and independent of whether or not the laser is exactly tuned to the resonance frequency. To date this method has been applied to measurements of sodium and rubidium isotopes. It is planned to extend the technique to measurement of isotopes of other alkali and alkaline earth metals and then to other selected elements. Methods for analysis of real world samples by photon-burst techniques are also being explored.

154. ANALYTICAL MASS SPECTROMETRY RESEARCH 3.3 02-02
R. L. Gordon, D. M. Robertson,
J. M. Kelley and J. J. Stoffels

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 methods for the control of surface work function of ion sources, develops techniques for application of mass spectrometry to real-time analysis, and establishes new ionization techniques. Surface analytical tools are used to establish physical and chemical properties of surface ionization sources and to identify chemical pathways responsible for ion production. The direct-inlet technique for real-time mass spectrometry uses innovations in ion sources, mass separators, and ion detectors. Laser-assisted ionization is being developed for new mass spectrometry ion sources.

Radiological Sciences Department, PNL, continued

155. ULTRASENSITIVE RADIOACTIVITY SPECTROMETRIC ANALYTICAL TECHNIQUES 0.5 02-02
J. H. Kaye

The objective of this program is to develop new and improved ultrasensitive and selective radioactivity spectrometric techniques for analysis of radionuclides. The current study involves an evaluation of time-of-event counting, a method wherein the time at which each counting event occurs is recorded as well as its pulse height. A computer simulation method has been developed which allows a large number of simulated counting experiments to be generated and analyzed in a few minutes' time. A comparison between the real and simulated data was made to verify that no difference was discernable. Advantages of the simulation approach are that a great deal of time is saved and the parameters of each simulation case can be exactly specified. A number of different data analysis methods are being evaluated. With the computer simulation approach, a comparison is being made between the detection limits obtainable with the time-of-event data analysis methods and with conventional, grouped-data counting techniques. Effects due to detector background and detector efficiency are being determined.

156. ANALYTICAL ATOMIC ABSORPTION SPECTROMETRY RESEARCH 1.3 02-02
D. L. Styris and J. H. Kaye

This program elucidates experimentally the mechanisms that control sample vaporization in furnace atomic absorption (FAA) spectrometry. Vaporization models that are developed from these results provide understanding of chemical treatment and furnace effects and thus establish the basis needed to help broaden and improve application of contemporary FAA spectrometric analysis. 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 order to model the vaporization of the Group IIA elements in presence of these furnace materials.

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

Total $100,000

157. LASER BASED ANALYTICAL METHODS 1.0 02-02
A. Owyoung, A.V. Smith, J.P. Hohimer

This research is directed toward the development of new, highly sensitive, species-specific laser-based analytical techniques with capabilities beyond the reach of conventional methods of analysis. To this end our program emphasizes (1) the determination of the utility and limitations of newly developed laser-based techniques (such as multiphoton ionization spectrometry, MPIS) in analytical applications, (2) the integration of such techniques with more conventional methods of anlaysis (such as mass spectrometry) to provide analytical capabilities of increased dimension, and (3) the exploration of entirely new laser-based concepts having potential utility for analytical applications. In the area of laser source development for MPIS we are now able to generate coherent vacuum ultraviolet radiation over the range 105-200 nm. A second-generation laser-ionization mass spectrometer is also being developed. This 1.0 meter time-of-flight instrument will allow the use of laser ionization and a molecular free-expansion jet and will be used to evaluate techniques for improving the sensitivity and selectivity of MPIS.

Chemical Engineering Sciences

Division of Applied Sciences
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total $230,000

158. TURBULENT COMBUSTION 2.5 02-04
F. Robben, R. K. Cheng
and L. Talbot

The effect of fluid mechanical turbulence on combustion is being studied experimentally for premixed fuel/air conditions in two idealized flow configurations: 1) turbulent boundary layer over a strongly heated wall where lean combustion occurs, 2) an unconfined v-shaped turbulent flame. Density and velocity fluctuations and several of their cross correlation parameters are measured using techniques based on laser Rayleigh scattering and laser Doppler velocimetry. These measurements are useful to characterize the features of the flame structures and their effects on the turbulent flow field. The initiation and development of combustion in the heated boundary layer are found to be dominated by the large-scale turbulence structures. Measurements of Reynolds stress in the v-shaped flame have shown that a mean-gradient transport model for production of turbulent kinetic energy is not appropriate for these flames.

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

Total $140,000

159. HIGH-PRESSURE PHASE EQUILIBRIA IN HYDROCARBON-WATER (BRINE) SYSTEMS 2.1 02-04
J. M. Prausnitz

Experimental and molecular-thermodynamic studies are directed toward better understanding of vapor-liquid and liquid-liquid equilibria for systems containing hydrocarbons with water (or brine). Such systems are of interest in the fossil-energy industry. Toward a quantitative description of equilibria in aquifers, an experimental apparatus is used to measure equilibrium compositions in the methane-water system at pressures to 2 kilobars in the region ambient to 350°C. Another apparatus is used to measure liquid-liquid equilibria in binary systems of water and selected hydrocarbons (such as toluene) in the region ambient to 250°C. Experimental data are correlated using semi-empirical molecular models.

Chemical Engineering Sciences

Theoretical Division
Los Alamos National Laboratory
University of California
P. O. Box]663
Los Alamos, New Mexico 87545

Total $70,000

160. THERMOPHYSICAL PROPERTIES OF MIXTURES 0.5 02-04

Jerome J. Erpenbeck

The evaluation of the thermophysical properties of mixtures of particles which interact through the hard sphere potential have been initiated using both the equilibrium techniques of Monte Carlo and molecular dynamics as well as nonequilibrium molecular dynamics. The properties under investigation are both the equations of state and transport properties, including mutual diffusion, shear and bulk viscosity and thermal conduction. These are currently under investigation at a number of densities and for several values of the diameter and mass ratio for binary mixtures. The equation of state is being compared with several approximate analytic theories, while the transport properties are compared with the Enskog theory.

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

Total $95,000

161. FUNDAMENTAL PROCESSES IN SORPTION PUMPING AND TRANSFER OPERATIONS USING DEEP BEDS OF SORBENTS 1.1 02-04
C. H. Byers, J. J. Perona

A fundamental framework for predicting the performance of deep-bed sorption systems is being developed for application to processes involving pumping, transfer, and storage of materials by sorption on deep beds of sorbents. Currently such techniques are utilized in a number of energy production and storage applications. An experimental program is in progress to determine the relative significance of heat and mass transfer, pressure drop, sorption equilibrium, and reaction kinetics. In the current phase, sorption processes at cryogenic temperatures in the molecular flow regime are controlled by mass transfer resistance. The assumptions used in an analytical solution to the problem are under experimental investigation in a recently reworked and expanded experimental system. Simultaneous numerical solutions are under development.

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

Total $220,000

162. ANALYSIS OF REACTING, TURBULENT FLOWS 1.5 02-04
W. Ashurst, P. Barr, B. Sanders

This research consists of the development of an unsteady turbulence computational procedure for application to reacting flows with high Reynolds number and large heat release. The fluid mechanics of turbulent mixing is computed by a discrete vortex transport technique, known as Vortex Dynamics. This procedure is unique in that it relaxes some of the restrictive assumptions which must be employed in most conventional turbulence models. Current research efforts are focusing on the influence of fluid transport length and time scales on flame propagation and scalar transport in turbulent, chemically-reacting systems. Analysis of the unsteady breakup of a round fuel jet has begun. In this study the three-dimensional transport is computed near the fuel nozzle. Statistics of scalar transport and intermittency will be characterized as probability density functions for use in diffusion flame models.

OFFSITE CONTRACTS

Photochemical and Radiation Sciences

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

163.	STUDY OF THE MOTION OF ELECTRONS IN NON POLAR CLASSICAL LIQUIDS G. Ascarelli Department of Physics	$69,708	01-01

In our effort to study the motion of electrons injected in insulating liquids we have measured the Hall mobility of electrons injected in neopentane along the liquid gas coexistence curve between the triple point and the critical point. The time of flight mobility (TOF) has been measured on the same sample over the same range of temperatures and is in good agreement with the results found in the literature. The ratio of these mobilities is 1.8 near the triple point, decreases linearly to 1.4 near 130°C and increases again to nearly 6 at the critical point. Such a temperature dependence cannot be understood as resulting from either a combination of known scattering mechanisms or from trapping by extrinsic impurities. The large increase of the mobility ratio near the critical point suggests the influence of density fluctuations that create localized states. The leading term of the mobility calculation by Basak and Cohen, coupled with the measured value of (dV_0/dn) as well as the room temperature compressibility predicts, without any adjustable parameters, a room temperature mobility that is only 30% higher than the experimental value.

DARTMOUTH COLLEGE
Hanover, New Hampshire 03755

164.	PHOTOEXCITED CHARGE PAIR ESCAPE AND RECOMBINATION Charles L. Braun Department of Chemistry	$81,539 24 mo. FY 83-84	01-01

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is being studied. The recombination of geminate charge pairs formed by the photoionization of solute molecules in low dielectric constant solvents is found to occur in picoseconds. This process is being studied by pump-probe conductivity techniques. Picosecond absorption measurements of the recombination kinetics are planned. The data are being compared with a detailed theory of the diffusive recombination of geminate charge pairs. The second key goal is to understand the mechanism of charge pair escape in electronically excited electron-donor-acceptor (EDA) materials. A number of donor-acceptor geometries are being explored in these solid state studies. The possible role of the lowest-energy, charge transfer (CT) state in the formation of separated charge pairs (current carriers) is of special interest. Steady-state and nanosecond pulse measurements of both photocurrents and fluorescence are being used to test mechanistic ideas.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

165.	STUDIES IN CHEMICAL REACTIVITY Robert W. Carr Department of Chemical Engineering and Materials Science	$70,305	01-01

Kinetics of elementary physical and chemical processes are being investigated by a number of experimental techniques. Flash spectroscopy and flash photolysis with time resolved mass spectrometry are being used to study the kinetics of atomic and free radical reactions in the gas phase. A flash spectroscopic study of the reaction $CF_2Cl + O_2$ has recently been completed. The collisional deactivation of highly vibrationally excited polyatomic molecules is being studied by chemical activation methods, and product analysis by gas chromatography. A photoionization method for direct detection of highly vibrationally excited molecules is being investigated. The variational method of sensitivity analysis recently developed in this laboratory is being applied to large kinetic mechanisms.

BOSTON UNIVERSITY
Boston, MA 02215

166.	INVESTIGATIONS OF THE TRIPLET STATES OF CHLOROPHYLLS Richard H. Clarke Department of Chemistry	$173,305 24 mo. FY 83-84	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.

UNIVERSITY OF COLORADO/BOULDER
Boulder, Colorado 80309

167.	SENSITIZING AND QUENCHING IN THE CONVERSION OF LIGHT ENERGY INTO CHEMICAL ENERGY Stanley J. Cristol Department of Chemistry	$61,800	01-01

Geometric, regiochemical and free-energy constraints for intramolecular excitation and electron transfer in bichromophoric molecules are being investigated. Factors being studied include modification of substituents present on the donor chromophore, which controls the electron-donating power of the first excited species, and the reduction potentials of the acceptor chromophores. Use of systems with rigid structures permits study of the effects of distance and geometry upon the rates of electron transfer (or the likelihood, in the case of short-lived intermediates). Work has begun on study of quantum-mechanical constraints on the electron-transfer process, that is, the question of whether electron transfer involves tunneling (electron jump) or prefers a through-bond mechanism. Substantial progress has been made in these areas.

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

168.	PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS Leon M. Dorfman Department of Chemistry	$75,525	01-01

The broad objective of this research program is to come to an understanding of the rates and mechanisms of chemical reactions induced by ionizing radiation. At the same time, the information generated about the reactive intermediates (free radicals, molecular cations and anions) is of interest in other areas of chemistry as well. Reaction is initiated by a high energy electron pulse of submicrosecond duration, and the reactive intermediates are directly observed by fast optical absorption measurement (time resolution 5 nanoseconds). These observations also provide the optical spectra of the reactive transients. Systems presently under study are: (a) organic molecular cations in solution. These ions, important in radiation-induced reactions, also play a key role in cationic polymerization. (b) Transition metal carbonyl radicals in solution, of which the absorption spectra and reactivities are determined. These free radicals play a role in homogeneous catalysis. Since the reactions are initiated by high energy electrons, the results obtained relate directly to radiation chemistry.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

169.	TIME-RESOLVED LASER STUDIES ON THE ENERGY TRANSFER AND THE CONFIGURATIONAL CHANGES IN BACTERIORHODOPSIN M. A. El-Sayed Department of Chemistry	$92,000	01-01

Bacteriorhodopsin is another photosynthetic system besides chlorophyll. The understanding of the primary photochemical and photophysical process is of current interest. We developed time-resolved resonance Raman techniques in order to record the vibration spectra of different transients formed following the initial photosynthetic absorption process. Questions such as: a. does energy migration take place to specific sites prior to photochemistry; b. does isomerization of retinal take place on the picosecond time scale, and c) when does the Schiff base lose its proton during the photochemical cycle, are among the questions we are attempting to answer. Very recently, we started using time-resolved optical spectroscopy of the protein and the retinal systems to identify the coupling between these two systems which results in the proton pumping required for photosynthesis in bacteriorhodopsin.

STANFORD UNIVERSITY
Stanford, California 94305

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

This program is examining energy transport processes in nontraditional systems using picosecond and other optical techniques and statistical mechanical theoretical methods. There are a wide variety of situations in both natural and man-made systems which cannot be modeled as periodic arrays of molecules. In many systems inherent disorder and characteristic size and shape play key roles in determining energy dynamics. We have developed the first accurate and detailed statistical mechanics theory of energy transport in disordered systems with finite volume. We are using a picosecond transient holographic grating technique and picosecond fluorescence mixing methods with conventional fluorescence and absorption experiments to study energy transport among dye molecules attached to long hydrocarbon chains organized in micelle solution, and to examine energy transport in chromophore containing polymers. These "clustered" chromophore systems permit extremely high local chromophore concentrations and therefore efficient energy transport, without the normal energy quenching associated with conventional concentrated dye solutions.

CLARKSON COLLEGE OF TECHNOLOGY
Potsdam, New York 13676

171.	PHOTOCHEMICAL SOLAR ENERGY CONVERSION IN SURFACTANT VESICLES Janos H. Fendler Department of Chemistry	$67,893	01-01

Utilization of surfactant vesicles for solar energy conversion continues to be the goal of this program. The main thrust of our research has been centered upon the development of polymerized vesicles. The recognized leakage from nonpolymerized vesicles as well as lack of long term stability necessitated this approach. Polymerized vesicles are stable yet remain fluid enough to allow for proton, electron, and hydrogen permeabilities. A number of polymerizable surfactants have been synthetized. Vesicles have been formed by sonication, and characterized by steady state and dynamic laser light scattering. Vesicle polymerization has been affected by steady state irradiation or by means of chemical initiators. Vesicle sizes did not alter appreciably upon polymerization. Research has been initiated for improving the performance of hydrogen generating colloidal catalysts. Attention has been initially focused on obtaining mechanistic insight into colloid formation in the confined space of water-in-oil microemulsions and vesicles. Colloidal platinum has been stabilized in polymerized vesicles. Efforts are underway for investigating vesicle stabilized semiconductors and their use in energy conversion, electron transfer, charge separation, and water splitting.

Photochemical and Radiation Sciences, continued

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

172. KINETICS OF FAST REACTIONS OF EXCITED SPECIES — $66,000 — 01-01
Richard F. Firestone
Department of Chemistry

Goals are identification of mechanisms for growth and decay of excited rare gas atoms and excimers in the presence and absence of foreign quenching agents using pulse radiolysis methods. Identities of excited atomic precursors of bound excimer states are sought by modelling of a multi-stage reversible collisional relaxation mechanism for rovibrationally excited excimer molecules in conformity with temporal behavior of excited atoms and rovibrationally relaxed excimers. Monitoring of excited species is done by emission spectrometry and tunable cw laser spectrophotometry. Kinetic parameters of selected 1s-2p state pairs are to be obtained by cw pumping coupled with absorption measurements at low power densities and at power densities sufficiently great to induce bleaching of the transition.

COLUMBIA UNIVERSITY
New York, New York 10027

173. 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. Fast hydrogen, chlorine, and deuterium atoms are being produced by pulsed excimer laser photolysis of gaseous diatomic molecules. These medium hot atoms cause vibrational excitation of stable molecules during collisions or react chemically to form products inaccessible to thermally cold species. Infrared fluorescence is being used to probe the broad spectral distribution of vibrationally and rotationally hot CO, CO_2, and CH_3F molecules produced in these atom-molecule encounters. An infrared laser diode is also employed to monitor, with a resolution of milliwavenumbers, the precise vibrational and rotational states excited during such collisions. Laser induced visible and U.V. fluorescence methods are being used to identify the species and to measure the distribution of final states formed as a result of chemical reaction.

UNIVERSITY OF TEXAS/AUSTIN
Austin, Texas 78712

174. ORGANIC REDOX PHOTOTRANSFORMATIONS AT CHEMICALLY MODIFIED SURFACES — $120,000, 24 mo., FY 82-83 — 01-01
Marye Anne Fox
Department of Chemistry

Exploratory and mechanistic studies of new chemical transformations of organic molecules at native and chemically modified surfaces represent the goal of this research program. New electrode materials are being prepared by adsorption, covalent attachment, polymerization, and mulling with electroactive or light-sensitive materials, and physical studies of the properties of these materials are being conducted. Both photocatalytic and photosynthetic organic reactions can be initiated by electron exchange induced by visible light excitation of either native chemically modified semiconductor surfaces. Several spectroscopic techniques are being used to evaluate intermediates and surface states: Fourier transform infrared spectroscopy, Resonance Raman spectroscopy, laser-induced flash coulostatic measurements, photochemically induced magnetic resonance, picosecond laser spectroscopy, rotating ring disc electrochemical techniques, and ESCA and Auger spectroscopy. New metal non-oxides and p-type semiconductors are also being investigated and the search for new reactions on these novel materials is continuing.

Photochemical and Radiation Sciences, continued

WASHINGTON UNIVERSITY
Saint Louis, Missouri 63130

175. REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS $86,000 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 reaction pathways influenced by the energy and electronic state of the free atoms and of 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 by pyrolysis and photolysis. In the past year a new silylene rearrangement, a transposition, has been shown to be mediated by alkyl and hydrogen shifts, with a disilene intermediate: $Me_3Si\text{-}\ddot{Si}\text{-}H \rightleftarrows Me_2Si{=}SiMeH \rightleftarrows Me_2HSi\text{-}\ddot{Si}\text{-}Me$. The ratio of transposition to intramolecular C-H insertion by the silylene has been determined as a function of temperature, and the results will permit the determination of the vibrational temperature of these intermediates when produced in recoil reactions. Rate measurements have been initiated via laser flash photolysis of the reactions of a silylene $Me\text{-}\ddot{Si}\text{-}Ph$ in solution.

TEMPLE UNIVERSITY
Philadelphia, Pennsylvania 19122

176. DYNAMIC ASPECTS OF THE DYE-SENSITIZED PHOTOCONDUCTIVITY OF SEMICONDUCTORS $66,579 01-01
Antonio M. P. Goncalves
Department of Chemistry

The objective of this program is 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 primarily on the use of subnanosecond time-resolved spectroscopic techniques: fluorescence and transient absorption or gain. The fluorescence lifetimes of several dyes adsorbed on semiconductors and insulators at high surface coverage are on the order of 50 picoseconds, as much as 30 times shorter than in solution. The fact that a similar lifetime reduction occurs for each dye both on semiconductor and insulator surfaces suggests that energy transfer quenching is primarily responsible for the short lifetimes. This is confirmed by preliminary fluorescence quantum yield measurements as a function of surface coverage: In the limit of very low surface coverage the quantum yield approaches the solution value on an insulator and a much smaller value on a semiconductor. These experiments indicate that injection occurs in a time on the order of 150 ps.

UNIVERSITY OF FLORIDA
Gainesville, Florida 32611

177. RADIATION CHEMISTRY OF HYDROCARBON AND ALKYL HALIDE SYSTEMS $65,000 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 hydrogen - carbon monoxide mixtures on alumina surfaces include measurement of both hydrocarbon and oxygen-containing products; certain yields are increased by 100 times or more in comparison to the gas phase. The radiolytic oxidation of propane shows many similarities to auto-oxidation in products and reaction pathways; computer modeling of the reaction scheme accounts for the oxygen pressure dependence of product yields. Measurements are being made on the rates of attack of OH radicals on hydrocarbon and halocarbon gases, using the pulse radiolysis method. Comparison of results at high and low water concentration yields data on the rates of OH + radical combination reactions in these systems. Photolysis of methyl iodide - perfluoromethyl iodide mixtures forms several products including methane and perfluoromethane, ethane and perfluoroethane, and several mixed products such as trifluoromethane, difluoroethylene, and trifluoroethane, along with HI and HF.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

178. STUDY OF INTERMEDIATES FROM TRANSITION METAL EXCITED-STATE ELECTRON-TRANSFER REACTIONS — $70,000 — 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 by means of continuous and flash photolysis or from the interaction of substrates with radiation-generated radicals using continuous and pulse radiolysis techniques. Emphasis is currently being placed on the modes of formation and decay of reduced viologens. Viologens form photoactive, luminescent charge-transfer complexes with sacrificial electron donors; the magnitude of complexation, photoreduction, and luminescence is being studied as a function of pH and solution composition. Ion-pairing and complexation have a significant effect on the quantum yield of reduced viologen when the system is photosensitized by tris-(2,2'-bipyridine)ruthenium(II) ion. In acidic solution, reduced viologens undergo hydrogenation in the presence and absence of catalytic platinum. The goal of the research is to understand the fundamental chemistry governing the generation of energy-rich charge-separated species.

OREGON GRADUATE CENTER
Beaverton, Oregon 97006

179. FUNDAMENTAL STUDIES IN CHARGE SEPARATION AT INTERFACES IN RELATION TO WATER PHOTOLYSIS — $90,000 16 mo. FY 83-84 — 01-01
James K. Hurst
Department of Chemistry & Biochemical Sciences

This research is directed at improving our conceptual understanding of the influence of microphase separation and compartmentation upon photostimulated redox processes. Three distinct activities are encompassed by these studies: examination of mechanisms of transmembrane redox across bilayer membranes, development of inorganic two-photon excitation schemes for transmembrane charge separation, and development of reversed micellar assemblies for water photolysis. Redox systems under study which exhibit net electron exchange across bilayers include lecithin-bound amphiphilic 4-alkylpyridinepentaammineruthenium$^{2+/3+}$ ions and dihexadecylphosphate-bound alkylviologen$^{+/2+}$ ions. Studies in two-photon excitation are based upon photoreduction of cupric ion to cuprous π-complexes which are capable of long-range photoinitiated electron transfer to oxidant sites. In reversed micelles, the relationship between O_2 and H_2 yields and the topographic organization of Zn(II) porphyrin sensitizers, viologen charge relays and colloidal RuO_2 and Pt sols is being explored. For all photoinitiated systems, pulsed laser spectrophotometry is being used to probe reaction dynamics.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

180. FORMATION OF FUEL VIA PHOTOCHEMICAL ELECTRON TRANSFER — $192,000 24 mo. FY 83-84 — 01-01
Guilford Jones, II
Department of Chemistry

This research involves investigation of photochemical electron transfer reactions which are of potential utility in photoformation of fuel or useful chemicals. New reagents are under development that would permit the separation of oxidation and reduction components through temporary storage of redox equivalents in stable photoproducts. Novel sulfur heterocycles capable of two-electron oxidation are of particular interest as electron relays for experiments involving bulk solution and electrode-electrolyte interfacial electron transfer. Studies also encompass photoinduced electron transfer reactions of organic dyes which are bound to water soluble polymers. Applications of electron transfer in photochemical decomposition of hydrogen sulfide, hydrogen halide, as well as water, are under consideration.

Photochemical and Radiation Sciences, continued

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

181. THEORETICAL STUDIES OF ELECTRON AND PROTON TRANSFER PROCESSES IN FLUIDS — $40,160 — 01-01
Neil R. Kestner
Department of Chemistry

This research program is designed to study electron and proton transfer processes in fluids, especially those which could be important in energy conversion. General theoretical studies are probing the role of temperature, pressure, and solvent effects on electron transfer rates. Our special attention is directed to such effects for reactions in the "abnormal" or highly exothermic regions. Related work is exploring structure-activity relations which are important in the related proton transfer processes. The general theories are being applied to specific reactions. In this regard we are determining very accurate water-water interactions and other intermolecular potentials, exploring in detail the role of basis set errors. These are being used to obtain accurate interaction energies between electron transfer species such as Fe(II) and Fe(III) in aqueous solutions. Other studies are directed at predicting electron transfer rates in glasses and highly viscous media.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF HOUSTON
Houston, Texas 77004

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

The objective of this research is to probe the molecular mechanistic and structural aspects of charge separation in photoredox reactions in micellar and vesicle systems in order to eventually couple this charge separation to chemical energy storage. Tetramethylbenzidine (TMB) has been photoionized to produce the cation radical in liquid and frozen micellar solutions of anionic, cationic and nonionic surfactants and in liquid and frozen synthetic, anionic and cationic vesicle solutions. The cation is observed by optical absorption, electron spin resonance and electron spin echo spectrometry. Cation-water interactions have been detected by electron spin echo modulation analysis and indicate stronger interactions in micellar compared to vesicular solutions. The photoproduced cation is deduced to be located asymmetrically within both the micellar and vesicular structures. Optical spectra of TMB in micellar and vesicular solutions indicate stronger hydrogen bonding interactions to TMB in the micellar solutions. Specifically deuterated surfactant molecules are being developed to better locate the photoproduced cations within these systems.

THE UNIVERSITY OF ALABAMA
Tuscaloosa, Alabama 35486

183. ELDOR INVESTIGATIONS OF RADIATION PROCESSES — $62,711 — 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, electron transport, 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 sugar, polyalcohol, carboxylic acid, and acetamide crystals are being studied to determine the effect of hydrogen bonding on radical stability and reaction mechanisms as a function of temperature in crystals containing (a) varying crystallographic forms, (b) rotational disorder, and (c) impurities. Preexisting electron traps, first observed by this research, are being studied in crystals of rhamnose and trehalose, radical intermediates have been identified in irradiated β-carotene and halogenated acetamide anions have been detected.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

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

The Office of Standard Reference Data of the National Bureau of Standards administers a collaborative interagency program for the preparation of compilations of physical and chemical reference data. Current projects within the scope of the Division of Chemical Sciences fall in the following areas: physical and thermodynamic properties of fluids, solubility, electrolyte properties, atomic data relevant to fusion, and thermodynamics of high-temperature systems. 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. Reviews are in press on high-temperature vaporization of alkali metal oxides, water solubility of polynuclear aromatic compounds, electrochemical equilibria in carbon-oxygen systems, and other topics.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

188.	ELECTRONIC RELAXATION PROCESSES IN POLYATOMIC MOLECULES Edward C. Lim Department of Chemistry	$76,330	01-01

The purpose of this research is to gain fundamental understanding of radiationless transitions in exciplexes and charge-transfer complexes, which are pertinent to photochemical energy conversion. Both the steady-state and time-resolved measurements of fluorescence and triplet formation are employed to study factors which influence various nonradiative decay channels in condensed phase. The results indicate that the dominant nonradiative decay channel of these species at moderately high temperatures (room temperature and above) may be internal conversion to the ground state. They also suggest that there is a propensity rule for singlet→triplet intersystem crossing in charge-transfer complexes. Thus, singlet→triplet intersystem crossing from a charge-transfer singlet state appears to be efficient only when a locally excited triplet state of a component molecule (donor or acceptor) lies below the charge-transfer singlet state, consistent with vanishingly small spin-orbit coupling between charge-transfer states.

BRANDEIS UNIVERSITY
Waltham, Massachusetts 02254

189.	PHOTOCHEMICAL REACTIONS OF COMPLEX MOLECULES IN CONDENSED PHASE Henry Linschitz Department of Chemistry	$90,000	01-01

The main purpose of this program is the identification and evaluation of factors governing the efficiency of primary radical formation in photochemical redox reactions. This is a general problem in photochemical energy conversion since charge-transfer kinetic intermediates may lead either to radical products or dissipative quenching. Reaction rates and quantum yields are measured by laser flash photolysis on redox systems including particularly porphyrins or anthraquinones, with inorganic anions as donors. The sharp increase in yield with anion concentration is attributable to changes in spin-orbit coupling within the primary reaction complex. Studies on covalently-linked porphyrin-quinone systems of known geometrical configuration are in progress to determine effects of donor-acceptor distance and orientation. Other research is concerned with photo-isomerization of dipyrrylmethenes and shifts in proton-transfer equilibria accompanying formation of rotational conformers.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

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

Studies are being conducted on two color laser spectroscopy. The experiments consist of exciting a molecule with one laser and then, with a second laser time-delayed with respect to the first one, inducing either a downward transition or an additional excitation. The downward transition permits the study of highly vibrationally excited states of the ground electronic state (stimulated emission pumping) and the additional excitation permits the investigation of the dynamics properties of electronically excited states. These studies are aimed at understanding the properties of highly excited vibrational and/or electronic states of molecules. Studies are also being conducted using variable angle electron impact spectroscopy to investigate spin forbidden electronic transitions in stable molecules and beams of free radicals. These transitions are difficult to induce by other means and the states produced play important roles in photochemistry, radiation chemistry, electric discharge chemistry and plasma chemistry.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

185.	THE FREE-RADICAL AND ION CHEMISTRY OF VOLATILE SILANES, GERMANES AND PHOSPHINES F. W. Lampe Department of Chemistry	$127,270	01-01

This research program consists of experimental studies of the chemical reactions initiated by the irradiation of gaseous silanes, germanes and phosphines with ionizing radiation, infrared laser radiation and vacuum-ultraviolet light. From the experimental studies fundamental reaction mechanisms relative to this new and unexplored chemistry are developed. In particular, the knowledge and understanding developed enables us to attempt useful exploitations of photochemical and radiation chemical techniques for the synthesis of amorphous solids of silicon, germanium, phosphine and mixtures thereof. Presently under study is the infrared laser photochemistry of SiH_4-HCl and SiH_4-PH_3 mixtures, CH_3SiH_3, the vacuum-ultraviolet photochemistry of GeH_4 and GeH_4-NO mixtures, and the ion chemistry of SiH_4-CH_3Cl, SiH_4-CH_2Cl_2, and GeH_4-C_2H_4 mixtures.

BROWN UNIVERSITY
Providence, Rhode Island 02912

186.	A UNIFIED APPROACH TO CHARACTERIZATION OF COLLISIONS BETWEEN REACTIVE RADICAL PAIRS IN SOLUTION Ronald G. Lawler Department of Chemistry	$60,000	01-01

A program is underway to systematically characterize the reactive and unreactive encounters between simple organic free radicals in aqueous and organic solvents. Three general techniques are being employed: (A) kinetics of bimolecular radical decay as measured by EPR, (B) measurement of bimolecular contributions, especially Heisenberg spin exchange, to electron relaxation times, and (C) determination of enhancement factors for chemically induced magnetic polarization (CIDNP and CIDEP). Radicals are generated at present primarily by pulse electron radiolysis of aqueous solutions of simple organic acids and alcohols using facilities at Argonne National Laboratory. Studies are being extended to organic solvents using peroxides as radical precursors and employing NMR and EPR detected laser flash photolysis. Theoretical models are being developed both to extract data from rapidly varying magnetic resonance spectra detected by pulsed methods and to interpret (A)-(C) in terms of molecular properties of the radicals and the medium in which they react.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

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

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) A study of the dependence on scavenger concentration of the efficiency of quenching geminate-ion recombination fluorescence of saturated hydrocarbon liquids in order to characterize the distribution function of electron-positive ion separation distances. (b) A study of the dependence on photon energy of the probability of photoionization and of the average range of the electron ejected from aromatic solutes in non-polar fluids via comparison with theory of the effect of an electric field to reduce the geminate-ion recombination fluorescence. (c) A study of the effect of perfluorocarbons to alter the distribution function of electron-positive ion separation distances by interaction with epithermal electrons as manifested by an altered electric field dependence of photocurrent.

DREXEL UNIVERSITY
Philadelphia, Pennsylvania 19104

191. A STUDY OF PHOTOSENSITIZED $55,000 01-01
REDOX REACTIONS IN MICROEMULSIONS
Raymond A. Mackay
Department of Chemistry

The objective of this research program is to explore the utility of microemulsions as media for solar energy conversion systems. An evaluation of the effect of sensitizer and reductant location in the microdroplet is being made by measuring the quantum yield of the photoreduction of methyl red by either ascorbate or hydrazobenzene in the presence of various surfactant porphyrin sensitizers. The mechanism of the enhancement, with respect to water, of the power output of a surfactant thionine-iron (II) thin layer photogalvanic cell employing an anionic microemulsion as the solvent is being investigated by means of flash photolysis and conventional spectroscopy. The use of auxiliary sensitizers in such photogalvanic cells is being concurrently examined by means of both steady-state irradiation experiments and energy transfer studies. The latter are being carried out in the very optically dense solutions required for effective cell operation.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

192. ENERGETICS OF THE FORMATION AND REACTIONS $90,000 01-01
OF GASEOUS IONS
G. G. Meisels
Department of Chemistry

Two areas are addressed. One uses threshold photoelectron-coincident photoion mass spectrometry to study ions whose internal energies are known within 0.025 meV. The energetics of the formation, isomerization and fragmentation of ions are measured. Nitromethane and nitrobenzene ions have activation barriers and rearrange before fragmentation. Modifications to allow study of collision processes are underway. The other area correlates ion residence times with the point of ionization by impact of 100 to 600 eV electrons. Linear ionization rates are highest at the point of entry and decrease smoothly with penetration. Ranges are derived; they are near the higher limits calculated by theoretical models, suggesting that the measured quantity lies between the real range and the electron path length.

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

193. ENERGY CONVERSION PROCESSES BASED ON MOLECULAR EXCITED STATES — $98,000 — 01-01
Thomas J. Meyer
Department of Chemistry

The research effort is based on the study and exploitation of excited states of transition metal complexes. A particularly important goal is the design and characterization of new classes of photosensitizers and their application to solar energy related problems. In technical detail the work involves the measurement of the photochemical and photophysical properties of excited states, the application of theory to such processes, synthesis of new types of potential photosensitizers, the preparations and properties of metallopolymers containing metal complex chromophores, the study of electron and energy transfer processes of the photosensitizers in solutions and polymeric films, and possible applications of these materials in photochemical and photoelectrochemical energy conversion processes.

NATIONAL BUREAU OF STANDARDS
Washington, DC 20234

194. PULSE RADIOLYTIC STUDIES OF INTER- AND INTRAMOLECULAR ELECTRON TRANSFER PROCESSES — $125,000 — 01-01
P. Neta, S.G. Lias, M. Mautner
Center for Chemical Physics

Studies of both intermolecular and intramolecular electron transfer processes are conducted using pulsed electron sources to generate the reactive intermediates, and time resolved absorption spectrophotometry to follow the kinetics of the ensuing reactions. Quantitative results are obtained detailing the effects on the rates of intramolecular electron transfer of the charge distribution within the molecule, electron affinities of substituents, steric effects, and other structural parameters. Intramolecular electron transfer reactions within metalloporphyrins are also studied because of the importance of these molecules in photosynthesis and because they allow a detailed analysis of the effect of driving force and other parameters on the rates of these processes. The mechanism and thermodynamics of intermolecular electron transfer reactions are studied using measurements of rate and equilibrium constants as a function of temperature to obtain quantitative information about activation energies, enthalpy and entropy changes associated with these processes. Comparison of values of liquid and gas phase systems will permit a more quantitative understanding of solvation effects in electron transfer processes.

CLEMSON UNIVERSITY
Clemson, South Carolina 29631

195. 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

The current research effort concentrates on coupling highly absorbing metal centers to potentially photoactive metal centers (e.g., metal dihydrides) by covalent bonding through bridging ligands. This is done in order to use low energy light to drive useful chemical reactions by intramolecular energy transfer processes. Major emphasis has been on bridging ligands that will chelate both metal centers, and form short, highly-conjugated links between the metal centers. One of these bridges, 2,2'-bipyrimidine (bpym) has been used to link a series of metal centers together to form a metallopolymer with the formula $[Ru(bpym)Cl_2]x(bpym)$, which is black in color and has two potential derivative sites on each metal center.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588-0304

196. HIGH ENERGY HALOGEN REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS $65,000 01-01
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 involving 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. The stereochemistry of exothermic halogen atom homolytic bimolecular substitution (S_H2) at the chiral centers of chiral 2-halopropionyl halides is currently studied. 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

197. SOLAR ENERGY CONVERSION IN HOMOGENEOUS SOLUTION $60,427 01-01
Robert M. Richman
Department of Chemistry

The goal of this project is to study the photochemistry of compounds that are likely to photodisproportionate. This mechanism has the potential for doing useful oxidations and reductions without the need for a non-dissociative long-lived charge transfer excited state. Irradiation of μ-oxo-bis((tetraphenylporphinato)-iron(III)) at $\lambda < 440$ nm yields the ferryl ion, FeOTPP. Irradiation with sunlight of a cyclohexene solution results in catalytic oxidation to cyclohexene-2-one with several thousand turnovers. Inclusion of thallium (III) benzoate may yield the epoxide. Flash photolysis allows direct observation of the transient FeOTPP. Analogous photochemistry is observed with $(FeTPP)_2N$ and $(FeTPP)_2C$. Use of charged porphyrins allows study in aqueous solution and may increase quantum yield by lowering back reaction rates. Irradiation in the presence of CoTPP may yield the novel mixed-metal FeTPP-O-CoTPP. Irradiation of $[Ru(NH_3)_5]_2O^{4+}$ results in substitution followed by reduction.

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

198. NUCLEAR METHODS IN CHEMICAL KINETICS $48,000 01-01
John W. Root
Department of Chemistry

This research program is designed to probe the chemical reactions of atomic fluorine. These reactions are initiated by recoiling radioactive fluorine-18 atoms produced using cyclotron induced nuclear reactions. The measured data include the distributions and the relative rates of formation of the labeled 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 fluorocarbons, these reactions probe center-of-mass collision energies in the range from ca. 2 to more than 25 eV. In the presence of excess inert moderator, these techniques also allow kinetic measurements to be performed for the reactions of thermal fluorine-18 atoms. Studies of this type are in progress with simple organic reagents.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

199. RESEARCH IN CHEMICAL KINETICS $170,000 01-01
F. S. Rowland
Department of Chemistry

This research program is directed toward the understanding of the rates and mechanisms of chemical reactions, including some of interest to atmospheric chemistry. The reactions of thermalized ^{18}F and ^{38}Cl atoms with gaseous $(CH_2=CHCH_2)M$ compounds are being studied for M=Sn, Ge, Si, C to determine the extent of restricted intramolecular energy flow ("non-RRKM") in such systems. Reactions of halogen atoms with haloolefins (X + $CH_2=CHY$; X=F,Cl; Y=F,Cl,Br) are furnishing rate information about radical lifetimes, and mechanistic information such as selectivity and isomerization. The temperature dependence of ^{38}Cl reactions with olefins is being studied over the 240-360 K temperature range. The mechanism of the direct gas-phase photolysis of $^{14}CS_2$ is being investigated with and without O_2 present. The rates and mechanisms of hydrolysis in aqueous solution are being measured for gases occurring in the atmosphere, including OCS, CH_3I and CH_3Br. The gas phase photolyses of PH_3 and P_2H_4 and the co-photolysis of PH_3 and NH_3 are being investigated. The possibilit of hot Cl abstraction by energetic ^{38}Cl atoms is being tested.

WORCESTER POLYTECHNIC INSTITUTE
Worcester, Massachusetts 01609

200. THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS $43,000 01-01
Alfred A Scala
Department of Chemistry

The objective of these studies is to gain a better understanding of how complex organic molecules react when they absorb the high energies characteristic of γ-radiolyses and vacuum ultraviolet photolyses. Emphasis is being placed on the reactions of heterocyclic compounds containing oxygen, nitrogen or sulfur. Since ions as well as neutrals are produced in these systems the rate constants for related ion-molecule reactions are being measured by photoionization mass spectrometry. This work has been extended to include chemical ionization at pressures in the vicinity of one atmosphere. This is an effort to produce even-electron ions of the type important in solution phase organic chemistry in order to facilitate evaluation of the role of the solvent in organic chemistry.

CHARLES F. KETTERING RESEARCH LABORATORY
Yellow Springs, Ohio 45387

201. PARTICULATE MODELS OF PHOTOSYNTHESIS $65,000 01-01
Gilbert R. Seely

The program consists of the investigation of photophysical and photochemical properties of chlorophyll, absorbed together with other amphiphilic molecules on 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, energy transfer among chlorophyll species, and photochemistry. With regard to the last, the behavior of particles with chlorophyll and oxidizing amphiphilic ligands is receiving particular attention.

UNIVERSITY OF PUERTO RICO/MAYAGUEZ
Mayaguez, Puerto Rico 00708

202. PHOTOELECTROCHEMISTRY OF NEW PHENOTHIAZINE DYE DERIVATIVES
Fernando A. Souto
Department of Chemistry
$125,000
24 mo.
FY 83-84
01-01

This program has been designed to study the potential of amphiphilic derivatives of thionine for a better understanding of photochemical energy conversion with aqueous systems in solution. The main objective is to investigate the kinetics associated with their photoreduction with ferrous ions. The work carried out thus far has consisted of the synthesis and the preliminary characterization of derivatives that are disulfonated, dimethyldisulfonated, trisulfonated, and with other groups. The uv-vis spectra of these dyes are similar to that of thionine (599 nm) with maxima in the range 570-625 nm, but with the exception that there is no evidence for wasteful self association at conc. c.a. 10^{-3}M. The solubility of the disulfonated thionines is about 10^{-2}M in 0.1N H_2SO_4 (thionine c.a. 5.10^{-5}M). The extinction and diffusion coefficients change with the nature and position of substituents on the thiazine nucleus, but no clear effects can yet be realized. The rate constants for the back reaction between the leucothiazines and ferric ion are all faster than the value of thionine, with one exception which merits further characterization. Work is in progress to further test these compounds in the presence of micellar assemblies.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

203. DYNAMICS AND MECHANISMS OF CATALYTIC PROCESSES AND HOT CHEMISTRY
Leonard D. Spicer
Department of Chemistry
$100,000
01-01

This research is designed to investigate reaction kinetics and mechanisms, collision dynamics, and energy transfer in thermal, photochemical, and hot reactions. Electronic excitation with and without photochemical rearrangement of active catalyst species is used to study the critical transition state for processes involving Wilkinson's catalyst and to generate new metal centered catalytic molecules. The kinetics of the photochemical processes are being modeled and include the formation of a new isomerization catalyst having a half life of several minutes. The active catalytic species is postulated to be a fluxional molecule having adjacent olefin and η^3-allyl ligands. Nuclear recoil chemistry is being used to study hot reaction dynamics. The recoil distribution for chlorine atoms from the $^{35}Cl(n,\gamma)^{36}Cl$ process is being determined from the reported prompt gamma ray spectrum. The cooling characteristics of recoil tritium atoms at high moderation in the presence of reactive hydrocarbons are also being modeled. The new material, ammonium trimethylsilylsulfite, from this laboratory is being tested as a standard for solid state NMR.

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

204. PHOTOELECTROCHEMISTRY WITH CHEMICALLY MODIFIED ELECTRODES
Thomas G. Spiro
Department of Chemistry
$80,300
01-01

The electrochemistry and photoelectrochemistry of metalloporphyrin electrode films is being explored, with a view toward catalyzing useful energy storage reactions, including the splitting of water to H_2O_2. Stable metalloprotoporphyrin films have been prepared via electroinitiated polymerization of the vinyl side-chains, and other porphyrin polymerization schemes are being explored. Cobalt porphyrins are being applied to the catalysis of H_2 production from water, while iron, chromium and manganese porphyrins are being explored in oxidative chemistry, with the eventual aim of catalyzing water oxidation.

MOUNT HOLYOKE COLLEGE
South Hadley, Massachusetts 01075

205.	PHOTOELECTROCHEMISTRY OF ORGANIC DYES Mark T. Spitler Department of Chemistry	$114,000 24 mo. FY 82-83	01-01

The oxidation of organic dyes adsorbed at semiconductor surfaces is being studied through photoelectrochemical techniques to determine the role of electron transfer in the quenching of the excited state of the dye. The utilization of an attenuated total reflection method enables an in situ determination of the quantum efficiency of current producing photoreactions at both metal and semiconductor surfaces. Photooxidation of dyes at ZnO, TiO_2, and $SrTiO_3$ single crystal surfaces is being investigated using dyes that show significant triplet character or tendency to form aggregates. Estimation of the degree of excitation quenching caused by this oxidation is also obtained through concomitant measurements of the fluorescence intensity of the adsorbed dye. The photoassisted oxidation of triphenylmethane dyes at Au and Pt electrodes is also being studied using an internal reflection technique which permits spectral characterization of reaction products.

UNIVERSITY OF ARIZONA/TUCSON
Tucson, Arizona 85721

206.	MECHANISMS OF PHOTOCHEMICAL ENERGY CONVERSION BY CHLOROPHYLL Gordon Tollin Department of Biochemistry	$160,627 24 mo. FY 83-84	01-01

The goals of this project are to elucidate the detailed mechanisms involved in light-induced one-electron transfer reactions involving chlorophyll (and related compounds) and electron donors and acceptors, and to determine the interactions between the elementary steps in these processes and environmental parameters such as viscosity, dielectric constant and homogenous vs. heterogeneous reaction matrices. The intent is 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. Current work involves the use of laser flash photolysis to monitor excited state and radical dynamics in lipid bilayer vesicle systems.

UNIVERSITY OF MASSACHUSETTS AT BOSTON
Boston, Massachusetts 02125

207. INVESTIGATION OF THE STRUCTURE OF PHOTOSYNTHETIC REACTION CENTERS $66,451 01-01
Hans van Willigen
Department of Chemistry

The research program concerns the study of the structure of photosynthetic reaction centers and model systems with the aid of magnetic resonance techniques. Measurements of the electron spin distribution in the photoexcited triplet state of these systems with the aid of Electron Spin Resonance (ESR) and Electron Nuclear Double Resonance (ENDOR) are used to obtain structural information. Research has focused on the ENDOR measurement of hyperfine interactions in the photoexcited triplets of a series of porphyrins. Also, the study has been concerned with the application of ESR and ENDOR in the study of aggregate formation of a number of water-soluble porphyrins. These systems are of interest because of their use as photo catalysts for the water splitting reaction $2 H_2O \rightarrow 2 H_2 + O_2$. Furthermore, they constitute ideal model systems for the investigation of the effects of aggregation on the photophysics and photochemistry of porphyrins.

UNIVERSITY OF ILLINOIS/CHICAGO
Chicago, Illinois 60680

208. EVALUATION OF THE ESE ENVELOPE MODULATION TECHNIQUE FOR STUDIES OF FREE RADICALS $38,000 01-01
Robert I. Walter
Department of Chemistry

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 samples can be prepared and observed. A series of nitroxide radicals which differ in deuterium labelling or in structural constraints on geometry, and three other nitrogen-centered radicals selected for small ^{14}N coupling constants (in the range 2.1 to 7.6 gauss) have been prepared. These radicals are examined in a random glassy matrix by the three-pulse electron spin echo technique; this part of the research is carried out at the Argonne National Laboratory under the supervision of James Norris. The ESEEM results are not consistent with the working hypothesis that small hyperfine coupling constants should appear in the spin echo modulation. Instead, the nuclear quadrupole moment of ^{2}D or ^{14}N dominates the echo modulation, and should be the major source of information about samples studied by this technique.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

209. ENERGY TRANSFORMATIONS IN TRANSITION METAL COMPLEXES — $82,863 — 01-01
Richard J. Watts
Department of Chemistry

The projects in this program are intended to explore basic photochemical and photophysical phenomena in transition metal complexes. Five primary areas of endeavor include: 1) Photochemical and photophysical consequences of metal-carbon bonding to acceptor ligands with extended π-systems; 2) Electronic relaxation phenomena between excited states of metal complexes; 3) Mechanisms of excited state electron transfer reactions; 4) Tuning of electronic excited states by extension of π-conjugation in N-heterocyclic ligand metal complexes; and 5) Photochemistry and photophysics of organometallic sandwich complexes. The primary techniques being applied in these projects include time-resolved emission spectroscopy, laser-induced transient and excited state absorption spectroscopy, and ^1H and ^{13}C nmr spectroscopy. Laser double resonance techniques are presently being developed for the purpose of characterizing electronic relaxation between excited states of metal complexes. Synthesis and characterizations of complexes containing metal-carbon bonds are being carried out in order to facilitate the projects in area 1) above.

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

210. APPLICATIONS OF PHOTOINDUCED ELECTRON TRANSFER AND HYDROGEN ABSTRACTION PROCESSES TO CHEMICAL AND ELECTROCHEMICAL CONVERSION PROCESSES — $76,445 — 01-01
David G. Whitten
Department of Chemistry

This research program involves studies of photochemical redox reactions occurring via electron transfer and hydrogen atom abstraction processes initiated by excitation of chromophores absorbing visible and near ultraviolet light. A part of the project involves direct study of photochemical reactions and external factors which can modify them. In addition, photoelectrochemical processes based on them are being investigated. Our studies of direct photochemical reactions have recently focused on photoredox reactions of certain indigo dyes. It develops that these dyes undergo net photoreduction processes with a variety of electron donors by, in some cases, a multiplicity of mechanisms. Among the most interesting mechanisms are a net hydride ion transfer which occurs via a sequence of electron, proton, and second electron transfer, all within the initially formed encounter complex. We are also investigating the effect of inclusion complex formation on reactivity using various amylose derivatives as selective hosts for a variety of reactive substrates. The photoelectrochemical studies are currently focusing on hydrogen atom abstraction reactions from alcohols occurring with substrates excited by visible light.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

211. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY — $21,019 24 mo. FY 82-83 — 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; and the role of neutralization processes in radical production in radiolyzed hydrocarbons.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37996

212.	STUDIES OF RADIATION-PRODUCED RADICALS AND RADICAL IONS T. Ffrancon Williams Department of Chemistry	$92,000	01-01

The basic objective of this program is to characterize important 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 typical 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, ethers, and organometals of Group IVB alkyls in fluorocarbon matrices. Electron spin resonance (ESR) spectroscopy is used to identify these paramagnetic species. Measurements of hyperfine coupling constants, including those of ^{13}C-labeled radicals, provide information about geometrical structure and spin density distribution. The chemical rearrangement of positive ions 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 catalysis and solar energy conversion.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

213.	PHOTOCHEMICAL ENERGY STORAGE: STUDIES OF INORGANIC PHOTOASSISTANCE AGENTS Mark S. Wrighton Department of Chemistry	$245,000	01-01

Light-driven, energy-storing chemical reactions are the object of study in this research program. Emphasis is on the use of semiconductor electrodes as the photoassistance agents for redox reactions such as the oxidation and reduction of H_2O. Fundamental studies of the nature of semiconductor/electrolyte interfaces to establish the energetics and kinetics for light-driven redox processes are one aspect of the program. Semiconductor materials under study in this connection include WS_2, InP, GaAs, Si, CdX (X=S, Se, Te), and amorphous hydrogenated Si. Another aspect of the program is chemical derivatization of the semiconductor surface for the purpose of improving durability and kinetics for the desired redox reaction. In the area of electrocatalysis surface modification with metals, oxides, and polymers is being studied. Catalysis of halide oxidation and H_2O reduction have received most attention. Exploratory studies to find unique interactions of redox reagents with semiconductor electrode surfaces, such as I_3^-/I^- with n-WS_2, are in progress. Such unique interactions are likely to lead to high efficiency for energy conversion and specific redox processes.

Chemical Physics

CORNELL UNIVERSITY
Ithaca, New York 14853

214. SHOCK TUBE PYROLYSIS OF AROMATIC HYDROCARBONS -- DETECTION OF SOOT PRECURSORS $52,142 01-02
Simon H. Bauer
Department of Chemistry

The objectives of the shock tube experiments are to determine the fragmentation patterns for structurally related di- and tri-cyclic aromatics, to measure the relative levels of soot produced, and to formulate semi-quantitative mechanisms for these processes. The experiments are performed in a single-pulse shock-tube with a coaxial laser beam absorption diagnostic. Gas chromatographic analyses are made of samples extracted from the downstream end of the shock tube. During the test time attainable with this configuration (700-900 μs) the quenched samples are kinetically limited. The shapes of the He/Ne transmission curves indicate that the attenuation of the beam is not due to loss by scattering from the final product but to absorption by precursor species, the concentrations of which first rise and then decline due to subsequent reactions. This technique presents a possibility for recording their extended absorption spectra.

THE UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

215. TOPICS IN FINITE TIME THERMODYNAMICS $70,000 01-02
R. Stephen Berry
Department of Chemistry and the James Franck Institute

The term "finite time thermodynamics" refers to the extension of traditional thermodynamics to the description of systems and processes whose constraints include finite times or nonzero rates of operation. In particular, the term refers to the determination of the extremal performance and the paths that would yield that performance, when the constraints of finite-time operation must be met. The recent progress of this group has included: the theoretical description of a new type of engine, based on a dissipative process; an analysis of heat engines subject to periodic boundary conditions (as with the diurnal variations of solar systems); the exploration of geometric formulation of thermodynamics based on the metric introduced by Weinhold; a first study of separation processes, involving an analysis of the use of multiple points of heat exchange in distillation columns as a means of minimizing the production of excess entropy, and finally, the extension of the concept of availability (exergy) to processes operating in finite time, and the application of this extended concept to extraction of work from a system not initially in internal equilibrium.

COLUMBIA UNIVERSITY
New York,NY 10027

216. ENERGY PARTITIONING IN ELEMENTARY GAS PHASE REACTIONS $35,000 01-02
Richard Bersohn
Department of Chemistry

The dynamics of the elementary reactions $A + BC \rightarrow AB + C$ and $A + BCD \rightarrow AB + CD$ are being studied by a two laser experiment. One laser generates the reactive atoms A (carbon, hydrogen,fluorine or sulfur) by photodissociation of a suitable parent molecule. The second laser probes the internal state distribution of the products. Reactions studied include: $S(^1D) + OCS$ and $F + RI$ where R=H,CH_3,C_2H_5,i-C_3H_7 and t-C_4H_9. For all R the abstraction product IF was probed and for R = CH_3 and C_2H_5 the iodine atom product of the Walden inversion was also found. Spectroscopic techniques are being developed for studying the time dependence of atomic concentrations,in particular of different atomic sublevels.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

217.	THEORETICAL STUDIES OF COMBUSTION DYNAMICS Joel M. Bowman Department of Chemistry	$59,000	01-02

The objective of this research is to develop and apply approximate but accurate quantum mechanical methods to reactions of interest in gas phase combustion. Such a theory has been developed and applied to the reactions $O(^3P) + H_2$, $O + D_2$ and $O + HD$ using an accurate ab initio potential energy surface. Extension of the theory to treat diatom + diatom reactions has been made and the first application will be to the $OH + H_2$ reaction. A surface will be obtained from new ab initio calculations that are planned by Dr. Thom Dunning. Work is also underway to calculate the vibrational energies and lifetimes of HCO and HOCO using an ab initio potential surfaces calculated by Harding. This work is based on a vibrational self-consistent field plus configuration interaction method developed here. The interaction of radiation with long-lived collision complexes is also being investigated and preliminary calculations indicate that stabilization by stimulated emission may be feasible for small systems using lasers of moderate power.

YALE UNIVERSITY
New Haven, Connecticut 06520

218.	SIMULTANEOUS MULTIPOINT MEASUREMENTS OF DENSITY GRADIENTS AND TEMPERATURE IN A FLAME R. K. Chang (Applied Physics), B. T. Chu and M. B. Long (Mechanical Engineering)	$63,000	01-02

Research is currently under way to develop and apply new optical diagnostic techniques to the characterization of turbulent reacting flows. Spontaneous Raman scattering is being used to map out the fuel gas concentration at 2500 points within a plane intersecting the flow in a single laser pulse (1.8 μsec). For this type of "Ramanography" experiment, a high-energy single-pulse laser system is required. A further requirement of the laser is that the peak power not be so high as to cause breakdown of the gases when the beam is focused. While this type of laser is not readily available commercially, the Diana dye laser available at the Combustion Research Facility (CRF) at Sandia National Laboratories in Livermore, California has the unique characteristics needed for this work. Experiments are therefore being carried out at the CRF and preliminary results demonstrate the feasibility of the technique. The ability of the technique to give the instantaneous fuel gas concentration distribution at many points within a plane is important for studying the interaction of the turbulence with the chemistry in these complex flows.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

219.	UNIMOLECULAR DECAY DYNAMICS F. Fleming Crim Department of Chemistry	$44,524 6 mo.	01-02

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 in conjunction with time resolved spectroscopic detection. Recent experiments determine the product quantum state distributions in the unimolecular decay of hydrogen peroxide (HOOH) and its partially deuterated analogue (HOOD) excited to the fifth overtone ($v = 6$) of the OH stretching vibration. These measurements also provide spectra of overtone vibrations which reveal rotational structure and combination transitions. The product state distributions appear to differ qualitatively for excitation of a combination transition compared to excitation of a pure stretching vibration. Statistical (phase space) calculations describe the essential features of the product state distributions except for the case of excitation of a combination band. This experimental technique is providing uniquely detailed data on the unimolecular reaction dynamics of selectively excited molecules.

SRI INTERNATIONAL
Menlo Park, California 94025

220. COMBUSTION RESEARCH PROGRAM: FLAME STUDIES, LASER DIAGNOSTICS AND CHEMICAL KINETICS $109,000 01-02
David R. Crosley
Molecular Physics Laboratory

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. In the LP/LIF technique, 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 over the range 800-1400 K. Measurements of the rate constant for $OH + C_2H_2$ at 1200 K show an abstraction mechanism, in contrast to the addition channel which dominates at room temperature. In a flow system, the laser spectroscopy of the $A^3\Pi_i - X^3\Sigma^-$ system of NH has been studied, yielding lifetime, quenching, and transition probability information.

WILLIAM MARSH RICE UNIVERSITY
Houston, Texas 77251

221. INFRARED ABSORPTION SPECTROSCOPY WITH COLOR CENTER LASERS $61,000 01-02
Robert F. Curl
Department of Chemistry

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. A magnetic rotation technique for the suppression of source noise combined with the long pathlengths obtainable with a White cell provides a high sensitivity absorption spectroscopy which is selective for free radicals. With this arrangement, the electronic spectrum of C_2H in a discharge through argon over polyacetylene, has been observed and assigned. The Ballik-Ramsay bands of C_2 have also been identified in this system. In the continuation of this work, efforts will focus upon the identification of other radical species present in the discharge over polyacetylene and the search for new radical spectra (CH_2, CH_2OH, HCCN, and N_2H_3). In addition, the development of a new high sensitivity spectroscopic method suitable for non-magnetic molecules using electro-optic tone modulation of the color center laser infrared output will be pursued.

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

222. COMPREHENSIVE MECHANISM FOR THE COMBUSTION CHEMISTRY OF ALCOHOLS: AN EXPERIMENTAL & NUMERICAL STUDY WITH EMPHASIS ON APPLIED SENSITIVITY ANALYSIS $79,117 01-02
Frederick L. Dryer
Dept. of Mech. and Aero. Engineering

With the exception of methanol, alcohols have received little attention with regard to mechanistic description of actual combustion chemistry. The current work addresses the development of a comprehensive detailed kinetic model for the pyrolysis and oxidation of ethanol. Intermediate temperature (ca. 1000 K) turbulent flow reactor data at atmospheric pressure are obtained to provide initial insights as to the phenomenology of these reactions, and these data are combined with higher temperature results (shock tubes, flames) in developing a detailed mechanism. Acetaldehyde appears as a major intermediate in this mechanism, and thus the work also provides a comprehensive pyrolysis and oxidation mechanism for this species. The mechanism development itself as well as the property behavior of the result are studied using the sensitivity analysis techniques developed by Rabitz and co-workers at Princeton.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

223. LASER PHOTOELECTRON SPECTROSCOPY OF IONS $57,000 01-02
G. Barney Ellison
Department of Chemistry

Laser photoelectron spectroscopy has been used to study a number of simple negative ions. Our experiments produ direct, reliable thermodynamic information such as electron affinities, radical and ion heats of formation, and bond dissociation energies. These are crucial data required for an understanding of combustion processes. We have completed careful studies of HNO^-, DNO^-, CH_2CCH^-, CH_2CCD^-, $CD2CCH^-$, CCO^-, $HCCO^-$ and $DCCO^-$. We have finished work on CH_2CN^-, CD_2CN^-, CH_2NC^-, and CH_3CHCN^-. Proposed research centers on polymeric carbon ions (C_n^-), allyl anion ($CH_2{=}CH{-}CH_2^-$), and CO_2^-.

UNIVERSITY OF OREGON
Eugene, Oregon 97403

224. LASER SPECTROSCOPY OF COMBUSTION INTERMEDIATES $28,500 01-02
Paul Engelking
Department of Chemistry

Molecular radicals important to combustion chemistry are being investigated by electronic spectroscopy. Besides providing wavelengths of optical transitions for practical use in the laser probing of flames and combustion environments, this research obtains basic information concerning the structure, the relative energies of electronic states, and the internal dynamics and reactivities of radical species. Current investigation includes a spectroscopic search for the lowest electronic state of CH, analogous to the newly discovered first excited state of CF, and an investigation of the spectroscopy of CH_3N. These species have been implicated in the fixation of nitrogen by flames.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

225. LASER-INDUCED ORGANIC REACTIONS IN THE GROUND ELECTRONIC STATE $54,000 01-02
18 mo.
FY 83-84
William E. Farneth
Department of Chemistry

This project is an investigation of the potential and present utility of high power infrared and visible 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 have been examined. The work attempts to define strategies for using the spatial, temporal or energetic resolution of the laser activation step to influence the rate and selectivity of subsequent chemical reactions. Specific systems investigated include: cyclopropane and oxacyclobutane derivatives with IR excitation, alcohols in the presence of CuO with IR excitation, and *t*-butylhydroperoxide with visible excitation. In the alcohol/CuO chemistry, for example, laser variables and system variables can be used to alter the ratio of dehydration to dehydrogenation from essentially exclusive dehydration in the homogeneous system to predominant dehydrogenation under certain heterogeneous conditions.

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

226. LOW ENERGY ION-MOLECULE REACTIONS AND CHEMIIONIZATION KINETICS — $65,000 — 01-02

James M. Farrar
Department of Chemistry

Molecular beam reactive scattering measurements of proton transfer reactions of the flame cations HCO^+ and H_3O^+ with neutral molecules present in hydrocarbon flames are being carried out to understand the dynamics of ionic processes occurring in flames. Measurements of product angular and kinetic energy distributions yield energy disposal in reactive collisions, inferences concerning preferred collision geometries, and in favorable cases, determination of specific quantum states of nascent reaction products. Proton transfer reactions to the substrates H_2O, CH_3OH, C_2H_5OH, and $(CH_3)_2C{=}O$ have been studied, indicating direct reaction dynamics. Unimolecular decay channels of protonated products are studied and decays involving bond cleavage, 1,3-hydrogen atom shifts, and elimination of molecular hydrogen across the C-O bond have been observed. In the latter case, variation of proton donor modifies the parent ion internal state distribution; such observations are being employed to assess the role of tunneling through the exit channel barrier in the elimination process. Work in progress involves hydride transfer reactions of CH_3^+.

AEROCHEM RESEARCH LABORATORIES, INC.
Princeton, New Jersey 08540

227. EXPERIMENTAL DETERMINATION OF RATE COEFFICIENTS FOR IMPORTANT COMBUSTION/FUEL CONVERSION REACTIONS BY A NOVEL HIGH-TEMPERATURE PHOTOLYSIS TECHNIQUE — $70,673 — 01-02

William Felder

The aim of this project is to measure the temperature-dependent rate coefficients for isolated, elementary reactions important in fossil fuel combustion and pollution processes. The flash photolysis/resonance fluorescence or absorption technique is used for rate coefficient measurements. The temperature range of this technique was extended in this work to permit measurements from room temperature (300 K) to practical combustion temperatures (up to 1800 K). Current work emphasizes reactions of OH radicals produced in the flash photolysis of water. Preliminary results for reaction of OH with benzene and methane yield $k(OH + C_6H_6) = (3.0 \pm 0.8) \times 10^{-11} \exp[-(2.32 \pm 0.30) \times 10^3/T]$ cm^3 $molecule^{-1}$ s^{-1} (840-1370 K) and $k(OH + CH_4) = (5.5 \pm 1.6) \times 10^{-11} \exp[-(2.9 \pm 0.36) \times 10^3/T]$ cm^3 $molecule^{-1}$ s^{-1} (970-1460 K). The first direct rate coefficient measurements on the reaction $H + H_2O \rightarrow OH + H_2$ were made above 1100 K. Our work shows that this reaction can interfere in any kinetic study on OH above ca. 1000 K if H_2O is used as a precursor. We obtain $k(H + H_2O) = (5.2 \pm 4.5) \times 10^{-10} \exp[-(11.2 \pm 1.1) \times 10^3/T]$ cm^3 $molecule^{-1}$ s^{-1} (1160-1390 K). Measurements at higher temperatures for these OH reactions are in progress.

RENSSELAER POLYTECHNIC INSTITUTE
Troy, New York 12181

228. KINETIC MEASUREMENTS ON ELEMENTARY FOSSIL FUEL COMBUSTION REACTIONS OVER WIDE TEMPERATURE RANGES — $80,000 — 01-02

Arthur Fontijn, Department of Chemical and Environmental Engineering

This, recently initiated, research program is aimed at providing kinetic data on important isolated elementary hydrocarbon molecule oxidation reactions. Emphasis is placed on measurements in the 1000-1800 K range, where accurate data are generally not available, but needed for development of improved fossil-fuel utilization methods. The high-temperature photochemistry (HTP) adaptation of the flash-photolysis resonance-fluorescense technique is further developed. Use is made of fast electronics, which allows rapid data taking and short residence times, and of on-line microcomputer data smoothing procedures which minimize the number of flashes required. The first objects for study are reactions between O atoms and C_2 hydrocarbons.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

229. STATE-TO-STATE DYNAMICS OF MOLECULAR ENERGY TRANSFER $75,000 01-02
W.R. Gentry and C.F. Giese
Departments of Chemistry and Physics

A novel pulsed molecular beam instrument has been constructed for the study of state-to-state vibrational and rotational energy transfer in collisions of atoms and molecules. The results are expected to lead to an understanding of molecular energy transfer on a microscopic level, including the dependence of energy transfer processes on the vibrational and translational energies of the colliding molecules. The first experiments measured the kinetic energy dependence of the vibrational excitation cross sections for I_2 + He collisions. Similar measurements have now been performed for I_2 + D_2 and I_2 + Ne collisions, in order to explore the effects of mass and features of the potential energy surface on the excitation dynamics. These experiments are being extended to other systems, including mode-specific excitation of polyatomic molecules.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

230. REACTION MECHANISMS IN COMBUSTION: FORMATION OF SOOT AND POLYCYCLIC AROMATIC HYDROCARBONS $70,000 01-02
William A. Goddard III
Department of Chemistry

We are examining the microscopic mechanisms of the gas phase and heterogeneous processes involved in the formation of soot and of polycyclic aromatic hydrocarbons during combustion. The emphasis this year has been on the development of methods for describing the dynamics of the heterogeneous processes involved in the growth of the soot particle. This has led to the Classical Stochastic Diffusion Theory in which the classical dynamical equations of motion are transformed to a generalized Langevin equation (involving explicitly only those atoms of the surface directly bonded to the adsorbate) which is solved by taking the Markovian limit appropriate to the long time scale for the growth processes. Detailed comparison of these first principles rate predictions with experimental rates for desorption shows excellent agreement.

UNIVERSITY OF ILLINOIS/CHICAGO
Chicago, Illinois 60680

231. KINETICS OF ELEMENTARY ATOM AND RADICAL REACTIONS $66,357 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, using sensitive, real time techniques to eliminate systematic errors. One system being studied is O+H_2, D_2 and HD. Measurements of the O+H_2 rate constant at 470K, using flash photolysis with resonance fluorescence detection of O atoms, show that previous values of the rate constant were 2-4 times too high. Accurate measurements of the rate constants for all three isotopes are being performed at temperatures up to 1000K. The intramolecular branching ratio for O+HD is being determined by using laser-induced fluorescence to measure the relative concentrations of OH and OD products. In a separate study the relaxation of highly excited molecules is being studied by using a CO_2 laser to excite a "donor" molecule while detecting IR fluorescence from a "receptor" molecule. Studies of SF_6 + N_2O and SF_6 + NO yield the VV transfer rate as a function of SF_6 excitation. The observation of a slower decay rate at higher excitation levels indicates the existence of an energy storage mechanism in the SF_6 molecule.

Chemical Physics, continued

BROWN UNIVERSITY
Providence, Rhode Island 02912

232. INTERACTIONS OF MOLECULES WITH SURFACES $65,000 01-02
E.F. Greene
Department of Chemistry

The rate of desorption of Cs,K,Na and Li atoms from the (100) and (111) surfaces of silicon is followed by surface ionization. The rates are markedly lower from surfaces stable in the temperature range 800-950K than they are from metastable ones supercooled below surface phase transitions. These are the well-known one for (111) at 1120±40K and one for (100) at 980±20K. On the metastable surfaces the desorption is first order and the atoms appear to be highly mobile. On the stable surface where the desorption is mixed first and second order the atoms are also highly mobile but concentrated at steps between terraces from which most of the desorption occurs. In a different experiment molecules of tetramethyldioxetane are given kinetic energy by being seeded into nozzle beams of hydrogen. This kinetic energy is converted by a single collision with a surface into internal energy of the molecules which then can decompose and emit light. The amount of light varies with the kinetic energy, the temperature of nozzle, and the nature of the surface. This experiment offers an effective method of activating the decomposition of gaseous molecules.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

233. THE STUDY OF COMBUSTION AND FLAME PROCESSES INITIATED BY IR LASER-INDUCED ABSORPTION $114,000 01-02
William A. Guillory
Department of Chemistry

The phenomenon of infrared multiple-photon absorption (IR MPD), subsequently leading to excited and ground state dissociation products, simulates non-equilibrium processes occurring in flames and other combustion systems. Using visible and UV laser-induced fluorescence diagnostics as probes of the reaction zone, highly sensitive time and wavelength resolved spectroscopy allow detailed determination of the mechanisms and energetics of a given system. The reactions of vibrationally excited ground electronic state CH and OH (produced by IR MPD) with O_2, N_2, NO and aliphatic and aromatic hydrocarbons are being studied. Also being studied is the efficiency and means of production, via IR MPD, of CH and OH from various precursors. New techniques, such as multi-photon absorption fluorescence, are being implemented to study amounts of and energy states of reactive and product species (CH_2, CH_3, CO, etc.). Discrete level and quasicontinuum energy transfer and relaxation in propynal, glyoxal and methylglyoxal are also being studied.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

234. STUDIES OF COMBUSTION KINETICS AND MECHANISMS $110,000 01-02
David Gutman
Department of Chemistry

The purpose of the research is to gain new quantitative knowledge of the kinetics and mechanisms of the reactions of polyatomic free radicals which are important in hydrocarbon combustion processes. The free radicals are generated in a heated tubular reaction by the multiple-photon-induced decomposition of suitable precursors by a CO_2 TEA laser. The ensuing reactions are monitored using a photoionization mass spectrometer capable of recording the time evolution of either reactants or products. The recombination of C_2H_5 radicals are being studied in detail. Special procedures to determine their initial concentrations are also being developed. The reactions of alkyl radicals with molecules are being investigated as a function of pressure as well as temperature. In particular the $C_2H_5+O_2$ reaction is being studied from 300-1000K and from 0.4 to 8 torr total pressure. Details of mechanism changes at elevated temperatures are being obtained.

STANFORD UNIVERSITY
Stanford, California 94305

235.	COMBUSTION GAS SPECTROSCOPY USING TUNABLE LASERS R. K. Hanson Department of Mechanical Engineering	$33,000 6 mo.	01-02

Objectives of this research are: (1) the measurement of fundamental spectroscopic parameters (absorption coefficients, band or oscillator 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 a discretely tunable CO laser. Species currently under study include HCN, CO, OH, C_2H_2, H_2O, NH, CH, NCO 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

236.	THE KINETICS OF SOME REACTIONS OF HCN AT HIGH TEMPERATURE Ronald K. Hanson and Craig T. Bowman Department of Mechanical Engineering	$65,000	01-02

The objective of this research program is to obtain high-temperature kinetic data for reactions involving HCN and the CN radical. These data are relevant to the formulation of reaction mechanisms for pollutant formation in flames. Reactions of interest include the thermal decomposition of HCN, the reactions of HCN with CN, H, O and OH, the thermal decomposition of C_2N_2 and the reactions of CN with O and O_2. A conventional shock tube technique is combined with spectroscopic diagnostics to study the mechanisms and rates of candidate reactions. Experimental data are compared with results obtained from empirical models.

HOWARD UNIVERSITY
Washington, District of Columbia 20059

237.	LASER STUDIES OF THE DYNAMICS OF ATOM MOLECULE REACTION William M. Jackson Department of Chemistry	$50,000	01-02

This program has been designed to use tunable dye lasers to measure reaction rates of CN free radicals as a function of their internal energy. The project is based upon unique photochemical sources of internally excited CN radicals that can be produced from the laser photolysis of C_2N_2, ClCN and BrCN. Each of these respective compounds produce CN radicals that are rotationally or vibrationally hot. The amount of rotational and vibrational excitation depends upon the compound used so that by measuring the rate constant as a function of particular source of CN, we hope to be able to obtain information about the effects of internal excitation on the rate constants for CN reaction.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

238. HIGH RESOLUTION INFRARED SPECTROSCOPY: DYNAMICS OF VIBRATIONALLY EXCITED STATES $64,000 01-02
Kenneth C. Janda
Department of Chemistry

Molecular beam laser photodissociation spectroscopy is used to characterize intramolecular energy redistribution in excited vibrational states of molecules. Van der Waals molecules are used as prototypes for this effect because deposition of one infra-red photon is enough to break a bond. The goal is to have a description of the interim molecular energy transfer in microscopic detail. It appears that vibrational predissociation of triatomic molecules is well described by Fermi's golden rule perturbation theory. This theory predicts that a HeI_2 molecule would have short-lived vibrationally excited states, 10^{-10} sec., while the $NeCl_2$ molecule would have long-lived vibrationally excited states, greater than 10^{-5} sec. This dramatic dependence of predissociation lifetime on molecular structure has now been observed. For larger molecules simple theories do not seem to apply. For example, a series of constituents were bound to ethylene. The series included Ne, Ar, HF, HCl, NO, C_2H_4. In spite of the broad distribution of molecular structures and binding energies in this series, the vibrational predissociation lifetimes are all on the picosec. timescale.

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

239. MULTIPHOTON DISSOCIATION SPECTROSCOPY AND PHOTOCHEMISTRY OF TRANSIENT SPECIES $74,357 01-02
Philip M. Johnson
Department of Chemistry

In order to investigate the characteristics of the photochemistry of mixed clusters of hydrocarbons and oxidants such as oxygen and nitrous oxide formed in a supersonic expansion, benzene and nitrous oxide or oxygen have been expanded together in around 20 atm of helium, resulting in large clusters containing up to around thirty benzene molecules and an indeterminate number of oxidant molecules. When irradiated with the 249 nm light from a KrF laser, the resulting mass spectrum contains only parent and fragments containing carbon and hydrogen. Upon 193 nm irradiation, however, masses are seen corresponding to inclusion of one to four oxygen atoms. In experiments to examine whether the oxidation products are the result of an ionic reaction or have a neutral precursor, a 193 nm pulse was used to irradiate the clusters initially. This photolytic pulse was followed by an ionizing probe pulse (249 nm) after a delay of up to 100 μsec. Even after this long time there is a substantial product containing oxygen, showing that either it or a precursor are stable neutral species.

UNIVERSITY OF NEW ORLEANS
New Orleans, Louisiana 70148

240. IDENTIFICATION AND TEMPORAL BEHAVIOR OF RADICAL INTERMEDIATES FORMED DURING THE COMBUSTION AND PYROLYSIS OF GASEOUS FUELS $55,000 01-02
Ralph D. Kern, Jr.
Department of Chemistry

The practical and environmentally acceptable use of fossil fuels containing aromatic hydrocarbons in furnaces and engines is dependent upon the control of soot formation. The chemical sequence of reactions which lead to soot are being investigated by recording the product profiles generated during the pyrolyses of toluene, benzene, allene, butadiene, and acetylene. The experimental technique utilized involves the dynamic sampling of the reflected shock zone by time-of-flight mass spectrometry. Data have been obtained over a wide range of temperature and fuel concentrations. Computer modeling has successfully fit many of the experimental profiles. The major findings are the dominance of the ring fragmentation routes as opposed to ring condensation steps in the pyrolyses of toluene and benzene, the limited amount of ring formation observed in the decompositions of allene and butadiene, and the absence of ring species formed during the polymerization of acetylene.

Chemical Physics, continued

UNIVERSITY OF ILLINOIS/CHICAGO
Chicago, Illinois 60680

241.	LASER SCHLIEREN, SHOCK TUBE STUDIES OF HIGH TEMPERATURE HYDROCARBON PYROLYSIS RATES John H. Kiefer Department of Chemical Engineering	$61,000	01-02

This project investigates the rates and mechanims of fuel pyrolysis reactions of importance in combustion at very high temperatures. Experiments use the shock tube in conjunction with laser-schlieren diagnostics capable of providing an accurate measure of initiation rates with 0.1 μs resolution as well as some secondary rates. Rates and mechanisms for the pyrolysis of propane, propene, ethane, ethylene/acetylene, and butadiene have been investigated. The ethane study strongly indicates that methyl-methyl reactions, other than recombination, do not occur at significant rates to 2700K. The butadiene study suggests a "low" heat of formation for vinyl radical ($\Delta H^{0}_{f,298} < 65$ kcal/mole), and an estimate for the high-T vinyl radical dissociation rate, a rate of considerable importance in combustion modeling.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

242.	DEPOPULATION RATES FOR COMBUSTION-RELATED SPECIES IN LONG-LIVED (τ>100μs) VIBRATIONALLY OR ELECTRONICALLY EXCITED LEVELS James L. Kinsey and Robert W. Field Department of Chemistry	$106,000	01-02

In this project, a new technique called Stimulated Emission Pumping (SEP) is being used to study individual levels of polyatomic molecules with chemically significant amounts (up to ~3.5eV) of vibrational excitation. Current effort focusses on the acetylene molecule, HCCH, in its electronic ground state ($\tilde{X}^1\Sigma_g^+$). Individual rotation-vibration levels as much as 28000 cm^{-1} above the vibrationless level are being studied to obtain information about the transition from regular to chaotic behavior in a molecular system. Parallel investigations are probing triplet levels of acetylene at ~45000 cm^{-1}, using Zeeman quantum beat spectroscopy and anticrossing spectroscopy. Among other things, these studies address the location of the $HCCH \rightarrow H + C_2H$ dissociation limit from the variation of the density of triplet levels.

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

243.	IONIC ASPECTS OF SOOT FORMATION Walter S. Koski Department of Chemistry	$64,983	01-02

Two classes of ion-molecule reactions frequently cited as pertinent to soot formation are being investigated in our laboratory. The first includes proton transfer reactions from HCO^+ and H_3O^+. The variation of cross section as a function of projectile energy is being studied for the reactions $HCO^+(H_2O,CO)H_3O^+$, $HCO^+(C_6H_6,CO)C_6H_7^+$, $D_3O^+(C_6H_6,D_2O)C_6H_6D^+$ and between D_3O^+ and napthalene. The second class of reactions being examined are condensation reactions. In examining the reaction of $C_2H_2^+$ with C_2H_2 the condensation product, $C_2H_4^+$, is observed in binary collisions as are the ions $C_4H_3^+$ and $C_4H_2^+$. Examination of the kinetic energy spectra of these products shows that the ion $C_4H_3^+$ results from the decomposition of $C_4H_4^+$. On the other hand, the ion $C_4H_2^+$ arises from a more direct process. In examining the reaction of $C_2H_3^+$ with C_2H_2, no condensation product ($C_4H_5^+$) is observed although this ion ($C_4H_5^+$) is observed in the mass spectra of flames. Other ionic products from this reaction, $C_4H_3^+$ and $C_4H_2^+$ are observed with small cross section. Similar results are being observed for C_6 products arising from the reaction of $C_4H_3^+$ and C_2H_2.

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

244.	MULTIPHOTON INTERACTIONS IN MOLECULES WITH PICOSECOND LASER PULSES Hoi-Sing Kwok Department of Electrical and Computer Engineering	$61,800	01-02

High power ultrashort CO_2 laser pulses are employed in this research program to study the multiphoton interaction behavior of polyatomic molecules. During the past year, multiphoton induced fluorescence in SO_2 was studied. Unimolecular decomposition of CF_3Br was also investigated in the presence of HI. Strong fluorescence was observed in both cases. Signals were observed with both 100 ns and 5 ns pulses. However, it was found that more energy was needed in our present laser system to extend the measurements to the low pressure/picosecond regime. Extensive modifications have been carried out to further this goal. A new plasma triggering device was invented. It makes use of a novel pin-resistor spark gap that produces photo-ionizing UV photons in large quantities. This device may have applications in UV spectroscopy. Also a silicon detector was explored as a monitoring device for the CO_2 laser. Techniques for generating high peak power (>500 MW) picosecond laser pulses are being pursued. Among them are high pressure (>10 atm) amplification and mode-locking. Semiconductor switching is also explored as a convenient method of producing picosecond laser pulses.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

245.	MEASUREMENT OF RADICAL SPECIES CONCENTRATIONS AND POLYCYCLIC AROMATIC HYDROCARBONS IN FLAMES BY FLUORESCENCE AND ABSORPTION USING A TUNABLE DYE LASER N.M. Laurendeau and D.W. Sweeney School of Mechanical Engineering	$88,000	01-02

New quantitative laser fluorescence techniques are being developed to measure flame radical and polycyclic aromatic hydrocarbon (PAH) concentrations. During the past year we have (1) demonstrated OH concentration measurements using laser-saturated fluorescence and the balanced cross-rate model at atmospheric pressure under stoichiometric, fuel-rich, and sooting conditions; (2) extended this saturated fluorescence technique to the NH radical; (3) developed a linear fluorescence technique for determining PAH concentrations in a vapor mixture; and (4) made the first reported fluorescence measurements of atomic hydrogen in flames using two-photon absorption. Current research includes (1) laser-saturated OH measurements, (2) development of a quantitative model relating measured fluorescence intensity to atomic species concentration, and (3) PAH measurements at flame conditions.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

246.	TIME-RESOLVED STUDIES OF FREE RADICALS AND LASER-INITIATED CHAIN REACTIONS Stephen R. Leone Department of Chemistry and Joint Institute for Laboratory Astrophysics	$65,000	01-02

Time and wavelength-resolved infrared emission techniques are used to study free radical production and reactions. Infrared emission spectra have been obtained and analyzed for combusting mixtures of low-pressure chlorine with hydrocarbons. A method has been developed to measure the absolute rate coefficients of methyl radical reactions with molecules such as chlorine and bromine. Intramolecular vibrational relaxation processes have been observed in the ground electronic state of hydrocarbons by exciting the first CH overtones and detecting the reduction in emission from these states. A multiple vibrational state analysis has been developed and applied to the extraction of rate information for very slow chain reactions.

Chemical Physics, continued

Kansas State University
Manhattan, Kansas 66506

247. DIFFUSION FLAME STUDIES OF THE CHEMICAL AND PHYSICAL MECHANISMS OF SOOT FORMATION FROM AROMATIC AND SUBSTITUTED AROMATIC FUELS, T.W. Lester, J.F. Merklin, C.M. Sorensen, Depts. of Nuc. Eng . & Physics — $56,000 — 01-02

This research program is intended to study the physical mechanisms and attendant chemistry that lead to the formation of large soot aggregates in flames. This past year, photon correlation spectroscopy (PCS) has been used to measure the diffusion constant of aerosol particles in flames. The soot aerosol data all lie in the transition Knudsen number regime, where the empirically based, Cunningham corrected Stokes-Einstein diffusion constant has been used commonly. However, the data all deviate from the theory by an order of magnitude. Possible errors in our interpretation of the experiment or experimental effects have been considered. These include, particulate polydispersity, various phoeretic effects, turbulence, and particulate change. None of these effects can explain the discrepancy. Rather the discrepancy may be due to a fundamental misunderstanding of particulate diffusion in gases when $Kn > 0$. Possible explanations we are currently considering include: experimental time scales compared to kinetic equilibrium time scales, correlated motion and velocity autocorrelation function long time tail effects, and particle-gas molecule interactions.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

248. EXPERIMENTAL STUDIES OF THE IONIZATIONS AND BONDING OF SMALL MOLECULES ATTACHED TO TRANSITION METALS — $35,000 6 mo. — 01-02
Dennis L. Lichtenberger
Department of Chemistry

This research project focuses on experimental investigation of the electronic mechanisms of bond activation of small molecules by transition metals. The primary experimental technique is gas-phase photoelectron spectroscopy, utilizing HeI, HeII, and X-ray excitation sources. Breakthroughs have been made with the HeI source in observing detailed vibrational structure in metal ionizations. An improved HeII source design has proven to be especially valuable in understanding the valence ionizations or organometallic molecules. Gas phase core photoelectron spectroscopy has also been developed and has shown important correlations between core and valence ionizations shifts. The systems receiving most attention involve metal interactions with small organic species that are proposed intermediates in water-gas shift and Fischer-Tropsch catalysis, such as alkyls, alkenes, alkynes, methylenes, and vinylidenes. An important new study involves investigation of metal-alkyl complexes that represent intermediate stages of carbon-hydrogen bond breaking and formation.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

249. LASER INDUCED CHEMICAL REACTIONS AND LASER-COLLISION PROCESSES — $65,000 — 01-02
John C. Light
James Franck Institute and
Department of Chemistry

Laser induced chemical processes of several types have been observed experimentally. Our research program is to develop theoretical methods to examine such processes and to permit accurate prediction of their dynamics. Methods to do exact (3-D) quantum calculations of single photon photodissociation of triatomic molecules have been developed and applied to ICN and HCN using model excited state potential energy surfaces. A new representation of the problem (discrete variable representation) simplifies the calculation considerably by taking advantage of the initial localized configuration of the molecule. Similar techniques are useful in the problem of dissociative attachment of an electron to a diatomic or triatomic molecule. For the problem of multiphoton dissociation of small polyatomic molecules a new transformation and approximation (rotating frame transformation) have been developed in order to follow the time evolution of the molecular system as it gains energy from the laser field. The technique is simple and accurate enough to permit the *ab initio* calculation of the dynamics of molecules such as O_3 in strong laser fields.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

250. MOLECULAR DESIGN PRINCIPLES FOR BIOMIMETIC SOLAR ENERGY CONVERSION SYSTEMS $84,207 01-02
Gerald M. Maggiora
Departments of Chemistry & Biochemistry

Ab initio quantum mechanical and empirical potential function procedures are being applied in an investigation of the physico-chemical factors underlying biological and biomimetic solar energy conversion, and these factors will be used to develop a set of molecular design principles which will enable chemists to formulate structures of potential biomimetic photoconversion systems possessing specified properties, more efficiently. Current studies are directed towards porphyrin dimer and trimer systems, especially hetero-dimers. Preliminary results indicate the existence of low-lying, non-radiative charge-transfer states in magnesium porphine-porphine dimers which may be sufficiently long-lived to facilitate electron transfer from these dimers to appropriate acceptors. The results are being further evaluated with regard to the effect of intermolecular geometry and microenvironment on the location and character of the charge-transfer states. Studies are also continuing on the evaluation of possible molecular candidates for the P700 and P680 photoactive species in the photoreaction centers of green plants. In addition, the development of new and improved theoretical methodologie and algorithms are being actively pursued.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

251. MOLECULAR BEAM STUDIES OF METASTABLE RARE GAS CHEMILUMINESCENT REACTIONS $52,000 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 eximer and excitation transfer lasers.

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

252. DYNAMICAL STUDIES IN MOLECULAR SYSTEMS $122,631 01-02
Herschel Rabitz
Department of Chemistry

The research program has two parts consisting of studies in chemical kinetics and collision dynamics. In the first part on chemical kinetics, the research is concerned with the development and application of sensitivity analysis tools for the understanding of complex chemical mechanisms. Both time and spatially dependent problems are under study with a special emphasis on combustion phenomena. In the latter case, sensitivity techniques are being developed for probing the role of rate constants, transport coefficients, initial conditions and boundary conditions on laboratory observables. The second part of the research in collision dynamics is concerned primarily with the development and application of collision scaling relationships. Scaling can be viewed as a form of inversion which takes laboratory data to a more fundamental underlying level such that it may be used again to produce new predicted observable collision phenomena. A hierarchical approach to collisional scaling is being taken whereby the scaling relations may be employed with various levels of sophistication. Applications to the inversion of collisional relaxation data are being considered.

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

253. A KINETIC STUDY OF RADICAL-AROMATIC HYDROCARBON REACTIONS $60,287 01-02
A. R. Ravishankara
Engineering Experiment Station

Improvements in the fundamental understanding of chemical reaction rates and pathways in radical-unsaturated hydrocarbon reaction 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 and olefinic hydrocarbon are being carried out as functions of temperature and pressure. By judicious interpretations of observed kinetic isotope effects, the yield and identity of certain products, the temporal profiles of reactant and product 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 have been elucidated. Furthermore, studies on aromatic free radicals have been initiated. Information gained from these studies is expected to help better utilization of hydrocarbons both as combustibles and as feedstocks for synthetic fuel production, as well as increasing our understanding of hydrocarbon combustion.

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45435

254. THE DIRECT DETERMINATION OF ATOM AND RADICAL CONCENTRATIONS IN THERMAL REACTIONS OF HYDROCARBONS AND OTHER GASES $55,190 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 in shock tube experiments using resonance absorption spectroscopy in the vacuum ultraviolet. Measurements made recently include H and D atom measurements in pyrolysis of dilute mixtures (in argon) of benzene-d_6, toluene-d_8, and mixtures of these compounds with 2,2-dimethylpropane (neopentane). In the experiments with mixtures, H atoms produced by dissociation of neopentane react with the deuterated aromatic compounds. Measurements of H and D concentrations help to clarify the reaction mechanisms. Experiments in which both H and D concentrations are measured in pyrolysis of partially deuterated propene are also being carried out.

RICE UNIVERSITY
Houston, Texas 77251

255. SUPERSONIC METAL CLUSTER BEAMS $120,000 01-02
R. E. Smalley
Department of Chemistry

Laser vaporization of a metal target within a pulsed supersonic nozzle is used in this research to prepare beams of transition metal clusters. This new technique (developed in the previous year of this DOE contract) is perfectly general for even the most refractory metals (eg. tungsten) and readily provides an intense source of bare metal clusters cooled to internal temperatures on the order of 5 K. Current research with this new source centers around the spectral study of small transition metal clusters in order to obtain accurate and definitive measurements of the the metal-metal bond (bond length, dissociation energy, electronic structure, bond angles, vibrational frequencies, etc.). Metal clusters studied thus far include Cr_2, V_2, Ni_2, Cu_2, Cu_3, and Mo_2. The results in the case of Cr_2 and V_2 indicate that the metal-metal bond in this region of the transition series is dominated by strong 3d orbital interaction, resulting in extremely short bond lengths. Nickel and copper, on the other hand, are found to be bound mostly through the 4s orbitals.

UNIVERSITY OF CALIFORNIA/SAN DIEGO
La Jolla, California 92093

256. SHOCK-TUBE STUDIES OF IMPORTANT COMBUSTION-REACTION STEPS INVOLVING RADICALS $60,493 01-02
Klaus G. P. Sulzmann
Energy Center

The aim of this research is twofold: (a) the use of shock-tube techniques for the rapid introduction of known intermediate and radical concentrations into a combustion environment in which the individual interactions of these species with other reactants and intermediates can be separated or enhanced for meaningful rate measurements of individual or sub-groups of reaction paths relevant to hydrocarbon combustion, and (b) the use of in situ quantitative spectroscopic measurement techniques for the determination of required species concentration-time histories. As a first step, the only partly understood fate and kinetics of the CH_3-radical is investigated during its donor-pyrolysis and its interactions with O_2 and O-atoms behind reflected shock-waves by using argon-diluted $CH_3CO_2CH_3$, $(CH_3)_2$, CH_3COCH_3 and/or CH_3N_2 as methyl radical donors. Oxidation reactions are initiated by admixing either O_2 or N_2O as an O-atom donor. Quantitative spectroscopic data are obtained by infrared emission (2 channels), by infrared HeXe-laser absorption at 3.508μ, by visible ultraviolet emission (10 channels), and/or by vacuum-ultraviolet absorption.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

257. VARIATIONAL TRANSITION STATE THEORY $65,000 01-02
Donald G. Truhlar
Department of Chemistry

This research program is an attempt to develop and implement new methods for calculating rate coefficients for chemical reactions from potential energy surfaces. Emphasis is being placed on gas-phase atom-transfer reactions, which are an important reaction type in combustion and atmospheric systems, as well as being of fundamental interest. We are also studying the effect of vibrational excitation of the reactants on chemical reaction rates, and we are studying kinetic isotope effects. A very important aspect of our studies is the inclusion of quantal effects in reaction rate calculations, with special emphasis on tunneling (barrier penetration) and on the dependence of vibrational frequencies on the reaction coordinate. We are developing methods to include tunneling contributions in the limits of small and large reaction-path curvature, as well as a least-action model that is applicable to all cases. Examples of our applications to reactions important in combustion are $OH + H_2 \rightarrow H_2O + H$ and $OH + O \rightarrow H + O_2$.

NATIONAL BUREAU OF STANDARDS
Washington, DC 20234

258. KINETICS DATA BASE FOR COMBUSTION MODELING $90,000 01-02
Wing Tsang and Robert F. Hampson
Chemical Kinetics Division

The aim of this research is to compile, evaluate and publish information on the rate constants for single step chemical processes which are pertinent to the detailed description of hydrocarbon combustion processes. The plan of attack is to start with the simplest molecular systems and then to expand into more complicated situations. All possible reactions are considered. Evaluation involves critical examination of experimental data, comparisons with analogous reactions and expectations from theory. Where data does not exist estimates are made. Results are presented on individual data sheets so as to permit periodic upgrading. Work on methane and ethane oxidation and pyrolysis have now been completed. It should be noted that these reactions form a subset of all combustion processes. Further work will involve continuous updating and expansion into NO_x, CH_3OH and higher hydrocarbon system.

Chemical Physics, continued

SURFACE ANALYTIC RESEARCH, INC.
Mountain View, California 94043

259. ELECTRONIC STRUCTURE OF HEAVY TRANSITION METAL CARBONYLS $62,000 01-02
Cary Y. Yang

The objective of this research program is twofold. Because of the inherent similarity between transition metal carbonyls and chemisorbed CO on a surface of the same metal, an improved understanding of the carbonyl electronic structure is likely to assist in the study of CO chemisorption. A comprehensive tool for calculating both bound and continuum states of molecules containing heavy elements such as the fifth-row transition metal carbonyls is needed and being developed. The first-year effort consists of ground-state calculations for $W(CO)_6$, $Re_2(CO)_{10}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$, and the formulation of Dirac-scattered-wave (DSW) continuum states. The metal $d_{3/2}$-$d_{5/2}$ hybridization, which can only be obtained with this fully relativistic SCF-Xα-DSW method, is considerably larger in tungsten, rhenium, and osmium carbonyls than in iridium or platinum ones. All four molecules have similar metal-ligand bonding mechanisms, namely, carbonyl-to-metal donation through 5σ, and back-donation through $2\pi^*$. The continuum states formulation is in progress, with the secular matrix being set up from the boundary conditions.

Atomic Physics

NEW YORK UNIVERSITY
New York, New York 10003

260. ENERGY-RELATED ATOMIC AND MOLECULAR STRUCTURE AND SCATTERING STUDIES $80,000 01-03
Benjamin Bederson
Department of Physics

A program to study atomic and molecular interactions with dc and ac electric fields is in progress, as well as one to study interactions of electrons with highly polar molecules. We have recently completed an extensive study of the electric dipole polarizabilities of selected alkali halide dimers, and are now completing a study of indium ($\sim 12 \times 10^{-24} cm^3$). Similar measurements on thallous halides, additional alkali halides, and some representative very heavy elements, are underway. We also completed our first scattering measurements, using a new scattering apparatus. These involve scattering of slow electrons (∿1 to 22 eV) by the highly polar CsBr molecule. Absolute values of "effective" cross sections have been obtained; these can be directly compared with computations by folding the latter into our known "apparatus functions". A systematic study of similar cross sections using molecules possessing a range of dipole moments is also in progress. Extension of ground-state measurements to excited states (for both polarizabilities and molecular scattering) using laser excitation, is now in the preliminary stages of development.

THE UNIVERSITY OF NEW MEXICO
Albuquerque, NM 87131

261. ATOMIC PHYSICS WITH RELATIVISTIC BEAMS $90,000 01-03
Howard C. Bryant
Department of Physics and Astronomy

Exploitation of the relativistic kinematics of an 800 MeV H^- beam at the Clinton P. Anderson Meson Physics Facility (LAMPF) at Los Almos allows the observation, with very little background, of the one and two electron continua and embedded resonant structures. The H^- system is being studied using Doppler-tuned laser probes and motional electric fields, which have so far ranged up to 7 MV/cm, far in excess of those possible using more conventional laboratory techniques. The behavior of the H^- system as a function of both excitation energy and applied field is being carefully mapped out. Energy scale calibration is provided by excitation, with single photon absorption, of the Lyman series in an H^0 beam, derived from the H^- beam by photodetachment. The studies of the ^1P resonant structures in H^- near n=2, the shape and Feshbach resonances, and that of the 2 electron threshold region are proving to be exceptionally challenging to atomic physics theory and more detailed measurements in these regions are planned.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

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

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. This research project will 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 cross-beam apparatus, with both polarized atom (Na) and polarized electron beams, is now in operation. In its first application the spin dependence of the threshold ionization process leading to a sodium ion plus two free electrons in spin selected states is being studied. Subsequent experiments will deal with ionization of the first excited state of sodium and the spin dependence in elastic scattering.

COLLEGE OF WILLIAM AND MARY
Williamsburg, Virginia 23185

263. COLLISIONAL DETACHMENT OF NEGATIVE IONS $75,000 01-03
R. L. Champion and L. D. Doverspike
Department of Physics

The fundamental goals of these experimental studies are to determine various cross sections and to develop a general understanding of the collisional dynamics for systems which involve negative ions. The energy range of the experiments is from a few electron volts up to 500 eV. The experiments include measurements of absolute total cross sections, doubly-differential cross sections, and the energy spectra of electrons which are liberated in collisional electron detachment. The processes under investigation include collisional detachment, charge transfer, reactive scattering and inelastic scattering. Emphasis is placed upon developing an understanding of the role of resonances in negative ion-molecule collisions and upon delineating the various collisional processes that may occur in collisions of negative ions with molecular targets. Studies have been completed on the systems $H^-(D^-) + H_2$, D_2, HD and are underway for $H^-(D^-) + C\ell_2$. The experimental results are coupled with theoretical models to provide a basis for understanding the role of negative ions in various experiments.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

264. MANY-BODY PROCESSES IN ATOMIC AND MOLECULAR PHYSICS $60,000 01-03
Shih-I Chu
Department of Chemistry

The fundamental goals of this project are to develop new theoretical formalisms and practical numerical methods for probing intense field atomic and molecular multiphoton processes and predissociation dynamics of van der Waals molecules. A *semi-classical many-mode Floquet theory* has been developed for nonperturbative treatment of the interaction of a quantum system with several monochromatic oscillating fields. Current work includes; (1) Spectral line shape analysis on the multiphoton absorption spectra of HF and CO molecules, (2) high precision rotational predissociation lifetime determination of Ar-H_2 and Ar-HD van der Waals molecules, (3) development of a *complex quasi-vibrational* energy and an *inhomogeneous differential equation* methods for the computation of two-photon dissociation cross sections of vibrationally excited states of H_2+.

UNIVERSITY OF TOLEDO
Toledo, Ohio 43606

265. SEMIEMPIRICAL STUDIES OF ATOMIC STRUCTURE $55,000 01-03
L. J. Curtis 24 mo.
Department of Physics and Astronomy FY 83-84

The structure and properties of very heavy and very highly ionized atoms is being studied through experimental measurements utilizing fast ion beam excitation and through the identification and exploitation of regularities in the data base using precise empirical parametrizations. The use of spectroscopic line intensities to determine thermonuclear plasma temperatures and densities requires laboratory observation and analysis of these systems. The spectroscopic accuracies required are difficult to achieve by purely *ab initio* theoretical methods for complex many electron systems in this highly relativistic regime. Through the acquisition and systematization of experimental data, regularities and linearities are being utilized to predict a wide variety of atomic structure properties, which are subsequently tested experimentally. During the past year, special emphasis has been given to the prediction of wavelengths and transition probabilities for metastable states in highly ionized atoms that decay by magnetic dipole, electric quadrupole, or spin-mixing processes, which are observed in tokamak spectra.

HARVARD-SMITHSONIAN CENTER FOR ASTROPHYSICS
Cambridge, Massachusetts 02138

266.	THEORETICAL STUDIES OF HIGHLY IONIZED SPECIES A. Dalgarno	$95,000	01-03

Collisions of multiply-charged ions with neutral gas affect the ionization structure, thermal balance, radiation losses and ion transport in plasmas containing a neutral component. Because the products of the collisions radiate, they can be detected and thereby provide unique diagnostic probes of the environment. We have extended our calculations of the efficiencies of the processes so that their accuracy can be assessed by comparison with experimental data, which are now becoming available. We have made estimates of charge transfer into individual fine-structure states because observations of astrophysical objects show that the separate emission lines can be distinguished readily. We have also explored collisions of positive and negative ions.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

267.	BASIC STUDIES OF ATOMIC DYNAMICS U. Fano Department of Physics and James Franck Institute	$94,000	01-03

This project aims at describing and predicting the correlations and the energy transfers among the variables of atomic and molecular systems. The observed but paradoxical stability of resonant states that are localized on top of potential barriers, rather than on valley bottoms, seems to have been eventually understood. It derives from a general property of light or particle beams focussed about a symmetry axis or plane. Whichever action produces the focussing also confines the associated transverse wave causing it to acquire a discrete stable spectrum. This concept is being applied initially to construct the theory of the quasi-Landau resonances of Rydberg spectra in a magnetic field, but it should bear on all atomic and molecular reactions. Other current research on novel aspects of electron mechanics is progressing regularly.

VANDERBILT UNIVERSITY
Nashville, Tennessee 37235

268.	THEORETICAL STUDIES OF ATOMIC TRANSITIONS Charlotte Froese Fischer Computer Science Department	$78,000	01-03

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, has been developed. Several transitions of current interest are being investigated. These include the E2 and M1 transitions between levels of $2p^3$ in the nitrogen isoelectronic sequence. Excellent agreement with the observed fine-structure splitting has been achieved for the $^2D_{5/2}$ - $^2D_{3/2}$ and $^2P_{3/2}$ - $^2P_{1/2}$ energy separations. Similar calculations for the $3p^3$ levels in the phosphorus sequence are under way. Allowed transitions between doubly excited states of B III are also under investigation. Preliminary studies of changes required to adapt MCHF procedures to photoionization calculations have been made.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

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

The objective of this project is to perform a theoretical analysis of the effects that intense laser pulses, possible 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. Under special study is the behavior of an otherwise free electron being subjected to two laser fields, propagating in different directions, with different amplitudes and frequencies. A classical treatment of the particle dynamics is being investigated preliminary to a full quantum mechanical treatment. Also under study is the nature of the radiation emitted by such a particle, the intensity of that radiation as a function of the pump laser parameters, its coherence, and also its spectral and angular distribution.

SRI International
Menlo Park, California 94025

270. STUDIES OF AUTOIONIZING STATES RELEVANT TO DIELECTRONIC RECOMBINATION — $72,000 — 01-03
Thomas F. Gallagher
Molecular Physics Laboratory

The goal of this program is 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 excitaiton 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. All theoretical models of dielectronic recombination, the inverse of autoionization, incorporate the above mentioned phenomena, and the data from these experiments should provide the means to make more stringent test of the theory.

UNIVERSITY OF OKLAHOMA
Norman, Oklahoma 73019

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

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.

Atomic Physics, continued

UNIVERSITY OF GEORGIA
Athens, Georgia 30605

272. QUANTUM MECHANICAL STUDIES OF HEAVY ION SCATTERING PROCESSES $48,000 01-03
T. G. Heil
Department of Physics and Astronomy

This research program concentrates on low to intermediate energy processes where a quantum mechanical description is most appropriate. Several heavy ion processes involving important constituent reactions that take place in terrestrial and astrophysical plasmas are being studied in detail. Inelastic collisions of protons with many-electron ions are being considered in a quasimolecular formulation. This type of reaction is being considered for use as a probe of proton density and temperature. Charge transfer processes between hydrogen atoms and multiply charged ions by both radiative and nonradiative mechanisms are also being studied. The charge transfer reactions [$C^{2+} + H \rightarrow C^{+} + H^{+} + h\nu$] and [$Al^{3+} + H \rightarrow Al^{2+} + H^{+}$] are being examined in detail.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803-4001

273. ELECTRON COLLISIONS WITH POSITIVE IONS $30,000 01-03
Ronald J.W. Henry
Department of Physics & Astronomy

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 Ti^{+3} and are in good agreement with measurements of Falk _et al_. Differential electron scattering cross sections for inelastic excitation of Zn^{+} are calculated at energies between 15eV and 100eV. Agreement of theory with the experiment of Chutjian at 75eV is excellent over the measured angular range of 4° to 16°.

ST. JOHN FISHER COLLEGE
Rochester, New York 14618

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

This research program is directed toward the studies of preparing multilevel atoms in high-lying levels using one or more laser pulses, and of multiphoton relaxation processes. The main results this year have been the discovery of unexpected population inversion procedures which give a generalized interpretation of adiabatic following, and the analytic formulation of specific pulse sequences incorporating both amplitude and phase modulation which give specific degrees of inversion of multilevel atoms. The precise analytic nature of these results opens the ways for a comprehensive study of multilevel photon-echo effects which are important for understanding multilevel relaxation processes.

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

278.	LOW ENERGY ION-NEUTRAL COLLISIONS J. J. Leventhal Department of Physics	$65,000	01-03

This experimental program is designed to investigate energy transfer and energy conversion in atomic and molecular interactions. Current emphasis is on interactions involving atoms in specific excited electronic states which are produced by laser photoexcitation. By using both spectral analysis of the radiation emitted by the reaction products and mass analysis of ionic products nearly complete characterization of the interactions can often be achieved. Of particular interest at this time is the examination of processes that are steps in the complicated sequence of microscopic reactions that collectively produce macroscopic effects, such as plasma formation, by coupling laser energy to gases or vapors.

UNIVERSITY OF ARKANSAS
Fayetteville, Arkansas 72701

279.	A THEORETICAL STUDY OF ELECTRON CAPTURE IN ION-ATOM COLLISIONS M. Lieber and F. T. Chan Department of Physics	$40,000 17 mo. FY 82-83	01-03

Electron capture processes in ion-atom and ion-ion collisions, e.g. $A^+ + B \rightarrow A + B^+$, are of importance to 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

280.	ATOMIC PHYSICS OF STRONGLY CORRELATED SYSTEMS Chii-Dong Lin Department of Physics	$78,933	01-03

This program is directed toward the understanding of correlations of two-electron atoms in hyperspherical coordinates and the development of practical codes for computing inelastic cross sections in ion-atom collisions. The Stark shift and Stark quenching of two-electron resonances in a strong external electric field are being investigated. A complete classification scheme for doubly excited states is being developed. The modified atomic-orbital model (AO+) is generalized to include excitation, charge transfer and ionization processes for calculating inelastic ion-atom collisions at intermediate and low velocities.

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

278. LOW ENERGY ION-NEUTRAL COLLISIONS $65,000 01-03
J. J. Leventhal
Department of Physics

This experimental program is designed to investigate energy transfer and energy conversion in atomic and molecular interactions. Current emphasis is on interactions involving atoms in specific excited electronic states which are produced by laser photoexcitation. By using both spectral analysis of the radiation emitted by the reaction products and mass analysis of ionic products nearly complete characterization of the interactions can often be achieved. Of particular interest at this time is the examination of processes that are steps in the complicated sequence of microscopic reactions that collectively produce macroscopic effects, such as plasma formation, by coupling laser energy to gases or vapors.

UNIVERSITY OF ARKANSAS
Fayetteville, Arkansas 72701

279. A THEORETICAL STUDY OF ELECTRON CAPTURE IN ION-ATOM COLLISIONS $40,000 01-03
17 mo.
FY 82-83
M. Lieber and F. T. Chan
Department of Physics

Electron capture processes in ion-atom and ion-ion collisions, e.g. $A^+ + B \rightarrow A + B^+$, are of importance to 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

280. ATOMIC PHYSICS OF STRONGLY CORRELATED SYSTEMS $78,933 01-03
Chii-Dong Lin
Department of Physics

This program is directed toward the understanding of correlations of two-electron atoms in hyperspherical coordinates and the development of practical codes for computing inelastic cross sections in ion-atom collisions. The Stark shift and Stark quenching of two-electron resonances in a strong external electric field are being investigated. A complete classification scheme for doubly excited states is being developed. The modified atomic-orbital model (AO+) is generalized to include excitation, charge transfer and ionization processes for calculating inelastic ion-atom collisions at intermediate and low velocities.

UNIVERSITY OF NEBRASKA/LINCOLN
Lincoln, Nebraska 68588-0111

281. HYPERSPHERICAL COORDINATE THEORY OF TWO-ELECTRON ATOMIC PROCESSES $60,000 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. The Fock coefficients have been obtained numerically and will be used to calculate photoabsorption by He and H^- as well as elastic electron scattering by H.

MOREHOUSE COLLEGE
Atlanta, Georgia 30314

282. THEORETICAL INVESTIGATION OF ELECTRON-ION INTERACTION $43,836 01-03
Alfred Z. Msezane
Department of Physics

The purpose of this investigation is to identify and calculate dominant physical mechanisms underlying the processes of electron impact excitation and ionization of ions using the close-coupling approximation. Both total and differential cross sections are calculated and compared with measurements. In particular, detailed numerical studies are carried out to investigate the extent of contribution of the physical processes of inner-shell excitation-autoionization, and inner-shell resonant-excitation-double autoionization to the total ionization cross section of Ti^{+3} important in CTR plasma. An accurate configuration - interaction wave function of the target is used, a wave function which is constructed to give the same values for the oscillator strengths in the length and velocity formulations.

NATIONAL BUREAU OF STANDARDS
Boulder, Colorado 80303

283. ATOMIC AND MOLECULAR COLLISION PROCESSES $93,000 01-03
David W. Norcross
Quantum Physics Division - 525

The focus of this program is the physics of low-energy collisions of electrons with atom, ions, 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. Core polarization effects as the cause of the serious discrepancy between theory and experiment for excitation of Be^+ are being investigated. The effects of zero-point averaging and polarization in vibrationally elastic scattering by HF have been shown to be small. A new parameter-free correlation-polarization model for molecular scattering based on free-electron-gas theory is being tested for several molecules, including H_2, N_2, and HCl. Calculations of vibrational excitation of HCl are in progress.

UNIVERSITY OF TENNESSEE/KNOXVILLE
Knoxville, Tennessee 37996

284.	PRODUCTION AND DESTRUCTION OF METASTABLE NEGATIVE IONS David J. Pegg Department of Physics	$42,000	01-03

This research program is designed to investigate the production and destruction of metastable negative atomic ions. In particular we begin our measurements on Ca^- where the $4s4p^2\ {}^4P$ state is theortically predicted to be bound and metastable against allowed radiative and autodetachment decay mechanisms. Our source of negative ions is a fast moving beam and we plan to use electron spectroscopic techniques to study the energy of electrons detached in flight by the processes of autodetachment, collisional detachment and photodetachment.

JACKSON STATE UNIVERSITY
Jackson, MS 39217

285.	SPECTROSCOPY OF TRAPPED MOLECULAR IONS J. Perkins, G. Miller Chemistry Department	$50,000	01-03

The goal of this project is to provide spectroscopic data that will help document those characteristics of molecular ions responsible for the large cross sections accompanying ion-molecule reactions. Using laser induced fluorescence (LIF), energy level and lifetime measurements are made of various small molecular ions, e.g., O_2^+, CO^+, CH^+ and CH_2^+. The ions are prepared by fragmentation of parent neutral gases through electron impact using a Pierce-type pulsed electron gun. The ions are mass selected by and trapped in a quadrapole ion trap long enough to carry out the spectroscopic measurements. Attempts are made to study intra- and intermolecular energy exchange involving electronic, vibrational and rotational motions of these ions. Light intensity measurements are made using a dye laser and the results are used to determine excited state lifetimes in the order of tens of milliseconds.

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

286.	NONLINEAR OPTICS WITH BROAD-BAND LASERS Michael G. Raymer The Institute of Optics	$59,831	01-03

Experiments are being carried out to understand the statistical properties of broad-band laser radiation, and the effects of using such radiation in several areas of nonlinear optics. Intensity fluctuations and mode correlations are being studied in both cw and pulsed broad-band dye lasers via intensity autocorrelation and spectral measurements. Such broad-band lasers are used to pump stimulated Raman amplification and coherent anti-Stokes Raman scattering in hydrogen gas. Intensity and field cross-correlations which develop between pump and probe laser beams in these processes are being observed using an intensity cross-correlator and a nonlinear interferometer based on the interference of beams produced at the sum-frequency of the two beams of interest.

Atomic Physics, continued

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

287. ATOMIC PHYSICS WITH HIGHLY CHARGED IONS $490,000 01-03
Patrick Richard
James R. Macdonald Laboratory
Department of Physics

High velocity, highly charged ions produced by the 6 MV KSU tandem Van de Graaff are used to study charge transfer, ionization and excitation in ion-atom collisions. During this contract period the impact parameter dependence of delta electrons, recoil ions, and Auger electrons have been studied for nearly symmetric F^{q+} - Ne collisions. The final state populations in single- and double-electron transfer have also been studied. Resonant transfer excitation is being studied by a high resolution x-ray spectroscopy method. The high velocity beams have been used to measure the 2s Lamb shift and the 1s Lamb shift in one-electron ions. The so-called "Thomas peak" in the angular distribution of the scattered ion in electron capture predicted by a second Born calculation has been observed for the first time in H^+ + He collisions. Energy gain spectroscopy and capture cross sections, using low velocity highly charged ions produced by the recoil ion method, have been studied for several systems with some emphasis on atomic hydrogen and Li targets.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

288. EXPERIMENTAL STUDIES OF ATOMIC INNER SHELL IONIZATION PHENOMENA $63,000 01-03
S. M. Shafroth
Department of Physics and Astronomy

This program is designed to study inner-shell vacancy production in ion-atom collisions, and subsequent decay via x rays or Auger electrons. Primary emphasis is on experiments relating to dielectronic recombination. Fast highly stripped ions are produced by the TUNL FN tandem Van de Graff and sputter ion source. Thus conditions in magnetic confinement fusion devices are simulated, except that the electrons corresponding to plasma electrons are bound in gas atoms and have relatively little kinetic energy whereas the fast ions have the same velocity as the plasma electrons which give rise to dielectric recombination. This process has been called Resonant Transfer and Excitation (RTE). Cross sections for RTE are being measured for a variety of collision systems by means of the x ray-charge changed beam coincidence method. A set of four parallel plate avalanche detectors has been constructed so that projectiles which have gained or lost one or two electrons can be measured in coincidence with projectile K x rays and radiative electron capture (REC) identified by radiation of a continuum type. REC gives a signature for nonresonant excitation of K electrons and electron capture (NTE). Extensive calculations for RTE and NTE are underway.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

289. NEAR-RESONANT ABSORPTION BY ATOMS IN INTENSE FLUCTUATING FIELDS $68,659 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. A hybrid system of electro-optic and acousto-optic modulators is used to impose laser bandwidths up to 30 MHz, and bandshapes out to 1 GHz from line center, on a single-mode laser beam. Lineshapes ranging from Gaussian to Lorentzian are synthesized 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).

Atomic Physics, continued

RICE UNIVERSITY
Houston, Texas 77251

290. ATOMIC AND MOLECULAR SCIENCES $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 collisonal effects of interest in plasma physics and controlled thermonuclear reaction technology. Specifically, time resolved spectroscopy of alkali-halide excimers excited by synchrotron radiation yields stimulated emission cross-sections, formation and quenching rates for excimer laser transitions. Experiments in a flowing afterglow apparatus are directed toward studies of Penning and photoionization of alkali atoms and small clusters, electron exchange in polarized electron-atom/molecule collisions, and new approaches to electron spin polarimetry. Recent theoretical results include cross sections for: radiative charge-transfer collisions between He^{++} ions and H atoms; inelastic electron-ion and ion-ion collisions in a dense, hot plasma; energy transfer in collisions of highly excited atoms with molecules; and Penning ionization of sodium atoms by metastable helium collisions.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

291. X-RAY EMISSION IN HEAVY-ION COLLISIONS $65,000 01-03
R. L. Watson
Cyclotron Institute and
Department of Chemistry

High resolution x-ray spectral measurements are being performed for the purpose of investigating (a) rapid electron transfer in light elements following multiple ionization by fast heavy-ion impact, (b) excitation and x-ray emission from np states of fast heavy ions in gaseous and solid media, and (c) alignment of P states in ion-atom collisions. Spectra are obtained using a variety of beams ranging from protons to argon ions provided by the Texas A&M variable energy cyclotron. The objectives of these experiments are to obtain a basic understanding of the processes responsible for chemical effects on x-ray satellite and hypersatellite structure, and to characterize solid state influences on x-ray emission from few-electron heavy ions, including alignment and possible coherence effects.

Chemical Energy

YALE UNIVERSITY
New Haven, Connecticut 06511

292.	STUDIES OF THE HYDROGENATION OF SMALL UNSATURATED MOLECULES USING ORGANOMETALLIC CLUSTER COMPOUNDS AS CATALYSTS Richard D. Adams Department of Chemistry	$78,000	02-01

This research project is focused on the mechanisms of activation and hydrogenation of small heteronuclear unsaturated molecules like CO and CO_2 by polynuclear transition metal complexes. Special emphasis is being placed on the importance of multinuclear bridging coordination forms in ligand activation. The products of selected reaction sequences are being investigated by IR and NMR spectroscopies and are being structually characterized by single-crystal x-ray diffraction analyses.

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

293.	HEATS OF FORMATION OF GAS PHASE ORGANOSULFUR MOLECULES AND IONS MEASURED BY PEPICO Tomas Baer and Slayton A. Evans, Jr. Department of Chemistry	$67,670	02-01

The goal of this research program is to determine accurate heats of formation and structures of organosulfur molecules and ions. The results obtained are of fundamental chemical interest, as well as of importance in the removal of sulfur containing molecules from coal. Some of the species being investigated include HCS^+, H_8CS^+, CH_2SS^+, and CH_3CHS. Heats of formation are obtained from fragment ion onsets in photoionization scans. In favorable circumstances, some structural information can be obtained from ion lifetime measurements obtained from Photoelectron photoion coincidence (PEPICO). However the more accurate structures are determined by <u>ab initio</u> calculations. These results are related to the fundamental bonding interactions between S-S and O-O bonds which are being investigated by ^{17}O and ^{33}NMR. The latter technique is also being developed into a rapid analytical method for determining the form of oxidized sulfur in organic mixtures.

Brigham Young University
Provo, Utah 84602

294.	METAL SUPPORT INTERACTIONS: THEIR EFFECTS ON CATALYTIC PROPERTIES OF COBALT Calvin H. Bartholomew Department of Chemical Engineering	$48,689 9 mo.	02-01

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, TPD, and TPR measurements. Recent results provide evidence that dispersion and support significantly influence adsorption and CO hydrogenation activity/selectivity properties of cobalt.

PURDUE UNIVERSITY
W. Lafayette, Indiana 47907

295. REDUCTION OF AROMATIC COMPOUNDS DERIVED FROM COAL BY CALCIUM — $55,000 — 02-01
Robert A. Benkeser
Department of Chemistry

A new reducing system consisting of calcium dissolved in a mixture of methylamine-ethylenediamine has been developed for the reduction of aromatic compounds that can be derived from coal. Hydrocarbons like tetralin, *m*- and *p*-xylene and indane are reduced in excellent yields by the calcium system to a crude product containing 88% or better of a single alkene. Optimal experimental conditions have been developed for the reduction of anthracene to 1,2,3,4,5,6,7,8,9,10-decahydroanthracene, tetralin to $\Delta^{9,10}$ octalin, *p*-xylene to 1,4-dimethylcyclohexene and indane to 4,5,6,7-tetrahydroindane. Surprisingly, durene is reduced by the calcium reagent to 1,2,4,5-tetramethyl-1,4-cyclohexadiene in excellent yield. The syntheses developed for the five aformentioned cyclic alkenes represent the best methods presently available for preparing these compounds. The calcium procedure fails almost entirely to reduce internal alkenes to alkanes. Internal alkynes, however, like 2-nonyne and 4-octyne are reduced quite cleanly to the corresponding *trans*-alkenes. The function of the dual solvent system is under active investigation.

UNIVERSITY OF PITTSBURGH
Pittsburgh, Pennsylvania 15261

296. THE CARBIDIC AD-LAYER AS RATE CONTROLLING FACTOR IN CO/H_2 CATALYSIS — $154,000, 24 mo., FY 83-84 — 02-01
Paul Biloen
Department of Chemical/Petroleum Engineering

The objective of this program is to assess the reactivity and abundance of reaction intermediates present at the surface of CO/H_2 converting catalysts during steady-state catalysis. The central question which is being addressed is to what extent carbonaceous side products control the abundancy of reaction intermediates. In a typical experiment the isotopic constitution of the feed is being changed abruptly (e.g., $^{12}CO/H_2 \rightarrow {}^{13}CO/H_2$). This leads to a transient phenomenon: the displacement of ^{12}C by ^{13}C, first in the catalyst ad-layer and then in the product. The rates of displacement contain transient-kinetic information regarding the abundancy and reactivity (i.e., lifetime) of reaction intermediates. With ^{12}CO and ^{13}CO exhibiting essentially identical reactivity, the steady-state of the system is essentially not affected by the isotopic switch. In the present setup, the rate of isotopic substitution in product is being monitored by on-line mass spectrometry. Under construction is a setup to combine this with an in-situ IR monitored rate of isotopic substitution in the reactive ad-layer.

STANFORD UNIVERSITY
Stanford, California 94305

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

The palladium catalyzed conversion of amorphous carbon to a graphitic form has been studied in vacuo and in situ by transmission electron microscope and electron diffraction. Throughout the process, the metal particles appear fluidlike but remain crystalline. There now appears a common thread through a number of phenomena involving a catalyst-carbon interface (CCI): the catalytic gasification of carbon, as reported by us last year, where carbon-carbon bonds are broken at the CCI; the formation of filamentous carbon where carbon-carbon bonds are formed at the CCI; and in the catalytic conversion of amorphous to graphitic carbon where carbon-carbon bonds are both broken and later re-made at different locations of the CCI. The link *between those phenomena is the acceleration by the catalyst of the breaking or making of carbon-carbon bonds* in the presence or in the absence of reactive gases adsorbed on the carbon or the metal.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

298. SYNTHESIS, STATIC, AND REACTIVE CHARACTERIZATION OF SUPPORTED ORGANOMETALLICS — Total $84,000 — 02-01
Alan Brenner
Department of Chemistry

Previous research dealing with the synthesis and reactivity of supported carbonyl complexes is being greatly expanded. During the past year glass reaction systems have been replaced with state of the art metal systems combining high purity and the ability to operate between 10^{-7} torr and 1000 psi. Studies of Fischer-Tropsch synthesis at typically 350 psi over catalysts derived from supported $W(CO)_6$ show activities 100-fold higher than for traditional (reduced salt) catalysts of W. Both Mo and W carbonyls also show large enhancements in activity for the hydrogenation of benzene compared to their traditional analogs. H_2-D_2 exchange over alumina and supported $Mo(CO)_6$ has been studied. Contrary to published data, reaction on alumina involves surface hydroxyl groups and the rate of exchange becomes very low if the alumina is activated above 1000 °C. $Mo(CO)_6$ activated to form $Mo(CO)_3$ is of low activity for exchange, but further decomposition results in very high activity. Photolytic activation of $Mo(CO)_6$ has also been studied as an alternative to thermal activation as a route to atomically dispersed metal. However, after facile removal of three ligands the rate of photolysis drops to a very low value.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

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

This project represents a study of the surface chemistry and catalytic activity of organoactinide complexes deposited on oxide supports. Two complexes, M = Th,U in $M[(CH_3)_5C_5]_2(CH_3)_2$ had been found to give very fast hydrogenation of propylene at -63°C and polymerization of ethylene at 25°C. $Th[(CH_3)_5C_5]_2H_2$ dimer has now been found to exhibit similar activity for hydrogenation, but $U[(CH_3)_5C_5]_2(CH_3)Cl$ has only 5% as much activity. Poisoning experiments with CO indicate that only a few percent of the U or Th atoms become active sites for the above reactions. During activation, a small fraction of $U[(CH_3)_5C_5]_2(CH_3)_2$ loses methane to form $U{=}CH_2$ probably stabilized by interaction with surface Al-O. It is not a good catalyst for olefin metathesis.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

300. THE PROPERTIES OF SUPPORTED METAL CATALYSTS — $65,000 — 02-01
John B. Butt, Robert L. Burwell, Jr. and Jerome B. Cohen
Ipatieff Laboratory

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. During the past year study of the hydrogenation of propylene as influenced by the nature of the pretreatment of Pt/SiO_2 and Pd/SiO_2 catalysts was completed. The preparation of Co, Rh and Co-Rh mixed elements on SiO_2 by decomposition of carbonyls was completed and the hydrogenolysis of methylcyclopropane on the Rh/SiO_2 was investigated. A combined synchrotron-x-ray diffraction EXAFS study was completed on Pt/SiO_2 and Pd/SiO_2, with special attention given to interactions with O_2. A new high-low temperature x-ray chamber was completed that allows in situ studies from -100 to +500 °C under reaction or pretreatment conditions. Current characterization is being carried out on the Co, Rh and Co-Rh systems.

UNIVERSITY OF WISCONSIN, MADISON
Madison, Wisconsin 53706

301. MECHANISTIC STUDIES RELATED TO THE METAL CATALYZED HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS
Charles P. Casey
Department of Chemistry
$170,000
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 studies of the synthesis and reactions of metal formyl compounds (M-CO-H) and hydroxymethyl metal compounds (MCH_2OH) [models for intermediates in the homogeneous hydrogenation of CO] are being carried out. Compounds with CH_3, CH_2, and CH groups bridging between two iron atoms have been synthesized as models for intermediate in the hetero-geneous catalysis of CO hydrogenation. Carbon-carbon bond forming reactions of the CH compounds with alkenes and with CO are being explored. 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

302. METAL ALKOXIDES - MODELS FOR METAL OXIDES
Malcolm H. Chisholm
Department of Chemistry
$146,500
24 mo.
FY 83-84
02-01

Structural analogies between polynuclear metal alkoxides and metal oxides have been noted, with the former providing models for subunits within the extended networks of the latter. An extensive organometallic chemistry supported by alkoxy ligands is emerging. Their facile interconversion between terminal and bridging positions and between σ^2 and $(\sigma^2 + \pi^2)$ donors allows for easy uptake and release of substrate molecules. Key findings during the 1982/83 period are: (i) the cleavage of C≡O to carbido and oxo tungsten alkoxide clusters; (ii) the coupling, co-coupling and sometimes metathesis-like reactions (M = W) between C≡C, C≡N and M≡M bonds in $M_2(OR)_6$ compounds; (iii) unusual β-hydrogen effects in dinuclear alkyl-alkoxides of molybdenum and (iv) the isolation of Mo-Mo quadruply bonded compounds supported by alkoxide ligands.

RENSSELAER POLYTECHNIC INSTITUTE
Troy, New York 12181

303. HOMOGENEOUS CARBON MONOXIDE FIXATION
Alan R. Cutler
Department of Chemistry
$185,000
24 mo.
FY 83-84
02-01

Organometallic complexes containing C_1 alkoxycarbonyl and C_2 carboalkoxymethyl ligands derived from terminally bound CO are being synthesized in order to delineate those coordinated ligand reactions and their intermediates that are viable for CO hydrogenation. The metalloester $FpCO_2CH_3$, derived from $FpCO^+$ or from Fp_2Mg/CO_2, serves as the common template in converting either CO or CO_2 into the C_1 *alkyl ligand on* $FpCH_2OCH_3$; $Fp = (\eta\text{-}C_5H_5)Fe(CO)_2$. The activated ester $FpC(OCH_3)_2{}^+$ thus adds hydride and gives its stable formylacetal $FpCH(OCH_3)_2$, which subsequently affords the desired $FpCH_2OCH_3$. The methylidene salt $FpCH_2{}^+$ (generated from $FpCH_2OCH_3$) picks up exogeneous CO, ascertained by a ^{13}C labeling study, and gives the stable $(\eta^2\text{-}C,C)$ ketene complex $Fp(CH_2CO)^+PF_6{}^-$; this complex abstracts methoxide from methanol (or even $FpCH_2OMe$) and provides the carbomethoxy methyl $FpCH_2CO_2CH_3$. This ketene complex, which effectively derives from two carbonyls, therefore serves as an efficient source of a C_2 alkyl ligand that is important in CO fixation studies.

Chemical Energy, continued

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

304. STUDIES OF NEW ELIMINATION REACTIONS OF METAL COMPLEXES — $89,657 — 24 mo. — FY 82-83 — 02-01
Mary Rakowski DuBois
Department of Chemistry

This project is investigating elimination and rearrangement reactions of alkyl substituents on μ_2-sulfido ligands in dimers of the general types $[CpMoSSR]_2{}^n$ and $[CpMo(SR)_2]_2{}^n$ (n=0,-1,-2). It has been proposed that the sulfido ligands and metal ions may participate in these reactions to provide low energy pathways for new reaction types. The complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$, I, has been synthesized, and each of its two one-e^- reduction products has been characterized. Protonation of $[I]^{-2}$ produces $(CpMo)_2(S_2CH_2)$-$(\mu\text{-}SH)(\mu\text{-}SCH_3)$, II, which reacts with protons to form hydrogen and I. II also reacts under N_2 at 70° to eliminate methane. Certain alkenyl substituents undergo unusual rearrangement reactions under nitrogen at 25°C in $CDCl_3$. For example, the 1,2 butene dithiolate ligand in $(CpMo)_2(\mu\text{-}S_2CH_2)(SCH{=}C(C_2H_5)S)$ isomerizes to form a coordinated 2-butene-3,4-dithiolate ligand. When the system is placed under hydrogen, *cis* 2-butene is produced exclusively, and under deuterium, deuterated (d_2-d_8) *cis* 2-butenes are formed. The relevance of these reactions to those catalyzed by metal sulfide surfaces is being investigated.

UNIVERSITY OF TEXAS/AUSTIN
Austin, Texas 78712

305. STUDY OF FISCHER-TROPSCH SYNTHESIS THROUGH THE USE OF SURFACE INTERMEDIATE SCAVENGERS — $54,965 — 02-01
John G. Ekerdt
Department of Chemical Engineering

The goals of this program are to identify reaction intermediates involved in synthesis gas conversion and to elucidate the reaction mechanisms. Pyridine is used to scavenge alkyl fragments from a silica supported iron catalyst during Fischer-Tropsch synthesis. The distribution of scavenged fragments establishes that alkyl fragments are the reaction intermediates involved in chain growth and are the immediate precursors to hydrocarbon products. Amines are being used in attempts to scavenge acyl species which may be present and may be involved in alcohol formation and/or chain growth. Direct CO hydrogenation into branched alkanes, isosynthesis, is being investigated over zirconia. Differential reactor studies establish the kinetics and primary products. These experiments suggest that normal and iso C_4 olefins form in a stepwise manner from a common intermediate. Temperature programmed studies of the interaction of synthesis gas with ZrO_2 suggest that CO reacts with surface hydroxyl groups to form formate and methoxide species at one atmosphere. The importance of these C_1 species in C_4 formation is being investigated.

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

306. CHEMICALLY MODIFIED CARBON, PLATINUM, AND NICKEL ELECTRODES — $60,000 — 02-01
C. Michael Elliott
Department of Chemistry

New chemically modified electrodes and related solution chemistry are under study in this research. The goals are to alter the kinetics of electrode reations in a useful way. 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 CALIFORNIA, IRVINE.
Irvine, California 92717

307. SYNTHESIS, CHEMISTRY AND CATALYTIC ACTIVITY OF LANTHANIDE METALS IN UNUSUAL OXIDATION STATES AND COORDINATION ENVIRONMENTS — $66,000 — 02-01
William J. Evans
Department of Chemistry

The objective of this research is to identify the special chemical properties of the lanthanide metals (14 heavy metals which are mined in California) and to exploit this unique chemistry to develop (a) new materials of potential practical importance, (b) more efficient and more selective catalytic systems, and (c) new stoichiometric and catalytic reactions presently not possible with conventional catalysts. Our study of the chemistry of the lanthanide-carbon bond has led to the first molecules containing lanthanide-hydrogen bonds. These lanthanide hydrides catalytically activate molecular hydrogen and we are studying the intermediates in this reaction to understand how to modify this reactivity in unusual ways. The reactions of the hydrides with nitriles, isocyanides, alkynes and alkenes provide new, structurally unusual complexes whose chemistry is being examined. We have developed an efficient conversion of bimetallic hydrides to structurally unique trimetallic tetrahydrides which may be of interest with respect to hydrogen storage. We are studying the extension of this synthesis to larger polymetallic lanthanide polyhydrides.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

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

The influence of alkali promoters on CO hydrogenation is being studied as a function of catalyst support, promoter preparation method and promoter concentration. Temperature-programmed reaction is being used to measure specific rates of CO and carbon hydrogenation and temperature-programmed desorption is used to study changes in CO and H_2 desorption rates. The activity and selectivity to higher hydrocarbons is being studied in a differential reactor with gas chromatography detection. On all nickel catalysts, the selectivity to higher hydrocarbons, particularly olefins, was increased by the addition of Na or K promoters. For approximately one percent potassium and ten percent nickel, the specific activity decreased and the activation energy changed on Ni/TiO_2, Ni/Al_2O_3 and Ni/SiO_2. On $Ni/SiO_2 \cdot Al_2O_3$, however, specific activity increased. Good agreement was obtained between TPR and differential reactor studies. On Ni/SiO_2, the rate of carbon hydrogenation and the strength of hydrogen bonding also decreased with promoter addition. The method of promoter addition had a small influence on the activity and selectivity.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

309. STUDIES RELATED TO THE HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT REACTION — $66,500 — 02-01
Peter C. Ford
Department of Chemistry

Research in these laboratories is directed toward elucidating fundamental mechanisms key to catalytic cycles including the water gas shift reaction and toward developing new homogeneous catalysts for such reactions. Studies in progress include kinetic investigations of important steps such as the nucleophilic activation of carbon monoxide coordinated to metal centers by a variety of species including the oxy anions HO^- and CH_3O^- ($M\text{-}CO + RO^- \rightarrow M\text{-}CO_2R^-$), the decarboxylation of hydroxy carbonyl adducts ($M\text{-}CO_2H^- \rightarrow M\text{-}H^- + CO_2$), the reductive elimination of H_2 from metal hydrides ($M\text{-}H^- + H_2O \rightarrow H_2 + M + OH^-$) and the substitution reactions of metal carbonyl complexes. Systems under investigation are largely drawn from those shown to have potential as homogeneous catalysts in the reactions of carbon monoxide. The elucidation of these mechanisms will provide guidelines for the molecular engineering of new and better catalysts for the production of fuels and other organic products from CO and other small molecule substrates.

CORNELL UNIVERSITY
Ithaca, New York 14853

310. ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS UNDER ULTRA-HIGH VACUUM CONDITIONS $50,000 02-01
Jack H. Freed
Department of Chemistry

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

311. RADICAL CHAIN AND REARRANGEMENT REACTIONS IN COAL LIQUEFACTION $68,000 02-01
Joseph J. Gajewski
Keven E. Gilbert
Department of Chemistry

This project focuses on providing fundamental data for the thermal reactions of aromatic compounds that may serve as a basis for understanding coal liquefaction. It has been shown that 1,3-diarylhydrocarbons and ethers decompose by free radical chain processes in the temperature range of 310 to 390°C. Some of these species will react with lower temperature free radical initiators and the kinetics and the thermodynamics of these reactions have been studied. Hindered phenols will inhibit radical chain reactions up to 200°C. We have also found that phenyl substituted tetralins cleave to smaller molecules via a complex series of radical rearrangements and phenyl shifts. Finally *p*-isotoluene and benzo-*p*-isotoluene, putative intermediates in the concerted retro-ene decomposition of 1,3-diphenylpropane, undergo thermal reactions with second order kinetics to give non-ene dimers and polymers respectively.

PENNSYLVANIA STATE UNIVERSITY
University Park, PA 16802

312. MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION $72,000 02-01
Gregory L. Geoffroy
Department of Chemistry

Mechanistic schemes for the metal surface catalyzed reduction of carbon monoxide to methanol and to hydrocarbons have been proposed, and the feasibility of these mechanisms are being tested by preparing and studying the chemistry of metal clusters which resemble the proposed surface intermediates. Initial focus has been on the preparation and reactivity studies of cluster complexes bearing formyl and acyl substituent groups. The stepwise reduction of CO to CH_4 on an Os_3 cluster via a formyl intermediate had been observed. More recently it has been found that $Os_3(CO)_{11}(\mu\text{-}CH_2)$, an isolatable intermediate in the preceding transformation reacts readily with CO to yield the first ketene substituted cluster, $Os_3(CO)_{12}(\eta^2(C,C),\mu_2\text{-}CH_2CO)$. This species has been characterized spectroscopically and by a single crystal X-ray diffraction study and its chemistry is now being explored in detail. A series of mixed-metal dinuclear complexes have been synthesized and their CO/H_2 reactivity is being examined. Focus is on dinuclear complexes containing one early and one late transition metal and held together by bridging $\mu\text{-}PR_2$ groups.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

313. THE NATURE OF THE CONTRIBUTION OF THE POLYMERS OF CELL WALLS OF THE HIGHER PLANTS TO COAL FORMATION

$50,000
02-01

Peter H. Given
Coal Research Section

The objective is to identify in peats the chemically altered forms of the plant polymers that constitute the input to coalification. Cores from four sites in the Florida Everglades and Okefenokee swamp have been obtained. About 30-50% of the organic matter in all levels of a peat derived from the red mangrove consists mostly of tissue from the rootlets and secondary roots of the tree. Specimens of these organs hand-picked from the upper layers of the peat show strong carbohydrate character, judging from FTIR and ^{13}C nmr spectra, but are not purely cellulosic. Nevertheless, the abundant rootlets from +40 mesh sieved material has a pronounced aromatic character, which resembles but is not identical with lignin, apparently because the rootlet material is encrusted with brown amorphous (humic?) substances. It has been found that oxidation with pertrifluoroacetic acid almost completely destroys cellulose but with lignin gives a good yield of a rather small number of simple polycarboxylic acids. The method has promise for the study of peats. In summary, the peat studied contains both carbohydrate- and lignin-related substances, but these are not identical with the natural polymers.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

314. 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 ($-CHO$, $=CHOH$, $=CH_2OH$, $\equiv C$, $\equiv CH$, $=CH_2$, $H_2C{=}O$, $-OCHO$, 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. Current studies are making extensive use of optically active substrates derived from easily resolved $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+ BF_4^-$. For instance, methylidene (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+ PF_6^-$ ((+)-(*S*)-1) couples to ethylene complex (+)-(*R*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+ PF_6^-$ with retention. This coupling also exhibits a remarkable degree of enantiomer self-recognition: the (+)-(*S*)-1 couples virtually exclusively with (+)-(*S*)-1, and (-)-(*R*)-1 couples virtually exclusively with (-)-(*R*)-1. The formate (+)-(*R*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$ decarboxylates at 70-130 °C to hydride (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ with retention. An X-ray structure study of $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]^+ PF_6^-$ has been submitted for publication.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

315. LIQUID AND SOLID CARBON-13 MAGNETIC RESONANCE STUDY OF HYDROCARBONS AND RELATED SUBSTANCES

$90,026
02-01

David M. Grant, Dept. of Chemistry
Ronald J. Pugmire, Dept. of Fuels Engrg.

This work focuses on both liquid and solid NMR methods to characterize carbonaceous compounds important in the energy industry. The methods are being calibrated using model organic compounds. Hydroaromatics, coal macerals, various fossil fuels and their precursors provide the main focus of this work. A portion of this project has focused on the conformational analysis of hydroaromatics using liquid NMR methods. The effect of dipolar-dephasing and cross-polarization methods on quantitative measurements are being studied. 2-Dimensional Fourier techniques may be used to differentiate and distinguish different spectral responses in solids. The most useful portrayal involves a chemical shift versus scalar coupling plot. Presently, the data is obtainable on solids with reasonably high internal motion. The dipolar decoupling power used in proton decoupling is insufficient at present to provide scalar coupling constants for very rigid solids. Spreading spectral information into a second dimension helps resolve otherwise overlapping spectral responses. Thus, quantitative estimates of coal composition will be enhanced by this development.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

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

The research is concerned with the activation and reduction of carbon monoxide. Group VI-B intramolecular metalloesters are synthesized from cationic transition-metal(II) carbonyl complexes employing intramolecular nucleophiles. Spectroscopic and X-ray crystallographic evidence confirm the general structure as an ester derived from the attack of an alkoxide at a carbonyl ligand. Equilibrium studies indicate that attack by an intramolecular nucleophile may be favored over that of an intermolecular one by at least four orders of magnitude. The optimum configuration for intramolecular nucleophilic attack is being investigated. One-electron electrochemical oxidation of an arene chromium carbonyl complex containing a pendant alcohol induces an interaction at bound CO. A family of Group IV ketene complexes have been synthesized as models for C-C coupling intermediates in CO reduction reactions.

YALE UNIVERSITY
New Haven, Connecticut 06520

317. SELECTIVITY ACTIVITY AND METAL-SUPPORT INTERACTIONS OF Rh BIMETALLIC CATALYSTS — $75,000 — 02-01
Gary L. Haller
Department of Chemical Engineering

This research program is designed to investigate the effects of a modifying second metal and/or the support on the selectivity and activity of Rh supported catalysts. A comparative extended X-ray absorption fine structure analysis of Rh-Ag/SiO_2 and Rh-Ag/TiO_2 indicates greater Rh-Ag interaction on the TiO_2 support than on SiO_2. This is reflected in the activity of structure sensitive reactions, e.g. hydrogenolysis, as a large decrease in activity as the Ag:Rh ratio is increased. The group VIII-TiO_2 support interaction behaves analogously to the group VIII-group lb, e.g. Rh-Ag, interaction with respect to kinetic parameters and relative effect on structure sensitive vs. structure insensitive reactions. The kinetics of the group VIII-TiO_2 interaction indicate a transport limited process at a fixed reduction temperature. From these results we have deduced that group VIII-TiO_2 interaction involves transport of a reduced species, TiO_x, onto metal particles which break up large ensembles of surface metal atoms necessary to constitute sites for structure sensitive reactions.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, CA 90024

318. METALLACARBORANES STRUCTURALLY ENGINEERED FOR THE REDUCTION OF CARBON MONOXIDE — $70,000 — 02-01
M.Frederick Hawthorne
Department of Chemistry

This research program has been designed to develop and evaluate various metallacarboranes as homogeneous catalysts for the transformation of CO into useful chemical feedstocks. Emphasis has been placed on several areas of interest: (1) the evaluation of the activity of rhoda- and ruthenacarborane complexes as catalyst precursors for the water gas shift reaction; (2) the synthesis of heterobimetallic metallacarboranes which possess both early and late transition metal vertices, as well as those which contain main group elements such as aluminum and gallium, for the study of metal-metal cooperativity in the reduction of CO; and (3) the preparation and screening of a series of rhodacarborane complexes as hydroformylation catalysts. The ability to synthetically engineer the structural and electronic properties of metallacarboranes has proven to be an indispensible tool. The catalyst precursors used in these studies have been shown to exhibit several novel structural features which include a structurally sensitive closo/exo-nido tautomerism, a key feature in the ability of these species to activate small molecules such as dihydrogen.

YALE UNIVERSITY
New Haven, Connecticut 06520

319.	THE ROLE OF d-ELECTRONS IN CHEMISORPTION AND METAL/SUPPORT INTERACTIONS STUDIED BY ELECTRON SPECTROSCOPY Victor E. Henrich Applied Physics	\$68,503 24 mo. FY 82-83	02-01

This research program utilizes model supported catalysts (small Rh particles deposited in situ on well characterized TiO_2 single-crystal surfaces) and surface-sensitive electron spectroscopies, including photoemission and Auger spectroscopy, to examine the role of d-electrons and support electronic structure in strong metal/support interactions. Core level binding energies of the Rh atoms are found to depend upon particle size. The primary cause is believed to be changes in screening of the core hole, although changes in the valence state of the Rh atoms cannot be ruled out. Inert gas sputter profiling of model catalysts has shown that heating the catalyst to 400°C results in a decrease in the amount of exposed Rh, possibly by the coverage of Rh particles by an oxide of Ti. Changes in the chemisorption of CO and H_2 for various catalyst treatments are currently being investigated in order to correlate the electronic and geometric effects that have been observed to strong metal/support interactions.

UNIVERSITY OF PITTSBURGH
Pittsburgh, Pennsylvania 15260

320.	STUDIES OF SUPPORTED METAL CATALYSTS David M. Hercules Department of Chemistry	\$80,000	02-01

During this period we have advanced the adaptation of spectroscopic techniques for studying catalytic surfaces demonstrating the utility of ESCA, ISS and LRS. LRS can give structural information about bulk phases whereas ESCA can give information about highly dispersed phases. We have demonstrated a correlation between ESCA, EXAFS and PAS measurements, giving valuable information about the site symmetry of transition metals on catalyst surfaces. We have shown a correlation between reducibility of catalytic species measured by ESCA and the same quantity measured classically. We have characterized Ni species on Al_2O_3 and SiO_2 when the preparation method and Ni content of the catalysts are varied. We have studied the nature of Co species on Al_2O_3 and how they are affected by Mo or Zn, or by sulfiding. We have determined how Mo species on an alumina catalyst are affected by sulfiding, by the presence of Co or by being supported on titania. We have studied tungsten on alumina; the catalytic W species differ from Mo for the same support.

SRI INTERNATIONAL
Menlo Park, California 94025

321.	HIGH TEMPERATURE CHEMISTRY OF COMPLEX VAPORIZATION/DECOMPOSITION PROCESSES Donald L. Hildenbrand Physical Sciences Division	\$94,961	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 Cs, 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.

THE PENNSYLVANIA STATE UNIVERSITY
University Park, PA 16802

322. CHARACTERIZATION OF ACTIVE SITES AND THEIR ROLE IN GAS-CARBON REACTIONS — $80,000 — 02-01
Robert G. Jenkins, Philip L. Walker, Jr. and Francis J. Vastola
Department 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. Previous work has shown that the steady state gasification rate at 0.1 MPa O_2 correlates with the total amount of surface oxide and that CO can inhibit the steady state gasification rate. Current work is focused on characterizing the surface oxide formed during steady state gasification under varying conditions of temperature, pressure, and duration of reaction. The C-O_2 reaction is significantly catalyzed by Pt, e.g., the rate is about 400 times larger for 1% Pt deposited on a graphitized carbon black compared to the uncatalyzed case at 775 K and 0.1 MPa air. The reaction rates (673-773 K and 0.01 to 0.1 MPa O_2) are found to depend on the amount of Pt on the sample. The Pt dispersions on various samples are being determined by an x-ray line broadening and O_2-CO titrations at 298 K. The rate constants are found to be independent of average Pt dispersion.

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

323. TRANSITION METAL ACTIVATION AND FUNCTIONALIZATION OF CARBON-HYDROGEN BONDS — $59,986 — 02-01
William D. Jones
Department of Chemistry

This research is directed towards the activation and cleavage of carbon-hydrogen bonds by homogeneous transition metal compounds. The possibilities for forming hydridometalaryl complexes and trapping these intermediates with isocyanides or acetylenes will be investigated. A reaction sequence involving trapping, insertion, and reductive elimination would yield imine or styrene products. These systems have the added feature that they can be catalytic, as the metal complexes are not consumed and the overall thermodynamics are favorable. The use of ω-arylacetylenes would permit the more facile intramolecular C-H activation, which would form fused ring systems if the proposed reaction sequence is followed. Metal complexes to be examined include $(C_5Me_5)RhL_2$, $(PR_3)_2ReH_7$, $(DMPE)_2TaH_5$, $H_5Ir(PMe_3)_2$, $Ru(PMe_3)_4$, $CpRe(PR_3)_2H_2$, $Mo(PMe_3)_4(N_2)_2$, and related molecules. The success of this project would result in a method for forming new carbon-carbon bonds.

OWENS-ILLINOIS, INC.
Toledo, Ohio 43666

324. INVESTIGATION OF SEMISYNTHETIC ESTERASES — $80,501 — 02-01
Melvin H. Keyes
Biotechnology Department

This research project is designed to study the nature of semisynthetic esterases, generated from nonesterase proteins, by means of conformational modifications induced by inhibitors of natural esterases. Two esterases are being generated from bovine pancreatic ribonuclease, using indolepropionic acid as the modifier, after perturbing the protein under acid pH and cross-linking with glutaraldehyde. The esterase activity is assayed using tryptophan ethyl ester as substrate and measuring the ethanol produced. The two esterases are distinguished by their distinct pH optima, substrate specificity and inhibition by tryptophan. After separation by ammonium sulfate precipitation, further purification of the esterases is being accomplished by gel filtration. The specificity of the esterases is being investigated using various esters, and amide substrates. Kinetic studies on the most appropriate substrates are being done.

LEHIGH UNIVERSITY
Bethlehem, Pennsylvania 18015

325. MECHANISMS AND CONTROLLING CHARACTERISTICS OF THE CATALYTIC OXIDATION OF METHANE
Kamil Klier and Gary W. Simmons
Department of Chemistry
$210,000
24 mo.
FY 83-84
02-01

The objective of this program is to investigate the role of metal and oxide catalysts on the product composition in partial and full oxidations of methane. Studies of both the gas phase free radical pathways and the surface catalyzed reactions, as well as the interplay of the two, are incorporated in this program, using spectroscopic characterization of gas phase intermediates (EPR, optical) and of surface intermediates (Auger/ESCA/EELS). The gas phase and surface reactions occurring during partial oxidation of methane are being analyzed separately, and the program is divided into four tasks: 1. Trapping, Detection, and Identification of Free Radicals; 2. Electron Spectroscopy of Surface Intermediates: Auger/ESCA/LEED/TPD studies of halogen-treated palladium crystal surfaces; 3. Kinetic and Mechanistic Study of the Catalyzed Combustion of Methane; and 4. Effects of Nitric Oxide.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

326. SOLID STATE, SURFACE AND CATALYTIC STUDIES OF OXIDES
Harold H. Kung
Department of Chemical Engineering
$145,000
24 mo.
FY 83-84
02-01

This program is to elucidate the interrelation among the solid state, surface and catalytic properties of oxides. Current emphasis is on the effect of crystallite size and surface atomic structure in surface chemistry and catalysis. In the former, Fe_2O_3 catalysts of average crystallite sizes ranging from 2.5 to over 100 nm were prepared. Mössbauer, x-ray, and magnetization measurements indicated the presence of only α-Fe_2O_3. When used as catalysts for butene oxidation, the selectivity for butadiene was found to decrease from about 80% to less than 40% with increasing crystallite size. In the study of surface atomic structure effect, single crystal planes of (0001), $(10\bar{1}0)$, $(40\bar{4}1)$, and $(50\bar{5}1)$ of ZnO were used in the decomposition of methanol, formaldehyde, and formic acid. The product distributions on $(10\bar{1}0)$, $(40\bar{4}1)$ and $(50\bar{5}1)$ were the same but the decomposition activity increased with step density. The primary reaction is the oxidation to formate which decomposed into CO, CO_2, H_2 and H_2O. On the (0001) surface, in addition to oxidation, a dehydrogenation pathway also exists to yield formaldehyde, H_2 and CO from methanol.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

327. CATALYSTS AND MECHANISMS IN SYNTHESIS REACTIONS
Jack H. Lunsford
Department of Chemistry
$93,579
02-01

A major part of this research program is devoted to understanding the structural and electronic factors which determine the catalytic properties of supported metals, such as palladium, for the formation of alcohols. Controlled modification of the support, for example by the addition of lithium ions, can transform an inactive catalyst into one which rivals commercial catalysts for methanol synthesis activity. Infrared experiments, using CO as a probe molecule, are underway to determine the relative amounts of Pd(111) and Pd(100) planes which are exposed on the supported catalysts. Another aspect of the research involves a study of matrix-isolated gas phase radicals which are produced on surfaces of catalytic importance. Recent work on magnesium oxide shows that surface defects which give rise to O^- ions (V-type centers) are active for the generation of methyl radicals from methane. These centers are present only on oxygen-rich surfaces which is surprising since magnesium oxide is normally considered to be a nonreducible oxide.

NATIONAL BUREAU OF STANDARDS
Washington, DC 20234

328. STRUCTURES AND REACTIVITY OF CHEMISORBED SPECIES AND REACTION INTERMEDIATES — $120,000 — 02-01
Theodore E. Madey, Richard D. Kelley

Surface Science Division

This program addresses the structure and reactivity of adsorbed molecules both on single crystal catalysts and high area catalysts using a variety of experimental methods. 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 molecular complexes adsorbed on metal and oxide surfaces is being studied using the electron stimulated desorption ion angular distribution (ESDIAD) method. 2) Vibrational spectroscopy of the adsorption, decomposition, and reaction kinetics of H_2O and NH_3 on single crystal metal and oxide 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 utility of NIS as an *in situ* probe of CO hydrogenation under reaction conditions has been demonstrated. 4) CO hydrogenation reactions over single crystal catalysts (refractory metals and Cu/Ni alloys) are under investigation.

STANFORD UNIVERSITY
Stanford, California 94305

329. MOLECULAR BEAM STUDIES OF THE DYNAMICS OF ACTIVATED ACTIVATED ADSORPTION OF N_2 ON W(110). — $218,504, 24 mo., FY 83-84 — 02-01
Robert J. Madix
Department of Chemical Engineering

The activated adsorption of N_2 on W(110) was studied using molecular beams to achieve translational energies from 2 to 30 kcal/gmol. The beams were formed in nozzles with and without helium seeding. For the lowest kinetic energy the probability of dissociation upon collision was about 10^{-3}, increasing to 2×10^{-1} at energies above 20 kcal/gmole. The dependence of the dissociation probability on nitrogen coverage suggested the process was direct in nature, not trapping dominated. The results show that adsorption is translationally activated and that the reactive collision is not adequately described by a one-dimensional barrier. As the beam energy was increased, the apparent saturation coverage by nitrogen increased, producing an unusual desorption state above a nitrogen atom coverage of 0.25. Nitrogen desorbed autocatalytically from this state in a fashion observed previously for high concentrations of oxygen from Pt(100). The emergence of this state at higher surface coverages indicates that the state of nitrogen adsorbed on tungsten and other metals may be quite different from the state normally observed in low pressure studies.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

330. THE PHOTOCHEMICAL PROPERTIES OF TRANSITION METAL-ARENE COMPLEXES. — $72,448 — 02-01
Kent R. Mann
Department of Chemistry

The photochemical reactivity of transition metal arene complexes will be studied by examining the mechanisms of the arene replacement reactions by NMR, laser flash photolysis and classical mechanistic techniques. The intermediate species generated in these reactions will be utilized as catalytic photoassistance agents and in the synthesis of novel organometallic complexes.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

331. REACTIONS OF IRON ATOMS WITH MOLECULES IN LOW TEMPERATURE MATRICES — $63,148 — 02-01
Ralph G. Pearson and Paul H. Barrett
Departments of Chemistry and Physics

The goal of this project is to study the reactivity of metal atoms and small clusters with molecules in low temperature matrices. Mössbauer and infrared spectroscopies are used to identify the reaction products. Reactions between Fe, Fe_2, and iron clusters and low temperature matrix isolated molecules of CO, C_2H_2, HCN, CH_4, CH_2N_2 and other small molecules are under investigation. This investigation includes the search for bond cleaving reactions of HX and CH_3X molecules and the study of CH_2, NH and O bound to iron atoms.

INDIANA UNIVERSITY-PURDUE UNIVERSITY
Indianapolis, Indiana 46223

332. STUDIES OF METAL-AMMONIA INTERACTIONS WITH AROMATIC SUBSTRATES — $47,000 — 02-01
Peter W. Rabideau
Department of Chemistry

Reduction and reductive alkylations effected by electron addition in dissolving metal systems such as sodium or lithium in liquid ammonia, can provide an important method for the solubilization of coal. This research is aimed at a better understanding of the fundamental nature of this reaction using aromatic and polynuclear aromatics as model compounds. The intermediates in these reactions are monoanions, radical anions and dianions, and efforts to study them involve direct and indirect methods. Direct studies include proton and carbon NMR with monoanions in liquid ammonia, whereas indirect studies involve determination of protonation sites (regioselectivity) and stereochemical outcome of alkylation. The conformational analysis of the reduced products (partially unsaturated six membered rings) is also being considered experimentally with proton and carbon NMR, as well as theoretically with force field calculations.

MARQUETTE UNIVERSITY
Milwaukee, Wisconsin 53233

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

This research is aimed at developing highly active and stable polymeric catalysts for use in aqueous/liquid organic two phase and aqueous/resin/liquid organic three phase reactions. Current effort is focusing on poly(ethylene glycols) and poly(ethylene glycol)-grafted copolymers as catalysts for promoting dehydrohalogenation, alkylation and saponification processes. Preliminary results indicate that significantly improved synthetic procedures are possible based on such catalysts, which should be amenable for a variety of laboratory as well as industrial applications.

UNIVERSITY OF NEBRASKA/LINCOLN
Lincoln, Nebraska 68588-0304

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

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, uranium, palladium, and platinum. The nickel powders have been found to react rapidly with benzylic halides and the resulting organonickel intermediate reacts with acid chlorides to yield benzyl ketones. Reactions of ROCOCOCl and benzylic halides with nickel powders yield dibenzyl ketones. These reactions proceed with a wide variety of substituents on the phenyl ring of the benzylic halides. Highly reactive uranium has been prepared and found to react with a variety of oxygen containing organic substrates such as nitrobenzene. Products are currently under investigation. Chemistry of cadmium, platinum, and palladium is also under investigation.

TEXAS A & M UNIVERSITY
College Station, Texas 77843

335. CATALYTIC BEHAVIORS OF MULTI-VALENT LANTHANIDE OXIDES $131,193 02-01
24 mo.
FY 83-84
Michael P. Rosynek
Department of Chemistry

This research program involves a systematic investigation of the influence exerted by selected lanthanide oxide supports, principally those of La, Ce, Pr, and Eu, on the catalytic behaviors of both well-dispersed (Pt, Ir, Rh) and poorly-dispersed (Fe, Co, Ni) transition metals, with a view toward identifying evidence for significant metal-support interactions. Supports being studied as a basis of comparison include silica, alumina, and titania. Catalytic behaviors of the various metals are being evaluated for appropriate diagnostic reactions, viz., CO hydrogenation and paraffin hydrogenolysis/dehydrocyclization, as a function of conditions and support identity. These results are being correlated with those of accompanying characterization studies, involving infrared and x-ray photoelectron spectroscopies, transmission and scanning electron microscopies, electron microprobe analyses, and selective chemisorption measurements, in an attempt to elucidate the nature and extent of metal-support interaction effects.

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

336. FUNDAMENTAL STUDY OF CATALYSTS USING LASER RAMAN, INFRARED, AUGER ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION $70,000 02-01
G. A. Sargent, Dept. of Met. Engr.
E. B. Bradley, Dept. of Elec. Engr.

The 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 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 was controlled by varying the gas pressure and exposure time. Surface dipoles (magnitude and orientation) are 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. Changes in band intensities are used to measure electric dipole orientation and thermal desorption characteristics. Thermal desorption experiments have been undertaken for each gas adsorbed on each surface using the linear temperature programming technique. The mass of the desorbed species is determined by a precision mass analyzer. The mass analyzer is also used to determine residual gas concentrations in the experimental chamber and to identify the structure of intermediate molecules.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

337. REDUCTION OF CARBON MONOXIDE — $215,000 — 02-01
Richard R. Schrock — 24 mo.
Department of Chemistry — FY 83-84

The object of this research is to learn how to reduce carbon monoxide catalytically and selectively to a two-carbon product such as ethanol, ethylene glycol, ethylene, or acetaldehyde. The approach is to discover how earlier transition metal hydride complexes can take part in unique reactions not possible with the later transition metals; i.e., what new principles of catalytic reduction of carbon monoxide remain to be discovered. The program involves the synthesis of new transition metal hydrido complexes and a detailed study of how they react with carbon monoxide. The program began with a study of a new dimeric tantalum hydrido complex which reacted with the carbon monoxide to give a μ-hydrido μ-formyl species. Analogous reactions employing metals which are less oxophilic are being sought. At present we are investigating some novel tungsten hydrido clusters and complexes containing linked cyclopentadienyl ligands including a late/early transition metal combination. The late/early transition metal complex is being tested for activity under typical syngas conditions.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

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

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. In addition, we have discovered the first catalysts for the room temperature copolymerization of carbon monoxide with olefins. The resultant polyketones constitute a new class of materials which are expected to have properties such as photo- and bio-degradability.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

339. STRUCTURE AND CHEMISTRY OF THE INTERACTION OF ORGANOMETALLICS WITH SURFACES — $90,000 — 02-01
Duward F. Shriver
Department of Chemistry

The objective of this research is to characterize organometallics attached to surfaces. The primary techniques include quantative analysis of gases evolved upon interaction of the organometallic with the surface, fourier transform infrared spectroscopy, Raman spectroscopy, and extended X-ray absorption fine structure. Initial studies will center on metal carbonyls attached to metal oxide surfaces. Parallel studies will be performed on molecular compounds which simulate the proposed surface species. Catalytic activity of some of the surface organometallics will be investigated.

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

340.	REACTIONS OF ALKYL PALLADIUM AND PLATINUM DIMERS. MECHANISMS OF DINUCLEAR ELIMINATION J. K. Stille Department of Chemistry	$65,000	02-01

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, palladium and rhodium complexes containing organic groups on adjacent bonded metals, and the reactions of these complexes, particularly the 1,2-reductive elimination rearrangement, oligomerizations and insertion reactions are being carried out. 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.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

341.	THE REACTIONS OF ELECTROPHILIC REAGENTS WITH BITUMINOUS COALS. THE CHEMISTRY OF THE REACTION PRODUCTS. Leon M. Stock Department of Chemistry	$81,061	02-01

The electrophilic reactions of bituminous coals are under investigation. Preliminary reactions with mercury (II), lead(IV) and ruthenium(VIII) have been carried out.
The plumbylation reaction of Illinois No. 6 coal yields a product which undergoes oxidative solvolysis to yield a material selectively enriched in aryl hydroxyl groups. The preliminary results suggest that this altered coal undergoes donor solvent liquefaction in tetralin to yield a product which is less soluble in pyridine but more soluble in hexane than the natural material.
The preliminary results of selective catalytic oxidations with ruthenium(VIII) are also most encouraging. Illinois No. 6 coal undergoes oxidation in 2 hours at ambient temperature in neutral solution in the presence of catalytic quantities of ruthenium(III) and an excess quantity of a cooxidant such as sodium periodate or sodium hypochlorite. About 225 different soluble carboxylic acid ester compounds are formed in the reaction.

THE PENNSYLVANIA STATE UNIVERSITY
University Park, PA 16802

342.	METAL-SUPPORT INTERACTIONS IN Ni, Pd, and Pt CATALYSTS M. Albert Vannice Department of Chemical Engineering	$81,564	02-01

This research proposal is directed toward a better understanding of the chemistry involved in the creation of metal-support interactions in certain systems, which have been found to have pronounced effects on adsorption and catalytic behavior. This is presumed to be due to modifications of the adsorbed state of reactant molecules, and this program involves a study of heats of adsorption and desorption energies for H_2, CO, and O_2 on Pt, Pd, and Ni using a modified differential scanning calorimeter and a thermal gravimetric analysis unit. Separate chemisorption experiments are being conducted in a volumetric adsorption system, and kinetic investigations being made on the hydrogen of carbon monoxide and aromatic hydrocarbons, beginning with benzene. Possible correlations between catalytic activity and adsorbate-metal bond strengths are being investigated. This multifaceted approach should provide a more complete explanation of both the much higher catalytic activities already found in certain reactions and the suppressed chemisorption which is observed after the SMSI state is induced. The possibility that special active sites are created at the metal-support interface is also being carefully examined.

YALE UNIVERSITY
New Haven, Connecticut 06511

343. ENERGIES OF ORGANIC COMPOUNDS $80,000 02-01
Kenneth B. Wiberg
Department of Chemistry

This research program is designed to provide information on the energies of organic compounds via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semi-empirical schemes for estimating energies of these compounds. The data also are being used to explore steric effects and other structural effects on energies. Reactions being studied include the hydration of alkenes, hydrolysis of ketals, reduction of ketones, and rearrangements of small ring hydrocarbons. Theoretical calculations (RHF) are being used to estimate energies of interesting compounds which have not as yet been prepared, and to obtain charge distributions which are needed in the semi-empirical calculations.

SRI INTERNATIONAL
Menlo Park, California 94025

344. ADSORPTION THERMODYNAMICS AND SURFACE TRANSPORT OF METAL CATALYSTS POISONS Total $71,997 02-01
Henry Wise and Jon McCarty
Materials Research Laboratory

This research has for its objective a fundamental understanding of the binding energy of sulfur and halogen adatoms to metal surfaces in order to relate catalysts poisoning and reactivation to covalent bond formation. The experimental measurements involve studies of equilibrium adsorption and surface diffusion on single crystals of different orientations and on highly dispersed metal catalysts. The techniques employed include classical studies of reversible adsorption at low surface coverages, Auger electron spectroscopy for diffusional transport, and low energy electron diffraction for determination of surface coordination and reconstruction.

UNIVERSITY OF PITTSBURGH
Pittsburgh, PA 15260

345. INFRARED STUDIES OF THE INFLUENCE OF ALKALI METALS ON THE C-O BOND IN CHEMISORBED CARBON MONOXIDE $186,555 19 mo. FY 82-83 02-01
John T. Yates, Jr.
Department of Chemistry

This research program is designed to probe the interaction of adsorbed alkali metals with adsorbed carbon monoxide on transition metal single crystal surfaces. Information obtained by Reflection IR Spectroscopy, X-Ray Photoelectron Spectroscopy, and Temperature Programmed Desorption will yield models of the interaction, and deeper understanding of the alkali promotion effects observed in catalytic chemistry on transition metals.

Chemical Energy, continued

ROCKWELL INTERNATIONAL
Canoga Park, California 91304

346. MOLTEN SALT INTERACTIONS IN COAL PROCESSING $160,000 02-01
S. J. Yosim and G. B. Dunks
Energy Systems Group

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. The current investigation is directed toward determining the effect of sulfur (a major constituent of coal) on the oxidation process. 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 mixed beds of sodium carbonate and sodium sulfate 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 TENNESSEE/KNOXVILLE
Knoxville, Tennessee 37996

347. SYSTEMATIC AND STRUCTURAL STUDIES OF POLYMERIC EXTRACTANTS FOR THE SEPARATION AND RECOVERY OF METAL IONS $46,913 02-02
Spiro D. Alexandratos
Department of Chemistry

The research is directed towards the synthesis and evaluation of polymer-supported extractants with emphasis on the properties of the polymeric support. In focusing on the development of polymeric extractants which will be commercially viable for large-scale applications to the recovery of strategically important metals and within nuclear waste reprocessing plants, the study is concerned with four major points: (1) develop an economical synthesis of the polymer support, (2) utilize polymers which display high chemical, mechanical, and radiation stability, (3) develop polymers with macroscopic properties allowing for a rapid rate of metal ion complexation, and (4) produce polymeric extractants with a high density of active sites in order to minimize bed volumes. The principle polymer support examined to date is polystyrene, in bead form, at various levels of crosslinker and macroporosity. Bonding phosphinic acid moieties to the styrenic network yields a polymer-supported extractant which is found to absorb large levels of metal ions from aqueous solutions even at low pH values.

Separations and Analysis, continued
UNIVERSITY OF MARYLAND
College Park, Maryland 20742

348. NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS $107,000 02-02
D. L. Anderson, G. E. Gordon,
W. B. Walters, and W. H. Zoller
Department of Chemistry

A low background thermal neutron-base facility has been constructed at the National Bureau of Standards (NBS) reactor for the purpose of elemental analysis in various matrices. Samples of masses of 10 mg to 2 g are placed in the beam and the prompt γ rays (0.1-11.0 MeV) are measured. The elemental concentrations of H, B, C, N, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Cd, Sm and Gd can be determined in many materials. The method is capable of measuring all major elements (except O) in most types of samples. Present studies include standardizing PCBs for Cl content, accurately measuring boron in scintered pellets used as burnable poisons in the startup cycle in power reactors, and the characterization of a number of USGS, NBS and IAEA geological and biological standards. Another study concerning the fate of boron in coal-burning is underway. Experiments using ^{252}Cf as a neutron source for a laboratory-based prompt-γ facility continue.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

349. CONTINUOUS REACTION CHROMATOGRAPHY $60,000 02-02
R. Aris
R. W. Carr
Department of Chemical Engineering
and Materials Science

Continuous reaction chromatography is a method for carrying out chemical reaction with simultaneous chromatography of reactants and products in a single continuous flow reactor. This can be accomplished by providing relative motion between the chromatographic packed bed and the feedstream. Investigations of the rotating cylindrical annulus for both liquid phase reaction - solid adsorbent and gas - solid catalytic reactions have been completed. Also, a detailed modelling study of the behavior of a countercurrent moving bed chromatographic reactor has been done. Experimental tests of a laboratory scale countercurrent moving bed reactor are being carried out. Analysis of reaction products is being done by conventional gas chromatography. Reactor performance is being compared with theoretical predictions.

BEND RESEARCH, INC.
Bend, Oregon 97701-8599

350.	FUNDAMENTALS OF COUPLED-TRANSPORT MEMBRANES Walter C. Babcock Membrane Separations Division	$91,786	02-02

The program objective 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 in the pores of a microporous polymeric support. This membrane separates two aqueous solutions of unequal concentrations. The complexing agent can pick up 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 efforts are focused on studying long-term performance of the membranes. The goal is to overcome problems of limited lifetime that are common with these membranes. Substantial progress has been made in developing a predictive model for the development of membranes with commercially practical lifetimes.

UNIVERSITY OF MASSACHUSETTS/AMHERST
Amherst, Massachusetts 01003/0035

351.	DYNAMICS OF, AND HEAT AND MASS TRANSFER IN, AN INDUCTION PLASMA Ramon M. Barnes Department of Chemistry	$60,000	02-02

This investigation involves the computer modeling and experimental verification of the inductively coupled plasma discharge operated at atmospheric pressure in argon and molecular gases. Calculation of flow and temperature fields for two major types of induction torches has been achieved with a new model using a velocity-pressure-temperature approach which has resulted in increased speed of convergence and stability. Conditions were simulated that were not possible with previous models. For argon and nitrogen discharges at 3 MHz, flow and temperature fields have been calculated for power levels between 5 and 20 kW and for central flows of 0 to 7 liter per minute. For spectrochemical torches at 0.75 kW, similar calculations were performed for frequencies between 13 and 40 MHz. In another calculation, flow and temperature fields were obtained including plasma particle interactions, especially heating loading effects and some changes of thermodynamic properties with vapor. Heavy loading of the 3 MHz plasma with up to 10 g/min Cu particles cooled the plasma, and extensive evaporation was observed with 40 micrometer particles. For alumina particles and water droplets only heat loading was considered. The particle interaction in the spectrochemical torch is being studied.

TEXAS TECH UNIVERSITY
Lubbock, Texas 79409

352.	METAL ION COMPLEXATION BY IONIC CROWN ETHERS Richard A. Bartsch Department of Chemistry	$112,500 21 mo. FY 83-84	02-02

The goals of this research are the synthesis of lipophilic crown ethers with pendant ionizable groups and the application of these compounds for selective metal ion complexation. A variety of lipophilic crown ether carboxylic acids are being prepared in which the following structural features are systematically varied: a) the size of the polyether cavity; b) the number and types of ethereal oxygens in the crown ether ring; c) the attachment site(s) for lipophilic groups; and d) the presence or absence of aromatic groups as polyether ring substituents. The first crown ether phosphonic and sulfonic acids are also being prepared. The efficiencies and selectivities of these lipophilic ionizable crown ethers in competitive solvent extraction, liquid surfactant (emulsion) extraction, and bulk liquid membrane transport of alkali and alkaline earth cations are being assessed.

AMHERST COLLEGE
Amherst, Massachusetts 01002

353.	ISOTOPE EFFECTS IN THE SOLUTION OF GASES IN LIQUIDS Bruce B. Benson Daniel Krause, Jr. Department of Physics	$47,080	02-02

The broad purpose of this research is to explore molecular interactions in dilute solutions of gases in liquids, especially water, by measuring the dependence of gas solubility on the isotopic masses of the solute and solvent. Measurements on the noble gases dissolved in H_2O have shown how the isotopic fractionation depends upon temperature, isotopic mass, and gas polarizability. Similar studies are being carried out on noble gas clathrate hydrates, in which the molecular structure of the hydrate is well known from x-ray analyses. A better understanding of the hydrogen bonded structure in liquid water may be obtained from a comparison of the extrapolations to 0°C of the results for the hydrates and liquid water. Gas solubilities in D_2O are being determined for comparison with previous results in H_2O

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

354.	FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY Jacob Bigeleisen Department of Chemistry	$98,000	02-02

Experimental and theoretical investigations are made of isotope effects in chemical and physical processes. When appropriate, applications are made to isotope separation processes and nuclear fuel cycles.Calculations have been made of the expected chemical properties of super-heavy isotopes of hydrogen, carbon, selenium and uranium as a guide in the search for such particles. Detailed calculations have been made of the separation expected of superheavy isotopic forms of CO by fractional distillation. Relations between the isotope chemistry of oxygen and molecular structure are being studied. Regularities are found by an analysis of the effect of isotopic substitution on the entropies and enthalpies of formation of the compound from the gaseous oxygen atom.

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

355.	SEPARATION OF SELECTED CATIONS BY LIQUID MEMBRANES James J. Christensen Department of Chemical Engineering Reed M. Izatt, Department of Chemistry	$64,754	02-02

Macrocycle-mediated cation transport using bulk, emulsion, and lipid vesicle liquid membrane systems is being investigated and modeled. In water-halocarbon-water bulk liquid membranes, proton coupled transport of alkali metal ions from two, three, and four cation mixtures is being studied using calixarene macrocycles as carriers. The relative fluxes of cations from cation mixtures in water-toluene-water emulsion membrane systems is under investigation using the carrier dicyclohexano-18-crown-6 and various complexing anions in the interior receiving phase. The transport in these emulsion systems of amphoteric metals as anionic species coupled to a pH gradient across the membrane is also being studied. Dicyclohexano-18-crown-6 is being incorporated into phospholipid vesicles as a means of making them selectively permeable to cations. The chemical and thermodynamic characteristics of the interaction of Pb^{2+} with these vesicles is being investigated.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

356. MULTIHETEROMACROCYCLES THAT COMPLEX METAL IONS $125,000 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. Rigid cyclic frameworks support attached heteroelements so their unshared electron pairs possess a convergent arrangement. Spherands are being studied whose cycles are composed of six to eight six-membered rings bonded to one another at their 1,3-positions, and carrying substituents in their 2-positions. Chorospherands are part crown and part spherand, and cryptospherands are part cryptand and part spherand. Spherands, chorospherands and cryptospherands are being studied which contain anisyl, pyridine, pyridine oxide, benzoquinone, thioanisyl, cyclic urea and benzenecarboxamide units. Metal ion and isotope-specific complexing agents are being sought.

BROWN UNIVERSITY
Providence, Rhode Island 02912

357. PHOTOCHEMICAL GENERATION OF THE OPTOACOUSTIC EFFECT $58,386 02-02
Gerald J. Diebold
Department of Chemistry

Research is being conducted into photochemical generation of the optoacoustic effect. The frequency, phase shift and amplitude dependence of the acoustic signal in nonlinear systems such as $C\ell_2$ are being experimenttally investigated. The effects of chemical inhibitors on the optoacoustic effect is also under investigation. The recently discovered chemical amplification of optoacoustic signals in chain reacting nonlinear systems is being extended to other photochemical systems that should be inherently linear. This should further establish the optoacoustic effect as a sensitive probe of photochemically generated exothermic reactions. In addition, a total internal reflectance optoacoustic effect is being studied for possible application as a spectroscopic or a trace detection method for gas phase species and bulk materials.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

358. FOURIER TRANSFORM PHOTOACOUSTIC SPECTROSCOPY $75,000 02-02
Edward M. Eyring
Department of Chemistry

Opaque solids of high surface area are being examined by Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS). Novel dopants (such as coordinative molybdenum and chromium carbonyls and trimethyloxonium salts) alter band gaps in electroconductive polymers such as polyacetylene, polyparaphenylene and their derivatives. Resulting infrared spectra are correlated with X-ray photoelectron spectra, solid state nuclear magnetic resonance spectra, and other spectral data to define the structure and reactivity of these materials. Multi-technique surface studies of high surface area heterogeneous catalysts such as sulfided $Co\text{-}Mo/Al_2O_3$ are also underway. Sample surfaces are selected for their properties that challenge the present capabilities of FT-IR/PAS and that force improvements such as photothermal beam deflection spectroscopy now also used in this laboratory.

Separations and Analysis, continued

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

359. REACTIONS OF METAL IONS AND THEIR CLUSTERS IN THE GAS PHASE USING LASER IONIZATION-ION CYCLOTRON RESONANCE SPECTROSCOPY — $82,127 — 02-02
Ben S. Freiser
Department of Chemistry

A laser ionization source is used in conjunction with ion cyclotron resonance spectroscopy to generate and study the gas phase chemistry of simple metal ions and their clusters. Using this technique metal ions are generated directly by focussing a high-powered pulsed laser onto the pure metal. The goals of this work have been 3-fold: determination of fundamental reaction mechanisms and trends in reactivity; comparison of gas phase to solution phase results; and development of metal ions as selective chemical ionization reagents. These goals have been pursued thus far in extensive studies of Cu^+ with esters and ketones, on Fe^+ with ethers and ketones, and on Fe^+, Ti^+, Co^+, Ni^+, Rh^+, V^+, Y^+, and Sc^+ with hydrocarbons. In addition work has been started on the effect of ligands on metal ion reactivity. Studies of $M\text{-}X^+$ ions, where X=O,S, CH_2, CH_3, and C_2H_4, for example, are well underway. This work has been catalyzed further with the acquisition of a Nicolet Fourier transform mass spectrometer (FTMS). Of particular importance is the application of collision-induced dissociation using FTMS to elucidate ion structures and reaction mechanisms.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

360. CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY — $74,286 — 02-02
Henry Freiser
Department of Chemistry

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.

UNIVERSITY OF MISSOURI
Rolla, Missouri 65401

361. AN EXTRACTION/SEPARATION PROCESS WITH EXTREME ENERGY EFFICIENCY — $63,564 — 02-02
S. E. Friberg and P. Neogi
Department of Chemistry

The purpose of this investigation is to examine the phase equilibria involved in an extraction/separation process with extremely low energy demand. The process uses the temperature dependent transitions of colloidal association structures in systems of water/polyethylene glycol dodecyl ethers/ aliphatic hydrocarbons to permit spontaneous extraction and separation with a temperature change of only 20°C. The main emphasis is placed on the role of liquid crystals to influence the kinetics of the extraction process.

UNIVERSITY OF VIRGINIA/CHARLOTTESVILLE
Charlottesville, Virginia 22901

362.	THE GLOW DISCHARGE AS AN ATOMIZATION AND IONIZATION SOURCE W.W. Harrison Department of Chemistry	$73,002	02-02

This project centers about the study of a glow discharge as an atomization and ionization source for trace element analysis of solids and solutions. Coupling of the glow discharge to a quadrupole mass filter results in a simple mass spectrometer system of considerable versatility. A variable duty pulsed discharge is being studied and shows advantages over direct current operation. The use of short, high intensity pulses produces enhanced sputter action and a greater ion yield. Time-resolved selection of ions generated only during the trailing pulse edge produces a strong atomic signal for the cathode sample with discrimination against background gases. The use of laser enhanced ionization within the glow discharge is also under investigation.

THE AEROSPACE CORPORATION
El Segundo, California 90245

363.	LASER FLUORESCENCE STUDIES OF METALLIC IONS IN FLAMES FOR IMPROVED DETECTION F. E. Hovis and J. A. Gelbwachs Chemistry and Physics Laboratory	$95,000 18 mo. FY 82-83	02-02

The use of fluorescence methods on neutral metal atoms in flames is a well established analytical technique. We propose to investigate laser induced fluorescence of metallic ions in high temperature flames for analytical applications. The first study involves the direct laser excitation of ionic fluorescence of the alkaline earth metals. A second experiment investigates neutral-ion energy transfer in metals as a means of sensitized ion fluorescence for multielement analysis. The use of sensitized ion fluorescence would allow simultaneous analysis of several metals using a single laser excitation line. The use of neutral-ion energy transfer is anticipated to yield superior detection limits to neutral-neutral energy transfer and to have good potential as a practical analytical tool. These studies will yield information of both practical and fundamental interest.

THE UNIVERSITY OF WYOMING
Laramie, Wyoming 82071

364.	SOLID SURFACE LUMINESCENCE ANALYSIS Robert J. Hurtubise Chemistry Department	$76,840	02-02

The main goal of this project is to develop a fundamental understanding of the physical and chemical interactions that induce strong room-temperature fluorescence and phosphorescence from organic compounds adsorbed on solid surfaces. Reflectance, infrared, nuclear magnetic resonance, and luminescence spectroscopy are being used to clarify the interactions. Luminescence polarization, and fluorescent and phosphorescent lifetime experiments are also being performed. The interactions in the initial wet solid-surface chemistry and their influence on the final luminescent signals in the dried solid matrix are being investigated. Experiments are being carried out to determine if the organic molecules are being held rigidly or if the solid matrix is preventing collisions with oxygen and water molecules. Basic and nonbasic nitrogen heterocycles and hydroxyl aromatics are being used as model compounds to develop total luminescence derivative spectroscopy as a new approach in organic trace analysis.

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

365. STABLE ISOTOPE STUDIES $108,370 02-02
Takanobu Ishida
Department of Chemistry

This project consists of basic studies of isotope effects (IE) and developmental investigations of methods for fractionating stable isotopes. A new mathematical method for directly correlating the zero-point energy (ZPE) to the forces and structures of molecules is applied to the ZPE of n-paraffins and the hydrogen/deuterium (H/D) IE in the ZPE of n-paraffins and halogen and oxygen compounds. A stainless steel packed column system is operated to determine ^{15}N separation characteristics of nitric oxide/dinitrogen trioxide process under pressures up to 15 atm. and temperatures between -15°C and 20°C. An electrochemical refluxer for the Nitrox ^{15}N separation process is developed to eliminate needs for chemical feeds and chemical waste disposal. Catalytic isotope exchange reactions between ammonia and hydrogen are studied. The ^{12}C/^{13}C and H/D vapor pressure isotope effects (VPIE) in liquid methlene difluoride and the ^{14}N/^{15}N and H/D VPIE in liquid and solid ammonia are measured using a differential manometry in a cryostat having a temperature stability and uniformity of one millidegree.

SAN DIEGO STATE UNIVERSITY
San Diego, California 92182

366. DEVELOPMENT AND OPTIMIZATION OF METHODOLOGIES FOR ANALYSIS OF COMPLEX HYDROCARBON MIXTURES $60,000 02-02
R. J. Laub
Department of Chemistry

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 the kinetics of mass transfer, 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. Also being studied are metal-modified silica LC packings, including in situ generation and alteration of the adsorbent surface. The utility of binary carriers in gas chromatography is being examined, where the second-interaction virial coefficients are predicted in advance from the McGlashan-Potter equation. Solute retentions are then calculated, where the separations achieved are a function both of the carrier pressure and composition. Work on establishment of a standard set of stationary phases for gas chromatography is being continued, where emphasis is being placed on newly-synthesized mesomorphic polysiloxane (MEPSIL) solvents.

University of Georgia
Athens, Georgia 30602

367. A Study of Mechanisms of Hydrogen Diffusion in Separation Devices $101,521 02-02
18 mo.
FY 82-83
M. Howard Lee
Department of Physics and Astronomy

This study centers on separating hydrogen from mixtures of light gases by means of diffusion through metals. The hydrogen diffusion is highly selective, showing nonclassical behavior. The metal-hydrogen systems have mean-field critical dynamics. To describe the hydrogen diffusion, a quantum mechanical model is constructed, based on cluster formation. The diffusion is regarded as a collective movement of clusters. The sizes of these clusters depend on interatomic forces and particle statistics. The observed reversed isotope effect is explained by different degrees of cluster formation in hydrogen and deuterium. The diffusion constants are calculated by solving the generalized Langevin equation via the method of recurrence relations.

KENT STATE UNIVERSITY
Kent, Ohio 44242

368. ADSORPTION AND DESORPTION OF HYDROCARBONS AT LOW CONCENTRATIONS $56,500 02-02
Richard Madey
Department of Physics

The aim of this research is to study the adsorption and diffusion of hydrocarbon gases through porous media adsorber beds. The approach involves calculations based on a mass-balance equation of the quantity of adsorbate adsorbed on an adsorbent, measurements of adsorption isotherms of hydrocarbons on activated carbon and polystyrene beads at selected temperatures, and studies of the dynamics of breakthrough curves with both a step-function and a pulse change of the input concentration. The breakthrough curves of binary mixtures exhibit interference phenomena where the output concentration of the weakly-adsorbed component increases above the input concentration until the other component elutes. An objective of this study is to provide a quantitative explanation of interference phenomena. The approach will be to obtain binary adsorption isotherms, to examine the mechanisms of intraparticle diffusion and longitudinal diffusion of the system, and to study the mathematical characteristics of the differential equation that governs the system.

UNIVERSITY OF MINNESOTA
St. Paul, Minnesota 55108

369. INTERFACIAL CHEMISTRY IN SOLVENT EXTRACTION SYSTEMS $80,000 02-02
Ronald D. Neuman
Department of Forest Products

This research project primarily aims at elucidating the interfacial behavior of extractant molecules and their interactions with metal ions using laser light-scattering techniques with a view to obtaining mechanistic insight into solvent extraction processes. Systematic investigations continue to examine the effect of pH of the aqueous phase, HDEHP concentration, and Ca^{2+} concentration on the interfacial properties of n-hexane/HDEHP/aqueous systems. The interfacial tension exhibits unusual behavior with increasing pH and suggests the presence of molecular aggregates. The fine structure of interfacial films is being examined by electron microscopy. Mass transfer studies on the extraction of Ca^{2+} from acidic aqueous solutions to n-hexane phase by HDEHP are being emphasized. Efforts are also being directed towards the study of spontaneous interfacial turbulence using Schlieren optical techniques. Attention is focusing on correlating interfacial properties with mass transfer rates and coalescence rates.

CALSPAN ADVANCED TECHNOLOGY CENTER
P.O. Box 400, Buffalo, New York 14225

370. ENERGY TRANSFER AND REACTION KINETICS OF VIBRATIONALLY PUMPED MOLECULES $49,000 02-02
J. William Rich
Physical Sciences Department

This is a program of experimental and analytical research into energy transfer and reaction kinetics of vibration-to-vibration (V-V) pumped molecules. Extreme V-V pumped vibrational population distributions in CO, NO and other gaseous species are produced by optical excitation. Special emphasis is being placed on isotopic enrichment reactions of V-V pumped CO, which yield products enriched in ^{13}C, ^{17}O, and ^{18}O. Processes limiting vibrational up-pumping in CO and NO are being studied, especially vibration-to-electronic energy transfer from the pumped ground electronic state of these molecules to low lying excited electronic states.

Separations and Analysis, continued

UNIVERSITY OF GEORGIA
Athens, Georgia, 30602

371. FUNDAMENTAL STUDIES OF SEPARATION PROCESSES — $ 77,445 — 02-02
L. B. Rogers
Department of Chemistry

There are three major areas of effort in this research. The first is concerned with the fundamental aspects of two different forms of liquid chromatography, adsorption and steric exclusion, especially with respect to interaction during a given separation. Non-porphyrin compounds of vanadium and nickel and commercial mixtures of oligomers of polystyrene are ideal solutes for these studies because each type of sample covers a wide range of molecular weights. A second area involves the identification of those non-porphyrin compounds using a variety of techniques. The third area is concerned with recycle chromatography, a promising approach to separations of isotopic species.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

372. INVESTIGATIONS ON MULTIPHOTON IONIZATION AND FAST-BEAM PHOTODISSOCIATION SPECTROSCOPY — $135,000, 24 mo., FY 82-83 — 02-02
David H. Russell
Department of Chemistry

The emphasis of this research program is the development of combined laser-mass spectrometry methods for probing the dynamics of dissociation reactions. The experimental hardware and techniques are being developed using model chemical systems which have been characterized by other experimental methods, e.g., $C_6H_6^{+\cdot}$, $C_4H_6^{+\cdot}$, $C_4H_4^{+\cdot}$, etc. Following these preliminary investigations, the experimental capabilities will be applied to chemical systems which this approach provides unique or unusual capabilities. These latter studies emphasize the structural characterization of large molecular systems (1,000-10,000 a.m.u.). These large molecules are ionized using fast-neutrals (8-10 KeV Xe) and fast-ions (8-10 KeV Cs^+), i.e., fast-atom bombardment (FAB) and secondary ion mass spectrometry (SIMS), directly from the solid state. Also, these latter studies will be performed using a high resolution tandem mass spectrometer (Kratos MS-50TA) with high mass range capabilities (3,000-5,000 a.m.u.) and a Fourier transform mass spectrometer (Nicolet FTMS-2,000).

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

373. COMPETITIVE ION KINETICS IN DIRECT MASS SPECTROMETRIC ORGANIC SPECIATION — $125,000 — 02-02
L. Wayne Sieck
Center for Chemical Physics

This research involves the measurement of fundamental properties of gas phase ions, including fragmentation and reaction mechanisms and rates, structures, and the thermochemistry associated with ionization, protonation, and reaction. This information is then used to suggest chemical ionization techniques which incorporate competitive ion kinetics and permit identification and/or assay of specific compounds or classes of compounds occurring in complex organic mixtures. The experimental program utilizes the NBS pulsed high pressure mass spectrometer system as the prime facility, and an ion cyclotron resonance instrument is also available. Work-in-progress includes determinations of enthalpies of protonation, hydration, and solvation of complex amines, ethers, and sulfur compounds, as well as systematic studies of the unimolecular kinetics associated with ion pyrolysis.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

374. MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES $67,000 02-02
S. A. Stern
Department of Chemical Engineering and Materials Science

The objective of this study is to obtain a basic understanding of the mechanisms of gas permeation through nonporous polymer membranes. A "free-volume" model of gas permeation was found to describe satisfactorily the transport of many gases and of a number of gas mixtures through polyethylene membranes. The model is applicable at temperatures above T_g, the glass transition of the polymer, over a wide range of pressures. The validity of the model is being tested with other polymer membranes. Simple correlations of free-volume parameters have been developed. These correlations permit the prediction of diffusion and permeability coefficients for many gases and components of gas mixtures; solubility data are also required for this purpose. The gas permeation model has been extended to glassy polymers by incorporating in it the "dual-sorption" behavior observed below T_g. The extended model is being examined by means of "time-lag" and absorption-desorption measurements with a number of gases in poly(*n*-butyl methacrylate) over a temperature range encompassing T_g.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

375. SELECTIVE METAL ION EXTRACTION FOR MULTIPLE ION LIQUID-LIQUID EXCHANGE REACTIONS $82,000 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 equilibria models for the system copper-iron-acid sulfate solutions extracted by β-alkenyl-8-hydroxy quinoline-xylene system are being determined. Iron extraction data have been obtained and analyzed to obtain a chemical equilibrium model. Kinetic experiments for the forward rate of the iron extraction are completed employing the liquid jet recycle reactor. Various models based on interfacial reaction mechanisms are under consideration. A one liter flow reactor system was designed, erected, and commissioned to acquire conversion and selectivity data. The system contains a photomicrographic assembly for drop size measurements, in situ membrane filtration for phase separation, and all wetted surfaces are inert to the process fluids. Simulation programs for predicting the extractor performance are on file to test the veracity of kinetic and extractor design models.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

376. PARTICLE DEPOSITION IN GRANULAR MEDIA $92,000 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

377.	MECHANISMS OF CAKE FILTRATION Frank M. Tiller Chemical Engineering-Univ. of Houston Maher Tadros Martin-Marietta Laboratories	$164,108	02-02

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 and integration of the areas of pretreatment, thickening, and separation are objectives of the research. A rough predictive method for calculating parameters involved in functions relating porosity and permeability to effective pressure has been developed. Quantities used in the correlations include, particle size and shape and degree of aggregation. An apparatus for simulating a continuous thickener by partially fluidizing a bed of fine particles has been developed. Initial cake structure of deposits as affected by surface charge, suspension concentration, and agitation is being studied in relation to resistance to flow. Pressure distributions are used to study flow mechanisms and fine particle migration. The theory of centrifugal filtration of compressible cakes has been developed.

COLUMBIA UNIVERSITY
New York, New York 10027

378.	UTILIZATION OF MAGNETIC EFFECTS AS A MEANS OF ISOTOPE ENRICHMENT Nicholas J. Turro Department of Chemistry	$62,000	02-02

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 restricted space provided by porous silica has proven to be an excellent environment for efficient separation of ^{13}C and ^{12}C based on the photolysis of dibenzyl ketone. It should now be possible to design a practical system to separate these isotopes.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

379.	STUDIES OF ISOTOPIC MASS EFFECTS IN CHEMISTRY Max Wolfsberg Department of Chemistry	$75,000	02-02

This project deals with theoretical studies of isotopic mass effects on molecular properties. Such work is usually carried out within the framework of the Born-Oppenheimer approximation. Exact expressions for the complete quantum mechanical Hamiltonian operator of molecules are being constructed to study this approximation. Statistical mechanical calculations of isotope effects on a variety of molecular properties require a knowledge of rotational-vibrational energies of molecules and of isotope effects on these energies. Such energies are being calculated by the variational method for formaldehyde, hydrogen cyanide and other molecules. The tunnelling phenomenon and isotope effects on tunnelling are being studied by an investigation of the vibrational energy levels of molecules with double-minimum potentials. Molecular dynamics calculations are being carried out on solutions of rare gases in water to elucidate isotope effects on Henry's law constants. The difference between gas phase and condensed phase infra-red spectra is being studied in connection with isotope effects on vapor pressures.

Separations and Analysis, continued

THE AEROSPACE CORPORATION
Los Angeles, California 90009

380. ISOTOPICALLY SELECTIVE, TWO-STEP, LASER PHOTODISSOCIATION OF MOLECULES $107,597 02-02

P. F. Zittel
Chemistry and Physics Laboratory

This research program is directed toward understanding those photophysical, energy transfer, and chemical processes relevant to isotope separation by two-step laser photodissociation of small molecules. The two-step technique involves the vibrational excitation of molecules containing a chosen atomic isotope with an infrared laser, followed by ultraviolet laser photodissociation and scavenging of the photofragments. A computer-interfaced, dual beam, IR absorption apparatus is used to measure the absorption of intense IR laser pulses as a function of pressure and laser fluence. Mass spectrometric analysis of the photoproducts of the subsequent UV photodissociation step reveals the effect of vibrational excitation on the photodissociation cross section and gives the isotope enrichments. Of particular interest are measurements of vibrationally state specific photodissociation cross sections for different vibrational modes. Two-step photodissociation of OCS has led to the separation of all stable isotopes of O, C and S, to a determination of the dependence of the 249 nm photodissociation cross section on the amount of ν_2(bending) vibrational excitation, and to a rate constant for the exchange of bending vibrational energy between different isotopic varieties of OCS.

Chemical Engineering Sciences

STANFORD UNIVERSITY
Stanford, California 94305

381. TRANSPORT CHARACTERISTICS OF SLURRIES IN PIPELINES: FLOW REGIMES AND PRESSURE DROP No Fund Extension 02-04

Andreas Acrivos
Department of Chemical Engineering

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. It is believed that this resuspension is due to the action of a shear induced diffusion of particles, and attempts are currently being made to measure the corresponding diffusion coefficient. The possible connection between this shear induced diffusion and the measured normal stresses in the suspension is being investigated.

COLUMBIA UNIVERSITY
New York, New York 10027

382. INTERACTION OF TURBULENCE and CHEMICAL REACTIONS $85,000 02-04
Rene Chevray
Department of Mechanical Engineering

Flow in a two-dimensional mixing layer is utilized to study a well known reaction with simple kinetic scheme. The flow represents a well-defined turbulent situation and additional complexities of finite heat release are avoided by use of small concentrations for the reaction chosen ($NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu + O_2$). Large Reynolds numbers, small dilution numbers, large reaction speed numbers and several concentration ratios are investigated. Conditional and conventional measurements are made of mean and fluctuating quantities for both the velocity and concentration fields by laser Doppler anemometry and absorption sprectroscopy, respectively. Simultaneous cinefilm recording is conducted in order to determine the convection velocity of the interface and hence the entrainment. Numerical simulation is set up to model directly the equations describing the evolution of the species concentrations in the shear layer.

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

383. PREDICTION OF THERMODYNAMIC PROPERTIES FOR COAL DERIVATIVES $81,000 02-04
Marc D. Donohue
Department of Chemical Engineering

The purpose of this project is to develop an equation of state to predict the thermodynamic properties of coal derivatives. The equation is based on perturbed-hard-chain theory but includes additional terms for multi-pole interactions. The equation allows prediction of vapor pressures, densities, 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 available. The applicability of the new equation to supercritical fluid extraction is being studied. Hydrogen bonding effects are being taken into account to predict properties of systems containing H_2O, alcohol, etc. High pressure vapor-liqui equilibrium measurements for CO_2- aromatic binary mixtures are being made.

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

384. STATISTICAL MODELING AND ANALYSIS OF CHEMICALLY REACTING TURBULENT FLOWS — $145,000 — 02-04
24 mo.
FY 82-83
H. A. Dwyer
W. Kollmann

The research program is aimed at developing new turbulent closure models for variable density turbulent flows and turbulent diffusion flames. The techniques used to accomplish this goal are physical and mathematical modeling and sensitivity analysis. The physical and mathematical modeling studies have focused on density-velocity correlations in flows with pressure gradients and conditional statistics for modeling boundary intermittency. Also, the existing models have been applied to new experimental measurements with good results. The other effort of sensitivity analysis has been applied to both the compressible and incompressible round jet for the k-ε model. It has been shown that the conservation properties of the turbulent jet dominate the turbulence modeling, and that the turbulent jet has similar sensitivities to all turbulent model coefficients.

NATIONAL BUREAU OF STANDARDS/BOULDER
Boulder, Colorado 80303

385. EXPERIMENTAL AND THEORETICAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF FLUID MIXTURES — $195,000 — 02-04
Howard J. M. Hanley
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 to 520 K are available. The temperature range is being extended. A VLE/LLE phase equilibria apparatus is undergoing testing: preliminary results will be forthcoming for water/alcohol systems. Phase equilibria VLE measurements of the system CO_2/i-butane have been completed. Theoretical studies include computer simulation of fluids under shear. Studies are underway to investigate shear induced melting.

STANFORD UNIVERSITY
Stanford, CA 94305

386. FUNDAMENTAL STUDIES OF HEAT TRANSPORT, FLUID MECHANICS, AND STABILITY IN POROUS MEDIA — $84,789 — 02-04
George M. Homsy
Department of Chemical Engineering

This program treats problems in flow and transport phenomena in porous media whose solutions are of interest in energy recovery processes. Broad categories of activities include macroscopic and microscopic descriptions. Regarding former, theoretical and experimental studies of the effect of graded mobility on instabilities of displacement fronts have continued. The theory is being extended to study important effects of flow-induced dispersion and adsorption loss of the mobility control agent. Preliminary experiments in a Hele-Shaw cell have been completed, showing the stabilization of displacements due to mobility gradation. A theory of finite - amplitude thermally driven instabilities in bounded porous regions has been completed which determines the form of convection which will be observed. Microscopic studies of two phase Hele-Shaw flows have been completed with good agreement between theory and experiment. Microscopic modelling of non-Newtonian flow in porous media has been studied, indicating that constitutive equations of the Oldroyd type are incapable of capturing the salient experimental features of these flows.

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

387. THERMODYNAMIC STUDY OF CO_2-ORGANIC COMPOUND INTERACTION AT HIGH PRESSURES AND TEMPERATURES. $129,982 24 mo. FY82-83 02-04
Reed M. Izatt, Department of Chemistry,
James J. Christensen, Department of Chemical Engineering

This research program is designed to gain increased understanding of the energetics associated with chemical interactions involving supercritical fluids. Emphasis is placed on reactions involving CO_2, Freons, and hydrocarbons. The quantities measured include heats of mixing of binary systems and heat capacities of individual components and mixtures. Flow calorimeters capable of operating to 673 K and 15 MPa are used to obtain the necessary experimental data. The variation of each measured quantity over the temperature and pressure ranges studied is described using equations involving existing theory and further theoretical development in our laboratory with particular emphasis given to critical point regions of the interacting fluid components.

THE CITY COLLEGE, C. U. N. Y.
New York, New York 10031

388. TURBULENCE AND THE DISTORTION OF REACTIONS $50,000 02-04
Joseph A. Johnson III
Department of Physics

Contact surfaces in a pressure-driven shock tube are used as a way of investigating the possibility of the manipulation of molecular recombinations. Turbulent bursts are produced. The reaction $2NO_2+X \rightarrow N_2O_4+X$ ($X=N_2$ or Ar) is unstable under some circumstances; fluctuations with amplitude incoherence and phase coherence are developed. Here, the use of standard reaction rate data proves to be inadequate. The histories of flow and mixture properties are determined using cross-beam correlations and fluorescence of NO_2 probed by the 4.88 nm line from an Ar^+ ion laser. The importance of the dynamical parameters of of turbulence is being measured, specifically, the impact of changing local viscosity, characteristic turbulence scale, and turbulence intensity. In addition, there is some speculation that reduced molecular chaos may te relevant to this kind of process. This possibility is given a quantitative formulation and tested in our data.

NATIONAL BUREAU OF STANDARDS
Washington, D. C. 20234

389. 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).

Chemical Engineering Sciences, continued

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

390.	TRANSPORT PROPERTIES OF MULTIPHASE SYSTEMS George Stell Department of Mechanical Engineering	$165,000 24 mo. FY 83-84	02-04

Ongoing research continues on the microscopic theory relating transport and structure in two-phase composite media, including new results on expected surface area and on quantitative comparisons of bounds and approximations that involve two-particle and three-particle correlations in such media. Research also continues on new statistical mechanical theories of transport at both liquid-state and gaseous-state densities. The liquid-state work includes the use of an entropy-maximization technique that leads to new quantitatively useful approximations for transport coefficients in the liquid state. The gaseous-state work includes the development of analytically tractable kinetic perturbation theories for useful model potentials. Finally, a kinetic approach to the theory of mixtures of interacting n-mers has yielded new exact results in the description of the gelation point and the post-gelation period for models that include and go beyond that of the Flory-Stockmayer theory.

CORNELL UNIVERSITY
Ithaca, New York 14853

391.	EXPERIMENTAL AND THEORETICAL STUDIES OF DENSE FLUID MIXTURES W.B. Streett and K.E. Gubbins School of Chemical Engineering	$180,000 24 mo. FY 82-83	02-04

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 in progress includes measurements of the PVT properties of CF_4 from 120 to 230 K and pressures to 1000 bars. The direct-weighing PVT apparatus, designed and built under this project, has been completely redesigned and reconstructed to extend the temperature and pressure ranges to 0-600 C and 0-2000 bars, respectively. Theoretical work has included development of statistical mechanical methods for calculating properties of fluid mixtures containing hydrogen, at pressures up to 1000 bars. These methods are tested against experimental phase equilibrium and PVT data measured by our group.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

392.	DYNAMICS OF VAPOR EXPLOSIONS B. Sturtevant Graduate Aeronautical Laboratories	$46,050	02-04

An experimental program to study an interfacial instability driven by rapid evaporation is continuing. The mechanism for the instability, which was discovered in previous experiments under this grant examining the vapor explosion of liquid butane heated to its superheat limit, is similar to that of the Landau instability of laminar flames. The previous experiments showed that the instability can cause the effective rate of vaporization of a single droplet of butane to be orders of magnitude greater than would be predicted by conventional theories of evaporating spherical bubbles. Recent calculations using an ad hoc Landau model have shown that the instability may be very sensitive to the ambient pressure, suggesting a method for controlling its effects. Presently, experiments are underway in a new apparatus that can be pressurized, in order to study the dependence of the vapor explosion of droplets of pentane on ambient pressure. Preliminary measurements of blast pressures indicate that the explosion is indeed qualitatively different at elevated pressures than it is at atmospheric pressure.

Basic Energy Sciences outlay funds are divided among operating, equipment and construction fudns. 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 1983 Equipment Funds were assigned as follows.

	Equipment Funds (K$)
Ames Laboratory	335
Argonne National Laboratory	885
Bartlesville Energy Technology Center	12
Brookhaven National Laboratory	1,383
Idaho National Engineering Laboratory	12
Lawrence Berkeley Laboratory	918
Lawrence Livermore National Laboratory	13
Los Alamos National Laboratory	52
Mound Facility	71
Notre Dame Radiation Laboratory	193
Oak Ridge National Laboratory	562
Pacific Northwest Laboratory	90
Pittsburgh Energy Technology Center	6
Sandia National Laboratories/Albuquerque	29
Sandia National Laboratories/Livermore	905
Solar Energy Research Institute	44

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 research resources for the general scientific community and qualified scientists from laboratories outside the host laboratory are encouraged to make use of them. However, any activity which can be carried out through commercially available laboratories is not appropriate for these DOE supported facilities.

The process by which an off-site scientist can 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. With the latter, the process is based on the need for collaboration by the off-site scientist with one or more in-house staff members.

Each of the facility summaries also gives the names of individuals to contact for further information, a general description of the facility and a list of technical data on the primary available instrumentation.

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 SPECTROSCOPY 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 2500-8500Å range and to produce coherent radiation between 1180 and 1250 Å 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 (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 x 10^5
5-meter Czerny-Turner spectrograph	>10^6
Tunable dye lasers	>10^6
Vacuum-ultraviolet coherent source	>10^7

Wavelength range, Å

30-foot Paschen-Runge spectrograph	2000-9000
5-meter Czerny-Turner spectrograph	1200-9000
Tunable dye lasers	2500-8500
Vacuum-ultraviolet coherent source	1180-1250

Physics Division
Argonne National Laboratory
Argonne, 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

Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

PREMIUM COAL SAMPLE PROGRAM

The purpose of the Premium Coal Sample Program is to provide the coal science research community with long term supplies of a small number of premium coal samples that can be used as standards for comparison. The premium coal samples produced from each coal and distributed through this program will be chemically and physically as identical as possible, have well characterized chemical and physical properties, and will be stable over long periods of time. Coals will be mined, transported, processed into the desired particle and sample sizes, and packaged in environments as free of oxygen as possible while maintaining the natural moisture content in order to insure that the coals will be in as pristine and stable a condition as possible.

AVAILABILITY

Initial samples are expected to be available in early 1984. Samples will be made available to research personnel at a nominal replacement cost. A very limited quantity of lump coal, stored under similar inert conditions will be available on special request for special physical property measurements. Distribution of these samples will be guided by policies established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres
Chemistry Division, Bldg. 200
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Phone: (312) 972-7374
FTS: 972-7374
Telex: TWX 910-258-3285 USDOE-CH ARGN

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 25 picoseconds to 10 microseconds. In liquids, transient concentrations up to 20 micromolar may be generated with the 25 picosecond pulse and concentrations in excess of 10 millimolar may be generated with the longest pulse. Instrumentation for measurement of 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
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

(312) 972-3471
FTS 972-3471

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 - 100 ns .25 - 10 microseconds

National Synchrotron Light Source
Brookhaven National Laboratory
Upton, N.Y. 11973

NATIONAL SYNCHROTRON LIGHT SOURCE

The National Synchrotron Light Source (NSLS) facility consists of a 750 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. A 6 pole superconducting wiggler magnet and a 38 pole permanent magnet undulator have been constructed, and several wiggler and undulator magnets are presently being designed which will significantly increase the photon intensity and brightness.

The NSLS is a facility where a wide range of reseach 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, radiography, fluorescence, interferometry, gas phase spectroscopy, photoemission, radiometry, 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.

PERSON TO CONTACT FOR INFORMATION

R. Klaffky (516) 282-4974
NSLS - Bldg. 510E (FTS) 666-4974
Brookhaven National Laboratory
Upton, New York 11973

National Synchrotron Light Source, BNL, continued

TECHNICAL DATA

Facilities	Key Features	Operating Characteristics
VUV electron storage ring	high brightness, continuous wavelengh range ($\lambda > 5$ Å) 16 beam ports.	0.75 GeV electron energy
X-ray electron storage ring	high brightness, continuous wavelength range ($\lambda > .5$ Å) 28 beam ports	2.5 GeV electron energy

Instruments

Monochromators:	
plane grating	$12\ \text{Å} < \lambda < 1500\ \text{Å}$; high resolution
zone plate	$8\ \text{Å} < \lambda < 100\ \text{Å}$; moderate resolution
toroidal grating	$10\ \text{Å} < \lambda < 2500\ \text{Å}$; high intensity, moderate and high resolution
extended range grasshopper	$20\text{Å} < \lambda < 2000\text{Å}$; high resolution
Wadsworth	$300\ \text{Å} < \lambda < 3000\ \text{Å}$; high intensity, moderate resolution
Seya & Czerny Turner	$1200\ \text{Å} < \lambda < 12000\ \text{Å}$; high intensity, moderate resolution
two crystal	$.04\ \text{Å} < \lambda < 2500\ \text{Å}$; high resolution, fixed exit beam
two crystal/two grating	$2.5\ \text{Å} < \lambda < 2500\ \text{Å}$; high resolution, fixed exit beam
Six circle spectrometer/ diffractometers	high positional and rotational accuracy
Experimental stations	photoemission, magnetic circular dichroism, fluourescence, gas phase spectroscopy, microscopy, lithography, holography, EXAFS, inelastic scattering, crystallography, radiometry, topography, small angle scattering
Superconducting wiggler	$\lambda > .1$ Å; high intensity
Permanent magnet undulator	$100\ \text{Å} < \lambda < 1000\ \text{Å}$; high intensity and brightness

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 $\sim$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
Notre 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	±5 mhos/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 faciltiy is used for both quantative 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° 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 both the development and applications 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 acommodating 250 people, a laboratory building housing 14 independent experiments, special facility laser systems, a dedicated VAX computer, and access to a Cray computer.

The facility is located in the San Fransicso 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 scientists with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are opportunities for faculty, post-doctoral scientists, 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

Dan 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 Feautures
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	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	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 (continued)

Universities (continued)

Industrial and Other Laboratories

INVESTIGATOR INDEX

United States
Department of Energy
Washington, DC 20545