

# Chemical Sciences Division

# ANNUAL REPORT 1991



September 1992

Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

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# **CHEMICAL SCIENCES DIVISION**

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## REMARKS BY THE DIVISION DIRECTOR

The Chemical Sciences Division (CSD) is one of ten research Divisions of the Lawrence Berkeley Laboratory, a Department of Energy National Laboratory. The CSD is composed of individual groups and research programs which are organized into five scientific areas: Chemical Physics, Inorganic/Organometallic Chemistry, Actinide Chemistry, Atomic Physics, and Physical Chemistry. The CSD is unique in that a good deal of our Division's research activity occurs in laboratories located on the campus of the University of California at Berkeley, involving students and faculty in the Department of Chemistry. Several large programs, notably the Actinide Chemistry Program and the Atomic Physics Program, are based at the Lawrence Berkeley Laboratory (LBL) site just east of and above the University campus. The two sites, the campus and the Laboratory, are linked by an efficient minibus system that transports students, faculty, staff, and visitors between the two institutions.

To the Laboratory and the Division the benefits of close ties with the campus are broad and numerous. One of the most important of these is the vigor, dedication, and high productivity that graduate student research assistants bring to our various research projects. In addition, the Laboratory has a staff of highly skilled engineers and crafts technicians who support the scientific mission, and it is the site of several major, world-class user facilities such as the Advanced Light Source (ALS). Combined, the two institutions represent a highly enriched research environment, attracting a large number of eminent scientists and leaders from all over the world—many of whom have close associations with the Chemical Sciences research programs.

In FY 1991 the Division continued to advance the Combustion Dynamics Initiative in support of DOE's national role in combustion research and chemical science. In conjunction with researchers at Sandia National Laboratories, the Division proposed the initiative to develop the knowledge and technology base needed to help solve the nation's combustion-related problems of the 21st century. The Laboratory's focus is on fundamental advances in understanding the structure and reactivity of critical reaction intermediates and transients and the dynamics of elementary chemical reactions. At this writing the initiative envisions both experimental and theoretical efforts that would lead to accurate and reliable models for predicting combustion properties to improve the design of engines, burners, and other combustion

devices. In FY 1991 the initiative was presented to the University of California President Gardner's "Scientific and Educational Advisory Committee" (SEAC) which recommended funding and characterized it as a "highly promising and very appropriate initiative which builds on the existing strength of Berkeley's campus faculty and LBL's long tradition in scientific instrumentation." Much of the leadership for this project, and to the Division, were due to Norman E. Phillips who served as the Chemical Sciences Division Director until October, 1991. We are much indebted to his efforts over the years.

Also, thanks to Norman Phillips' considerable energies, the Division participated strongly in the upgrading of the environmental health and safety program at the Laboratory. We continued to make substantial progress, particularly in the areas of corrective actions, staff training, and in the conduct of our operations. All staff is to be commended for the dedication and zeal with which they participated in training programs, conducted inspections in their laboratories, and corrected weaknesses or implemented needed changes. The effort was time-consuming and costly, but everyone agreed that it was eminently worthwhile and have carried that spirit into ongoing practice.

Awards and honors received by CSD investigators in FY 1991 include:

- Neil Bartlett received the American Chemical Society Award for Creative Work in Fluorine Chemistry.
- Robert G. Bergman was a Kolthoff Lecturer at the University of Minnesota.
- Y.T. Lee was an Acheson Series Lecturer at the State University of New York, a NASA Lecturer at the Case Western University, a Linus Pauling Lecturer at the California Institute of Technology, and a Stevenson Lecturer at the Washington State University.
- C. Bradley Moore received the U.C. Berkeley Staff Assembly Excellence in Management Award.
- David A. Shirley was a Cohen-Ofer Memorial Lecturer at the Hebrew University.

Charles B. Harris  
Division Director  
Chemical Sciences Division



# FUNDAMENTAL INTERACTIONS

## PHOTOCHEMICAL AND RADIATION SCIENCES

### Photochemistry of Materials in the Stratosphere\*

*Harold S. Johnston, Investigator*

#### INTRODUCTION

This research is concerned with global change in the chemistry of the atmosphere, including theoretical and experimental gas-phase and heterogeneous photochemistry.

Five graduate students completed their work on this project during the last 1.5 years and prepared 13 draft articles based on their theses. These draft articles were between 10% and 90% ready for submission to journals. Since retiring from teaching at the University of California on July 1, 1991, the principal investigator on this project has put major effort into revising these draft papers for submission to the journals. Also, the principal investigator has studied the problem of stratospheric sulfate aerosols and their possible role in activating chlorine chemistry in the global lower stratosphere and has proposed a new mechanism involving nitrosyl sulfuric acid,  $(\text{ONO})(\text{HO})\text{SO}_2$  or  $\text{NOHSO}_4$ , in converting inactive  $\text{HCl}$  to photochemically active  $\text{ClNO}$ . The thermodynamic and kinetic, necessary and sufficient conditions are worked out for the occurrence of this heterogeneous catalytic process.

The principal investigator is an advisor to the Upper Atmosphere Research Program, Atmospheric Effects of Stratospheric Aircraft, of the National Aeronautics and Space Administration (NASA).

#### 1. Fluorescence of Nitrate Free Radical (Publication 7)

*B. Kim, P.L. Hunter, H.S. Johnston*

The fluorescence emission spectra of  $\text{NO}_3$  excited at 14742, 15109, 15882, 16053, and 16555  $\text{cm}^{-1}$  are reported. On the basis of fundamentals, overtones, and combination

of five vibrational frequencies (368, 753, 1053, 1500, and 2010  $\text{cm}^{-1}$ ), we assign 18 out of 20 observed bands. The fluorescence bands exhibit two different shapes, one shows a sharp spike overlapped with a broad band, and the other shows a broad band only. From the literature a potential energy surface is obtained that has  $\text{D}_{3h}$  symmetry with three identical shallow minima each representative of a local  $\text{C}_{2v}$  structure and located with three-fold symmetry around the central axis. Such a potential energy function can split degenerate  $\text{D}_{3h}$  vibrational modes, giving "pseudo-rotations," as a structure with one long and two short bonds permutes around the three minima. On the time scale of molecular rotations, vibrational motions average over the three local  $\text{C}_{2v}$  structures to give  $\text{D}_{3h}$  structure and rotational spectra. This model qualitatively explains both the 5 fundamental frequencies observed by fluorescence and the definite  $\text{D}_{3h}$  properties of high resolution infrared spectra.

#### 2. Stratospheric Photochemistry and Proposed Supersonic Aircraft (Publication 2)

*H.S. Johnston, M.J. Prater, and R.T. Watson*

The steady-state distribution of natural stratospheric ozone is primarily maintained through production by ultraviolet photolysis of molecular oxygen, destruction by a catalytic cycle involving nitrogen oxides ( $\text{NO}_x$ ), and relocation by air motions within the stratosphere. Nitrogen oxides from the exhausts of a commercially viable fleet of supersonic transports would exceed the natural source of stratospheric nitrogen oxides if the aircraft should be equipped with 1990 technology jet engines. This model-free comparison between a vital natural global ingredient and a proposed new industrial product shows that building a large fleet of passenger stratospheric aircraft poses a significant global problem. NASA and aircraft industries have recognized this problem and are studying the redesign of jet aircraft engines in order to reduce the nitrogen oxides emissions. In 1989 atmospheric models identified two other paths by which the ozone destroying effects of stratospheric aircraft might be reduced or eliminated: (1) *Use relatively low supersonic Mach numbers and flight altitudes.* For a given rate of nitrogen oxides injection into the stratosphere, the calculated reduction of total ozone is a strong function of altitude, and flight altitudes well below 20 kilometers give relatively low calculated ozone

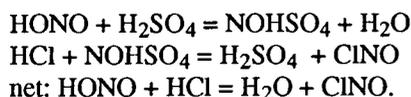
\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

reductions. (2) *Include heterogeneous chemistry in the two-dimensional model calculations.* The first test of this suggestion, made in 1991, included a single heterogeneous reaction and gave results encouraging for the future of stratospheric aviation.

### 3. Heterogeneous Reactions in the Stratosphere (Publication 9)

*J.D. Burley and H.S. Johnston*

From information found in the atmospheric and chemical literature, it appears that nitrosyl sulfuric acid (NSA),  $\text{NOHSO}_4$ , may play an important role in stratospheric chemistry. NSA is formed from several reactions between  $\text{NO}_y$  species and sulfuric acid, if the acid is above 70 wt% at room temperature and above 60% at stratospheric temperatures. NSA is a nonvolatile solid, melting at 346 K and boiling with decomposition at 633 K. Over a period of time, it could accumulate as a solution in the liquid aerosol, and upon reaching solubility saturation (about 3% under lower stratospheric conditions) precipitate out as solid crystals, which permits indefinite further accumulation. In one study, stratospheric NSA has been observed as a slurry of crystals in about a third of the particles collected between 15 and 20 km. If the reaction probability per collision of NO is  $10^{-4}$ , 20% of the sulfuric acid would be converted to NSA within three months at 20 km altitude. At room temperature, HCl gas reacts with NSA, either the solid or in sulfuric acid solution, to form gaseous nitrosyl chloride, ClNO, which is rapidly photolyzed in the atmosphere to nitric oxide and atomic chlorine. HONO is one of many reactants that form NSA; its reaction is the simplest expression of this heterogeneous catalytic cycle:



The catalytic cycle is thermodynamically favorable under stratospheric conditions if the unknown value of  $\Delta_f G_{298}^\ominus(\text{NSA})$  is between  $-505$  and  $-535$   $\text{kJ mol}^{-1}$  and  $S_{298}^\ominus(\text{NSA}) \approx 142$   $\text{J mol}^{-1} \text{K}^{-1}$ . If the second order rate constant for  $(\text{HCl} + \text{NOHSO}_4 = \text{H}_2\text{SO}_4 + \text{ClNO})$  in sulfuric acid solution is greater than  $5 \times 10^{-18}$   $\text{cm}^3 \text{molec.}^{-1} \text{s}^{-1}$  at 20 km altitude, the rate of reaction of HCl with NSA is faster

than that with hydroxyl radicals. In this case, this heterogeneous catalysis is expected to affect the balance of nitrogen species, chlorine species, and ozone in the lower stratosphere. The  $\text{NOHSO}_4$  mechanism calls for new laboratory studies, new atmospheric observations, and new atmospheric modeling. To carry out some of these needed studies, this project is collaborating with CSD investigators at Berkeley and with others at Livermore and at Boulder, Colorado.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. K.O. Patten, Jr., J.D. Burley, and H. S. Johnston, "Radiative Lifetimes of Nitrogen Dioxide for Excitation Wavelengths from 400 to 750 nm," *J. Phys. Chem.* **94**, 7960 (1990); LBL-28435.

### Other Publications

2. H.S. Johnston, M.J. Prather, and R.T. Watson, "The Atmospheric Effects of Stratospheric Aircraft," NASA Reference Publication 1250, January 1991; LBL-31860.
3. H.S. Johnston, "Trends in Ozone Profile Measurements," Chapter 5 in *Report of the International Ozone Trends Panel 1988*, World Meteorological Organization Global Ozone Research and Monitoring Project-Report No. 18, 1990.

### LBL Reports

4. C.E. Miller (Ph.D. Thesis), "The Photodissociation of R- $\text{NO}_2$  Molecule," LBL-30540.
5. K.O. Patten (Ph.D. Thesis), "Collisional Energy Transfer from Excited Nitrogen Dioxide," LBL-30599.
6. J.D. Burley (Ph.D. Thesis), "Part I. Kinetic Energy Dependencies of Selected Ion-Molecule Reactions. Part II. Photochemistry of  $(\text{FSO}_3)_2$ ,  $\text{FSO}_3$ , and  $\text{FNO}$ ," LBL-31027.
7. B. Kim, P.L. Hunter, and H.S. Johnston, " $\text{NO}_3$  Radical Studied by Laser Induced Fluorescence," to be published in *J. Chem. Phys.*, LBL-30869.
8. J.D. Burley and H.S. Johnston, "Photoabsorption Cross Sections of  $(\text{FSO}_3)_2$  and  $\text{FSO}_3$ ," to be published in *J. Photochem. Photobiol. A*, LBL-31547.
9. J.D. Burley and H.S. Johnston, "Nitrosyl Sulfuric Acid and Stratospheric Aerosols," submitted to *Geophys. Res. Lett.* LBL-31660.

# CHEMICAL PHYSICS

## Energy Transfer and Structural Studies of Molecules on Surfaces\*

Charles B. Harris, Investigator

### INTRODUCTION

The goal of this research is to understand the dynamics of excited electronic states on surfaces, at interfaces, and in condensed phases. The research program is both theoretical and experimental in character. It includes nonlinear optical and ultrafast laser techniques in the picosecond to femtosecond regime, in addition to more conventional surface science instruments for characterizing surfaces and adsorbate-surface interactions. Recent work has focused on the development of new techniques to probe the dynamics of electrons at interfaces and carrier diffusion in semiconductors, as well as proton transfer and photodissociation of transition metal carbonyls in solution. The results of this program have a direct bearing on high speed technological devices and materials and on other problems of general interest such as the dynamics of electrical transmission in conductors on ultrafast time scales and the optical properties of thin films.

#### 1. Electronic Dynamics at Metal-Insulator Interfaces (Publication 6)

C.B. Harris, R.E. Jordan, W. R. Merry, and D.F. Padowitz

New prospects for the study of electron dynamics at interfaces and in thin films are emerging from a combination of ultrafast lasers and electron spectroscopy. Time- and angle-resolved two-photon photoemission spectroscopy probes the band structure and femtosecond dynamics of *excited* electronic states at surfaces and interfaces. Electrons excited just below the photoemission threshold of a metal may remain bound at the metal surface by the *image potential*. We have found that these image potential states persist in the presence of adsorbed molecules. Electrons in the image potential states, localized in the microscopic region just outside the surface and interacting strongly with adsorbed molecules, provide a

unique probe of the potential at the metal-insulator interface and of the dynamics of electrons in atomically thin films.

Using a recently developed angle-resolved two-photon photoemission spectrometer having unprecedented energy resolution, we initiated a systematic study of adsorbate-induced changes in the binding energies, dispersion, and linewidths of the image potential states on a metal surface. We have looked at Ag(111) with adsorbed mono- or multilayers of xenon, benzene, cyclohexane, and water. For a monolayer of xenon or hexanes the  $n = 1$  image state binding energy ( $-0.75 \pm 0.05$  eV) was unchanged or slightly increased, while dispersion became free-electron-like with a reduction in effective mass from  $m^*/m_e = 1.4$  to  $1.0 \pm 0.05$ . These simple results are at odds with early models and indicate a significant alteration of the molecule's electronic distribution due to contact with the metal.

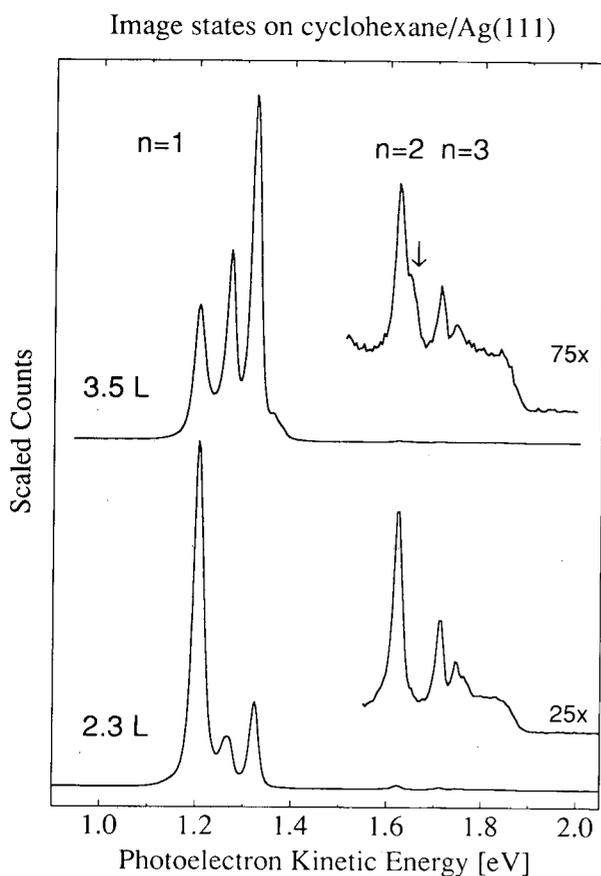
Remarkable results have been observed for the interaction of an electron with multilayer adsorbates. Successive doses of cyclohexane produced the series of photoelectron peaks as shown in Figure 1-1. We interpret the progression of peaks as corresponding to successive reductions in the binding energy for image electrons on discrete layers of cyclohexane. For a given dose there was a set of distinct peaks that suggest surface regions with thicknesses differing by one or two layers. These spectra have excellent resolution, and the higher quantum states can easily be observed. The expanded portion of Figure 1-1 shows the spectra of the higher quantum states of the bound electron. The  $n = 2, 3,$  and  $4$  states are easily visible and are not perturbed by the first two to three adsorbate layers. A slight shoulder on the  $n = 2$  peak begins to appear only after a 3.5 L dose. Figure 1-2 illustrates the basis for the extreme sensitivity of the image states to the detailed electron-adsorbate-surface interaction. The overlap of the electron in the image state with the adsorbed film changes for each molecular layer and varies with the quantum state of the image electron.

#### 2. Ultrafast Thermal Expansion and Diffusivity of the GaAs Surface (Publication 4)

D.M. Pennington and C.B. Harris

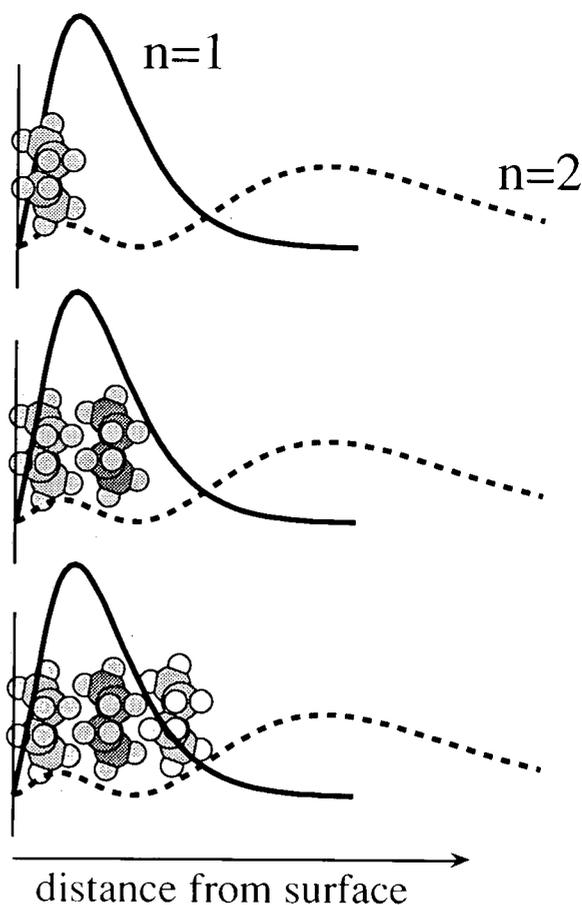
Two-color reflection transient grating spectroscopy was used for the first time to time resolve the ultrafast thermal expansion of a GaAs (100) surface. Understanding the dynamics of transient thermal expansion is of technological importance in fields such as heteroepitaxial semiconductor structures and optical coating design. For

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.



**Figure 1-1.** Schematic comparing the spatial extent of probability amplitudes  $|\Psi|^2$  for electrons bound outside a metal surface in the first two quantum levels of the image potential and the dimensions of cyclohexane layers adsorbed on the surface. (XBL 928-5351)

example, the biaxial stress due to different rates of thermal expansion between two semiconductor layers can alter the band structure of the materials, leading to a change in energy relaxation rates. By utilizing a 100-fsec ultraviolet probe with visible excitation beams, the electronic effects that dominate single color experiments become negligible; thus surface expansion due to heating and the subsequent contraction caused by cooling provide the dominant effect on the diffracted probe. The diffracted signal is composed of two components, heat conduction into the bulk perpendicular to the surface and heat flow parallel in the plane of the surface that fills in the nulls of the transient grating. Our initial experiments were performed using a large grating periodicity, resulting in a diffracted signal due entirely to expansion perpendicular to the surface. These results were then modeled theoretically with excellent agreement. For many materials it will be possible to measure the parallel expansion component as well by decreasing the periodicity to less than the skin depth of the excitation beams.



**Figure 1-2.** Two-photon photoemission spectra for approximately 2.5 and 3.5 layers of cyclohexane on a Ag(111) surface. The  $n = 1$  image state is split into several distinct peaks that correspond to shifts in the image electron's binding energy for regions covered by 2, 3 or 4 molecule thick cyclohexane layers. The expanded region shows that the  $n = 2$  and higher image states are not perturbed by the first two layers, consistent with the electron's greater distance away from the surface, but a shoulder on the  $n = 2$  peak appears for 3-4 layers of adsorbate. (XBL 928-5352)

### 3. Ultrafast Dynamics in Solution (Publications 1, 2, and 3)

*C.B. Harris, R.L. Hoff, J.A. King, M.E. Paige, E. Peterson, D.J. Russell, K.A. Schultz, B.J. Schwartz, and J.Z. Zhang*

The fast excited state intramolecular proton transfer of 3-hydroxyflavone has recently been investigated. By using picosecond stimulated emission and transient absorption spectroscopies, tautomer formation has been demonstrated, and hence, the proton transfer can be monitored by 620-nm transient absorption. By studying the 620-nm transient absorption with femtosecond time resolution, it has been determined that the proton transfer takes place in 240 fsec

in a nonpolar solvent environment. In a polar solvent, however, the proton transfer takes place in a time faster than the 125 fsec instrument response function. The difference in proton transfer rate of 3-hydroxyflavone between the two solvent environments can be explained in terms of a simple wavepacket picture.

In addition, the vibrational relaxation dynamics of large molecules undergoing photodissociation have been investigated, specifically, transition metal carbonyls. Such complexes as  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{W}(\text{CO})_6$ , and  $\text{Cr}(\text{CO})_6$ , have been systematically studied. All of these species dissociate in less than 1 psec. After the early dissociation dynamics are complete, the  $\text{Mn}_2(\text{CO})_9$  and  $\text{Cr}(\text{CO})_5$  species undergo vibrational cooling through two channels, a fast one on a 15-psec time scale and a slower one on a time scale of 180 psec.  $\text{Re}_2(\text{CO})_9$  and  $\text{W}(\text{CO})_5$ , in contrast, show only a single rapid vibrational energy transfer process. The striking differences in the relaxation of these species is explained with a simple model of the kinematics of the coupling between the heavy metal atom centers and the CO vibrations.

Finally, the relaxation dynamics of vibrationally excited ground state azulene molecules have been examined in a variety of different solvents including hexane, chloromethanes, methanol,  $\text{CClF}_3$ , Xe, and Kr. Experimental results indicate that the vibrational cooling rate is strongly solvent dependent, with cooling times of approximately 20 psec in molecular solvents and 150 psec in atomic solvents. Comparison of the rates in Xe and Kr at constant number density demonstrates the strong effect of solvent mass on energy transfer. The effect of solvent temperature on vibrational cooling is minimal, as is the effect of solvent density. The latter result is quite surprising in light of earlier experiments on simpler molecular systems, such as  $\text{I}_2$  in Xe, and predictions of Isolated Binary Collision Theories. An explanation is offered from large scale molecular dynamics simulations of the system. In effect, azulene forms an "ordered Xe cluster" with xenon atoms; the xenon number density normal to the azulene molecular plane is independent of solvent density.

#### 4. Work in Progress

The dynamics of  $e^-$ - $h^+$  pairs in graded and alloy semiconductors, i.e.,  $\text{CdS}_x\text{Se}_{1-x}$ , are under continuing investigation. First, photoluminescence decays have been shown to display fast ( $<200$  ps) lifetimes at room temperature. The data was analyzed to elucidate the influence of surface recombination on the observed dynamics. More importantly, however, the data demonstrated explicit dependence of the carrier localization on compositional disorder. The results from the studies of

homogeneous  $\text{CdS}_x\text{Se}_{1-x}$  samples were applied to the modeling of carrier diffusion in inhomogeneous graded samples, i.e., samples with a composition and band gap gradient. These studies probe the effects of a macroscopic potential gradient, as well as local potential fluctuations, on the carrier dynamics. The full analysis is currently in progress. Secondly, a fluorescence upconversion spectrometer with 1-ps time resolution was designed and built. This system utilizes a synchronously pumped dye laser, computer-controlled optical delay and data collection, and single photon counting methods to extend our current time resolution.

The work on electron dynamics at interfaces is progressing rapidly. An adsorbate charge-transfer state or negative ion, heretofore unobserved in two-photon photoemission, may have been detected in benzene on silver. A nondispersive feature has been seen in angle-resolved two-photon photoemission from the  $n = 1$  image state on bilayer films of n-hexane and n-heptane. This may be evidence of 2D localization of electrons. In addition, these experiments are ideal for examining metal-insulator transitions and metal-semiconductor Schottky barriers.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. J.Z. Zhang and C.B. Harris, "Photodissociation Dynamics of  $\text{Mn}_2(\text{CO})_{10}$  in Solution on Ultrafast Time Scales," *J. Chem. Phys.* **95**, 4024 (1991); LBL-30736.<sup>†‡</sup>
2. M.E. Paige and C.B. Harris, "Ultrafast Studies of Chemical Reactions in Liquids: I. Validity of Gas Phase Vibrational Relaxation Models and II. Density Dependence of Bound Electronic State Lifetimes," *Chem. Phys.* **149**, 37 (1990); LBL-29164.<sup>†§</sup>
3. D.J. Russell, M.E. Paige, and C.B. Harris, "Energy Dissipation in Chemical Reactions on Ultrafast Time Scales," *Ber. Bunsenges. Phys. Chem.* **95**, 299 (1991); LBL-29735.<sup>†§||</sup>

### LBL Reports

4. R.L. Hoff (Ph.D. thesis), "Ultrafast Studies of Photophysics of Phenyl Substituted Butadienes in Liquids," (1991); LBL-31152.<sup>†‡</sup>

### Invited Talks

5. C.B. Harris, "Energy Dissipation in Chemical Reactions on Ultrafast Timescales," LBL Joint seminar, Berkeley, CA, October 18, 1990.
6. C.B. Harris, "Fundamental Studies of Chemical Reactions in Liquids on Ultrafast Timescales," *Molecular Dynamics*

Symposium honoring Hochstrasser, University of Pennsylvania, January 4, 1991.

7. C.B. Harris, "Energy Dissipation in Chemical Reactions on Ultrafast Timescales," Photoinduced Proton Transfer Dynamics in Chemistry, Biology and Physics honoring Michael Kasha, FL, January 6-9, 1991.
8. C.B. Harris, "Spectroscopy of Electrons at Metal-Insulator Interfaces," Gordon Conference on the Dynamics of Gas-Surface Interaction, Andover, NH, August 6, 1991.
9. C.B. Harris, "Energy Transfer in Liquid State Chemical Reactions on the Femtosecond Timescale," ACS Symposium on Energy Transfer and Relaxation in Condensed Phases, New York, NY, August 25-30, 1991.
10. D.F. Padowitz, "Two-Photon Photoemission from Excited Electronic States at Surfaces," Department of Chemical Engineering, Stanford, CA, March, 1991.
11. J.Z. Zhang, "Picosecond Time-Resolved Study of the Photodissociation Dynamics of  $\text{Mn}_2(\text{CO})_{10}$  in Solution," Seventh Interdisciplinary Laser Science Conference (ILS-VII), Monterey, CA, September 22-26, 1991.

<sup>†</sup>National Science Foundation Program using DOE equipment.

<sup>‡</sup>Office of Army Research Program Using DOE equipment.

<sup>§</sup>Office of Naval Research Program using DOE equipment.

<sup>||</sup>Calculations performed at the San Diego Supercomputer Center.

# Laser Sources and Techniques\*

*Andrew H. Kung, Investigator*

## INTRODUCTION

This research program focuses on the development of novel laser and spectroscopic techniques in the IR, UV, and VUV regions to study combustion related molecular dynamical processes at the microscopic level. Laser spectroscopic techniques have been proven to be extremely powerful in studying molecular processes that require high sensitivity and selectivity. The key to the success of these techniques is high spectral brightness, which is currently not readily available in the two regions of most interest to molecular dynamics: the infrared region beyond three microns and the VUV region. Our approach is to use quantum electronic and nonlinear optical techniques to extend the spectral coverage and to enhance the optical power of ultrahigh resolution laser sources so as to obtain and analyze photoionization, fluorescence, and photoelectron spectra of jet-cooled free radicals and of reaction products resulting from unimolecular or bimolecular dissociation. New spectroscopic techniques are developed with these laser sources for the detection of optically thin and often short-lived species. This program also provides scientific and technical support within the Chemical Sciences Division to the development of LBL's Combustion Dynamics Initiative.

### 1. Development of Ultranarrow Bandwidth VUV-XUV Laser System (Publication 3)

*E. Cromwell, T. Trickl, Y.T. Lee, and A.H. Kung*

An ultrahigh brightness laser system was developed a few years ago for applications in spectroscopy and dynamics in the VUV-XUV region. The laser utilizes pulse amplification of a single-mode ring dye laser, together with frequency multiplication in nonlinear crystals and a pulsed jet to get to the short wavelength region. The utility of this laser system was demonstrated in an ultrahigh resolution (1 + 1) photoionization study of krypton where the hyperfine structure and isotope shift of several Rydberg states of Kr were measured with very high precision, and in state-selected ionization of nitrogen where selectively vibrationally excited N<sub>2</sub> ions were

produced in large quantities. More recently the laser system has been used in product state distribution mapping in H<sub>2</sub> elimination from cyclohexadiene (see below) and from ethylene (Y.T. Lee group).

### 2. Dynamics of H<sub>2</sub> Elimination from Cyclohexadiene (Publications 1,2)

*E. Cromwell, D.J. Liu, M.J.J. Vrakking, A.H. Kung, and Y.T. Lee*

A comprehensive study of the dynamics of H<sub>2</sub> elimination from 1,4- and 1,3-cyclohexadiene has been completed. Rotational and vibrational quantum state distributions for the H<sub>2</sub> product were measured that complement translational energy distribution studies. State specific detection of H<sub>2</sub> was accomplished via (1 + 1) REMPI. The vibrational and rotational energy distributions indicate a tight and symmetric transition state that is supported by theoretical calculations. The distribution of H<sub>2</sub> translational energy, both for a given rovibrational state and for all the populated quantum states, confirms the concerted and synchronous nature of the dissociation process and the dominance of the potential barrier to the release of the translational energy of the H<sub>2</sub> product. A (v,J) correlation for H<sub>2</sub> with VIIJ primarily is observed from anisotropy in the Doppler profiles. This correlation between the velocity and rotational angular momentum vectors indicates that the H<sub>2</sub> moves away from the transition state complex with a helicopter-type motion. The study shows the significant utility of the high resolution laser system in understanding the dynamics of primary photodissociation of polyatomic molecules.

### 3. Work in Progress

Recent workshops and reviews have identified that fundamental studies in the primary dissociation and spectroscopy of free radicals of hydrocarbons are essential to understand the processes that underlie combustion of fossil fuels. These studies can best be performed using infrared sources both to produce the free-radicals by multiphoton excitation and to probe the reactive intermediates. We are investigating methods to generate moderately high power infrared that will permit demonstration of the feasibility of multiphoton excitation in an isolated molecular setting and allow some of the critical experiments to be performed. The focus will be on evaluating the use of nonlinear optical techniques such as high order Raman shifting of high power visible

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tunable lasers to produce high resolution nanosecond infrared pulses. The goal is to obtain a high repetition rate infrared source tunable from 3 to 10 microns, with pulse energy of greater than 25 mJ, and with near-transform-limited resolution.

A picosecond UV/VUV laser system has been developed for the study of unimolecular dynamics. The system provides two independently tunable picosecond pulses for UV excitation and time delayed VUV ionization. Over the last year, greater than 40 microjoules near 266 nm and greater than  $10^8$  photons near 119 nm (measured after a VUV monochromator) with a cross correlation of the precursor pulses of less than 4 picoseconds have been achieved. Work is in progress to obtain the instrument response function by studying the photodissociation of methyl iodide. The molecule is pumped near 266 nm, and after a variable delay, all species present are ionized by a 119 nm 1 photon process. The ions are separated by Time-of-Flight Mass Spectrometry and the appearance rate of  $I^+$  and  $CH_3^+$  ions is measured. Preliminary results yield a response of

~5 ps. Further work will focus on the photodissociation of halogenated benzenes using the same technique.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. E.F. Cromwell, D.J. Liu, M.J.J. Vrakking, A.H. Kung, and Y.T. Lee, "Dynamics of  $H_2$  Elimination from 1,4-Cyclohexadiene," *J. Chem. Phys.* **92**, 3230 (1990).
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### Other Publications

3. A.H. Kung and Y.T. Lee, Spectroscopy and Reaction Dynamics Using Ultrahigh Resolution VUV Lasers, in Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters, C.Y. Ng, ed., World Scientific Publishing Company, Singapore (1991), pp. 487-502.

# Crossed Molecular Beams\*

Yuan T. Lee, Investigator

## INTRODUCTION

The major thrust of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and to unravel the mechanism of complex chemical reactions or photochemical processes that play important roles in many macroscopic processes. Molecular beams of reactants are used to study individual reactive encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy, angular and state distributions. Recent activities are centered on the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons, the dynamics of endothermic substitution reactions, the dependence of the chemical reactivity of electronically excited atoms on the alignment of excited orbitals, the primary photochemical processes of polyatomic molecules, intramolecular energy transfer of chemically activated and locally excited molecules, the energetics of free radicals that are important to combustion processes, the infrared-absorption spectra of carbonium ions and hydrated hydronium ions, and the bond-selective photodissociation through electronic excitation.

### 1. Reactions of Ground-State and Electronically Excited Sodium Atoms with Methyl Bromide (Publication 6)

*P.S. Weiss, J.M. Mestdagh, H. Schmidt, M.H. Covinsky, and Y.T. Lee*

The reactions of ground- and excited-state Na atoms with methyl bromide ( $\text{CH}_3\text{Br}$ ) and chlorine ( $\text{Cl}_2$ ) have been studied by using the crossed molecular beams method. For both reactions, the cross sections increase with increasing electronic energy. The product recoil energies change little with increasing Na electronic energy, implying that the product internal energies increase substantially. For  $\text{Na} + \text{CH}_3\text{Br}$ , the steric angle of acceptance opens with increasing electronic energy.

### 2. 193-nm Photodissociation of Acetylene (Publication 8)

*B.A. Balko, J. Zhang, and Y.T. Lee*

The product translational energy distribution  $P(\text{ET})$  for acetylene photodissociation at 193 nm was obtained from the time-of-flight spectrum of the H atom fragments. The  $P(\text{ET})$  shows resolved structure from the vibrational and electronic excitation of the  $\text{C}_2\text{H}$  fragment; comparison of the translational energy release for given excited states of  $\text{C}_2\text{H}$  with the known energy levels of these states gives  $D_0(\text{HCC-H}) = 131.4 \pm 0.5$  kcal/mol. This value is in agreement with that determined previously in this group from analogous studies of the  $\text{C}_2\text{H}$  fragment and with the latest experimental and theoretical work. The high resolution of the experiment also reveals the nature of  $\text{C}_2\text{H}$  internal excitation. A significant fraction of the H atoms detected at moderate laser power were from the secondary dissociation of  $\text{C}_2\text{H}$ . The  $P(\text{ET})$  derived for this channel indicated that most of the  $\text{C}_2$  is produced in excited electronic states.

### 3. Dynamics of $\text{H}_2$ Elimination from Cyclohexadiene (Publication 9)

*E.F. Cromwell, D.-J. Liu, M.J.J. Vrakking, A.H. Kung, and Y.T. Lee*

A comprehensive study of the dynamics of  $\text{H}_2$  elimination from 1,4 and 1,3 cyclohexadiene is reported. Rotational and vibrational quantum state distributions as well as translation energy distributions for the  $\text{H}_2$  product are measured. State specific detection of  $\text{H}_2$  is accomplished with a transform limited vacuum ultraviolet-extreme ultraviolet laser system via  $(1 + 1)$  resonance enhanced multiphoton ionization (REMPI). Rate constants for the  $\text{H}_2$  elimination and 1,4 to 1,3 isomerization reactions are derived. A  $(v, J)$  correlation for  $\text{H}_2$  with  $v \parallel J$  primarily is observed from anisotropy in the Doppler profiles. A clear picture of the transition state configuration of 1,4 cyclohexadiene is provided from the information obtained.

### 4. Photodissociation of $\text{H}_2\text{S}$ and the HS Radical at 193.3 nm (Publication 10)

*R.E. Continetti, B.A. Balko, and Y.T. Lee*

Photodissociation of  $\text{H}_2\text{S}$  has been studied at 193.3 nm using H atom photofragment-translational spectroscopy with mass-spectrometric detection.  $\text{H} + \text{HS}(v)$  product

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branching ratios are reported that are not in quantitative agreement with other recent experimental results. Secondary photodissociation of HS radicals has also been observed, showing that both  $S(^3P)$  and  $S(^1D)$  are produced via perpendicular transitions. The HS bond energy was found to be  $3.62 \pm 0.03$  eV.

#### 5. Molecular Beam Studies of the Photolysis of Allene and the Secondary Photodissociation of the $C_3H_x$ Fragments (Publication 11)

*D.S. Anex, R.E. Continetti, B.A. Balko, and Y.T. Lee*

Angle resolved time-of-flight (TOF) measurements produced when allene is photolyzed at 193 nm are described. The two primary processes that have been identified from these measurements are the  $H + C_3H_3$  and the  $H_2 + C_3H_2$  channels. The quantum yields for these first steps are 0.89 and 0.11, respectively. Subsequent photolysis of the  $C_3H_3$  radical produces  $H_2 + C_3H$ ,  $C_3H_2 + H$ , and  $C_2H_2 + CH$ , while the  $C_3H_2$  produces  $C_3 + H_2$ ,  $C_2H + CH$ , and  $C_2H_2 + C$ . The translational energy distributions for each one of these steps have been derived using the forward convolution technique. These energy distributions reveal the exit barriers and other constraints on the potential energy surfaces that lead to the above stated products.

#### 6. Reaction Geometry from Orbital Alignment Dependence of Ion Pair Production in Crossed-Beam $Ba(^1P_1) + Br_2$ Reactions (Publication 12)

*A.G. Suits, H. Hou, H.F. Davis, Y.T. Lee, and J.-M. Mestdagh*

Strong orbital alignment dependence was observed for  $Ba^+$  produced in crossed-beam reaction of  $Ba(^1P_1)$  with  $Br_2$ . The peak of this dependence varied strongly with scattering angle for alignment of the p orbital in the scattering plane, with the maximum flux seen for perpendicular alignment with respect to the relative velocity vector. The measured  $Ba^+$  was always favored by alignment of the orbital in the scattering plane, regardless of laboratory scattering angle. The experimental results suggest that this charge-transfer process is dominated by large impact-parameter collisions that achieve collinear nuclear geometry and  $\Sigma$  orbital alignment at the crossing point. Orbital locking is probably not important owing to the large internuclear distance of the crossing region.

#### 7. Dynamics of $Ba-Br_2$ Chemiionization Reactions (Publication 13)

*A.G. Suits, H. Hou, H.F. Davis, and Y.T. Lee*

The formation of  $BaBr^+$  ions in reaction of  $Ba(^1S_0, ^1P_1)$  with  $Br_2$  was studied as a function of laboratory scattering angle and product translational energy in a crossed-beam experiment. The contour map of  $BaBr^+$  flux obtained for the ground-state reaction at 1.1 eV collision energy showed a backscattered angular distribution (relative to the barium beam) with a substantial fraction of the available energy appearing in translation. Laser excitation strongly inhibited this channel at 1.1 eV. These experimental observations suggest that for the chemiion reaction head-on, collinear collisions and proximal crossings of the potential energy surfaces are necessary to preclude escape into the dominant neutral pathways. At 1.6 eV collision energy a new laser-dependent source of  $BaBr^+$  appeared. This laser-enhanced  $BaBr^+$  showed a laboratory angular distribution substantially narrower than for the ground-state reaction, indicating a smaller translational energy release. The angular distribution was  $\sim 70\%$  backscattered and displayed a clear dip at the center of mass. This new  $BaBr^+$ , produced from electronically excited barium at higher translational energy, is ascribed to secondary collisions of  $BaBr + Br$  initially formed in low impact parameter collisions. Reaction of electronically excited barium with  $Br_2$  also yielded an associative ionization product  $BaBr_2^+$  at both collision energies studied, with a cross section about  $1/100$ th that of the chemiion channel.

#### 8. The Reaction Dynamics of Sodium with Ozone (Publication 17)

*M.H. Covinsky, A.G. Suits, H.F. Davis, and Y.T. Lee*

The reaction of sodium atoms (Na) with ozone ( $O_3$ ) has been studied using crossed molecular beams at a collision energy of 18 kcal/mole. The only product observed was NaO. The reaction occurs via an electron-transfer mechanism that yields NaO that is forward scattered with respect to the sodium beam. The translational energy distribution peaks near the forward stripping limit but extends out to the maximum allowed by energy conservation. The fragmentation ratio of NaO upon electron bombardment ionization  $I(NaO)/[I(NaO^+) + I(Na^+)]$  as a function of translational energy has been measured for an electron energy of 200 V.

## 9. IR Multiphoton Dissociation of Anisole: Production and Dissociation of Phenoxy Radical (Publication 18)

*A.-M. Schmoltner, D.S. Anex, and Y.T. Lee*

The infrared multiphoton dissociation (IRMPD) of anisole in a molecular beam was studied using pulsed CO<sub>2</sub> laser radiation. The only primary process identified was the dissociation into phenoxy and methyl radicals. Under conditions of higher laser fluence, secondary dissociation of the phenoxy radical into carbon monoxide and C<sub>5</sub>H<sub>5</sub> was observed. The product recoil energy distribution was measured using the time-of-flight technique.

## 10. The Dynamics of Electronically Inelastic Collisions From 3-Dimensional Doppler Measurements (Publication 19)

*A.G. Suits, P. de Pujo, O. Sublemontier, J.-P. Visticot, J. Berlande, J. Cuvellier, T. Gustavsson, J.-M. Mesidagh, P. Meynadier, and Y. T. Lee*

Flux-velocity contour maps were obtained for the inelastic collision process Ba(<sup>1</sup>P<sub>1</sub>) + O<sub>2</sub>, N<sub>2</sub> Ba(<sup>3</sup>P<sub>2</sub>) + O<sub>2</sub>, N<sub>2</sub> from Doppler scans of scattered Ba(<sup>3</sup>P<sub>2</sub>) taken over a range of probe laser directions in a crossed beams experiment. Collision with O<sub>2</sub> resulted in sharply forwarded scattered Ba(<sup>3</sup>P<sub>2</sub>), with efficient conversion of initial electron energy into O<sub>2</sub> internal energy and little momentum transfer. Collision with N<sub>2</sub> was dominated by wide-angle scattering with most of the available electronic energy appearing in product translation. The results suggest the importance of large impact parameter collisions and a near-resonant energy transfer in the case of O<sub>2</sub>, while for N<sub>2</sub> close collisions dominate despite the presence of an analogous near-resonant channel. The results represent the first direct experimental demonstration of a near-resonant quenching process.

## 11. The Dynamics of H<sub>2</sub> Elimination from Ethylene (Publication 20)

*A. Stolow, B.A. Balko, E.F. Cromwell, J. Zhang, and Y.T. Lee*

The dynamics of H<sub>2</sub> elimination in the photodissociation of ethylene at 193 nm were investigated through measurements of the translational energy distribution and rovibrational state distribution of H<sub>2</sub> products. Using 1,1-D<sub>2</sub>C = CH<sub>2</sub> and 1,2-HDC = CDH, it was shown that both four-centered and three-centered

elimination of H<sub>2</sub> could take place with an acetylene to vinylidene formation ratio of approximately two-thirds. Limited 1,2 hydrogen atom migration occurred during the fragmentation, presumably through an ethylidene-type structure. The relatively high rotational excitation of the H<sub>2</sub> fragment suggests that the transition is not symmetric; as the two ethylene hydrogen atoms approach each other and reach the transition state, one C-H bond should be significantly longer than the other. The vibrational energy distributions can be roughly characterized by a vibrational temperature of 4800 K and an average translational energy, which is dependent on the rovibrational state of H<sub>2</sub>, exceeding 20 kcal mol<sup>-1</sup>.

## 12. Reaction Dynamics From Orbital Alignment Dependence and Angular Distributions of Ions Produced in Collision of Ba(<sup>1</sup>P) with NO<sub>2</sub> and O<sub>3</sub> (Publication 22)

*A.G. Suits, H. Hou, H.F. Davis, and Y.T. Lee*

Angular distributions, orbital alignment dependence and energy dependence of the relative cross sections of various ions produced in crossed beams collisions of electronically excited barium with O<sub>3</sub> and NO<sub>2</sub> were used to explore the dynamics of these reactions. The Ba<sup>+</sup> product from both reactions showed strong dependence on alignment of the Ba(<sup>1</sup>P) p orbital with respect to the relative velocity vector. The Ba<sup>+</sup> was generally forward or forward-sideways scattered, with the latter favored by the dominant perpendicular orbital alignment. Similar results for Ba<sup>+</sup> from both O<sub>3</sub> and NO<sub>2</sub> suggests that electron transfer is favored for large impact parameter collisions in which the Ba p orbital is directed toward the molecule at the critical configuration, regardless of the symmetry of the available orbital in the isolated molecule. BaO<sub>2</sub><sup>+</sup> from the O<sub>3</sub> reaction exhibited angular distributions and energy dependences that were reminiscent of the Ba<sup>+</sup> albeit two orders of magnitude lower in intensity, indicating a close relationship between these two channels. Important differences in the dynamics for the Ba<sup>+</sup> channel were suggested in the angular distributions, which show a substantial backscattered component, as well as the alignment effects and energy dependence. These indicate that the BaO<sup>+</sup> probably derives from neutral BaO\* that is sufficiently internally excited to undergo vibrational autoionization.

## 13. Work in Progress

The first complete investigation of chemical reactions that involve reagent state specification and state resolved

angular distribution measurements on  $D + H_2 \rightarrow DH(v',J') + H$  is expected to become fruitful in the coming year. The efforts in the understanding of electron transfer in chemical reactions will move from divalent atoms to polyvalent transition metals. Reaction dynamics of polyatomic radicals that play important roles in combustion chemistry and atmospheric chemistry will still be our main focus in the near future.

In the area of the primary dissociation and photochemical processes, we will focus on the unsaturated ring compounds. The aspect of isomerization of these molecules prior to dissociation will be studied in detail. Those series of investigations will include aromatic, heterocyclic compounds as well as cyclopentadiene. The mode specificity in the dissociation of  $ClO_2$  through electronic excitation that was discovered recently will be further investigated for other systems. Photodissociation of polyatomic radicals and dissociation of molecules at wavelength shorter than 2000 Å will be explored.

IR absorption spectra of solvated metallic ions, and solvated anions, especially hydroxides and halides, will be investigated using our unique tandem mass spectrometer, ion trap apparatus. Intramolecular dynamics of molecular ions containing weak bonds will be investigated from the variance of the branching ratio in a process initiated by overtone excitation of C-H stretching mode.

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  44. Y.T. Lee, "VUV Laser Probing of the Dynamics of H<sub>2</sub> Elimination from Simple Organic Molecules," Department of Chemistry, Beijing University, Beijing, China, May 18, 1991.
  45. Y.T. Lee, "Electron Transfers in Chemical Reactions," Laser Chemical Physics Workshop, Dalian Institute of Chemical Physics, Dalian, People's Republic of China, May 20, 1991.
  46. Y.T. Lee, "Dynamics of H<sub>2</sub> Elimination from Ethylene," Laser Chemical Physics Workshop, Dalian Institute of Chemical Physics, Dalian, People's Republic of China, May 20, 1991.
  47. Y.T. Lee, "Solvation of Hydronium and Ammonium Ions by IR Absorption Spectroscopy," Laser Chemical Physics Workshop, Dalian Institute of Chemical Physics, Dalian, People's Republic of China, May 21, 1991.
  48. Y.T. Lee, "Search for Dynamical Resonances in D + H<sub>2</sub> → DH + H," XIII International Symposium on Molecular Beams, El Escorial, Madrid, Spain, June 2-7, 1991.
  49. Y.T. Lee, "Probing of Reaction Dynamics Using Dye Lasers," 25 Years, Schloss Ringberg, Germany, June 10, 1991.
  50. Y.T. Lee, "Lasers in Chemical Dynamics," Laser '91 Laser International Laser Symposium, Munich, Germany, June 13, 1991.
  51. Y.T. Lee, "Dynamic Resonances in D + H<sub>2</sub> → DH(v'J) + H Reaction," First International Conference on Atomic and Molecular Dynamics, Taipei, Taiwan, People's Republic of China, July 5, 1991.

### Invited Talks

29. Y.T. Lee, "Molecular Beam Chemistry, Acheson Series Lecturer," State University of New York, Buffalo, NY, October 13, 1990.
30. Y.T. Lee, "Crossed Molecular Beams Studies of Elementary Chemical Reactions," Case Western University, Cleveland, OH, October 25, 1990.
31. Y.T. Lee, "Research Activities of Molecular Beam Laboratory at Berkeley," Institute for Molecular Science, Myodaiji, Okazaki, Japan, November 2, 1990.
32. Y.T. Lee, "Crossed Molecular Beam Studies on Elementary Reactions," Korea Advanced Institute of Science and Technology, Seoul, Korea, November 8, 1990.
33. Y.T. Lee, "Molecular Beam Studies on Primary Photochemical Processes," Korea Advanced Institute of Science and Technology, Seoul, Korea, November 9, 1990.
34. Y.T. Lee, "Dynamics of Chemical Reactions," Milan Welcomes Nobel Laureates, Milan, Italy, November 12, 1990.
35. Y.T. Lee, "Electron Transfers in Reactions of Ba Atoms with Triatomic Molecules," Brookhaven National Laboratory, Upton, LI, NY, November 26, 1990.

52. Y.T. Lee, "The Dynamics of H<sub>2</sub> Elimination from Ethylene," XVth International Conference on Photochemistry, Paris, France, July 29, 1991.
53. Y.T. Lee, "Dynamics of One and Two Electron Transfer in the Reaction of Ba with Simple Molecules," International Union of Pure and Applied Chemistry Conference, Budapest, Hungary, August 19, 1991.
54. Y.T. Lee, "Molecular Beam Studies of Chemical Vapor Deposition of Diamond Film," Department of Chemistry, University of Singapore, Singapore, September 9, 1991.
55. Y.T. Lee, "Concerted Decomposition of Organic Molecules," Department of Chemistry, University of Singapore, Singapore, September 10, 1991.

# Molecular Interactions\*

William A. Lester, Jr., Investigator

## INTRODUCTION

This research program is directed at extending fundamental knowledge of atoms and molecules including their electronic structure, mutual interaction, collision dynamics, and interaction with radiation. The approach combines the use of *ab initio* methods—Hartree-Fock (HF), multiconfiguration HF, configuration interaction, and the recently developed quantum Monte Carlo (QMC)—to describe electronic structure, intermolecular interactions, and other properties, with various methods of characterizing inelastic and reactive collision processes and photodissociation dynamics. Present activity is focused on the development and application of the QMC method.

### 1. Theoretical Study of the CO Interaction with 3d-Metal Surfaces (Publication 1)

A.C. Pavão,<sup>†</sup> M. Braga,<sup>†</sup> C.A. Taft,<sup>‡</sup> B.L. Hammond,<sup>§</sup> and W.A. Lester, Jr.

*Ab initio* molecular orbital calculations of the M-CO systems (M = Sc to Cu) combined with Pauling's resonating-valence-bond theory indicate that CO adsorption only on Sc, Ti, V, Cr, Mn, and Fe surfaces will be dissociative, and nondissociative on Co, Ni, and Cu surfaces, in agreement with the experimental evidence. The nature of the chemical bond, charge-transfer, Fermi level, and other parameters of the CO interaction with 3d-metal surfaces is analyzed. The CO dissociation is described as a charge-transfer process with bonds resonating among the metal, C, and O atoms. CO dissociation in activated catalytic processes on modified 3d surfaces is discussed.

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<sup>‡</sup>Permanent address: Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, Brazil.

<sup>§</sup>Present address: Fujitsu America, Inc., San Jose, CA.

### 2. Multidimensional Wave-Packet Analysis: Splitting Method for Time-Resolved Property Determination (Publication 2)

P. Pernot<sup>†</sup> and W.A. Lester, Jr.

The present paper is concerned with the application of the splitting method to time-resolved product analysis. The splitting method is an approach for preventing unphysical behavior of a wave-packet at the edges of its coordinate space representation grid. Extension of the method to multidimensional systems has to contend with the existence of product internal states. In order to take full advantage of asymptotic propagation efficiency, it is necessary to decompose the wave-packet on internal-state basis sets. On the other hand, it is possible to avoid asymptotic propagation if one is not interested in energy- or momentum-resolved information. We propose here a simplified analysis method to treat this case. We outline and discuss these points in the paper.

Accuracy of time-resolved information obtained by the splitting method depends particularly on the frequency of splitting and on the form of the transfer function connecting the interaction grid to the asymptotic grid. We investigate these parameters and the accuracy of the method for a general 1D example. We also treat a 2D example of He scattering by H<sub>2</sub>(B).

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### 3. Quantum Time-Dependent Treatment of Molecular Collisions: Scattering of He by H<sub>2</sub>(B <sup>1</sup>Σ<sub>g</sub><sup>+</sup>) (Publication 3)

P. Pernot,<sup>†</sup> W.A. Lester, Jr., and C. Cerjan<sup>‡</sup>

Computational limitations of using a time-dependent quantum method to study He + H<sub>2</sub>(B) scattering are presented with an analysis of the consequences of the approximation to a 2D model.

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<sup>‡</sup>Permanent address: Lawrence Livermore National Laboratory, Livermore, CA.

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

#### 4. Theoretical Study of the CO Interaction with the Fe(100) Surface (Publication 4)

A.C. Pavão,<sup>†</sup> M. Braga,<sup>†</sup> C.A. Taft,<sup>‡</sup> B.L. Hammond,<sup>§</sup> and W.A. Lester, Jr.

*Ab initio* unrestricted Hartree-Fock, Effective Core Potential, and Multiple Scattering-X $\alpha$  molecular cluster calculations have been performed in order to study the interaction of CO with an Fe(100) surface. The calculated Fe  $\rightarrow$  CO charge-transfer in the systems FeCO and Fe<sub>5</sub>CO is correlated to the observed CO stretching frequencies of Fe(100). The increasing values of the Fe  $\rightarrow$  CO charge-transfer obtained as the molecule inclines in relation to the surface are consistent with the assignment of the low stretching frequency (1210 cm<sup>-1</sup>) to the precursor state of CO dissociation on the iron surface.

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#### 5. On Quantum Monte Carlo for the Electronic Structure of Molecules (Publication 5)

B.L. Hammond,<sup>†</sup> M.M. Soto, R.N. Barnett,<sup>‡</sup> and W.A. Lester, Jr.

We present recent advances in the quantum Monte Carlo (QMC) method for the electronic structure of atoms and molecules. The QMC method used here is a procedure for solving the Schrödinger equation stochastically based on the formal similarity between the Schrödinger equation and the classical diffusion equation. Quantum mechanical expectation values are obtained as Monte Carlo averages over an ensemble of random walkers undergoing diffusion, drift (from importance sampling), and branching. The power of the QMC method is that it is inherently an N-body method that can capture all of the dynamic correlation of the electrons. The approach yields highly accurate energies and has been used to determine other properties including dipole moments and molecular geometry energy gradients. We present a description of the QMC method that we employ and give representative results. In addition we discuss recent progress on the calculation of transition dipole moments and developments with the "damped-core" QMC method that enables studies of molecular systems containing heavy atoms without reliance on pseudopotentials.

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<sup>‡</sup>Present address: Department of Chemistry, University of California, Berkeley.

#### 6. Work in Progress

A systematic study of the structure and energetics of CH-containing systems has been initiated that draws on the broad range of recently developed QMC methods. Systems planned for the present effort are CH, C<sub>2</sub>H, and C<sub>2</sub>H<sub>2</sub>, as well as C<sub>2</sub>. The primary effort will use the fixed-node short-time approximation QMC approach with optimized trial functions.

### FY 1991 PUBLICATIONS AND REPORTS

#### Refereed Journals

1. A.C. Pavão, M. Braga, C.A. Taft, B.L. Hammond, and W.A. Lester, Jr., "Theoretical Study of the CO Interaction with 3d-Metal Surfaces," *Phys. Rev. B* **43**, 6962 (1991); LBL-29601.
2. P. Pernot and W.A. Lester, Jr., "Multidimensional Wave-Packet Analysis: Splitting Method for Time-Resolved Property Determination," *Int. J. Quant. Chem.* **40**, 577 (1991); LBL-28591.
3. P. Pernot and W.A. Lester, Jr., "Quantum Time-Dependent Treatment of Molecular Collisions: Scattering of He by H(B <sup>1</sup> $\Sigma_u^+$ )," *Comp. Phys. Commun.* **63**, 259 (1991); LBL-28590.
4. A.C. Pavão, M. Braga, C.A. Taft, B.L. Hammond, and W.A. Lester, Jr., "Theoretical Study of the CO Interaction with Fe(100) Surface," *Phys. Rev. B* **44**, 1910 (1991); LBL-29489.
5. B.L. Hammond, M.M. Soto, R.N. Barnett, and W.A. Lester, Jr., "On Quantum Monte Carlo for the Electronic Structure of Molecules," *J. Molec. Struct. (Theochem)* **234**, 525 (1991); LBL-30151.

#### LBL Reports

6. Z. Sun, R.N. Barnett, and W.A. Lester, Jr., "Optimization of a Multideterminant Wave Function for Quantum Monte Carlo," accepted by *J. Chem. Phys.*; LBL-31429.
7. R.N. Barnett, P.J. Reynolds, and W.A. Lester, Jr., "Monte Carlo Determination of the Oscillator Strength and Excited State Lifetime for the Li 2 <sup>2</sup>S  $\rightarrow$  2 <sup>2</sup>P Transition," accepted by *Int. J. Quant. Chem.*; LBL-30152.
8. J.W. de M. Carneiro, P.R. Seidl, J.G.R. Tostes, C.A. Taft, B.L. Hammond, M.M. Soto, and W. A. Lester, Jr., "The Effects of Lone Pairs on Charge Distribution in the Tetracyclic Norbornyl Derivatives," submitted to *Chem. Phys. Letters*; LBL-31893.
9. J.S. Francisco, Y. Zhao, W.A. Lester, Jr., and I.H. Williams, "Theoretical Studies of the Structure and Thermochemistry for FO<sub>2</sub> Radical: Comparison of Moller-Plesset Perturbation, Complete-Active-Space Self-Consistent Field, and Quadratic Configuration Interaction Methods," submitted to *J. Chem. Phys.*; LBL- 32800.

## Invited Talks

10. W.A. Lester, Jr., "Quantum Monte Carlo for Molecules," University of Florida, Gainesville, April 12, 1991.
11. W.A. Lester, Jr., "Theoretical Studies of Molecular Interactions," 1991 DOE Combustion Research Meeting, Lake Geneva, WI, May 28-31, 1991.
12. W.A. Lester, Jr., "Variational Monte Carlo for Atoms and Molecules," CECAM Planning Meeting on Quantum Simulation for Atoms, Molecules, and Solids, University of Paris-South, Orsay, France, July 27, 1991.
13. W.A. Lester, Jr., "Monte Carlo Calculation of Small Molecules," Fall 1991 Frontiers in Chemistry Series, Wayne State University, Detroit, Michigan, September 23, 1991.

# Theory of Atomic and Molecular Collisions Processes\*

William H. Miller, Investigator

## INTRODUCTION

This research is primarily involved with the development and application of theoretical methods and models for describing atomic and molecular collision processes and chemical reaction dynamics. Specific topics of interest have included 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.

Most recently, research has focused on the development of theoretical methods for a first principles treatment of dynamics in *polyatomic* molecular systems. The goal is to develop approaches that can utilize *ab initio* quantum chemical calculations of the potential energy surface (in the Born-Oppenheimer approximation) as direct input into the dynamical treatment, and thus, to as great an extent as possible, have a truly predictive theory.

The potential application of these methods is almost without limit. In this group hydrogen atom transfer processes have been studied in a variety of systems. Other research groups have used these approaches to describe a variety of reactions that are relevant to the primary steps in combustion.

### 1. Transition State Theory, Siegert Eigenstates, and Quantum Mechanical Reaction Rates (Publication 4)

T. Seideman and W.H. Miller

The "good" action variables associated with a transition state (i.e., the saddle point of a potential energy surface), on which a general semiclassical transition state theory is based, are shown to be the semiclassical counterpart of the Siegert eigenvalues of the system. (Siegert eigenvalues are the complex eigenvalues of the Schrödinger equation with outgoing wave boundary conditions.) By using flux correlation functions, it is then

\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

shown how the exact quantum mechanical reaction rate can be expressed in terms of the Siegert eigenvalues (and eigenfunctions). Applications to some test problems show these Siegertbased rate expressions to be rapidly convergent with respect to the sum over the Siegert states.

### 2. Classical Trajectory Studies of the Molecular Dissociation Dynamics of Formaldehyde: $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ (Publication 10)

Y.-T. Chang, C. Minichino,<sup>†</sup> and W.H. Miller

Classical trajectory calculations have been carried out to simulate the unimolecular decomposition of formaldehyde in the ground electronic state ( $S_0$ ). Global potential energy surfaces were constructed using the empirical valence bond (EVB) approach. Two sets of *ab initio* input were used to characterize two different EVB potential energy surfaces, and trajectory calculations using one of these gives excellent agreement with experimental data for the product state distributions of  $\text{H}_2$  and  $\text{CO}$ . The trajectory study of vector correlations with prompt dissociation of the parent molecule provides understanding of the dissociation dynamics in the molecular frame. From comparison with some of the experimental results and information from a few *ab initio* calculations, some improvements for the current potential surfaces are suggested.

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### 3. Reaction Dynamics in Polyatomic Molecular Systems: Some Approaches for Constructing Potential Energy Surfaces and Incorporating Quantum Effects in Classical Trajectory Simulations (Publication 11)

W.H. Miller

This paper deals with the two essential tasks necessary to model chemical reactions theoretically: obtaining the potential energy surface (i.e., the electronic energy of the molecular system as a function of nuclear positions) and then determining the dynamical motion of the nuclei/atoms governed by it.

It is sometimes possible to model the potential energy surface for a chemical reaction *locally*, e.g., a harmonic valley along the *reaction path* that passes through the transition state (saddle point on the potential energy surface) connecting reactants and products. More generally, though, it is necessary to have a *global* potential

energy function that is not restricted to the vicinity of reaction path. Many completely empirical potential functions have been developed for nonreactive molecular motions, and it is shown here how the *empirical valence bond* (EVB) idea can be used to combine these nonreactive potential functions, which describe reactant and product regions individually, with *ab initio* calculations for the transition state region and thus obtain a global potential energy surface for a chemical reaction.

Although the dynamics of nuclear motion should in principle be treated quantum mechanically, the difficulty of doing so is prohibitive for polyatomic systems. Most dynamical treatments employ classical mechanics which, though an excellent approximation in many regards, has some serious deficiencies. One such problem discussed here has to do with zero point vibrational energy and the other with tunneling of light (e.g., hydrogen) atoms. Though quite rigorous semiclassical theories exist that would in principle solve these problems, we describe in this paper more approximate approaches that are intended to be suitable for direct incorporation into classical simulation algorithms.

#### 4. Calculation of the Cumulative Reaction Probability via a Discrete Variable Representation with Absorbing Boundary Conditions (Publication 13)<sup>†</sup>

*T. Seideman and W.H. Miller*

A new method is suggested for the calculation of the microcanonical cumulative reaction probability *via* flux autocorrelation relations. The Hamiltonian and the flux operators are computed in a discrete variable representation (DVR) and a well-behaved representation for the Green's operator,  $G(E^+)$ , obtained by imposing absorbing boundary conditions (ABC). Applications to a one-dimensional-model problem and to the collinear H+H<sub>2</sub> reaction show that the DVR-ABC scheme provides a very efficient method for the *direct* calculation of the microcanonical probability, circumventing the need to compute the state-to-state dynamics. Our results indicate that the cumulative reaction probability can be calculated to a high accuracy using a rather small number of DVR points, confined to the vicinity of the transition state. Only limited information regarding the potential-energy surface is therefore required, suggesting that this method would be applicable also to higher dimensionality problems, for which the complete potential surface is often unknown.

<sup>†</sup>This work is also supported in part by the National Science Foundation Grant CHE8920690.

#### 5. Quantum Mechanical Reaction Probabilities via a Discrete Variable Representation–Absorbing Boundary Condition Green's Function (Publication 14)<sup>†</sup>

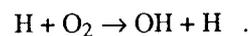
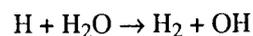
*T. Seideman and W.H. Miller*

The use of a discrete variable representation (DVR) and absorbing boundary conditions (ABC) to construct outgoing Green's function  $G(E^+) \equiv \lim_{\epsilon \rightarrow 0} (E + i\epsilon - H)^{-1}$ , and its subsequent use to determine the cumulative reaction probability for a chemical reaction, has been extended beyond our previous work in several significant ways. In particular, the present paper gives a more thorough derivation and analysis of the DVR-ABC approach, shows how the same DVR-ABC Green's function can be used to obtain state-to-state (as well as cumulative) reaction probabilities, derives a DVR for the exact, multidimensional Watson Hamiltonian (referenced to a transition state), and presents illustrative calculations for the three-dimensional H+H<sub>2</sub> reaction with zero total angular momentum.

<sup>†</sup>This work is also supported in part by the National Science Foundation Grant CHE8920690.

#### 6. Work in Progress

The new ways developed for computing the *cumulative reaction probability* in a direct (yet rigorous) fashion is being applied to the reactions



This methodology will allow absolutely rigorous calculations of the rates of simple reactions (given a potential energy surface).

#### FY 1991 PUBLICATIONS AND REPORTS

##### Refereed Journals

1. W.H. Miller and J.Z.H. Zhang, "How to Observe the Elusive Resonances in  $\text{H}$  or  $\text{D} + \text{H}_2 \rightarrow \text{H}_2$  or  $\text{HD} + \text{H}$  Reactive Scattering," *J. Phys. Chem.* **95**, 12 (1991); LBL-29939.
2. W.H. Miller, "Some New Approaches to Semiclassical and Quantum Transition State Theory," *Ber. Bunsenges Phys. Chem.* **95**, 389 (1991); LB-29938.

3. D.L. Yeager and W.H. Miller, "Complex Log-Derivative Method for NonReactive Coupled-Channel Scattering Calculations," *J. Phys. Chem.* **95**, 8212 (1991).
4. W.H. Miller and T. Seideman, "Transition State Theory, Siegert Eigenstates, and Quantum Mechanical Reaction Rates," *J. Chem. Phys.* **95**, 1768 (1991); LBL-30639.
5. W.H. Miller, "Comment on: Semiclassical Time Evolution without Root Searches," *J. Chem. Phys.* **95**, 9428 (1991).
6. T. Uzer and W.H. Miller, "Theories of Intramolecular Vibrational Energy Transfer," *Phys. Rep.* **199**, 73 (1991).
7. J.Z.H. Zhang, W.H. Miller, A. Weaver and D. Neumark, "Quantum Reactive Scattering Calculations of Franck-Condon Factors for the Photodetachment of  $\text{H}_2\text{F}^-$  and  $\text{D}_2\text{F}^-$  and Comparisons with Experiment," *Chem. Phys. Lett.* **182**, 283 (1991).
8. R.A. Harris, C.J. Grayce, N. Makri, and W.H. Miller, "A Corrected Exponential Power Series Expansion of the Position Matrix Elements of the Time Evolution Operator for a System in the Presence of a Vector Potential," *J. Chem. Phys.* **94**, 4682 (1991).

#### LBL Reports

9. W.H. Miller, "Quantum Mechanical Scattering for Chemical Reactions," in *Methods in Computational Molecular Physics*, ed. S. Wilson and G. H. F. Diercksen, NATO ASI; LBL-31627.
10. Y.T. Chang, C. Minichino, and W.H. Miller, "Classical Trajectory Studies of the Molecular Dissociation Dynamics of Formaldehyde:  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ ," *J. Chem. Phys.*, in press; LBL-31623.
11. W.H. Miller, "Reaction Dynamics in Polyatomic Molecular Systems: Some Approaches for Constructing Potential Energy Surfaces and Incorporating Quantum Effects in Classical Trajectory Simulations," in *The Role of Computational Models and Theories in Bio-Technology*, ed. J. Bertran, NATO ARW; LBL-31626.
12. W.H. Miller, "S-Matrix Version of the Kohn Variational Principle for Quantum Scattering Theory of Chemical Reactions," in *Advances in Molecular Vibrations and Collision Dynamics*, ed. J.M. Bowman, JAI Press; LBL-31625.
13. T. Seideman and W.H. Miller, "Calculation of the Cumulative Reaction Probability via a Discrete Variable Representation with Absorbing Boundary Conditions," *J. Chem. Phys.*, in press; LBL-31624.
14. T. Seideman and W.H. Miller, "Quantum Mechanical Reaction Probabilities via a Discrete Variable Representation-Absorbing Boundary Condition Green's Function," submitted to *J. Chem. Phys.*; LBL-32180.
15. W.H. Miller and T. Seideman, "Cumulative and State-to-State Reaction Probabilities via a Discrete Variable

Representation—Absorbing Boundary Condition Green's Function," in *Time Dependent Quantum Molecular Dynamics: Experiments and Theory*, ed. J. Broeckhove, NATO ARW; LBL-32181.

#### Invited Talks

16. W.H. Miller, "Some New Developments and Aspects of Transition State Theory," Kasha Conference on Proton Transfer Dynamics in Chemistry, Biology, and Physics, Tallahassee, FL, January 6–9, 1991.
17. W.H. Miller, "Quantum Reactive Flux Correlation Functions – Some New Developments," Meeting on Chemical Dynamics in the Time Domain, Oxford, England, March 20–23, 1991.
18. W.H. Miller, "Complex Kohn Variational Treatment of Reactive Scattering: Recent Advances and Applications," American Physical Society Spring Meeting, Washington, D.C., April 22–25, 1991.
19. W.H. Miller, "Recent Developments and Applications of Quantum Mechanical Reactive Scattering," Canadian Symposium on Computational Chemistry, Oxford, Quebec, May 19–22 1991.
20. W.H. Miller, "Reaction Dynamics in Polyatomic Molecular Systems: Some Approaches for Constructing Potential Energy Surfaces and Incorporating Quantum Effects in Classical Trajectory Simulations," NATO Advanced Research Workshop on the Role of Computational Models and Theories in Biotechnology, Saint Felieu de Guixols, Spain, June 13–19, 1991.
21. W.H. Miller, "Some Recent Developments in Quantum Mechanical Reactive Scattering and in Quantum Transition State Theory," Meeting on Recent Methodological Advances in Dynamical and Correlation Calculations, Peyresq, France, June 27–29 1991.
22. W.H. Miller, "Quantum Theory of Chemical Reactions: Some Recent Developments in Reactive Scattering and in Transition State Theory," Conference on the Dynamics of Molecular Collisions, Lake George, NY, July 7–12, 1991.
23. W.H. Miller, "Scattering Calculations Using Basis Set Expansions (4 Lectures)," NATO Advanced Study Institute on Methods in Computational Molecular Physics, Bad Windsheim, Germany, July 21–August 3, 1991.
24. W.H. Miller, "Semiclassical Methods in Chemical Dynamics," 4th Topsoe Summer School on Time Dependent Methods in Quantum Mechanics, Copenhagen, Denmark, August 19–23, 1991.
25. W.H. Miller, "Quantum Theory of Chemical Reactions: Reactive Scattering and Transition State Theory," Symposium on Comparison of *Ab Initio* Quantum Chemistry with Experiment (North American Chemical Congress), New York, NY, August 25–30, 1991.

# Selective Photochemistry\*

C. Bradley Moore, Investigator

## INTRODUCTION

The fundamental goals of this program are to understand the photophysics and photochemistry that occur following selective excitation of molecules and during the reactions of free radicals. Of particular interest are the chemical reactions of specifically excited states and the dynamics of energy transfer, both within a molecule and to surrounding molecules.

Molecules produced in bound excited singlet states may fragment following the conversion of electronic excitation energy into vibrational energy. Intersystem crossing to triplet states is often in competition with internal conversion to singlet states. In this work the dynamics of intersystem crossing and reaction of the triplet state are studied for both unimolecular and bimolecular systems.

For low levels of vibrational excitation in small molecules, individual quantum states may be excited, enabling the measurement of reaction and energy-transfer rate constants for each quantum state. For larger or more highly excited molecules, it is usually not possible to excite single eigenstates. Instead, a number of eigenstates are excited simultaneously, and a redistribution of the initial vibrational excitation occurs. This process, known as intramolecular vibrational energy redistribution (IVR), is extremely rapid and severely limits the realization of truly mode-specific unimolecular reactions. Advances in mode-specific chemistry will come from a more complete understanding of the IVR process and the parameters that control its efficiency. By being able to predict the rates of IVR and the path of vibrational energy flow through a molecule, experiments can be designed utilizing molecular systems that maximize the possibilities for mode-specific effects. Studies designed to elucidate the coupling mechanisms and dominant pathways for IVR are currently under way on a number of model systems. High resolution measurements as a function of energy reveal the dynamics of passage through the transition state. The rates and mechanisms of free-radical reactions, such as are important in combustion, are often best studied by flash kinetic spectroscopy using lasers for thermal heating, for photolyzing, and for spectroscopic probing. Reactions can be studied as a function of individual quantum states. A fundamental understanding of the rate constants and product distributions for these reactions is sought to serve as a basis for modeling combustion processes.

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SFO098.

## 1. Kinetics of Intramolecular Carbon Atom Exchange in Ketene (Publication 1)

E.R. Lovejoy, S.K. Kim, R.A. Alvarez, and C.B. Moore

Intramolecular carbon atom exchange in highly vibrationally excited ketene was studied by monitoring the carbon monoxide fragments ( $^{12}\text{CO}$  and  $^{13}\text{CO}$ ) from the photodissociation of  $^{12}\text{CH}_2^{13}\text{CO}$  and  $^{13}\text{CH}_2^{12}\text{CO}$ ; Figure 1-1 shows the reaction energetics and species. Two experimental techniques were employed. In one set of experiments the IR transient absorptions of  $^{12}\text{CO}$  and  $^{13}\text{CO}$  were measured following pulsed excimer excitation of ketene  $^{13}\text{C}$  isotopomers, giving carbon atom exchange yields at 351 and 308 nm in a low pressure gas cell. In the other set of experiments, jet-cooled ketene  $^{13}\text{C}$  isotopomers were excited with tunable near-UV radiation, and the CO products were detected by monitoring their VUV laser-induced fluorescence. Carbon atom exchange yields were measured for energies extending from below the triplet decomposition threshold ( $\text{CH}_2\text{CO} \rightarrow \text{CH}_2(X^3B_1) + \text{CO}(X^1\Sigma^+)$ ) to about  $4000\text{ cm}^{-1}$  above the singlet threshold ( $\text{CH}_2\text{CO} \rightarrow \text{CH}_2(a^1A_1) + \text{CO}(X^1\Sigma^+)$ ). The exchange yields range from 4 to 19% and the energy dependence of the yield exhibits pronounced structure, with maxima at the triplet and singlet decomposition threshold, Figure 1-2. Kinetic measurements of the appearance of the CO products were also performed. The time constant for the appearance of the exchanged CO (e.g.,  $^{13}\text{CO}$  from  $^{13}\text{CH}_2^{12}\text{CO}$ ) is significantly longer than that for the direct CO fragment (e.g.,  $^{12}\text{CO}$  from  $^{13}\text{CH}_2^{12}\text{CO}$ ). All the experimental observations are consistent with a simple reaction mechanism involving ketene isomerization,  $^{13}\text{CH}_2^{12}\text{CO} \rightleftharpoons ^{12}\text{CH}_2^{13}\text{CO}$ , and dissociation,  $^{13}\text{CH}_2^{12}\text{CO} \rightarrow ^{13}\text{CH}_2 + ^{12}\text{CO}$  and  $^{12}\text{CH}_2^{13}\text{CO} \rightarrow ^{12}\text{CH}_2 + ^{13}\text{CO}$ . The isomerization rate

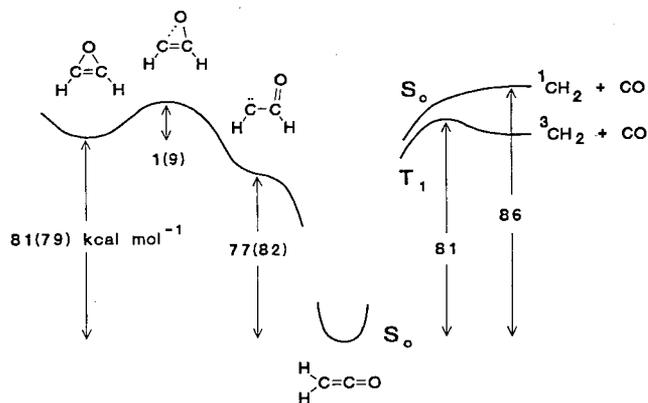
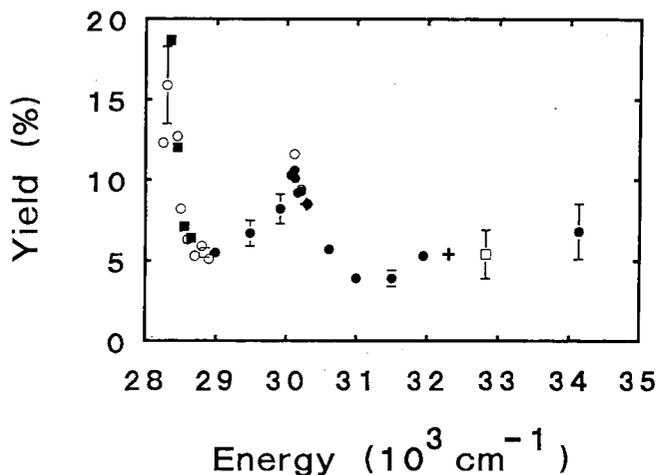


Figure 1-1. *Ab initio* energies for  $\text{C}_2\text{H}_2\text{O}$  isomers relative to ground state ketene including zero point energies. The ketene dissociation energies are our experimental values. (XBL 928-6189)



**Figure 1-2.** Carbon atom exchange yield as a function of the ketene excitation energy. (O)  $^{13}\text{CH}_2^{12}\text{CO}$  pulsed-jet/VUV LIF; (●)  $^{12}\text{CH}_2^{13}\text{CO}$  pulsed-jet/VUV LIF; (■) pulsed-jet/VUV LIF,  $^{12}\text{CO}$  and  $^{13}\text{CO}$  kinetics ( $^{13}\text{CH}_2^{12}\text{CO}$ ); (□) excimer photolysis/transient IR absorption; (+) low pressure (<10 torr) gas cell measurements by Russell and Rowland with  $^{14}\text{CH}_2\text{CO}$ . All the gas cell excitation energies have been adjusted for an average ketene internal energy of  $350 \text{ cm}^{-1}$  at 300 K. The error bars correspond to the 95% confidence limits for precision. (XBL 928-6190)

constant was determined by analyzing the CO kinetics and the carbon atom exchange yields in terms of the simple isomerization mechanism. A fit of the energy dependence of the isomerization rate constant to the results of tunneling-corrected RRKM calculations gave the threshold ( $28360 \pm 60 \text{ cm}^{-1}$ ) for the isomerization process.

## 2. Gas-Phase Rates of Alkane C-H Oxidative Addition to a Transient CpRh(CO) Complex (Publication 2)

*E.P. Wasserman, C.B. Moore, and R.G. Bergman*

The gas-phase irradiation of  $\text{CpRh}(\text{CO})_2(\text{Cp} = \eta^5\text{-C}_5\text{H}_5)$  was examined in order to study the rates of reaction of the 16-electron intermediates presumed to be involved in the C-H oxidative addition of alkanes. "Naked" (unsolvated) CpRh(CO) was detected, and direct measurements of the rates of reaction of this very short-lived complex with alkane C-H bonds were made. Activation of C-H bonds occurs on almost every collision for alkanes of moderate size, and intermediates in which the alkanes are bound to the metal centers, without their C-H bonds being fully broken, are implicated as intermediates in the overall reaction.

## 3. Work in Progress

Energy transfer and chemical reaction rates are being studied for triplet  $\text{CH}_2$  radicals. A diode laser infrared flash kinetic spectrometer is being used to study the reaction with  $\text{O}_2$  in order to identify product states and intermediates. Reaction rates for radical-radical reactions are being measured.

Unimolecular reaction dynamics are being studied by photofragment spectroscopy. Fragmentation on the triplet potential energy surface of ketene is being studied by detection of CO fragments using a tunable photolysis laser below the threshold for singlet fragmentation. Steps in the reaction rate allow vibrational energy levels of the transition state to be identified. The yield and rates for carbon atom exchange are studied by photolysis of  $^{13}\text{CH}_2\text{CO}$ . Rates are measured as a function of photolysis energy with  $\text{cm}^{-1}$  resolution.

Infrared and ultraviolet spectra of intermediates in organometallic photochemistry in gas and liquid phase are being studied jointly with R.G. Bergman. Emphasis is on CH activation chemistry. Studies of CH activation systems in liquid Kr and Xe are proceeding well.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. E.R. Lovejoy, S.K. Kim, R.A. Alvarez, and C.B. Moore, "Kinetics of Intramolecular Carbon Atom Exchange in Ketene," *J. Chem. Phys.* **95**, 4081 (1991).
2. E.P. Wasserman, C.B. Moore, and R.G. Bergman, "Gas-Phase Rates of Alkane C-H Oxidative Addition to a Transient CpRh(CO) Complex," *Science* **255**, 315 (1992).

### Invited Talks

3. C.B. Moore, "Unimolecular Reactions in the Quantum State Desolved Limit," University of Florida, Gainesville, FL, February 20, 1991.
4. C.B. Moore, "Chemical Bond Breaking," University of Florida, Gainesville, FL, February 22, 1991.
5. C.B. Moore, "Breaking Chemical Bonds," University of Nevada, Reno, Nevada, March 1, 1991.
6. C.B. Moore, DOE/BES Chemical Sciences Review, LBL, March 5, 1991.
7. C.B. Moore, "Unimolecular Reaction Dynamics," ACS Symposium Comparison of Ab initio Quantum Chemistry with Experiment: State-of-the-Art, New York City, August 25-30, 1991.
8. C.B. Moore, "A Spectroscopic View of Transition States in Unimolecular Reactions," Princeton University, New Jersey, November 15, 1991.

# Photodissociation of Free Radicals\*

Daniel M. Neumark, Investigator

## INTRODUCTION

While many photodissociation studies of stable molecules have been performed in recent years, it has proved difficult to extend these experiments to studies of reactive free radicals. This is largely due to the difficulty of implementing a clean, well-characterized source of free radicals. We have developed a novel approach to this problem by setting up an experiment in which free radicals are generated by photodetachment of a mass-selected anion beam, rather than the more conventional strategies in which radicals are formed by photolysis of a stable precursor or by a chemical reaction. Since nearly all radicals have a positive electron affinity, this approach should be quite general.

In the experiment, an 8-keV beam of cold mass-selected anions is photodetached with a pulser laser. The resulting neutral radicals are photodissociated with a second pulsed laser, and the photofragments are detected with high (~50%) efficiency using a microchannel plate detector that lies about 100-cm downstream from the photodissociation laser. The center of the detector is blocked so that the undissociated radicals do not impinge on it, but the photofragments move off the beam axis and strike the detector. The experiment can be operated in several modes. We can measure the total photofragment signal as a function of dissociation laser wavelength, thereby mapping out the dissociative electronic transitions of the radical. We can measure the time-of-flight distribution of the photofragments, thereby obtaining an approximated kinetic energy distribution at a fixed photodissociation wavelength. Finally, using a two-particle position and time sensing detector, we can determine detailed photofragment energy and angular distributions.

### 1. Fast Beam Studies of $N_3$ Photodissociation (Publication 8)<sup>†</sup>

R.E. Continetti, D.R. Cyr, R.B. Metz,<sup>‡</sup> and D.M. Neumark

A new fast radical beam apparatus has been used to study the photodissociation cross section of  $N_3$  as a function of wavelength. Neutralization of a fast negative

ion beam by photodetachment is used to create a beam of cold, mass-selected radicals, with subsequent photodissociation and efficient detection of the neutral fragments.  $N_3$  was observed to predissociate throughout the first electronic absorption near 270 nm. High-resolution predissociation spectra were obtained that show rotationally resolved structure. Time-of-flight measurements of the kinetic energy release confirm that the lowest energy dissociation pathway that occurs is the first spin-allowed channel producing  $N(2D) + N_2(1\Sigma_g^+)$ . The photoelectron spectrum of  $N_3^-$  was also obtained, yielding an electron affinity of  $2.68 \pm 0.01$  eV for  $N_3$ .

<sup>†</sup>Equipment and partial operating expenses for this work were provided by the National Science Foundation under Grant No. CHE-8803729.

<sup>‡</sup>Department of Chemistry, University of Wisconsin, Madison, WI 53706

### 2. Adiabatic Three-Dimensional Simulations of the $IHI^-$ , $BrHI^-$ , and $BrHBr^-$ Photoelectron Spectra (Publication 12)<sup>†</sup>

R.B. Metz<sup>‡</sup> and D.M. Neumark

In order to better characterize the transition state region for the  $I + HI$ ,  $Br + HI$ , and  $Br + HBr$  reactions, the photoelectron spectra of  $IHI^-$ ,  $IDI^-$ ,  $BrHI^-$ ,  $BrHBr^-$ , and  $BrDBr^-$  have been simulated using a three-dimensional adiabatic approach. This method of simulation uses a Born-Oppenheimer separation in time scales between the fast hydrogen atom motion and the slow halogen atom motion to greatly simplify the computational of the photoelectron spectrum. The resulting simulations are compared to the experimental photoelectron and threshold photodetachment spectra of these anions, and to "exact" simulations of the  $IHI^-$  and  $IDI^-$  spectra. The comparison with the exact simulations shows that the adiabatic method is reasonably accurate and is a considerable improvement over previous approximate simulation schemes. Potential energy surfaces for the  $I + HI$  and  $Br + HI$  reactions are evaluated based on a comparison between the simulated and experimental spectra. A three-dimensional surface for the  $Br + HBr$  reaction that reproduces the experimental photoelectron spectrum is constructed by extending a fitted collinear surface to three dimensions.

<sup>†</sup>Partial support from the Air Force Office of Scientific Research under Grant No. AFOSR910084.

<sup>‡</sup>Department of Chemistry, University of Wisconsin, Madison, WI 53706.

### 3. Work in Progress

Thus far, we have performed dissociation cross section and time-of-flight measurements of the  $N_3$ ,  $NCO$ , and  $CH_2NO_2$  radicals. We found that the  $A(2\Sigma^+) \leftarrow X(2\Pi)$

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

transitions in  $N_3$  near 270 nm results in predissociation to the spin-allowed  $N(^2D) + N_2$  channel. In contrast, in NCO, the  $B(^2\Pi) \leftarrow X(^2\Pi)$  transition leads to predissociation to the spin-forbidden  $N(^4S) + CO$  channel for dissociation wavelengths above 260 nm; at lower wavelengths, the spin-allowed  $N(^2D) + CO$  channel opens and is the dominant channel. From these results, we obtain  $\Delta H_f(NCO) = 30.5$  kcal/mole, about 5 kcal/mole lower than the literature value. Our experiments on  $CH_2NO_2$  photodissociation at several wavelengths indicate that the primary products are  $CH_2 + NO_2$ , and that the  $NO_2$  is most likely electronically excited.

We have recently begun experiments with our two-particle position and timesensing detector in which  $O_2$  photodissociated via the Schumann-Runge band. We form vibrationally excited  $O_2$  by photodetachment of  $O_2^-$  and excite rotationally predissociating transitions of the  $v' = 7 \leftarrow v'' = 4$  band near 210 nm. This work has shown that the current energy resolution of the detector is 50 meV. Preliminary studies of  $N_3$  dissociation with this detector yield resolved peaks in the photofragment kinetic energy distribution due to the  $N_2$  vibrational state distributions associated with the various N atom electronic states. We find that a small amount of  $N(^4S) + N_2$  is produced when the (000) vibrational level of the  $N_3A(^2\Sigma^+)$  state dissociates, but this spin-forbidden channel is quenched when the (010) level dissociates. A new anode design for this detector that should yield considerably improved energy resolution is now being tested.

## FY 1991 PUBLICATIONS AND REPORTS

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1. A. Weaver, D.W. Arnold, S.E. Bradforth, and D.M. Neumark, "Examination of the  $^2A_2$  and  $^2E$  States of  $NO_3$  by Ultraviolet Photoelectron Spectroscopy of  $NO_3^-$ ," *J. Chem. Phys.* **94**, 1740 (1991).
2. R.B. Metz, D.R. Cyr, and D.M. Neumark, "Study of the  $^2B_1$  and  $^2A_2$  States of  $CH_2NO_2$  via Ultraviolet Photoelectron Spectroscopy of the  $CH_2NO_2^-$  Anion," *J. Phys. Chem.* **95**, 2900 (1991).
3. T.N. Kitsopoulos, C.J. Chick, Y. Zhao, and D.M. Neumark, "Study of the Low-Lying Electronic States of  $Si_2$  and  $Si_2^-$  Using Negative Ion Photodetachment Techniques," *J. Chem. Phys.* **95**, 1441 (1991).
4. T.N. Kitsopoulos and D. M. Neumark, "Photoelectron Spectroscopy of  $Si_2^-$ ," *Mat. Res. Symp. Proc.* **206** (1990 Fall Meeting), Materials Research Society (1991), p. 71.
5. T.N. Kitsopoulos, C.J. Chick, Y. Zhao, and D.M. Neumark, "Threshold Photodetachment Spectroscopy of  $C_5^-$ ," *J. Chem. Phys.* **95**, 5479 (1991).
6. S.E. Bradforth, D.W. Arnold, R.B. Metz, A. Weaver, and D.M. Neumark, "Spectroscopy of the Transition State: Hydrogen Abstraction Reactions of Fluorine," *J. Phys. Chem.* **95**, 8066 (1991).
7. J.Z.H. Zhang, W.H. Miller, A. Weaver, and D. Neumark, "Quantum Reactive Scattering Calculations of Franck-Condon Factors for the Photodetachment of  $H_2F^-$  and  $D_2F^-$  and Comparisons with Experiment," *Chem. Phys. Lett.* **182**, 283 (1991).
8. R.E. Continetti, D.R. Cyr, R.B. Metz, and D.M. Neumark, "Fast Beam Studies of  $N_3$  Photodissociation," *Chem. Phys. Lett.* **182**, 406 (1991); LBL31879.
9. R.B. Metz, S.E. Bradforth, and D.M. Neumark, "Transition State Spectroscopy of Bimolecular Reactions Using Negative Ion Photodetachment," *Adv. Chem. Phys.* **81**, 1 (1992).
10. A. Weaver and D. M. Neumark, "Negative Ion Photodetachment as a Probe of Bimolecular Transition States: The  $F + H_2$  Reaction," *Faraday Discuss. Chem. Soc.* **91**, 5 (1991).
11. D.W. Arnold, S.E. Bradforth, T.N. Kitsopoulos, and D.M. Neumark, "Vibrationally Resolved Spectra of  $C_2-C_{11}$  by Anion Photoelectron Spectroscopy," *J. Chem. Phys.* **95**, 8753 (1991).

### LBL Reports

12. R.B. Metz and D.M. Neumark, "Adiabatic Three-Dimensional Simulations of the  $IHI^-$ ,  $BrHI^-$  and  $BrHBr^-$  Photoelectron Spectra," submitted to *J. Chem. Phys.*; LBL-31880.

### Invited Talks

13. D.M. Neumark, "Transition-State Spectroscopy in the Time of Frequency Domains," Conference on Chemical Dynamics in the Time Domain, Oxford, England, March 1991.
14. D.M. Neumark, "Negative Ion Photodetachment as a Probe of Bimolecular Transition States: The  $F + H_2$  Reaction," Faraday Discussions Meeting, Nottingham, England, March 1991.
15. D.M. Neumark, "Transition-State Spectroscopy of Fluorine Atom Reactions Using Negative Ion Photodetachment," American Chemical Society Meeting, Atlanta, GA, April 1991.
16. D.M. Neumark, "Vibrationally Resolved Photodetachment Spectra of Polyatomic Silicon and Carbon Cluster Anions," American Chemical Society Meeting, Atlanta, GA, April 1991.
17. D.M. Neumark, "Recent Results of Experimental Studies of the Transition State in Chemical Reactions," American Physical Society Meeting, Washington DC, April 1991.
18. D.M. Neumark, "Studies of Transition States and Clusters with Negative Ion Photodetachment," University of Chicago, May 1991.

19. D.M. Neumark, "Fast Beam Photodissociation Studies of Free Radicals," DOE Contractors Meeting, Lake Geneva, WI, May 1991.
20. D.M. Neumark, "Studies of Transition States and Clusters with Negative Ion Photodetachment," University of Perugia, Italy, June 1991.
21. D.M. Neumark, "Vibrationally Resolved Photodetachment Spectroscopy of Carbon and Silicon Clusters," Gordon Conference on Metal and Semiconductor Clusters, Wolfeboro, NH, August 1991.
22. D.M. Neumark, "Fast Beam Studies of Free Radical Photodissociation," Gordon Conference on Molecular Electronic Spectroscopy, Wolfeboro, NH, August 1991.
23. D.M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," Yale University, New Haven, CT, September 1991.
24. D.M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," University of California, Davis, CA, October 1991.
25. D.M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," U.S.-Japan Workshop for Young Investigators, Institute for Molecular Science, Okazaki, Japan, October 1991.
26. D.M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," IBM Almaden, NJ, November 1991.
27. D.M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," University of Southern California, November 1991.
28. D.M. Neumark, "Studies of Transient Species Using Negative Ion Photodetachment," University of Florida, Gainesville, December 1991.

# Physical Chemistry with Emphasis on Thermodynamic Properties\*

*Kenneth S. Pitzer, Investigator*

## INTRODUCTION

The purpose of this program is the discovery and development of methods of calculation of thermodynamic and related properties of important chemical systems by the use of quantum and statistical mechanics together with experimental measurements for key systems. Current emphasis is on fluid systems that include ionic components in novel ranges of conditions, including near-critical and supercritical temperatures and compositions extending from pure water or other polar solvent to pure fused salt. A very recent study concerned a novel ionic system with a critical point near room temperature where it was possible to measure with high precision the near-critical properties including the critical exponent  $\beta$ . Earlier advances yielded improved equations for electrolyte solutions that are now being applied to a wide variety of systems of industrial or geological interest, including geothermal brines. Other recent research involved the development of a feasible method of relativistic quantum mechanical calculation for molecules containing very heavy atoms and its application to important examples. This method is now in wide use. The closely related results of items 1 and 2 below are the most significant accomplishment of FY 1991.

### 1. Virial Coefficients and Equations of State for Mixed Fluids; Application to $\text{CH}_4\text{-H}_2\text{O}$ (Publication 5)

*K.S. Pitzer, A. Anderko, and S.M. Sterner*

The statistical mechanics of both pure and mixed fluids yields expressions in terms of virial series. The composition dependencies of various virial coefficients are well established, as are the integrals expressing their values in terms of intermolecular potentials. These expressions are simple for the second virial coefficient but increase in complexity so rapidly for higher coefficients that it is not yet feasible to generate a complete equation of state from

intermolecular potentials by this method. But it is shown that these properties for the second, third, and fourth virial coefficients can be combined in a very useful manner with information from the complete equations of state for the component pure fluids to yield a form for the equation for the mixed fluid that maintains consistency with all of the pertinent principles. This is in contrast to many of the more complex equations in current use that violate the basic statistical requirement for the composition dependency of the second virial coefficient. As an example, the new equation is applied to the very demanding and important system  $\text{CH}_4\text{-H}_2\text{O}$ . Figures 1-1a-d show the excellent agreement obtained.

### 2. Equation of State for Pure Fluids and Mixtures Based on a Truncated Virial Expansion (Publication 3)

*A. Anderko and K.S. Pitzer*

The equation proposed in item (1) above was applied to an array of 20 pure fluids that are nonpolar or weakly polar. These results are generalized using the critical temperature, the critical pressure, and the acentric factor as characterizing properties. The result is a general equation valid for any normal fluid. Application is then made to various mixtures of normal fluids and several mixtures of  $\text{H}_2\text{O}$  with light hydrocarbons. It is shown that a very small number of experimental measurements for a specific system suffice for a reliable prediction of both volumetric properties and phase relationships.

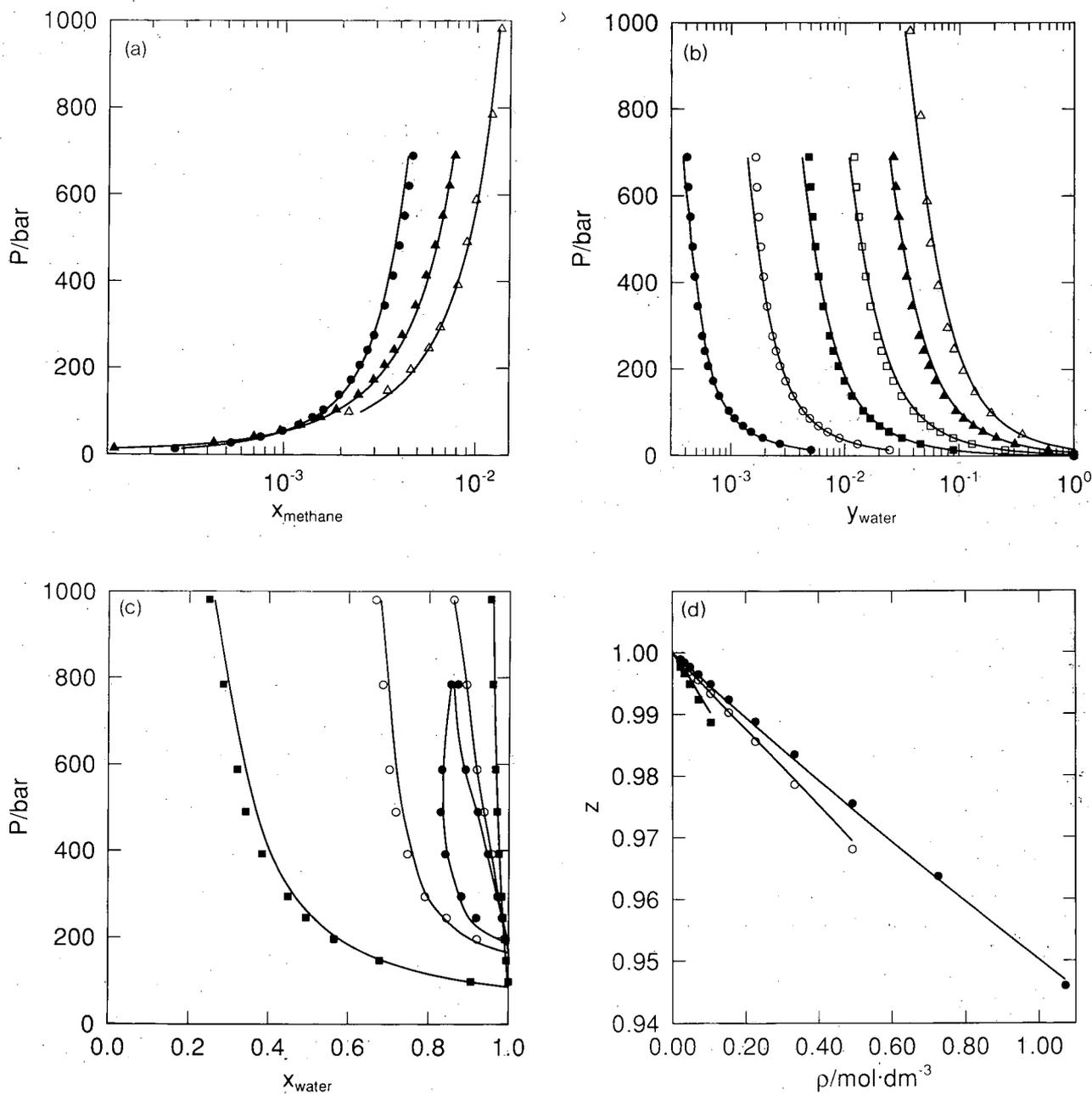
### 3. Thermodynamics of Very Concentrated Aqueous Electrolytes: $\text{LiCl}$ , $\text{ZnCl}_2$ , and $\text{ZnCl}_2\text{-NaCl}$ at $25^\circ\text{C}$ (Publication 2)

*R.G. Anstiss and K.S. Pitzer*

The effectiveness of extended ion-interaction equations in the treatment of activity and osmotic coefficients for very concentrated electrolytes is explored for the examples  $\text{LiCl-H}_2\text{O}$ ,  $\text{ZnCl}_2\text{-H}_2\text{O}$ , and  $\text{NaCl-ZnCl}_2\text{-H}_2\text{O}$ . For the two pure electrolytes the results are very satisfactory. Although satisfactory agreement is also obtained for the solubility of  $\text{NaCl}$  in the ternary system, this is too limited a data base to justify general conclusions.

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\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.



**Figure 1-1.** Comparison of calculated curves with experimental data (points) for the system CH<sub>4</sub>-H<sub>2</sub>O. (a) P-x comparison for the aqueous phase at 310.93 K (circles), 444.26 K (solid triangles) and 473.15 K (open triangles); (b) P-x comparison for the methane-rich phase at 310.93 K (solid circles), 344.26 K (open circles), 377.59 K (solid squares), 410.93 K (open squares), 444.26 K (solid triangles), and 473.15 K (open triangles); (c) vapor-liquid equilibria at 573.15 K (solid squares), 623.15 K (open circles), and 633.15 K (solid circles); (d) compressibility factor for equimolar mixture in the gas phase at 398.15 K (solid squares), 460.65 K (open circles), and 498.15 K (solid circles). (XBL 928-5353)

#### 4. Thermodynamics of Aqueous Sodium Sulfate for the Temperatures 273 to 373 K and Mixtures of Aqueous Sodium Sulfate and Sulfuric Acid at 298.15 K (Publication 10)

J.K. Hovey, K.S. Pitzer, and J.A. Rard<sup>†</sup>

New isopiestic vapor pressure measurements on the mixed aqueous system  $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$  along with earlier measurements give data for the complete composition range. These results have been analyzed in terms of the ion-interaction (Pitzer) equations. For pure aqueous  $\text{Na}_2\text{SO}_4$ , data over the range 273–373 K were similarly analyzed, and the results used for the mixed system. Two sets of ion-interaction parameters were presented for the mixture: the first yields high accuracy for total sulfate molalities up to that of saturation for pure  $\text{Na}_2\text{SO}_4$  ( $4 \text{ mol}\cdot\text{kg}^{-1}$ ) while the second gives less precise results for the entire range of data considered that extends to  $15 \text{ mol}\cdot\text{kg}^{-1}$  for  $\text{H}_2\text{SO}_4$ . Examples of relevant calculations using these results are given.

<sup>†</sup>Lawrence Livermore National Laboratory.

#### 5. Work in Progress

A comprehensive equation of state is being developed for the system  $\text{NaCl-H}_2\text{O}$  at high temperatures that is very important geologically and industrially and very complex theoretically. Recent advances in the statistical mechanics of mixed fluids of dipolar molecules are employed. The equation is required to yield the correct compositions and densities of both vapor and liquid phases as well as the density of the single-phase supercritical fluid and the solubility of solid  $\text{NaCl}$  over the very wide range from 573 to 1073 K and to 5000 bar in pressure. The form of the equation is one which is readily extended to more complex fluids with three or more components.

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2. R.G. Anstiss and K.S. Pitzer, "Thermodynamics of Very Concentrated Aqueous Electrolytes:  $\text{LiCl}$ ,  $\text{ZnCl}_2$ , and  $\text{ZnCl}_2\text{-NaCl}$  at  $25^\circ\text{C}$ ," *J. Sol. Chem.* **20**, 849 (1991); LBL-30621.
3. A. Anderko and K.S. Pitzer, "Equation of State for Pure Fluids and Mixtures Based on a Truncated Virial Expansion," *AIChE J.* **37**, 1379 (1991); LBL-30586.

4. S.M. Sterner and R.J. Bodnar, "Synthetic Fluid Inclusions. X: Experimental Determination of P-V-T-X Properties in the  $\text{CO}_2\text{-H}_2\text{O}$  System to 6 KB and  $700^\circ\text{C}$ ," *Am. J. Sci.* **291**, 1 (1991); LBL-29455.<sup>†</sup>

#### LBL Reports

5. K.S. Pitzer, A. Anderko, and S.M. Sterner, "Virial Coefficients and Equations of State for Mixed Fluids; Application to  $\text{CH}_4\text{-H}_2\text{O}$ ," invited talk presented at the 11th Symposium on Thermophysical Properties, University of Colorado, Boulder, June 23-27, 1991. *Fluid Phase Equilibria* (in press); LBL-30899.
6. A. Anderko and K.S. Pitzer, "Equation of State for Pure Sodium Chloride," 11th Symp. on Thermophysical Properties, University of Colorado, Boulder, June 23-27, 1991. *Fluid Phase Equilibria* (in press); LBL-30861.
7. K.S. Pitzer and S.M. Sterner, "Equations of State for Solid  $\text{NaCl-KCl}$  and Liquid  $\text{NaCl-KCl-H}_2\text{O}$ ," 11th Symp. on Thermophysical Properties, University of Colorado, Boulder, June 23-27, 1991. *Fluid Phase Equilibria* (in press); LBL-30916.<sup>‡</sup>
8. I.-M. Chou, S.M. Sterner, and K.S. Pitzer, "Phase Relations in the System  $\text{NaCl-KCl-H}_2\text{O}$ . IV: Differential Thermal Analysis of the Sylvite Liquidus in the  $\text{KCl-H}_2\text{O}$  Binary, the Liquidus in the  $\text{NaCl-KCl-H}_2\text{O}$  Ternary, and the Solidus in the  $\text{NaCl-KCl}$  Binary to 2 Kilobars Pressure," *Geochim. et Cosmochim. Acta* (in press); LBL-31058.<sup>‡</sup>
9. S.M. Sterner, I.-M. Chou., R.T. Downs, and K.S. Pitzer, "Phase Relations in the System  $\text{NaCl-KCl-H}_2\text{O}$ . V: Thermodynamic-PTX Analysis of Solid-Liquid Equilibria at High Temperatures and Pressures," *Geochim. et Cosmochim. Acta* (in press); LBL-31059.<sup>‡</sup>
10. J.K. Hovey, K.S. Pitzer, and J.A. Rard, "Thermodynamics of Aqueous Sodium Sulfate from 273 to 373 K and Mixtures of Aqueous Sodium Sulfate and Sulfuric Acid at 298 K," 47th Annual Calorimetry Conf., Northern Illinois Univ., DeKalb, IL, July 28-August 1, 1991. *J. Chem. Thermodyn.* (in press); LBL-31194.
11. K.S. Pitzer, "Thermodynamics of Natural and Industrial Waters," (invited talk) 47th Annual Calorimetry Conf., Northern Illinois Univ., DeKalb, IL, July 28-August 1, 1991. *J. Chem. Thermodyn.* (in press); LBL-31210.

#### Invited Talk

12. K.S. Pitzer, "Critical Properties of Ionic Fluids," Gordon Research Conference on the Chemistry and Physics of Liquids, Plymouth, N.H., August 12-16, 1991.

<sup>‡</sup>This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering and Geosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

# Chemical Physics at High Photon Energies\*

David A. Shirley, Principal Investigator

## INTRODUCTION

This program addresses both experimental and theoretical aspects of electron spectroscopy for the investigation of electronic structure of matter in the gaseous and condensed phases. Research is conducted using both laboratory sources at LBL and synchrotron radiation in the 5–5000 eV energy range available at SSRL and NSLS, with emphasis on developing the high-resolution spectroscopy in the 20–1000 eV energy range by using both modified toroidal grating monochromator (TGM) and spherical grating monochromators at SSRL. Effects are emphasized that can be refined and extended with the advent of third-generation light sources; e.g., threshold and near-edge photoexcitation phenomena, very fast processes, and processes requiring very high intensity and energy resolution. Electron correlations in atoms and molecules are studied, especially in the adiabatic (low-energy) limit, where the electronic structure of the continuum is important. Time-of-flight measurements with synchrotron radiation are used to measure angular distributions of photoelectrons and resonant photoemission phenomena in the gas phase. Of special interest are ultrahigh resolution absorption and threshold photoemission studies. 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, this program examines the electronic structure of solids. The program also studies the geometric and electronic structure of surface-adsorbate systems using photoelectron diffraction, angle-resolved photoemission extended fine structure (ARPEFS).

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\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098. It was performed at the National Synchrotron Light Source (NSLS) and Stanford Synchrotron Radiation Laboratory (SSRL), which are supported by the Department of Energy's Office of Basic Energy Sciences.

## 1. A Detailed Study of $c(2\times 2)$ Cl/Cu(001) Adsorbate Geometry and Substrate-Surface Relaxation Using Low-Temperature Angle-Resolved Photoemission Extended Fine Structure (Publication 1)

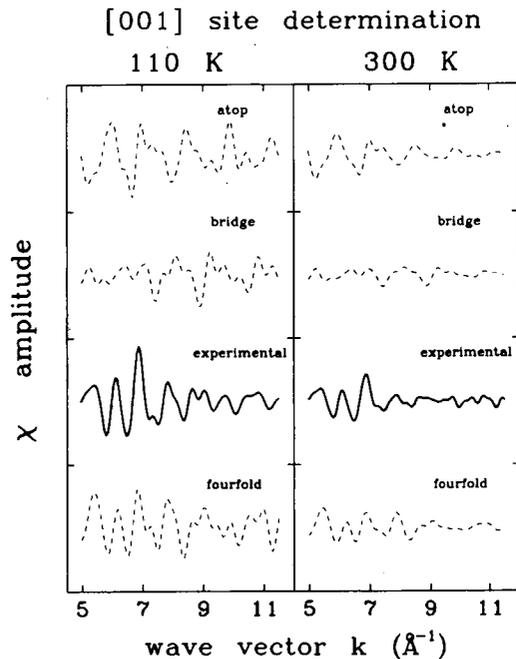
L.-Q. Wang, A.E. Schach von Wittenau, Z.G. Ji, L.S. Wang, Z.Q. Huang, and D.A. Shirley

A detailed structural study of the  $c(2\times 2)$ Cl/Cu(001) adsorbate system was made, using the angle-resolved photoemission extended-fine-structure (ARPEFS) technique at low temperature, which yields both more accurate surface structural information and near-surface structural information for deeper substrate layers. Electrons were detected along two emission directions, (001) and (011), and at two temperatures, 110 and 300 K. The Cl atoms were found to adsorb in the fourfold hollow site, 1.604(5) Å above the first copper layer, with a Cl-Cu bond length of 2.416(3) Å (in which the errors in parentheses are statistical standard deviations only). These values are in excellent agreement with a previous low-energy electron diffraction study by Jona et al. The  $c(2\times 2)$  Cl-covered first copper layer showed no relaxation with respect to the bulk position. However, a small corrugation of the second copper layer was found: The second-layer copper atoms below the Cl atoms move 0.042(12) Å away from the surface, while those in open positions remain in their bulk positions. The distances from the Cl atoms to the third and fourth copper layers were found to be 5.222(25) and 7.023(22) Å, respectively, yielding a bulk-like inner layer spacing (see Figure 1-1). Thus the depth sensitivity of the low-temperature ARPEFS facilitated definitive referencing of near-surface atomic positions to the underlying lattice.

## 2. Surface Structure of $\sqrt{3}\times\sqrt{3}R\ 30^\circ$ Cl/Ni(111) Determined Using Low-temperature Angle-resolved Photoemission Extended Fine Structure (Publication 2)

L.-Q. Wang, Z. Hussain, Z.Q. Huang, A.E. Schach von Wittenau, D.W. Lindle, and D.A. Shirley

A surface structural study of the  $\sqrt{3}\times\sqrt{3}R\ 30^\circ$  Cl/Ni(111) adsorbate system was made using low-temperature angle-resolved photoemission extended fine structure. The experiments were performed along two emission directions, (111) and (110), and at two temperatures, 120 and 300 K. The multiple-scattering spherical-wave analysis determined that the Cl atom adsorbs in the fcc threefold hollow site, 1.837(8) Å above the first nickel layer, with a Cl-Ni bond length of



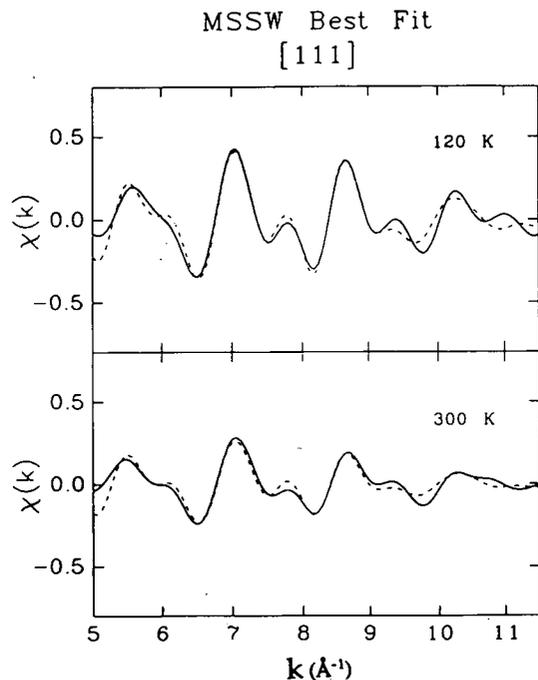
**Figure 1-1.** Absorption site determination for the [001] geometry at two temperatures. The experimental curves (solid lines) are compared to the multiple-scattering spherical wave (MSSW) calculated curves (dashed lines) for three unreconstructed adsorption geometries (atop, bridge, and fourfold hollow). The experimental data most closely resemble the fourfold hollow calculations at both temperatures. (XBL 928-6176)

2.332(6) Å, and an approximate 5% contraction between the first and the second nickel layers (the errors in parentheses are statistical standard deviations only; see Figure 2-1).

### 3. Reevaluation of the p(2×2)S/Cu(001) Structure Using ARPEFS (Publication 3)

*A.E. Schach von Wittenau, Z. Hussain, L.-Q. Wang, Z.Q. Huang, Z.G. Ji, and D.A. Shirley*

The experiment was performed using low-temperature (110–160 K) angle-resolved photoemission extended fine structure studies of p(2×2)S/Cu(001). Analysis based on multiple scattering spherical wave calculations indicates that S adsorbs into a fourfold hollow site 1.32 Å above the Cu surface, with near-surface reconstruction of the Cu layers in general similar to recent LEED and medium-energy ion-scattering results, removing an earlier discrepancy (see Figure 3-1). The S-Cu bond length is determined to be 2.26 Å. The second-layer Cu(001) plane appears to be corrugated more than indicated by the other methods. Additional reconstruction may be present in this system.



**Figure 2-1.** The best fits of the MSSW calculations (dashed curves) to the filtered (10.0 Å) ARPEFS data (solid curves) for the [111] geometry at two temperatures, 120 and 300 K. (XBL 928-6177)

### 4. Amplitudes and Phase Shifts in Electron-Atom Forward Scattering: Strong Dependence on Atomic Valence Electrons

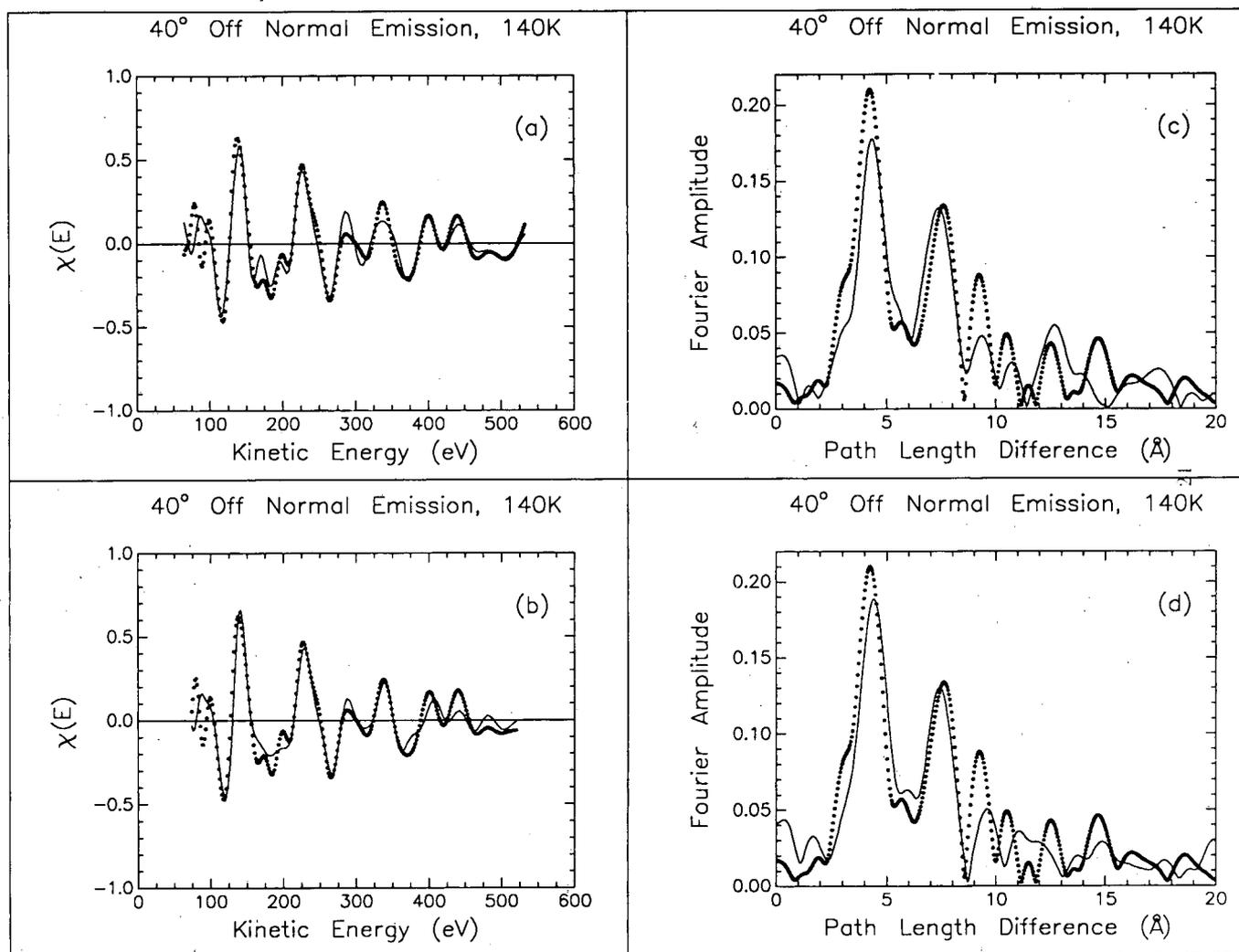
*Y. Zheng, Z. Hussain, and D.A. Shirley*

Forward-scattering amplitudes and phase shifts for intermediate-energy electrons were systematically calculated for selected elements throughout the Periodic Table. Characteristic variations in the forward-scattering amplitudes with atomic number were found (see Figure 4-1) that differ from those observed in backscattering amplitudes. Strong effects of atomic valence electrons on the forward-scattering process are evident.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

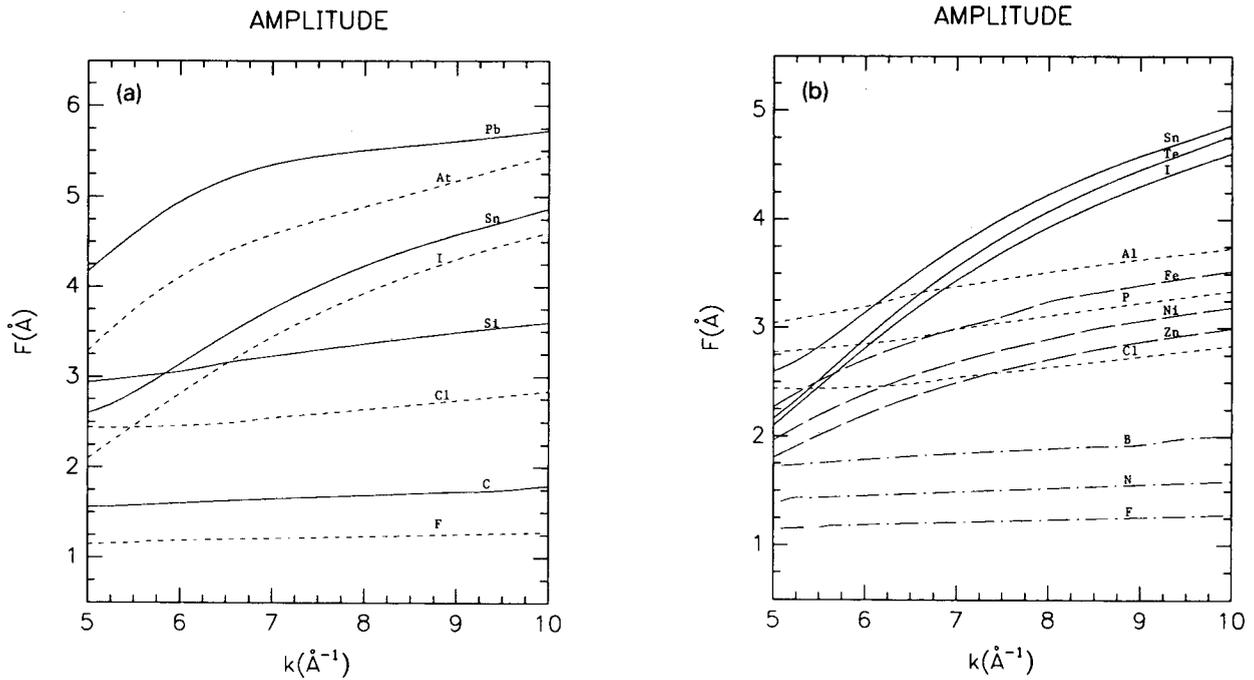
1. L.-Q. Wang, A.E. Schach von Wittenau, Z.G. Ji, L.S. Wang, Z.Q. Huang, and D.A. Shirley, "A Detailed Study of c(2×2)Cl/Cu(001) Adsorbate Geometry and Substrate Surface Relaxation Using Low-Temperature Angle-Resolved Photoemission Extended Fine Structure," *Phys. Rev. B*, **44**, 1292 (1991); LBL-28731.



**Figure 3-1.** Results of fitting the 40° off normal emission (140 K) data in k-space and R-space. The k-space curves are Fourier filtered at  $2.1 \text{ \AA} < R < 15.4 \text{ \AA}$ . (a) and (c): Comparison of data (dots) and theory (solid line) curves. Fit performed in k-space. (b) and (d): Comparison of data (dots) and theory (solid line) curves. Fit performed in R-space. (XBL 928-6178)

2. L.-Q. Wang, Z. Hussain, Z.Q. Huang, A.E. Schach von Wittenau, D.W. Lindle, and D.A. Shirley, "Surface Structure of  $\sqrt{3} \times \sqrt{3} R 30^\circ \text{ Cl/Ni(111)}$  Determined Using Low-Temperature Angle-Resolved Photoemission Extended Fine Structure," *Phys. Rev. B.* **44**, 13711 (1991).
3. M. Domke, C. Xue, A. Puschmann, T. Madel, E. Hudson, D.A. Shirley, and G. Kaindl, "Extensive Double Excitation States in Atomic Helium," *Phys. Rev. Lett.* **66**, 1306 (1991).
4. A.E. Schach von Wittenau, Z. Hussain, L.-Q. Wang, Z.Q. Huang, Z.G. Ji, and D.A. Shirley, "Reevaluation of the  $p(2 \times 2)S/Cu$  Structure Using ARPEFS," *Phys. Rev. B.*, in press; LBL-31501.
5. Y. Zheng, Z. Hussain, and D.A. Shirley, "Amplitudes and Phase Shifts in Electron-Atom Forward Scattering: Strong Dependence on Atomic Valence Electrons," *Chem. Phys. Lett.* (in press); LBL-31818.
6. L.J. Medhurst (Ph.D. Thesis), "Photoelectron and Photodissociation Studies of Free Atoms and Molecules, Using Synchrotron Radiation," LBL-31466.
7. L.J. Medhurst, P.A. Heimann, M.R.F. Siggel, D.A. Shirley, C.T. Chen, Y. Ma, S. Modesti, and F. Sette, "Vibrationally Resolved Threshold Photoemission of  $N_2$  and CO at the N and C K-edges," LBL-30354.
8. L.Q. Wang, "Surface Structures and Surface-Atom Vibrations Determined Using Photoelectron Diffraction," Ph.D. Thesis; LBL-31081.
9. A.E. Schach von Wittenau (Ph.D. Thesis), "ARPEFS as an Analytic Technique," LBL-30769.

#### LBL Reports



**Figure 4-1.** (a) Calculated forward-scattering amplitudes of elements in columns IV and VII. (b) Calculated forward-scattering amplitudes of elements in rows II-IV. (XBL 928-6179)

#### Invited Talks

10. D. Shirley, "ALS at Berkeley," Workshop on the Synchrotron Light Source, Paul Scherrer Institute, Switzerland, July 1991.
11. Z. Hussain, "High Resolution Soft X-Rays: Where Are They and How Can We Use Them?" SSRL User's Meeting, Stanford, CA.

# ATOMIC PHYSICS

## High Energy Atomic Physics\*

*Eugene B. Commins and Harvey Gould, Investigators*

### INTRODUCTION

The goals of this program are to understand atomic collisions of highly relativistic heavy ions, to search for a permanent electron electric dipole moment (EDM) and to test quantum electrodynamics in a strong static Coulomb field. Recent results include a new technique for determining electron impact ionization cross sections of highly ionized atoms, as well as achieving the best upper limit to the electron EDM. Finding an electron EDM would be proof of new physics, not contained in the Standard Model, and would be as significant a discovery as the results expected from the Superconducting Super Collider. Present activities include (1) an attempt to observe, measure, and accurately calculate the differential cross sections for capture from pair production, a new relativistic atomic collisions process, in which an electron is captured by a relativistic (bare) ion, when the electron is produced as part of an electron positron-pair by the motional Coulomb fields of the relativistic ion passing within atomic distances of a target nuclei; (2) developing a more sensitive EDM experiment; and (3) continued adherence to applicable standards for environment, health, safety, and procedure in all activities.

#### 1. Relativistic Electron Impact Ionization of Highly Stripped Heavy Ions Determined from Projectile Electron Loss in H<sub>2</sub> and He (Publication 3)

*B. Feinberg, Harvey Gould, W.E. Meyerhof,<sup>†</sup> A. Belkacem, H.-P. Hülskötter,<sup>†</sup> J.R. Alonso, L. Blumenfeld, E. Dillard,<sup>†</sup> N. Guardala,<sup>†</sup> G.F. Krebs, M.A. McMahan, M.J. Rhoades-Brown,<sup>‡</sup> B.S. Rude, J. Schweppe, D.W. Spooner,<sup>†</sup> K. Street,<sup>§</sup> P. Thieberger,<sup>‡</sup> and H. Wegner<sup>‡</sup>*

Until now, the only way to measure electron impact ionization of the heaviest highly stripped heavy ions has been by using the high density of quasi-free electrons along a crystal channel. Here we present an alternative technique using the loosely bound electrons of low-Z

atomic targets, such as hydrogen and helium, as a moderately dense target. This method has the advantage of using a lower density, large thickness target whose parameters are well characterized and accurately controlled.

Stripping a tightly bound electron from a projectile requires an energy transfer high enough to overcome the ionization energy,  $I$ . For very large values of  $I$ , the size of the projectile and the impact parameter are much smaller than the K-shell of the low-Z target. The projectile electron loss cross section under these conditions is the sum of a contribution from the electron(s) and a contribution from the nucleus without interference. Because the target electron binding energy is very small compared to the energies involved in the process, one can ignore the binding energy and assume that the electron is quasi-free.

Since the nuclear contribution to the ionization cross section is proportional to  $Z^2$ , while the target electron contribution is proportional to the number of electrons,  $Z$ , measurements of the total ionization cross sections in both H<sub>2</sub> and He may be combined to yield the electron impact ionization.

We measured the one-electron loss cross sections for U<sup>86+</sup> at 405 MeV/u and Au<sup>52+</sup> at 100 and 380 MeV/u, all in H<sub>2</sub> and He, at the Bevalac. The ions pass through a 241-cm long, 40-cm diameter gas cell target filled with up to 5 Torr of H<sub>2</sub> or He gas. We determine the one-electron loss cross section by measuring the growth of the Au<sup>53+</sup> and U<sup>87+</sup> peaks, respectively, as a function of gas pressure.

We obtain a cross section of  $91 \pm 28$  barns for the electron impact ionization cross section of U<sup>86+</sup> by 222-keV electrons (in the projectile reference frame), and cross sections of  $7.5 \pm 3.0$  kbarns and  $4.5 \pm 1.4$  kbarns for the electron impact ionization of Au<sup>52+</sup> by 54.9- and 208-keV electrons, respectively.

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<sup>‡</sup>Brookhaven National Laboratory, Upton, NY 11973.

<sup>§</sup>Berkeley High School, Berkeley, CA 94704.

#### 2. Work in Progress

In a relativistic charged particle collision, the large transient Coulomb field can produce electron-positron pairs. If the collision involves a highly stripped ion, the electron may be captured by the ion. This process, "electron capture from pair production," was first suggested by Gould in 1984. Unlike all other known electron capture processes, the cross section for electron

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

capture from pair production is predicted to increase at relativistic energies. Thus at highly relativistic energies, it is expected to become the dominant capture process. Although the cross section for capture from pair production may be estimated semiclassically, the estimate is almost certainly inaccurate. An accurate calculation must take into account the extremely strong fields, the large probability for producing the pairs, and the small impact parameters required to transfer the large energies necessary to produce the pairs.

The signature of electron capture from pair production is the change in charge state of the projectile (from  $U^{92+}$  to  $U^{91+}$ , for example) with the simultaneous production of a positron. For  $U^{92+}$  on a gold target, the cross section for electron capture from pair production at 1 GeV/n is expected to be about 1 barn. The energy and angular distribution of the positrons will be measured using a magnetic spectrometer (in coincidence with the charge change of the projectile) to yield a doubly differential cross section. The projectile charge states will be measured by the same Bevalac magnetic spectrometer, used for all earlier charge changing experiments. A positron spectrometer of a new and novel design will be specially built to measure the positron energy and angle.

An apparatus for performing the first observation and measurement of electron capture from pair production was fabricated, assembled, and tested with energetic electrons and positrons from radioactive sources. The heart of the apparatus, the Advanced Positron Spectrometer (APS), incorporates several new and novel features to measure the doubly differential cross section (positron energy and angle) with >70% efficiency at all energies and angles of interest.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. J. Schweppe, A. Belkacem, L. Blumenfeld, N. Claytor, B. Feinberg, H. Gould, V.E. Kostroun, L. Levy, S. Misawa, J.R. Mowat, and M.H. Prior, "Measurement of the Lamb Shift in Lithiumlike Uranium ( $U^{89+}$ )," *Phys. Rev. Lett.* **66**, 1434 (1991); LBL-30370.
2. H.-P. Hülskötter, B. Feinberg, W.E. Meyerhof, A. Belkacem, J.R. Alonso, L. Blumenfeld, E. Dillard, H. Gould, N. Guardala, G.F. Krebs, M.A. McMahan, M.J. Rhoades-Brown, B.S. Rude, J. Schweppe, D.W. Spooner, K. Street, P. Thieberger, and H. Wegner, "Electron-electron Interaction in Projectile Electron Loss," *Phys. Rev.* **A44**, 1712 (1991); LBL-31815.

3. E.D. Commins, "Berry's Geometric Phase and Motional Fields," *Am. J. Phys.* **59** (12) 1077 (1991).

### LBL Reports

4. B. Feinberg, H. Gould, W.E. Meyerhof, A. Belkacem, H.-P. Hülskötter, J.R. Alonso, L. Blumenfeld, E. Dillard, N. Guardala, G.F. Krebs, M.A. McMahan, M.J. Rhoades-Brown, B.S. Rude, J. Schweppe, D.W. Spooner, K. Street, P. Thieberger, and H. Wegner, "Relativistic Electron and Proton Impact Ionization of Highly Stripped Heavy Ions Determined from Projectile Electron Loss in  $H_2$  and He," submitted to *Phys. Rev. Lett.*; LBL-31022.
5. H. Gould, K. Abdullah, C. Carlberg, E.D. Commins, and S.B. Ross, "A New Experimental Limit on the Electron Electric Dipole Moment," abstract for the Spring Meeting of the American Physical Society, *Bull. Am. Phys. Soc.* **36**, 1336 (1991); LBL-30219 Abstract.
6. C.R. Vane, S. Datz, P.F. Dittner, H.F. Krause, A. Belkacem, B. Feinberg, H.A. Gould, R. Schuch, H. Knudsen, P. Hvelplund, "Measurement of Pair Production in Relativistic Heavy Particle Coulomb Collisions," abstract for the Spring Meeting of the American Physical Society, *Bull. Am. Phys. Soc.* **36**, 1390 (1991).
7. B. Feinberg, H. Gould, W.E. Meyerhof, A. Belkacem, H.-P. Hülskötter, J.R. Alonso, L. Blumenfeld, E. Dillard, N. Guardala, G.F. Krebs, M.A. McMahan, M.J. Rhoades-Brown, B.S. Rude, J. Schweppe, D.W. Spooner, K. Street, P. Thieberger, and H. Wegner, "Relativistic Electron and Proton Impact Ionization of Highly Stripped Heavy Ions Determined from Projectile Electron Loss in  $H_2$  and He," submitted to the 12<sup>th</sup> DOE Atomic Physics Program Workshop, Manhattan, KS, Oct. 15-16, 1991; LBL-31816 Abstract.
8. E.D. Commins, H. Gould, and S.B. Ross, "Improvements to the Electron Electric Dipole Moment Experiment," submitted to the 12<sup>th</sup> DOE Atomic Physics Program Workshop, Manhattan, KS, Oct. 15-16, 1991; LBL-31817 Abstract.

### Invited Talks

9. H. Gould, "A New Limit on the Electric Dipole Moment of the Electron," Fermi Lab, Batavia, IL, May 2, 1991.
10. H. Gould, "A New Limit on the Electric Dipole Moment of the Electron," Stanford Linear Accelerator Laboratory, Stanford, CA, May 20, 1991.
11. H. Gould, "Measurement of the Lamb Shift in Lithiumlike Uranium," Notre Dame University, Notre Dame, IN, May 1, 1991.
12. H. Gould, "Relativistic Electron and Proton Impact Ionization of Highly Stripped Heavy Ions Determined from Projectile Electron Loss in  $H_2$  and He," at the 12<sup>th</sup> DOE Atomic Physics Program Workshop, Manhattan, KS, Oct. 15-16, 1991.

13. H. Gould and E.D. Commins, "Search for the Electric Dipole Moment of the Electron," UC Berkeley Chemistry Dept. Colloquium, Berkeley, CA, March 1991; UC Physics Dept. Colloquium, Santa Barbara, CA, April

1991; University of Notre Dame, IN, September 1991; Symposium on Time Reversal, University of Michigan, Ann Arbor, MI, October 1991.

## Atomic Physics\*

Michael H. Prior, Investigator

### INTRODUCTION

This program performs studies of the structure and interactions of atomic systems, to provide the most detailed description of their behavior and to challenge and stimulate theoretical understanding of the observed phenomena. Emphasis is placed upon research topics that are best addressed with unique research tools and expertise available at LBL. Often topics selected have relevance to plasma behavior and diagnostics in tokamak devices or advanced laser technology. Collaborative associations with investigators from outside LBL form an essential means of bringing resources to the program, forming stimulating scientific exchange and efficiently utilizing experimental facilities.

Currently the program exploits the ability of state-of-the-art electron cyclotron resonance (ECR) ion sources at LBL to produce intense, highly charged beams for conduct of ion-atom collision and Auger spectroscopic studies. Work is carried out using the atomic physics facilities jointly established by LBL and LLNL at the LBL ion sources. These include three beamlines, several electron and optical spectrometers, a multipurpose scattering chamber with precision controlled rotating table, and data collection instrumentation. Work to date has used ion beams from the original LBL ECR source constructed in 1984 by the LBL Nuclear Science Division (NSD) to provide heavy ions for acceleration by the LBL 88-Inch Cyclotron. Two beamlines are in operation with this source; the third is attached to the recently constructed Advanced ECR source located nearby. The proximity of the two sources and facilities allows efficient use of instrumentation at either and quick switchover from one source to the other. The enhanced performance of the AECR will allow mounting of experiments that require the increased intensity and/or higher charged beams available from this source.

The program is presently providing the most detailed experimental description of multiple electron capture in slow ion-atom collisions. In the past, nearly all multiple electron capture experiments have consisted of total cross-section measurements into unresolved or only partially resolved final states. Thus, whereas theorists can calculate population amplitudes into fully defined quantum states of

the products, summing and averaging over much of this detail is required to obtain a total or partial cross section to compare with the much less detailed experimental data. A large part of our research program is addressed to performance of experiments that describe double (or more) electron transfer between uniquely characterized final states so that theoretical predictions can be tested at the finest scale possible.

The program also provides energy level structure, and decay modes of highly excited states, and insight into novel population mechanisms in ion-atom collisions, for a wide range of multiply charged ions.

#### 1. Magnetic Substates Populated in Double Electron Capture (Publication 1)

R.A. Holt,<sup>†</sup> M.H. Prior, K.L. Randall,<sup>‡</sup> R. Hutton,<sup>§</sup>  
J McDonald,<sup>||</sup> and D. Schneider<sup>¶</sup>

We have observed striking variations of magnetic substate populations formed in double electron capture by H-like  $C^{5+}$  ions from He target atoms. We see large deviations from a uniform distribution that change substantially over the collision velocity range  $\approx 0.25-0.50$  au ( $1 \text{ au} = 2.19 \times 10^8 \text{ cm/sec}$ ). Capture from the He atoms populates the doubly excited  $1s2\ell 2\ell'$  configuration of the Li-like  $C^{3+}$  product ion. Since the two electrons are captured from a spin singlet state (the He ground state), and their spin is conserved in the capture process, the only unpaired electron in the Li-like product is from the projectile and thus only states of the type  $1s(2\ell 2\ell')^2L$  are produced. We have measured the anisotropy, with respect to the projectile beam direction, of the Auger emission from both the  $1s(2s2p^1P)^2P$  and  $1s(2p^2)^2D$  states of both product ions. Since the final state of the projectile ion, after Auger emission, is He-like  $1s^2$  (spherically symmetric as is the recoiling  $He^{++}$  target nucleus), the Auger electron carries away complete information on the magnitude of the alignment of the state formed in the collision. Auger spectra were obtained with a simple parallel plate, 90 degree spectrometer mounted on a rotatable table, with the He gas jet located on the axis.

From the measured Auger anisotropies, one can determine the magnetic substate populations (that is, the relative number of product ions in a definite  $|L, M_L\rangle$  state). The substate population fractions can be compared directly with theoretical treatments; this is shown in Figure 1-1 for the  $1s2p^2^2D$  state, where theoretical calculations of J.-P. Hansen and K. Taulbjerg are shown for the  $C^5 + He$  collision. These calculations were stimulated by the measurements.

One may also use the substate population fractions derived from the anisotropy measurements to construct a

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

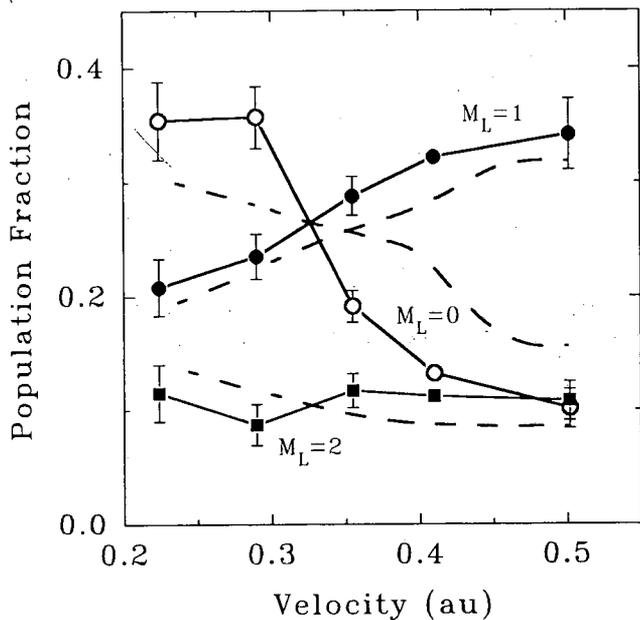


Figure 1-1. Velocity variation of the population fractions of the  $M_L$  substates of the  $1s2p^2 \ ^2D$  states of  $C^{3+}$  formed by double electron capture from He atoms onto  $C^{5+}$  ions. The dashed lines are calculations by J.-P. Hansen (U. Bergen, Norway) and K. Taulbjerg (U. Aarhus, Denmark). (XBL 924-770)

picture of the doubly excited electron charge cloud around the projectile ion core before the Auger emission. This is a way of "seeing" the outcome of the double capture process on an atomic scale. Figure 1-2 shows the results of such a construction made from our measurements. Since our work determines only the absolute value of the population amplitudes, these pictures, while resulting from the most detailed study to date, do not give a complete description because relative phase information is not present. This means that the plots in Figure 1-2 are cuts through the charge cloud that have been averaged over all rotations about the beam direction. Future work will be addressed to achieving a complete description of the final state wavefunction.

Our measurements have stimulated theoretical work by two groups; each has had some success in reproducing our observations, especially at the higher velocities. This is encouraging, but the calculations are complex and computer intensive; more work is needed, and one hopes to reach a more physical, qualitative understanding of the variations observed. From a practical point of view it is essential to know the angular dependence of Auger spectra if one is to infer reliable production cross-sections from measurements made at fixed angles. Our

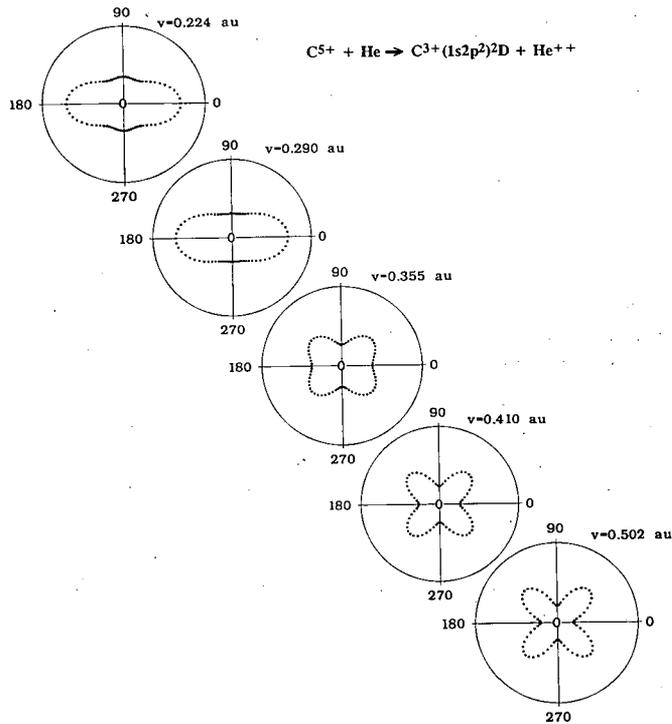


Figure 1-2. Velocity variation of the shape of the azimuthal averaged charge cloud following double capture to  $1s2p^2 \ ^2D$  state by  $C^{5+}$  from He atoms. The projectile beam is along the 0 degree direction, and the shapes are contours of constant density for the charged cloud averaged over all azimuthal orientations about this axis. (XBL 924-771)

measurements show that enormous errors can be made if the angular distributions are ignored.

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<sup>‡</sup>LLNL V-Division and Wesleyan University, Middletown, CT.

<sup>§</sup>On leave at LBL Chemical Sciences Division and LLNL V-Division from U. Lund, Sweden.

<sup>||</sup>LLNL V-Division and U. Texas, Austin.

<sup>¶</sup>LLNL V-Division.

## 2. Isoelectronic Study of Double-electron Capture in Slow Ion-Atom Collisions (Publication 2)

R. Hutton,<sup>†</sup>D. Schneider,<sup>‡</sup> and M.H. Prior

This work reports a survey study of Na-like core-excited configurations produced by electron capture from He atom targets. Beams of Fluorine-like (9 electrons) projectiles  $Si^{5+}$ ,  $Ar^{9+}$ ,  $Sc^{12+}$ ,  $Ti^{13+}$ ,  $Fe^{17+}$ , and  $Cu^{20+}$  were produced by the LBL ECR ion source and

transported through a gas cell containing He target atoms. Auger electrons emitted in the direction of the ion beam (0 degrees) were analyzed by a hemispherical McPherson electron spectrometer. The goals of the measurements were to establish trends in the Auger spectra of the Na-like projectile final states and the double electron capture process. In many cases the Auger spectra were observed for the first time.

The Fluorine-like projectile has the valence configuration  $2p^5$ , thus the Na-like core excited states are of the form  $2p^5 n l n' l'$ . Since single electron capture can populate the Ne-like metastable states  $2p^5 3s \ ^3P_{0,2}$  whose lifetimes are long enough to permit a second single electron capture within the gas cell, it is possible to produce Na-like states via this double collision process as well as by direct double electron capture in a single collision. For this reason, separate studies were made using Ne-like projectile beams (which generally contain a significant metastable fraction) as a aid to separating the two production modes.

As an example of this work, Figure 2-1 shows the Auger spectra from Na-like  $Cu^{18+}$  produced using a beam of  $Cu^{20+}$  ions. It contains the prominent line from the  $2p^5 3s 3p \ ^4D_J$  term, which was observed in all the other cases except from  $Si^{3+}$ . This term is the lowest lying quartet state (total spin 3/2) and the  $J = 7/2$  level is metastable against radiative decay (there are no lower quartet states) and the continuum final state  $2p^6 \ \epsilon l$ , with

spin 1/2, cannot be reached by Coulomb autoionization. The level does autoionize slowly via the spin-spin part of the Breit interaction. The energy of this line was measured for the Na-like ions of Ar, Ti, Fe, and Cu; there is very good agreement between results of multiconfiguration Dirac Fock (MCDF) calculations by M.H. Chen and the measured values. Since this state is the lowest quartet, it is significantly populated, especially in the higher charged members of the sequence, by radiative cascades from higher lying levels. Generally the total spin is not a good quantum number because of mixing by the fine structure interaction, this is particularly true for the higher lying states, thus radiative cascade feeding is allowed from high states that are populated in the double capture via their doublet ( $S=1/2$ ) components into  $2p^5 3s 3p \ ^4D_{7/2}$ . The  $J = 7/2$  level of this term is, however, a nearly pure quartet state since it has the maximum  $J$  allowed and hence there are no other nearby even parity states of the same  $J$  with which it can be mixed.

The large number of weaker features in Figure 2-1 have been partially identified with levels arising from configurations such as  $2p^5 3s \ n l$ , with  $n$  ranging up to about 9.

†On leave at LBL and LLNL from U. Lund, Sweden.

‡LLNL V-Division 3.

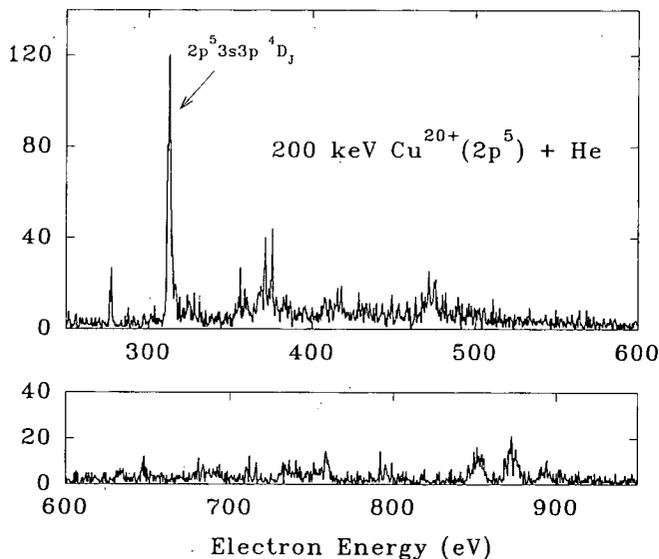


Figure 2-1. Auger spectrum from Na-like core excited states of  $Cu^{18+}$  populated by double electron capture onto 200 keV  $Cu^{20+}$  ions from He atoms. (XBL 924-772).

### 3. Anisotropy of Auger Electron Emission Following Double Capture

*H. Khemliche,† M.H. Prior, and D. Schneider‡*

We are working to modify our experiment on Auger electron anisotropy following double electron capture, to provide both phase and magnitude information on the substate amplitudes. This requires determination of the scattering plane of the collision. The technique will also measure the recoil momentum for each event, and hence we will obtain the impact parameter dependence of the anisotropy. To carry out this work efficiently, modifications will be made to the electron spectrometer to allow position sensitive detection in the exit plane; and a novel recoil ion detector will be constructed to simultaneously measure the velocity and  $q/m$  of the target product ion.

†Graduate student of U. Pierre et Marie Curie, Paris.

‡LLNL V-Division.

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1. R.A. Holt, M.H. Prior, K.L. Randall, R. Hutton, J. McDonald, and D. Schneider, "Magnetic Substates Populated by Double-Electron Capture," *Phy. Rev. A* **43**, 607 (1991).
2. R. Hutton, D. Schneider, and M.H. Prior, "Isoelectronic Study of Double-Electron Capture in Slow Ion-Atom Collisions," *Phys. Rev. A* **44**, 243 (1991).

### Other Publications

3. M.H. Prior, D. Schneider, K.L. Randall, and R. Holt, "Magnetic Substates Populated in Double Electron Capture," *Bull. Am. Phys. Soc.* **36**, 1309 (1991).

4. M.H. Prior, R.A. Holt, D. Schneider, K.L. Randall, and R. Hutton, "Alignment of Magnetic Substates in Double Electron Capture Collisions," XVII International Conference on the Physics of Electronic and Atomic Collisions, I.E. McCarthy, W.R. MacGillivray, and M.C. Standage, eds., p. 425 (1991).
5. D.H.G. Schneider, R. Hutton, and M.H. Prior, "Production of Na-like Auger States in Si, Ar, Sc, Ti, Fe, and Cu Following Double Electron Capture in Slow Ion-Atom Collisions," XVII International Conference on the Physics of Electronic and Atomic Collisions, I.E. McCarthy, W.R. MacGillivray, and M.C. Standage, eds., p. 466 (1991).
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# PROCESSES AND TECHNIQUES

## CHEMICAL ENERGY

### High Energy Oxidizers and Delocalized-Electron Solids\*

Neil Bartlett, Investigator

#### INTRODUCTION

The main aim of this program is the synthesis and characterization of new materials that may have utility in efficient storage or usage of energy. The novel materials include two-dimensional networks of light  $\pi$ -bonding atoms (boron, carbon, and nitrogen) with structures akin to graphite. Of these the more metallic have possible applications as electrode materials for high-energy-density batteries and those that are semiconducting could be useful in converting light to electrical energy. Good ionic conductors are also being sought, with emphasis on lithium-ion and fluoride-ion conductors, since batteries based on lithium and fluorine would be unsurpassed in their energy density features. In addition novel oxidation-state fluorides are being synthesized and structurally characterized to provide a comprehensive basis for better theoretical models, from which an improved capability to predict physical and chemical behavior ought to be forthcoming. Previously unknown or little studied high-oxidation-state species constitute a large part of this effort. Such species are also investigated for their efficiency and specificity as chemical reagents.

#### 1. Structural and Magnetic Properties of Some $\text{AgF}^+$ Salts<sup>+</sup> (Publication 3)

W.J. Casteel, Jr., G. Lucier, R. Hagiwara, H. Borrmann, and N. Bartlett

New salts of the one-dimensional polymeric  $(\text{Ag-F})^{n+}_n$  species have been prepared and shown to be metallic, this behavior being compatible with the extraordinary oxidizing power of cationic  $\text{Ag(II)}$ , which is akin to that of the F atom.

Single crystals of the salt  $\text{AgF}^+ \text{BF}_4^-$  were grown in anhydrous hydrogen fluoride (AHF) by the interaction of molecular  $\text{F}_2$  with  $\text{AgBF}_4$  under a  $\text{BF}_3$  over-pressure. The single-crystal x-ray structure of the salt illustrated in Figure 1-1 shows a linear  $\dots\text{Ag-F-Ag-F}\dots$  chain with the F ligand symmetrically linked to its two  $\text{Ag(II)}$  neighbors, at 2.002(3) and 2.009(3)Å. Each cation chain is surrounded tetragonally by four columns of close-stacked  $\text{BF}_4^-$ . The magnetic susceptibility is nearly temperature independent from 6 to 300 K, this being indicative of a partially filled band. A small field dependence of the susceptibility (illustrated in Figure 1-2) below 163 K is caused by  $\text{AgF}_2$  impurity (~1.5%). The optical properties also fit metallic behavior. Absence of Peierls distortion may be due to the unsymmetrical field at each  $\text{Ag(II)}$ , since the four close  $\text{BF}_4^-$  all are centered on one plane to one side of the cation. The Peierls distortion, for this  $d^9$   $\text{Ag(II)}$  case, requires disproportionation  $2 \text{Ag(II)} \rightarrow \text{Ag(I)} + \text{Ag(III)}$ , each in a centrosymmetric environment, and the observed unsymmetrical anion distribution may be frustrating that. In the  $\text{AgF}^+ \text{AsF}_6^-$  and  $\text{AgF}^+ \text{AuF}_6^-$  salts a sharp reduction, at 63 K, in the otherwise temperature independent susceptibility of the salts, probably signals a Peierls distortion and the structure of these salts is more

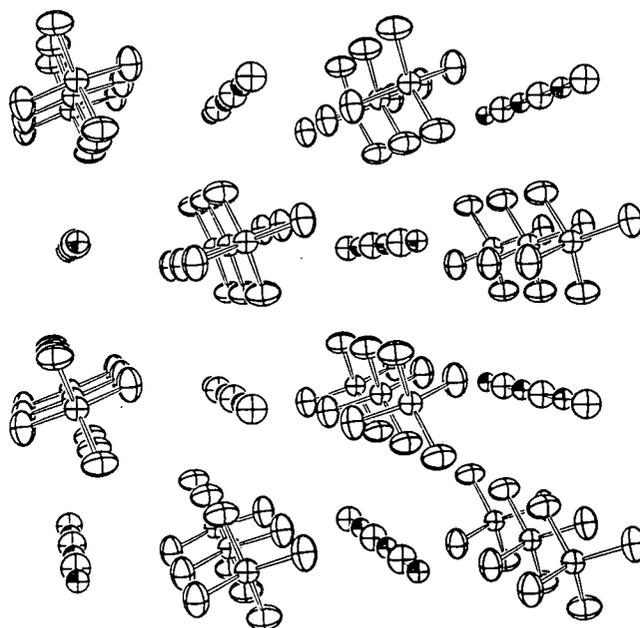


Figure 1-1. The  $\text{AgFBF}_4$  extended structure (50% probability ellipsoids). (XBL 928-6167)

\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

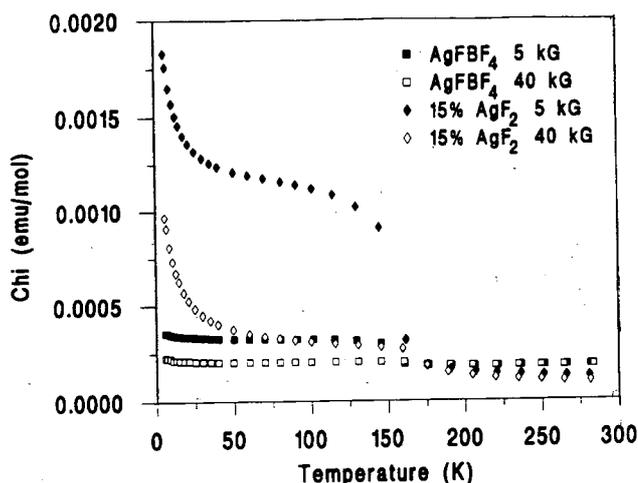


Figure 1-2. Magnetic susceptibility data of  $\text{AgFBBF}_4$ , at two field strengths, compared with dilute  $\text{AgF}_2$  (15%  $\text{AgF}_2$ , 85%  $\text{CaF}_2$ ).  $\text{AgF}_2$  is ferromagnetic with a Curie temperature of 163 K. (XBL 929-5359)

conductive to such an event than that of the  $\text{AgF}^+\text{BF}_4^-$  salt. The salt  $\text{AgFAuF}_4$  probably contains a linear cationic chain, since it is isostructural with  $\text{CuFAuF}_4$ , in which the cation chain is known to be linear, but the salt  $\text{Ag}(\text{AuF}_4)_2$  like its relative  $\text{Ag}(\text{AgF}_4)_2$ , is a magnetically dilute paramagnet, the magnetic susceptibility of which departs very little from the Curie law between 6 and 280 K.

All of the  $\text{AgF}^+$  salts oxidize hexafluorobenzene to  $\text{C}_6\text{F}_6^+$  at 208 K, in AHF, and quantitatively convert perfluoropropene to perfluoropropane at the same temperature.

## 2. The Preparation and Structure of Ruthenium Tetrafluoride and a Structural Comparison with Ruthenium Trifluoride and Ruthenium Pentafluoride

W.J. Casteel,<sup>†</sup> A.P. Wilkinson,<sup>‡</sup> H. Borrmann,<sup>†</sup> R.E. Serfass,<sup>§</sup> and N. Bartlett<sup>†</sup>

A structural study has been carried out to test the validity of an apparent lack of dependence of M-F bond character on oxidation state of M. Novel synthetic approaches were employed to ensure reliable stoichiometry and absence of oxygen contamination. The remarkable constancy of the M-F bond character appears to be general for transition elements of the second and third transition series, from groups V through VIII of the periodic table. Changes in the van der Waals interactions of the ligands are evidently more important than changes in the electron configuration.

The structure of  $\text{RuF}_5$  (which is tetrameric) and structure of  $\text{RuF}_3$  (which is a three-dimensional Ru-F-Ru bridged polymer) have been redone to provide the necessary higher precision for comparison with the structure of  $\text{RuF}_4$ . The last has been found to be of a new type for elements of the second or third transition series and is compared with the  $\text{RuF}_5$  tetramer in Figure 2-1. The  $\text{RuF}_5$  and  $\text{RuF}_3$  structures are compared in Figure 2-2. The Ru atom, in all three fluorides, is surrounded by six F ligands on an octahedral framework, and the bridging interatomic distances in the three fluorides have been found to be:  $\text{RuF}_3$ , 1.982(6)°;  $\text{RuF}_4$ , 2.00(1) and 2.00(3)°;  $\text{RuF}_5$ , 1.995(1), 1.999(1), 2.003(1), and 2.007(1)°. The Ru-F-Ru angles are:  $\text{RuF}_3$ , 136(1)°;  $\text{RuF}_4$ , 133(1)°;  $\text{RuF}_5$ , 136.8(1) and 140.8(1)°. The nonbridging interatomic distance of  $\text{RuF}_4$  has Ru-F = 1.82(2)°, these two ligands being above and below the Ru atom of the fluorine-bridged, puckered sheet, of composition  $(\text{RuF}_2)_n$ . These match closely the nonbridging Ru-F distances of the  $\text{RuF}_5$  tetramer that are perpendicular to the eight-membered Ru-F-Ru bridged ring. Those non-bridging distances are 1.817, 1.821, 1.823, and 1.824 Å [(all occurring twice, with  $\sigma = 0.001(\text{Å})$ ), whereas the nonbridging Ru-F distances equatorial to the ring are slightly shorter, with two each at 1.793, 1.795, 1.796, and 1.798 Å (all  $\sigma = 0.001\text{Å}$ )]. Since the Ru-F-Ru bridge-bonding is essentially the same in  $\text{RuF}_3$ ,  $\text{RuF}_4$ , and  $\text{RuF}_5$ , as is the Ru-F nonbridging bonding in  $\text{RuF}_4$  and  $\text{RuF}_5$ , the decrease in the number of  $d$  electrons from Ru(III) (which is  $d^5$ ) to Ru(V) (which is  $d^3$ ) is seen to have negligible impact on the bonding. The slight stretching of the M-F-M bridging distances in the pentafluoride, relative to the trifluoride, here and in the molybdenum and rhodium fluorides, must be a consequence of the repulsive interaction of the bridging-F ligand with its neighbors, these being closer in the pentafluoride, because they are nonbridging.

<sup>†</sup>University of California, Berkeley, CA 94720.

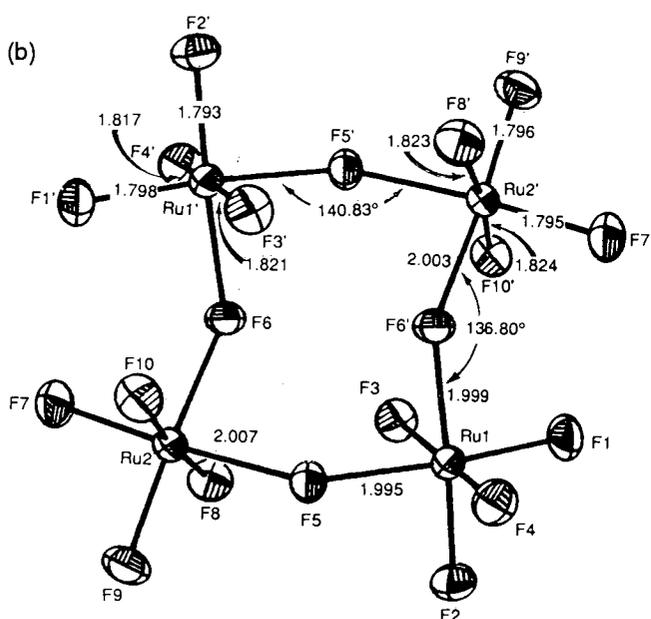
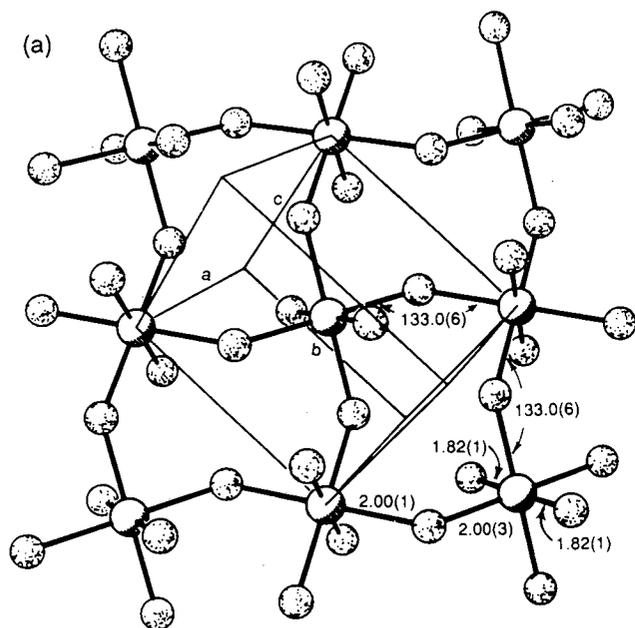
<sup>‡</sup>University of Oxford, England.

<sup>§</sup>Princeton University, New Jersey.

## 3. Concerning the Metallic Nature of $(\text{BN})_{3.1}^+$ $\text{SO}_3\text{F}^-$ (Publication 6)

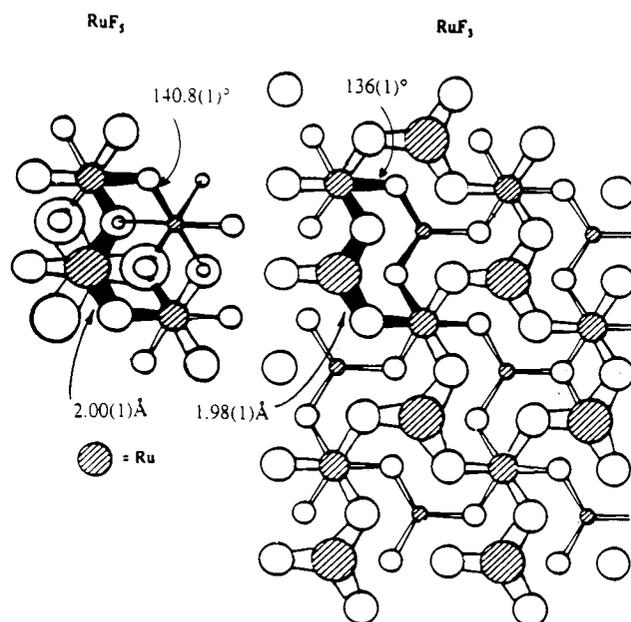
C. Shen, S.G. Mayorga, and N. Bartlett

Electrical conductivity measurements, using the four-probe technique, have been carried out on monolithic pieces of boron nitride intercalated by the powerful oxidizer  $\text{SO}_3\text{F}$  to provide the first-stage salt of composition  $(\text{BN})_{3.1}^+ \text{SO}_3\text{F}^-$ . The deep blue solid, under an argon atmosphere, was stable at 295 K, and at that temperature had a specific conductivity ( $\sigma$ ) of 1.5 S  $\text{cm}^{-1}$ ,



**Figure 2-1.** (a) View of the puckered-sheet structure of  $\text{RuF}_4$  with interatomic distances ( $\text{\AA}$  units) and bridge-bonding angles (degrees). (b) The tetrameric structural unit of  $(\text{RuF}_3)_4$  (70% probability ellipsoids) with interatomic distance ( $\sigma = 0.001 \text{\AA}$  units) and bridge-bonding angles (degrees). (XBL 928-6168)

which is about  $10^4$  lower than that of graphite. Since the conductivity increased steadily with decreasing temperature,  $\sigma$  at 95 K, being 1.7 times that at 295 K, the compound appears to be metallic, the low value of the specific conductivity probably deriving from low



**Figure 2-2.** Relationship of the  $(\text{RuF}_5)_4$  geometry to an element of the  $\text{RuF}_3$  infinite hexagonal nearly-close-packed F atom array. (XBL 928-6169)

mobility of the charge carriers. It is probable that the heteronuclear character of boron nitride is responsible for this low mobility, the remarkably high mobility in its structural relative, graphite, being attributable to the highly effective  $\sigma$  bonding associated with the homonuclear atomic network.

#### 4. Work in Progress

Lewis acids ( $\Delta$ ) such as  $\text{AsF}_5$ ,  $\text{BF}_3$ , and  $\text{HF}$  in combination with elemental fluorine are proving to be potent electron oxidizers and fluorinating agents. This is a consequence of the high  $\text{F}^-$  affinity of the Lewis acids with, e.g.,  $\Delta\text{H}^\circ (\text{F}^-_{(\text{g})} + \text{AsF}_5_{(\text{g})} \rightarrow \text{AsF}_6^-_{(\text{g})}) \approx -113 \text{ kcal mole}^{-1}$ , the low bond dissociation energy of the  $\text{F}_2$  molecule with  $\Delta\text{H}^\circ_{\text{f}} (\text{F}_{(\text{g})}) = 18.5 \text{ kcal mole}^{-1}$  and the high electron affinity of the F atom ( $\text{E.A.} = 80 \text{ kcal mole}^{-1}$ ). It appears as though the  $\text{F}_2$  molecule in association with  $\Delta$  (the initial bonding need only be very weak) provides for electron transfer from even poor Lewis bases (donor,  $\text{D}$ ) to this molecular combination,  $\text{F}_2\text{-}\Delta$ . It should be noted that the lowest unoccupied molecular orbital (LUMO) of  $\text{F}_2$  is  $\sigma^*$ . Donation of electrons into this  $\sigma^*$  orbital must lead to breaking of the F-F bond, hence the interaction of Lewis base ( $\text{D}$ ) with the  $\text{F}_2\text{-}\Delta$  combination results in F-F bond breaking and  $\Delta\text{F}^-$  anion formation. Any bonding of

$\underline{D}^+$  with F will, of course, assist the interaction. Such reactions appear to be favorable even for the weak Lewis base xenon (Xe). Interaction of Xe with  $F_2-\underline{A}$  to yield  $XeF^+ \underline{A}F^-$  is energetically favorable for all  $\underline{A}$  cited and proceeds without apparent activation. This is consistent with the orbital symmetry for the interaction  $\underline{D} + LUMO F_2 + \underline{A}$  which allows for smooth transition to the products  $\underline{D}F^+ \underline{F}\underline{A}^-$ . These reactions are carried out at low temperatures to minimize the unfavorable impact of the entropy change.

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1. B. Žemva, K. Lutar, A. Jesih, W.J. Casteel, Jr., P. Wilkinson, D.E. Cox, R.B. Von Dreele, H. Borrmann, and N. Bartlett, "Silver Trifluoride: Preparation, Crystal Structure, Some Properties, and Comparison with  $AuF_3^+$ ," *J. Am. Chem. Soc.* **113**, 4192 (1991).
2. R. Hagiwara, F. Hollander, C. Maines, and N. Bartlett, "The Crystal Structure of  $[Ag(XeF_2)]_2AsF_6$  Formed in Oxidation of Xe by  $AgFAsF_6$ ," *Eur. J. Solid State Chem.* **28**, 855 (1991).

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3. W.J. Casteel, Jr., G. Lucier, R. Hagiwara, H. Borrmann, and N. Bartlett, "Structural and Magnetic Properties of Some  $AgF^+$  Salts\*," *J. Solid State Chem.* (in press); LBL-30919.
4. W.J. Casteel, Jr., A.P. Wilkinson, H. Borrmann, R.E. Serfass, and N. Bartlett, "The Preparation and Structure of Ruthenium Tetrafluoride and a Structural Comparison with Ruthenium Trifluoride and Ruthenium Pentafluoride," *Inorganic Chemistry* (in press); LBL-31263.
5. M. Lerner, R. Hagiwara, and N. Bartlett, "Synthesis of Main-Group Graphite Fluoroanion Salts with Chlorine-Assisted Oxidation by Lewis-Acid Fluorides," *J. Fluorine Chem.* (in press); LBL-31912.
6. C. Shen, S.G. Mayorga, and N. Bartlett, "Concerning the Metallic Nature of  $(BN)_3^+SO_3F^-$ ," LBL-32138.

### Invited Talks

7. N. Bartlett, "Concerning the Generation and Stabilization of High-Oxidation-State Cations by Fluoro-anions," 74<sup>th</sup> Canadian Chemical Conference, Hamilton, Ontario, Canada, June 3, 1991.
8. N. Bartlett, Imperial Oil Distinguished Lecturer Chemistry Department, University of Toronto, "Synthetic Metals from Graphite," Toronto, Canada, November 15, 1991.

# Catalytic Hydrogenation of CO\*

Alexis T. Bell, Investigator

## INTRODUCTION

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

### 1. Isotopic Tracer Studies of Hydrocarbon Chain Initiation, Growth, and Termination During Fischer-Tropsch Synthesis over Ru/TiO<sub>2</sub> (Publication 14)

K.R. Krishna and A.T. Bell

Transient response isotopic tracer experiments have been carried out to determine the rate coefficients for the initiation, growth, and termination of hydrocarbon chains during Fischer-Tropsch synthesis over Ru/TiO<sub>2</sub>. The coverage of the metal surface by growing hydrocarbon chains has also been determined from these experiments. At 463 K, the rate coefficients for chain initiation, propagation, and termination are 0.02 s<sup>-1</sup>, 0.2 s<sup>-1</sup>, and 0.05 s<sup>-1</sup>, respectively. The activation energy for chain termination is found to be 8 kcal/mol, whereas that for chain propagation is 20 kcal/mol. The higher activation energy for chain termination than propagation explains the observed decrease in the probability of chain growth with increasing temperature. The surface coverages of adsorbed species determined from an analysis of the transient response curves are in close agreement with those measured independently by temperature-programmed reduction.

Separate isotopic tracer experiments have been carried out to identify the extent to which olefins produced by Fischer-Tropsch synthesis are adsorbed and thereby influence the chain growth process. Ethylene is found to adsorb extensively and to act as a chain initiator, as well as a source of C<sub>1</sub> species for chain growth. For example, when 1.2% <sup>12</sup>C<sub>2</sub>H<sub>4</sub> is added to a feed containing 10% <sup>13</sup>CO and 30% H<sub>2</sub>, all of the C<sub>3+</sub> products are found to be initiated by a C<sub>2</sub> unit derived from the added ethylene, and the ethylene contributes 45% of the C<sub>1</sub> species responsible for chain growth. These results suggest that ethylene produced during Fischer-Tropsch synthesis can be recycled to initiate and propagate additional chain growth, and thereby contribute to a higher average molecular weight of the products.

### 2. Quantitative Structural Analysis of Dispersed Vanadia Species in Anatase-Supported V<sub>2</sub>O<sub>5</sub> (Publication 10)

G.T. Went, L.-J. Leu, and A.T. Bell

Vanadia dispersed on titania has been characterized by in-situ laser Raman spectroscopy and temperature-programmed reduction (TPR) and oxidation (TPO). Quantitative Raman and TPO analysis of the oxidized samples show that these materials consist of a distribution of monomeric vanadyls, polymeric vanadates, and crystallites of V<sub>2</sub>O<sub>5</sub>. At low loadings, the predominant species are monomeric vanadyls, with the remaining vanadia being present in the form of polymeric vanadates. As the surface concentration of vanadia increases, a maximum concentration of the polymeric vanadates is detected. Crystallites of V<sub>2</sub>O<sub>5</sub> form at the expense of polymeric vanadates as the loading is raised above the dispersive capacity of the support. Raman and TPR/TPO studies of the reduction process indicate that the terminal V = O groups of the polymeric species are reduced preferentially to the bridging oxygen atoms of the polymeric species. The maximum loss of oxygen upon reduction is one oxygen atom per vanadium atom.

### 3. Raman Investigations of the Interactions of NH<sub>3</sub> with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (Publication 11)

G.T. Went, L.-J. Leu, S.J. Lombardo, and A.T. Bell

The interaction of NH<sub>3</sub> with anatase and anatase-supported vanadia has been investigated using thermal desorption and Raman spectroscopies. NH<sub>3</sub> adsorbs on TiO<sub>2</sub> by coordinating to Ti<sup>4+</sup> Lewis acid sites. Upon heating, most of the adsorbed NH<sub>3</sub> desorbs intact, with

\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

only a small amount of  $N_2$  being produced. At vanadia loadings well below a monolayer, the dispersed vanadia is present in the form of vanadyl and polymeric vanadate species.  $NH_3$  adsorbs on vacant  $Ti^{+4}$  sites not covered by the vanadia, and  $V^{+5}$  sites associated with the monomeric vanadyl species. Temperature-programmed desorption of  $NH_3$  from titania-supported vanadia samples indicates that  $NH_3$  is more strongly bound to the surface of these materials, and displays a higher tendency to dissociate prior to desorbing. Increasing the coverage of vanadia species to a monolayer results in a weaker  $NH_3$  bond. Desorption studies show that substantial quantities of  $NO$  and  $N_2O$  are evolved by the oxidation of the adsorbed  $NH_3$  and reduction of the sample. Raman spectra recorded in the presence of  $NH_3$  at high temperatures indicate that the terminal oxygen atoms of the polyvanadate species and clustered monomeric species are removed preferentially, resulting in the reduction of these species. On the other hand, isolated monomeric vanadyls are not reduced by the adsorbing  $NH_3$ . These results suggest that the dissociation of  $NH_3$  is accelerated by the presence of adjacent  $V = O$  groups.

#### 4. Infrared and Isotopic Tracer Studies of the Interactions of $CO_2$ with $Cu/SiO_2$ (Work in Progress)

*D. Clarke, I. Suzuki, and A.T. Bell*

Infrared spectroscopy and isotopic tracer techniques have been used to characterize the interactions of  $CO_2$  with silica-supported  $Cu$ . Adsorbed  $CO_2$  exhibits a band at  $2340\text{ cm}^{-1}$  attributable to weakly adsorbed species bonded through both oxygen atoms with the surface of  $Cu$ . Even at room temperature,  $CO_2$  dissociates to form  $CO$  and atomic oxygen, the latter species causing a partial oxidation of the catalyst surface. Isotopic tracer experiments reveal that  $CO$  and  $CO_2$  rapidly exchange oxygen atoms via the process  $CO_{2,s} = CO_s + O_s$ .

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Programmed Desorption Kinetics," *Surf. Sci.* **245**, 213 (1991); LBL-29460.

4. E. Shustorovich and A.T. Bell, "An Analysis of Fischer-Tropsch Synthesis by the Bond-Order-Conservation-Morse-Potential-Approach," *Surf. Sci.* **248**, 359 (1991); LBL-29418.
5. E. Shustorovich and A.T. Bell, "Analysis of Methanol Synthesis from  $CO$  and  $CO_2$  on  $Cu$  and  $Pd$  Surfaces by the Bond-Order-Conservation-Morse-Potential-Approach," *Surf. Sci.* **253**, 386 (1991); LBL-29624.
6. G.T. Went and A.T. Bell, "Laser Raman Spectroscopy of  $NH_3$  and  $ND_3$  Adsorbed on  $TiO_2$  (Anatase)," *Catal. Letts.* **11**, 111 (1991); LBL-30567.
7. G.H. Yokomizo, K.R. Krishna, and A.T. Bell, "Comments on 'Evaluation of the Intrinsic Rate Parameters of the Fischer-Tropsch Synthesis'," *J. Catal.* **132**, 571 (1991); LBL-31380.

#### Other Publications

8. A.T. Bell, "Reflections on the Current Status and Future Directions of Chemical Reaction Engineering," in *Perspectives in Chemical Engineering—Research and Education*, C.K. Colton, Ed., *Adv. Chem. Eng.* **16**, Academic Press, New York, 1991, p. 205; LBL-25857.
9. A.T. Bell, "Relationships of Reaction Energetics to the Mechanism and Kinetics of Heterogeneously Catalyzed Reactions," in *Metal-Surface Reaction Energetics*, E. Shustorovich, Ed., VCH Publishers, New York, p. 191; LBL-30137.

#### LBL Reports

10. G.T. Went, L.-J. Leu, and A.T. Bell, "Quantitative Structural Analysis of Dispersed Vanadia Species in  $TiO_2$ (Anatase)-Supported  $V_2O_5$ ," *J. Catal.* (in press); LBL-30656.
11. G.T. Went, L.-J. Leu, S.J. Lombardo, and A. T. Bell, "Raman Spectroscopy and Thermal Desorption of  $NH_3$  Adsorbed on  $TiO_2$ (Anatase)-Supported  $V_2O_5$ ," *J. Phys. Chem.* (in press); LBL-30568.
12. G.T. Went, L.-J. Leu, R. Rosin, and A.T. Bell, "The Effects of Structure on the Catalytic Activity and Selectivity of  $V_2O_5/TiO_2$  for the Reduction of  $NO$  by  $NH_3$ ," *J. Catal.* (in press); LBL-30569.
13. K.R. Krishna and A.T. Bell, "Isotopic Tracer Studies of Chain Propagation and Termination During Fischer-Tropsch Synthesis over  $Ru/TiO_2$ ," *Proc. 10th Int. Cong. Catal., Akademiai Kiado, Budapest*, (in press); LBL-31707.
14. K.R. Krishna and A.T. Bell, "Estimates of the Rate Coefficients for Chain Initiation, Growth, and Termination During Fischer-Tropsch Synthesis over  $Ru/TiO_2$ ," submitted to *J. Catal.*; LBL-31801.
15. K.R. Krishna (Ph.D. Thesis), "Isotopic Tracer Studies of Fischer-Tropsch Synthesis over  $Ru/TiO_2$  Catalysts"; LBL-31822.

## Invited Talks

16. A.T. Bell, "Opportunities for Fundamental Research in Support of Industrial Catalysis," 12th North American Meeting of The Catalysis Society, Lexington, KY, May 6, 1991.
17. A.T. Bell, "Catalysis Looks to the Future," The Industrial Affiliates Program, Departments of Chemistry and Chemical Engineering, Stanford University, Stanford, CA, May 28, 1991.
18. A.T. Bell, "Applications of NMR Spectroscopy to the Study of Catalyst Systems," Tenth International Meeting on NMR Spectroscopy, St. Andrews, Scotland, July 10, 1991.
19. A.T. Bell, "Mechanistic Studies of Hydrocarbon and Alcohol Synthesis from CO and CO<sub>2</sub>," BP International Ltd., Sunbury-on-Thames, England, July 15, 1991.
20. A.T. Bell, "Recent Advances in Catalytic Science and Engineering and Future Opportunities," The 13th Seminar on Frontier Technology, The Association for the Progress of New Chemistry, Hakone, Japan, July 23, 1991.
21. A.T. Bell, "Selective Catalytic Reduction of Nitric Oxide," W. R. Grace & Co., Columbia, MD, September 16, 1991.
22. A.T. Bell, "Effects of Catalyst Structure on the Performance of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalysts for NO Reduction by NH<sub>3</sub>," Gas Research Institute Inorganic Chemistry Review, Chicago, IL, October 9, 1991.
23. A.T. Bell, "Applications of the Bond-Order-Conservation-Morse-Potential Approach in the Field of Catalysis," BIOSYM Technologies, Inc., La Jolla, CA, October 24, 1991.
24. A.T. Bell, "Effects of Catalyst Structure on the Performance of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalysts for NO Reduction by NH<sub>3</sub>," Ethyl Corp., Baton Rouge, LA, November 26, 1991.
25. A.T. Bell, "Future Direction in Catalysis," 8th DOE/BES Heterogeneous Catalysis and Surface Chemistry Meeting, Santa Monica, CA, March 13, 1991.
26. A.T. Bell, "Raman Studies of the Interactions of NO and NH<sub>3</sub> with V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalysts," ACS Meeting, Atlanta, GA, April 1991.
27. A.T. Bell, "Activation of Ammonia on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalysts Used for the Selective Reduction of NO," ACS Meeting, New York, NY, August 1991.
28. A.T. Bell, "Effects of Catalyst Structure on the Performance of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalysts," ACS Meeting, New York, NY, August 1991.
29. A.T. Bell, "Isotopic Tracer Studies of Oxygen Exchange on Silica-Supported Cu," AIChE Annual Meeting, Los Angeles, CA, November 1991.
30. A.T. Bell, "The Influence of Vanadia Structure on the Activity and Selectivity of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalysts for NO Reduction by NH<sub>3</sub>," AIChE Annual Meeting, Los Angeles, CA, November 1991.
31. A. T. Bell, "Isotopic Tracer Studies of Chain Propagation and Termination During CO Hydrogenation over Ru/TiO<sub>2</sub>," AIChE Annual Meeting, Los Angeles, CA, November 1991.

# Transition Metal-Catalyzed Conversion of CO, NO, H<sub>2</sub>, and Organic Molecules to Fuels and Petrochemicals\*

Robert G. Bergman, Investigator

## INTRODUCTION

The goal of this program is the development of new chemical reactions in which transition metals interact with organic materials and the understanding of how these reactions work. A recent discovery on this project was the finding that certain cyclopentadienyliridium and -rhodium complexes undergo oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons ( $M + R-H \rightarrow R-M-H$ ). This finding was the first example of a long-sought "alkane C-H activation" reaction; research is now being directed at examining the scope, selectivity, and mechanism of the process, extending it to other systems and developing ways to convert the activated metal complexes X-M-H into functionalized organic molecules. During the current year, progress was made on exploring C-H oxidative addition/reductive elimination and related reactions of noncyclopentadienyl-containing ruthenium complexes. A number of novel transformations, including the synthesis of unique low-valent ruthenium benzyne and hydroxide complexes, were uncovered, and significant progress was made in understanding the mechanisms of these reactions.

### 1. The Structure, Synthesis, and Chemistry of $(PMe_3)_4Ru(\eta^2\text{-Benzene})$ . Reactions with Arenes, Alkenes, and Heteroatom-containing Organic Compounds. Synthesis and Structure of a Monomeric Hydroxide Complex

J. F. Hartwig, R. G. Bergman, and R. A. Andersen

Thermolysis of  $(PMe_3)_4Ru(Ph)(Me)$  or  $(PMe_3)_4Ru(Ph)_2$  leads to the ruthenium benzyne complex

$(PMe_3)_4Ru(\eta^2-C_6H_4)$  (**1**) by a mechanism that involves initial reversible dissociation of phosphine. The structure of **1** was determined by x-ray diffraction (Figure 1-1). In many ways its chemistry is analogous to that of early rather than late organotransition metal complexes. Thus, compound **1** undergoes apparent  $\sigma$ -bond metathesis reactions with the C-H bonds of benzene, toluene, or acetophenone, as well as with the N-H bond in aniline and the O-H bonds of *p*-cresol, isopropanol, and water. Several of these reactions are illustrated in Figure 1-2. The monomeric hydroxide complex **2** resulting from addition of water has also been characterized by x-ray diffraction (Figure 1-3). Compound **1** undergoes insertion reactions with a variety of unsaturated organic molecules, including ethylene, di-*p*-tolylacetylene, benzaldehyde, and benzonitrile. Qualitative mechanistic studies on the O-H addition of *p*-cresol and the insertion of benzaldehyde and benzonitrile have been carried out.

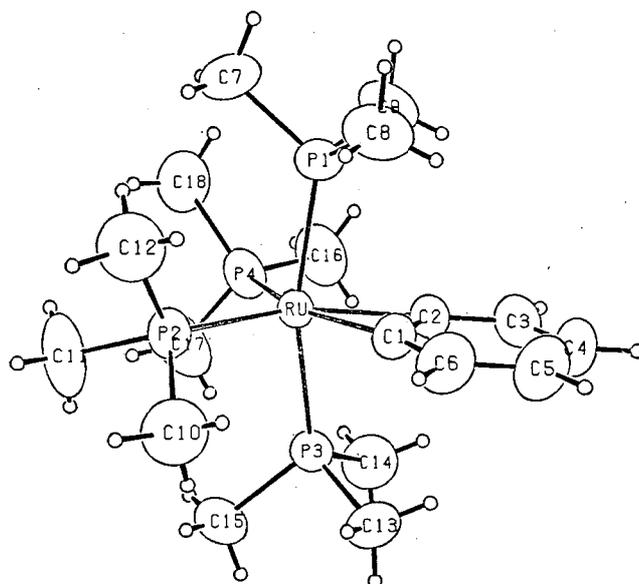


Figure 1-1. ORTEP drawing illustrating the results of the X-ray diffraction study of ruthenium benzyne complex **1**. (XBL 928-6170)

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

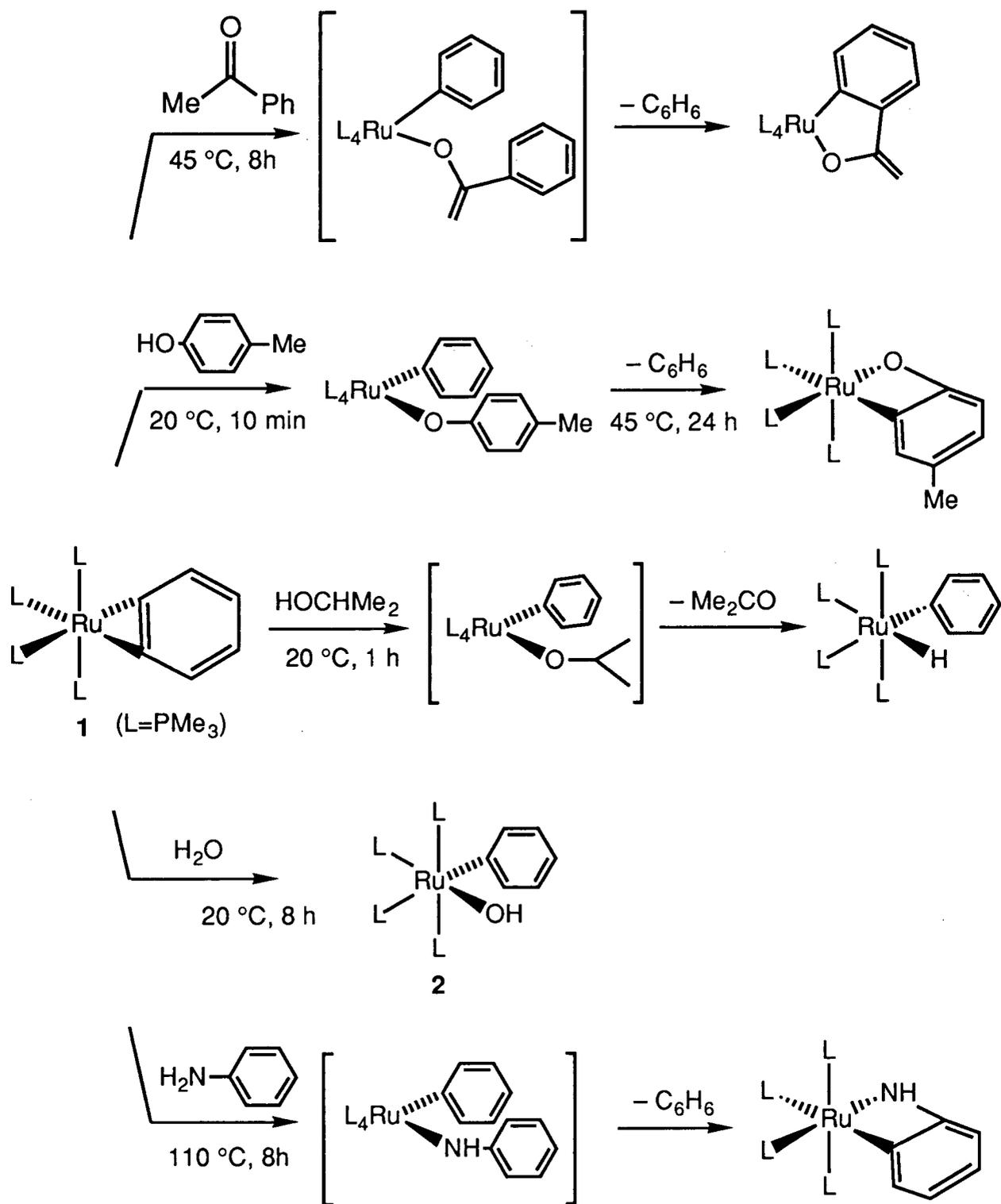


Figure 1-2. Reactions of benzyne complex 1. (XBL 928-6171)

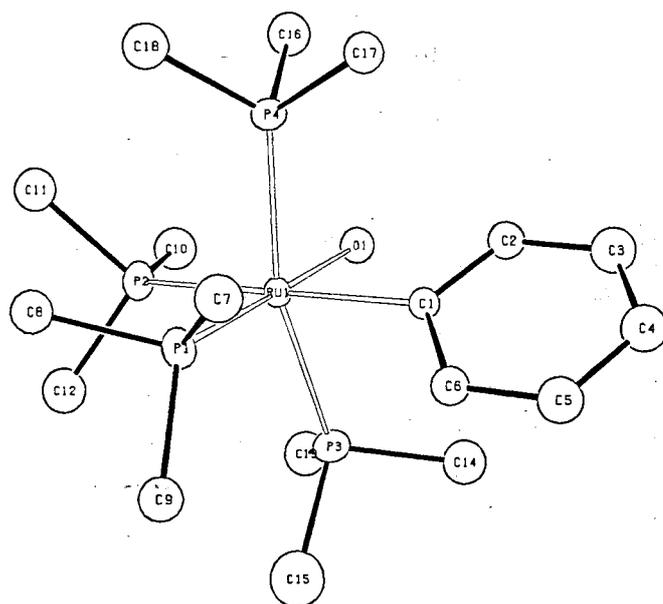


Figure 1-3. ORTEP drawing illustrating the results of the x-ray diffraction study of ruthenium phenyl hydroxide **2**. The hydrogen atoms have been removed for clarity. (XBL 928-6172)

## 2. Alkyl, Aryl, Hydrido, and Acetate Complexes of $(\text{DMPM})_2\text{Ru}$ [DMPM = *bis*-(dimethylphosphino)methane]: Reductive Elimination and Oxidative Addition of C-H bonds

*J.F. Hartwig, R.A. Andersen, and R.G. Bergman*

Complexes of the general formula  $(\text{DMPM})_n\text{Ru}(\text{X})(\text{Y})$  [DMPM = 1,2-*bis*-(dimethylphosphino)methane] were investigated. Addition of excess DMPM to the ruthenium triphenylphosphine compound  $(\text{PPh}_3)_2\text{Ru}(\text{OAc})_2$  led to formation of the mononuclear *tris*-DMPM complex with the formula  $(\eta^1\text{-DMPM})_2(\eta^2\text{-DMPM})\text{Ru}(\text{OAc})_2$ . Addition of two equivalents of DMPM to the starting ruthenium bis-triphenylphosphine diacetate gave the dimeric complex  $(\eta^1\text{-DMPM})_2(\eta^2\text{-DMPM})_2\text{Ru}_2(\text{OAc})_4$ , and thermolysis of this material led to formation of the monomeric product *cis*- $(\eta^2\text{-DMPM})_2\text{Ru}(\text{OAc})_2$ . This monomeric diacetate was used as a precursor to the dihydride *cis*- $(\eta^2\text{-$

$\text{DMPM})_2\text{Ru}(\text{H})_2$  (**1**) by addition of lithium aluminum hydride, and as a precursor to diaryl and dialkyl complexes *cis*- $(\eta^2\text{-DMPM})_2\text{Ru}(\text{R})_2$  by addition of aluminum and magnesium alkyl and aryl reagents. As shown in Figure 2-1, irradiation of the dihydride **1** in benzene solvent led to extrusion of hydrogen and formation of the phenyl hydride complex *cis*- $(\eta^2\text{-DMPM})_2\text{Ru}(\text{Ph})(\text{H})$  (**2**). Addition of methanesulfonic acid to **1** generated the hydrido methanesulfonate *trans*- $(\eta^2\text{-DMPM})_2\text{Ru}(\text{H})(\text{OSO}_2\text{Me})$  (**3**) that gave *trans*- $(\eta^2\text{-DMPM})_2\text{Ru}(\text{H})(\text{Me})$  (**4**) upon addition of trimethylaluminum at  $-78^\circ\text{C}$ . This alkyl hydride was unstable at room temperature, eliminating methane to form phenyl hydride complex **2** in arene solvents. Phenyl hydride **2** undergoes exchange reactions at room temperature with toluene- $d_8$  solvent to form a series of tolyl hydride products (Figure 2-1). These C-H oxidative additions proceed through the  $(\text{DMPM})_2\text{Ru}$  intermediate, also formed photolytically from dihydride **1**, as determined by isotopic labeling studies.

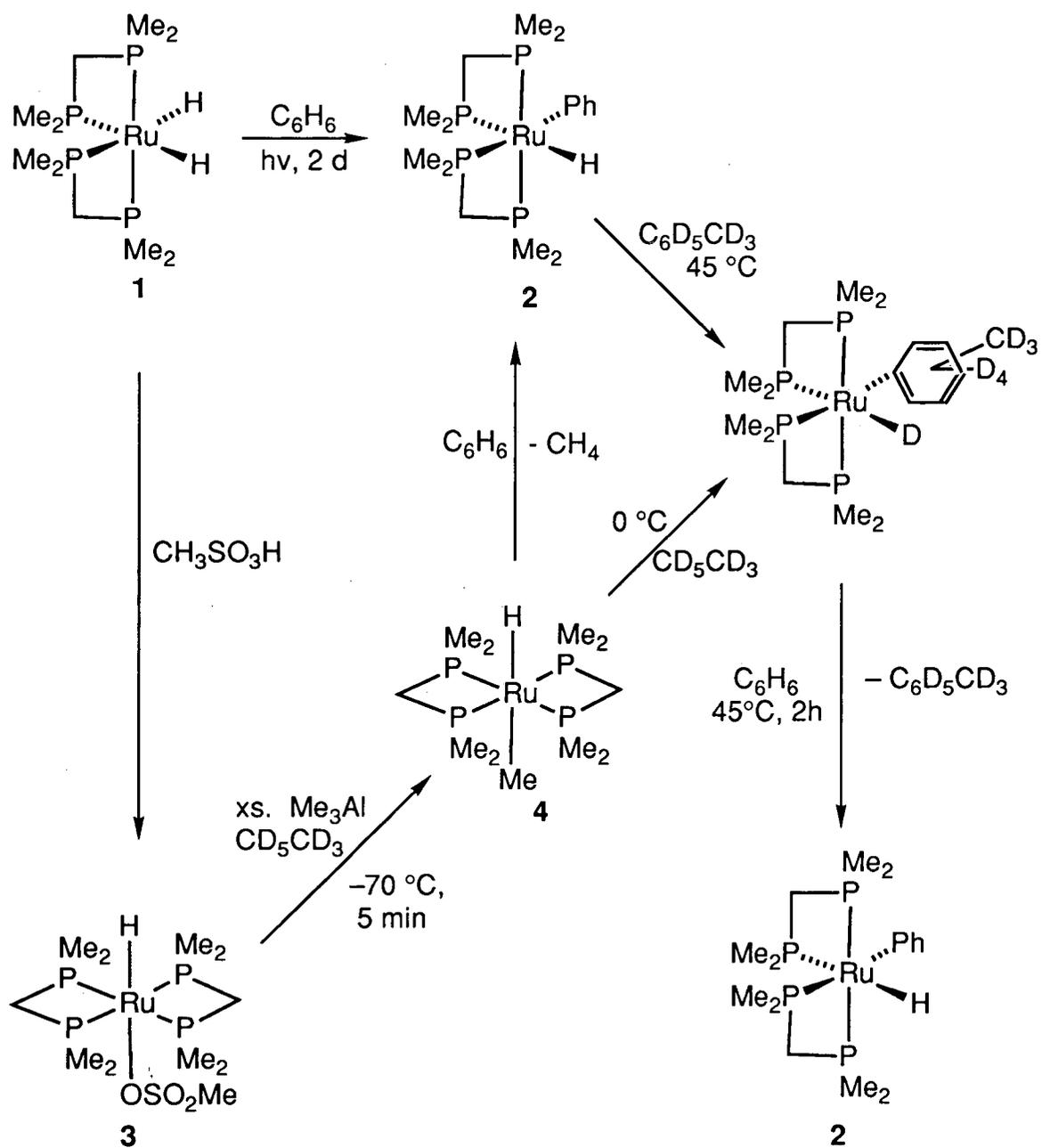
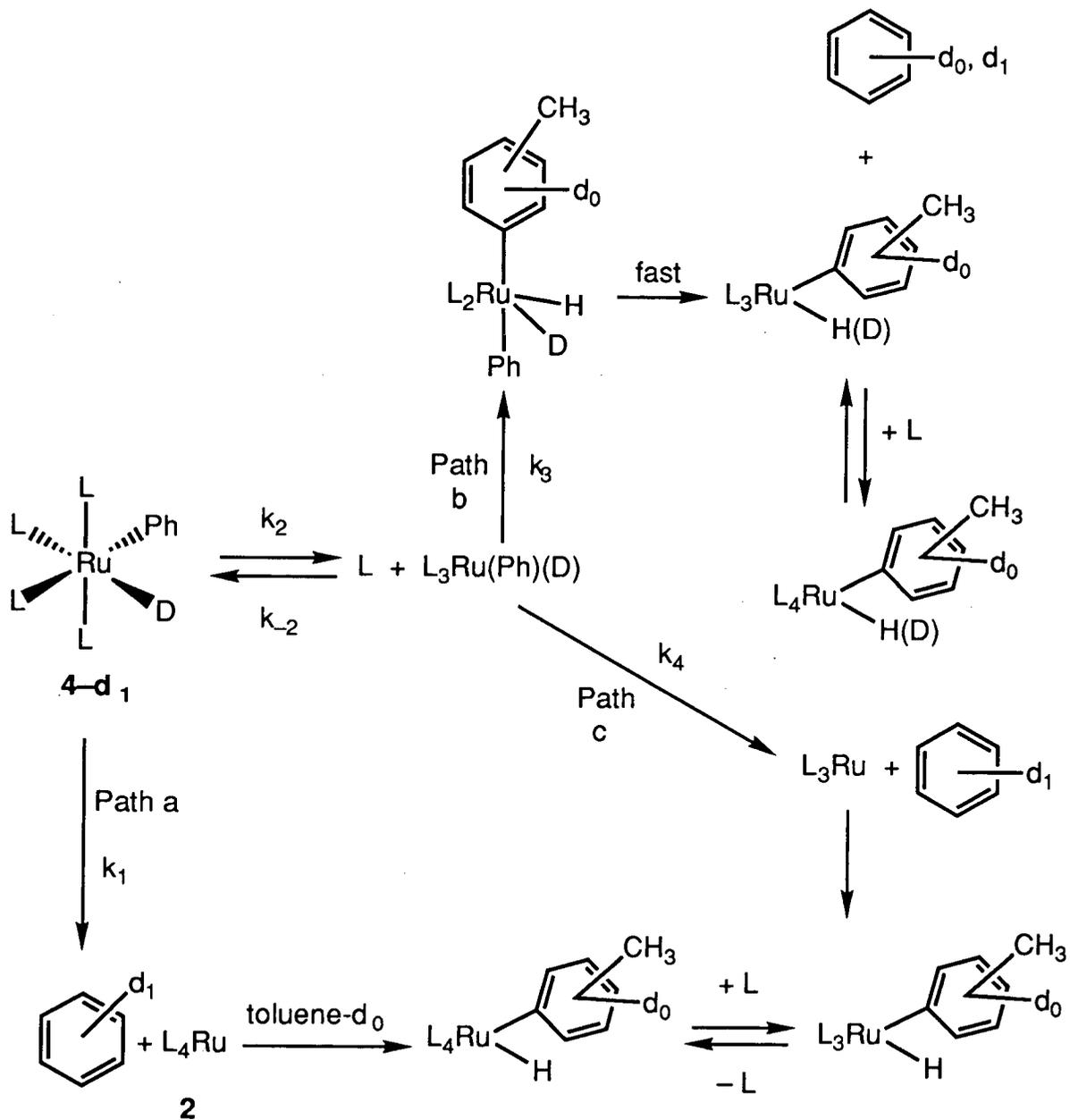


Figure 2-1. Selected chemistry of ruthenium dihydride **1** and methyl hydride **4**. (XBL 928-6173)





**Figure 3-2.** Potential mechanisms for the thermal decomposition of ruthenium phenyl deuteride  $4-d_1$  illustrating the fate of the deuterium label predicted by each pathway. (XBL 928-6175)

#### 4. Work in Progress

Research is in progress in the following areas: (1) expansion of the use of liquefied noble gases in preparative C-H activation chemistry; (2) infrared and uv-visible flash kinetic studies of the rapid steps involved in C-H oxidative addition reactions in liquefied noble gas solvents; (3) exploration of processes potentially leading to C-F activation reactions; (4) studies of rearrangements proceeding through weak complexes formed between metal centers and alkanes; and (5) development of reactions that can potentially convert the products of C-H oxidative addition reactions into functionalized organic molecules.

#### FY 1991 PUBLICATIONS AND REPORTS

##### Refereed Journals

1. J.F. Hartwig, R.G. Bergman, and R.A. Andersen, "The Structure, Synthesis and Chemistry of  $(PMe_3)_4Ru(\eta^2\text{-Benzynes})$ . Reactions with Arenes, Alkenes, and Heteroatom-containing Organic Compounds. Synthesis and Structure of a Monomeric Hydroxide Complex," *J. Am. Chem. Soc.* **113**, 3404 (1991); LBL-29636.
2. J.F. Hartwig, R.A. Andersen, and R.G. Bergman, "Alkyl, Aryl, Hydrido, and Acetate Complexes of  $(DMPM)_2Ru$  [ $DMPM = bis\text{-}(dimethylphosphino)methane$ ]: Reductive Elimination and Oxidative Addition of C-H Bonds," *Organometallics* **10**, 1710 (1991); LBL-29637.
3. J.F. Hartwig, R.A. Andersen, and R.G. Bergman, "Inter- and Intramolecular C-H Bond Forming Cleavage Reactivity of Two Different Types of Poly(trimethylphosphine)ruthenium Intermediates," *J. Am. Chem. Soc.* **113**, 6492 (1991); LBL-29635.

##### LBL Reports

4. R.G. Bergman, "Activation of Carbon-Hydrogen Bonds in Alkanes and Other Organic Molecules Using Organotransition Metal Complexes," *Am. Chem. Soc. Advances in Chem.* (in press); LBL-31443.
5. E.P. Wasserman, C. B. Moore, and R. G. Bergman, "Gas-Phase Rates of Alkane C-H Oxidative Addition to a Transient CpML Complex," *Science* (in press) (1991); LBL-31099.
6. T. Foo and R.G. Bergman, "Synthesis and C-H Activation Reactions of  $\eta^5\text{-Indenyl-(tri-methylphosphine)iridium Alkyl and Hydride Complexes}$ ," submitted to *Organometallics*; LBL-31249.

7. T. Foo and R.G. Bergman, "Migratory Insertion Reactions of Indenyliridium Dialkyls and Alkyl and Aryl Hydrides," submitted to *Organometallics*; LBL-31250.
8. J.F. Hartwig (Ph.D. Thesis), "Synthesis and Reactivity of Compounds Containing Ruthenium-Carbon, -Nitrogen, and -Oxygen Bonds"; LBL-30200.

##### Invited Talks

9. R.G. Bergman, "The Role of Alkane Complexes in the Oxidative Addition of C-H Bonds to Transition Metal Centers," William S. Johnson Symposium in Organic Chemistry, Stanford University, Stanford, CA, October 5, 1990.
10. R.G. Bergman, "The Role of Alkane Complexes in C-H Activation Reactions," Union Carbide, Charleston, W. Va., April 2, 1991.
11. R.G. Bergman, "Using Kryptochemistry to Deal with Xenophobia: Alkane C-H Activation in Liquefied Noble Gas Solvents," Department of Chemistry, Yale University, New Haven, CT, October 31, 1990; Department of Chemistry, Brown University, Providence, RI, November 1, 1990; Department of Chemistry, Wellesley College, Wellesley, MA, November 2, 1990; Kolthoff Lecturer, Department of Chemistry, University of Minnesota, Minneapolis, February 18, 1991.
12. R.G. Bergman, "Stoichiometric and Catalytic Reactions of Early-Late Heterobimetallic Complexes," Kolthoff Lecturer, Department of Chemistry, University of Minnesota, Minneapolis, February 20, 1991.
13. R.G. Bergman, "Transformations of Organic Compounds Mediated by Complexes with Metal-Heteroatom Multiple Bonds," Kolthoff Lecturer, Department of Chemistry, University of Minnesota, February 22, 1991.
14. R.G. Bergman, "Transformations of Organic Compounds Mediated by Organotransition Metal Complexes," Marvel Symposium, University of Arizona, Tucson, March 12, 1991; American Chemical Society Convention, New York, August 26, 1991.
15. R.G. Bergman, "Synthesis and Reactions of Complexes with Single and Multiple Metal-Heteroatom Bonds," Dalton Symposium, London, United Kingdom, April 9, 1991.
16. R.G. Bergman, "Metal-Mediated Transformations of Organic Compounds," Garvan Symposium, American Chemical Society Convention, Atlanta, GA, April 15, 1991.
17. R.G. Bergman, "Stoichiometric and Catalytic Reactions of Complexes with Metal-Heteroatom Multiple Bonds," American Chemical Society Convention, Atlanta, GA, April 17, 1991.
18. R.G. Bergman, "C-H Activation in Noble Gas Solvents: The Role Played by Alkane and Xenon

- Complexes," DOE/BES Organometallic Chemistry and Homogeneous Catalysis Research Conference, University of Wisconsin, Madison, WI, June 3, 1991; Seminar at AMOCO, Naperville, IL, June 6, 1991.
19. R.G. Bergman, "The Use of Organotransition Metal Complexes in the Formation and Cleavage of Bonds to Carbon, Nitrogen, and Oxygen," Breslow Symposium, American Chemical Society Convention, New York, NY, August 24, 1991.
  20. R.G. Bergman, "Photoinduced C-H Activation in Metal Organic Systems," American Chemical Society Convention, New York, NY, August 27, 1991.
  21. R.G. Bergman, "Stoichiometric and Catalytic Carbon-Nitrogen Bond-Forming Reactions Mediated by Organotransition Metal Imido Complexes," Los Alamos National Laboratory, Los Alamos, NM, February 8, 1991.

# Formation of Oxyacids of Sulfur from $\text{SO}_2^*$

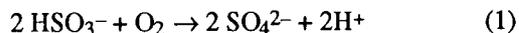
Robert E. Connick, Investigator

## INTRODUCTION

The research is concerned with the basic chemistry of inorganic sulfur species in aqueous solution. Sulfur dioxide produced in coal-burning power plants is the major source of acid rain. Currently the primary method of removing it from flue gas is by absorption into aqueous scrubber solutions as bisulfite ion. The present research is focused on understanding the kinetics and mechanism of oxidation of bisulfite ion by oxygen—a reaction of importance not only in flue gas desulfurization but also in the formation of sulfuric acid from sulfur dioxide in atmospheric water droplets.

### 1. Work in Progress

The oxidation of bisulfite ion by oxygen:



proceeds by a chain reaction whose mechanism is not known in spite of much research over the last 60 years. In the pH region 3 to 6, roughly half of the sulfur forms disulfate ion,  $\text{S}_2\text{O}_7^{2-}$ , as an intermediate that hydrolyzes to sulfate and hydrogen ions with a lifetime of about a

minute. When this unusual intermediate was also found to be formed by the reaction of peroxymonosulfate ion,  $\text{HSO}_5^-$ , with bisulfite ions it could be concluded that reaction (1) proceeds through peroxymonosulfate ion, a speculation made by several researchers in the past. The rate law for the reaction:



has now been found to contain three terms, all of which are first order in peroxymonosulfate ion and bisulfite ion concentrations. One term is first order in hydrogen ion concentration, another independent of hydrogen ion, and the third inversely proportional to the hydrogen ion concentration. For the first two terms it appears that 90% of the reaction goes through the intermediate  $\text{S}_2\text{O}_7^{2-}$  while 10% reacts directly to the products shown in (2). For the third term no evidence was found for formation of  $\text{S}_2\text{O}_7^{2-}$ .

A study of the inhibition of the reaction of Equation (1) by alcohols and arsenious acid has revealed a most remarkable kinetic behavior in the pH region around 4.5. With increasing concentration of these inhibitors the rate of reaction falls off quite abruptly with the rate appearing to have greater than an inverse fourth power dependence on inhibitor concentration. This behavior can be accounted for, however, if the chain initiation occurs by the reaction of peroxymonosulfate ion with bisulfite ion, along with reasonable propagation and termination steps. This striking evidence for  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  initiation is in accord with a prior conclusion based on free energies that the  $\text{HSO}_5^-$ - $\text{HSO}_3^-$  reaction was the only plausible reaction that could bring about initiation.

\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

# Potentially Catalytic and Conducting Polyorganometallics\*

K. Peter C. Vollhardt, Investigator

## INTRODUCTION

Soluble organotransition metal clusters have great potential as catalysts for known and new organic transformations, and as building blocks for novel electronic materials. While much is known about how such clusters are assembled and disassembled, their chemistry is largely unpredictable and/or uncontrollable. This project constitutes an interdisciplinary approach to the designed construction of polymetallic arrays, anchored rigidly on novel  $\pi$ -ligands that enforce hitherto unprecedented metallic topologies. For this purpose, new synthetic organic methodology has been developed that allows the stepwise chemo-, regio-, and loco- (i.e., identity of the metal sequence in heterometallic systems) specific buildingup of cluster-chains. Many of their physical and chemical properties are unparalleled and include extreme ligand deformations, highly strained metal-metal bonds, intramolecular organic fragment migrations, intrachain electron transfers, and thermally reversible photochemical storage processes.

### 1. Unique Reactivity of Heterodimetallic Fulvalene Complexes: First Reversible Conversion of a "Side-on"- to Semi-Bridging Alkenylidene Ligand (Publication 5)

R. Boese,<sup>†</sup> M.A. Huffman, and K.P.C. Vollhardt

This report contains the first clear evidence for the proposal that heterodimetallic fulvalene (Fv) complexes should show novel reactivity compared to their homodimetallic counterparts.

Irradiation of FvMoRu(CO)<sub>5</sub> (1) in the presence of diphenylethyne (THF, 300 nm, 5.5 h) gave **2** (48%) and traces of **3** (see Figure 1-1). The former is readily carbonylated (CO, 1 atm, 23°C, 100%) to its likely precursor **3**, a process that is reversible (75°C). The analogs **4-6** were prepared in the same way (20-56%). The unusual end-on, parallel (to the Fv ligand) assignment

of the two-electron-donating alkynes in **3** and **6** rests on the <sup>1</sup>H and <sup>13</sup>C NMR spectra, revealing the symmetrical patterns expected for **3** and the appropriate lack thereof for **6**. In contrast, NMR indicates that the four-electron donor alkynes in **2**, **4**, and the two (inseparable) isomers of **5** (**5a**:**5b** = 7:1) adopt a terminal, perpendicular configuration, a conclusion corroborated by an x-ray structural analysis of **2** (see Figure 1-2).

Interestingly, **2** and **4** exhibit fluxionality via two different processes, one that equilibrates the two sides of the Fv ligand [i.e., C(14,15,20,19) with C(13,12,17,18)] at the same rate as CO(9) with *one* [presumably CO(8)] of the Ru carbonyls ( $\Delta G^\ddagger_{25^\circ\text{C}} = 15.5 \pm 0.1 \text{ kcal mol}^{-1}$ ), a second ( $\Delta G^\ddagger_{25^\circ\text{C}} = 17.6 \pm 1.0 \text{ kcal mol}^{-1}$ ) that in addition reveals coalescence of the signals of the respective arylcarbyne halves of the alkynes. The most plausible mechanism for the first involves stereospecific access to a hitherto undetected doubly bridging carbonyl [e.g., CO(8) and CO(9)] intermediate containing a perpendicular terminal alkyne group, the second process being alkyne rotation. The latter should interconvert **5a** and **b**, an expectation verified through spin saturation transfer experiments at 50°C.

In contrast, photosubstitution of **1** with terminal alkynes [e.g., C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H or (CH<sub>3</sub>)<sub>3</sub>SiC<sub>2</sub>H] provided the first heterodinuclear, side-on bridging four-electron-donating alkenylidenes **7a,b** and **8a,b** (as pairs of interconverting diastereomers, 40-50%). The phenyl-substituted system **7** crystallizes in only one form (see Figure 1-3).

The diastereoisomerization of **7** and **8** was probed using the parent structure **9**, available by ready protodesilylation of **8a,b** (Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>, THF, 23°C, 65%). On heating **9**, the <sup>1</sup>H NMR signals for the two vinylidene hydrogens ( $\delta = 2.37, 2.84 \text{ ppm}$ ,  $J = 14 \text{ Hz}$ ) suffer extensive line broadening, while the Fv absorptions remain unchanged. Spin-saturation transfer techniques establish the occurrence of vinylidene H-H site exchange (20-60°C;  $\Delta H^\ddagger = 14.8 \pm 0.8 \text{ kcal mol}^{-1}$ ;  $\Delta S^\ddagger = -15.3 \pm 2.4 \text{ cal K}^{-1}\text{mol}^{-1}$ ,  $\Delta G^\ddagger = 19.4 \pm 0.1 \text{ kcal mol}^{-1}$ ), most likely via vinylidene rotation.

That the precursors to **7** and **8** are most likely terminal alkyne complexes was indicated by protodesilylation of **5a,b** at -78°C to give first **10a** and **b**. Remarkably, even at -40°C, these compounds are unstable with respect to isomerization to **7**, a facility that is unprecedented. Exposure of **7** to CO (5 atm, CH<sub>3</sub>COCH<sub>3</sub>, 75°C, 20 h) effected monocarbonylation (60%) to

\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

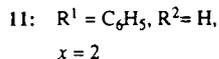
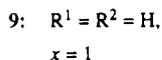
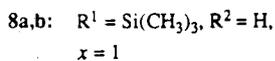
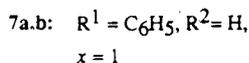
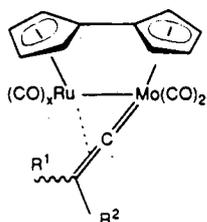
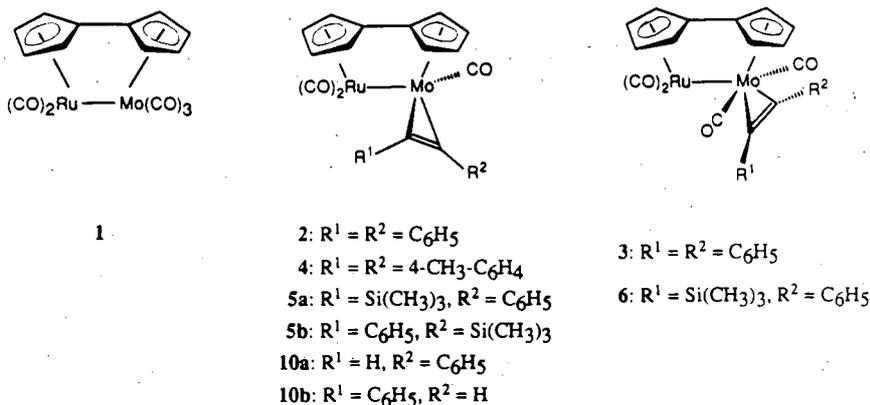


Figure 1-1. Products of the photosubstitution of 1 by alkynes. (XBL 928-6180)

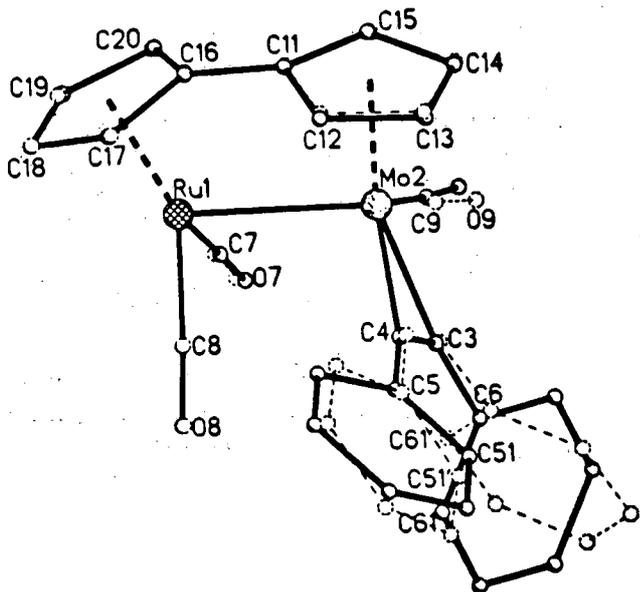
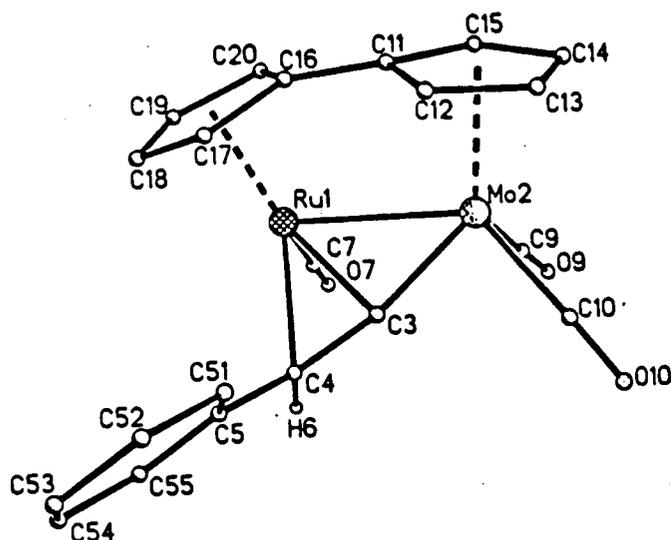
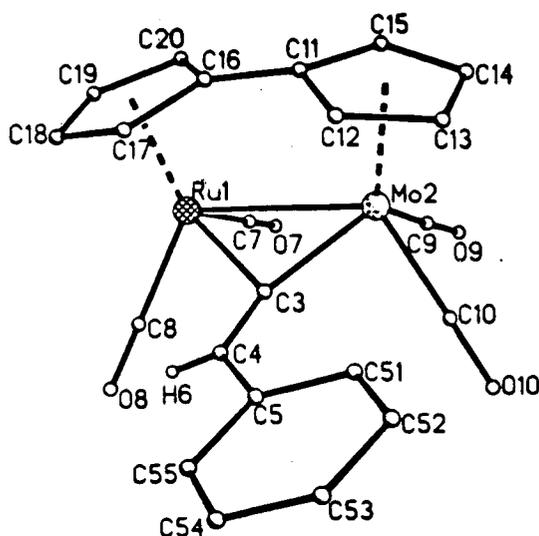


Figure 1-2. Molecular structure of 2, hydrogen atoms omitted. The two independent molecules are drawn superpositioned (fitted on the metal atoms and the fulvalene moiety), with the coordinates of the atoms of one molecule inverted (dashed lines). Atomic labeling is given for only two atoms of the phenyl rings. Selected bond lengths (Å) and angles (°) (interplanar angles defined as best planes of the given atomic positions in parentheses, separated by virgules): Ru1-Mo2 2.840(1), Ru1'-Mo2' 2.860(1), Mo2-C3 2.055(5), Mo2'-C3' 2.060(5), Mo2-C4 2.026(4), Mo2'-C4' 2.023(5), C3-C4 1.304(7), C3'-C4' 1.322(5), C3-C6 1.466(7), C3'-C6' 1.464(5), C11-C16 1.451(7), C11'-C16' 1.453(6); Mo2-Ru1-C7 92.0(2), Mo2'-Ru1'-C7' 93.8(2), Mo2-Ru1-C8 86.0(2), Mo2'-Ru1'-C8' 84.7(2), Ru1-Mo2-C9 90.2(1), Ru1'-Mo2'-C9' 93.8(1), Ru1-Mo2-C3 106.6(1), Ru1'-Mo2'-C3' 107.7(1), Ru1-Mo2-C4 105.4(1), Ru1'-Mo2'-C4' 107.7(1), C3-Mo2-C4 37.3(2), C3'-Mo2'-C4' 37.8(2), C3-C4-C5 141.3(4), C3'-C4'-C5' 138.7(5), C4-C3-C6 138.0(4), C4'-C3'-C6' 142.1(5), (C11-C15)/(C16-C20) 29.1, (C11'-C15')/(C16'-C20') 27.2, (C3,C4,C5,C6)/(C5,C51-C55) 147.5, (C3',C4',C5',C6')/(C5',C51'-C55') 14.9, (C3,C4,C5,C6)/(C6,C61-C65) 43.6, (C3',C4',C5',C6')/(C6',C61'-C65') 56.5, C12-C1'-C16-C17 0.7, C12'-C11'-C16'-C17' -2.4, C3-C4-C5-C51 -24.2, C3'-C4'-C5'-C51' 12.7, C4-C3-C6-C61 -36.8, C4'-C3'-C6'-C61' 123.0. (XBL 928-6181)



**Figure 1-3.** Molecular structure of **7**, hydrogen atoms except H6 omitted. Selected bond lengths (Å) and angles (°) (interplanar angles given as in Fig. 1-2): Ru1-Mo2 2.847(1), Mo2-C3 1.918(4), Ru1-C3 2.091(4), C3-C4 1.388(5), C4-C5 1.478(5), C11-C16 1.452(6); Mo2-Ru1-C7 103.3(1), Ru1-Mo2-C9 88.9(1), Ru1-Mo2-C3 47.3(1), Mo2-Ru1-C3 42.4(1), Ru1-C3-Mo2 90.4(1), C3-C4-C5 123.6(4), (C11-C15)/(C16-C20) 26.7, (C3,C4,C5)/(C5,C51-C55) 1.5, (Ru1-Mo2-C3)/(C3-C4-C5) 69, C12-C11-C16-C17 -7.2, C3-C4-C5-C51 1.1. (XBL 928-6182)



**Figure 1-4.** Molecular structure of **11**, hydrogen atoms except H6 omitted. Selected bond lengths (Å) and angles (°) (interplanar angles given as in Fig. 1): Ru1-Mo2 2.906(1), Mo2-C3 2.053(2), Ru1-C3 2.191(3), C3-C4 1.340(4), C4-C5 1.478(4), C11-C16 1.452(5); Mo2-Ru1-C7 81.2(1), Mo2-Ru1-C8 116.3(1), Ru1-Mo2-C9 96.3(1), Ru1-Mo2-C3 48.8(1), Mo2-Ru1-C3 44.8(1), Ru1-C3-Mo2 86.3(1), C3-C4-C5 129.2(3), (C11-C15)/(C16-C20) 25.4, (C3,C4,C5)/(C5,C51-C55) 2.3, (Ru1-Mo2-C3)/(C3-C4-C5) 160, C12-C11-C16-C17 4.2, C3-C4-C5-C51 2.6. (XBL 928-6183)

isomerically pure **11**, reversible under vacuum. An x-ray structural analysis revealed the presence of a semi-bridging  $C_6H_5CHC$ -moiety (see Figure 1-4). Most notable are the asymmetric disposition of the alkenylenecarbon, C(3), the tilting of C(4) toward the Ru atom, and the large change in the "twist" angle of the terminal methylene group relative to the metallacyclopropane core when going from **7** ( $69^\circ$ ) to **11** ( $160^\circ$ ). The equilibrium  $7 \rightleftharpoons 11$  is the first of its kind to be observed.

In stark contrast to the chemistry of **1**, under the same conditions its homodinuclear analogs give rise to distinctly different products.

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## 2. Selective Metal Redox Recognition in the Heterodinuclear Fulvalene Complexes $[WM(\text{fulvalene})(CO)_5]$ , M = Fe or Ru (Publication 6)

*M.-H. Delville-Desbois, † D.S. Brown, K.P.C. Vollhardt, and D. Astruc†*

One-selection oxidation of  $[Fe(C_5Me_5)_2]$  has provided the first example of a molecular ferromagnet. In the search for oligometallic analogs, the redox behavior of metal-metal bonded fulvalene dimetals  $FvM_1M_2(CO)_n$  was investigated. While the homodimetallic systems ( $M_1 = M_2 = Ru, Cr, Mo, W$ ) enter well-behaved two-electron ( $\vec{E}C\vec{E}$ ) redox cycles, the title compounds behave differently: the two metals are either reduced or reoxidized at well-separated potentials, each system following a distinct reaction path (see Figures 2-1 and 2-2).

Thus, cyclic voltammetry indicates that the W center of **1** is reduced first to a radical anion that dimerizes to the tetranuclear dianion **B1**. The latter is then reduced to the classical dianion **A1** that is directly reoxidized by an ( $\vec{E}C\vec{E}$ ) process to **1**.

In contrast, **2** is reduced in a two-electron ( $\vec{E}C\vec{E}$ ) process to the dianion **A2**, the one-electron reoxidation of which gives the tetranuclear dianionic species **B2** (analogous to **B1**). The oxidation of the proposed intermediate **B2** could eventually give **2**, via an unstable oligomeric intermediate. Support for these schemes was obtained by the chemical trapping of **B1** to give **3**, and of **A2** to give **4**. The unique electron-transfer reactivity of **1** and **2** suggest intriguing possibilities for their higher cyclopentadienologs.

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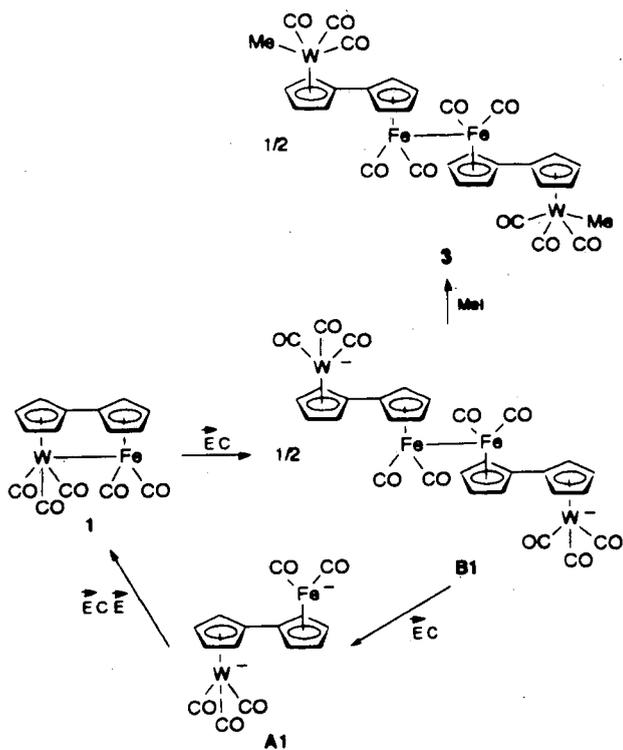


Figure 2-1. The electrochemistry of 1. (XBL 928-6184)

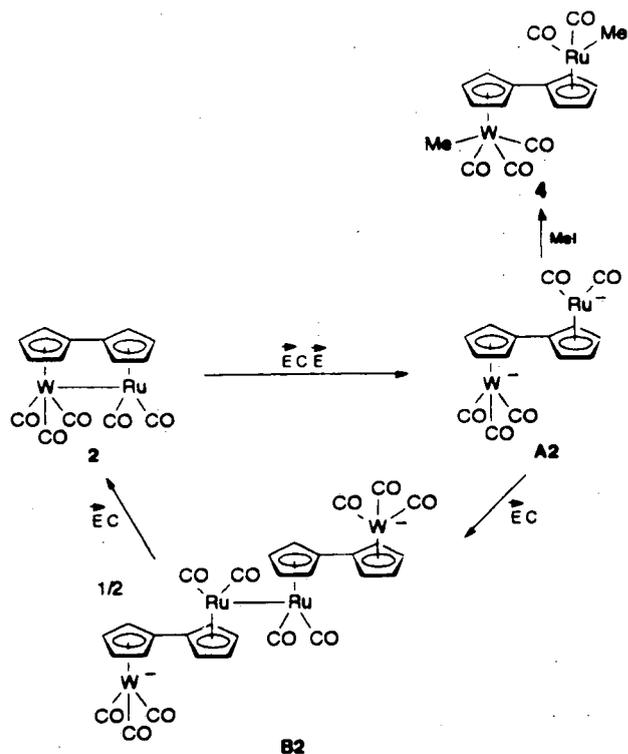


Figure 2-2. The electrochemistry of 2. (XBL 928-6185)

### 3. First Addition of Alkynes to Metal-Metal Quadruple Bonds (Publication 4)

M.C. Kerby,<sup>†</sup> B.W. Eichhorn,<sup>‡</sup> L. Doviken, and K.P.C. Vollhardt

The reaction between  $\text{Mo}_2(\text{O}_2\text{CMe})_4(\text{M}^4\text{M})$  and terminal arylalkynes in ethylenediamine (en) represents the first example of an alkyne addition to a metal-metal

quadruple bond. The coordinated alkyne ligands in these complexes are thermally hydrogenated and extruded as alkenes via an unusual amine-to-alkyne hydrogen transfer reaction (see Figure 3-1).

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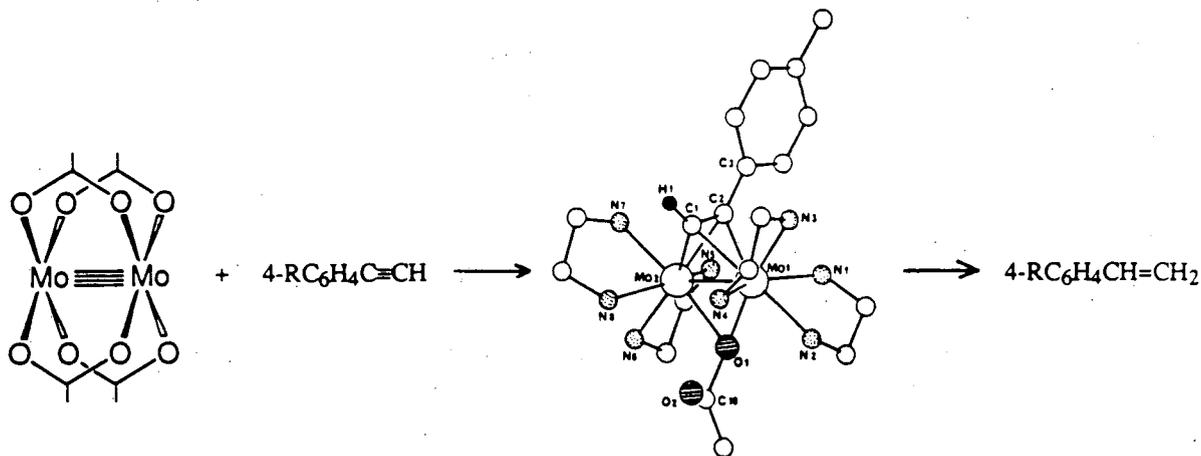


Figure 3-1. The addition of arylalkynes to a Mo-Mo quadruple bond. The scheme includes a Chem-X view of the (4-methylphenyl)ethyne complex,  $[\text{Mo}_2(\mu\text{-4-MeC}_6\text{H}_4\text{CCH})(\mu\text{-O}_2\text{CMe})(\text{en})_4]^{3+}$ . (XBL 928-6186)

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. J. Blum, G. Bitan, S. Marx, and K.P.C. Vollhardt, "Transfer Hydrogenation of Diarylacetylenes by Polymethylhydrosiloxane in the Presence of the  $\text{RhCl}_3$ -Aliquat 336 Catalyst," *J. Mol. Cat.* **66**, 313 (1991); LBL-31924.
2. Y. Badrieh, J. Blum, I. Amer, and K.P.C. Vollhardt, "Cyclo-oligomerization and Rearrangement of Some Phenylated Dienes by the  $\text{RhCl}_3$ -Aliquat 336 and by the  $\text{H}_2\text{PtCl}_6$ -Aliquat 336 Catalysts Under Phase Transfer Conditions," *J. Mol. Cat.* **66**, 295 (1991); LBL-31923.
3. K.P.C. Vollhardt, "Metallacyclopentadiene and Metallacyclopentene Complexes by Cyclodimerization of Alkynes with Alkynes or Alkenes," A. P. Hagen, J.J. Zuckerman, Eds., *Inorganic Reactions and Methods*, Verlag Chemie: New York, **12A**, p 247 (1991); LBL-31986.
4. M.C. Kerby, B.W. Eichhom, L. Doviken, and K.P.C. Vollhardt, "Activated Mo-Mo Quadruple Bonds. 2. First Example of Alkyne Additions to Metal-Metal Quadruple Bonds," *Inorg. Chem.* **30**, 156 (1991); LBL-31987.
5. R. Boese, M.A. Huffman, and K.P.C. Vollhardt, "Unique Reactivity of Heterodinuclear Pentacarbonyl(fulvalene) molybdenumruthenium with Alkynes: Fluxionality, Rearrangements, Structures, and First Reversible Conversion of a 'Side-on'- to a Semi-Bridging Alkenylidene Ligand," *Angew. Chem.* **103**, 1542 (1991); *Angew. Chem., Int. Ed. Engl.* **30**, 1463 (1991); LBL-31988.
6. M.-H. Delville-Desbois, D.S. Brown, K.P.C. Vollhardt, and D. Astruc, "Redox Chemistry of the Heterodinuclear Fulvalene Complexes  $[\text{WM}(\text{fulvalene})(\text{CO})_5]$ , M = Fe or Ru: Selective Metal Redox Recognition," *J. Chem. Soc., Chem. Commun.* 1355 (1991); LBL-31989.
7. A. Stanger and K.P.C. Vollhardt, "Synthesis and Fluxional Behavior of  $[\text{Bis}(\text{trialkylphosphine})\text{nickeliolanthracene}(\text{Alkyl} = \text{Et, Bu})]$ ," *Organometallics* **11**, 317 (1992); LBL-31990.

### LBL Reports

8. R.L. Myrabo (Ph.D. Thesis), "The Synthesis and Reactivity of Tercyclopentadienyl Diheterotrimetallic Complexes," LBL-31944.

9. M.J. West (Ph.D. Thesis), "Photochemistry and Thermal Reactivity of (Fulvalene)diiridium Complexes," LBL-31945.
10. R.H. Radde, (Ph.D. Thesis), "The Total Syntheses of Angular [4]- and [5]phenylene," LBL-31947.

### Invited Talks

11. K.P.C. Vollhardt, "Transition-metal Mediated Total Synthesis of Natural and Unnatural Products," 4th Symposium on the Latest Trends in Organic Synthesis, Blacksburg, VA, Oct. 14-17, 1990; University of California, Los Angeles, Los Angeles, CA, Nov. 1, 1990; Sandoz Phanna AG, Basel, Switzerland, Nov. 22, 1990; Bayer AG, Bayerwerk, Germany, Nov. 23, 1990; Plenary Lecturer, CONCOORD XXI, Bordeaux, France, May 13-16, 1991; University of Bordeaux, France, May 16, 1991; University of Toulouse, France, May 17, 1991; University of Rennes, France, May 29, 1991; University of Brest, France, May 31, 1991.
12. K.P.C. Vollhardt, "Oligocyclopentadienyl-metals: Remarkable Organometallic Materials," University of Bordeaux, France, May 28, 1991.
13. K.P.C. Vollhardt, "Oligocyclopentadienyl-metals: Remarkable Organometallic Materials," University of Rennes, France, June 3, 1991.
14. K.P.C. Vollhardt, "Cyclopentadienylmetals in Organic and Inorganic Synthesis: Award Lecturer, ACS A.C. Cope Scholar Award, 4th Chemical Congress of North America, New York, NY, Aug. 25-30, 1991.
15. K.P.C. Vollhardt, "Metal-Mediated Making and Breaking of Carbon-Carbon Bonds," Plenary Lecturer, GECCO XXXIII, Village de Lozari, Corsica, Sept. 1-6, 1991.
16. K.P.C. Vollhardt, "The Iterative Construction of Novel Extended  $\pi$ -Systems: An Exercise in the Interphase Between Organic and Organometallic Chemistry," Plenary Lecturer, Binational Humboldt Colloquium, Berkeley, CA, Sept. 22-24, 1991.

# HEAVY ELEMENT CHEMISTRY

## Actinide Chemistry\*

Richard A. Andersen, Norman M. Edelstein, and  
Kenneth N. Raymond, Investigators

### INTRODUCTION

Development of new technological processes for the use, safe handling, storage, and disposal of actinide materials relies on the further understanding of basic actinide chemistry and the availability of a cadre of trained personnel. This research program is a comprehensive, multifaceted approach to the exploration of actinide chemistry and to the training of students. Research efforts include synthetic organic and inorganic chemistry for the development of new chemical agents and materials; the chemical and physical elucidation through various characterization techniques; and thermodynamic and kinetic studies for the evaluation of complex formation.

The development and understanding of complexing agents that specifically and effectively sequester actinide ions is one program aspect. Such agents are intended for the decorporation of actinides in humans, in the environment, and in systems related to the nuclear fuel cycle. Extensive studies are underway to prepare organometallic and coordination compounds of the f-block elements that show the differences and similarities among the f-elements, and between the f- and d-transition series elements. Optical and magnetic studies on actinides as isolated ions in ionic solids, and in molecules, provide information about electronic properties as a function of atomic number.

### SPECIFIC SEQUESTERING AGENTS FOR THE ACTINIDES

The coordination chemistry of the actinides and lanthanides is being studied in order to create agents that selectively and strongly bind f transition elements in their +4 and +3 oxidation states. Characterization of these compounds includes the use of NMR spectroscopy, x-ray crystallography, potentiometric and spectrophotometric titrations, and electrochemistry. Possible applications for these ligands include magnetic resonance imaging (MRI),

\* This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

plutonium decorporation, uranium extraction from sea water, and waste actinide extraction and long-term storage.

### 1. Stereognostic Coordination Chemistry: The Design and Synthesis of Chelators for the Uranyl Ion (Publication 11)

*T.S. Franczyk, K.R. Czerwinski, and K.N. Raymond*

A new approach to the molecular recognition of metal oxo cations is introduced based on a ligand design strategy that provides at least one hydrogen bond donor for interaction with oxo group(s) as well as conventional electron pair donor ligands for coordination to the metal center. This concept of stereognostic coordination of oxo metal ions is exemplified in the design of four tripodal ligands: tris[2-(2-carboxyphenoxy)ethyl]amine [NEB], tris[3-(2-carboxyphenoxy)propyl]amine [NPB], tris[3-(2-carboxynaphth-3-oxy)propyl]amine [NPN] and tris [3-(2-carboxy-4-octadecylphenoxy)propyl]amine [NPoDB], for sequestration of the uranyl ion. The ligands NEB, NPB, NPN form 1:1 complexes with  $UO_2^{2+}$ . The bidentate coordination of carboxyl groups of these compounds is indicated by the infrared spectra, which offer some support for the presence of a hydrogen bond to the uranyl group. Mass spectral data corroborate CPK model predictions that more than five intervening atoms between the tertiary nitrogen atom and the carboxylate groups are required for metal ion incorporation and monomeric complex formation. Solvent extraction of aqueous  $UO_2^{2+}$  into chloroform solutions of the ligands have shown them to be powerful extractants. In the case of the very hydrophobic ligand NPoDB the stoichiometry of the complexation reaction is shown to be a 1:1  $UO_2$ /ligand complex formed by the release of three protons. The extraction is quantitative at pH 2.5 and an effective extraction coefficient of about  $10^{11}$  is estimated for neutral aqueous solutions of  $UO_2^{2+}$ .

### 2. Pu(IV) Coordination (Publication 12)

*J. Xu, L.C. Uhlir, and K.N. Raymond*

Previous workers have determined that the tetracatecholates are not optimal ligands for decorporation of Pu(IV) due to their high pKa's.<sup>1</sup> However, the catechol ligands that are terephthalamides have lower pKa's and improved water solubility.<sup>2</sup> New terephthalamide ligands have been synthesized. Some of these new terephthalamide ligands are able to remove more than

70% of Pu(IV) from mice as test animals. Another type of octadentate terephthalamide ligand has been synthesized employing a backbone composed of four primary amines in the shape of an H, this ligand is not as efficient at removing Pu(IV) from mice as those previously mentioned. The crystal structure of the first tetraterphthalamide trimacrocyclic  $\text{Me}_8\text{BHCAM}$  has been determined.

A new hexadentate 3-hydroxy-4-pyridone has been synthesized. The protonation and ferric ion binding constants of the resulting TREN-3,4-HOPO-N have been determined using potentiometric and spectrophotometric methods. The  $\log \beta_{110}$  and pM values are 34.4 and 28.9, respectively. An octadentate analog of this ligand has also been synthesized, BISTRENOX-3,4-HOPO-N.

1. M.J. Kappel, H. Nitsche, and K.N. Raymond, *Inorg. Chem.* **24**, 606 (1985).
2. T.M. Garret, P.W. Miller, and K.N. Raymond, *Inorg. Chem.* **28**, 128, 1989.

### 3. Work in Progress

$[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$  is the only lanthanide containing MRI agent approved by the FDA. Neutral derivatives of this complex are of interest as they are non-ionic, which reduces toxicity, and have been shown to be relatively more stable than  $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$  in the presence of physiological concentrations of  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{H}^+$  (Ref. 1). The x-ray crystal structure of  $[\text{Gd}(\text{DTPA-bisethylamide})(\text{H}_2\text{O})]$ , studied in collaboration with a research group at Salutar, Inc. has revealed that both amide oxygens are bound to the metal.<sup>2</sup> Analogous bis-amide macrocyclic chelators are being synthesized in order to fully encapsulate the metal, and to explore the factors influencing the relative stability and isomerization processes.

In addition, stability constant measurements and NMR spectroscopy of the lanthanide complexes are in progress in order to determine their solution state coordination geometry and mechanism of ligand exchange Pu(IV) Coordination.

Catechoylamides and terephthalamides are also being covalently bound to solid substrates (polystyrene and silica gel) in attempt to produce a material that can

1. W.P. Cacheris, S.C. Quay, and S.M. Rocklage, *Mag. Reson. Imag.* **8**, 467 (1990).
2. M.S. Konings, W.C. Dow, D.B. Love, K.N. Raymond, and S.C. Quay, *Inorg. Chem.* **29**, 1488 (1990).

selectively remove Pu(IV) from solution. Characterization of these materials is underway.

## PHYSICAL AND SPECTROSCOPIC PROPERTIES

### 4. Observation of Strong Electron-Phonon Coupling Effects in $\text{YbPO}_4$ (Publication 18)

*P.C. Becker, G.M. Williams, N.M. Edelstein, J.A. Koningstein, L.A. Boatner, and M.M. Abraham*

Coupling between the electronic states of rare earth ions doped in a crystal and the vibrational modes of the lattice are usually weak due to the effective shielding of the 4f electrons of the rare earth ions. In the present work surprising results are presented for the system  $\text{YbPO}_4$ , which show a temperature dependent electron-phonon coupling (see Figure 4-1) with coupling strengths an order of magnitude larger than any previously reported. The effect is observed using electronic Raman spectroscopy, which uncovers in a precise fashion the character of the low-lying energy states. The underlying cause of the anomalously large electron-phonon coupling effects is not understood, nor is it clear why the effect is restricted to the ytterbium ion. Phenomenological calculations, based on the low-lying energy level structure of  $\text{Yb}^{3+}$ , are presented, which qualitatively account for the temperature dependence of the splitting of the  $E_g$  phonon at  $310 \text{ cm}^{-1}$  (see Figure 4-2). The novel effects reported here should have implications for the physics of electron-phonon coupling in rare earth systems.

### 5. Analysis of the Optical Spectra and Magnetic Susceptibilities of $\text{Li}_7\text{UO}_6$ , $\text{Ba}_3\text{NpO}_6$ , and $\text{Li}_5\text{PuO}_6$ (Publication 6)

*Y. Hinatsu and N. Edelstein*

The absorption spectra and magnetic susceptibilities of  $\text{Li}_7\text{UO}_6$ ,  $\text{Ba}_3\text{NpO}_6$ , and  $\text{Li}_5\text{PuO}_6$  obtained from published data have been reanalyzed on the basis of an octahedral crystal-field model with and without a small tetragonal distortion. The spin-orbit coupling constants obtained for  $\text{Li}_7\text{UO}_6$ ,  $\text{Ba}_3\text{NpO}_6$ , and  $\text{Li}_5\text{PuO}_6$  from this work give reasonable values for  $\text{U}^{5+}$ ,  $\text{Np}^{6+}$ , and  $\text{Pu}^{7+}$ , and show an increase with atomic number and/or oxidation state, which is consistent with the results of the theoretical

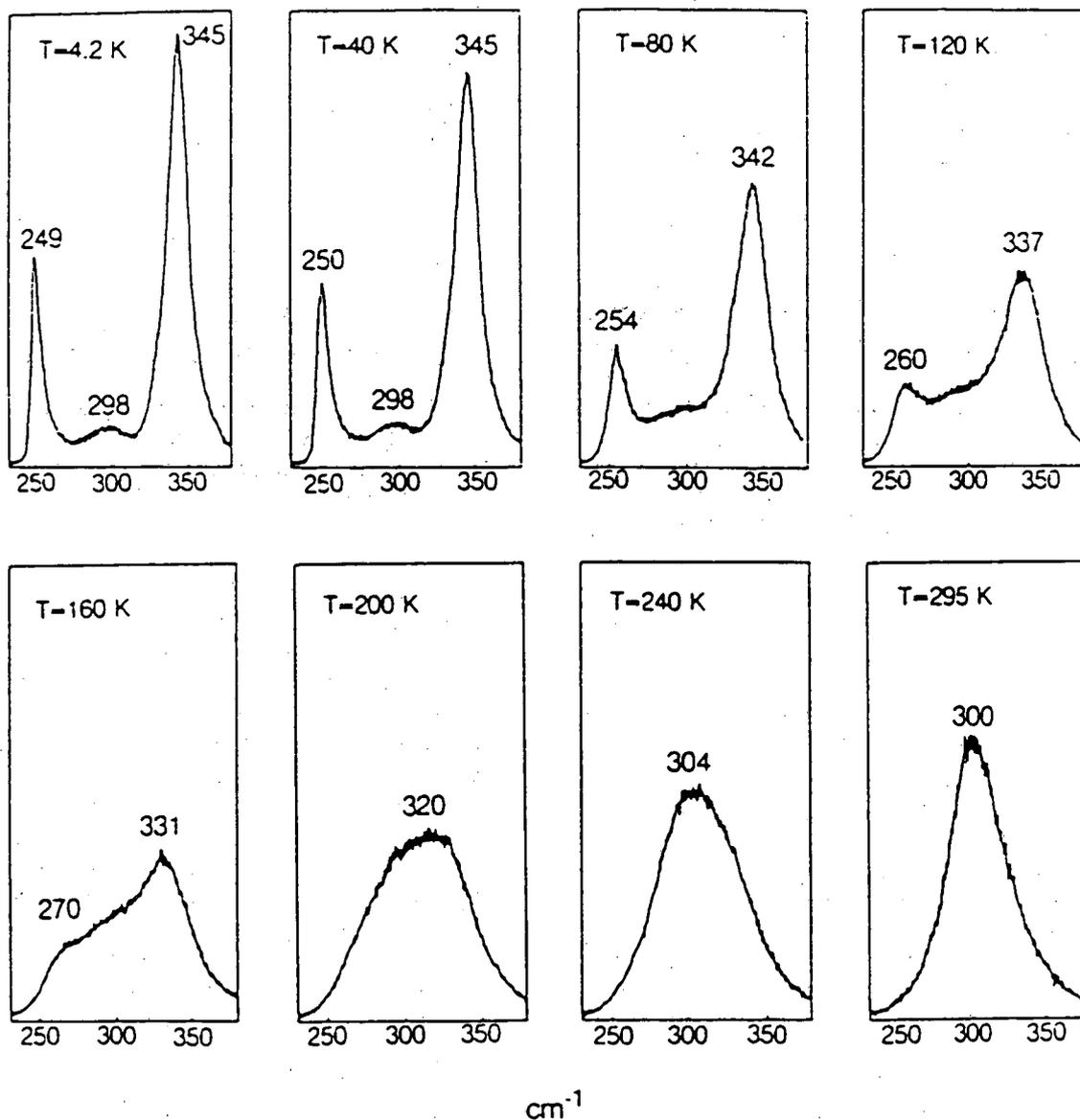


Figure 4-1. Raman spectra of the crystal  $\text{YbPO}_4$  in the  $\text{Y(XZ)X}$  configuration, in the  $300 \text{ cm}^{-1}$  region, as a function of temperature between room temperature and  $T = 4.2 \text{ K}$ . The numbers in the figures are peak positions in  $\text{cm}^{-1}$ . (XBL 923-538)

calculations. The covalency effect in chemical bonding has been taken into account by the use of orbital reduction factors in the calculation of energy levels and magnetic susceptibilities. Although the orbital reduction factors determined ( $k$  and  $k'$ ) may not be the unique values for each compound, the results indicate that  $k'$  should be much smaller than  $k$ , which is consistent with the theoretical view. To obtain a satisfactory fit of the magnetic susceptibility data as a function of temperature, an added empirical temperature-independent paramagnetism (TIP) was needed for all of the compounds. It is suggested the reduced actinide ions with

the  $[\text{Rn}]5f^2$  configuration, i.e.,  $\text{U}^{4+}$ ,  $\text{Np}^{5+}$ , and  $\text{Pu}^{6+}$ , are responsible for this extra TIP. These latter ions in an octahedral coordination are known to show a temperature-independent paramagnetism over a wide temperature range. With this hypothesis and from the comparison of the extra TIP between compounds, it was found that a considerable amount of  $\text{Pu}^{6+}$  ions (which are much more stable than  $\text{Pu}^{7+}$  ions) exists in  $\text{Li}_3\text{PuO}_6$ . The crystal-field splitting  $\Delta$ , which is very sensitive to the magnetic properties of the compounds, increases with atomic number (from  $\text{U}^{5+}$  to  $\text{Np}^{6+}$  to  $\text{Pu}^{7+}$ ) as expected.

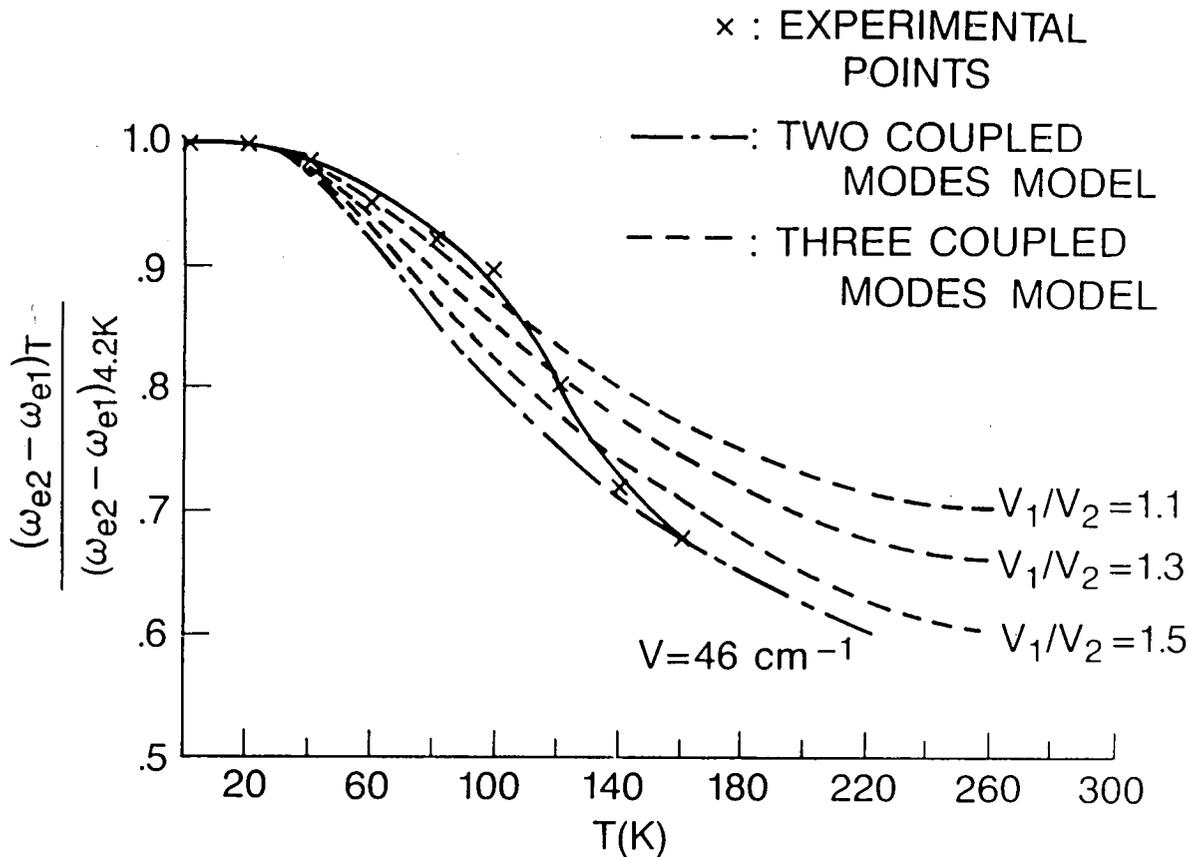


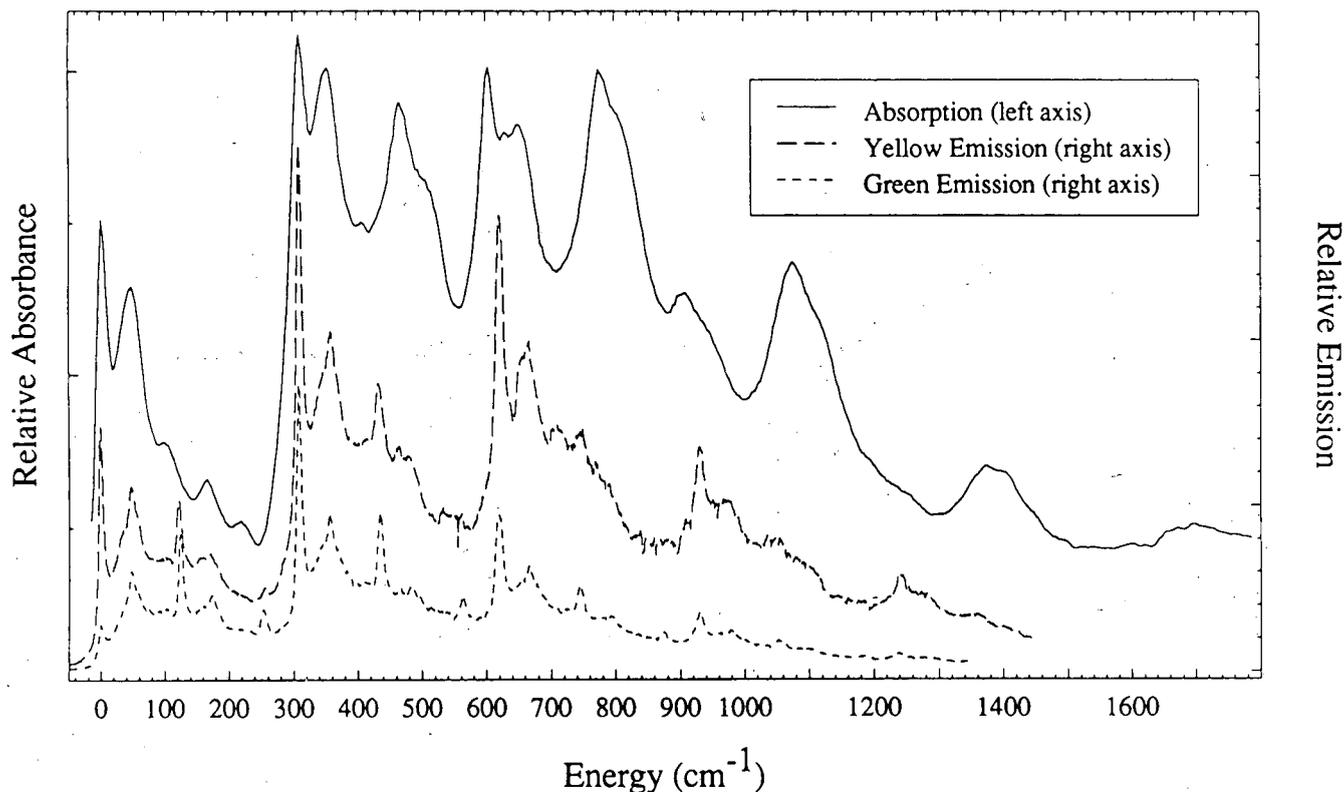
Figure 4-2. Splitting of the coupled modes of YbPO<sub>4</sub>, as a function of temperature, in  $\Gamma_5$  symmetry. Experimental and calculated curves are shown. The smooth curve drawn through the experimental points is a guide to the eye.  $V_1$  and  $V_2$  represent the interaction potentials, respectively, between the two electronic excitations of energies  $E_1$  and  $E_2$  with the 310 cm<sup>-1</sup> E<sub>g</sub> phonon. (XBL 923-539)

## 6. The 5f → 6d Absorption Spectrum of Pa<sup>4+</sup>/Cs<sub>2</sub>ZrCl<sub>6</sub> (Publication 15)

*N. Edelstein, W.K. Kot, and J.-C. Krupa*

The 5f<sup>1</sup> → 6d<sup>1</sup> absorption spectrum of <sup>231</sup>Pa<sup>4+</sup> diluted in a single crystal of Cs<sub>2</sub>ZrCl<sub>6</sub> has been measured at 4.2 K. Three bands corresponding to the 6d( $\Gamma_{8g}$ ,  $\Gamma_{7g}$ , and  $\Gamma_{8g}$ ) levels are assigned. Values of  $\zeta_{6d} = 1860$  cm<sup>-1</sup> and 10 Dq ~18,600 cm<sup>-1</sup> are obtained from an analysis of the data. Extensive vibronic structure has been observed for the lowest 5f → 6d transition and this structure is compared to that recently reported for the 6d<sup>1</sup> → 5f<sup>1</sup> emission spectra in the same system as shown in Figure

6-1. Two major differences are observed between the emission spectra and the absorption spectrum. The first is the absence of features in the absorption spectrum that can be attributed to e<sub>2g</sub> and t<sub>2g</sub> vibrations, although these features are present in the emission spectra, and the second is the broadening and relative increase in intensity of the vibronic features at ~170-200 cm<sup>-1</sup> compared to the bands at 0-60 cm<sup>-1</sup> in the higher progressions of the absorption spectrum. In the emission spectra these vibronic features in the higher progressions decrease in intensity (relative to each other) without noticeable broadening. These differences are attributed to the different potential-energy surfaces in the ground 5f configuration and the excited 6d configuration.



**Figure 6-1.** Comparison of the vibronic structure observed for  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  in the absorption spectrum (zero-phonon line at  $19,947 \text{ cm}^{-1}$ ) with the vibronic structure in two emission bands: the yellow band (zero-phonon line at  $17,847 \text{ cm}^{-1}$ ) and the green band (zero-phonon line at  $19,954 \text{ cm}^{-1}$ ). The abscissa for the absorption data represents the differences between the vibronic data and the zero-phonon line; the abscissa for the emission data represents the differences between the respective zero-phonon lines and the vibronic data. (XBL 923-537)

## 7. Studies of $f^1$ and $d^1$ Configurations in the Lanthanide and Actinide Series (Publication 8)

*N.M. Edelstein*

At the beginning of both the  $4f$  and  $5f$  electron series, the possible electron configurations for atoms or ions with one electron outside the xenon or radon core are very close in energy. As the degree of ionization increases for the one electron (outside the closed shells) ions, the  $4f$  or  $5f$  configuration becomes stabilized with respect to the other possible configurations. The free ion data for  $\text{RaII}$  ( $\text{Ra}^{1+}$ ) to  $\text{UVI}$  ( $\text{U}^{5+}$ ) are shown in Figure 7-1. The one electron ions,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{4+}$ ,  $\text{Th}^{3+}$ ,  $\text{Pa}^{4+}$ , and  $\text{U}^{5+}$  form accessible chemical compounds.  $\text{Pa}^{4+}$  is a stable

oxidation state for element 91, but the naturally occurring isotope  $^{231}\text{Pa}$  is part of the  $^{235}\text{U}$  decay chain and handling this element and its compounds is difficult, primarily due to the radioactivity of the  $^{231}\text{Pa}$  daughters. There is only one known structurally characterized compound of  $\text{Th}^{3+}$ . For compounds of  $\text{PrV}$  ( $\text{Pr}^{4+}$ ) or  $\text{UVI}$  ( $\text{U}^{5+}$ ) only the ground  $4f$  or  $5f$  configurations are accessible by conventional optical techniques. This paper reviews recent studies of the optical and/or magnetic data of  $\text{Ce}^{3+}$ ,  $\text{Th}^{3+}$ , and  $\text{Pa}^{4+}$  in compounds or crystals for which information is available on both the ground and the first excited configurations. As an example of the data available, Figure 7-2 shows the  $4f$  and  $5d$  energy levels for the  $\text{Ce}^{3+}$  ion in a number of different crystals.

## FY 1991 PUBLICATIONS AND REPORTS

### Refereed Journals

1. K.N. Raymond, "Template Synthesis and Ligand Design for f-Metal Ligands," *Eur. J. Solid State Inorg. Chem.* **28**, 225 (1991); LBL-31867.
2. G.N. Stradling, S.A. Gray, J.C. Moody, A. Hodgson, K.N. Raymond, P.W. Durbin, S.J. Rodgers, D.L. White, and P.N. Turowski, "The Efficacy of DFO-HOPO, DTPA-DX and DTPA for Enhancing the Excretion of Plutonium and Americium from the Rat," *Int. J. Radiat. Biol.* **59**(5), 1269 (1990); LBL-31868.
3. D. Piehler, W.K. Kot, and N. Edelstein, "The 6d  $\rightarrow$  5f Fluorescence Spectra of  $\text{PaCl}_6^{2-}$  in a  $\text{Cs}_2\text{ZrCl}_6$  Crystal," *J. Chem. Phys.* **94**, 942 (1991); LBL-29451.
4. K. Yunlu, P.S. Gradeff, N. Edelstein, W. Kot, G. Shalimoff, W.E. Streib, B.A. Vaartstra, and K.G. Caulton, "Photoreduction of Ce(IV) in  $\text{Ce}_2(\text{O}^i\text{Pr})_8(\text{PrOH})_2$ . Characterization and Structure of  $\text{Ce}_4\text{O}(\text{O}^i\text{Pr})_{13}(\text{PrOH})$ ," *Inorg. Chem.* **30**, 2317 (1991); LBL-30168.
5. C.S. Yoo, H.B. Radousky, N.C. Holmes, and N.M. Edelstein, "Luminescence of  $\text{Sm}^{2+}$  Ions as a Probe of Pressure-Induced Phase Transitions in  $\text{SrF}_2$ ," *Phys. Rev. B* **44**, 830 (1991); LBL-30130.
6. Y. Hinatsu and N. Edelstein, "Analysis of the Optical Spectra and Magnetic Susceptibilities of  $\text{Li}_7\text{UO}_6$ ,  $\text{Ba}_3\text{NpO}_6$ , and  $\text{Li}_5\text{PuO}_6$ ," *J. Solid State Chem.* **93**, 173 (1991); LBL-31137.
7. H. Reddmann, H. Schultze, H.-D. Amberger, G.V. Shalimoff, and N. M. Edelstein, "The Electronic Structure of Metalloorganic Compounds of f-Elements XXVII. Interpretation of the Optical, Magnetic, EPR, and NMR Spectroscopic Properties of the Neutral Base Adducts of  $\text{Tris}(\eta^5\text{-cyclopentadienyl})\text{Nd}(\text{III})$ ," *J. Organomet. Chem.* **411**, 331 (1991); LBL-30167.
8. N. Edelstein, "Studies of  $f^1$  and  $d^1$  Configurations in the Lanthanide and Actinide Series," *Eur. J. Solid State Inorg. Chem.* **28**, 47 (1991); LBL-29652.
9. D. Piehler, "Electronic Coherent Anti-Stokes Raman Spectroscopy in  $\text{CeF}_3$ ," *J. Opt. Soc. Am. B* **8**, 1889 (1991); LBL-29802.

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10. G. N. Stradling, S. A. Gray, M. Ellender, J. C. Moody, A. Hodgson, M. Pearce, I. Wilson, R. Burgada, T. Bailly, Y.G.P. Leroux, D. El Manouni, P. Durbin, and K. N. Raymond, "The Efficacies of 3,4,3-LIHOPO and DTPA for Enhancing the Excretion of Plutonium and Americium from the Rat: Comparison with Other Siderophore Analogues," submitted to *Int. J. Rad. Biology*, LBL-31871.
11. T. S. Franczyk, K. R. Czerwinski, and K. N. Raymond, "Stereognostic Coordination Chemistry: The Design and Synthesis of Chelators for the Uranyl Ion," LBL-32174.
12. J. Xu, L. C. Uhlir, and K. N. Raymond, "Pu(IV) Coordination," LBL-32175.

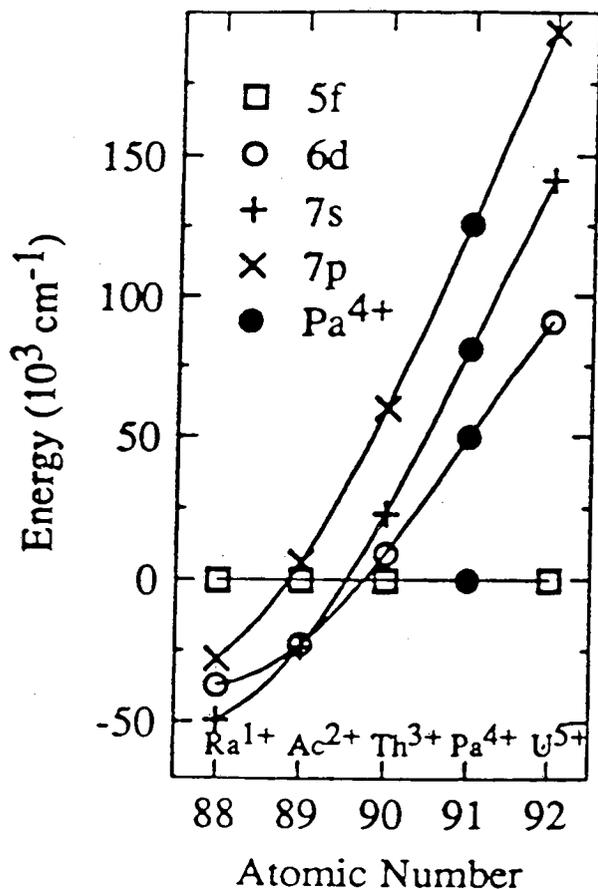


Figure 7-1. Relative energies of the lowest levels of various one electron configurations for a number of one electron ions at the beginning of the actinide series. The points for  $\text{Pa}^{4+}$  are interpolated. (XBL-923-541)

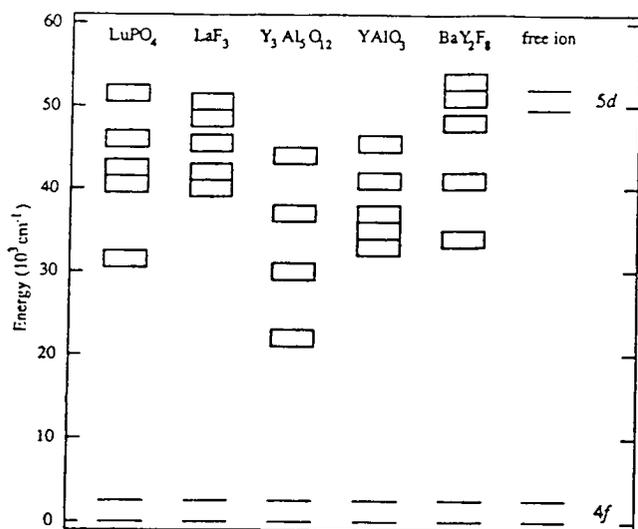


Figure 7-2. Approximate 4f and 5d crystal field energy levels for  $\text{Ce}^{3+}$  in several different crystals. Only four of the five 5d levels are observed below the band gap of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  that begins at  $\sim 50,000 \text{ cm}^{-1}$ . (XBL 923-540)

13. K.N. Raymond and P.W. Durbin, "The Design, Synthesis and Evaluation of Sequestering Agents Specific for Plutonium(IV)," presented at The First Hanford Separation Science Workshop, Hanford, Washington, July 23-25, 1991, LBL-31872.
14. P.T. Matsunaga (Ph.D. Thesis), "Bis (pentamethylcyclopentadienyl)-ytterbium: Electron-Transfer Reactions with Organotransition Metal Complexes," LBL-31491.
15. N. Edelstein, W.K. Kot, and J.-C. Krupa, "The  $5f \rightarrow 6d$  Absorption Spectrum of  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ ," *J. Chem. Phys.*, (in press); LBL-31108.
16. W.K. Kot (Ph.D. Thesis), "Electronic Structure in the Actinides—Three Case Studies," LBL-30652.
17. H. Reddmann, H. Schultze, H.-D. Amberger, G.V. Shalimoff, and N.M. Edelstein, "The Electronic Structure of Organometallic Complexes of the f Elements XXVIII. Interpretation of the Optical and Magnetochemical Data of a Cyclohexylisocyanide Adduct Derived from  $\text{Tris}(\eta^5\text{-Cyclopentadienyl})\text{-Samarium(III)}$ ," in *Proceedings of the 19th Rare Earth Research Conference*, Lexington, Kentucky, July 14-19, 1991, *J. of Less-Common Metals*; LBL-30570.
18. P.C. Becker, G.M. Williams, N.M. Edelstein, J.A. Koningstein, L.A. Boatner, and M.M. Abraham, "Observation of Strong Electron-Phonon Coupling Effects in  $\text{YbPO}_4$ ," *Phys. Rev. B* (in press); LBL-32117.
22. K.N. Raymond, "Metal-Ion Specific and Stereognostic Coordination Chemistry," American Cyanamid Company, Stamford, CT, May 1, 1991.
23. K.N. Raymond, "Metal Ion-Specific and Stereognostic Coordination Chemistry," Princeton University, Princeton, NJ, May 2, 1991.
24. K.N. Raymond, "Metal-Ion Specific and Stereognostic Coordination Chemistry," Czechoslovakia, May 11-18, 1991.
25. K.N. Raymond, "Microbes as Coordination Chemists: Iron Transport in Bacteria and Man," and "Metal Ion Specific Complexing Agents; Stereognostic Coordination Chemistry," Technische Universität Berlin, June 13-14, 1991.
26. K.N. Raymond, "The Design, Synthesis and Evaluation of Sequestering Agents Specific for Plutonium(IV)," First Hanford Separations Workshop, July 23-25, 1991, Richland, WA.
27. K.N. Raymond, "Iron and Vanadium Complexes of Siderophores or Siderophore Analogs" Marine Bioinorganic Symposium, ACS Meeting, New York, Aug. 25-27, 1991.
28. K.N. Raymond, "Microbes, Plutonium and Stereognosis," American Chemical Society, California Section, Berkeley, CA, Sept. 24, 1991.
29. K.N. Raymond, "Metal Ion Molecular Recognition," University of California, Berkeley, CA, Oct. 29, 1991.
30. K.N. Raymond, "Metal Ion Molecular Recognition," Salutar, Inc, Sunnyvale, CA, Dec. 16, 1991.
31. R.A. Andersen, "Organometallic Chemistry of the f-Block Elements," Dow Chemical Co., Midland, MI, March 25, 1991; Hope College, Holland, MI, Mar. 27, 1991; Calvin College, Grand Rapids, MI, March 28, 1991; Raychem Corp., Menlo Park, CA, May 1, 1991.
32. N.M. Edelstein, "I. Magnetic and Optical Properties of the Actinides. II. Transactinium Science at the Advanced Light Source," Institute for Transactinium Science Advisory Council Meeting, Lawrence Livermore National Laboratory, July 11, 1991.

#### Invited Talks

19. K.N. Raymond, "Biomimetic Sequestering Agents for Iron and Vanadium," Metals in Biology Gordon Conference, Ventura, CA, Jan. 30, 1991.
20. K.N. Raymond, "Metal-Ion Specific and Stereognostic Coordination Chemistry," University of Utah, Salt Lake City, UT, Feb. 12, 1991.
21. K.N. Raymond, "Stereognostic Coordination Chemistry: Uranyl Complexation," Metal Specific Ligands Symposium, ACS Meeting, Atlanta, GA, Apr. 16, 1991.

# CHEMICAL ENGINEERING SCIENCES

## Molecular Thermodynamics for Phase Equilibria in Mixtures\*

John M. Prausnitz, Investigator

### INTRODUCTION

Phase equilibria are required for design of efficient large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries. In this context, "efficient" refers to optimum use of raw materials and to conservation of energy.

Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all equilibria from experiment. Therefore, the objective of this research is development of molecular thermodynamics for interpretation and correlation of reliable experimental data toward confident prediction of phase equilibria for engineering. The correlations are expressed through semi-theoretical, physicochemical models in a form suitable for computer-aided design. Particular attention is given to those materials that may be useful for innovative low-energy-consuming separation processes such as polymers and gels, and polyelectrolyte systems with possible applications in biotechnology. However, attention is also devoted to conventional materials for applications in fuel technology and for recovery of solutes from wastewater.

Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it requires simultaneous awareness of progress in molecular science and of realistic requirements for engineering design.

#### 1. Correlation of High-Pressure Phase Equilibria in the Retrograde Region with Three Common Equations of State (Publication 1)

R. Dohrn, W. Künstler, and J.M. Prausnitz

Phase equilibria in the retrograde regions were calculated for the methane-n-decane binary system and for a realistic natural-gas system (methane-Kensol-16). Calculations were performed using three equations of

state (EOS): Peng–Robinson, Redlich–Kwong–Soave, and Perturbed Hard–Chain; calculations were compared to experiment. Liquid-drop-out curves and pressure-temperature diagrams were calculated between 301 and 369 K and pressures to 90 MPa. The binary system was represented best by the Peng–Robinson EOS. For the natural-gas system, the Perturbed Hard–Chain equation yielded the best results, although all equation of state showed appreciable deviations. Good results could only be obtained when binary coefficients were fitted to the experimental retrograde data.

#### 2. Three-Phase Flash Calculations for Multicomponent Systems (Publication 2)

A.P. Bünz, R. Dohrn, and J.M. Prausnitz

A three-phase flash algorithm<sup>1</sup> has been incorporated into a program for calculating high-pressure phase equilibria.<sup>2</sup> The method presented here includes the a priori determination of the number of phases present and the solution of the flash equations once the number of phases have been determined. Although an extension to more than three coexisting phases is possible, the method given here is restricted to multicomponent systems with a maximum of three phases in equilibrium. To illustrate the method, phase-equilibrium calculations are shown for the ternary systems hexadecane-water-hydrogen and toluene-water-hydrogen at elevated pressures and temperatures.

1. Nelson, *Computers Chem. Eng.* **11**, 581 (1987).

2. Dohrn and Brunner, *Chem. Technik* **41**, 65 (1989).

#### 3. Swelling Equilibria for Weakly Ionizable, Temperature-Sensitive Hydrogels (Publication 3)

S. Beltrán, J.P. Baker, H.H. Hooper, H.W. Blanch, and J.M. Prausnitz

Swelling equilibria in aqueous citrate-phosphate buffer solutions are reported for thermally sensitive poly(N-isopropylacrylamide) hydrogels containing weakly-ionizable groups. The comonomers containing these groups were sodium acrylate and 2-(dimethylamino)ethyl methacrylate to produce gels with, respectively, acidic and basic character. Gel swelling was measured as a function of pH, ionic strength, and temperature. With increasing ionization, the temperature range over which the gel volume changes is greatest becomes larger and shifts to higher temperatures.

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76F00098.

#### 4. Monte Carlo Study of Polyelectrolyte Adsorption. Isolated chains on a Planar Charged Surface (Publication 4)

*S. Beltrán, H.H. Hooper, H.W. Blanch, and J.M. Prausnitz*

Monte Carlo simulations are presented for the adsorption of a lattice-model isolated polyelectrolyte on an impenetrable, oppositely charged surface. We consider the effects of chain ionization, chain hydrophobicity, surface charge density, and solution ionic strength on the conformation and interfacial properties of the model system. The overall conformational properties of the model polyelectrolytes in the adsorbed state are similar to those of isolated polyelectrolytes in solution; however, the adsorbed chains are conformationally anisotropic. This anisotropy is described here by calculating the components of the polymer end-to-end distance in directions parallel and orthogonal to the interface. Detailed structural features of the adsorbed chains are described by the distributions of tails, trains, and loops. Tails are favored at low degrees of chain ionization, while trains become more favorable at high degrees of ionization. The number of adsorbed chain segments (e.g., degree of adsorption) increases with the surface charge density and decreases with increasing solution ionic strength; for some conditions, this degree of adsorption is a strong function of solution and surface properties.

#### 5. Binary Liquid-Liquid Equilibria from a Double-Lattice Model (Publication 5)

*Y. Hu, H. Liu, D.S. Soane, and J.M. Prausnitz*

Freed's lattice field theory is used to establish a double-lattice model for the Helmholtz energy of mixing for strongly nonideal binary liquid mixtures. The coefficients of Freed's expansion terms are adjusted such that the calculated coexistence curve for the simple Ising lattice is in excellent agreement with that calculated from the Padé-approximant coefficients for spontaneous magnetization proposed by Scesney. For a variety of binary systems, two parameters ( $\epsilon/k$  and  $r_2$ ) are obtained from experimental critical consolute points; here  $\epsilon/k$  is the interchange energy and  $r_2$  is the number of lattice sites required by molecule 2, with  $r_1 = 1$ . Calculated coexistence curves are generally in good agreement with experiment for fluid mixtures without specific (oriented) interactions, much better than those calculated using Flory-Huggins theory, especially near critical consolute points. Introducing a secondary lattice to account for highly oriented interactions (hydrogen bonding), requires

an additional energy parameter  $\delta\epsilon/k$  and an empirical parameter  $c_{10}$ . With these parameters coexistence curves are fitted well for systems having a miscibility loop with both lower and upper critical solution temperatures.

#### 6. Cloud-Point Curves of Polymer Solutions from Thermo-optical Measurements (Publication 6)

*Y.C. Bae, S.M. Lambert, D.S. Soane, and J.M. Prausnitz*

Thermo-optical analysis (TOA) provides a simple, rapid, and reliable experimental method to determine cloud-point curves of binary polymer/solvent systems. Phase diagrams have been obtained for different molecular weights of polystyrene in cyclohexane, methyl acetate, ethyl acetate, and *tert*-butyl acetate and for poly(ethylene glycol) in water. Polystyrene solutions exhibit both upper and lower critical solution temperatures, while aqueous poly(ethylene glycol) solutions give closed-loop phase diagrams. The TOA apparatus described here uses very small samples (0.02 cm<sup>3</sup>); for a binary system, upper and lower cloud-point curves can be easily obtained in about one hour.

#### 7. Double-Lattice Model for Binary Polymer Solutions (Publication 7)

*Y. Hu, S.M. Lambert, D.S. Soane, and J.M. Prausnitz*

Freed's lattice-field theory provides a basis for a double-lattice model for the Helmholtz energy of mixing for binary polymer solutions. When Freed's series-expansion terms for the simple Ising lattice and for the Flory-Huggins lattice with  $r_1 = 1$  and  $r_2 = 100$  are revised slightly, predicted liquid-liquid coexistence curves are in excellent agreement with those calculated from Scesney's Padé-approximant coefficients and from computer simulation results by Madden, Pesci, and Freed; here  $r_1$  and  $r_2$  are the numbers of sites required by molecule 1 and molecule 2, respectively. For real systems, the interchange energy ( $\epsilon/k$ ) and  $r_2$  are adjusted to fit the experimental concentration dependence of the Flory-Huggins parameter  $\chi$  determined by vapor sorption, osmotic pressure, light scattering, or sedimentation. To account for highly oriented interaction between segments, a secondary lattice is introduced. This secondary lattice requires an additional parameter ( $\delta\epsilon/k$ ) related to the energy of the oriented interaction and one empirical parameter  $c_{10}$ . With the double-lattice theory, coexistence curves can be reproduced for systems having an upper critical solution temperature (UCST), a lower critical solution temperature (LCST), or a miscibility loop with both UCST and LCST.

## FY 1991 PUBLICATIONS AND REPORT

### Refereed Journals

1. R. Dohrn, W. Künstler, and J.M. Prausnitz, "Correlation of High-Pressure Phase Equilibria in the Retrograde Region with Three Common Equations of State," *Canadian J. Chem. Eng.* **69**, 1200 (1991); LBL-28324.
2. A.P. Bünz, R. Dohrn, and J.M. Prausnitz, "Three-Phase Flash Calculations for Multicomponent Systems," *Computers and Chem. Eng.* **15**(1), 47 (1991); LBL-28763.
3. S. Beltrán, J.P. Baker, H.H. Hooper, H.W. Blanch, and J.M. Prausnitz, "Swelling Equilibria for Weakly Ionizable, Temperature-Sensitive Hydrogels," *Macromolecules* **24**, 549 (1991); LBL-29053.
4. S. Beltrán, H.H. Hooper, H.W. Blanch, and J.M. Prausnitz, "Monte Carlo Study of Polyelectrolyte Adsorption. Isolated Chains on a Planar Charged Surface," *Macromolecules* **24**, 3178 (1991); LBL-29238.
5. Y. Hu, H. Liu, D.S. Soane, and J.M. Prausnitz, "Binary Liquid-Liquid Equilibria from a Double-Lattice Model," *Fluid Phase Equilibria* **67**, 65 (1991); LBL-29997.
6. Y.C. Bae, S.M. Lambert, D.S. Soane, and J.M. Prausnitz, "Cloud-Point Curves of Polymer Solutions from Thermo-optical Measurements," *Macromolecules* **24**, 4403 (1991); LBL-31890.
7. Y. Hu, S.M. Lambert, D.S. Soane, and J.M. Prausnitz, "Double-Lattice Model for Binary Polymer Solutions," *Macromolecules* **24**, 4356 (1991); LBL-31892.

### Other Publications

8. S.F. Matzke (M.S. Thesis), "Structural Aspects of Protein Solubilization in Reverse Micelles" (jointly with Prof. H.W. Blanch), June 1991.
9. L.Y. Chou (M.S. Thesis), "Buffer Effects on Aqueous Swelling Kinetics of Polyelectrolyte Gels" (jointly with Prof. H.W. Blanch), June 1991.
10. A.M. Ting (M.S. Thesis), "The Extractive Crystallization of Sodium Chloride and Sodium Sulfate with N,N-Diethylmethylamine" (jointly with Prof. S. Lynn), September 1991.

### LBL Reports

11. P. Magin, M. Bonnin, and J.M. Prausnitz, "Separation of Salt from Water-Soluble Polymers Using High-Pressure Carbon Dioxide," LBL-30819.

12. J.P. Baker, D.R. Stephens, H.W. Blanch, and J.M. Prausnitz, "Swelling Equilibria for Acrylamide-Based Polyampholyte Hydrogels," accepted by *Macromolecules*; LBL-30830.
13. L.Y. Chou, H.W. Blanch, and J.M. Prausnitz, "Buffer Effects on Aqueous Swelling Kinetics of Polyelectrolyte Gels," accepted by the *J. Appl. Polymer Sci.*; LBL-31083.
14. J.J. de Pablo, M. Bonnin, and J.M. Prausnitz, "Vapor-Liquid Equilibria for Polyatomic Fluids from Site-Site Computer Simulations: Pure Hydrocarbons and Binary Mixtures Containing Methane," accepted by *Fluid Phase Equilibria*; LBL-31167.
15. A. Ting, S. Lynn, and J.M. Prausnitz, "Liquid-Liquid Equilibria for Aqueous Systems Containing N,N-Diethylmethylamine and Sodium Chloride of Sodium Sulfate," accepted by the *J. Chem. Eng. Data*; LBL-31307.
16. Y.C. Bae, J.J. Shim, D.S. Soane, and J.M. Prausnitz, "Representation of Vapor-Liquid and Liquid-Liquid Equilibria for Binary Systems Containing Polymers. Applicability of an Extended Flory-Huggins Equation," accepted by the *J. Appl. Polymer Sci.*; LBL-31891.
17. D.K. Brenner, E.W. Anderson, S. Lynn, and J.M. Prausnitz, "Liquid-Liquid Equilibria for Saturated Aqueous Solutions of Sodium Sulfate in Contact with 1-Propanol, 2-Propanol, and Tertiary Butanol," submitted to the *J. Chem. Eng. Data*; LBL-31900.

### Invited Talks

18. J.M. Prausnitz, "Putting the Pieces Together. The Synthetic Character of Molecular Thermodynamics," Iowa State University, Ames, October 1990; Georgia Institute of Technology, Atlanta, November 1990; University of Delaware, Newark, April 1991; University of Texas at Austin, April 1991; University of Calgary, Canada, June 1991.
19. J.P. Baker, "Swelling Equilibria for Weakly-Ionizable Temperature-Sensitive Hydrogels," American Institute of Chemical Engineers Annual Meeting, Chicago, IL, November 1990.
20. J.M. Prausnitz, "New Developments in Molecular Thermodynamics: Polymers, Gels and Biotechnology," European Conference on Applied Thermodynamics, Spandau, Germany, April 1991.
21. J.M. Prausnitz, "Phase Equilibria for Petroleum Production," Reservoir Engineering Research Institute, Palo Alto, CA, August 1991.

**Exploratory Research  
and Development Funds**

# Technical Evaluation of Beamlines and Experimental Stations for Chemical Dynamics Applications at the ALS\*

Investigators: Yuan T. Lee, and Andrew H. Kung

## INTRODUCTION

The high brightness and high flux of photons that are becoming available from next-generation synchrotron sources offer new and exciting possibilities for gas-phase chemical-physics studies. It is the goal of this project to perform a detailed evaluation of various synchrotron beamline technologies and examine improvements to synchrotron light output that will respond to specific needs of gas phase chemical research at synchrotron facilities. Specific objectives include a numerical study of monochromator layout and choice of grating designs to achieve an exceptionally high resolution of 1 part in 50,000 while maintaining a high throughput, and a feasibility evaluation and design of a high-order suppressor to achieve a spectral purity of 1 part in 100,000 in undulator output for these applications.

Bend magnet and undulator beamline arrangements using normal incidence monochromators were studied by numerical ray tracing to obtain detailed focusing characteristics of each optical design option. The result is an optimized design that meets the conditions: (1) at the specimen center, the width of the undulator beam spot in the horizontal direction must be kept extremely small, (2) the height of the beam from the floor should be 1.5 m, and (3) an identical monochromator design will be adapted for the bend magnet beamline and the undulator beamline. Various options for the approach to grating design will be examined critically. The merits of ruled gratings, variable spaced gratings, and holographic gratings will be compared. Their scientific, technical, and economic trade-offs will be carefully evaluated to arrive at a final design recommendation.

It is an important target to achieve a spectral purity of 1 part in 100,000. A number of options are examined: gas filters, dielectric coated mirrors, and thin-film windows. The criteria to be used for evaluation are high throughput, broad and continuous tunability, cost, compactness, and compatibility with the experiments. The options are studied quantitatively and in conjunction with the optics arrangement of the beamlines. The result should be a

highly optimized filter design for the purposes of chemical dynamics research at synchrotron sources.

## 1. Advanced Light Source Chemical Physics Beamline

M. Koike, and A.H. Kung

The initial beamline design for the bend magnet and the U10 undulator was reexamined to meet design conditions that were revised in user workshops held in 1991. A new design has been proposed. In the new design, the width of the ALS beam spot in the horizontal direction at the molecular beam sample is kept at less than 10 microns. The height of the beam from the floor is reduced to match that of the ALS at approximately 1.5 meters. It was discovered that by reducing the deviation angle at the monochromator grating from 15 degrees to 10 degrees the astigmatism of the beam at the sample location can be improved, ranging from 20% at 125 nm to a factor of 2.2 at 200 nm and 2.7 at 50 nm. Calculations used in the new design required development of capability for doing ray-tracing of optical designs for the bend magnet beamline and for the undulator beamline. The work involves design studies of the monochromator and the overall beamline.

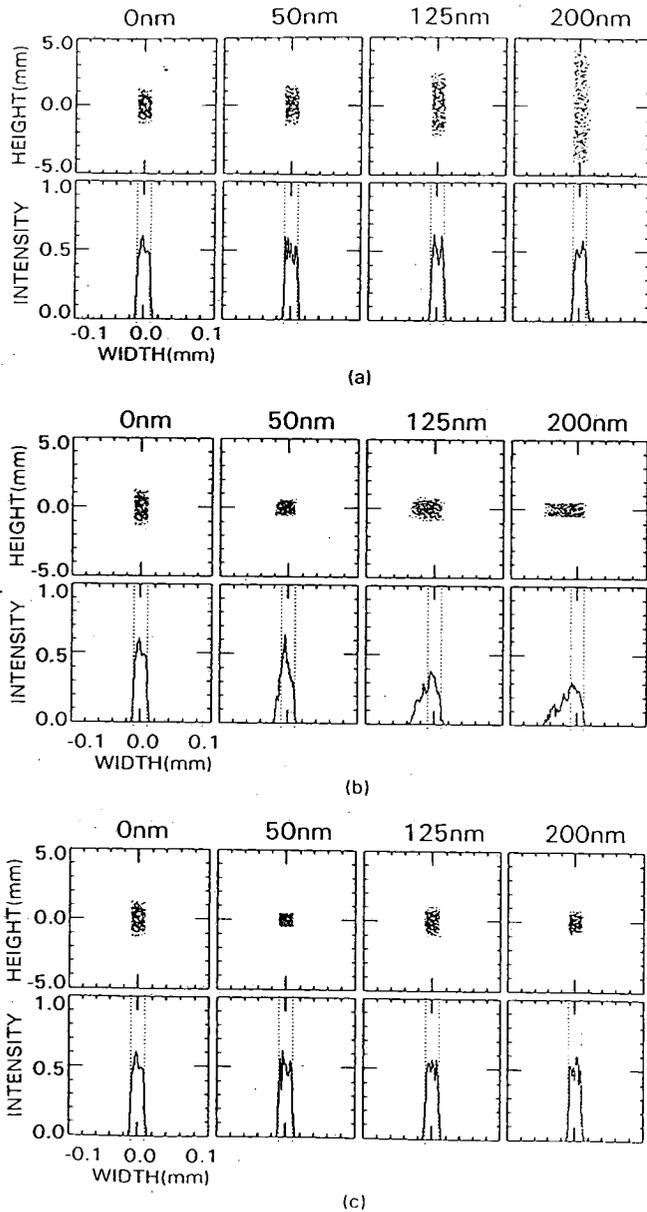
### A. Monochromator Design

We had started our investigation from the evaluation of the in-plane Eagle monochromator in 1990. A conventional spherical grating with equal spacing grooves had been assumed in the original designs. In this case, the deviation angle subtended from the grating to the entrance and exit slits is exclusively only one geometrical factor to determine the amounts of the astigmatism, and the travel distance of the grating that relates to the deflection of the beam at nonfocal points. The latter may cause two major defects to the system: (1) the increase of the capacity of the gas filter chamber and (2) the decrease of the effect of the compensation of the astigmatism with the prefocus and/or refocus systems.

To overcome these shortcomings, we investigated the possibility to use ruled gratings with variable spacing and curved grooves, and holographic gratings by assuming 5-m, 2400 lines/mm grating. For this purpose, we applied a new design method utilizing analytical expression of the spot diagrams, as well as a merit function that closely represents the rms spread of the spots formed when an infinite number of rays are traced.

Figure 1-1 shows the ray-traced spot diagrams and line profiles constructed for the monochromator using a

\* This work was supported by the Director's, Exploratory Research and Development funds of the Lawrence Berkeley Laboratory under Contract No. DE-AC03-76SF00098.



**Figure 1-1.** Ray traced spot diagrams and line profiles at the exit slit for the U10 beamline monochromator equipped with (a) conventional grating, (b) holographic grating, and (c) ruled grating with variable spacing and curved grooves. (XBL 928-6187)

10- $\mu$ m slit width and equipped with a conventional grating (a), the holographic grating (b), or the ruled grating with variable spacing and curved grooves (c). The ruled grating with variable spacing and curved grooves provides the most satisfactory result, with both coma and astigmatism well-corrected. The results show a resolving power  $\sim 90,000$  over a wavelength range of 0–200 nm. Furthermore, the amount of grating travel and collateral changes in the direction of exiting beam are 49 mm and

0.08°, respectively, and these values are a factor of three less than those for the conventional grating. The rather wide linewidth for the holographic grating are the results of the trade-off between correction of astigmatism and coma, illustrating the limitation of the current spherical wavefront recording and suggesting the need of aspherical wavefront recording for future improvement. Furthermore, a ruled variable spacing grating is available from few suppliers. However, a grating with variable spacing and curved grooves comes from only one supplier. So we should investigate the other options more seriously for securities.

## B. Overall Beamline Design

The overall beamline designs were reexamined for the bending magnet and the U10 undulator sources. Here, we describe the process of the improvement of the performance of the bend magnet beamlines: the original design (C1), the revised design (C2), and the secondly revised design employing the conventional grating (C3), and the design employing a ruled grating with variable spacing grooves (V1), the design employing a ruled grating with variable spacing and curved grooves (V2), and the design employing a holographic grating (H1).

The C2-design is a revised design of the C1-design in the refocus system. For the C3-design, we reinvestigated the refocus systems in greater detail and designed the system to consist of two identical toroidal mirrors. The outgoing beam from the exit slit is focused at the intermediate point of the mirrors where the gas filter is installed. This focus is essential to reduce the volume of the filter chamber. The C3-, H1-, and V1-designs have the same layout except for the category of gratings. Therefore, the differences in the performance are due to the specifications of the grating and its motion in wavelength scanning.

At the workshop held on August 15, 1991, the following design conditions were newly assessed: (1) at the specimen center, the width of the beam spot in the horizontal direction must be kept extremely small, (2) the height of the beam from the floor should be 1.5m, (3) to save construction cost, the same monochromator design is adapted to both the bend magnet and the undulator beamlines. To reduce the astigmatism, the deviation angle was changed from 15° to 10° and the adaptability of a ruled grating with variable spacing and curved grooves for this purpose was investigated. The V2-design is the final design that realizes these requirements. The results from an evaluation by means of tracing rays and the rms spot sizes at the specimen center thus obtained are listed in Table 1-1. The V2-design has the

Table 1-1. The rms spot size of each beamline design at the specimen center.

Design	Deviation Angle (degree)	0 nm		50 nm		125 nm		200 nm	
		V (mm)	H (mm)						
C1	15	---	---	0.097	0.716	0.115	0.858	0.202	1.12
C2	15	---	---	0.069	0.921	0.028	0.337	0.168	2.013
C3	15	0.007	0.371	0.008	0.500	0.006	0.586	0.007	1.292
H1	15	0.007	0.326	0.013	0.392	0.016	0.618	0.017	0.448
V1	15	0.007	0.590	0.009	0.626	0.007	0.371	0.006	0.703
V2	10	---	---	0.006	0.229	0.007	0.310	0.006	0.338

best resolution and the minimum astigmatism over the whole wavelength range.

The results show a spectral resolving power of 90,000 over a wavelength range of 0 to 200 nm. It is therefore possible to meet the stringent requirements of gas-phase chemical-dynamics applications. However, there is only one supplier of a grating with variable spacing and curved grooves. A holographic grating gives a factor of two to three wider linewidth at the specimen center. In situations where this can be tolerated, the holographic grating may be the best compromise for the sake of its easier availability. This design incorporates use of toroidal mirrors to refocus the exit beam to create an intermediate focus to accommodate a high order suppressor on the undulator beamline.

## 2. Differential Gas Filter for Suppression of Higher-Order Undulator Light

*T.T. Miao and Y.T. Lee*

High-order suppression of undulator light is studied in detail. It is discovered that a combination of reflection filtering and rare gas filter will provide a spectral purity of better than 1 part in 100,000 for the energy range of 5–30 eV. Reflection filter consists of using normal incidence and slightly off-grazing incidence metal mirrors in the beamline that cuts off all the photons with energy higher than 30 eV. A differentially pumped rare gas filter then serves to eliminate the unwanted orders from the undulator emission. A molecular beamless gas filter has

been designed (Figure 2-1). The filter employs an active length of 10 cm using up to 30 Torr of a rare gas. For full protection of the synchrotron storage ring and delicate beamline optics from potential contamination by the gases used, the filter is enclosed in a compact, triply differentially pumped chamber. Molecular beam chokes and side vents are incorporated to prevent gas streaming into the synchrotron source or the experimental chamber. Calculation shows that a baseline pressure of  $3 \times 10^{-9}$  Torr can be achieved. This pressure is compatible with the residual gas pressure in the beamline vacuum. Presence of this filter also will prevent corrosive gas molecules that will be used in the experiment from getting to the beamline optics and storage ring section. As an extension of this project, funding has been received from the Department of Energy to construct and test a prototype of this high-order suppressor for the purpose of evaluating its efficacy at the ALS.

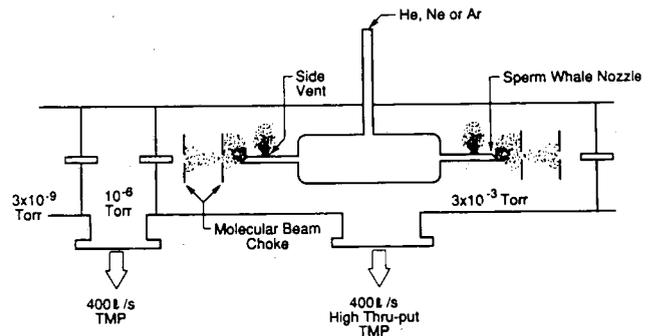


Figure 2-1. Schematic of molecular beamless gas filter. (XBL 928-6188)

# Molecular Beam Threshold Time-of-Flight Spectroscopy of Rare Gas Atoms\*

David A. Shirley, Investigator

## INTRODUCTION

The subject of this project was the utilization of synchrotron radiation to conduct spectroscopic measurements on rare-gas atoms. This effort will contribute to the quantitative understanding of electron-electron correlation in highly-excited states, elucidation of the three-body problem in important prototype atoms, and determination of the structure of continuum states in which two-electron resonances are embedded.

A chamber was designed by John Allman of the CSD High Energy Chemical Physics Group, which incorporated supersonic molecular beam source, a beam catcher, and a differentially-pumped threshold electron analyzer. It also accommodated an ion yield spectrometer that was provided by the U. Becker Group of the Fritz Haber Institute, Berlin, and was mounted on the FU Berlin SX 700 II beamline of the Kaindl Group, FU Berlin. This chamber was manufactured at UCB/LBL and tested at LBL prior to shipment to Berlin. Mr. Allman traveled to Berlin, arriving with the chamber, and was joined later by Dr. Tobias Reich and Mr. Barry Petersen of this group.

The plan was to collaborate with the Becker and Kaindl groups in studying rare gas atoms, beginning with helium, by collecting several different kinds of spectra simultaneously: photoionization, ion yield, and threshold photoemission. Of these, the photoemission spectra would be by far the most challenging and probably the most valuable as well. To maximize our chances for

success, the supersonic molecular beam source was the interaction region between the crossed photon and atomic beams, and the run was scheduled during "single bunch" running time, a two-week period in May, because of the time-of-flight requirement of our detector.

The molecular beam source was completed and transported to Berlin, where it was mounted together with equipment from the Becker Group, of the Fritz Haber Institute on the Free University of Berlin SX700/II beamline at BESSY and used in a "single bunch" run during two weeks in May and June, 1991. Several difficulties were overcome to perform the experiment. The LBL group could not afford vacuum pumps, which were provided by the FHI and FUB groups and mounted after the molecular beam chamber reached Berlin. Similarly, the time-of-flight analyzer could not be tested before going on line. In addition, a campus-based German-speaking machinist was taken to Berlin for last-minute changes, when this was judged necessary.

The apparatus was successfully assembled. It held a very good vacuum, in the  $10^{-10}$  range, and the (innovative) thin window design was successful. After the adjustment the TOF detector worked, and first experiments were tried on argon. Each step of the experiment was carried through to completion, and all components appeared to be in working order—a triumph in itself, considering the large number of new components. In particular, the electron energy resolution appeared to be improved as hoped, although it was not practical to close the monochromator slits enough to quantify this result. We were not able to obtain any final data, however, because the counting rate was disappointingly low, and attempts to improve it were unsuccessful.

Our final conclusion was that a more intense light source will be needed in order to carry out this experiment successfully.

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\*This work was supported by the Director's Exploratory Research and Development funds of the Lawrence Berkeley Laboratory under Contract No. DE-AC03-76SF00098.

**Work for Others**

# UNITED STATES OFFICE OF NAVAL RESEARCH

## Normal and Superconducting Properties of High- $T_c$ Systems\*

Vladimir Z. Kresin, Investigator

### INTRODUCTION

This research is concerned with different aspects of superconductivity such as the mechanisms of high- $T_c$ , properties of new oxides, the effect of oxygen depletion, behavior in an AC Field, etc.

A theoretical method has been developed to study the charge transfer between different structural units. This charge transfer leads to a strong correlation between microstructure, oxygen content, and properties of the high- $T_c$  oxides. Spectral properties appear to be very sensitive to oxygen ordering.

The strength of the coupling has been determined; this property is directly related to the problem of the origin of high- $T_c$  superconductivity.

#### 1. Correlation between Structure, Oxygen Content and Properties at the High- $T_c$ Oxides (Publications 4, 5, 6, 8 and 9)

V. Kresin, S. Wolf,<sup>†</sup> and G. Deutcher<sup>‡</sup>

The theoretical model capable of calculating the superconducting properties (e.g.,  $T_c$ , energy gaps, etc.) of materials such as  $Y_1Ba_2Cu_3O_7$  that consist of two conducting subsystems (planes and chains) is developed. The system is characterized by two energy gaps. The interplay of two channels (phonon-mediated processes and the intrinsic proximity effect) inducing the superconducting state in the chains is studied. The proximity effect combined with the phonon-mediated channel appears to be favorable for superconductivity. The theory describes the effect of the oxygen ordering on  $T_c$ , and the induced gap and allows us to explain in number of experiments including the plateau in  $T_c$  versus oxygen, the large residual microwave losses, zero-bias

anomalies, and the temperature dependence of the penetration depth.

<sup>†</sup>Naval Research Laboratory, Washington, D.C.

<sup>‡</sup>Department of Physics and Astronomy, Tel-Aviv University, Tel-Aviv, Israel.

#### 2. Strength of the Coupling and the Origin of High- $T_c$ (Publications 1, 3, 6, 7 and 10)

V. Kresin, M. Reeves,<sup>†</sup> S. Wolf,<sup>†</sup> and H. Morawitz<sup>‡</sup>

The strength of the electron-phonon coupling in Y-Ba-CuO-O compound has been determined from the heat capacity data; the coupling constant appears to be large.

A feature of electron-energy-loss spectroscopy (EELS) in layered materials is predicted. Contrary to the usual isotropic case, EELS becomes temperature dependent. This result, obtained by using thermodynamic Green's function, arises from the unusual structure of the layer plasmon bands.

High- $T_c$  is due to strong electron-phonon coupling to soft optical modes and to a weakening of the Coulomb repulsion due to the layered quasi-2D plasmons.

<sup>†</sup>Naval Research Laboratory, Washington, D.C.

<sup>‡</sup>IBM, Almadin Research Center, San Jose, CA.

#### 3. Microwave Properties (Publication 2)

V. Kresin

Microwave properties of the high- $T_c$  oxides are studied. The frequency and temperature dependences of the impedance are obtained. Short coherence length leads to large losses. The effects of impurities and multi-gap structures are discussed. The impedance of the proximity system is calculated.

Oxygen depletion leads to an appearance of residual losses.

### FY 1991 PUBLICATIONS AND REPORTS

#### Refereed Journals

1. V. Kresin and H. Morawitz, "Electron-Energy-Loss Spectroscopy of Layered Systems," *Phys. Rev. B* **43**, 2591 (1991).
2. V. Kresin, "High- $T_c$  Superconductor in an AC Field," *IEEE Trans. on Magnetics* **27**, 888 (1991).

\*This work was supported by the U.S. Office of Naval Research under Contract No. N00014-90-FOO06, and carried out at the Lawrence Berkeley Laboratory under Contract No. DE-AC03-SF00098.

3. H. Morawitz, I. Bozovic, G. Rietveld, D. van der Marel, and V. Kresin, "The Plasmon Density of States of a Layered Electron Gas," submitted to *Phys. Rev. Lett. B* (1991).
4. V. Kresin, S. Wolf, and G. Deutcher, "Correlation between Microstructure and Properties of High- $T_c$  Application to Microwave Properties of High- $T_c$ , *J. Mat. Sci. and Eng. B* (in press) (1991).
5. V. Kresin, S. Wolf, and G. Deutcher, "The Effect of Phonon-Mediated Transfer and Internal Proximity Effect on the Properties of Multigap Cuprate Superconductors," *Physica C* (in press) (1991).

#### Other Publications

6. V. Kresin, S. Wolf, M. Reeves, and G. Deutcher, "Correlation between Structure and Properties of High- $T_c$  Cuprates," B. Raveau, K. Wasa, R. Suryanaryanan, Eds., in *ICMAS-91, IITP, Paris, France*, p. 167 (1991).
7. V. Kresin, "Unified Approach to High- $T_c$  Cuprates Including a Generalized Phonon Mechanism: Strong Coupling to Phonon and Phonon-like Plasmon Modes," *APS Bulletin* **36**, 374 (1991).
8. S. Wolf and V. Kresin, "Two Gap Superconductivity," *APS Bulletin* **36**, 375 (1991).
9. G. Deutcher, V. Kresin, and S. Wolf, "Two Superconducting Systems and Zero-Bias Anomalies in Y-Ba-Cu-O," *APS Bulletin* **36**, 373 (1991).
10. H. Morawitz and V. Kresin, "Nonlinear Electron-Phonon Effects in Strong Coupling Superconductors," *APS Bulletin* **36**, 613 (1991).
11. V. Kresin and S. Wolf, "Multigap Structure and Tunneling," in *Proceedings of International Conference on Electronics Italy (1991)*, World Scientific Publishing, Singapore (in press).
12. V. Kresin and S. Wolf, "A Unified Approach to the Description of High- $T_c$  Oxides," in *High Temperature Superconducting Compounds*, by S. Whang, A. Das Gupta, and E. Collings, eds, TMS, Warrendale, PA (1991).

#### Invited Talks

13. V. Kresin, "Microwave Properties of High- $T_c$  Oxides," ASC, Aspen, CO, October 1990.
14. V. Kresin, "Mechanisms of High- $T_c$ ," International Conference; Miami, FL, January 1991.
15. V. Kresin, "Unified Approach to High- $T_c$  Cuprates," American Physical Society; March 1991.
16. V. Kresin, "Major Parameters of the High- $T_c$  Oxides and Origin of High- $T_c$ ," International Conference, Stockholm, Sweden, May 1991.
17. V. Kresin, "Correlation between Structure and Properties of the High- $T_c$  Oxides," EMS-91, Strasbourg, France, May 1991.
18. V. Kresin, "Unified Approach to High- $T_c$  Superconductivity," Seminar at Office Naval Research, Washington, D.C., July 1991.
19. V. Kresin, "Theoretical Aspects of High- $T_c$  Superconductivity," Superconducting Digital Circuits and Systems Conference, Washington, D.C., September 1991.
20. V. Kresin, "Proximity Effect," SC Global, San Diego, CA, January 1991.
21. V. Kresin, "Properties of High- $T_c$  Materials and Their Structure," TMS Meeting, New Orleans, LA, April 1991.
22. V. Kresin, "Two Gap Spectrum and Tunneling," International Conference on Electronics, Napoli, Italy, September 1991.
23. V. Kresin, "Correlation between Microstructure and Properties of the High- $T_c$  Oxides," International Conference; ICMAS-91, Paris, France, September 1991.
24. V. Kresin, "Properties of High- $T_c$  Oxides," Royal Institute of Technology, Stockholm, Sweden, May 1991.
25. V. Kresin, "Spectroscopy of the High- $T_c$  Oxides," Max Planck Institute, Stuttgart, Germany, June 1991.
26. V. Kresin, "Theory of High- $T_c$ ," Cambridge University, Cambridge, MA, September 1991.
27. V. Kresin, "High- $T_c$  Films," Xerox Research Corporation, Palo Alto, CA, April 1991.



# APPENDIX A

## DIVISION PERSONNEL

### 1991 Scientific Staff

Investigators	Postdoctoral and Other Scientists	Graduate Students	Guests, Affiliates
Neil Bartlett	R. Hagiwara	W.J. Casteel	B.-C. Shen H. Borrmann G. M. Lucier
Alexis T. Bell		D.B. Clarke K.R. Krishna R.M. Pittman	M.J. Sandoval G.T. Went H. Abe C.S. Gittleman T. Komaya I. Suzuki
Robert G. Bergman		A.M. Baranger K.N. Bharucha M.J. Burn M.D. Butts T.A. Hanna J. Hartwig	M.J. Hostetler S.Y. Lee R.I. Michelman R.E. Minto R.D. Simpson P.J. Walsh R.J. Morris M.W. Nee R.N. Yrtis
Robert E. Connick	S. Lee		
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Richard A. Andersen	B. Campion	W.W. Lukens, Jr. P.T. Matsunaga	M.E. Smith M. Weydert M.R. Smith C. Sofield
Kenneth N. Raymond		T.S. Franczyk S.J. Franklin	L.C. Uhlir T.M. Dewey B.A. Lulay-Bryan M.P. Neu L. Tunstad D.W. Whisenhunt, Jr. J. Xu
Andrew Streitwieser, Jr.		T.R. Boussie M.C. Holmes	C.H. Jenson H. Gonzalez
David H. Templeton			L.K. Templeton

Investigators	Postdoctoral and Other Scientists	Graduate Students		Guests, Affiliates
Harvey A. Gould	A. Belkacem M. Klapisch			M. Cohen G.P. Segre A.N. Sorensen
Eugene D. Commins		S.B. Ross		
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Harold S. Johnston	C.E. Miller K.O. Patten, Jr.	J.D. Burley P.L. Hunter	C.E. Miller K.O. Patten, Jr.	
Yuan T. Lee	A.H. Kung	B. Balko D.W. Boo A.S. Bracker J.D. Chesko P.M. Chu E.F. Cromwell H.F. Davis H. Hou	T.-T. Miao J.D. Myers S.W. North J. Price L.A. Smoliar A.G. Suits M.J.J. Vrakking J. Zhang	D.S. Anex M.J. Cote D. Gosalvez K.A. Prather A. Stolor D. Stranges
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Vladimir Z. Kresin				
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Daniel M. Neumark		D.R. Cyr	R.B. Metz	D.W. Arnold S.E. Bradforth R.E. Continetti D.R. Cyr
Norman E. Phillips				

Investigators	Postdoctoral and Other Scientists	Graduate Students	Guests, Affiliates
Kenneth S. Pitzer	A.M. Anderko R. Anstiss S. Sterner		J.K. Hovey
John M. Prausnitz		E.W. Anderson J.P. Baker	L.Y. Chou A.P. Sassi
Michael H. Prior			P. Beiersdorfer R.D. Dubois R.A. Haar D. Ivie H. Khemliche J.W. McDonald K.L. Randall
Richard J. Saykally		R.C. Cohen N. Pugliano	J. Scherer
David A. Shirley	Z. Hussain	J.C. Allman M.P. Blackwell R.S. Fellers Z. Huang E.A. Hudson W.R.A. Huff S.A. Kellar	L.J. Medhurst E.J. Moler B. Niu B.L. Petersen A.E. Schach Von Wittenau L. Wang M.A. Ziegeweid
K. Peter C. Vollhardt	J.-P. Gotteland E. West	R. Faust M. Malaska	M. West

## Support Staff

### Division Administrative Staff

Division Administrator: Linda R. Maio\*

#### Administration

L. Aubert  
A.W. Backus  
J. Edgar\*  
T. Lynem-Paynes

#### Personnel/Financial

A. Backus  
K. deRaadt\*  
M. Graham  
T. Lynem-Paynes  
S. Nasman\*  
M. Smith\*  
S. Waters\*

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I. Katsumoto  
E.A. Lawhead  
B. Moriguchi-Iwai  
V. Narasimhan

M. Noyd  
T.C. Peoples  
S. Schmitt  
P. Southard  
K. Steele  
P. Takahashi  
K. Wong

\*Materials Sciences Division effective 10/1/90.

# APPENDIX B

## LIST OF DIVISIONAL SEMINARS

### Chemical Dynamics Seminars

<u>Date</u>	<u>Speaker and Affiliation</u>	<u>Seminar Title</u>
10-15-90	A. Burshstein, Thermochemical Laboratory, Novosibirsk, USSR	Non-Adiabatic Electron Transfer: Frictional Effects in Chemical Reactions in Solution
11-9-90	R.D. Coalson, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA	Theory of Optical Spectra in Condensed Media
11-12-90	E.E. Nikitin, Institute of Chemical Physics, Soviet Academy of Sciences, Moscow, USSR	Semiclassical Theory for the Scattering of Polarized Atoms
11-14-90	A. van der Avoird, Vakgroep Theoret. Chem., Faculteit Natuurwetenschappen, Toernooiveld, 6525 ED Nijmegen, The Netherlands	<i>Ab initio</i> Potential Surfaces and Many-Body Dynamics of Binary Complexes: ArH <sub>2</sub> O and ArNH <sub>3</sub>
11-19-90	H. Kroto, School of Chemistry and Molecular Sciences, The University of Sussex, England	A Postbuckminsterfullerene View of the Chemistry, Physics and Astrophysics of Carbon
1-7-91	Dr. Stephen J. Harris, General Motors Research Laboratories, Warren, MI	Kinetics of Diamond Film Growth
1-23-91	Professor Joe Chaiken, Syracuse University, Department of Chemistry, Syracuse, NY	Probing Intramolecular Energy Transfer in Isolated Organometallic Molecules Using Multiphoton Dissociation
2-25-91	Dr. R.D. Suenram, Molecular Physics, Div., National Inst. of Standards and Technology, Washington, DC	Using Van der Waals Complexes to View Reaction Pathways
3-11-91	Professor Peter Hess, Institute für Physikalische Chemie, Universität Heidelberg, Germany	Chemistry and Dynamics of the Growth of Hydrogenated Amorphous Silicon
3-14-91	Professor Paul Marie Guyon, LURE Laboratoire, Université de Paris XI, Orsay, France	Selected Ion-Molecule Reactions Studied by the Tpepico Coincidence Method
3-19-91	Dr. Sean C. Smith, Institut für Physikalische Chemie, Universität Göttingen, Germany	Microcanonical Variational Transition State Theory: New Methods of Rapid State Counting in Loose Transition States

<u>Date</u>	<u>Speaker and Affiliation</u>	<u>Seminar Title</u>
4-10-91	Professor David Singel, Harvard University, Department of Chemistry, Cambridge, MA	The Glories of Spin-Echo Modulations; Structural Studies of Apoferritin and N-ras p21
4-11-91	Dr. András Lőrincz, The Hungarian Academy of Sciences, Institute of Isotopes, Budapest, Hungary	Interaction of Strong Femtosecond Electric Fields with Molecules
5-28-91	Dr. Alexander Efros, Physics Department, Technical University, Munich, Germany	Optical Properties of Zero-Dimensional Semiconductor Structures
6-21-91	Dr. Jeremy Hutson, Department of Chemistry, The University of Durham, England	Intermolecular Forces from Spectra of Van der Waals Dimers and Trimers
8-20-91	Professor Henryk Wozniakowski, Department of Computer Science, Columbia University, New York, NY	Multivariate Integration: Complexity in Different Settings
9-16-91	Professor James A. Anderson, Department of Chemistry, Pennsylvania State University, University Park, PA	Exact Quantum Monte Carlo for Many-Electron Systems
9-27-91	Professor R.A. Ryabov, Institute of Spectroscopy, USSR Academy of Sciences, Moscow, USSR	Vibrational Energy Redistribution in IR Laser Excited Polyatomic Molecules. Effect of IVR and Collisions

### Other Seminars Hosted

10-1-90	P.J. Reynolds, Physics Division, Office of Naval Research, Arlington, VA	Acceleration Methods in Quantum Monte Carlo
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# APPENDIX C

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\*Boldface numbers indicate investigators' main programs.

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University of California  
Technical Information Department  
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1975-1976  
1977-1978  
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