

# Working Group on Chemical Dynamics

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## 1. Introduction

The field of chemical dynamics studies the elementary chemical reactions that underlie virtually all macroscopic chemical systems. It is a strongly coupled experimental-theoretical effort that can provide a solid foundation for understanding the gas-phase chemical processes on which predictive models of combustion and atmospheric chemistry must rely. The objective of this section is to identify exciting opportunities for chemical dynamics and to investigate how the Advanced Light Source (ALS) can help in achieving the scientific goals. Tremendous advances in the areas of lasers and molecular beams have already made a substantial impact in this field, but the unique features of the ALS make it possible to solve a number of previously unreachable problems in the following key areas:

- Combustion: Radical Chemistry and Dynamics.
- New Molecules.
- Atmospheric Chemistry and Global Change.
- Astrochemistry.
- Clusters/Interfacial Chemistry.
- Plasma Chemistry.
- Chemistry in Real Time.
- Photoionization Dynamics of Complex Molecules.

The Chemical Dynamics Beamline (Beamline 9.0.2) at the ALS represents a unique facility, the first in the world to combine dedicated, intense undulator radiation with state-of-the-art molecular-beam machines for a broad range of studies of fundamental chemical processes. The beamline achieved full operation in November 1995 with the installation and commissioning of the U10 undulator, which

is the world's most intense source of continuously tunable vacuum-ultraviolet (VUV) light. The scientific promise afforded by the new Chemical Dynamics Beamline is now just beginning to be realized. A report ["Application of Synchrotron Radiation in Chemical Dynamics," P. Heimann, M. Koike, A. H. Kung, C. Y. Ng, M. G. White, and A. Wodtke, LBL-34131, May 1993] outlined the initial goals of the program. Many of the milestones mentioned in that report have been achieved as the scientific program has begun in earnest and as outside users have come to Berkeley to take advantage of the facility. The end stations are now fully operational, the normal-incidence monochromator has demonstrated world-record resolution, and breakthroughs have been achieved in photoionization studies, photochemistry, and, recently, crossed-beam reactive scattering. Visitors have come from Cornell University, Brookhaven National Laboratory, the University of North Carolina, the University of Waterloo, Purdue University, State University of New York at Stony Brook, and University of California, Davis to take advantage of the facility, and the user base is ramping up rapidly. The scientific advances recently achieved and the promising future directions are outlined below.

## 2. Opportunities in Chemical Dynamics

### 2.1 Combustion: Radical Chemistry and Dynamics

Despite the short time since it has come on line, the end stations at the Chemical Dynamics Beamline have already begun to have a significant effect on our understanding of combustion chemistry. The high flux of the ALS available at the crossed-molecular-beam end station has allowed sensitive universal detection of reaction products, while the tunability of the ALS has been used to discriminate among competing product channels. The high resolution available from use of the Eagle monochromator has opened the door to a new generation of studies on the photoelectron spectroscopy of radicals. Future developments can extend the techniques available for exploration of new systems. The subsections below describe some recent work and future directions.

#### 2.1.1 Reaction of Radicals with Hydrocarbons

Crossed-beam reactions of halogen atoms with saturated hydrocarbon molecules have recently been investigated by the Suits group using soft-VUV ionization for direct measurement of the hydrocarbon-radical fragment for the first time. Radical abstraction of primary or secondary hydrogen atoms from hydrocarbon molecules represents a crucial aspect of the dynamics of these reactions, important for developing a predictive understanding of combustion systems. The crossed-beam reaction of chlorine with propane showed clear energy-dependent dynamics indicating abstraction of secondary hydrogen atoms that led to forward-scattered, internally cold propyl radicals. The backscattered component, which moved to sideways scattering at higher collision energy, indicated reaction of the primary hydrogen atoms was mediated by an entrance barrier. Reaction with n-pentane showed similar behavior with one striking difference: the forward-scattered product was unambiguously the 2-pentyl radical, which was formed even colder than in the propyl case. The backscattered pentyl radicals, however, showed a translational-energy release nearly 1 eV lower than the forward-scattered products, dramatically showing the involvement of the carbon skeleton in the collision. Past studies of these reactions have relied on state-resolved laser probing of the HCl product, with the assumption of uncoupled energy and angular distributions being used to allow reconstruction of the differential cross sections, an assumption we see is of limited validity. The laser experiments are thus blind to these key aspects of the reaction. Universal probing of the radical fragment via undulator radiation allows the complete picture of the dynamics to emerge.

This work demonstrates that the crossed-molecular-beam end station is already having an impact on combustion dynamics. It should now be possible to investigate many other radical-molecule reactions with good detection sensitivity in a state-of-the-art molecular-beam system.

### 2.1.2 Photodissociation of Hydrocarbons

The photodissociation and chemistry of hydrocarbons and related species is of considerable interest in modeling combustion processes. As the complexity of these species increases, however, they become less accessible to investigation by “standard” techniques. For example, state-resolved laser-based methods are rarely practical for probing hydrocarbon systems beyond  $\text{CH}_3$ . Furthermore, in a conventional crossed-beam instrument with electron-impact ionization, product identification is greatly complicated by dissociative ionization of parent masses, and discrimination between different product isomers of the same mass is not possible. Using tunable VUV undulator radiation as a universal but selective probe, both of these issues can be addressed. Dissociative ionization can be prevented by tuning the photon energy below the onset of dissociation. Background interference is thus nearly eliminated. Furthermore, if two product isomers have different ionization potentials, as is often the case, they can be distinguished using tunable VUV ionization.

As an example, the Neumark group has investigated the photodissociation at 193 nm of allene ( $\text{CH}_2\text{CCH}_2$ ) and propyne ( $\text{CH}_3\text{CCH}$ ) on End Station One of the Chemical Dynamics Beamline. Both have the chemical formula  $\text{C}_3\text{H}_4$ , and both undergo primary dissociation to  $\text{C}_3\text{H}_3 + \text{H}$ . However, the chemical identity of  $\text{C}_3\text{H}_3$  is unclear; it could be the propargyl radical ( $\text{CH}_2\text{CCH}$ ) or the propynyl radical ( $\text{CH}_3\text{CC}$ ). One expects and finds exclusively the propargyl product from dissociation of allene, as shown in the upper panel of Figure 1, but either product is possible from dissociation of propyne. However, breaking the acetylenic bond in propyne takes 40 kcal/mol more energy. The two channels can be distinguished because their ionization potentials are quite different: 8.7 eV for propargyl and 10.8 eV for propynyl. As shown in the lower panel of the figure, there is significant dissociation of propyne to propynyl, indicating substantial bond-selectivity in which the stronger bond breaks.

Other recent examples are provided by the studies of Lee and co-workers on the photodissociation of dimethyl sulfoxide and of Hall and coworkers on acrylonitrile and vinyl chloride. As in the allene and propyne examples, complex, multichannel dissociations are analyzed by taking advantage of the fact that tunable ultraviolet ionization produces reduced cracking of the parent molecule and permits both selective detection of different species with the same mass and low-resolution spectroscopy of internal energies. Momentum matching has been exploited in the dissociation of these molecules to give quantitative dissociation energies and recombination barriers for radicals such as  $\text{H}_2\text{CCl}$ ,  $\text{H}_2\text{CCH}$ , and  $\text{CH}_3\text{SO}$ . Future experiments can be optimized to investigate unimolecular decomposition and isomerization of energetic free radicals.

### 2.1.3 High-Resolution Molecular Photoionization

Recent developments at the high-resolution photoionization and photoelectron end station at the Chemical Dynamics Beamline of the ALS have made possible ultrahigh-resolution measurements using the photoionization, threshold photoelectron (TPE), and pulsed-field-ionization (PFI) zero-kinetic-energy photoelectron (ZEKE) spectroscopic techniques. Energetic and spectroscopic data for gaseous ions can now be measured routinely at resolutions of  $2\text{ cm}^{-1}$  to  $5\text{ cm}^{-1}$  using this facility, making it a unique apparatus for VUV photoionization and photoelectron studies of gaseous molecules in the photon-energy range of 6 eV to 27 eV. The energetic information for molecular ions

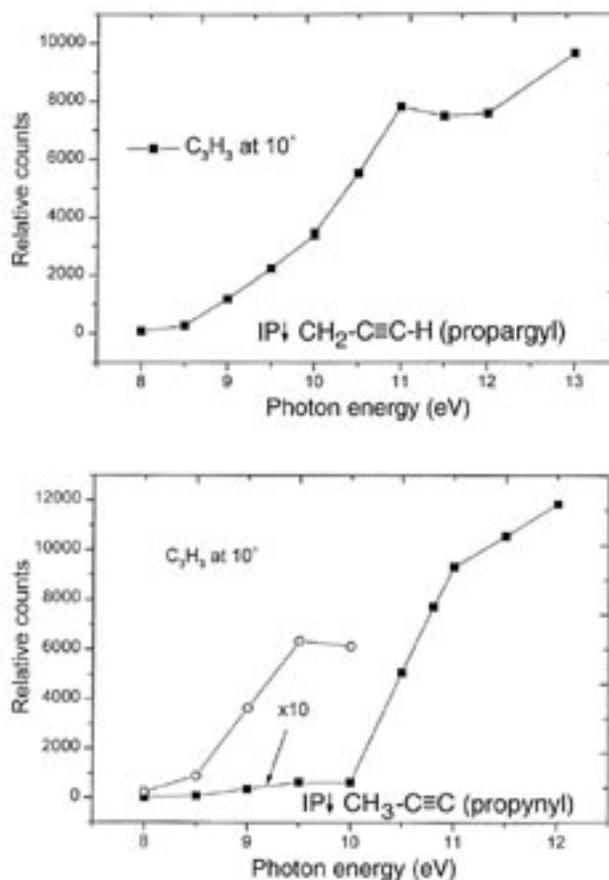


Figure 1. Hydrocarbon photodissociation at the ALS. Allene (top) and propyne (bottom) are photodissociated at 193 nm. The product scattered at various laboratory angles is ionized with VUV radiation and mass-analyzed. The figure shows the ionization efficiency of the mass-39 product at  $10^\circ$  (CH-bond fission) produced from both precursors. The product species clearly have different ionization potentials. The propargyl radical is produced from allene, and the propynyl radical is produced from propyne. The latter channel is particularly interesting since it represents dissociation of the much stronger (by 40 kcal/mol) C-H bond in propyne. [Figure courtesy of D. Neumark, University of California, Berkeley.]

thus obtained can be used in thermochemical cycles to derive highly accurate heats of formation, as well as dissociation energies for neutral molecules. Since accurate energetic and structural data for radicals are lacking in the literature, the photoionization and photoelectron capability of the Chemical Dynamics Beamline should play an important role in providing these data for key reactive intermediates relevant to combustion, plasma, atmospheric, and interstellar chemistry.

Rotationally resolved (or partially resolved) photoelectron spectra of small radical hydrides, e.g., CH, CH<sub>2</sub>, NH, NH<sub>2</sub>, HCO, CH<sub>3</sub>O, and C<sub>2</sub>H, are of particular interest because these species are important intermediates in combustion chemistry. Polyatomic hydrocarbon radicals are another class of intermediates relevant to combustion and planetary chemistry. Photoionization studies of polyatomic hydrocarbon radicals provide fundamental information about the vibrational excitation in hydrocarbon cations and about transitions from classical to nonclassical structures, e.g., bridged hydrogen in ethyl and propargyl cations.

Accurate energetic and spectroscopic data obtained for open-shell and highly correlated radical and ionic species also provide tests of state-of-the-art *ab-initio* calculations. High-resolution, rotationally resolved photoelectron measurements allow the testing of symmetry-selection rules and the angular-momentum balance involved in photoionization processes. These fundamental data, which can be obtained routinely in a high-resolution photoelectron experiment, can be used to elucidate cation geometries and vibronic couplings.

High-resolution photoelectron studies of polyatomic radicals will require the further development of radical sources. Many polyatomic radicals can be produced readily in electrical discharge, photodissociation, and thermal-pyrolysis. However, radicals thus formed often coexist with their precursors and with secondary reaction products. The photoelectron spectrum of a radical in a mixture of other species can be isolated with high sensitivity using the threshold photoelectron-photoion coincidence (TPEPICO) scheme.

Mass-selected threshold-ion (MATI) spectroscopy involves the detection of ions formed by the PFI of high- $n$  Rydberg species. Preliminary efforts in the measurement of the MATI spectra for molecules at the Chemical Dynamics Beamline have been partially successful, and changes in the ion optics based on the experience gained in these preliminary studies are under way. Since MATI is a threshold-ionization technique, it provides the same spectroscopic capabilities as ZEKE, with the tremendous added advantage of clear identification of the species responsible for the spectrum. This mass labeling of the high-resolution photoelectron spectrum makes the MATI technique perfect for high-resolution photoelectron spectroscopic studies of radicals and clusters, which are usually prepared in a source coexisting with other impurities.

An entirely new type of threshold ionization spectroscopy, similar in spirit to ZEKE or MATI, has recently been demonstrated using coherent VUV light in the laboratories of John Hepburn of the University of Waterloo. This technique, called threshold ion-pair-production spectroscopy (TIPS), is based on the Rydberg-like behaviour of very high vibrational levels in ion-pair potentials. The existence of these levels means that one can make a very precise determination of the threshold for ion-pair formation using pulsed-field ionization with a MATI-type spectrometer. In fact, exactly the same ion optics are used for MATI and TIPS. Since TIPS determines the precise energetic threshold for  $AB \rightarrow A^+ + B^-$  to an accuracy of  $1 \text{ cm}^{-1}$ , if the ionization efficiency of A is measured by ZEKE/MATI and the electron affinity of B is measured by precise ion-beam techniques, the TIPS result can determine the bond energy of neutral A–B to wavenumber accuracy, as has been demonstrated by Hepburn's group for  $O_2$ , HF, and HCl. The broad tuning range and superior VUV flux at the Chemical Dynamics Beamline will allow for studies of polyatomic molecules, where frequently bond energies are not well known. Since ion-pair formation is a common process in molecules, TIPS should be widely applicable. Some examples of very interesting systems to study are  $CH_3F$ ,  $CF_4$ , and HCN. In addition, because TIPS is a spectroscopic technique, it can measure the spectrum of the molecular-ion fragment if the other ionic fragment is an atomic ion. For example, the TIPS spectrum of  $HCC \rightarrow HCC^- + H^+$  will reveal the spectrum of the  $HCC^-$  anion, along with the dissociation energy of the  $HCC-H$  bond. Because of the higher electric fields involved in typical applications of TIPS or MATI, the energy resolutions are usually on the order of  $2 \text{ cm}^{-1}$  to  $4 \text{ cm}^{-1}$ , making these two techniques perfectly suited for the Chemical Dynamics Beamline at the ALS. Because of the high flux and tuning range in the VUV, implementation of TIPS and MATI at the ALS is very important.

## 2.2 New Molecules, New Chemistry

The “soft-ionization” feature made available by the tunability of the ALS allows one to detect weakly bound molecular systems without fragmenting them. In addition, one-photon ionization is a universal probe requiring no prior spectroscopic information. This powerful combination of selectivity and universality makes it possible to detect and characterize new radicals and metastable molecules, as discussed in the next section.

### 2.2.1 New Radicals

The weakly bound radical product ClCO has been directly observed for the first time, using End Station One of the Chemical Dynamics Beamline and the undulator “white” beam. This radical is believed to play a critical role in combustion of halogen containing wastes and in the formation of photochemical smog. The use of soft ionization by tunable undulator radiation allowed for direct observation of this unstable radical and, for the first time, the measurement of its photoionization-efficiency curve (Figure 2). Other weakly bound or highly reactive radicals might similarly be investigated.

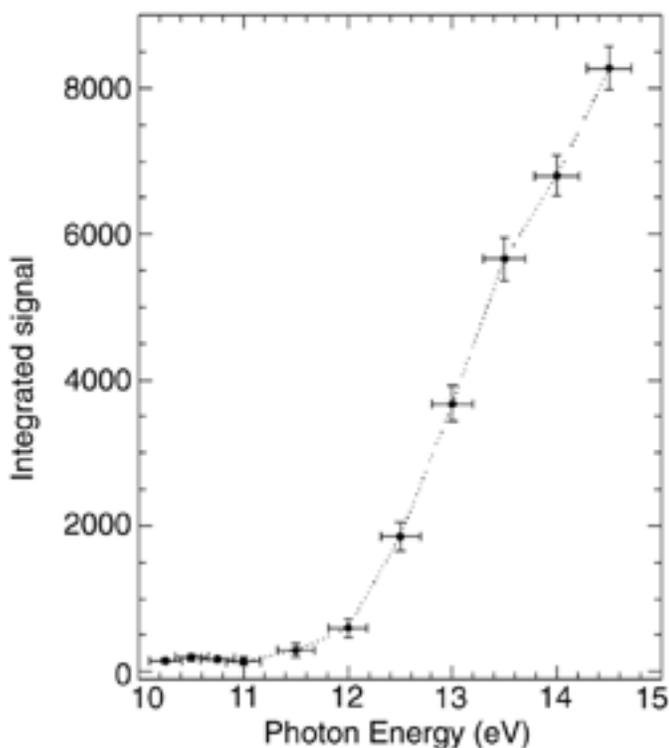


Figure 2. Photoionization-efficiency spectrum for ClCO from 193-nm dissociation of oxalyl chloride. [Figure courtesy of Arthur Suits, LBNL.]

### 2.2.2 New Molecules

Recent work has suggested the possible formation of energetic, metastable tetraoxygen species produced in the nonequilibrium combination of a pulsed discharge with a supersonic expansion. The use of tunable undulator radiation will allow for direct one-photon probing of this species to determine its energy and to aid in assigning its structure. These “physical synthesis” methods, similar to those that produced  $C_{60}$ , might conceivably produce other such novel molecules. The combination (described in Section 3) of a high-throughput monochromator system and the imaging end station will be well suited to the investigation and characterization of such species using simple photoionization-efficiency measurements or imaging photoelectron spectroscopy.

### 2.2.3 New Chemistry

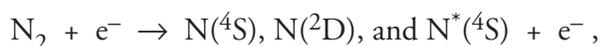
Molecular beams enable one to prepare highly reactive species under carefully controlled conditions, allowing one to study the elementary reactions that combine to yield the macroscopic chemistry taking place in the atmosphere, in an engine, or in interstellar space. Often these reactions will involve new chemistry with novel reactants or products. The recent crossed-beam study of the reaction of carbon atoms with acetylene is a case in point—the dynamics of these reactions and their importance to interstellar chemistry were unknown and the product  $C_3H$  isomers not well characterized. As detailed further in the section on astrochemistry below, tunable soft VUV ionization in End Station One will allow direct insight into this new chemistry because product isomers and electronic states may be identified directly and compared to ab initio calculations. Similar considerations apply to studies in combustion chemistry. As new molecular-beam sources of radicals or excited atoms are developed, new reactions will inevitably be revealed. This underscores the importance of parallel laboratory development of molecular-beam sources of radicals.

## 2.3 Atmospheric Chemistry and Global Change

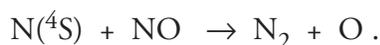
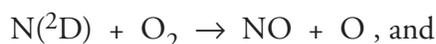
Substantial opportunities exist for increased understanding of the fundamental reactions involved in atmospheric chemistry and global change. The availability of soft x-ray radiation can be used to characterize aerosols, and the tunability in the ultraviolet can be used for selective ionization to determine branching ratios in key reactions. Since photoabsorption cross sections as a function of wavelength for such important classes of molecules as CFCs and HCFCs are not known, both the Working Groups on Atomic, Molecular, and Optical Physics and on Chemical Dynamics have recognized the important role the ALS has to play in atmospheric chemistry (see also Section 2.2.5 of the report of the Working Group on Atomic, Molecular, and Optical Physics).

### 2.3.1 Electron Scattering from $N_2$

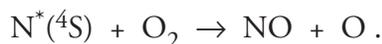
The NO budget in the upper atmosphere depends critically on the product state distribution resulting from dissociative electron scattering with  $N_2$ . In the 10-eV to 20-eV range, we have



where  $N^*$  refers to translationally excited nitrogen atoms. These nitrogen atoms result in the production and depletion of NO via



In addition, translationally hot  $N^*(^4S)$  can form NO via



Calculations shown in Figure 3 demonstrate that the concentration of NO changes by over an order of magnitude if the branching ratio for production of  $N(^2D)$  and  $N^*(^4S)$  atoms changes by only a few percent from a ratio around 0.5. It would therefore be very useful to measure the branching ratio in the laboratory as a function of electron energy. This experiment can be performed by introducing a low-energy electron gun into either End Station One or the new proposed end station (see Section 3) and then using tunable VUV ionization to detect selectively the various electronic states of the atomic-nitrogen products.

### Atmospheric chemistry: the NO budget



$\therefore$  deviations from 50%  $N(^4S)$ ,  $N(^2D)$   
have large effects on [NO]

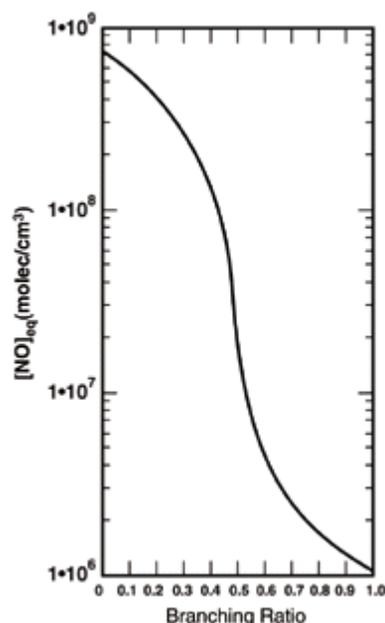
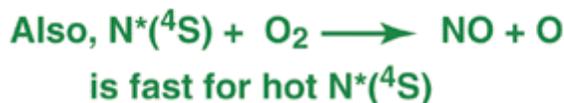


Figure 3. Calculations show that the concentration of stratospheric NO varies strongly with the branching ratio for production of  $N(^2D)$  vs.  $N^*(^4S)$  in the dissociative electron scattering from nitrogen. [Figure courtesy of S. Solomon, NOAA, University of Colorado.]

### 2.3.2 Aerosols

Combustion aerosols from crude-oil flaming, from Diesel motors or other industrial combustion, and from wood smoke from forest or savanna fires have the potential at some atmospheric altitudes to counteract the warming effects of anthropogenic gases ( $CO_2$ , CFC,  $CH_4$ ,  $N_2O$ ,  $O_3$ ), while at other altitudes they pose a serious public-health threat. Submicron carbonaceous particles ( $0.03 \mu m$ ) containing primarily organic and/or black carbon material can often combine with sulfur compounds, the major component of aerosols. These particles then cause cooling perturbations on the overall greenhouse warming and also influence regional anomalies of the climate. Understanding these particles is thus an important component of our ability to understand and predict climate change.

One pressing issue is to investigate the mixing of these particles with water droplets in clouds and to examine their reactivity with atmospheric gases under solar radiation. The photochemical reactions on the surface of such aerosols represent a new class of heterogeneous chemical reactions whose understanding is necessary for inclusion in atmospheric models. There are various types of aerosols to be considered: pure carbonaceous particles, pure water aerosols, hydrophilic carbonaceous particles, carbonaceous particles seeded with metal ions (such as iron) or inorganic material (Ca, SiO<sub>2</sub>), etc. The oxidation of SO<sub>2</sub> by water to produce sulfates or the reactions involving NO<sub>x</sub>-NO<sub>y</sub> cycles are typical processes to be considered. According to current laboratory experiments investigating chemiluminescent reactions on very large rare-gas clusters (several thousands of atoms), the reaction rarely involves a one-to-one molecular interaction but rather the formation of dimers or trimers or even microclusters of reactants. It would be ideal to build an experiment incorporating a direct probe of such microclusters by in-situ x-ray absorption [near-edge x-ray absorption fine structure (NEXAFS, also known as XANES) or extended x-ray absorption fine structure (EXAFS)]. The tunability and the brightness of the ALS in the soft-ray and x-ray spectral regions would provide the chemical selectivity necessary to select the microclusters out of the other products in the small region of the reaction. The x-ray absorption spectrum would give directly the structural and chemical-bonding information that is impossible to obtain using normal laboratory instruments.

Novel types of experiments can also be envisaged based on carbonaceous, soot-like aerosols produced by infrared laser pyrolysis of hydrocarbons that are quite representative of a combustion process. Reactant gases might be incorporated onto the surface of these aerosols by the “pick-up” technique or by a crossed beam method. At the center of the reactor, a cw visible-UV laser can be switched on to trigger the photoreaction. Several probe techniques such as mass spectrometry and visible chemiluminescence can be used together with the synchrotron x-ray probe to complement the determination of the reaction mechanism.

## 2.4 Astrochemistry

As a third-generation synchrotron source, the ALS offers many unique opportunities for advancement in understanding processes important in planetary atmospheres, in astrophysics, and even in the cosmology associated with the planet formation. The ALS can be used to study branching ratios for the production of different photochemical products as a function of the wavelength of the light (see Section 2.1.2). The unique capability stems from selective ionization based on the tunability of the undulator radiation.

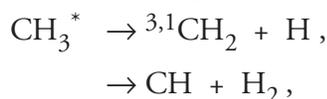
### 2.4.1 Photochemical Branching Ratios as a Function of Wavelength

Branching ratios for photodissociation and photoionization are important for understanding comets and planetary atmospheres. First, consider saturated hydrocarbons. These molecules are important in the atmospheres of the giant planets and their satellites, in comets, and in the interstellar medium. The most important wavelength for studying them is Lyman- $\alpha$ . Even with four-wave mixing and resonant sum or difference frequency mixing, it is difficult for laboratory lasers to obtain more than 10<sup>11</sup> photons per laser pulse at this wavelength. The low flux precludes determining branching ratios among possible dissociation channels of hydrocarbons. Although the dissociation of methane has recently been reinvestigated by detecting the hydrogen atoms with laser-induced fluorescence (LIF) and by imaging, these studies did not adequately distinguish between the four processes of

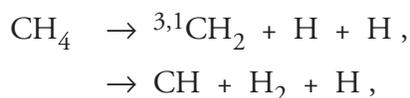
(1) simple C-H bond fission leading to stable  $\text{CH}_3$  radicals,



(2) sequential dissociation into three fragments,



(3) simultaneous dissociation into three fragments,



or (4) molecular elimination,



The ability to determine the velocity of the heavy fragment would certainly aid in sorting out these possibilities. The imaging apparatus at the ALS could use the first harmonic to dissociate the  $\text{CH}_4$  and the second harmonic to detect the heavy fragments. Similar problems occur for the photolysis of other saturated hydrocarbons, such as ethane and propane, and for alkynes, such as acetylene.

## 2.4.2 Reaction Dynamics

Recent work by Arthur Suits and Yuan Lee at LBNL and the University of California, Berkeley, using the crossed-molecular-beam technique has shown the importance of neutral reactions in the synthesis of carbon-bearing molecules in interstellar space. These studies were hampered by the inability to identify the radical product isomers directly. The crossed-beam method is ideal for detailed study of these reactions involving highly reactive radicals and atoms, since products are detected before subsequent chemistry takes place obscuring the processes of interest. End station one, with the tunable VUV probe, will aid greatly in identifying the primary products of these reactions, helping to unravel the complex chemistry in interstellar clouds and planetary atmospheres.

## 2.5 Cluster Dynamics and Spectroscopy

The high photon flux of the ALS allows coincidence measurements that can greatly improve our understanding of the spectroscopy and dynamics of clusters, clearly an exciting area of opportunity for chemical dynamics and AMO physics in the VUV (see also Section 2.1 of the report of the Working Group on Atomic, Molecular, and Optical Physics).

### 2.5.1 Photoionization/Photoelectron Coincidence Spectroscopy of Clusters

Photoelectron spectroscopy of size-selected clusters reveals how electronic and vibrational structure evolves from the molecular to the macroscopic, therefore bridging the gap between small-molecule chemical physics and materials science. Numerous experiments of this type have been performed on negative cluster ions of carbon, silicon, germanium, and mixed species, such as gallium arsenide and indium phosphide. However, analogous studies of neutral clusters have been far more difficult to perform because such clusters cannot be mass-selected prior to spectroscopic interrogation. To deal with this issue, we propose to perform photoelectron-photoion coincidence studies on these clusters at the ALS. Clusters will be generated in a laser ablation/molecular beam source using a high repeti-

tion rate (about 1 kHz) laser. The experiments can best be carried out on the proposed chemical-dynamics imaging end station with the high-throughput medium-resolution monochromator (see Section 3), since 10-meV resolution is about what one needs.

### 2.5.2 Inner Electron Spectroscopy and Photodissociation of Ion Clusters

Studies of ion clusters are appealing because they are readily size-selected, so that there is no ambiguity concerning their mass. However, since ion clusters are typically produced in much lower quantities than neutral species, all spectroscopy experiments performed to date have been restricted to the visible and near ultraviolet, where powerful lasers are available. The high photon flux and low emittance of the ALS will allow us to extend these studies to the vacuum ultraviolet region and beyond. The VUV spectroscopy of ion clusters offers a novel probe of their electronic structure. Specifically, one can map out the evolution of the more tightly bound orbitals and compare their energies to those of the highest occupied molecular orbitals (HOMOs) probed in the visible/near UV. This measurement can be done for clusters ranging from rare-gas cluster ions to carbon and semiconductor ions. Experimentally, the most feasible means of performing these experiments is to detect photodissociation products. One can collinearly overlap a mass-selected cluster-ion beam with the beam from the ALS, and use a secondary-mass spectrometer to analyze and detect product-ion fragments.

### 2.5.3 Helium/Argon Droplets

Another experiment along these lines involves generating a beam of very large, cold helium clusters (10,000 to 100,000 atoms) and passing it through a graphite oven; the result will be exceedingly cold carbon clusters adsorbed onto (or absorbed into) a much larger helium cluster. Studies to date in France and in the U.S. have typically used detection of laser-induced fluorescence or chemiluminescence to probe the dynamics in these systems, but clear opportunities exist for applications of synchrotron radiation to probe the products directly using photoionization, photoelectron spectroscopy, or fluorescence methods. One could then measure the ionization potentials, photoelectron spectra, and ion-fragmentation spectra for these clusters. An intriguing possibility is to probe these species with much higher photon energies (about 1 keV) to perform EXAFS and other x-ray based spectroscopies; the resulting structural information would complement more common experiments in the visible and ultraviolet.

## 2.6 Plasma Chemistry

Studies of plasma chemistry are relevant to the semiconductor industry, planetary atmospheres, and material research. The modeling of plasma processes requires accurate absolute total cross sections or rate constants of ion-molecule and ion-radical reactions in the kinetic energy range from thermal to about 100 eV. Because these quantities are also of fundamental interest, this area of research is also important to the atomic, molecular, and optical physics community (see Section 2.1 of the report of the Working Group on Atomic, Molecular, and Optical Physics). Since the temperature varies greatly in different plasmas, it is necessary to measure absolute cross sections of internally excited atomic and molecular ions over a wide range of collisional and vibrational energies. The high sensitivity in photoionization achieved using the photoion-photoelectron apparatus at the ALS would allow the reactivity studies of ions in very high vibrational states. Owing to the very high photoelectron-energy selectivity demonstrated in PFI-ZEKE measurements, the further development of the photoion-photoelectron apparatus associated with the Chemical Dynamics Beamline will offer unique capa-

bilities for studies of mode- or state-selected ion-molecule reaction dynamics. Specifically, the reaction cross sections involving diatomic and simple polyatomic hydride cations should be measurable at the rotationally state-selected level.

Cross-section measurements for ion-radical reactions are an unexplored field. Owing to the high VUV flux of ALS undulator radiation ( $10^{16}$  photons/sec at 2.2% bandwidth), the preparation of state-selected neutral atoms and radicals for reactive studies should be possible. Atoms and radicals in specific internal states can be prepared by photodissociation of appropriate precursor molecules. Knowing the photodissociation cross sections would allow the reliable determination of the number density for the photoproduct thus prepared.

### 2.6.1 Photodissociation of State- or Energy-Selected Molecular Ions

Spectroscopic and thermochemical information about gaseous ions may be obtained using laser-photodissociation spectroscopy, which involves the monitoring of daughter ions as a function of the energy of the laser radiation. Earlier experiments used electron-impact ionization for ion preparation, and the ions thus formed were thermally excited over a distribution of rotational and vibrational states. The thermal excitation of the precursor ions makes the analysis of the photodissociation spectrum difficult. In addition, hot-band excitations also shift the dissociation threshold to a lower energy.

These problems can be overcome by use of molecular photoionization and molecular beams. Photoionization favors processes with a small change in rotational quantum number, so that molecular ions in the ground vibrational state can be efficiently prepared with negligible rotational excitation in a free jet by photoionization at photon energies near the ionization threshold. State-selected or energy-selected molecular ions can be prepared by photoelectron-photoion coincidence (PEPICO) techniques for photodissociation studies. Baer and coworkers have applied the PEPICO technique to energy-select ions and subsequently photodissociate them with a pulsed excimer laser. The kinetic-energy-release distributions derived for the product ions provide information about the dynamics of unimolecular dissociation. We plan to develop this technique for routine studies of the photodissociation dynamics of vibrational- and electronic- state-selected diatomic and triatomic ions.

### 2.6.2 Dynamics of State-Selected Ion-Molecule Reactions

The U10 undulator, in connection with a high-resolution monochromator, is particularly useful for experiments requiring highly monochromatic radiation of high intensity and makes it feasible to perform chemical-dynamics experiments that were previously impossible. As described above, the system is particularly well suited for preparing ions in well-defined states. One area of future investigation is to explore state- or energy-selected ion reactions.

Studies of the chemistry of state- or energy-selected ions are important for the fundamental understanding of ionic processes relevant to organic, inorganic, atmospheric, interstellar, plasma, and materials chemistry. Many ion-molecule reactions relevant to the Earth's ionosphere involve electronically excited atomic oxygen and nitrogen ions. Because of the difficulties in preparing these ions, reliable cross sections for many important atmospheric ion-molecule reactions have not been examined in detail. We plan to develop a PEPICO apparatus for ion-molecule reactions that incorporates mass-spectrometric and rf-octopole ion-guide techniques in order to measure for state-selected cross sections of ion-molecule reactions of planetary interest.



optimum density of information. The future lies in understanding and predicting the behavior of systems of greatly increased complexity (large molecules, clusters, solvated reactants, molecules at interfaces) where the number of degrees of freedom is too numerous to allow accurate computation and high-resolution frequency-domain data may not be amenable to analysis. Most needed are ultrafast techniques that enable one to investigate selectively only those degrees of freedom that are important to the chemical process. The most obvious such information concerns the positions of the nuclei and the electronic state of the reacting partners. In solution, solids, or clusters, we must know the positions of the neighbor atoms and molecules. It would appear that inner-shell excitation and level shifts may be a particularly effective probe to provide this time-dependent structural information. This will require the development of intense, tunable, ultrafast light pulses in the ultraviolet/near x-ray region. The third- and fourth- generation light sources may have a truly unique role to play in this endeavor.

## 2.8 Photoionization Dynamics of Complex Molecules

Photoionization is becoming increasingly important as a probe of chemical systems, be they complex molecules, transition states, clusters, or radicals. What is not as obvious is that the photoionization dynamics for molecular systems provides a useful means of developing a deeper understanding of molecular scattering. For both of these reasons, the ALS will be a useful tool for developing a clear understanding of how electrons are ejected from molecular systems and, in so doing, how electronic and nuclear degrees of freedom are coupled in fundamental and theoretically tractable systems. It should be noted that a fundamental understanding of electron-ejection dynamics for simple systems has already led to important applications; for example, the field of NEXAFS spectroscopy of adsorbates on surfaces. It is very likely that an understanding of photoejection dynamics can lead to analogous applications to more complex materials and biological systems. A clear understanding of photoelectron dynamics for complex systems, such as polyenes and heterocyclic ring structures, can be of fundamental interest in chemical and molecular physics.

There are at least two possible experiments that one can envision, although it is likely that many others will emerge. First, it would be of great interest to obtain vibrationally resolved photoelectron spectra on polyatomic systems over a broad energy range for both valence- and core-electron ejection in order to study how the ionization process responds to changes in molecular geometry. Second, it would be informative to study how the ionization dynamics behave far from threshold for molecular clusters. Both of these experiments have the potential of understanding how electrons become quasibound in real systems, and such information is not accessible via other means. The high resolution of the ALS beam on end-station two should make interesting studies possible on such complex systems.

Related studies on dissociative ionization processes and the decay dynamics of superexcited states promise insights into the nature of the coupling among the electronic states at these energies above the first ionization potential, as well as providing valuable data for thermochemical cycles. The imaging apparatus and high-throughput monochromator system mentioned above will enable coincidence measurements of the complete energy and angular distributions for these processes, thereby providing unprecedented insight into the lifetimes, decay pathways, product branching, and coupling mechanisms in these systems.

### 3. Future Capabilities

The ALS represents the world's most intense source of continuously tunable VUV light in the 5-eV to 30-eV region. This high intensity has been exploited in two branch lines on Beamline 9.0.2, one of which incorporates a 6.65-m Eagle monochromator to perform very high-resolution studies of photoionization dynamics and threshold photoelectron spectroscopy, while the other relies on the broadband "white beam" of the undulator with its inherent 2.2% energy bandwidth to perform selective soft ionization of reaction products. An important innovation for chemical-dynamics studies at the ALS is to take advantage of the new velocity-map imaging technique in conjunction with a high-throughput monochromator system. This combination will considerably expand the experimental opportunities and broaden the appeal of studies on the beamline to a larger community in the field of chemical dynamics. New experimental opportunities include spectroscopy and photodissociation dynamics of radicals (Section 2.1), cluster dynamics and spectroscopy (Section 2.5), identification and characterization of novel metastable molecules and superexcited states and their decay mechanisms (Section 2.2), and new approaches to the study of photoionization dynamics in complex systems (Section 2.8).

A moderate-resolution, high-throughput monochromator system has been designed for application on the beamline in conjunction with an end station based on ion imaging. The monochromator, whose performance is summarized in Table 1 along with the characteristics of the existing branchlines, has a high-efficiency, moderate-resolution 3-m Eagle design. The new end station incorporates dual imaging detectors for recording energy and angular distributions of electrons and ions, singly or in coincidence. This combination, joining many of the strengths of the two existing end stations with the powerful imaging technique, promises greatly enhanced experimental versatility. This versatility comes from the inherent multiplexing nature of the imaging technique and the high flux of the monochromator.

Table 1. Characteristics of Chemical Dynamics Branch Lines

Branch Line	1	2	3 (proposed)
Source	"White Beam"	6.65-m Eagle	3-m Eagle
Resolution, E/ $\Delta$ E	35 to 50	3000 to 75,000	50 to 1000
Flux (at resolution)	$10^{16}$ 50	$10^{12}$ 3000	$10^{14}$ 1000

### 4. Summary

The Chemical Dynamics Beamline at the ALS along with its dedicated end stations has already begun to make a substantial impact of in the area of combustion. As the user base grows and as the new opportunities in atmospheric chemistry, cluster chemistry, plasmas, and astrochemistry augment further advances in combustion, many more of the unique features of the beamline will be exploited to extend the depth and range of chemical dynamics. The high likelihood of major advances and the importance of the problems being addressed argue strongly for increased support of the Chemical Dynamics Beamline.