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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Application of Synchrotron Radiation in Chemical Dynamics

Workshop Report
February 5–6, 1993
Claremont Hotel, Oakland, CA

P. Heimann, M. Koike, A.H. Kung, C.Y. Ng,
M.G. White, and A. Wodtke

May 1993

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Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Workshop on Application of Synchrotron Radiation in Chemical Dynamics
February 5-6, 1993
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11:30 am	End-station 2: Preliminary Specifications and Design *Mike White*, Brookhaven National Laboratory
12:00 noon	Facility Lasers *Andy Kung*, LBL
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Workshop on Application of Synchrotron Radiation in Chemical Dynamics
February 5-6, 1993
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List of Participants

David Attwood
Center for X-Ray Optics
Materials Sciences Division
Lawrence Berkeley Laboratory

Joseph Berkowitz
Chemistry Division
Argonne National Laboratory

Michael Bowers
Chemistry Department
University of California, Santa Barbara

David Chandler
Combustion Research Facility
Sandia National Laboratory

William Chupka
Chemistry Department
Yale University

Fleming Crim
Chemistry Department
University of Wisconsin

Charles Harris
Chemistry Department
University of California, Berkeley, and
CSD, Lawrence Berkeley Laboratory

Philip Heimann
Advanced Light Source
AFRD, Lawrence Berkeley Laboratory

Paul Houston
Chemistry Department
Cornell University

William Jackson
Chemistry Department
University of California, Davis

Brian Kincaid
Advanced Light Source
AFRD, Lawrence Berkeley Laboratory

Masato Koike
Center for X-Ray Optics
Materials Sciences Division
Lawrence Berkeley Laboratory

Andrew Kung
Chemical Sciences Division
Lawrence Berkeley Laboratory

Yuan Lee
Chemistry Department
University of California, Berkeley, and
CSD, Lawrence Berkeley Laboratory

C. Bradley Moore
Chemistry Department
University of California, Berkeley, and
CSD, Lawrence Berkeley Laboratory

Daniel Neumark
Chemistry Department
University of California, Berkeley, and
CSD, Lawrence Berkeley Laboratory

Cheuk Ng
Chemistry Department
Iowa State University

Philip Ross
Materials Sciences Division
Lawrence Berkeley Laboratory

Alfred Schlachter
Advanced Light Source
AFRD, Lawrence Berkeley Laboratory

Frank Tully
Combustion Research Facility
Sandia National Laboratory

Michael White
Chemistry Department
Brookhaven National Laboratory

Alec Wodtke
Chemistry Department
University of California, Santa Barbara

I. Introduction

In October, 1992, funding was approved by the Chemical Sciences Division, Office of Basic Energy Sciences of the Office of Energy Research in the Department of Energy to begin construction of a beamline and two end stations to support chemical dynamics experiments at LBL's Advanced Light Source (ALS). On February 5–6, 1993, a workshop was organized to develop specifications and plans and to select a working team to design and supervise the construction project. The target date for the start of scientific experiments is January 1995. The conclusions of the workshop and representative experiments proposed in earlier workshops to form the basis for beamline plans and end-station designs are summarized in this report.

Technological advances over the last decade have made it increasingly possible to study chemical and molecular phenomena under well-characterized conditions. The ALS, a new 1–2-GeV synchrotron-radiation source, is one of two third-generation U.S. synchrotron-radiation facilities designed to exploit the properties of electromagnetic radiation emitted from wigglers and undulators. Scheduled for completion in 1993, the source will produce beams of very high intensity and extreme brightness delivered in very short pulses. This light will offer many new opportunities for fundamental scientific research. The beamline from a 10-cm-period undulator (U10) at the ALS will be optimized to produce output from 10 to 100 eV in the region suitable for probing chemical and molecular interactions. On a time-averaged basis, this undulator will be the brightest source available in this photon-energy range.

A participating research team (PRT) has been organized to explore applications of synchrotron radiation at the ALS in chemical dynamics and to provide the experimental facilities needed for this exploration. The ALS will be used as a photo-analysis source to produce high yields of vacuum ultraviolet (VUV) photoionized products. If operated in conjunction with powerful lasers, the ALS will additionally be a powerful tool for the study of chemical processes induced by single and multiphoton absorption. Its time structure permits the study of ultrafast processes. These studies will culminate in research to:

- Determine the microscopic details of the mechanisms and dynamics of primary dissociation processes and elementary chemical reactions.
- Explore the chemistry of molecules excited to a Rydberg state or to other superexcited states.
- Study the structure, energetics, and chemical reactivity of highly reactive polyatomic radicals and unusual transient species.
- Probe the nature of inter- and intra-molecular energy relaxation.
- Search for bond-selective or mode-selective means to modify and manipulate chemical reactivity.

A particularly effective approach to studying the energetics and spectroscopy of chemical intermediates (neutral and ionic) important in combustion, atmospheric, and interstellar chemistry is through mass and electron spectroscopies following interaction with VUV radiation. Historically, photoionization mass spectrometry and photoelectron spectroscopy utilizing dispersed VUV radiation from laboratory discharge sources have provided many reliable values for radical heats of formation and bond energies, which are extremely difficult to obtain by other methods. The ALS undulator coupled to a large (6.65-m) VUV monchromator will fully exploit the beam brightness and provide very intense ($\geqq 10^{11}$ photons/s), tunable radiation (6–30 eV) at very high resolution ($\geqq 5 \times 10^4$) and should make it possible to investigate with unprecedented resolution and sensitivity the VUV photoinduced processes of highly reactive species that can only be produced at very low concentrations.

In this report, a synopsis of the proposed experiments is described in Section II. The workshop summary is presented in Section III.

II. Scientific Opportunities

In this section, we review the types of experiments that will be made possible by the proposed ALS chemical-dynamics beamline. The experiments reflect a broadly based scientific program that was developed over the last five years in a series of workshops including:

- Chemical Applications of Undulator Radiation Workshop (May 1987, Tom Baer, organizer)
- Chemical Reaction Dynamics Workshop (October 1988, Y.T. Lee, organizer)
- Combustion Dynamics Facility Workshop (April 1990, organized by LBL/SNL)
- Photoion-Photoelectron and Free Radicals Processes Workshop (July 1991, Tom Baer, organizer)
- Clusters and Ionic Beam Processes Workshop (September 1991, Mike Bowers, organizer)
- Application of Molecular Beams Workshop (June 1992, Y.T. Lee and G. Scoles, organizers)

and the workshop described in this report.

The following are representative experiments that exemplify the spectrum of scientific activities to be performed at the chemical-dynamics beamline at the ALS.

Primary Dissociation of Hydrocarbons

The high flux from the ALS is ideally suited for the study of primary photodissociation processes that require a very low background. In high-temperature combustion processes, dissociation of hydrocarbons precedes the oxidation processes; thus, it is necessary to understand thermal dissociation of hydrocarbons into smaller molecules and radicals. By using a high-power IR laser and synchronizing with a TEA CO_2 laser, it is possible to dissociate almost all medium-sized (~6–10 atoms) and large molecules using IR multiphoton dissociation in a molecular beam.

Two examples of experiments include the dissociation of aromatic hydrocarbons and the dissociation of CH_2=CH–C≡CH. The dissociation of aromatic hydrocarbons often involves extensive isomerization processes prior to dissociation, and they are not well-understood. The tunable IR laser will allow excitation of aromatic hydrocarbons that do not absorb CO_2 laser photons. The dissociation dynamics of CH_2=CH–C≡CH will reveal important mechanisms of addition reactions involving two acetylenes. Whether the formation of CH_2=CH–C≡CH involves the initial isomerization of CH≡CH to CH_2=C: or occurs through a molecular reaction to form the •CH=CH–CH=CH•

diradical followed by a 3,1-H shift can be answered by measuring the translation energy distribution of the products of the reverse reaction. The ALS U10 beam will selectively probe the product radical.

VUV Photodissociation Dynamics

The ALS should extend the possibilities of bond-selective chemistry in the UV. In the photodissociation of CH_2IBr, for example, it has been shown possible to selectively dissociate the stronger C–Br bond and keep the weaker C–I bond intact by exciting the nonbonding electrons of bromine to an antibonding orbital of the C–Br bond. It will be very interesting to learn whether a trend can be established by breaking the C–Cl bond in CH_2BrCl in an analogous way. This excitation, which requires wavelengths much shorter than 2000 Å, can be carried out with the ALS undulator beamline at low resolution, used essentially as a cw source without the monochromator. To ensure sufficient signal-to-noise, cross-correlation modulation can be employed, using a beam chopper to modulate the photons from the beamline.

In the area of high-energy excitation, the tunable IR laser is a potentially powerful preparative tool for exploring unique regions of electronically excited potential-energy surfaces. Vibrationally mediated photodissociation experiments, in which a second photon dissociates a highly vibrationally excited molecule prepared by vibrational overtone excitation, have shown that excitation from the vibrationally excited state reaches regions of the excited potential energy surface that are otherwise inaccessible. To date, this approach has been restricted to the excitation of light-atom stretching motions; however, the IR laser could extend it to include lower-frequency, large-amplitude motions. For example, exciting one or a few quanta of bending vibration might produce good Franck-Condon factors for vibrational states. Such experiments could reveal new bound excited states and illuminate unique aspects of dissociation dynamics.

High-Resolution Molecular Photoionization

The high-resolution capabilities of the U10 normal-incidence monochromator will make it possible to investigate the final-state distributions of molecular cations with an energy resolution of ~1 cm^{-1}. For small radical systems, this energy resolution will provide rotational state information on the cation; while for larger polyatomics, complete vibronic resolution will be possible. Such results can be contrasted with current synchrotron-radiation-based measurements, which are limited to resolutions ≥80 cm^{-1} by a combination of monochromator-bandpass and electron-spectrometer resolution. Whereas laser-based, nonlinear mixing techniques can produce ultra-narrow-band VUV radiation (0.01 cm^{-1}), the limited tuning range of these methods restricts their applicability to a small range of molecular systems. The wide scanning capabilites of the monochromator on the U10 beamline will

allow studies of ground-state free radicals that have first ionization energies of 6eV and electronically excited cation states with energies typically lying between 12 eV and 16 eV.

High-resolution measurements of cation state distributions directly probe the symmetry-selection rules and angular-momentum balance involved in the photoionization process and provide spectroscopic data that can be used to elucidate cation geometries and vibronic couplings. Cation spectroscopic data, including Franck-Condon factors for $(v_1^+, v_2^+,...) \leftarrow (v_1'', v_2'',...)$ vibrational transitions, often yield complementary spectroscopic and geometric information on the neutral ground state. This information is particularly valuable and difficult to obtain for reactive species. Rotationally resolved measurements will focus on the radical hydrides, e.g., CH, CH_2, NH, NH_2, HCO, CH_3O, and C_2H, which are extremely important as reactive intermediates in combustion and atmospheric chemistry, yet are amenable to study by high-resolution photoionization techniques and fully *ab initio* theoretical methods. The open-shell and often highly correlated nature of the ground and low-lying excited states means that photoionization will often be accompanied by cation stabilization and large geometry changes, e.g., bent-to-linear ionization transitions for NH_2 and HCO. In addition to exploring the ionization dynamics of these species, rotational assignments will also yield ionization potentials to very high accuracy (±2–5 cm^{-1}). The latter can be used in thermochemical cycles to obtain accurate heats of formation and dissociation energies used in reaction-rate kinetics involving these radical species.

For polyatomic species, high-resolution photoionization studies will focus on the vibronic spectroscopy of hydrocarbon radical cations found in combustion processes, e.g., $C_xH_3^+$, in an effort to obtain new information concerning their vibrational structure and geometry and to determine accurate ionization energies. Previous photoelectron measurements on such systems were performed at relatively low resolution (≥50 meV), and, except for a few examples, their vibrational structure has not been resolved. Of particular interest is vibrational excitation in the cation indicating photoionization transitions from classical to nonclassical structures, e.g., bridged hydrogen in ethyl and propargyl cations. A very recent high-resolution resonance-enhanced multiphoton ionization [(1+1) REMPI], threshold-photoelectron (TPE) study of the benzyl radical also suggests the possibility of studying low-frequency vibrational modes in larger aromatic systems.

Photoelectron-Photoion Coincidence Measurements of Radicals and Clusters

Many radicals can be produced readily in electrical discharge, photodissociation, and thermal-pyrolysis sources, coexisting with their precursors and secondary reaction products. Norwood and Ng have demonstrated that the photoelectron spectrum of a radical in a mixture of other species can be measured with high sensitivity by using a pulsed photoelectron-photoion coincidence (PEPICO) scheme. When radicals, especially polyatomic

radicals, are prepared by conventional methods under effusive beam conditions, their internal excitations are difficult to assess, making it difficult to estimate the hot band effects on the measured ionization energies. Progress in the photoionization study of polyatomic radicals may require the use of a supersonically cooled radical source. Recent preliminary experiments by Ng and co-workers using a laser-photodissociation, supersonic, pulsed radical source indicate that vibrational excitation up to 40 kcal/mole can be relaxed efficiently in a supersonic expansion. Polyatomic radicals often exist in many isomeric forms. A major advantage of using the photodissociation-radical source is that specific isomers can be prepared from different molecular precursors.

PEPICO measurements of van der Waals clusters are hindered by fragmentation problems due to the weak binding energies of ionized van der Waals clusters. These problems should be greatly alleviated in the proposed studies of covalently bound clusters such as carbon, silicon, and transition-metal clusters. These can be prepared in a laser ablation source. The PEPICO spectra of covalently bound clusters will provide information about vibrational frequencies and ionization energies for the ground and excited electronic states of the corresponding cluster ions.

The full width at half maximum of the radical beam pulse, as measured by VUV photoionization, was found to be ≥800 μs. The construction of a high-repetition-rate (1-kHz) pulsed source, together with use of a high-repetition-rate (500-Hz) excimer laser, will allow the preparation of a quasi-continuous radical or cluster source with a >40% (800-μs, 500/s, 100%) duty factor. With the incorporation of the reflectron time-of-flight (TOF), mass-spectrometric method for extending the mass range and resolution and with the resolution and sensitivity provided by the U10 beamline, it will be possible to measure the photoionization and PEPICO spectra of radicals and size-selected clusters routinely.

Photodissociation of State- or Energy-Selected Molecular Ions

Laser photodissociation spectroscopy, which involves the monitoring of daughter ions as a function of the energy of the laser radiation, is capable of providing spectroscopic and thermochemical information about gaseous ions. Earlier experiments used electron-impact ionization for ion preparation, and ions thus formed were thermally excited, with distributions of rotational and vibrational states. Rotational and vibrational excitations of the precursor ions make the analysis of the photodissociation spectrum difficult. Hot band excitations also shift the dissociation threshold to a lower energy.

Molecular photoionization favors processes with a small change in rotational quantum number. Thus, 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 PEPICO techniques

for photodissociation studies. Baer and co-workers have applied the PEPICO technique to energy-selected ions and subsequently photodissociate these ions with a pulsed excimer laser. The derived kinetic-energy-release distributions of the product ions provide information about the dynamics of unimolecular dissociation. Baer used an excimer-pumped dye laser system with a repetition rate of 50 Hz. This PEPICO-photodissociation method is potentially a very useful technique if the duty factor of the dye laser can be increased or if cw dye lasers are used as the photodissociation source. For simple diatomic and polyatomic molecular ions, where the vibrational states can be resolved by the PEPICO method, the photodissociation spectra for these ions can be measured as a function of the ion vibrational energy level. We plan to develop this technique for routine studies of the photodissociation dynamics of vibrational and electronic state-selected diatomic and triatomic ions of interest in the study of planetary atmospheres. By incorporating the ion trap and reflectron TOF methods, the fragmentation of excited cluster ions can be examined. The reflectron TOF arrangement is useful for identifying the daughter fragment ions and for measuring unimolecular decay rates.

Direct Identification of Photofragments and Reaction Products

The identification of photodissociation and reaction-product channels and product branching ratios are important to the understanding of atmospheric and combustion chemistry. The photoion efficiency spectrum is an unambiguous means to identify photofragments and reaction products and provides structural information on the photofragments. With the greater than tenfold improvement in photoion-detection sensitivity at the U10 beamline, primary photofragments from molecules with very low cross sections can be observed. We plan to determine the primary product channels for the reactions between oxygen atoms and a series of hydrocarbons, such as C_2H_2, C_2H_4, and C_3H_6. A specially designed coaxial reactor is needed for this study. Detailed product branching ratios for this set of reactions are fundamental to the modeling of combustion chemistry in oxygen/hydrocarbon flames.

Molecular Spectroscopy and Reaction Dynamics of Rydberg and Superexcited Molecules

The complete range of photophysics and photochemistry of the highly excited states of polyatomic molecules can be studied with high precision. The high intensity of the U10 beamline will enable measurements of photoionization quantum yields and cross sections for

- total absorption,
- total ionization,
- partial ionization, and
- optical emission

as a function of the photon energy ranging from 10 eV to 30 eV, with a resolution of 1 meV. It will be easy to measure both optical emission spectra and photoelectron spectra.

It will be possible to measure these cross sections for clusters to elucidate the effect of van der Waals potentials on photoionization and photoexcitation. Time-resolved dissociation processes with a higher energy resolution will also be studied. For example, rotational-energy-resolved observation of the pre-ionization of superexcited H_2 will be possible. Furthermore, higher synchrotron-radiation intensities have been required for the measurement of bimolecular processes. The study of highly state-selected bimolecular processes will be possible at this beamline.

Infrared Spectroscopy of Gas-Phase Free Radicals

The availability of the ALS and high-power laboratory IR laser systems provides exceptional new opportunities for the measurement of ionization potentials and IR absorption spectra of gas-phase free radicals. Adiabatic ionization potentials of radicals are key ingredients in many thermodynamic calculations of bond energies and reaction energetics, but these potentials are often poorly known. Infrared absorption spectroscopy of gas-phase radicals is still poorly developed because of the difficulty of creating a sufficient number-density of radicals, detecting the absorption spectrum, and identifying the spectral carrier. Infrared absorption spectra can provide important structural information and a critical test of quantum chemical calculations. Rotationally resolved, higher-resolution spectra will yield detailed geometric information and assignments of narrow spectral lines that can be used for *in situ* laser diagnostics in flame and combustion studies.

The unique combination of the ALS and laboratory lasers will permit a comprehensive program in IR spectroscopy of unstable species cooled in supersonic expansions. Species of particular interest include hydrocarbon radicals such as ethynyl, vinyl, ethyl, and propargyl, as well as small organometallic species such as partially ligated transition-metal atoms. The generality of IR-UV resonance-ionization detection will be limited primarily by the experimenter's ingenuity in designing suitable radical sources.

Alternatively, Hg sensitization reactions can be used to produce a clean source of free radicals without worrying about secondary photolysis. These free radicals can be cooled in an expanding beam and then photolyzed with the light from the ALS. In this manner, one can measure the absorption cross sections of free radicals as a function of wavelength in the VUV region. One can also study the photodissociation of these free radicals. Products such as C_2 from C_2H, NH from NH_2, and C_3 from C_3H_2 can be measured by laser-induced fluorescence (LIF) with continuously tunable dye lasers. Other radical intermediates important in the semiconductor industry such as SiH or GeH could also be studied.

High-resolution IR measurements will be carried out with cw IR lasers, e.g., F-center laser or Ti:Sapphire, which provide a 100% duty cycle with the quasi-cw ALS pulse train (12.2-Mhz, 8-bunch mode) and have sufficient energy (10 mW) for efficient pumping of rovibronic transitions. Such lasers are limited to excitation energies greater than 2800 cm^{-1}, useful for excitation of CH, OH, and NH stretches and combination bands. Since the main interest is rotational resolution for determining structure, this limitation is not serious. The experiments are carried out by selecting the VUV energy to lie below the ionization threshold of the vibrationless cation and detecting parent ions with sufficient internal energy (provided by the IR absorption) to be ionized. In cases of poor Franck-Condon overlap with the ground vibronic state of the cation, it may be more sensitive to detect dissociative ionization products, which can only be produced from vibrationally excited neutrals. It has been demonstrated that all of the vibrational energy residing in the neutral precursor can be used to surmount the dissociation energy. This latter approach has the added advantage of near-zero background ions in the absence of IR excitation. It is crucial that higher-order (n = 2, 3, ...) VUV radiation from the U10 beamline be suppressed to 10^{-6} of the first-order beam in order to eliminate interfering background ions. It should also be possible to use the unmonochromatized U10 radiation for cases in which a narrow VUV bandwidth is unnecessary or higher sensitivity is needed. The natural bandwidth for the U10 is 2.5% (1600 cm^{-1} at 8 eV), and selective ionization can be achieved for vibrational excitations within about 2000 cm^{-1} of the radical ionization potential.

Ion-Molecule Collisions and Two-Photon Experiments

The U10, in connection with a high-resolution monochromator, is particularly useful for experiments requiring highly monochromatic radiation of high intensity. Undulators are particularly useful for such purposes as they automatically produce monochromatic radiation. The larger bandwidth of such radiation is not necessarily a drawback because there are many cases for which such resolution is sufficient but which could not be handled using normal synchrotron sources because of their low intensity.

Chemical-dynamics experiments that were previously impossible to perform thus become feasible. Such techniques are particularly well suited for investigating ion reactions in which the ions are prepared in well-defined states. Also, two-photon experiments, in which one photon is generated by the synchrotron and the second by a suitable laser, are now within the reach of the experimentalist.

Another area of investigation is the following: The high intensity of undulator radiation should make it possible to perform two-photon experiments, in which the first photon (from the synchrotron) is used to excite a molecule or cluster into an intermediate state, while the second photon (from a high-power laser) subsequently ionizes the particle. This method may be used

to select different isomers in complex molecules and clusters in order to produce isomer ions for use in reaction experiments or as a means of detection.

Reactive Studies of C_{60}

Crossed-beam reactive studies of C_{60} will employ the VUV light from the ALS as a photoionization source for TOF mass spectrometry. The beams will be continuous, and the sources of the two beams will rotate about the interaction region. This source would be gentle, a characteristic that can help to prevent dissociative ionization of any of the $C_{60}X_n$ product. Two types of products can be formed. If the X molecule adds to the surface of the C_{60}, it could be weakly bound and dissociative ionization could destroy it. If it is an endohedral product, it should be more tightly bound.

Metastable Excitation for TOF and Angular-Distribution Measurements of CO and Other Small Molecules

The intensity of the U10 beamline is sufficient to carry out metastable TOF detection of chemical-reaction and energy-transfer products created by two continuous, crossed molecular beams in a universal molecular-beam machine. For example, H + OCS, SH + CO could be studied. The VUV radiation would be tuned to excite specific vibrational states of the CO product, and TOF would be carried out through cross-correlation techniques. A study of this type would give the first information on reaction-product vibrational quantum-state correlation. In this and other experiments, several considerations must be given special attention.

First, the 6–10-eV energy range is of crucial importance. It is in this region that there are many metastable states which are below the dissociation limit of the molecule. It is very important that this photon-energy range be readily accessible.

Second, tunability must be a user-friendly operation. For this experiment, it is anticipated that new wavelengths will be chosen approximately every 15 minutes. It is extremely important that tuning of the magnet gap not be so involved as to be the bottleneck in the experiment.

Third, from time to time, low-resolution spectral scans of the magnet gap would be highly desirable. The magnet gap should be continuously tunable for such experiments.

Ion-Pair Formation in an Ice Matrix

The ALS could be used to irradiate dilute frozen mixtures of methane, ammonia, formaldehyde, etc. in an ice matrix. At short wavelengths, ion-pair formation should occur when the electrons formed by photoionization escape the cage and recombine with a radical to form a negative ion. Laser ablation of the ice with a pulsed infrared laser could be the method for interrogating the

sample. TOF analysis of the positive and negative ions can determine which ion pairs are formed. This problem is important in understanding the processing of ice grains in the interstellar medium that go to form protoplanets.

State-Selected, Ion-Molecule Reaction Dynamics

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. The introduction of the radio-frequency (rf) octopole ion guide has played an important role in reliable, absolute, cross-section measurements. Much of the vitality in the study of state- or energy-selected ion-molecule reaction dynamics is owed to the development of sophisticated, photoelectron–secondary-ion coincidence techniques.

As a consequence of recent advances on the experimental and theoretical fronts, the field of state-selected ion-molecule reaction dynamics is ready to probe more complex ion-molecule systems. Absolute reaction cross sections for ion-molecule reactions involving state- or energy-selected reactant ions and stable neutral reactants can now in principle be measured from below thermal energy to well beyond 10 eV.

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 ion-molecule reaction apparatus, incorporating mass spectrometric and rf octopole ion-guide techniques, for state-selected cross-section measurements of ion-molecule reactions of planetary interest.

A survey of the literature indicates that studies of reactions between state- or energy-selected ions and atoms (other than the rare gas atoms) or radicals remain an unexplored research area. Thus, the studies of ion-atom and ion-radical reactions can be considered as a frontier in ion-molecule reaction dynamics. For this reason, we intend to devote efforts to cross-section measurements of state-selected ion-atom and ion-radical reactions.

The aim is to investigate ion-molecule and ion-cluster dynamics by using ions in electronically well-defined states. Reactions are of the type X^+ (state selected) + BC $\rightarrow$ XB^+ + C, where X is a rare gas (He, Ne, Ar, Kr, Xe) and BC is a diatomic or polyatomic molecule (e.g., CO, CO_2, CH_4, ...). A particular state is selected by using an ion-electron coincidence technique, which distinguishes between different electronic states. This method can also be applied to produce molecular ions in a particular vibronic state (e.g., NO, N_2O, ...) to use as reagent ions in ion-molecule reactions. The investigation of reactions between state-selected ions and clusters is also considered in order to study energy and charge-transfer processes in such systems.

III. Workshop Summary

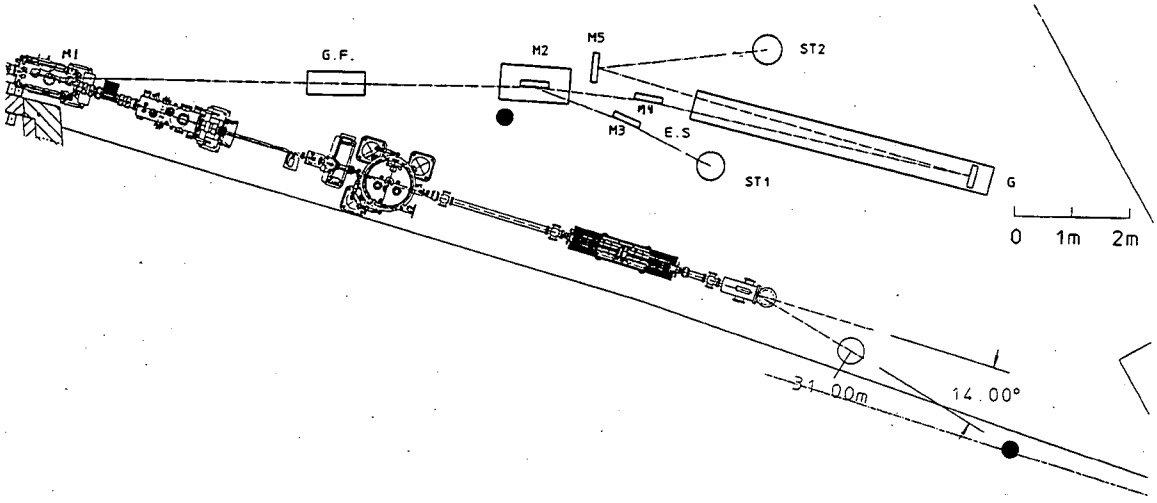
Beamline Design (Phil Heimann, Group Leader)

The preliminary design of the beamline was developed by Masato Koike and Philip Heimann. The beamline consists of a gas filter, focusing and branching mirrors, and a high-resolution, normal-incidence monochromator. High-flux, 2.5%-bandwidth radiation will be directed toward the first end station for photodissociation, while lower-intensity, highly monochromatized radiation will be sent to the second end station for spectroscopy and energetics. The energy range covers 5 to 30 eV at both end stations.

The flux of the U10 was presented at the workshop and compared to that of the ALS 8-cm-period undulator (U8). Initially, this U8 will be installed in the chemical-dynamics sector of the ALS storage ring. Following its completion in April 1995, the U10 will replace the U8 during the next ALS shutdown. The important advantage of the U10 is that the photon energy can reach 5 eV without changing the storage-ring energy or using a magnetic field larger than the field of a bending magnet. For the U10, the photon flux is 2.5×10^{15} photon/s at 15 eV in a 0.1% bandwidth. Because the undulator operates at a high K value, many higher harmonics are present in the spectrum. These harmonics at higher energies will be greatly reduced primarily by the gas filter and additionally by the reflectivities of the optics.

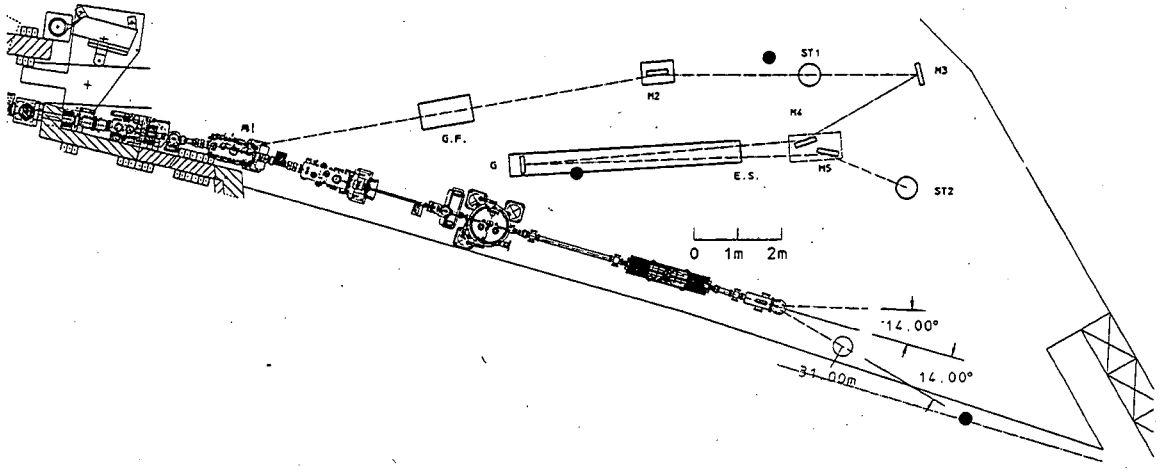
Two alternative optical layouts were presented for discussion. In the first layout, Option 1, the synchrotron-radiation beam is directed alternatively to End Station 1 or to End Station 2 (Figure 1). The monochromator is located between the two end stations. In the second layout, Option 2, the beam passes through End Station 1 before entering the monochromator and is then directed toward End Station 2 (Figure 2). The monochromator is situated between this beamline and the ALS U8 branchline presently under construction. With Option 2, experiments could take place in both end stations simultaneously. However, workshop participants were seriously concerned about the potential downtime of the end stations and decided that alternately directing the beam to End Station 1 or 2, as allowed by Option 1, was preferable. A concern was also expressed that with Option 1 the space allocated to End Station 1, 2 m × 5 m, is too small. Space is always a limited resource at synchrotron facilities. Currently, a new optical layout is being developed in which the space is arranged similarly to Option 2 but the beam is alternatively directed to one end station at a time.

The photon flux at both end stations was calculated for each optical layout. The mirror reflectivities were derived from tabulated values of the indices of refraction (Palik, *Handbook of Optical Constants*). The grating efficiency was calculated using the scalar theory. The flux at End Station 1 was predicted to be 10^{16} photons/s (at 2.5% bandwidth), with the result being quite similar for both options. This intensity represents the power of the undulator fundamental



Optic	Figure	θ (deg)	Magnification	Focusing Direction
M1	Toriod	85	0.31	Both
M2	Toroid	80 (87)	1.0 (0.79)	V (H)
M3	Sphere	87	0.4	H
M4	Cylinder	87	0.22	V
G	Sphere	3–17	1	Both
M5	Toroid	12.5	1	Both

Figure 1. Preliminary beamline layout for chemical-dynamics research at the ALS. Option 1: Synchrotron beam is directed alternatively to End Station 1 or End Station 2.



Optic	Figure	θ (deg)	Magnification	Focusing Direction
M1	Toriod	80	0.31	Both
M2	Toroid	85	0.7	Both
M3	Sphere	15	1.8	H
M4	Cylinder	77.5	0.27	V
G	Sphere	3–17	1	Both
M5	Toroid	77.5	1	Both

Figure 2. Preliminary beamline layout for chemical-dynamics research at the ALS. Option 2: Synchrotron beam passes through End Station 1 and then is directed to End Station 2.

reduced only by a factor of four by grazing-incidence reflections. At End Station 2, the intensity is further reduced by additional mirrors and by the throughput of the monochromator. The photon flux at End Station 2 was predicted to be 4×10^{11} (at 1/50,000 bandwidth), with the result for Option 2 being about an order of magnitude lower. The reduced intensity with Option 2 is a consequence of having an additional mirror and two mirrors at increased incidence angles. The throughput of the new optical layout is being analyzed to optimize the intensity at End Station 2.

A 6.65-m off-plane Eagle design was chosen for the monochromator. In an off-plane Eagle monochromator, aberrations are small because of the Rowland mount and the near-normal incidence. The mechanical motion required is relatively simple; the slits remain fixed, while the grating rotates about a horizontal axis and translates horizontally. This design has been proven in spectrographs used for absorption measurements at the SURF and Photon Factory synchrotron facilities. The 6.65-m Eagle monochromator has a theoretical resolving power of 50,000 at 16 eV and 100,000 at 8 eV by use of a 2400 l/mm grating. This instrument will be one of the highest-resolution VUV monochromators at any synchrotron laboratory in the world.

The higher harmonics of the undulator will be suppressed by mirror reflectivities and by the gas filter. The grazing-incidence mirrors leading to End Station 1 provide a cut-off at about 200 eV, while the near-normal-incidence grating essentially eliminates radiation above 30 eV. The gas cell chamber consists of a tube filled with a rare gas such as argon and differential pumping at both sides. Individual harmonics are reduced to the 1–2 percent level, or below, by the gas cell. The combination of optical reflectivities and the gas cell will suppress harmonics to a level of 0.01% or less for End Station 2 and to an effective level for End Station 1.

The focus in the end stations can be ~250 μm × 50 μm (FWHM) from optical considerations. Discussion at the workshop suggested that the ideal spot size for both types of experiments is 1 mm^2, defined by the dimensions of the molecular beams. A further request for End Station 1 was to be able to direct the beam either to the molecular-beam source or to the ionization region. This flexibility will be provided by a retractable plane mirror.

A general plan for the construction of the beamline was presented. It was proposed that McPherson Corp., which has much experience in high-resolution VUV monochromators, build the monochromator. The rest of the beamline design and assembly, involving nonstandard mirror chambers and the analysis of high heat loads, would be done at LBL. The projected completion date is December 1994.

End Station 1: Photodissociation Studies (Alec Wodtke, Group Leader)

We reached a consensus on the desirability of a molecular beam machine with the following features:

- Photoionization detector using the U10 undulator output. The detector will use 10^{16} photons/s for pseudo-cw ionization. It is anticipated that experiments will be routinely carried out with little or no background, opening many new avenues of scientific pursuit.
- Optional electron-bombardment ionization.
- Dual, rotating, crossed molecular-beam sources (fixed at 90 degrees with respect to one another). Laser access to each source will be included to allow free-radical photolysis sources as well as laser ablation of low-vapor-pressure material for formation of covalently bound clusters. Laser access to the crossing region of the two beams will be standard.
- Optional VUV mirror for crossing output of U10 undulator with one or both of the crossed molecular beams in the main chamber.
- Conventional LIF or REMPI probes of the molecular-beam crossing region.

Possible Areas of Experimentation

The following general areas of experimentation would be possible at a level of resolution, selectivity, and sophistication that is not available in any existing laboratory nor would be possible in the foreseeable future in a single investigator's lab:

Core Areas with Short-Term Questions

1. Reaction-mechanism determinations: Free-radical beam sources will be adopted from existing groups or developed in order to carry out crossed-molecular-beam studies that will unambiguously give the primary reaction products of important combustion intermediates.
2. Photofragmentation-translation spectroscopy that will allow upper limits to be determined for the bond energies of many species and will thereby give information on the heats of formation of many radicals.
3. VUV photofragmentation-translation spectroscopy serving a similar purpose as (b.) but for a class of molecules that absorb light when no laser sources are possible (6–30 eV).

Long-Term Issues

1. Role of nonequilibrium states in chemical systems: The apparatus will allow vibrationally and electronically metastable molecules to be prepared

for study in crossed-beam reactions. This will allow study of the chemistry of high-energy compounds that may be of importance to combustion.

2. Chemical and thermochemical characterization of covalently bound carbon and other covalently bound clusters.
3. Photoionization detection of isomerization and universal detection of hydrocarbon isomers.

General Description of the Machine

The basic idea is that of a rotating-source beam machine modelled after an existing machine shown in Figure 3. Two crossed molecular beams fixed at 90 degrees to one another will rotate with respect to a differentially pumped photoionization-based, "universal," mass-spectrometric detector. The two beams will cross in a volume of 3 mm (along flight path) × 5 mm (along rotation axis) × 1 mm (determining angular resolution), providing a large interaction region, high angular resolution, and superior time resolution. The flight length to the photoionization detector will be a minimum of 15 cm and can be extended. The ionization volume will be 0.5 mm long (giving a limit to $\Delta t/t < 0.003$, 10 times better than any existing machine) and 0.1 mm high (providing an inherent limit on angular resolution to 0.04 degree, 20 times better than any existing machine). The solid angle subtended by the detector is 2.2×10^{-5} steradian. The solid angle into which products will be scattered must be assumed, but a typical and conservative estimate is 1 steradian. The ionization efficiency is 2×10^{-4} (assuming a 10^{-17} cm^2 photoionization cross section). Consequently, it is anticipated for feasibility calculations that 2×10^8 product molecules/s in the interaction volume will lead to 1 ion count per second in the detector.

Laser access to every chamber in the machine (except the differential pumping chambers of the detector but including the ionization chamber) will be designed into the machine.

Description of the Beam Sources

Source 1: A high-throughput source for use with pseudo-cw laser-ablation sources of covalently bound species or laser-photolysis, free-radical sources. This source is compatible with all other more conventional applications. The required throughput is 20,000 l/s at 10^{-4} torr. Laser access will be available.

Source 2: A conventional source with laser access requiring 6,000 l/s at 10^{-4} torr.

Differential Pumping Chambers: Each of these will be equipped with one magnetically suspended 300 l/s turbo pump. Laser access will be available.

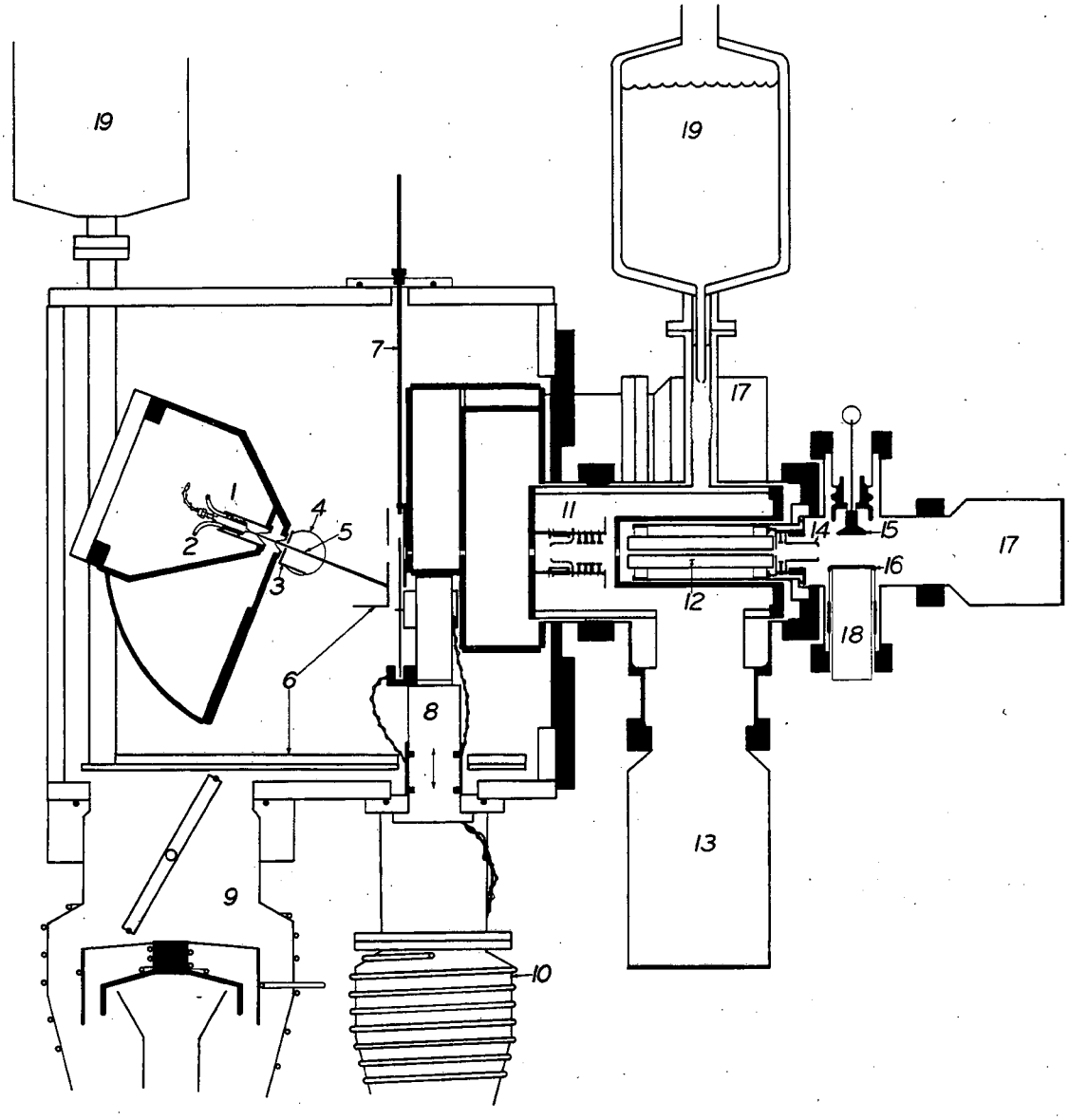


Figure 3. Schematic of model rotating-source beam machine for End Station 1. Critical components: (1) rotating beam source; (3) background suppressor; (5) molecular/laser beam crossing region; (6) LN_2 cooled panels; (7) gate-valve assembly for detector; (8) chopper wheel; (11) electron impact ionizer; (12) quadrupole mass filter; (14), (15), (16) Daly detector parts; (9), (10), (13), (17) high-vacuum pumps.

Description of the Main Chamber

Cryopumping will be extensive in addition to that provided by a 2000 l/s turbo pump. This will include liquid-nitrogen cooling of false interior walls and liquid helium background gobbler. Laser access will be available at the crossing region of molecular beams. In addition, the U10 output can also intersect with the molecular-beam crossing volume. LIF or REMPI detection of the crossing volume of the molecular beams will also be included.

Detector

Three stages of differential pumping will necessitate two 350-l/s turbo pumps and one 500-l/s turbo pump in the ionization region. A fourth chamber for the Daly detector ion counter requires one more 350-l/s turbo pump. The main feature of the detector is the use of the U10 output as a photoionization source, which will be located in a liquid-helium-cooled Dewar. The photoionization volume will also have laser access. Electron bombardment ionization will be available as an option.

End Station 2: Photoelectron and Photoionization Processes (Mike White and Cheuk Ng, Group Leaders)

End Station 2 will be optimized for the following types of experiments:

- Photoionization mass spectrometry,
- TPE spectroscopy
- Threshold PEPICO spectroscopy
- PEPICO-photodissociation spectroscopy
- State-selected ion-molecule reaction dynamics
- IR/VUV double resonance.

A major component of the experimental program will be the development of radical sources utilizing pyrolysis, photolysis, and discharge techniques. Major design considerations are: (1) sufficient pumping for high-throughput cw molecular beam (1 torr/liter-s) and effective differential pumping, (2) shortest possible distance from nozzle source to interaction volume to maximize molecular-beam intensity (10^{12} particles/cm^3), (3) laser access to nozzle expansion region for photolysis or IR pumping, (4) interchangeable chambers and detectors for relatively easy reconfiguration of apparatus.

The proposed experimental apparatus (Figure 4) is configured around a three-chamber apparatus, with each chamber pumped by turbomolecular and/or cryopumps. The source chamber will be pumped by two 2200-l/s turbomolecular pumps, while the second chamber containing the beam-collimating aperture is pumped by a 500-l/s turbomolecular pump. The

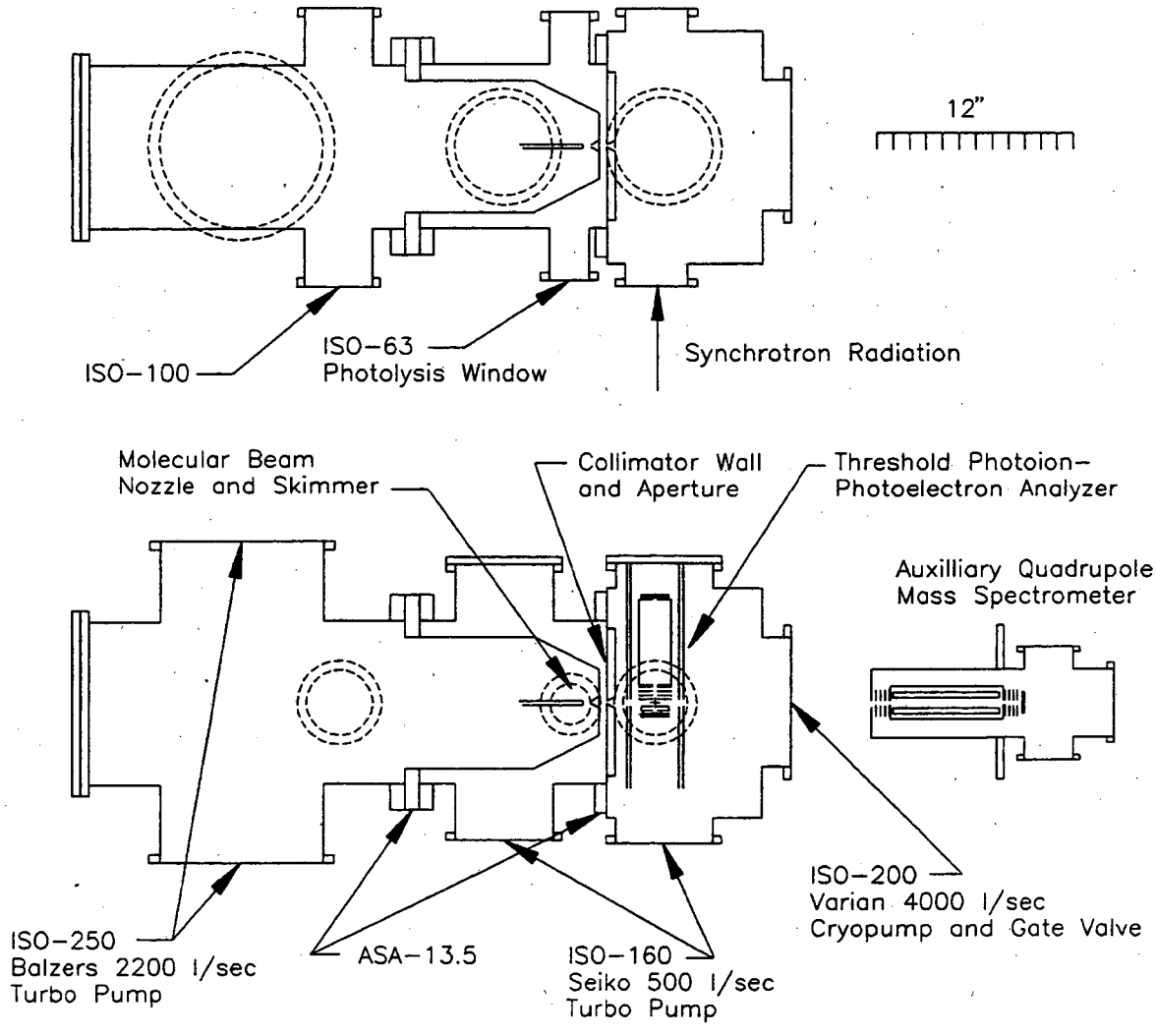


Figure 4. Schematic of vacuum-chamber arrangement for End Station 2.

experimental chamber will be pumped by a combination of a 1600-l/s turbomolecular pump and a 10,000 l/s cryopump. Background pressures in the three chambers with a cw molecular beam are expected to be 10^{-4} torr (source), 10^{-6} torr (collimator), and $<5 \times 10^{-7}$ torr (experimental). Chambers will be closed and joined by standard ISO (O-ring seals) and conflat flanges (metal seals) so that experimental configurations can be quickly changed by interchanging components mounted on these flanges. Modular components will include a PEPICO setup, threshold-field-ionization (TFI) photoelectron spectrometer, etc. A PEPICO detector assembly based on TOF-TPE and photoion analyzers is shown schematically in the experimental chamber in Figure 5.

Threshold Photoelectron-Photoion Coincidence Spectrometer

It has long been recognized that the high collection efficiency and high-resolution capabilities of photoelectron spectrometers that detect near-zero-kinetic-energy electrons (ZEKEs) are ideal for PEPICO measurements of molecular cations. Because true ZEKEs will only have momentum parallel to the small extraction field, threshold spectrometers reject other fast photoelectrons by inserting "steradiancy" analyzers between the ionization volume and the detector. Photoelectrons with momentum components perpendicular to the extraction field are blocked from reaching the detector by using collimated hole structures or field-free flight paths with small entrance and exit apertures. The limitation on resolution for TPE detection is the ability of the spectrometer to select true ZEKEs from "fast" electrons moving parallel to the extraction field. For cw sources, this has been accomplished with a secondary electrostatic velocity analyzer at the exit to steradiancy separation or by the TOF time of arrival, which can distinguish true zero-energy electrons originating from pulsed ionization sources.

TOF spectrometers have been used quite successfully at synchrotron-radiation sources that have appropriate pulse repetition rates for field-free flight times of up to 200–500 ns and energy resolutions of 10 meV (80 cm^{-1}). TOF-TPE spectrometers are also efficient and quite simple to construct. Again, the limit on resolution is determined by how finely the analyzer can distinquish the TOF of true ZEKEs, which is most often limited by the radiation pulse width (0.5–1 ns at most synchrotron facilities). The very short pulse at the ALS (30 ps) allows the timing resolution to improve significantly, so that an energy resolution of 1 meV (8 cm^{-1}) can be obtained for TOF-TPE spectroscopy. This resolution can be accomplished with a 1-V/cm extraction field, an acceleration and drift length of less than 22 mm, and an overall timing resolution of 100 ps. The short flight length is a result of the 82-ns period between ALS synchrotron-radiation pulses in the timing (eight-bunch) mode of operation. A 100-ps timing resolution is currently state of the art and will require some electronics development effort by LBL.

Threshold electrons falling within the 100-ps time gate will then act as triggers for pulsed extraction of photoions from the ionization volume. The photoions are then mass-analyzed by their TOF and detected in coincidence with

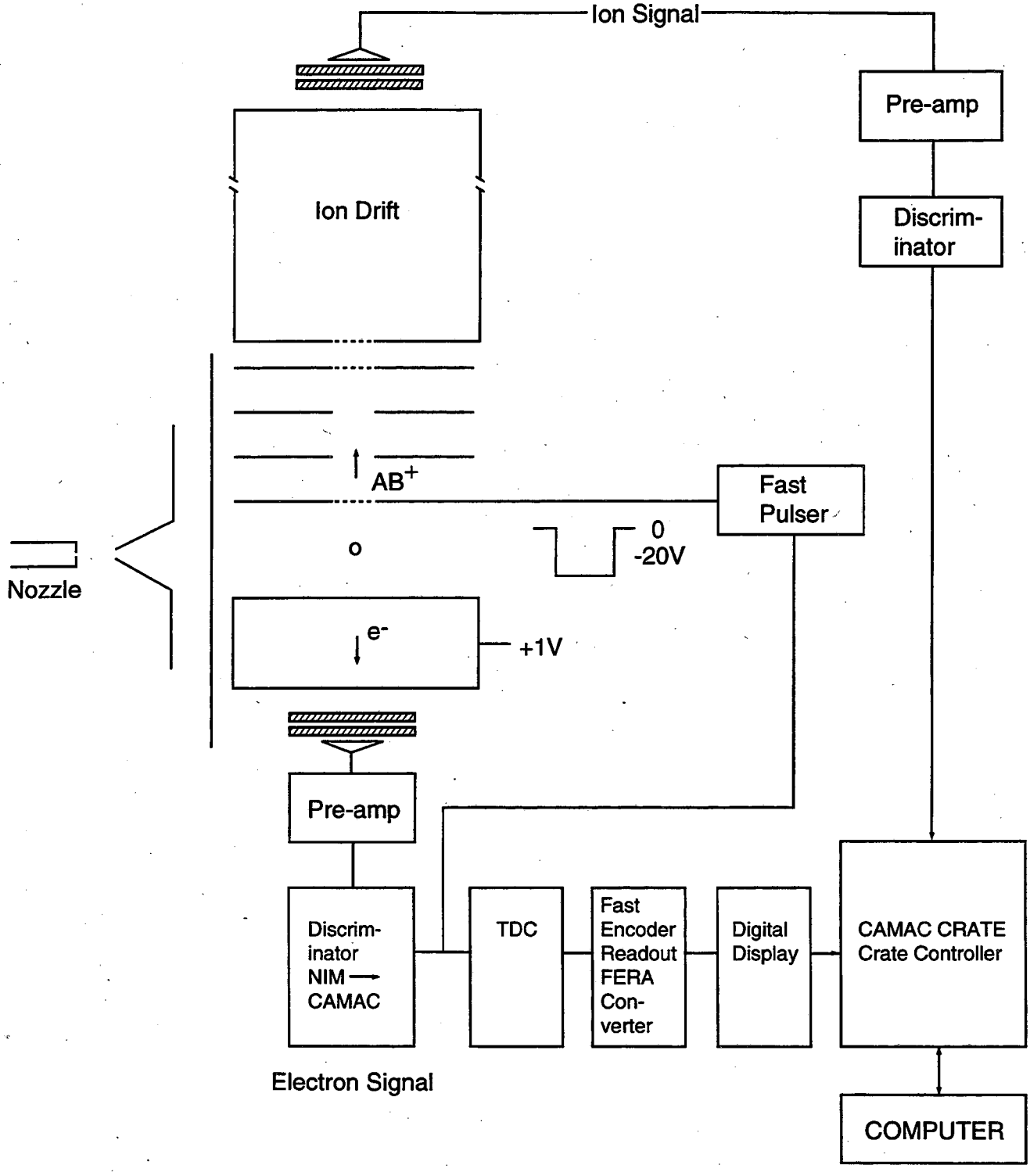


Figure 5. Schematic of TOF-PEPICO apparatus.

the photoelectrons. Linear or reflectron TOF photoion analyzers will be used, depending on the application and resolution required. The coincidence process determines the internal energy of the detected photoion within the photoelectron resolution. This technique can be used to prepare the cation for subsequent ion-molecule reactions or follow its unimolecular decay as a function of internal energy. Conversely, by reversing the basis of coincidence from photoelectron to photoion, it will also be possible to obtain high-resolution TPE spectra for specific cations. The latter technique is especially useful for obtaining spectra of radicals, which often can only be produced in beam sources containing many other spectrally interfering species. The study of state-selected ion-molecule reactions by PEPICO requires additional ion optics and placement of a gas collision cell prior to mass analysis of the charged products. Such an apparatus has recently been developed. A schematic of the TOF-PEPICO setup is shown in Figure 5.

TFI Electron Spectrometer

Although TPE spectroscopy at the ALS will provide a significant improvement in resolution over previous spectrometers, it is still not capable of providing sufficient resolution to determine the rotational state distribution of the cation (2 cm^{-1}). Recently, laser-based analogues of TPE based on the delayed pulsed-field ionization of high-n Rydberg states lying within a few wave numbers of the ionization threshold have demonstrated sub-wave-number resolution for cation spectroscopy. These techniques, falling under the name ZEKE spectroscopy, have been applied in (n + 1) REMPI as well as coherent VUV measurements of molecular photoionization with low-repetition-rate lasers.

The main advantage of this approach over TPE is that the pulsed nature of the excitation source allows one to wait for "fast" and prompt near-ZEKEs, which arise from direct ionization and autoionization processes, to be removed from the ionization volume before extraction takes place. Low-energy electrons produced by prompt ionization processes cannot be separated from true ZEKEs by TPE methods, since a spectrometer with wave-number resolution would be required. This is virtually impossible because all electron spectrometers are subject to stray fields that are always much greater (typically 1–5 meV). The very high repetition rate of the ALS limits the separation between excitation pulses to 100 ns, a time that is insufficient to effect separation by delayed pulsed-field ionization. Based on a recent development by Zhu and Johnson, however, it is possible to configure an asynchronous TFI spectrometer that uses the velocity of the molecular beam to effect separation of prompt- and field-ionization events. A schematic of the proposed TFI spectrometer is shown in Figure 6.

The molecular beam containing the molecules of interest is directed down the axis of the spectrometer where the molecules are photoexcited in the first field region defined by V_1. Prompt electrons as well as electrons originating from field ionization of states very near the threshold (~$6\sqrt{V_1}$ cm^{-1}) are decelerated along the path from the spectrometer, while the subset of long-lived Rydberg states surviving the V_1 field move along with the molecular beam.

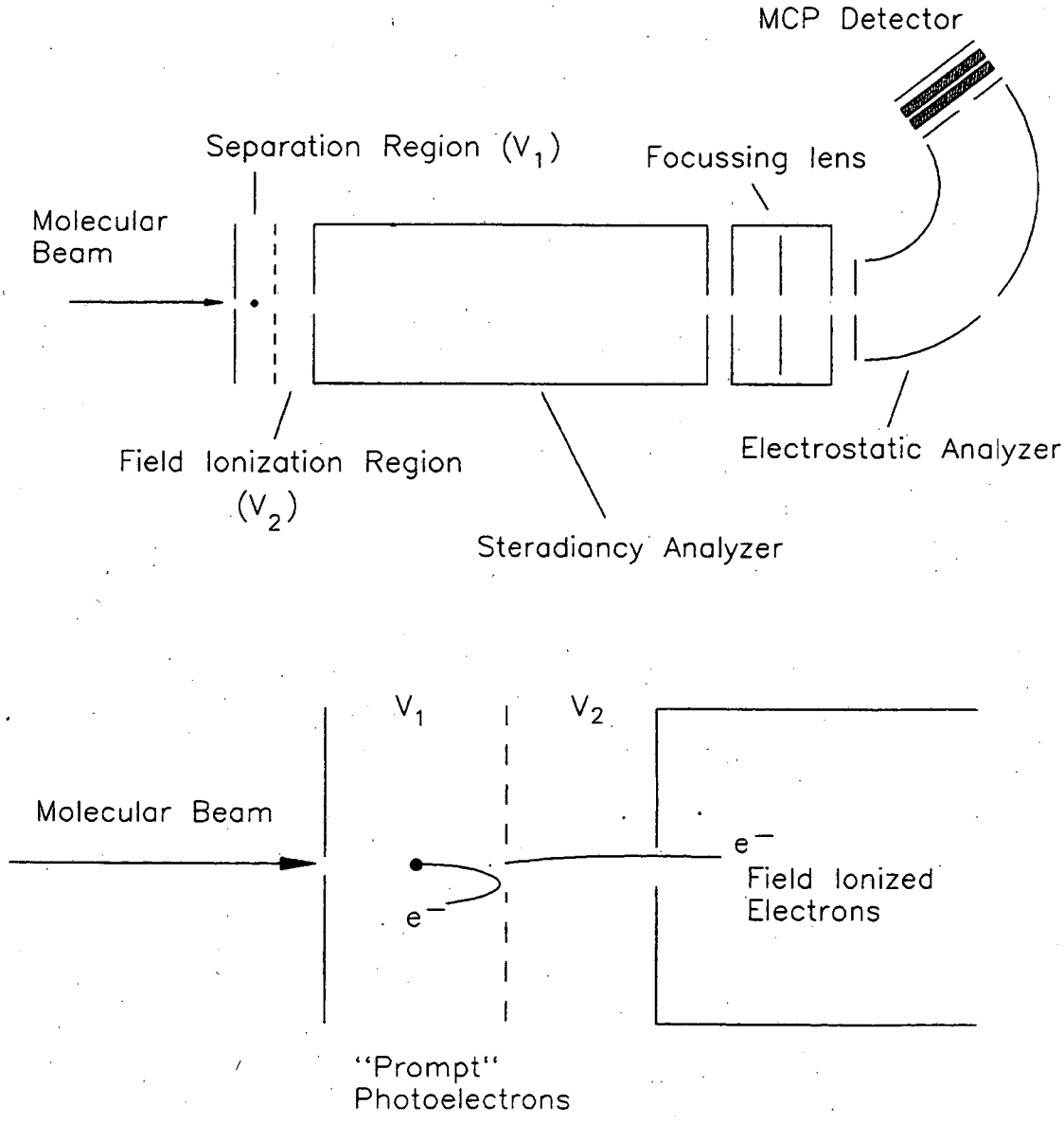


Figure 6. Proposed TFI spectrometer for End Station 2.

This subset is subsequently field-ionized at the second grid and accelerated towards the detector by the second field region V_2 ($\geq V_1$) of opposite sign. The field-ionized electrons are separated by an electrostatic filter from any remaining "fast" electrons with kinetic energies exceeding the retarding field V_1 before being detected by the multiplier. Unlike asychronous TPE, the bandwidth of the ZEKEs seen by the detector is not determined by the resolution of the electrostatic filter, since all near-ZEKEs have been removed in the first field region. The overall resolution of the spectrometer is given approximately by $6\sqrt{(V_1 - V_2)}$ cm^{-1}, which approaches the 2 cm^{-1} bandwidth of the U10 monochromator. Detailed particle-trajectory calculations will be necessary to optimize the design for efficient electron collection.

Tandem Mass Spectrometer

The use of a quadrupole-octopole-quadrupole apparatus has become the standard setup for absolute cross-section measurements of ion-molecule reactions. An apparatus of a similar design (not shown here) will be developed as a portable experimental chamber for the end station. Such an apparatus can also be used for PEPICO-photodissociation studies of state-selected molecular ions and PEPICO studies of radicals.

Molecular Beam Sources

The free radicals will be generated through a variety of techniques including pyrolysis, discharge, or high-repetition-rate excimer photolysis. Chen and co-workers have developed both cw and pulsed pyrolysis sources and identified many precursor systems that yield small hydrocarbon radicals with high yield. These include propargyl, ethyl, methyl, vinyl, cycloproenylidene, and o-benzyne. An excimer photodissociation supersonic radical beam source has been used sucessfully to prepare polyatomic radicals for photoionization studies. Excimer photolysis of suitable precursors is also effective for producing CH, CH_2, HCO, OH, NH, NH_2, NCO, C_2H, CH_3O, and others that are of primary interest in this project. With the use of a 500–1000-Hz excimer laser and pulsed jet, it will be possible to produce a molecular beam of radicals with a 50% duty cycle. Laser ablation from solid targets such as carbon, co-expanded in the presence of other gases, should be useful for photoionization and PEPICO studies.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720