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Publication Date

1999-02-01

LBNL-42816

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Chemical Sciences Division

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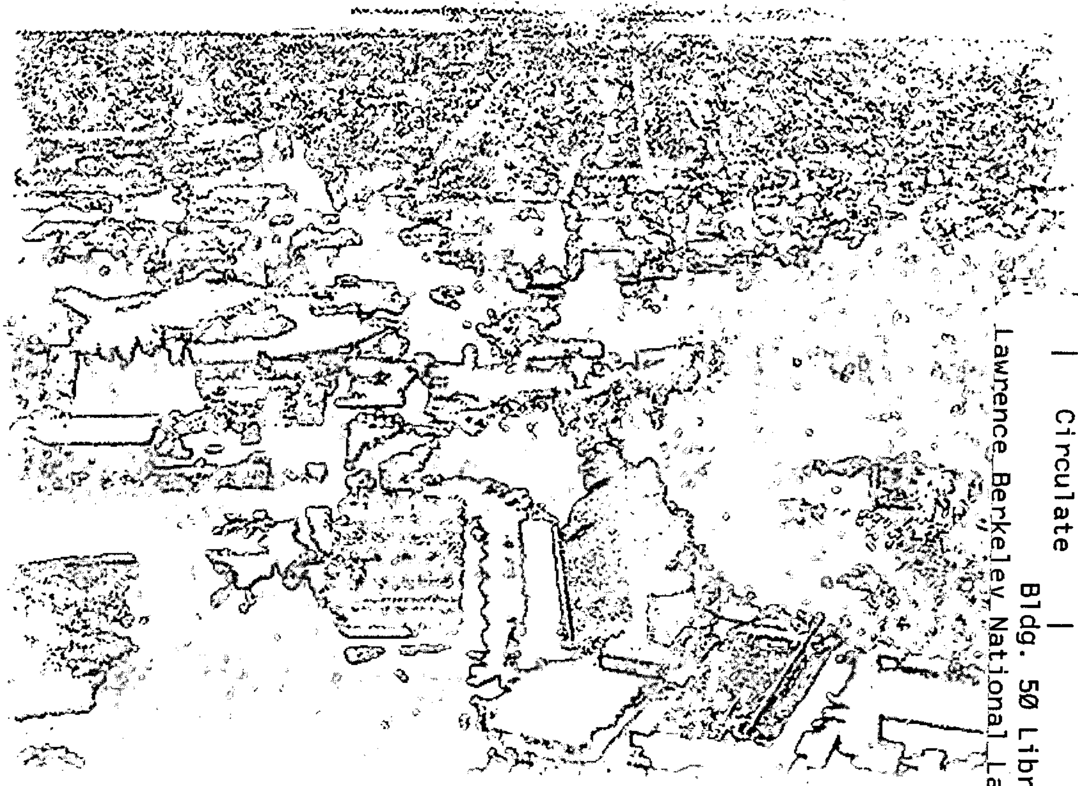

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Program Retreat Report
January 15, 1999

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

Chemical Dynamics at the Advanced Light Source

Program Retreat Report
January 15, 1999

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Abstract

A day-long retreat was held January 15, 1999 to chart the future directions for chemical dynamics studies at the Advanced Light Source. This represents an important period for the Chemical Dynamics Beamline, as the hardware is well-developed, most of the initial experimental objectives have been realized and the mission is now to identify the future scientific priorities for the beamline and attract users of the highest caliber. To this end, we have developed a detailed scientific program for the near term; identified and prioritized the long range scientific opportunities, identified essential new hardware, and outlined an aggressive outreach program to involve the chemical physics community.

Executive Summary

The Chemical Dynamics Beamline at the ALS was established by the Chemical Sciences Division of the US Department of Energy as a national user facility providing world-class experimental resources for probing fundamental chemical phenomena. A unique combination of state-of-the-art molecular beam machines and commercial lasers with the world's most intense source of continuously tunable vacuum ultraviolet radiation is now opening new doors in the study of chemical reaction dynamics, photoionization dynamics and high resolution photoelectron spectroscopy. A February 1993 workshop defined scientific priorities with the broadly stated goals:

- To determine the mechanisms and dynamics of uni- and bi-molecular chemical reactions.
- To explore the chemistry of molecules excited to Rydberg states or to other superexcited states.
- To study the structure, energetics and chemical reactivity of highly reactive polyatomic radicals and unusual transient species.
- To probe the nature of inter- and intra-molecular energy relaxation processes.
- To search for bond-selective or mode-selective means to modify chemical reactivity.
- To study molecules important in combustion, atmospheric and interstellar chemistry.

Virtually all of these goals have been addressed in published studies conducted on the Beamline, and the promise of the application of third-generation synchrotron radiation to frontier areas of chemical dynamics has clearly been demonstrated. The mission is now to identify the future scientific priorities and attract users of the highest caliber. To this end, a day-long retreat was held January 15, 1999. We have developed a detailed scientific program for the near term; identified and prioritized the long range scientific opportunities, identified essential new hardware, and outlined an aggressive outreach program to involve the chemical physics community.

The scientific program will focus on several areas of Beamline excellence and outstanding scientific promise:

- Photodissociation dynamics of complex molecules
- Photoionization experiments on He droplets and other clusters
- Radical photochemistry and reaction dynamics
- UV-VUV spectroscopy
- Radical photoionization studies
- Threshold photoelectron-photoion coincidence studies
- Threshold photoelectron spectroscopy of aqueous solutions.

A prospective schedule of users and studies through the June, 1999 shutdown was developed and included in the report.

The Chemical Dynamics Beamline is at a natural stage of its evolution, turning now from a period of demonstration and exploration requiring more intensive development and frequent hardware modification, to routine use and ready application to experiments for visitors. An aggressive outreach program is being implemented to bridge the culture gap between the chemical physics community and the world of synchrotron radiation research. This outreach program consists of the following components:

- The principal means of acquainting the scientific community with the resources on the Beamline is through presentations at national and international meetings, and publication of results in leading journals. Resources will be allocated to ensure that all large-impact meetings will feature presentations of Beamline results, and that these presentations will contain relevant outreach information such as resources and contacts.
- A mailing is being developed to remind leading practitioners in the field of experimental chemical physics of the available resources here and the ease with which experiments may be proposed and undertaken.
- Perceived barriers to ready use of the facility by outside users are being met and dealt with preemptively, whether they relate to housing, transportation costs, or available support personnel.
- Needed resources for priority experiments must be promptly secured.

This program, combined with adequate funding for first time users, should stimulate the intense, constructive competition that will lead to the highest quality research results from the Beamline.

1. Introduction and Background

The Chemical Dynamics Beamline at the Advanced Light Source was established by the Chemical Sciences Division of the US Department of Energy as a national user facility providing world-class experimental resources for probing fundamental chemical phenomena. A unique combination of state-of-the-art molecular beam machines with an array of laser resources and the world's most intense source of continuously tunable vacuum ultraviolet radiation was envisioned to open new doors in the study of chemical reaction dynamics, photoionization dynamics and high resolution photoelectron spectroscopy. Funding for the Beamline was approved in 1992, and in February 1993, a workshop was held to develop the specifications and plans for the beamline, and to identify a working team responsible for completing the detailed design and construction. The target date set of January 1995 for completion of the beamline and endstation construction was met, with regular beamline operation beginning in November 1995 following the installation of the U-10 undulator in ALS sector 9. The initial workshop report outlined a series of scientific priorities with the broadly stated goals:

- To determine the microscopic details of the mechanisms and dynamics of primary dissociation processes and elementary chemical reactions.
- To explore the chemistry of molecules excited to Rydberg states or to other superexcited states.
- To study the structure, energetics and chemical reactivity of highly reactive polyatomic radicals and unusual transient species.
- To probe the nature of inter- and intra-molecular energy relaxation processes.
- To search for bond-selective or mode-selective means to modify chemical reactivity.
- To study energetics and spectroscopy of molecules important in combustion, atmospheric, and interstellar chemistry through mass- and electron-spectroscopies.

As will be documented below, virtually all of these objectives have been addressed, and the promise of the application of third-generation synchrotron radiation to frontier areas of chemical dynamics has been demonstrated.

The Chemical Dynamics Beamline has reached a natural stage in its evolution, turning now from a period of demonstration and exploration requiring more intensive development and frequent hardware modification, to more routine use and ready application to experiments for visitors. It is an appropriate time to define the future course of scientific study in detail, to develop and prioritize work in areas that have been opened and those that remain to be explored, and to make the transition to becoming a major national user facility. To this end, on January 15, 1999, a Program Retreat was held to examine these issues; this document presents the conclusions of this retreat.

This report is organized as follows: after this introduction, Section 2, "Accomplishments," presents an overview of scientific highlights from beamline research in the context of the goals sketched above; Section 3, "Scientific Opportunities," presents a detailed description of near-term scientific priorities as well as some key areas for longer-range development; Section 4, "User Program," discusses the visitor program and outlines an aggressive outreach program to involve the chemical physics community; Section 5 summarizes the conclusions of the report.

2. Accomplishments

We will briefly review the scientific achievements at the Beamline to date with reference to the goals stated in the 1993 workshop report. Detailed reports with literature citations may be found on the Chemical Dynamics Beamline Web site, http://www.lbl.gov/chemicaldynamics as well as in review chapters in forthcoming books[1].

Microscopic features of primary dissociation and reaction dynamics

This broad area represents the principal focus of Endstation 1, and many significant contributions have been made here. Endstation 1 is a universal crossed-molecular beam machine employing VUV photoionization-based product detection rather than electron impact. As a consequence, it achieves a unique combination of *universality* in product detection, while at the same time preserving *selectivity* through the tunability of the VUV probe. One characteristic has emerged from studies of primary dissociation dynamics using this apparatus, exemplified in recent work on dimethyl sulfoxide, vinyl chloride, and carbon disulfide. These are all molecules that have been intensely studied by other methods, and in all three cases both state-resolved laser studies and EI-based photofragment translational spectroscopy have been used to investigate the primary dissociation dynamics. For all of these well-studied molecules, textbook cases of polyatomic photodissociation dynamics, studies on Endstation 1 have shown that previous work was entirely in error in some cases, or that important product channels were overlooked, or that answers were found when alternative studies even using the same techniques had come to opposing conclusions.

In the case of DMSO, for example, studies of its UV photodissociation dynamics relying on state-resolved laser probing of the methyl radical fragments had concluded that the dissociation was concerted, with simultaneous departure of both methyl radicals. Beamline studies, however, clearly showed this to be incorrect. Instead, a rich array of dissociation pathways was documented, including unambiguous observation of the sulfonyl intermediates implying a stepwise dissociation process. In vinyl chloride, one of the most widely studied polyatomic molecules in the literature of photochemistry, the global dissociation dynamics were obtained for the first time. Again, earlier laser based studies were able to probe some of the fragments for this system, but the PI studies, with momentum matching of both product fragments, allowed for careful measurement of all primary processes including both H and Cl atomic elimination and H_2 and HCl molecular elimination. In addition to these primary processes, secondary decomposition of the radical products was observed and used to characterize the thermochemistry and

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[1] A. G. Suits, "Photodissociation and Reaction Dynamics using third-generation synchrotron radiation," in *Chemical Applications of Synchrotron Radiation*, T. K. Sham, ed., (World Scientific, Singapore, in press); C. Y. Ng, "Advances in Photoionization and Photoelectron Studies using third generation synchrotron radiation and UV/VUV lasers," in *Photoionization and Photodetachment*, Adv. Ser. Phys. Chem., 10A (in press).

dynamics of these species: Finally, a recent study of the UV dissociation dynamics of carbon disulfide highlights unique strengths of Endstation 1. Previous studies using high-resolution EI-based photofragment translational spectroscopy had come to dramatically differing conclusions concerning the branching between the S(^{1}D) and (^{3}P) products. Using the tunable VUV probe, detection of either the excited atom alone, or both states together was used with momentum-matching to the CS cofragment to map the photochemistry unambiguously for the first time.

In addition to unraveling complex dissociation mechanisms in polyatomic molecules, unique studies of hydrogen abstraction dynamics have been carried out on Endstation 1. These measurements, providing extremely detailed information on the reaction of chlorine atoms with saturated hydrocarbons, yield the identity of the primary reaction products and details of the energy disposal in the reaction. The use of tunable undulator radiation provided the unprecedented ability to probe the reactive hydrocarbon radical fragment directly in these reactions. Initial studies of the reaction of chlorine with propane suggested different dynamics for the forward- and backward-scattered products. More recent studies on reaction of chlorine with n-pentane show that the forward-scattered products are clearly associated with the formation of the lowest energy 2-pentyl radicals, while the backscattered-products arise from close collisions preferentially involving the terminal carbons. The forward scattered products are formed extremely cold, largely beyond the limit for production of the 1-pentyl radicals indicating a "stripping"-type mechanism and a loose transition state for this component of the reaction. For the backscattered-products, however, virtually all of the energy of the collision is deposited into the pentyl radical product, producing extremely hot, reactive products. This is very different from what was observed in other related systems. In fact, previous studies relying on state-resolved laser probing of the HCl have often assumed that no energy is deposited into vibration of the radical product. Beamline results dramatically show that this is incorrect.

Chemistry of Rydbergs and superexcited states

The spectroscopy and decay dynamics of highly excited molecular states has been probed in unprecedented detail in studies on the beamline, and this remains an important area for future exploration. Specifically, breakthroughs achieved on the beamline in coupling pulsed-field ionization photoelectron (PFI-PE) spectroscopy with the high resolution 6.65-m Eagle monochromator have led to the ability to achieve rotationally resolved photoelectron spectroscopy for many molecules on a routine basis. Furthermore, spectra have been recorded for vibrational levels up to the ionic dissociation limits, and for both ground and excited ionic states for many molecules. This is discussed in greater detail in the section below on structure, energetics and reactivity of radicals and transient species.

A further example of new direction on the Beamline is a recent imaging study of SF_6 dissociative ionization dynamics. In this work, detailed energy and angular distributions were obtained for all ionic fragments of SF_6 dissociative ionization from 15.5 to 23 eV. The results provide clear insight into the dissociation dynamics, showing unambiguously that all products result from initial formation of SF_5^+ + F, with subsequent ionic fragments arising from sequential loss of F atoms. This work complements a coincidence study performed on Endstation 2 that is discussed below.

Structure, energetics and reactivity of radicals and transient species

Several aspects of radical energetics and reactivity have been probed in experiments on Endstation 1. Among these are many of the photochemistry studies mentioned above, in which radicals play a significant role as primary photoproducts. In this case, low-resolution photoionization efficiency curves have routinely been obtained for these photofragments, while the energetics and dissociation dynamics are inferred from secondary decay processes. This has been shown for many radicals including propynyl, propargyl, vinyl, chlorovinyl, methylsulfonyl and numerous others. In addition to the photochemistry studies, the Cl abstraction dynamics discussed above represent a model for understanding H abstraction by OH radicals, a key combustion reaction.

As discussed below in the section on molecular structure and spectrscopy, breakthroughs have been achieved in high resolution threshold photoelectron spectroscopy on the beamline that promise unprecedented combination of broad wavelength tunability and laser-like resolution. These techniques will be applied to study the spectroscopy and energetics of radicals in the immediate future.

Inter- and intra-molecular energy relaxation

To date, this has not been a principal focus of the Beamline, although insight into competing relaxation pathways often result for the complex photochemistry studies as mentioned above.

Bond-selective or mode-selective manipulation of molecules

The power of Endstation 1 to reveal complex primary dissociation processes was reviewed in the first section above. Another compelling example of this is in a recent study of the photodissociation of the hydrocarbon isomers propyne (H_3CCH) and allene (H_2CCCH_2). This study relied upon the distinct ionization potentials of the two possible radical products propargyl (H_2CCCH) and propynyl (H_3CCC) to show clearly that the two parent isomers dissociate to give distinct radical isomers as products. Furthermore, in the case of propyne photodissociation this is clearly a bond-selective process, in that the much stronger acetylenic bond is preferentially broken yielding the propynyl radical. Such examples of bond-selective chemistry are rare.

The photoelectron-photoion coincidence (PEPICO) scheme is the combination of the photoionization mass spectrometric and photoelectron spectroscopic methods for the detection of correlated mass-selected ions and energy-selected photoelectrons. It is well established that the PEPICO technique is a general method for state- or energy-selected unimolecular dissociation dynamics studies and is useful for measuring the photoelectron spectrum for a minor radical or size-selected cluster species produced in a radical or cluster source. An extension of this coincidence technique for the correlated detection of energy-selected photoelectrons and secondary ion formed in collisional processes has also been demonstrated as a powerful method for the study of state- or energy-selected ion-molecule reaction dynamics. The development of effective, high-resolution PEPICO scheme is an important scientific direction at the Chemical Dynamics Beamline. Along this direction, we have successfully performed a high-resolution kinetic energy release measurement on SF_n^+ (n=2-5) observed in a PEPICO study of SF_6.

Molecular energetics and spectroscopy

Photoionization mass spectrometry and photoelectron spectroscopy have played a major role in providing accurate energetic and spectroscopic information for atomic and molecular cations. Through proper energetic cycles, highly accurate energetic information for neutral molecular species can also be deduced from photoionization and photoelectron measurements. Energetic information, such as ionization energies (IEs) for molecular species, in which photoionization mass spectrometry and photoelectron spectroscopy have played a major role, is used for prediction of chemical reactivity, and is of fundamental importance to chemistry.

The photoelectron spectrum of a polyatomic molecule usually contains more information on the energetics and spectroscopy of the resulting cation than that revealed in it photoion spectrum. For this reason, the development of high-resolution photoelectron spectroscopic techniques has been a primary pursuit in the field of photoionization and photoelectron studies. Employing the high-resolution VUV facility at the ALS, we have developed a multi-bunch synchrotron based pulsed field ionization-photoelectron (PFI-PE) detection scheme. In this synchrotron based technique, high-n ($n \geq 100$) Rydberg states are field ionized by a small electric field pulse applied in the dark gap of a synchrotron ring period. Using an electron spectrometer equipped with a stearadiancy analyzer and a hemispherical energy analyzer arranged in tandem, we have shown that PFI-PEs can be detected with little prompt electron background for a delay of only ≈8 ns with respect to the beginning of the dark gap. This in essence overcomes the requirement for a delay in the μs range in laser PFI-PE studies. The photon energy range of 6-30 eV obtained in synchrotron studies is far greater than VUV laser sources, meaning that vibronic photoelectron progressions arising from valence shell ionization of all molecular species can be studied in their entirety with near rotational resolution. Using this synchrotron based PFI-PE technique, we have obtained detailed rotationally resolved PFI-PE spectra for O_2, CO, NO, N_2, H_2, HD, D_2, OCS, CO_2, CS_2, and NO_2.

Recently, we have further simplified and improved the PFI-PE detection using a time-of-flight (TOF) selection scheme. This scheme is shown to be more effective in suppressing the hot-electron background. In addition to attaining a high PFI-PE transmission, a major advantage of this TOF scheme is that it allows the use of a smaller pulsed electric field and thus results in a higher instrumental PFI-PE resolution. We have demonstrated a PFI-PE resolution of 1.0 cm^{-1} (FWHM) at 12 eV, corresponding to a resolving power of 100,000. The high resolution, together with the broadly tunable capability demonstrated in synchrotron based PFI-PE experiments, has made the Chemical Dynamics Beamline a world center for research in photoelectron spectroscopy.

3. Scientific Opportunities

The accomplishments outlined above demonstrate the power of the beamline to address fundamental issues in chemical physics, and to open broad fields of study. In this section, we detail some of the specific scientific issues that will be explored on the beamline in coming months. This is by no means an exhaustive list, and a number of additional opportunities have been outlined in the March, 1998 Workshop Report.

Photodissociation of complex molecules.

As demonstrated in the Accomplishments section, one of the most useful and general capabilities of Endstation 1 is in the area of ultraviolet photodissociation of complex molecules. The goal of these experiments is to determine the identity of the photoproducts and to characterize the partitioning of available energy amongst the product degrees of freedom. While this is relatively straightforward to do for small molecules, larger molecules with multiple product channels present a real challenge. The use of tunable VUV ionization of scattered photoproducts instead of electron impact greatly facilitates interpretation of the photodissociation dynamics, because dissociative ionization processes are largely eliminated and one can even distinguish between product isomers with the same mass but different ionization potentials.

As examples of work in progress in this area, the photodissociation of anisole and 1,3 butadiene at 193 nm are being investigated. A prior investigation of anisole using electron impact indicates exceedingly complex dynamics involving as many as 7 distinct channels. Work done at the ALS so far indicates that several of these were essentially due to dissociative ionization, and that the dynamics are actually considerably simpler. In the case of butadiene, there are four distinct product channels involving different product mass combinations. In one of these $C_4H_6 \rightarrow C_4H_4 + H_2$, the identity of the C_4H_4 product is not at all clear, but measurement of the photoionization efficiency curve shows it is most likely due to cyclobutadiene rather than $H_2C{=}C{=}C{=}CH_2$.

These experiments are relatively straightforward and it should be possible to complete them in about 4 weeks, on the average. Thus, this capability of Endstation 1 should be of considerable interest to the large community of chemical physicists interested in photodissociation. This class of experiment represents an excellent opportunity to bring outside users to the ALS for the first time so that they can see firsthand what can be done here.

Photoionization experiments on He droplets

One of the most exciting developments in chemical physics has been the use of ultracold He droplets as a spectroscopic "matrix". These droplets are generated by expanding He cooled by a liquid He refrigerator into a vacuum. They typically consist of ~ 5000 atoms and are ~ 20 Å in diameter with a characteristic temperature of 0.3 K. Several groups (Toennies, Scoles, R. Miller) have shown that these droplets readily absorb (or adsorb) molecules and molecular clusters. Optical spectroscopic measurements on such systems probe a very low temperature regime not generally available to spectroscopists, yielding both spectroscopic simplicity and new physics.

We propose to use the ALS to perform photoionization measurements of molecules, radicals, and clusters on He droplets. The proposed experiments range from investigating the fundamental of ionization of these species to using them as a means of eliminating hot band and isomerization issues that have plagued radical and cluster spectroscopy. In the basic experiment, He droplets pass through a "pickup" source in which they take up the species of interest. One can then measure the photoionization efficiency, the photoelectron spectrum, or perform coincidence experiments. The source is continuous, and therefore is compatible with the cw light coming out of the ALS. The proposed experiments could be performed on Endstation 3 (initial lower resolution, higher signal studies) and Endstation 2 (higher resolution, lower signal).

This project is reasonably long range and will require some source and ion optical development, but will represent an exciting scientific opportunity with true "breakthrough" potential. We envision a collaboration involving several PI's, including D. Neumark (Berkeley), T. Baer and R. Miller (North Carolina), B. Ruscic (Argonne), K. Janda (Irvine), and G. Scoles (Princeton).

Radical Sources and Spectroscopy

In order to extend the now clearly demonstrated basic capabilities of all three endstations, and to begin to fully exploit their outstanding potential, the development and implementation of a variety of radical sources emerges as a clear scientific priority. The overall goal of this effort is multifaceted, and ranges from a variety of direct spectroscopic studies of radicals and other unstable species generated by these sources, to studies of their reactive properties, revealed via photodissociation studies and/or dynamics of chemical reactions. The planned photoionization spectroscopic studies of radicals, which will employ mass-selected photoionization, ZEKE, MATI, PEPICO, etc., are aimed primarily toward deeper understanding of the spectroscopic and thermodynamic properties of key transient species. These species play key roles in a variety of important chemical reactions, ranging from combustion-related processes and related subsequent atmospheric chemistry to those that have direct industrial applications, such as reactions used in semiconductor manufacturing. The spectroscopic data obtained from these studies will determine the photoionization properties of these ephemeral species and hence provide a plethora of basic spectroscopic data, as well as facilitate the determination of their structures, tie into the cycles used to determine thermochemical quantities (IEs), prepare data needed for diagnostic purposes (photoionization efficiency curves, differentiation of isomers via their IEs), etc. Although the primary intent is to carry out these spectroscopic studies on Endstation 2, which exploits its outstanding high-resolution capability, parallel studies directed to obtaining medium-resolution photoionization yield curves complemented by application of imaging techniques will be carried out on Endstation 3, and finally photochemical and reaction dynamics studies will be conducted on Endstation 1. The goal of these studies is a deeper understanding of the important role that these species have in chemical reactions, as well as the development of detection techniques which can be applied to real systems such as flames or internal combustion engines.

On Endstation 2, currently underway is the design and assembly of a laser photodissociation source that will produce thermally equilibrated radicals in a quasi-continuous fashion. Although its primary use will be in the production of radicals equilibrated at 300 K, the source can be easily cooled down to the condensation temperature of the precursor compound, or heated up to 1200 K. Immediately following this development will be the assembly of a laser photodissociation source that exploits the cooling capabilities of jet expansion, hence producing radicals that are quite cold rotationally and at least partly vibrationally relaxed. These two initial laser photodissociation sources will be further complemented by implementing a microwave discharge source and a source that exploits the in situ abstraction reactions with fluorine or hydrogen atoms generated in a microwave discharge. This *in situ* chemical reaction approach has been proven in other laboratories to be a clean source of a very large variety of radicals. Further developments should bring to the beamline additional sources that have been demonstrated to produce a variety of interesting radicals and metastable species, such as an effusive pyrolysis source, corona discharge source, a pyrolysis source coupled to jet expansion from a nozzle, etc. Finally, this set of sources of transient and unusual species will be complemented by the implementation of a high-temperature effusive source, based on a modified Knudsen cell, which will allow the study of high-temperature species.

On Endstations 1and 3, the implementation of a variant of a fluorine atom source based on a DC discharge (rather than microwave discharge) is currently underway. This will be coupled to an *in situ* chemical reaction source of radicals. Implementation of other sources similar and parallel to those described above in conjunction with Endstation 2 will follow briefly.

In a separate development, the coupling of various radical sources with the proposed He droplet source discussed above appears to be potentially a very exciting development. One of the reasons to attempt such coupling emanates from the fact that it is normally very difficult to produce radicals (or other species) that are truly thermally equilibrated to some known sub-cryogenic temperature. This is mainly related to the fact that expansion in a jet, which is the dominant way of generating cold species, is quite efficient in cooling rotational excitations, but significantly less efficient in producing molecules that are vibrationally cold. Furthermore, the final distribution of both rotational and vibrational states is not at all guaranteed to be simply describable in terms of a single-temperature Boltzmann distribution. The idea here is to produce radicals in a variety of sources that are described above, and adsorb these species onto He droplets. Once adsorbed or embedded, the species are expected to be energetically well-equilibrated with the temperature of the super-cold cluster. These adsorbed radicals can then be studied as such, or transformed into free (desorbed) species by stripping the He atoms.

In conjunction with the immediate plans of developing laser photoionization sources, followed by chemical abstraction schemes, a list of about a dozen or so early candidates for study, to be understood only as a brief illustration of the planned activities, is given below:

CH_3 - For a number of reasons this is a very good first candidate for testing the photodissociation source. It has been recently shown that the spectrum of CH_3 is replete with rotational autoionization in the threshold region. This effect is temperature-dependent (through the temperature-dependent population of rotational levels in the initial state) and at lower resolution produces a shift in the apparent photoionization threshold. It is very important to fully understand such an effect if one hopes to use photoionization to detect hot CH_3 radicals in a real system (such as an actual flame). High-resolution photoionization spectra of CH_3, which are fully thermally equilibrated at several temperatures and their comparison to PE spectra obtained on the same machine and using the same conditions, should allow us to fully understand this phenomenon.

CH_2 - Only one photoionization spectrum from the triplet state is known (and none so far from the singlet state), and no PFI-PE data exists for this important radical. Furthermore, it appears that this radical also demonstrates rotational autoionization in the threshold region, similar to that found in CH_3. The photodissociation approach is known to be able to produce selectively only the triplet state or both the triplet and the singlet state of CH_2.

HOCO - This very important radical has a very unfavorable Franck-Condon envelope for ionization, and the current experimental value is known to be only an upper limit to the true IE. The correct value for the IE is desperately needed to complete the thermochemical cycle that provides the heat of formation of HOCO. The number of active modes of vibration and the change in geometry also makes this species very interesting from the spectroscopic and computational viewpoint. Good high resolution photoionization and PFI-PE spectra would significantly aid in solving these open questions.

C_2H_3 - This important species also suffers from unfavorable Franck-Condon factors. One of the current experimental values is believed to be correct, but needs to be verified in order to help anchor the thermochemistry of this species. Hence, for arguments similar to those forwarded for HOCO, high-resolution photoionization and PFI-PE spectra would be highly desirable.

CH_3O -The triplet ground state of CH_3O^+ is strongly predissociated by crossing with a singlet dissociative surface leading to $HCO^+ + H_2$. This results in a metastable CH_3O^+ ion, existing apparently only in the lowest vibrational state. High resolution photoionization and PFI-PE spectra should help understand this important intersystem crossing.

CN- no PFI-PE or photoionization data for this important radical have been reported.

C_2H - no PFI-PE or photoionization data for this important radical have been reported.

CH - no PFI-PE or photoionization data for this important radical have been reported.

CF_3 - This is again a case of very unfavorable Franck-Condon factors. Here direct measurements were always providing only an upper limit to the correct IE, and the more recent lower limit to the IE value inferred indirectly has been subsequently challenged by advocates of a very low IE value.

NH - no PFI-PE or photoionization data for this important radical presently known.

C_3H_3 - The photoionization spectrum of the propargyl radical, including the fragmentation properties, is important for both diagnostic and thermodynamic purposes.

HO_2 - No PFI-PE for this important radical have been reported. Furthermore, a high resolution photoionization study would elucidate the rich autoionization resonances displayed in medium-resolution spectra.

C_2H_5O - although some of the isomers with a C-C-O skeleton have been studied, a thorough high-resolution study of CH_2CH_2OH, which suffers from unfavorable Franck-Condon factors, using both photoionization and PFI-PE would help understand its spectroscopic and thermochemical properties. High resolution photoionization and PFI-PE of the other isomers is also extremely interesting.

Elementary Reactions Of Radicals

One of the central problems in chemistry concerns the determination of elementary reaction mechanisms. Fundamental questions regarding the identity of chemical reaction products and the branching between competitive pathways need to be answered before any deeper understanding of these reactions is possible. Moreover, developing a molecular understanding of chemistry related to combustion will never be possible if these most basic questions cannot be answered.

The crossed molecular beam technique is one of the great technical breakthroughs allowing detailed investigations of elementary chemical reactions and, over the years, has provided perhaps the most powerful approach to the solution of such problems. The study of elementary chemical reactions, particularly the reactions of free radicals, was one of the central goals for which the Chemical Dynamics Beamline was envisioned. Indeed, Endstation 1 was designed specifically with this in mind.

VUV photoionization detection of chemical reaction products in crossed beams experiments offers a number of advantages over conventional electron bombardment ionization detection previously used in crossed beams work. It allows use of a cryogenically cooled detector (15K) resulting in a dramatic background reduction at many masses. Photoionization generally results in limited ion fragmentation meaning that the detected ion has the same mass as the neutral product, simplifying data analysis. Because of the photoionization's tunability, neutrals that result in ions of the same mass-to-charge ratio can be distinguished by differences in their ionization thresholds.

We have demonstrated that ES1 is capable of performing crossed molecular beams experiments with photoionization detection. Specifically, the reactions $Cl + C_3H_8$ and $Cl + C_5H_{12}$ have been carried out; the results of these studies have been presented in the Accomplishments section above. These results give us valuable information for the design and execution of future experiments on chemical reactions of radicals. Clearly these experiments are more difficult than photofragmentation experiments described elsewhere in this document. Two considerations are therefore of utmost importance: 1) optimization of the sensitivity of Endstation 1, and 2) development of ultrahigh intensity radical beam sources.

The NH + NO reaction is well-suited to experiments of this kind on ES1. This prototypical radical-radical reaction (which has been identified as an important reaction in thermal DeNOx) possesses a large reaction cross-section and exhibits competitive chemical branching,

$$\begin{aligned} NH + NO &\rightarrow H + N_2O \\ &\rightarrow OH + N_2. \end{aligned}$$

There remain fundamental unresolved questions concerning its mechanism. A very intense pulsed molecular beam of $NH(X^3\Sigma)$ has recently been developed in Alec Wodtke's laboratory and the kinematics of the reaction are favorable for a crossed molecular beams experiment. A pulsed NH beam (operating at 100 Hz) will be chopped by a slotted chopping wheel to limit the interaction time in the crossing region to $\sim 10^{-5}$ s. This beam will be crossed by a pulsed NO beam. Reaction products will be ionized by the ALS 15 cm away from the crossing region. Measurements of the branching ratio, angular distribution and translational energy distributions will be carried out at two collision energies. We expect that these preliminary studies of NH Chemistry will open up a gold mine of new experiments on reactions of NH with more complex molecules.

A proposal has also been received from Prof. H. F. Davis at Cornell University to use Endstation 1 to study singlet methylene insertion reactions. Prof. Davis has extensive experience in crossed-beam reaction dynamics, and has constructed an apparatus in his laboratory that is quite similar to Endstation 1 but relying on laser and EI based detection. They are currently optimizing the radical source in their laboratory. Once the source is fully optimized, beamline studies of methylene insertion into hydrocarbons can begin, complementing their laboratory studies of reactions producing low-IE products.

Two-color UV-VUV Spectroscopy

One of the important applications in combining third-generation synchrotron radiation with lasers is the use of a tunable laser to excite a molecule to some excited vibrational or electronic state, with the VUV used to ionize, selectively, those that have undergone resonant excitation. A sensitive, ionization-based probe results for excitation in wavelength regions from the near-IR to the UV. Our first application of this method is planned using the new Endstation 3, in a study of the spectroscopy of metastable O_2 (c $^1\Sigma_u^-$) through the little-known ($1^1\Pi_g$) valence state. Recent studies of O_4 photoionization have suggested that this transition is a fully allowed but overlooked, since the upper state was believed to be repulsive.

Threshold Photoelectron Photoion Coincidence Studies

Experimental Development of TPEPICO

State of the art TPEPICO studies with 1 meV energy resolution of internally cold molecules are planned for the spring of 1999. Breakdown diagrams (mass selected fractional ions counts as a function of ion internal energy) obtained from TPEPICO are the most accurate means for obtaining dissociative photoionization onsets ($AB \rightarrow A^+ + B$) through the thermochemical cycle:

$$\text{Fragment Ion Appearance Energy} = \Delta H_f(A^+) + \Delta H_f(B) - \Delta H_f(AB)$$

The key to high resolution involves the use of electron time-of-flight energy analysis and the production of vibrationally cold molecules in the ion source. Even higher resolution may be possible by combining proven PFI-PE techniques with ion detection in coincidence with zero energy electrons.

Planned Studies – Free Radical Heats of Formation

Dissociative photoionization Studies of Alkyl Halides

A considerable body of ion heats of formation for such species as $C_2H_5^+$, $C_3H_7^+$, t-$C_4H_9^+$, etc. has been collected by ion-equilibrium studies and exists in the literature in the form of the proton affinity scale. However, these proton affinities (which can be converted to ion heats of formation) are more accurate relative to each other than they are to an absolute scale. Some key heats of formation that are best obtained through the above mentioned breakdown diagrams anchor the whole scale. Thus, by measuring very accurate dissociative ionization onsets for reactions such as: $RI + h\nu \rightarrow R^+ + I$, we will establish accurate benchmark heats of formation of the R^+ ions which can be used to anchor the proton affinity scale. This study will be done in conjunction with a research group in Madrid, Spain, which will determine accurate heats of formation of the alkyl iodide neutrals by bomb calorimetry.

Once the proton affinity scale is better established on an absolute basis, we can use these values with accurate ionization energies of free radicals (determined on end-station 2) to determine accurate heats of formation of neutral free radicals. Among those to be investigated is the t-butyl radical whose neutral heat of formation is still not well established. These studies will also permit us to determine the first experimental heats of formation of numerous alkyl iodide molecules.

Cluster Studies

The photoionization of dimers will be used to measure free radical heats of formation by the following scheme:

$$B + RH \rightarrow R\text{-}H\cdots R + h\nu \rightarrow BH^+ + R\cdot + e^-$$

where B is a molecule with a strong proton affinity (i.e. a base such as NH_3). By 'pre-dissociating" the R-H molecule within the cluster, the R· group will be in a geometry poised to dissociate with a geometry similar to the free R·. The dimer ion will thus dissociate with no reverse activation barrier. This feature is very important for a free radical such as t-butyl in which the geometry changes considerably upon ionization. Numerous BH^+ ions have well known heats of formation, which should permit the scheme to be applied to numerous reactions.

Threshold Photoelectron Spectroscopy of Aqueous Solutions

M. Faubel and coworkers have pioneered a technique of introducing liquid water and aqueous solutions into vacuum for experiments such as direct sampling of evaporative processes and photoelectron spectroscopy of the liquid. A very recent demonstration experiment has shown the successful application of this remarkable method on Endstation 2, and this clearly represents an exciting area for future work. Important topics include direct probing of energy and structure of ion hydration shells, and insight into the prediction from molecular dynamics simulations that large ions may lose their hydration shells on the water surface. Another important issue amenable to study using tunable synchrotron radiation is the depth profiles of solvated species. These are all experiments that take advantage of the high flux and brightness of the third-generation source.

Essential Hardware

One of the most important priorities to come out of the March, 1998 Workshop was the importance of developing a high-flux, medium-resolution imaging branchline that could serve a variety of users in different experimental modes. This 'Endstation 3' is now being commissioned, with the 3-m Eagle monochromator installation scheduled for June, 1999. This will add important experimental range for many of the experiments listed below.

A clear priority for Chemical Dynamics at the ALS that arises from discussions at the present Retreat, is the urgent need for a small-gap vacuum chamber for beamline 9.0. This is owing to the routine demand for photon energies down to 6 eV, which is currently only accessible when the storage ring operates at energies of 1.5 GeV or lower. As the ALS has moved to ever-increasing demand for 1.9 GeV operation, this represents a serious challenge to our ability to do radical studies in the future. As the 1.9 GeV operation is clearly a priority for ALS, and a small gap vacuum chamber would allow access to low photon energies regardless of the storage ring energy, the possibility of cost sharing with the Advanced Light Source seems feasible.

4. User Program

As demonstrated in the foregoing sections, most of the original experimental objectives for the Chemical Dynamics Beamline have been demonstrated, and a clear vision exists both for the short-term scientific program and long-range scientific goals. Results of these experiments are beginning to show a substantial impact in the scientific literature; beamlines at SuperACO in Paris, the SRRC in Taiwan, and BESSY-II in Germany are duplicating various aspects of the Chemical Dynamics Beamline hardware; and users have come to the beamline from around the world to do experiments. Table I shows a summary of Beamline visitors and their experiments since commissioning in 1995. Table II shows an approximate near-term schedule for the beamline endstations through the next shutdown in June, 1999. Considerable flexibility is built in so that if, for example, the methylene radical source at Cornell is deemed ready for preliminary studies, time can be allocated quickly.

The time is now ripe for new users to take advantage of the unique resources of the facility. One difficulty that arises is a well-known culture gap between the chemical physics community in general and the world of synchrotron radiation research. Researchers in chemical physics have traditionally operated in a single-PI mode very different from the mode of operation at a user facility. Consequently, there is a substantial barrier to undertaking the first experiments on the beamline. Despite this culture gap, several leaders in the chemical physics community have had their first exposure to synchrotron-based experiments in their work on the Beamline, and we have witnessed how this initial exposure has been able to generate enthusiasm for future work at the facility. In light of this observation, one possible solution proposed at the retreat is the development of a competitive funding opportunity for first-time users of the facility. DOE program officers may wish to consider this possibility.

In any event, an aggressive outreach program will be necessary to ensure that an intense, constructive competition exists that fosters the development of the highest quality proposals for work on the Beamline. This outreach program consists of the following components:

- The principal means of acquainting the scientific community with the resources on the Beamline is through presentations at national and international meetings, and publication of results in leading journals. This is a natural outcome of Beamline research, but efforts will be made and resources allocated to ensure that all large-impact meetings will feature presentations of beamline results, and that these presentations will contain relevant outreach information such as resources and contacts.
- A mailing is being developed to remind leading practitioners in the field of experimental chemical physics of the available resources here and the ease with which experiments may be proposed and undertaken.
- Any perceived barriers to ready use of the facility by outside users must be met and dealt with preemptively, whether they relate to housing, transportation costs, or available support personnel.
- Needed resources for priority experiments must be promptly secured.

The Chemical Dynamics Beamline is at an important stage of its development, changing from a program of exploration and demonstration to one of more routine use as a national resource for performing state-of-the-art investigations into chemical reaction dynamics. A vigorous outreach program will ensure that the highest caliber science is undertaken on the beamline.

5. Conclusions

The Chemical Dynamics Beamline at the Advanced Light Source, a unique combination of state-of-the-art molecular beam machines with an array of laser resources and the world's most intense source of continuously tunable vacuum ultraviolet radiation, has clearly opened new doors in the study of chemical reaction dynamics, photoionization dynamics and high resolution photoelectron spectroscopy. The time is now ripe for outside users to come to Berkeley to take advantage of these resources. This report summarizes the recent scientific achievements of the Beamline, and charts a future course including both detailed scientific priorities and an aggressive outreach program to ensure that the Beamline remains at the forefront of research in chemical dynamics.

Table I. Beamline visitors 1996-1999.

Date	Visitors	Experiments	Estation	Weeks
5/15/96 - 6/21/96	Dr. Tom Baer Jeff Keister	TPEPICO setup TPEPICO study of 1,3-butadiene methylcyclopropene dimethylamine dimer	2	5
8/96-10/96	Dr. Simon North Dr. Greg Hall	CH_3CN Photodissociation C_2H_3CN	1	8
6/1/96-6/21/96	Prof. Paul Houston	Vibrationally inelastic scattering	1	3
11/12/96 - 11/20/96	Dr. John Hepburn Dr. Michael White Dr. Ed Grant Dr. Phil Johnson	PFI-PE study of acetone benzene & d6-benzene cyclopropane NO_2 HCl	2	1
3 weeks-96	Prof. Wm Jackson	VUV Photochemistry	1	3
4/9/97 - 4/19/97	Dr. John Hepburn Dr. Ralph Shiell	PFI-PE study of CH4, CO, Xe, HCl, & C_4H_6 TPEPICO study of CH_4	2	2
3 weeks-97	Prof. Wm Jackson	VUV Photochemistry	1	3
4/1/98-6/8/98	Prof. D. Neumark	UV Photodissociation C_3H_3Br C_3H_4	1	8
8/24/98 - 9/24/98	Dr. Rick Lafleur (Dr. Tom Baer)	2-bunch ZEKE setup	2	4
10/6/98-10/29/98	Prof. S. North	Photodissociation of CS_2, $CHBr_3$	1	3
12/8/98-12/15/98 1/6/99-1/25/99	Prof. D. Neumark	Photodissociation of Anisole	1	4
12/8/98 - 12/22/98	Dr. Ed Grant	PFI-PE study of NO_2	2	2
1/10/99 - 1/18+/99	Dr. Manfred Faubel Mirko Dittmar	H_2O jet setup & photoelectron studies	2	2

Table II. Chemical Dynamics Beamline visitor schedule January-June, 1999.

Week	ALS Mode	Visitors	Experiments	Estation
Jan 4-10	1.9 GeV MB	Prof. M. Faubel	Water Jet TPES	2
		Prof. D. Neumark	Anisole Photochemistry	1
Jan 11-17	1.9 GeV MB	Prof. M. Faubel	Water Jet TPES	2
		Prof. D. Neumark	Anisole Photochemistry	1
Jan 18-24	1.9 GeV MB	Prof. M. Faubel	Water Jet TPES	2
		Prof. D. Neumark	Anisole Photochemistry	1
Feb 1-7	1.9 GeV MB	Dr. B.Ruscic	Laser Radicals	2
		Dr. B. Ruscic	Discharge radicals	3
Feb 8 -14	1.9 GeV MB	Dr. B.Ruscic	Laser Radicals	2
		Dr. B. Ruscic	Discharge radicals	3
Feb 15-22	1.9 GeV MB	Dr. B. Ruscic	Laser Radicals	2
Feb 23-28	1.9 GeV MB	Prof. K. Weitzel Prof. T. Baer	PFI-PE	2
Mar 1-7	1.9 GeV 2B	Prof. T. Baer Prof. K. M. Weitzel	TPEPICO	2
Mar 8-14	1.9 GeV 2B	Prof. T. Baer Prof. K. M. Weitzel	TPEPICO	2
Mar 15-21	1.9 GeV MB	Prof. T. Baer	PFI-PE/TPEPICO	2
Mar 22-28	1.9 GeV MB	Prof. T. Baer Prof. K. M. Weitzel	PFI-PE/TPEPICO	2
Mar 29-Apr 4	1.9 GeV MB	Prof. T. Baer	TPEPICO	2
Apr 5-11	1.5 GeV MB	Prof. T. Baer	TPEPICO	2
Apr 5-11	1.5 GeV MB	Prof. D. Neumark	Anisole/Butadiene	1
Apr 12-18	1.9 GeV MB	Prof. T. Baer	PFI-PE/TPEPICO	2
Apr 19-25	1.9 GeV MB	Prof. T. Baer	PFI-PE/TPEPICO	2
Apr 26-May 2	1.9 GeV MB	Prof. T. Baer Dr. B. Ruscic	TPEPICO/Radicals	2
May 3-9	1.5 GeV MB	Prof. T. Baer Dr. B. Ruscic	TPEPICO/Radicals	2
May 3-9	1.5 GeV MB	Prof. R. Bersohn	CH4 VUV PD	3

May 10-17	1.9 GeV MB	Prof. T. Baer Dr. B. Ruscic	TPEPICO/Radicals	2
May 18-24	1.9 GeV MB	Prof. R. Bersohn	CH4 VUV PD	3
May 18-24	1.9 GeV MB	Prof. T. Baer Dr. B. Ruscic	TPEPICO/Radicals	2
May 25-30	1.9 GeV MB	Prof. R. Bersohn	CH4 VUV PD	3
May 25-30	1.9 GeV MB	Prof. T. Baer	TPEPICO	2

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098