

1. Introduction

Application of the universal crossed molecular beams method to problems in bimolecular scattering and photodissociation have had a profound impact on our understanding of the underlying mechanisms of chemical reactions.¹ In most cases these experiments achieve universality in product detection by means of electron impact (EI) ionization.² Product angular and translational energy distributions are measured by time-of-flight of the neutral products. With the use of EI, a very steep price is paid to achieve the universality that has led to so many successful experiments. Principal among these shortcomings of EI based experiments is fragmentation of the neutral molecules leading to appearance of the product ion at a different mass-to-charge ratio than that of the neutral. This greatly complicates interpretation of the experimental results, particularly for complex molecules and hydrocarbons where fragmentation is especially troublesome. The development of third generation synchrotron radiation sources with associated VUV photon fluxes greater than 10^{18} photons/cm²/s has opened the door to a new era in universal crossed-beam scattering studies relying on VUV photoionization (PI) rather than EI. A universal crossed molecular beam endstation employing tunable undulator radiation for product photoionization based detection has recently been constructed on the Chemical Dynamics Beamline³ at the Advanced Light Source.⁴ This chapter will be devoted to introducing this apparatus and documenting the range of experiments that can be carried out.

2. Experimental

The endstation is based in principle on a single molecular beam source apparatus⁵ employing EI detection that has been used very successfully for photochemistry studies. The design has been adapted to feature two crossed molecular beams along with oil free pumping to ensure compatibility with the synchrotron storage ring vacuum requirements.

The machine, shown schematically in Fig. 1, features two differentially pumped molecular beam sources each of which is pumped by 2000 l/s high throughput magnetic bearing turbomolecular pumps. The sources are fixed at 90° and housed in a chamber that rotates about an axis parallel to the undulator probe beam. The molecular beams cross inside a main chamber pumped by a 2000 l/s turbopump. Scattered products fly out of the interaction region and those that enter a small aperture pass into a

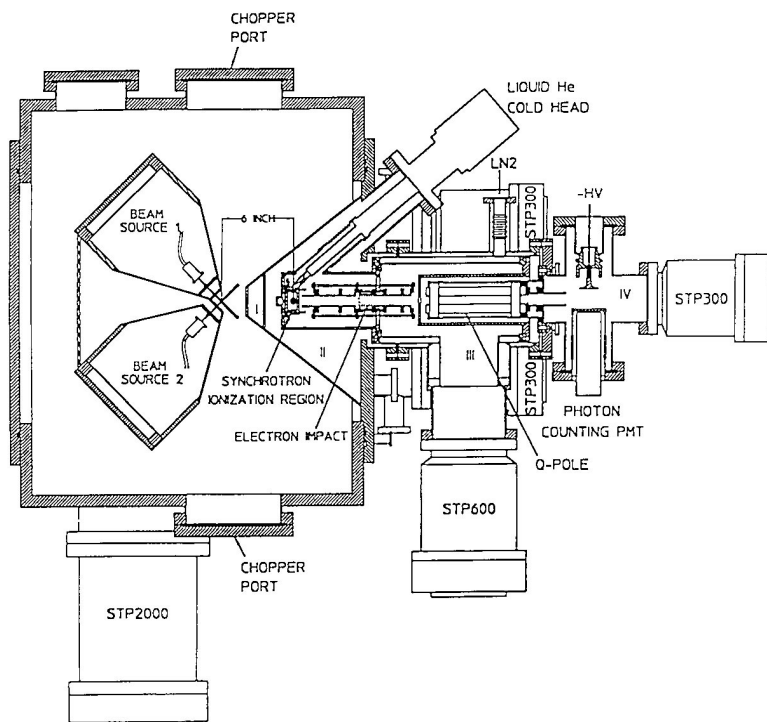


Fig. 1. Schematic diagram of the universal crossed molecular beams apparatus with synchrotron photoionization product detection (Endstation 1).

triply differentially pumped UHV detector region which with pressures maintained typically about 10^{-10} Torr. Product detection is accomplished by ionization of the neutral fragments some 15 cm from the interaction region by tunable undulator light. The characteristics of the undulator radiation “white beam” are a flux of 10^{16} photons/second with an energy spread of 2.2% FWHM. The resulting ions are then extracted from the ionization region, mass selected by means of a quadrupole mass filter and then counted using a Daly ion detector. The data is then recorded as a function of time and scattering angle to reconstruct the primary product velocity distributions from the scattering or photochemical event. The use of tunable undulator radiation based PI in place of EI has many compelling advantages. First, as mentioned earlier, EI leads to dissociative ionization of parent and product molecules resulting in very large backgrounds at certain masses greatly complicating interpretation of the experimental results. Universal PI

based detection, on the other hand, can be used in such a way that it is at once selective and universal. The photon energy can be tuned so that the molecule of interest can be detected but below the threshold for any dissociative ionization process. A second shortcoming of EI is that hot filaments are used to produce the flux of electrons. These filaments typically operate at temperatures of around 2000°C, resulting in much higher partial pressure of background gases and further contributing to background interference problems. Yet another difficulty of EI is that, in order to minimize space charge problems, the size of the ionization region has to be large, typically on the order of 1 cm. As a result, this leads to an associated uncertainty in the point of ionization and a corresponding uncertainty in the velocity inferred from the time of flight measurement. The undulator beam from a third generation synchrotron source, on the other hand, can be focused to yield a very small ionization volume. In this apparatus it is on the order of 0.25 mm in length. In consequence the location of the ionization region is very well determined, so that this contribution to the velocity uncertainty is negligible. Finally, the use of a cold photon beam in place of the hot filament allows us to use liquid helium cooling for cryopumping around the ionization region. In addition to the practical advantages sketched above for photoionization vs. EI, PI offers new opportunities simply not available to EI based systems. In particular, photoionization efficiency (PIE) curves for products can be measured, providing some information on the ionization thresholds for products, and insight into the internal energy content or electronic state of the product.

Figure 2 illustrates some of the advantages of PI over EI based studies. This figure shows a pair of time-of-flight spectra resulting from photodissociation of methylamine at 193 nm, specifically looking at the methyl + NH₂ channel. This channel is a minor channel, less than 1% of the total dissociation yield. Using EI, the methyl at m/e 15 is notoriously difficult to detect owing to interference from methane, a common contaminant in most machines. This methane contaminant also contributes signal at mass 16, where NH₂ would appear, making detection of either of these species extremely problematic in EI based machines. As can be seen in Fig. 2, very good signal-to-noise is obtained with just 4×10^5 laser shots for both of these species, despite the fact that this is a minor channel. The solid lines show excellent momentum matching between the two cofragments. In addition to the improved signal-to-noise from reduced background contributions, there is no evidence of dissociative ionization that would complicate

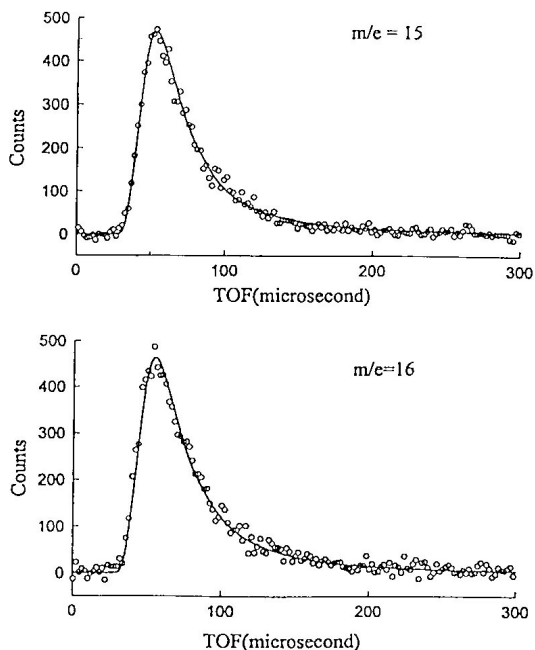


Fig. 2. Time-of-flight (TOF) spectra of photodissociation products of methylamine ($\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3^+\text{NH}_2$) at 193 nm: the upper trace shows the TOF spectrum for the CH_3 radical detected at $m/z = 15$; the bottom trace results from the NH_2 radical, detected at $m/z = 16$. There is no evidence of the much more likely H atom loss channels because dissociative ionization of the CH_2NH_2 or CH_3NH radicals is suppressed by use of photoionization. Note that detection of reaction products at $m/z = 15$ and 16 is easily accomplished despite the large residual CH_4 background.

interpretation of these spectra. The dominant photoproduct in these experiments would be CH_2NH_2 , the H loss channel, which in EI studies would overwhelm both the mass 15 and mass 16 primary products.

Figure 3 illustrates an additional feature of PI: the product internal states can be probed by varying the wavelength of the probe light. Shown in Fig. 3 are a series of time-of-flight spectra for the O_2 product from ozone photodissociation at 193 nm. The peaks are marked showing the dominant channels assigned in previous work.⁶ The use of the tunable VUV allows for discrimination successively between the ground state O_2 (X) product (the fastest peak) the O_2 $a(^1\Delta_g)$ state (the dominant peak at the low photon energy), and the $b(^1\Sigma_g^-)$ state, and finally highly vibrationally excited levels of the ground state. No practical analogy exists in EI based studies.

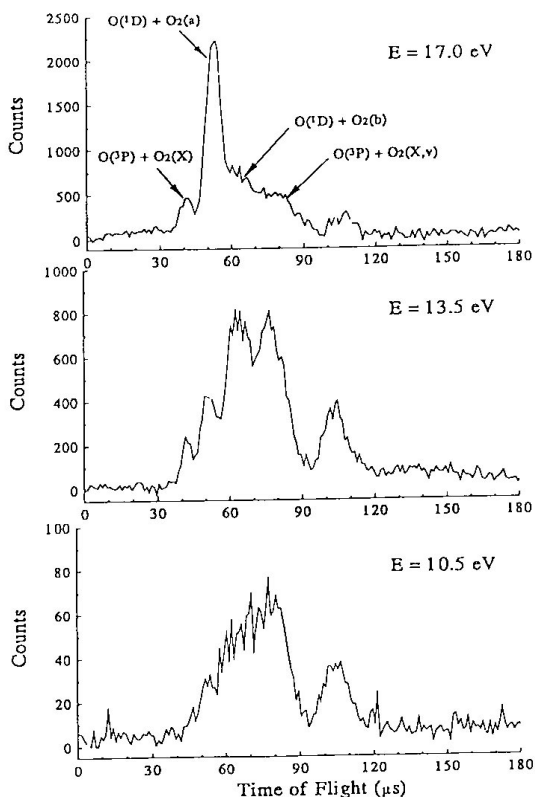


Fig. 3. Time of flight spectra of $m/e = 32$ from ozone photodissociation at 193 nm detected at $\Theta = 20^\circ$. Upper: ionization energy 17 eV, middle: 13.5 eV, lower: 10.5 eV. TOF peaks are labeled consistent with results from Ref. 2. D. Stranges, X. Yang, J. D. Chesko and A. G. Suits, *J. Chem. Phys.* **102** (15), 6067 (1995).

3. Photochemistry

3.1. Dimethyl Sulfoxide

Among the compelling advantages of PI-based photodissociation studies using photofragment translational spectroscopy (PTS) is the ability to study complex systems and complex dissociation processes in great detail. This is well illustrated in the recent study⁷ of the photodissociation of dimethyl sulfoxide (DMSO). Earlier investigations based on state-resolved resonance enhanced multiphoton ionization (REMPI) probe of the methyl radical in conjunction with laser induced fluorescence (LIF) studies on