

Photodissociation Dynamics Studies Using Molecular Beams

The studies of bimolecular and unimolecular reactions using molecular beam techniques have greatly improved our understanding of chemical reactions. The angularly resolved time of flight (TOF) method for reactive scattering studies gives us the information that is needed to understand the detailed dynamics of reactive processes. VUV light sources have been extensively used as an ionization tool in chemical dynamics studies. Intense VUV light sources up to 17 eV photon energy can now be obtained using various nonlinear optical methods. Using coherent VUV light as the ionization detection tool in TOF measurements, instead of high energy electrons (~60 eV), has many advantages over the widely used electron bombardment ionization method, such as species detection selectivity as well as universal detection ability. However, in order to make the VUV ionization a universal detection tool for chemical dynamics research, it has to meet the following two criteria: high VUV photon flux (high enough sensitivity) and wide range tunability. The third generation synchrotron radiation source at the National Synchrotron Radiation Research Center (NSRRC) has provided us with such an ideal light source.

The NSRRC is one of the first low emittance, third generation synchrotron radiation facilities available. The design of the NSRRC is optimized for insertion devices (undulators, wigglers) which produce tunable VUV to X-ray radiations with much higher photon fluxes than bending magnets. A U9 (9 cm period magnets) undulator has been constructed for the generation of VUV light. A beamline dedicated for chemical dynamics research has been constructed using the U9 undulator, providing $\sim 10^{16}$ photon/s (2% bandwidth) VUV light, tunable from 5 to 30 eV. The higher order radiations of the light generated in the undulator are filtered out by a gas filter. The fundamental undulator radiations are then directed to the rotating source, crossed molecular beam machine on the white light beamline.

The new rotating source, crossed molecular

beam apparatus has been set up primarily for two types of experiments: (1) crossed molecular beam reactive scattering studies using synchrotron radiations or electron impact ionization as the detection scheme; (2) photodissociation studies using synchrotron radiations or electron impact ionization as the detection method. The main detector is, therefore, equipped with a VUV ionization detector. Figure 1 shows the crossed molecular beam apparatus at the chemical dynamics beamline of the NSRRC. It has three main parts: the rotatable source, the main chamber and the detector. The rotating source has two source chambers, each of which has a differentially pumped region. The main chamber can be maintained at 10^{-8} Torr vacuum. In order to isolate the ionization region from the main chamber, two differential regions are present. Region I is the first differential region that isolates the main chamber and the detector. Region II is the ionization region, which includes a VUV ionizer, an electron bombardment ionizer and ion optics to transport ions. This region is cooled

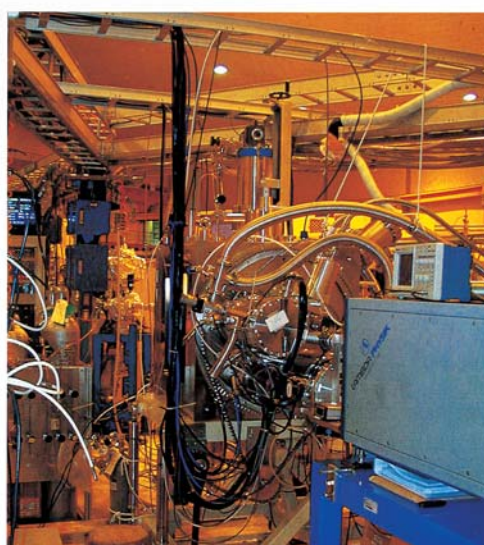


Fig.1: The rotating source crossed molecular beam apparatus at the chemical dynamics beamline of the NSRRC.

down to the liquid nitrogen temperature with a 10 K cryopump, capable of creating an ultimate vacuum of 3×10^{-12} Torr. Quadrupole (Extrel) mass selection then follows in region III which also houses a standard Daly ion detector.

This apparatus has been used to study photodissociation dynamics of many interesting molecules recently. In this highlight, we would like to provide a couple of examples that exhibit interesting dynamics in the photodissociation processes.

Photodissociation of Cyclopropane: Concerted Triple Dissociation

Photodissociation of cyclopropane at 157 nm has been studied using the molecular beam apparatus at the chemical dynamics beamline. Four different dissociation channels have been observed: H atom formation channel, H₂ formation channel, C₂H₄ + CH₂ channel and C₂H₃ + CH₃ channel.

One of the most interesting dynamical information obtained is the observation of the triple H atom elimination channel. Kinetic energy distribution (KED) for the H atom product could be obtained from fitting the TOF spectra at mass 1 assuming that the H atom is from a binary dissociation. The kinetic energy distribution determined from fitting mass 1 TOF spectra is shown in Fig. 2. Signals at mass 40 can also be simulated assuming that the signals are from a binary H atom loss channel. In this way, we assume that the mass 41 parent products from the binary H atom elimination are not stable upon VUV ionization and they subsequently crack to lower mass products. The kinetic energy distribution determined from fitting the TOF spectra at mass 40 is also shown in Fig. 2, assuming all these signals are from a binary H atom elimination channel. The two kinetic energy distributions obtained from mass 1 and mass 40 apparently show very significant differences. The difference between the kinetic energy distributions obtained from mass 1 and mass 40 is clearly not due to any strange experimental artifact. It is rather from the peculiar dissociation dynamics of the two photofragments.

From careful analyses, we conclude that these products could not come from a simple binary H atom dissociation channel simply because kinetic

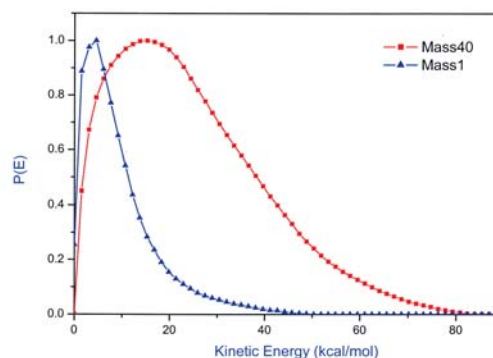


Fig. 2: The kinetic energy distributions obtained from simulating the TOF spectra of masses 1 and 40, assuming both products are from the H-atom elimination process.

energy distributions for the two products could not match each other. From the energetic limit of the H atom product, the H atom products are more likely to come from a triple product channel in which two hydrogen atoms are eliminated. There are a few possible pathways shown in the energetic diagram: allene (=C=C) + 2H, propyne (CH₃C≡CH) + 2H, and *c*-C₃H₄ + 2H. Energetically, since the cut-off of the KED for the H atom products is about 40 kcal/mol, the H product is likely produced by the first two processes, which have available energies of about 45 kcal/mol, and not by the *c*-C₃H₄ + 2H process, which has an available energy of only 23 kcal/mol. Both of the first two reaction pathways involve the ring-opening and new bond formation processes. However, additional H-migration process is also needed for the formation of propyne. Therefore, the allene + 2H dissociation channel might be more favorable than the channel that involves propyne. Such a process could also account for the observation that the mass 40 signals appear to be noticeably faster than a simple binary H atom dissociation because the C₃H₄ radical receives kicks from two H atoms rather than a single H atom. The observation of a concerted dissociation mechanism for the two H atoms from cyclopropane is very interesting.

It is expected that soft VUV ionization will cause much less fragmentation than electron impact ionization at high energies, thus making the detection and analysis of multiple channel reaction processes more straightforward. Since the VUV synchrotron radiations are tunable, different photon energies are conveniently used to ionize the reaction products in order to clarify the

dissociative ionization problem. Figure 3 shows the TOF spectra of masses 26, 27 and 28 from cyclopropane photodissociated at 157 nm, and with its dissociation products photoionized at three different VUV energies from 11 eV to 13 eV. From this figure, it is obvious that the dissociative ionization is significantly reduced as the photon energy decreases. The signals at mass 26 in the TOF spectra are clearly due to dissociative ionization from the parent products of mass 28 (C_2H_4) and mass 27 (C_2H_3). Relatively, signals at mass 26 are significantly smaller at 11 eV ionization energy, in comparison with those at 12 or 13 eV.

Photodissociation of CH_3Cl : Direct Molecular HCl Elimination

Photodissociation of CH_3Cl has been studied previously at 193.3 nm, 157.6 nm, and 121.6 nm. Previous experimental studies show that the dominant dissociation channel is the C(Cl bond fission at wavelengths longer than 157 nm, while the C(H bond fission becomes more important at 121.6 nm. However, no experimental results on dissociation channels other than the $CH_3 + Cl^*/Cl$ and $H + CH_2Cl$ channels have been reported. In the present study, we have used the molecular beam apparatus at the chemical dynamics beamline to investigate

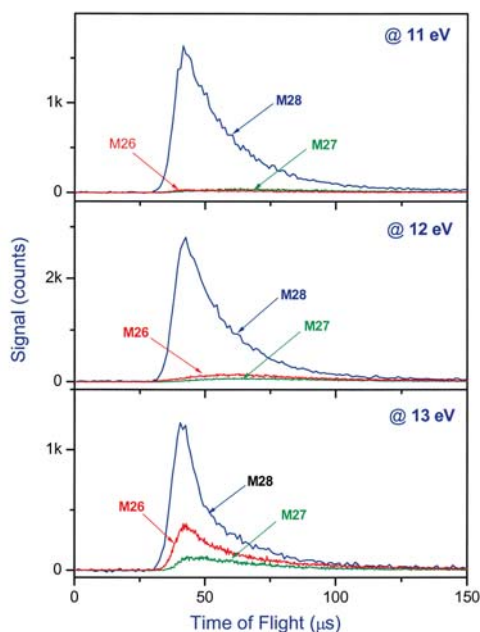


Fig. 3: The TOF spectra of masses 26 to 28 using three different VUV ionization energies from 11 to 13 eV.

the CH_3Cl photodissociation dynamics at 157.6 nm. Three dissociation channels have been observed: the $CH_3 + Cl$ channel, the $H + CH_2Cl$ channel, and the $HCl + CH_2$ channel. The $CH_3 + Cl$ channel and the $H + CH_2Cl$ channel are found to be very fast dissociation processes on repulsive potential surfaces, similar to the dissociation process through the A band. In addition, molecular HCl elimination channel has also been observed.

TOF spectra (Fig. 4) of mass 14 at the laboratory angle of 70° with ionization photon energies from 10.3 eV to 13.8 eV were also measured. A careful experimental measurement indicates dissociative ionization of CH_3 caused by VUV ionization is very small. This result implies that the signal observed at mass 14 (CH_2^+) from photodissociation of CH_3Cl is due to the CH_2 product from HCl elimination. Two peaks (fast/slow) are observed at higher ionizing photon energies. The fast peak becomes weaker and almost disappears at lower ionizing photon energies. Similar double peak structures are also observed in the TOF spectra at mass 36 (HCl^+). The $P(E_T)$'s and the relative branching of fast/slow $CH_2 + HCl$ channels obtained are shown in Fig. 5. The TOF spectra of mass 36 detected at photon energies from 15 to 21 eV can also be simulated using the same $P(E_T)$'s. The fast $P(E_T)$ peaks at 80 kcal/mol are very close to the energetic limit of the $CH_2\tilde{X}^3B_1 + HCl$ dissociation channel, indicating that this component is due to the triplet methylene $CH_2\tilde{X}^3B_1 + HCl$ channel, while the slow peak is

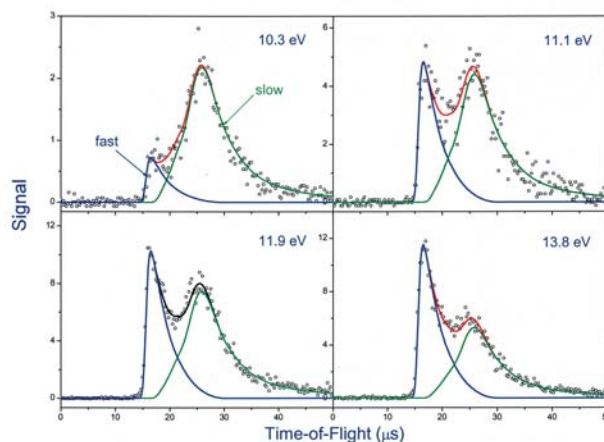


Fig. 4: The TOF spectra of mass 14 detected at ionizing photon energies of 10.3 eV, 11.1 eV, 11.9 eV, and 13.8 eV at 70° lab angle. Circles: experimental data; solid lines: simulation. The simulation uses the $P(E_T)$ shown in Fig. 5a and the weighting shown in Fig. 5b.

attributed to the $\text{CH}_2(\tilde{a}^1\text{A}_1) + \text{HCl}$ channel.

One of the most interesting observations for the $\text{CH}_2\tilde{\text{X}}^3\text{B}_1 + \text{HCl}$ channel is that the majority (75%) of the available energy is deposited to the translational degree of freedom, implying that this channel is more or less a direct and fast dissociation process. The average internal energy of the products is only about 23 kcal/mol. This is quite surprising for a molecular elimination channel since molecular elimination processes normally exhibit a more statistical type of behavior in which the majority of the available energy is deposited into the internal degrees of freedom. The distance between H and Cl in the parent molecule is much longer (2.4 Å) than that of HCl (1.3 Å) in its ground state. The low internal excitation of the HCl product indicates a transition state with H—Cl distance more similar to the HCl product. After passing through this transition state, a repulsive potential energy surface is likely responsible for a large translational energy deposition. For the slow $\text{CH}_2(\tilde{a}^1\text{A}_1) + \text{HCl}$ channel, the $P(E_T)$ peaks at about 30 kcal/mol with an available energy

of about 80 kcal/mol. Therefore, the majority (~ 63%) of the available energy is distributed into the internal degrees of freedom for this channel, which implies that the dissociation of this channel occurs most likely on the ground state potential.

From the above two examples, we have shown the advantages of using VUV synchrotron radiations as a tool for chemical dynamics research. In addition to these two systems, many other interesting systems have also been investigated using this apparatus. We are also planning to develop interesting radical sources for crossed molecular beam, reactive scattering studies in the near future.

Beamline:

21A1 U9/Chemical Dynamics beamline

Experimental Station:

Chemical dynamics end station

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Publications:

- C. C. Wang, J. Shu, J. J. Lin, Y.T. Lee, and X. M. Yang, *J. Chem. Phys.* **117**, 153 (2002).
- S. H. Lee, Y.-Y. Lee, Y. T. Lee, and X. M. Yang, *J. Chem. Phys.* **119**, 827 (2003).
- J. J. Lin, Y. Chen, Y. Y. Lee, Y. T. Lee, and X. M. Yang, *Chem. Phys. Lett.*, (accepted).
- I.-C. Lu, J. J. Lin, S.-H. Lee, Y. T. Lee, X. M. Yang, *Chem. Phys. Lett.*, (in press).
- Y. Y. Lee, Y. T. Lee, and X. M. Yang, (in preparation).
- R. E. Continetti, B. A. Balko, and Y. T. Lee, *J. Chem. Phys.* **89**, 3383 (1988).

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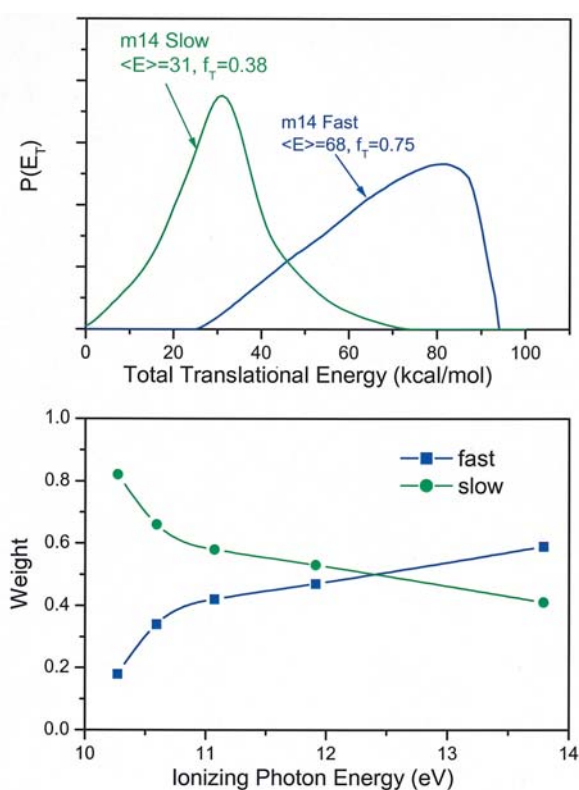


Fig. 5: a) The translational energy distributions for fast and slow $\text{CH}_2 + \text{HCl}$ channels. b) The weighting of the fast and slow $\text{CH}_2 + \text{HCl}$ channels used in the simulation at various ionizing photon energies.