

Universal Detection of Reaction Products

The combination of a time-of-flight (TOF) mass spectrometer with a photon ionizer using tunable vacuum-ultraviolet (VUV) light has achieved universal detection of reaction products. Compared with the similar experimental setup at the Advanced Light Source in Berkeley, the crossed-molecular-beam apparatus at NSRRC has higher detection sensitivity. NSRRC Chemical Dynamics beamline can provide VUV light at high flux, albeit low resolving power, as an ionization source and allows scientists to distinguish two species having almost identical mass but from different reaction pathways. Products from photodissociation of several polyatomic molecules have all been successfully detected thus their branching ratios, kinetic-energy distributions, and angular anisotropies are measured unambiguously. This detection scheme is also applicable to crossed-beam reactions.

The success in probing reaction products relies on a powerful experimental setup. A molecular-beam apparatus coupled with an ionizer is common equipment in chemical dynamics research; electron-impact ionization and photoionization are two typical approaches in detecting products in the gas phase. The detection scheme of electron-impact ionization has been widely employed in mass spectrometers due to affordable cost and universality. However, a typical electron ionizer with electron energy of ~ 60 eV can cause fragmentation of species after ionization (i.e., dissociative ionization) and has no resolving power in species and quantum states. By contrast, photoionization has less dissociative ionization and larger resolving power due to its tunability and small bandwidth in photon energy. The Chemical Dynamics beamline at NSRRC can provide VUV photons at $\sim 1 \times 10^{16}$ photons s^{-1} and a bandwidth ($\Delta E/E$) of $\sim 3\%$ for ionization of reaction products. The photon energy is tunable from 5 eV to 100 eV. Direct VUV ionization is a universal detection method, i.e., all species can be ionized with a single VUV photon as long as the photon energy is higher than the ionization energy of the species.

Figure 1 shows the crossed-molecular-beam machine that consists of a main chamber, a rotating source assembly, a chopper assembly, a set of ion optics, a quadrupole mass filter, a Daly-type ion counter, a liquid nitrogen trap, a He refrigerator, and many vacuum pumps. The source assembly can generate two molecular beams crossing at 90° for a collision reaction and is rotatable from -20° to 110° with respect to the detection axis. For an experiment of molecular photodissociation, laser light used for photolysis propagates into the molecular-beam machine and perpendicularly intercepts a molecular beam. After a flight along a path of 100 mm, reaction products are ionized with the VUV synchrotron radiation. The ion optics extracts

product ions into the quadrupole mass filter for the selection of a mass-to-charge ratio. Subsequently, the Daly-type ion counter transfers the ion signals to a multichannel scaler to display the signals with respect to the flight time. The homemade quadrupole mass filter has a larger size and thus a greater throughput than a commercial one (EXTREL) by a factor of 2.2. The use of a liquid nitrogen trap and a He refrigerator reduces background pressure in the ionization region to 5×10^{-12} Torr, which makes the detection of H_2 product feasible.

A quadrupole mass filter coupled with an electron ionizer cannot distinguish two species with almost identical mass unless they have a large difference in kinetic energy and thus can be separated completely in TOF distributions. Ionization using tunable VUV photons has selectivity on species and quantum states, depending on the



Fig. 1: Photograph of the crossed-molecular-beam apparatus. Laser light propagates from the left to the right while ionization light (i.e., synchrotron radiation) counter propagates with a horizontal offset of 100 mm from the laser light.

energy resolution of the VUV photons and the difference in ionization cross sections of the species.

In the following, three examples on the photodissociation of ethene (CH_2CH_2), propene (CH_3CHCH_2), and methanol (CH_3OH) at 157 nm are discussed to elucidate the merits of this experimental approach using photofragment translational spectroscopy coupled with tunable VUV ionization.

In the photolysis of ethene and its isotopomers, four dissociation channels namely $\text{C}_2\text{H}_3 + \text{H}$, $\text{C}_2\text{H}_2 + 2\text{H}$, $\text{C}_2\text{H}_2 + \text{H}_2$, and $\text{CCH}_2 + \text{H}_2$ have been identified in the VUV region. Nascent C_2H_3 fragment can further decompose to C_2H_2 and H , if C_2H_3 has enough internal energy to overcome its dissociation barrier. A mechanism of four-center (1,2) elimination of H_2 leads to the production of C_2H_2 (ethyne) and of three-center (1,1) elimination leads to the production of CCH_2 (vinylidene). Lin *et al.* have investigated the photodissociation of ethene using a photofragment translational spectrometer and an electron-impact ionizer. However, only the TOF spectra of atomic H and H_2 were reported; products of C_2H_3 , C_2H_2 and CCH_2 suffer from too severe dissociative ionization to be successfully detected. In our experiment we can detect all the

fragments using tunable VUV ionization. Figure 2 shows the TOF spectra of H , H_2 , C_2H_2 , and C_2H_3 from photolysis of ethene with an excellent ratio of signal to noise. The observed C_2H_3 product has a narrow TOF distribution because internally hot C_2H_3 with small kinetic energy decomposes to $\text{C}_2\text{H}_2 + \text{H}$. The C_2H_2 component appears in the lower right panel of Fig. 2. We have partitioned the TOF spectrum of atomic H into three components (not shown here); one component is primary H correlating with the survived C_2H_3 and the other two components are primary H and secondary H after a process of three-body dissociation. As a result, the rapid component of C_2H_2 correlates with H_2 and the slow component of C_2H_2 is due to 2H elimination. Because the rapid component of C_2H_2 , which includes CCH_2 , has larger internal energy than the slow component, we can observe the former by using VUV photons at 9.5 eV. We have determined branching ratios, kinetic-energy releases, and angular anisotropy parameters of all products and revealed their site and isotopic effects. We conclude that at 157 nm ethene is excited either to the 1^1B_{1u} state or to the 1^1B_{1g} state that borrows intensity from the former; subsequently, ethene relaxes back to the electronic ground state through internal conversion followed by fragmentation.

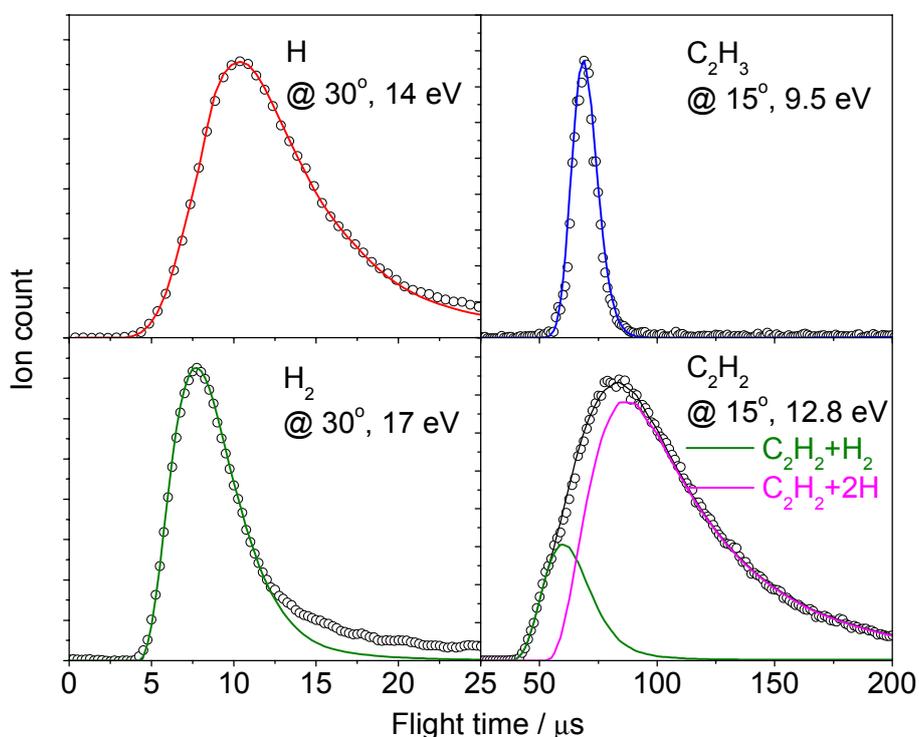


Fig. 2: TOF spectra of H , H_2 , C_2H_2 , and C_2H_3 produced from photolysis of ethene at 157 nm. Laboratory angle and ionizing photon energy are shown in the panels. Only the leading part of atomic H correlates with C_2H_3 ; the rest is due to 2H elimination. The rapid component (green) of C_2H_2 correlates with H_2 and the slow component (magenta) of C_2H_2 reflects 2H elimination.

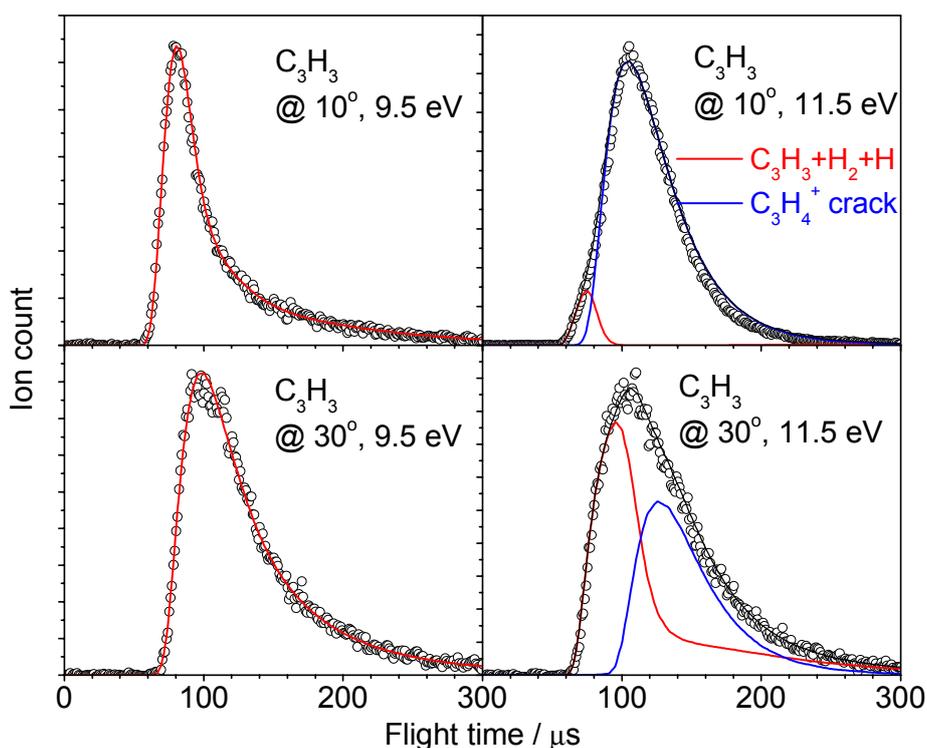


Fig. 3: TOF spectra of mass 39 (C_3H_3) produced from photolysis of propene at 157 nm. These TOF spectra were recorded at laboratory angles 10° and 30° using 9.5-eV and 11.5-eV photons. In the 9.5-eV panels, only the C_3H_3 product (red line) is observed. A slow component (blue line) appears in the 11.5-eV panels and is attributed to dissociative ionization of the C_3H_4 product.

To demonstrate the capability of the experimental apparatus, we have performed an extensive experiment on the photodissociation dynamics of propene and its isotopomer CD_3CHCH_2 at 157 nm. Upon photolysis of propene, we observed 11 fragments correlating with eight dissociation channels: $C_3H_5 + H$, $C_3H_4 + 2H$, $C_3H_4 + H_2$, $C_3H_3 + H_2 + H$, $C_2H_4 + CH_2$, $C_2H_3 + CH_3$, $C_2H_2 + CH_4$, and $C_2H_2 + CH_3 + H$ with a branching ratio of 0.01, 0.07, 0.002, 0.17, 0.06, 0.04, 0.05, and 0.60, respectively. Due to the large excitation energy, three-body dissociation, particularly $C_2H_2 + CH_3 + H$, dominates in the multi-channel decomposition of propene. To our best knowledge, this is the only available example so far to produce methane from photolysis of hydrocarbons. The work on photolysis of CD_3CHCH_2 reveals a site effect on elimination of atomic and molecular hydrogen and indicates that a fraction (25%) of propene undergoes hydrogen migration prior to fragmentation. We have measured kinetic-energy distributions and angular anisotropies of products in addition to branching ratios. Figure 3 shows the TOF spectra of the C_3H_3 radical. C_3H_3 has an ionization energy of 8.67 eV for propargyl (CH_2CCH) radical and of 10.8 eV for propynyl (CH_3CC) radical. We have successfully detected the C_3H_3 product with photon energy at 9.5 eV. However, the TOF spectrum of C_3H_3 dramatically changes when the photon energy increases to merely 11.5 eV. The abrupt change is

due to cracking of the C_3H_4 product after photoionization. No doubt it is impossible to detect C_3H_3 using an electron-impact ionizer without a severe interference of C_3H_5 and C_3H_4 . The successful measurements of all photofragments outline the whole picture of photodissociation of propene. We deduce that propene is excited to the $2^1A'$ ($\pi-3p$) state at 157 nm and subsequently dissociates on the electronic ground-state following internal conversion.

The last example describes the photolysis of methanol. After excitation at 157 nm, methanol undergoes dissociation with five possible channels: $CH_3 + OH$, $CH_3O/CH_2OH + H$, $CH_2O + 2H$, $CH_2O/HCOH + H_2$, and $CO + 2H_2$. Harich *et al.* have investigated the dissociation dynamics of methanol using photofragment translational spectroscopy coupled with electron-impact ionization. From photolysis of isotopomers of methanol, CH_3O and $HCOH$ have been identified to be the dominant products among their isomers after elimination of atomic and molecular hydrogen. However, Harich *et al.* did not indicate the detection of CH_3O (methoxy) and CO products owing to severe dissociative ionization and large detection background. In our experiment, all fragments are detectable using selective photoionization. Figure 4 shows the TOF spectra of CH_3O , H , and CO using ionizing photons at 9.8 eV, 14 eV, and 14.8 eV, respectively. After elimination of atomic H , internally hot CH_3O

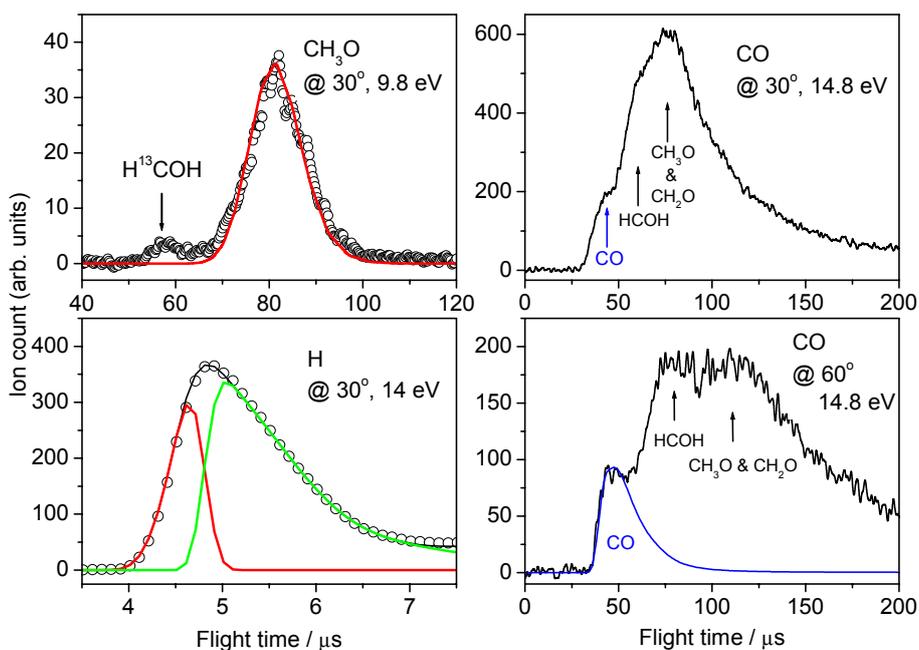


Fig. 4: TOF spectra of CH_3O , H , and CO produced from photolysis of methanol at 157 nm. The observed CH_3O radical correlates only with the rapid component (red line) of atomic H . The internally hot CH_3O , correlating with the slow component (green line) of atomic H , decomposes to $\text{CH}_2\text{O} + \text{H}$. The rapid component (blue line) of CO reflects elimination of two H_2 molecules and the slow component of CO is attributed to dissociative photoionization of HCOH , CH_3O , and CH_2O products.

further decomposes to $\text{CH}_2\text{O} + \text{H}$ and thus the survived CH_3O radical correlates only with the leading part of H atom. A fraction of CH_3O still decomposes to HCO^+ and CH_2O^+ following ionization even by using photons at 9.5 eV. Moreover, dissociative ionization of CH_3O , CH_2O , and HCOH products to CO^+ is considerable and a continuous background at mass 28 is large using electron-impact ionization, which inhibits the observation of CO . In our experiment, using VUV ionization the CO product is clearly distinguishable from other contributions. Methanol is excited to the $^1\text{A}''$ ($n\text{-}3\text{p}$) state at 157 nm, which produces a transition dipole moment perpendicular to the $\text{C}\text{-O}$ bond and thus leads to $\beta = -0.75$ for the $\text{CH}_3 + \text{OH}$ channel, $\beta = -0.26$ for the $\text{CH}_3\text{O} + \text{H}$ channel, and $\beta = -0.36$ for the $\text{HCOH} + \text{H}_2$ channel.

In addition, other interesting systems of photodissociation have been investigated by using this experimental apparatus and the selective photoionization scheme. Universal detection on photofragments has been achieved by combining a powerful molecular-beam machine with the intense VUV light at NSRRC. Up to date, products created from a crossed-beam reaction are also detectable using this setup.

BEAMLINE

21A1 U9/Chemical Dynamics beamline

EXPERIMENTAL STATION

Crossed molecular beam apparatus end station

AUTHOR

S.-H. Lee
National Synchrotron Radiation Research Center,
Hsinchu, Taiwan

PUBLICATIONS

- S.-H. Lee, Y.-Y. Lee, X. Yang, and Y. T. Lee, *J. Chem. Phys.* **119**, 827 (2003).
- S.-H. Lee, Y. T. Lee, and X. Yang, *J. Chem. Phys.* **120**, 10983 (2004).
- S.-H. Lee, H.-I. Lee, and Y. T. Lee, *J. Chem. Phys.* **121**, 11053 (2004).

CONTACT E-MAIL

shlee@nsrrc.org.tw