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Volume 1 of *Advances in Photochemistry* appeared in 1963. The stated purpose of the series was to explore the frontiers of photochemistry through the medium of chapters written by pioneers who are experts. As editors we have solicited articles from scientists who have strong personal points of view, while encouraging critical discussions and evaluations of existing data. In no sense have the articles been simply literature surveys, although in some cases they may have also fulfilled that purpose.

In the introduction to Volume 1 of the series, the editors noted developments in a brief span of prior years which were important for progress in photochemistry: flash photolysis, nuclear magnetic resonance, and electron spin resonance. A quarter of a century later in Volume 14 (1988) the editors noted that since then two developments have been of prime significance: the emergence of the laser from an esoteric possibility to an important light source; the evolution of computers to microcomputers in common laboratory use of data acquisition. These developments have strongly influenced research on the dynamic behavior of excited state and other transients. We can look forward to significant developments to include at the end of another quarter century.

With an increased sophistication in experiment and interpretation, photochemists have made substantial progress in achieving the fundamental objective of photochemistry: Elucidation of the detailed history of a molecule which absorbs radiation. The scope of this objective is so broad and the systems to be studied are so many that there is little danger of
exhausting the subject. We hope that the series will reflect the frontiers of photochemistry as they develop in the future.

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Volume 22
ULTRAVIOLET PHOTODISSOCIATION STUDIES OF ORGANOSULFUR MOLECULES AND RADICALS: ENERGETICS, STRUCTURE IDENTIFICATION, AND INTERNAL STATE DISTRIBUTION

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Sulfur occurs naturally in crude oil and in coals in amounts of 0.2 to 10%. Volatile organosulfur molecules such as dimethylsulfide (CH$_3$SCH$_3$) and methylmercaptan (CH$_3$SH) are major industrial pollutants emitted to the atmosphere because of incomplete combustion of coal and oil [1-5]. A great deal of effort has been directed toward the desulfurization of coals and oil to minimize the emission of sulfur-containing species to the atmosphere. Comparable sulfur emission into the atmosphere by natural oceanic sources in the form of volatile organosulfur molecules is also well known [6-8]. Oxidation of these organosulfur molecules ultimately leads to the formation of SO$_2$. Acid rain results when sulfur-containing compounds, including SO$_2$, are removed from the atmosphere by rain or snow [9-11]. Many of these organosulfur species have strong absorption bands in the ultraviolet (UV) wavelength region of $\approx$ 190–250 nm [7-20]. Previous UV photolysis studies suggest that the primary photodissociation of organosulfur species involves the breaking of the C-S, S-H, and S-S bonds [11,17,21-27]. Organosulfur radicals formed in UV photolysis are expected to be responsible for the increase in oxidation rate for organosulfur compounds and are recognized as important intermediates in the atmospheric sulfur cycle [6-8,28-31]. Thus, laboratory UV photodissociation studies of volatile organosulfur species are relevant to modeling of the atmospheric sulfur chemistry.

Owing to advances in laser technology, spectroscopic techniques, and molecular beams, laboratory photodissociation studies of many triatomic molecules have been performed at state-to-state levels [32-34]. Over the past decade, much experimental progress has also been made toward detailed photodissociation studies of simple polyatomic species. In addition to detailed dynamics studies, a primary and long-standing motivation for photochemical studies is to learn about the factors that control the outcome of a photochemical process. As demonstrated in the excimer laser photodissociation study of CH$_2$IBr [35], either the C-I or C-Br bond can be photodissociated by choosing the excitation wavelength which corresponds to the electronic excitation of an electron localized on either bond. By selectively exciting a bonding electron of the C-I or C-Br bond to an antibonding orbital, prompt dissociation of the corresponding C-I or C-Br bond is
observed. The short-lived repulsive state involved does not allow energy randomization and results in selective bond breaking. Without doubt, similar selective UV and vacuum UV (VUV) photodissociation processes exist for other molecular species. Another approach, often referred to as "mode-selective" chemistry, involves the preparation of a vibrationally excited molecule which has photochemistry favoring the breakage of a selected chemical bond. The overtone photochemical study of HOD by Crim and co-workers [36] is an excellent example of this scheme. They show that overtone excitation of the O-H (O-D) stretch, followed by photodissociation of the vibrationally excited molecules, produces dominantly OD + H (OH + D) products. The underlying principle of this approach is to photoexcite the molecule onto the repulsive part of an excited potential surface that favors the formation of a specific product channel. A third method potentially useful for controlling the branching ratios of photoproduct channels is based on the principle of coherent control [37,38]. An experimental demonstration of coherent control in the molecular photoionization processes of HI has recently been made [39]. However, a discussion concerning overtone spectroscopy and coherent control is beyond the scope of this review.

Small polyatomic organosulfur molecules are excellent molecular systems for detailed experimental studies of photodissociation dynamics because of their high photodissociation cross sections in a wide UV range, matching the output of commercial lasers. Because of this and other practical interests, the UV photochemistry of simple stable organosulfur molecules has received much experimental [40–61] and theoretical [48–50, 56–59, 62–69] attention in recent years. As summarized below, the UV photodissociation of simple polyatomic organosulfur species displays bond-breaking selectivity similar to that observed in the photodissociation of CH$_2$IBr.

To obtain information concerning energy disposals, product kinetic and internal energy distributions, and identification of primary product structures resulting from the UV photolysis of organosulfur pollutants, we have performed UV laser photodissociation and photoionization mass spectrometric studies of a series of sulfur-containing species in recent years [40–45, 49, 50, 54–61]. Ab initio calculations [49, 50, 55–59, 65, 66, 69] have also been made to compare with the energetic measurements and to interpret the experimental observations. This review mostly summarizes and evaluates the results of these experimental and theoretical studies. Related results obtained by other laboratories are also discussed.

We have developed a rotating molecular beam source, variable flight path, laser photofragmentation apparatus to measure the translational energy distributions of neutral photofragments produced in the UV laser photolysis of supersonically cooled molecules [70]. Using this apparatus, we have measured specific C-S, S-H, and S-S bond dissociation energies at 0 K ($D_0$) and the partition of translational and internal energies involved in the 193-nm photodissociation of selected organosulfur molecules [40–45, 56, 70].
We have used the laser resonance-enhanced multiphoton ionization (REMPI) method to probe the final state distributions of S atoms formed in the 193-nm photodissociation of several organosulfur molecules and radicals [58–60]. Using the rate-equation scheme and calibrating with the known photodissociation cross sections for the formation of \( S(3P_{2,1,0}, 1D_2) \) in the 193-nm photodissociation of \( \text{CS}_2 \), we have estimated the absolute cross sections for the photodissociation of organosulfur radicals \( \text{HS} \) [59,60] and \( \text{CH}_3\text{S} \) [58,60] leading to the formation of \( S(3P_{2,1,0}; 1D_2; 1S_0) \).

The method of inducing a photochemical reaction in the high-pressure region of a free jet and measuring the ionization energies of cold product species is a novel technique for identifying the isomeric structures of polyatomic photo- or reaction products when only a small fraction of precursor molecules is seeded in an unreactive carrier gas so that secondary reactions can be minimized [49,50,55]. This, the gas-phase analog of the matrix isolation technique, is expected to be generally applicable for structural determinations of polyatomic photofragments, as demonstrated in the recent experiments concerning 193-nm laser photodissociation of diethyl sulfide (\( \text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3 \)) [49], dimethyl disulfide (\( \text{CH}_3\text{SSCH}_3 \)) [50], and thiophene (\( \text{C}_4\text{H}_4\text{S} \)) [55]. Comparing the ionization energy (IE) measurements for polyatomic photofragments formed in a He- (or Ar-) seeded supersonic beam with IE predictions from high-level \textit{ab initio} calculations, we have been able to identify nascent isomeric structures for the primary radical photoproducts.

In recent high-resolution, pulsed-field ionization–photoelectron (PFI–PE) spectroscopic studies of laser-initiated radicals, such as \( \text{SH} \) [61] and \( \text{CH}_3\text{S} \) [54] formed in the laser photodissociation of \( \text{H}_2\text{S} \) and \( \text{CH}_3\text{SH} \) and \( \text{CH}_3\text{SSCH}_3 \), respectively, we have demonstrated that the PFI–PE spectroscopic technique is potentially useful for probing nascent state distributions of primary products formed in photochemical or reactive processes.

The different experimental techniques, when applied to the same molecule, yield complementary results. Since the specific information obtained depends on the experimental schemes, the experiments presented here are grouped based on the experimental method used.

II. LASER PHOTOFRAGMENTATION TIME-OF-FLIGHT MASS SPECTROMETRY

The pioneering work of Wilson and co-workers [71–75] established crossed-laser and molecular-beam photofragmentation spectroscopy with time-of-flight (TOF) mass-spectrometric detection as a universal and detailed
method for investigating photodissociation dynamics. In recent years, several groups [70,76–78] have adopted the rotating quadrupole mass-spectrometric detector design. The unique feature of our apparatus is the translationally movable mass spectrometer, which allows the flight path to be varied. At a high signal level, a long flight path can be used to achieve high-resolution TOF measurements. Several new techniques have been developed for photofragmentation studies, noticeably, the laser-ionization imaging method [79], high-\(n\) Rydberg TOF spectroscopy [80], and fast-beam photodetachment techniques [81]. For specific photodissociation processes, these new techniques offer significantly higher sensitivity and resolution than that obtainable from the Wilson design [71] equipped with an electron-impact mass spectrometer. However, we emphasize that the conventional Wilson design is in principle a universal technique applicable to all molecular systems.

A. Rotating Beam Source Photofragmentation Apparatus

We describe below the rotating-beam-source-photofragmentation apparatus [70] of the Wilson design used in our laboratory (see Fig. 1). The apparatus can be divided into three main components: an excimer excitation laser, a photodissociation chamber in which a rotatable supersonic molecular beam intersects the laser beam, and a linearly movable, ultrahigh vacuum-electron ionization mass spectrometer detector.

The molecular beam source chamber is pumped by a 20-in. diffusion pump (DP) (Varian HS20) with a pumping speed of 20,0001/s. For a nozzle (1) diameter of 0.125 mm and a nozzle stagnation pressure \(P_0\) of 800 Torr for a rare gas-seeded beam, a pressure of \(<1 \times 10^{-4}\) Torr is maintained in the beam source chamber. The beam has an angular divergence of 3°, defined by the opening of the conical skimmer and the circular aperture, as it passes through the differential pumping chamber (7) into the photodissociation chamber (4). The 3° angular spread of the beam corresponds to a beam width of 3 mm in the photodissociation region. The differential pumping chamber is evacuated by a liquid-nitrogen (LN\(_2\)) trapped 6 in. DP (Varian VHS6) with a pumping speed of \(\approx 2000\) l/s, while the photodissociation chamber is pumped by a freon-trapped 10 in. DP (Varian VHS10) having a pumping speed of \(\approx 5000\) l/s. The photodissociation chamber has two LN\(_2\) cold traps, (5) and (11). When these cold traps are cooled to LN\(_2\) temperature, the photodissociation chamber has a base pressure of \(1 \times 10^{-8}\) Torr. During the experiment, the pressures in the differential and photodissociation chambers are maintained at \(\approx 1 \times 10^{-5}\) and \(<8 \times 10^{-8}\) Torr, respectively.
Figure 1. Cross-section view of the rotating-beam-source-photofragmentation apparatus: (1) nozzle, (2) rotatable molecular beam source chamber, (2a) shaft, (3) excimer laser beam, (4) photodissociation chamber, (5) liquid-nitrogen-cooled cold trap, (6) rotatable differential pumping chamber, (7) differential pumping chamber, (8) molecular-beam source chamber, (9) bearing, (10) detector axis, (11) liquid-nitrogen cold trap, (12) flexible bellow, (13) valve, (14) extension tube, (15) adjustable aperture, (16) detector chamber, (17) first differential pumping region, (18) second differential pumping region, (19) ionization region, (20) ionizer, (21) turbomolecular pump (Balzer TPU310), (22) to ion pump (Ultek DI pump, 220 l/s), (23) quadrupole mass filter, (24) photomultiplier assembly, (25) to liquid-nitrogen-trapped turbomolecular pump (Balzer TPU50), (26) ion target. Taken from ref. 70.

The nozzle is mounted on a rotatable-beam source chamber (2) which is coupled to the molecular-beam source chamber (8) using a bearing (9) and rotating "O"-ring seal assembly. The rotatable differential pumping chamber (6) is fabricated from a stainless-steel tube. One end of the rotatable differential pumping chamber is rigidly attached to the rotatable molecular-beam source chamber, while the other end opens to the differential pumping chamber. The seal between the rotatable differential pumping chamber and the photodissociation chamber is accomplished by a rotating O-ring seal as shown in the figure. A shaft (2a) secured to the center of the rotatable-beam source chamber and placed along the common axis of the rotatable-beam source and rotatable differential pumping chambers makes possible the rotation of the molecular beam in a plane perpendicular to the common axis. Since the rotatable-beam source and rotatable differential
pumping chambers rotate together, differential pumping for the molecular-beam production region is achieved without the rotation of any pumps. The rotation of the shaft outside the vacuum chamber can be made manually or by a stepping motor.

The laser beam [XeCl (308 nm), KrF (248 nm), or ArF (193 nm)] from a commercial excimer laser enters the differential pumping chamber through a MgF₂ focusing lens and traverses along the central axis of the rotatable differential pumping chamber before intersecting the molecular beam at 90° in the photodissociation region. The fact that the molecular beam intersects the common central axis of the rotatable-beam source and the rotatable differential pumping chambers ensures the crossing of the laser and the molecular beam for all directions of the beam.

The mass spectrometric detector has four stages of differential pumping. The first (17) differential pumping region is evacuated by a 310 l/s turbomolecular pump (Balzer TPU310), while the second (18) differential pumping chamber is pumped by the combination of a 220 l/s ion pump (Utek DI pump) and a 560 l/s turbomolecular pump (Leybold Turbvac 600). The ionizer (20) is mounted inside the ionization chamber, which is cooled to LN₂ temperature during the experiment. The ionizer is an axial ionizer of the Brink design which has an aperture of 9 mm in diameter and a length of 2 cm. The ionization region (19) is pumped by a combination of a 120 l/s ion pump (Utek DI pump) and a 500 l/s turbomolecular pump (Balzer TPU520) and has a base pressure of $2 \times 10^{-11}$ Torr. The apertures between the first differential, second differential, and ionization chambers are 5 mm in diameter. During the experiment, the pressures in the three chambers are $\approx 2 \times 10^{-8}$, $2 \times 10^{-10}$, and $\leq 5 \times 10^{-11}$ Torr, respectively. The quadrupole mass filter (QMF) is constructed of four stainless-steel rods of 1.9 cm diameter and 21 cm length, which are symmetrically held in a circle of 3.55 cm diameter. The Daly-type scintillation ion detector consists of an ion target (26) and a scintillator–photomultiplier assembly (24). The ion-detector chamber is separated from the second differential pumping region by the QMF and a sheet metal wall. The vacuum in the ion detector chamber is maintained by a LN₂ trapped 50 l/s turbomolecular pump (Balzer TPU50).

The detector chamber (16) is mounted on a platform supported on a linearly movable rail assembly (not shown in the figure). Using the rail assembly, the flight distance ($L$) between the photodissociation region and the ionizer can be varied continuously in the range of $\approx 35$–110 cm. The molecular beam axis in the horizontal direction and the central axis of the ionizer define the detector axis. The positions of the platform and rail assembly are carefully adjusted so that the central axis of the ionizer remains in alignment with the detector axis as the detector chamber moves along the
full range of the rail. The laboratory angle ($\theta_{\text{lab}}$) is the angle between the molecular beam and the detector axis. The detector chamber is coupled to the photodissociation chamber with a flexible bellows (12) which serves to relieve the strain of any slight mechanical misalignment of the two chambers. The detector and photodissociation chambers can be isolated by valves (13). To change $L$, an extension tube of the desired length can be placed between the valves. The isolation valves allow the extension tube to be replaced without venting the detector and the photodissociation chambers.

In addition to two apertures on the differential pumping walls in the detectors, there are two more defining apertures along the detector axis. The first aperture (3 mm in diameter) is attached to the LN$_2$ cold trap (11) in the photodissociation chamber. The adjustable aperture (15), located between the extension tube and the isolation valve of the detector chamber, has an aperture 5 mm in diameter in the normal photodissociation experiment. When it is necessary to orient the molecular beam toward the detector ($\theta_{\text{lab}} = 0^\circ$), such as when measuring the velocity distribution of the molecular beam, the adjustable aperture is reduced to a diameter of 0.127 mm.

The TOF spectrum is recorded on a multichannel scaler (MCS) (Stanford Research Model SRT430) with a minimum channel width of 5 ns. The MCS is started by a trigger pulse signifying the firing of the laser. Time-of-flight spectra have also been recorded using a pulsed molecular-beam valve. In such experiments, the firing of the excimer laser is delayed appropriately with respect to the triggering pulse for opening the pulse valve. The delay timings are controlled by a digital delay unit (Stanford Research Model DG 535).

In the TOF measurements of neutral photofragments, the neutral photofragments are ionized in the electron impact ionizer before mass filtering and detection. We find that the conditions of the ionizer can affect significantly the appearance of the TOF spectrum of a photofragment. For example, in Figures 2a and b, we compare the TOF spectra of S formed in the 193-nm photodissociation of CS$_2$ recorded at extraction voltages of 8 and 0 V, respectively. The ion-extraction voltage is the difference in the voltages applied to the grid cage where the ions are formed and the ion extraction lens next to the cage. To extract ions from the cage, the potential of the ion-extraction lens is lower than that of the cage. Other than the extraction voltage, these two spectra are recorded under the same experimental conditions. The spectrum in Figure 2a exhibits two steplike structures and a sharp peak, whereas the spectrum in Figure 2b reveals only a single broad peak. Furthermore, the onset of the spectrum in Figure 2b is delayed by $\approx 80 \mu$s compared to that of the spectrum in Figure 2a. The delay of the onset of S observed in Figure 2b is mostly likely due to the space charge effect in the ionizer at 0 V ion-extraction voltage. Under this condition the
Flight time (ps)

Figure 2. TOF spectra for S obtained using an ion extraction voltage of (a) 8 V and (b) 0 V with respect to the ionizer cage \([L = 72.7 \text{ cm}, \theta_{\text{lab}} = 15^\circ, P_0 = 150 \text{ Torr (pure CS}_2), T_0 = 298 \text{ K, electron energy} = 50 \text{ eV, laser power} = 20-120 \text{ mJ}].\) Taken from ref. 70.

S\(^+\) and other ions trapped by the space charge potential in the ionizer may be responsible for washing out the TOF structure of the neutral photofragment. The comparison of TOF spectra recorded at different ion-extraction voltages suggests that it is important to reduce the effect of the space charge potential minimum in the ionizer by applying a sufficiently high ion-extraction voltage when performing TOF measurements.

1. Velocity Distribution of the Parent Molecular Beam. To obtain the translational velocity distribution from TOF spectra of photofragments, it is necessary to measure the velocity distribution of the parent molecular beam. In these measurements, the parent molecular beam is set at \(\theta_{\text{lab}} = 0^\circ\) and the detector is reduced to 0.127 mm. Two methods are used here. The first uses a TOF chopper wheel to chop the parent beam to generate a narrow parent gas beam pulse. The TOF spectrum resulting from this gas
pulse, which travels from the chopper wheel to the detector, yields information about the velocity distribution of the parent gas beam. In such an experiment, an aluminum chopper wheel with a diameter of 20 cm and two slot openings is placed between the photodissociation region and the first aperture along the detector. The two open slots on the edge of the wheel are 0.2 mm wide and 5 mm deep and are separated by 180°. For a chopper frequency of 200 Hz, the chopper produces a parent molecular-beam pulse of 1.6 μs width every 2.5 ms. The MCS is initiated by a trigger pulse from a photodiode which marks the production of the parent beam pulse by the chopper wheel.

The second method is the laser hole-burning method. By firing the excimer laser at the parent molecular beam, the intensity of the parent molecules along the detector axis is reduced for a time equal to the pulse width (full width = 16 ns) of the laser. The reduction of the parent beam signal is due to the dissociation of the parent molecule induced by the absorption of a 193-nm photon. The laser burn hole recorded by the MCS gives an accurate measure of the velocity spread and the most probable speed \( v_0 \) of the parent molecular beam traveling from the photodissociation region to the ionizer.

To obtain the \( v_0 \) value for the parent molecular beam, the speed profile for the parent molecular beam obtained by the chopper wheel or the laser hole-burning method is fitted to an assumed number density distribution of the form:

\[
f(v) \approx v^2 \exp\left[\frac{-(v - v_0)^2}{(\Delta v)^2}\right],
\]

where \( \Delta v \) is a measure of the width of the speed profile.

As an example, we show in Figure 3a–d the laser hole-burning spectra of CS\(_2\) observed at \( L = 84.5 \) cm for: (a) a cw pure CS\(_2\) beam at \( P_0 = 150 \) Torr, (b) a cw CS\(_2\)/Ne seeded beam of 517 Torr, (c) a cw CS\(_2\)/He seeded beam at \( P_0 = 362 \) Torr, and (d) a cw CS\(_2\)/He seeded beam at 776 Torr [70]. Since the masses of the carrier gases are lighter than that of CS\(_2\), values for \( v_0 \) for the seeded beams are greater than that for the pure CS\(_2\) beam. As expected, the ratio \( \Delta v/v_0 \) for the CS\(_2\)/He seeded beam at \( P_0 = 776 \) Torr is a smaller, \( \approx 0.4 \) times that for the pure CS\(_2\) beam. Considerable amounts of CS\(_2\) dimer and clusters are formed in the CS\(_2\)/He seeded beam at 776 Torr. The laser hole-burning spectrum for (CS\(_2\))\(_2\) formed in the CS\(_2\)/He seeded beam at \( P_0 = 776 \) Torr is depicted in the lower panel of Fig. 3d. Owing to the slippage effect in the seeded supersonic beam, the velocity of (CS\(_2\))\(_2\) is slightly lower than that of CS\(_2\). It is interesting to note that the \( \Delta v/v_0 \) for (CS\(_2\))\(_2\) is smaller than that for CS\(_2\).

It is more difficult to obtain a hole-burning spectrum for a pulsed molecular beam because of pulse to pulse intensity fluctuations. A hole-burning spectrum for a pulsed-molecular beam can be achieved by operating the pulsed-molecular beam at twice the repetition rate of that for the
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Figure 3. Laser-hole-burning spectra for CS$_2$ in (a) a pure CS$_2$ beam ($P_0 = 150$ Torr), (b) a CS$_2$/Ne seeded beam ($P_0 = 517$ Torr), (c) a CS$_2$/He seeded beam ($P_0 = 362$ Torr), and (d) CS$_2$/He seeded beam (upper spectrum) ($P_0 = 776$ Torr); and laser hole-burning spectrum for (CS$_2$)$_2$ in CS$_2$/He seeded beam (lower spectrum) ($P_0 = 776$ Torr). $L = 84.5$ cm. Taken from ref. 70.

excimer laser, and then taking the difference of the molecular beam pulses recorded by the MCS when the laser is on and off. This can be achieved by using the “toggle-add and toggle-subtract” modes, a feature of the Stanford Research MCS. This feature allows the TOF data to be added to and subtracted from the previously accumulated data when the laser is on and off, respectively. As an example, we show in Figure 4 the laser hole-burning spectrum for SO$_2$ produced in a SO$_2$/Ar seeded pulsed beam. The TOF spectrum for the SO$_2$/He pulsed beam is also plotted in the figure for comparison with the hole-burning spectrum. Since the supersonic cooling for molecules attained in a pulse beam depends on their temporal location within the beam pulse, the hole-burning technique is the most appropriate method for obtaining the velocity distribution of the ensemble of molecules which are actually dissociated by the excimer laser.

The ion drift times through the quadrupole mass filter can also be determined in the hole-burning experiment. By taking the hole-burning spectra of the parent and fragment ions formed in electron impact ionization of the parent molecule, the corresponding arrival times ($t$) and masses ($m$) of these ions are used to fit the equation: $t = Am^{1/2} + t_0$, where $t_0$ is the flight time of the parent molecule from the photodissociation region to the
ionizer and $A$ is a constant. The procedure allows the determination of $A$ and thus the ion drift time through the quadrupole mass filter. The actual flight times of photofragments were corrected for the corresponding ion drift times.

2. Factors Influencing the Resolution of TOF Measurements. The width of the TOF ($\Delta T_{\text{TOF}}$) for photofragments with a nominal flight time $t_F$ traveling a distance $L$ depends on the length of the ionizer ($L_1 = 2\,\text{cm}$), $\Delta v$ of the parent molecular beam, and the temporal width of the laser pulse ($\Delta \tau = 16\,\text{ns}$). Considering that $T_F$ is usually $>50\,\mu\text{s}$, we can ignore the contribution of $\Delta \tau/T_F$ to $\Delta T_{\text{TOF}}/T_F$. It can be shown that

$$\left(\frac{\Delta T_{\text{TOF}}}{T_F}\right)^2 \approx \left(\frac{L_1}{L}\right)^2 + \left(\frac{\Delta v}{v_{\text{lab}}}\right)^2 = \left(\frac{L_1}{L}\right)^2 + \left[v_0(\Delta v/v_0) \cos \frac{\theta_{\text{lab}}}{v_{\text{lab}}}\right]^2$$

(1)

For fixed $L_1$ and $L$, the overall resolution $\Delta T_{\text{TOF}}/T_F$ depends on $\theta_{\text{lab}}$, $\Delta v/v_0$, $...
and $v_0/v_{\text{lab}}$. If the second term in Eq. 1 can be made sufficiently small, the highest solution achieved for the rotating beam source TOF mass spectrometer [70] is expected to be $\Delta T_{\text{TOF}}/T_F \approx L_1/L_{\text{max}} = 0.018$, where $L_{\text{max}} = 110 \text{ cm}$. We note that to achieve $\Delta v/v_0 < 0.05$ in a supersonic expansion requires a careful experimental effort.

3. Angular Distribution Measurements. The kinematics of a laser photodissociation experiment using a rotating beam source apparatus is illustrated in Figure 5. Here, the detector is fixed along the $z$ axis and the laser beam propagates along the $y$ axis (perpendicular to the $x$-$z$ plane, not shown here) with its electric field $[E = E(\hat{i} \sin \epsilon + \hat{k} \cos \epsilon)]$ lying on the $x$-$z$ plane. The molecular beam source rotates in the $x$-$z$ plane. Since the molecular beam source axis (and $\mathbf{v}_0$) and the detector axis (and $\mathbf{v}_{\text{lab}}$) are both on the $x$-$z$ plane, the center-of-mass (c.m.) velocity of the fragment can be expressed as $\mathbf{u} = u(\hat{i} \sin \delta + \hat{k} \cos \delta)$, where $\delta = \theta_{\text{c.m.}} - \theta_{\text{lab}}$. Figure 5 also shows the relationship $\gamma = \theta_{\text{c.m.}} + \epsilon - \theta_{\text{lab}} = \delta + \epsilon$, where $\gamma$ is the angle between $\mathbf{E}$ and $\mathbf{u}$; $\theta_{\text{c.m.}}$ is the angle between $\mathbf{v}_0$ and $\mathbf{u}$; and $\epsilon$ is the angle between $\mathbf{E}$ and the detector axis.

It is assumed that the c.m. flux for a photofragment channel $I_{\text{c.m.}}(E_{\text{c.m.}}, \theta_{\text{c.m.}})$, which depends on the c.m. translational energy ($E_{\text{c.m.}}$) of...
the photofragments and $\theta_{c.m.}$, can be factored [72] as

$$I_{c.m.}(E_{c.m.}, \theta_{c.m.}) = P(E_{c.m.})\omega(\gamma) \tag{2}$$

where $P(E_{c.m.})$ and $\omega(\gamma)$ are functions that depend only on $E_{c.m.}$ and $\gamma = \delta + \epsilon$, respectively. For photodissociation on a single electronic surface, the photofragments formed upon one-photon electric dipole excitation of an ensemble of randomly oriented parent molecules recoil with an angular distribution of the form [72,82]

$$\omega(\gamma) = (1/4\pi)[1 + \beta P_2(\cos \gamma)] \tag{3}$$

where $P_2(\cos \gamma) = (1/2)(3\cos^2\gamma - 1)$ is the second Legendre polynomial and $\beta$ is the anisotropy parameter. Depending on the symmetry of the electronic excitation and the dynamics of the dissociation process, $\beta$ has a value between $-1$ and 2, which correspond to the transition dipole moment $\mu$ being aligned perpendicular or parallel to the fragment recoil direction, respectively. Strictly speaking, Eq. 3 is applicable only for photofragments with a single well-defined velocity. Here, $\beta$ is also assumed to be independent of $\mu$.

For an unpolarized laser, we must average $E$ over $\epsilon$ from 0 to $2\pi$, that is,

$$I(E_{c.m.}, \theta_{c.m.}) = (1/4\pi)(1/2\pi) \int_0^{2\pi} P(E_{c.m.})[1 + \beta P_2(\cos \gamma)] d\epsilon \tag{4}$$

Since

$$\cos \gamma = \sin \epsilon \sin \delta + \cos \epsilon \cos \delta$$

and

$$\langle \cos^2 \gamma \rangle = \langle \sin^2 \epsilon \rangle \sin^2 \delta + \langle \cos^2 \epsilon \rangle \cos^2 \delta = 1/2$$

it can be shown [83] that

$$I(E_{c.m.}, \theta_{c.m.}) = (1/4\pi)P(E_{c.m.})[1 + \beta/4] \tag{5}$$

This result indicates that when an unpolarized laser is used, $\beta$ contributes merely to the normalization factor and $I(E_{c.m.}, \theta_{c.m.})$, proportional to $P(E_{c.m.})$, is independent of $\theta_{c.m.}$.

Commercial excimer lasers are not polarized. A convenient way to linearly polarize the excimer laser radiation is to use a crystal or a stack of quartz plates set at the Brewster angle. With a 10-plate set, $>90\%$
polarization can be achieved. Using a half-wave retarder at a specific
excimer laser wavelength, $\varepsilon$ can be rotated with no change in the laser
intensity and beam geometry.

When a polarized laser is used together with the rotating-beam source
apparatus, two common methods are used for the determination of the $\beta$
parameter. One method suggested by Frey and Felder [83] involves
measurements of the TOF spectra of a photofragment at $\varepsilon = 0^\circ$ and $90^\circ$ at
a fixed $\theta_{\text{lab}}$ value. For a given value of $u$, the $\gamma$ values corresponding to $E$
perpendicular ($\gamma_{\perp}$) and parallel ($\gamma_{||}$) to the detector differ by $\pi/2$, that is,
$\gamma_{\perp} = \gamma_{||} + \pi/2$.

$$I_{||}(E_{\text{c.m.}}, \theta_{\text{c.m.}}) = [P(E_{\text{c.m.}}/4\pi][1 + \beta P_2(\cos \gamma_{||})]$$

or

$$I_{||}(u, \theta_{\text{c.m.}}) = [P(u)/4\pi][1 + \beta P_2(\cos \gamma_{||})]$$

$$I_{\perp}(E_{\text{c.m.}}, \theta_{\text{c.m.}}) = [P(E_{\text{c.m.}})/4\pi][1 + \beta P_2(\sin \gamma_{||})]$$

or

$$I_{\perp}(u, \theta_{\text{c.m.}}) = [P(u)/4\pi][1 + \beta P_2(\sin \gamma_{||})]$$

(6a)

(6b)

$$I_{||} + I_{\perp} = [P(u)/2\pi][1 + \beta/4]$$

(7)

$$I_{||} - I_{\perp} = [P(u)/4\pi][(3\beta/2) \cos 2\gamma]$$

(8)

$$(I_{||} - I_{\perp})/(I_{||} + I_{\perp}) = [3\beta/(4 + \beta)] \cos 2\gamma$$

(9)

Since the laboratory to c.m. flux transformation is $I_{\text{lab}}(v_{\text{lab}}, \theta_{\text{lab}}) = (v_{\text{lab}}/u)^2 I_{\text{c.m.}}(u, \theta_{\text{c.m.}})$ (if the averaging effect due to the finite angular and
energy resolution is ignored), Eq. (9) can be applied directly to the
laboratory data without transforming the TOF data into the c.m. system.
Experimentally, the TOF spectra corresponding to $\varepsilon = 0^\circ$ and $90^\circ$ must be
measured at the same laser pulse energy and the same number of laser
pulses.

A straightforward approach to measuring the angular distribution of a
given photodissociation channel is to acquire the TOF spectrum of the
corresponding photofragment as a function of $\varepsilon$ at a fixed number of laser
shots, assuming that the laser is operating in the constant-pulse energy
mode. The $\beta$ parameter can then be obtained by fitting the experimental
data using Eq. (3).

For the analysis of angular distribution measurements involving two
electronic surfaces, readers are referred to refs. 83 and 84.