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Molecular Beam Study of Multiphoton Dissociation of SF_6†

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Crossed molecular and CO_2 laser beams were used to study collisionless multiphoton dissociation of SF_6. Dissociation products were found to be SF_5 and F. Angular and velocity distributions of the SF_5 fragment were measured. The results indicate that the average excess energy absorbed by an SF_6 molecule beyond the dissociation limit was definitely less than 8000 cm^{-1} and the activation energy for dissociation was less than 70 cm^{-1}.

The discovery of multiphoton dissociation of polyatomic molecules in an intense laser field is one of the most exciting developments in recent years.[1,2] The potential applicability of this method in promoting selective chemical reactions for chemical synthesis, in separation of isotopes, and in many other branches of chemistry has led to an intensive effort towards an understanding of the dissociation process. In spite of numerous detailed experimental studies[1-3] and the recently improved theoretical understanding[1,4] of the nature of multiphoton absorption, many important questions have remained unanswered. For example, in the multiphoton dissociation of SF_6 molecules, the fragments have not yet been positively identified although it was believed that the major products could be either $SF_5 + F$, or $SF_4 + F_2$, or others depending on the laser intensity. It is also not sure how many photons a single molecule can absorb beyond the dissociation limit, and how the excess energy is distributed among the fragments. Furthermore, little is known about the dynamics of multiphoton molecular dissociation, the existence of an activation barrier in the exit channel beyond the dissociation limit and the effect of molecular collisions. These questions and many others can, however, be answered by studying multiphoton dissociation with a molecular beam machine.[5] We have recently carried out such an experimental study on SF_6 with crossed laser and molecular beams. In this Letter, we report some preliminary results of our new venture, providing identification of the primary fragments along with their angular and velocity distributions. Information about absorbed excess energy in SF_6 and activation energy beyond the dissociation limit was deduced.

The molecular beam apparatus used is shown schematically in Fig. 1. The molecular beam was formed by expansion of pure SF_6 at ~75-Torr stagnation pressure from a 0.1-mm-diam quartz nozzle. Three stages of differential pumping were used along with two conical skimmers and a final collimating aperature to produce a well defined beam of ~2 mm in diameter. The molecular beam had a very sharply delineated angular distribution of 1.2° full width at half-maximum (FWHM). The velocity distribution of the beam could be characterized by a Mach number of ~6, a peak velocity of 3.6×10^4 cm/sec, and a FWHM of 25% of the peak velocity. The density of molecules in the beam was $\sim 3 \times 10^{11}/cm^3$. A Tachisto

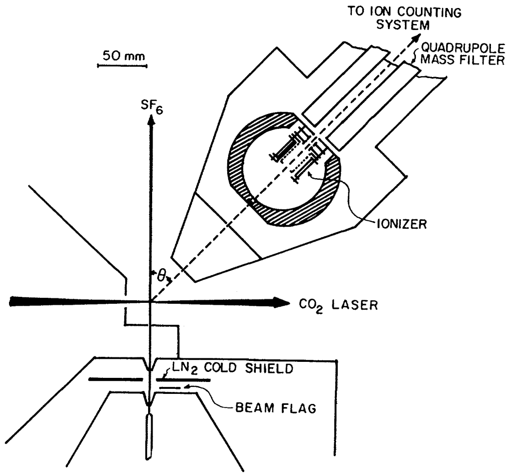

FIG. 1. Schematic of the apparatus used for the measurement of angular distribution of the fragments from multiphoton dissociation of SF_6. The molecular beam is triply differentially pumped, allowing a low pressure (10^{-7} Torr) to be maintained in the fragmentation region.

TAC II grating tuned CO_2 transverse-excitation-atmospheric laser (~1.0 J/pulse) was used in our experiments as the excitation source. The laser beam was admitted into the vacuum chamber via a ZnSe lens with a 25.4-cm focal length. It crossed the molecular beam near the focal region with a focal diameter of 0.35 mm. The fragments produced by multiphoton dissociation of SF_6 at the small interaction region were detected by a triply differentially pumped quadrupole mass spectrometer utilizing electron bombardment ionization and ion counting. The angular position of the mass spectrometer around the beam intersection point could be varied so that the angular distribution of the fragments could be measured. The mass filter was always adjusted to provide better than unit mass resolution. External triggering at 0.5 Hz was used to fire the laser and to enable a dual-channel scaler for recording counts of fragments from the mass spectrometer. Separate adjustments of delay and gate times were made to ensure that one scaler channel recorded only background (i.e., with the laser pulse off) while the other recorded both background and signal. Typically, 50–100 laser shots were used to measure the fragments produced at each laboratory angle θ (see Fig. 1). The angular resolution of the measurements was ~0.5°. Velocity distributions of the SF_6 beam and the fragments were measured with a 256-channel scaler (4 μsec/channel width).

Our observation of dissociation products from the beam interaction region gives a direct confirmation of the suggestion that multiphoton molecular dissociation is a unimolecular process.[4-6] Figure 2(a) shows the measured angular distributions of four species found in the ionization chamber of the mass spectrometer, SF_5^+ (127), SF_4^+ (108), SF_3^+ (89), and F^+ (19) (the numbers in parentheses specifying their respective mass-to-charge ratios m/e). No F_2^+ species was detectable. These data represent the average of several angular scans of the mass spectrometer. The $P(18)$ line of the CO_2 laser was used in the experiment with a peak power density of $\sim 5\times10^9$ W/cm^2 in the beam interaction region. Throughout the angular range, the signal of SF_5^+ was always the most intense. It should be noted that this signal was always correlated with the laser pulse. To within experimental error, the angular distributions of the four fragments shown are the same. Because of the difference in kinematic relations, the angular distribution of a fragment in molecular dissociation is a very sensitive function of its mass and recoil velocity, and thus the invariance of the angular distributions shown in Fig. 2(a) for different species clearly

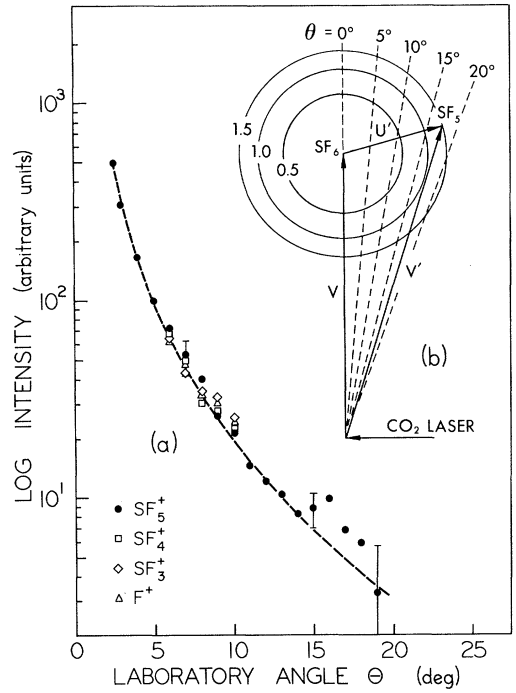

FIG. 2. (a) Angular distribution of the fragment products. (b) Kinematic diagram for fragments of SF_6. The circles show the total amount of translational energy released (in kcal) when the SF_5 is found in the phase space which lies on the circle.

implies that they are all from the same parent molecule, SF_5. This result then unambiguously identifies the primary dissociation products as SF_5 and F.

The translational energy released in the dissociation of SF_6 can be found easily from the angular distribution by using conservation of energy and linear momentum. Because of the mass difference, the F fragment should have a recoil velocity 6.7 times larger than the corresponding SF_5 fragment and hence a much broader angular distribution. Only a negligible fraction of the F^+ signal detected came from the F fragment directly. Figure 2(b) shows a kinematic diagram of the dissociation process. The concentric circles centered on the tip of the SF_6 velocity vector represent the maximum recoil velocity in the center-of-mass coordinates that an SF_5 fragment can have for a given amount of released translational energy. Since the majority of SF_5 fragments were detected within 20° of the beam, the average energy is much less than 1.5 kcal/mole, which is the maximum translational energy of $SF_5 + F$ observed. Confirmation of this was obtained by measuring the velocity distribution of the SF_5 fragments which at $\theta = 3°$ has a peak velocity at 3.6×10^4 cm/sec and a FWHM of 43% of the peak velocity compared with 25% for the SF_6 beam. It is, as yet, not certain to what extent the excess absorbed energy is redistributed among the fifteen vibrational degrees of freedom of SF_6 prior to its dissociation. However, even assuming complete randomization, the average excess energy absorbed by SF_6 under present experimental conditions would be less than 23 kcal/mole (8000 cm^{-1}/molecule), or less than nine infrared photons per molecule. Since SF_6 is a central symmetric molecule, we can expect the rotational excitation of SF_5 to be small.[7]

Because of the presence of the strong SF_6 beam, it was not possible to measure dissociation fragments produced within an angle of 2.5° from the beam axis. However, it appears that the angular distribution of the SF_5 fragment peaks at or near 0°. Kinematically, such a result would indicate that no substantial activation barrier beyond the dissociation limit (<0.2 kcal/mole or 70 cm^{-1} per molecule) exists for the dissociation of SF_6 into $SF_5 + F$.

Finally, a study was made of the dependence of the SF_5 fragment signal as a function of SF_6 beam stagnation pressure. Over the range from 50 to 600 Torr, no increase in intensity was seen beyond that due to the increased beam flux. If the measured signal had been due to the breakup of SF_6 dimers (or longer clusters) formed during the gas expansion, a noticeable enhancement of these species should have resulted from the increased stagnation pressure. That no such increase could be measured indicates that dissociation of van der Waals type complexes of SF_6 is not the origin of the fragment signal.

We are currently in the process of making detailed measurements and analysis on how the laser intensity, power, polarization, and wavelength may affect the dynamics of multiphoton dissociation of SF_6. We also plan to use the scheme to study multiphoton dissociation with the SF_6 beam at different vibrational and rotational temperatures. The results should yield detailed information about dissociation dynamics, and internal energy distribution and energy transfer of an excited molecule before dissociation, and hence a better understanding of the physical mechanism of multiphoton dissociation.

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Observation of High-Resolution Differential Cross Section of Polarized, Rotationally State-Selected LiF on Ar[†]

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We report high-resolution differential cross sections at thermal energy for polarized, rotationally state-selected LiF on Ar. They were 2–8% larger with LiF in the $J=|M|=1$ orientation along the relative velocity than in the $J=1$ unpolarized state. The differential cross section in the present case is much more sensitive to change in polarization than is the total cross section. The high-frequency oscillations of the differential cross sections were found substantially independent of J when the present $J=1$ data were compared with non-state-selected data for $\bar{J}=15$ or $\bar{J}=25$.

The measurement of the variation of total scattering cross section with polarization in state-selected beams has given information about the angular dependence of intermolecular potentials.[1,2] However, the effects of change of polarization upon the received signal are small. Because long integrating times are necessary, it is difficult to obtain the velocity dependence of the difference in total cross section due to polarization, which gives further information about the radial dependency of the angular dependent terms in the intermolecular potential. This laboratory has recently performed measurements of the velocity variation of the differential cross section for atom-atom[3] and atom-molecule[4] scattering. LiF-Ar was studied[4] in the thermal energy range under conditions of very high resolution in which all features of the quantum mechanical scattering were observable, although the rotational states of the molecule were thermally distributed. Observation of damped high-frequency (diffraction) and low-frequency (rainbow) oscillations[5] permitted a determination of the spherically averaged potential and some characteristics of the angular dependent potential. The present experiments combine the observational advantages of both state selection and high-resolution differential cross sections.

The use of a seeded high-temperature supersonic source to cool the LiF beam translationally and rotationally, and the use of quadrupole fields to provide finite-aperture ($f/100$) optics made possible the observation of the differential cross section of a state-selected molecular beam at intensities of about $\frac{1}{5}$ that of a non-state-selected molecular beam previously used and with no sacrifice in geometrical angular resolution. A supersonic Ar jet carried 0.5-Torr superheated LiF as it expanded from 300 Torr at 1750 K from an indirectly heated graphite oven through a 0.15-mm thin orifice. It was skimmed by a 50° full angle, 0.5-mm-diam truncated cone.[6] Rotational and translational temperatures ranged from 25 to 85 K. Differential pumping was provided by a 100-l/sec booster and by 4200- and 200-l/sec diffusion pumps, sequentially, to a pressure of 1×10^{-7} Torr in the first refocuser chamber. The chamber containing the second refocuser and the scattering apparatus was pumped by a 600 l/sec ion pump supplemented by liquid hydrogen cryopumping and Ti sublimation pumping to a pressure of 3×10^{-8} Torr. The state selectors were two 180° refocusing "three-quarter" quadrupoles together with apertures for velocity selection (8.5% stan-