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THE EXTENT OF ENERGY RANDOMIZATION IN THE
INFRARED MULTIPHOTON DISSOCIATION OF SF₆

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ABSTRACT

Crossed laser and molecular beams were used to obtain the recoil-energy distribution of fragments in the study of multiphoton dissociation of SF₆. An average dissociation lifetime of ~100 nsec was estimated from the laser pulse width dependence of the dissociation product. The results are in good agreement with the theoretical prediction of the RRKM model for unimolecular dissociation assuming an average excitation of ~16 kcal per molecule beyond the dissociation threshold and complete energy randomization in the excited molecule before dissociation.
INTRODUCTION

The decomposition of polyatomic molecules by infrared multiphoton absorption is a subject which is under extensive investigation in many laboratories. The process has been shown to be efficient, isotopically selective and collisionless.\(^1\) Considerable progress has been made toward elucidating the mechanism by which an isolated molecule under intense infrared laser irradiation can absorb a large number of photons.\(^2\) However, one very important question which remains to be answered is the relation between the dynamics of the laser induced unimolecular dissociation and the distribution of vibrationally energized states, i.e., the question of whether or not the excitation energy is completely randomized before dissociation. The observation of electronically excited fragments in the dissociation of halogenated hydrocarbons\(^3\) and the apparent detection of SF\(_4\) and F\(_2\) fragments in the decomposition of SF\(_6\)\(^4\) have been the basis of some recent speculation that the excitation energy might not be randomized. On the other hand, newer results of Bloembergen et al.,\(^5\) based on absorption measurements, suggest that multiphoton dissociation is a statistical process.

In a recent paper,\(^6\) we reported the results of a crossed laser-molecular beam experiment that provided the first unambiguous characterization of the primary products of the multiphoton dissociation of SF\(_6\) as SF\(_5\) and F. In addition, this work showed that, on the average, the recoil energy of the products was less than 2 kcal. These results have been confirmed by the recent findings of Wittig et al.\(^7\) and Weston et al.\(^8\) that chemiluminescence, characteristic of the reaction of slow fluorine atoms with H\(_2\), occurs in SF\(_6\) - H\(_2\) mixtures.
We have extended our study to include direct time-of-flight measurements of fragment velocities. These results, combined with the angular distributions reported earlier have enabled us to obtain the center of mass recoil energy distribution and hence information about energy disposal. In addition, the time dependence of the apparent formation and subsequent destruction of SF$_5$ seen with variations in laser pulse length has provided an estimate of the dissociative lifetime of SF$_6$.

The experimental recoil energy distribution and dissociative lifetime have been compared to the corresponding theoretical predictions of a detailed RRKM calculation. It was found that the multiphoton results for both recoil energy distribution and lifetime were completely consistent with a statistical model for the unimolecular decomposition of SF$_6$ for an assumed energization of six photons (16 kcal) above the dissociation threshold.

EXPERIMENTAL

The experimental setup was identical to that described previously. A molecular beam of SF$_6$ was crossed by the output at 10.6 μm from a Tachisto CO$_2$ TEA laser. For the SF$_5$ fragment measurements the laser was operated at an output energy of 1 joule with a pulse duration of ~50 nsec full width half maximum. Additional studies of the secondary dissociation of SF$_5$ to SF$_4$ were carried out with laser pulses of the same energy widened to 500 nsec. The laser beam was focused by a
25 cm focal-length lens. Its intensity was varied by means of attenuators and by defocusing.

The fragment velocity distributions were obtained by determining arrival time of each fragment at the detector relative to the time origin defined by the laser pulse. This was done by multisampling the mass spectrometer output signal. Typically, an eight µsec channel width was used in a scan over two msec (256 channels).

RESULTS AND DISCUSSION

The angular distribution together with a typical time-of-flight spectrum for the SF₅ product is shown in Fig. 1. The measured time-of-flight spectra taken at different angles were combined with the angular distribution and deconvoluted from the velocity distribution of the molecular beam to obtain the center of mass recoil energy distribution. The result for SF₅ is shown in Fig. 2. Two qualitative but important conclusions can readily be drawn from these data:

(1) The average recoil energy is low, approximately 1.7 kcal, indicating that, if SF₆ absorbs more than one photon above the dissociation threshold, a substantial fraction of that excess energy must be retained by the SF₅ fragment in its internal degrees of freedom.

(2) The experimental recoil energy distribution peaks at or very near zero. This confirms our earlier observation that the relevant dissociation channel has little or no "exit barrier."
It also rules out a mode-selective "explosive" dissociative mechanism for which a velocity distribution skewed to higher energy would be expected.

In addition, identical results were seen for laser polarizations both parallel and perpendicular to the detection plane. This indicates that the product recoil direction has no dependence on the polarization of the laser field and/or that the lifetime of the excited molecule is many rotational periods.

We have calculated a theoretical recoil energy distribution using the RRKM statistical model for unimolecular dissociation. The molecule was assumed to have been excited to a certain level of energization above the dissociation threshold and the excitation energy was assumed to be completely randomized in all vibrational degrees of freedom. As shown in Fig. 2, correspondence between the experimental data and the theoretical curve for an energization by six photons (16 kcal) in excess of the dissociation threshold is very good. This, therefore, strongly suggests the validity of the statistical model for collisionless multiphoton dissociation.

The theoretical lifetime for an excess energy of 16 kcal is about 100 nsec, as shown in Table I. We have been able to obtain an experimental estimate for the dissociative lifetime of SF₆ from an apparent pulselength dependence for the collisionless reaction mechanism. With laser pulses of ~50 nsec FWHM the dissociation products were exclusively SF₅ and F. When the pulses were lengthened to 150 nsec (with no change in the integrated energy output), we
observed an appreciable decrease of the SF$_5$ signal and a corresponding increase of the SF$_4$ signal. With 400 nsec laser pulses, the SF$_5$ signal completely disappeared, and the SF$_4$ signal was greatly enhanced. No F$_2$ signal has ever been detected in this experiment. A broad angular distribution for SF$_4$ was observed in the long pulse case, a typical example is shown in Fig. 1. This information combined with the absence of F$_2$ and the correlation between the appearance of SF$_4$ signal and the disappearance of SF$_5$ indicates a two step mechanism for the production of SF$_4$:

\begin{align}
\text{SF}_6 + n\nu &\rightarrow \text{SF}_6^{**} \rightarrow \text{SF}_5^* + F \quad \text{(1)} \\
\text{SF}_5^* + n'\nu &\rightarrow \text{SF}_5^{**} \rightarrow \text{SF}_4^* + F \quad \text{(2)}
\end{align}

where * and ** denote, respectively, internal excitation below and above the dissociation threshold. That the angular distribution of SF$_4$ in Fig. 1 peaks at 0° again indicates the absence of an "exit" barrier for the dissociation of SF$_5$. The dissociative lifetime of SF$_6^{**}$ in reaction (1) can be determined from the observed difference between the long and short laser pulses: Production of SF$_5$ from excited SF$_6$ must begin to be significant on a timescale of 150 nsec and must be essentially complete by 400 nsec. Thus the average dissociative lifetime of SF$_6$ at our level of excitation must be in the neighborhood of 150 nsec. This agrees well with our prediction of ~100 nsec based on the statistical model and the experimentally observed recoil energy distribution.

These results, therefore, provide fairly conclusive evidence that, under our experimental conditions, SF$_6$ absorbs, on the average, six
photons beyond the dissociation threshold. The very steep energy
dependence of the lifetimes listed in Table I suggests that this level
of excitation may arise as a consequence of a lifetime limitation in
the multiphoton absorption process for SF$_6$. Such a limitation would
occur for the case where continued pumping to higher levels with
shorter lifetimes becomes increasingly difficult due to dissociative
loss of excited molecules. This would result in the very important
effect that the level of excitation would not vary significantly over
a wide range of laser powers. We have found in our experiment that
this was indeed the case for SF$_6$.\textsuperscript{10}

In summary, we have found that the experimental recoil energy
distribution for SF$_5$ fragments produced in the multiphoton dissociation
of SF$_6$ is characteristic of that predicted for a statistical unimole-
cular dissociation. It agrees well with one calculated for the
absorption of six photons beyond the dissociation threshold. The
experimentally determined lifetime also agrees with statistical pre-
dictions for the same level of excitation. Finally, we have observed
that SF$_5$, produced in the first dissociation step, is unstable with
regard to secondary absorption and dissociation, consistent with the
speculation that it carries away a substantial fraction of the excess
energy of the primary reaction as internal excitation. The body of
experimental evidence combined with the statistical rate theory
calculations clearly indicates that the multiphoton absorption and
dissociation process in SF$_6$ proceeds statistically.
ACKNOWLEDGMENT

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Table I. RRKM Unimolecular Rate Constants and Lifetimes for the Production of SF$_5$.

<table>
<thead>
<tr>
<th>Energy $(E^*-E^0)$ in excess photons</th>
<th>$k(E^*)$ a$^{-1}$ sec$^{-1}$</th>
<th>$\tau$ nsec</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$7.4 \times 10^3$</td>
<td>135,000</td>
</tr>
<tr>
<td>3</td>
<td>$1.0 \times 10^5$</td>
<td>10,000</td>
</tr>
<tr>
<td>4</td>
<td>$7.4 \times 10^5$</td>
<td>1,351</td>
</tr>
<tr>
<td>5</td>
<td>$3.6 \times 10^6$</td>
<td>278</td>
</tr>
<tr>
<td>6</td>
<td>$1.3 \times 10^7$</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>$3.7 \times 10^7$</td>
<td>27</td>
</tr>
<tr>
<td>8</td>
<td>$9.8 \times 10^7$</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>$2.3 \times 10^8$</td>
<td>4</td>
</tr>
</tbody>
</table>
Fig. 1. Angular and time of flight distributions for products of the multiphoton dissociation of SF\textsubscript{6}: ●, SF\textsubscript{5} product with ~50 nsec laser pulse; ▲, SF\textsubscript{4} product (detected as SF\textsubscript{3}\textsuperscript{+}) with 500 nsec laser pulse (see text).

Fig. 2. Fragment recoil energy distributions for SF\textsubscript{6} → SF\textsubscript{5} + F. Data points ● are experimental results. Curves are statistical rate theory predictions for: ——, 4 photons; ———, 6 photons; ————, 8 photons absorbed above the dissociation threshold.
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