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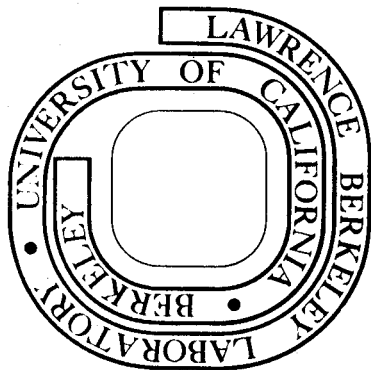
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THE EXTENT OF ENERGY RANDOMIZATION IN THE
INFRARED MULTIPHOTON DISSOCIATION OF SF₆

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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 hydrocarbons³ and the apparent detection of SF₄ and F₂ fragments in the decomposition of SF₆⁴ 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 SF₆ as SF₅ 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 H₂, occurs in SF₆ - H₂ 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.⁹ 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.⁶ 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 multi-scaling the mass spectrometer output signal. Typically, an eight μ sec 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 SF_5 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 SF_5 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 SF_6 absorbs more than one photon above the dissociation threshold, a substantial fraction of that excess energy must be retained by the SF_5 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."

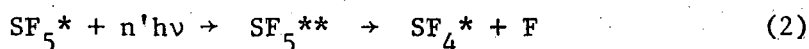
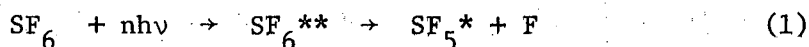
It also rules out a mode-selective "explosive" dissociative mechanism for which a velocity distribution skewed to higher energy would be expected.

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 SF_6 from an apparent pulselength dependence for the collisionless reaction mechanism. With laser pulses of ~50 nsec FWHM the dissociation products were exclusively SF_5 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 :



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 .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 unimolecular 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 predictions 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.

0 0 0 0 4 7 1 0 3 8 5

-7-

ACKNOWLEDGMENT

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REFERENCES

1. See, for example, papers on the subject presented at the Nordfjord Conference on Tunable Lasers and Applications (June 1976), and references therein.
2. (a) N. Bloembergen, Optics Comm. 15, 416 (1975); (b) D. M. Larsen and N. Bloembergen, Optics Comm. 17, 254 (1976); (c) R. V. Ambartzumian, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Poretzkii, ZhETF Pis. Red. 23, 26 (1976); (d) S. Mukamel and J. Jortner, Chem. Phys. Lett. 40, 150 (1976) and J. Chem. Phys. 65, 5204 (1976); (e) C. D. Cantrell and H. W. Galbraith, Optics Communications 18, 515 (1976); (f) V. S. Letokhov and A. Makarov (to be published); (g) T. P. Cotter (to be published).
3. R. V. Ambartzumian, N. V. Shekalin, V. S. Letokhov and E. A. Ryabov, Chem. Phys. Lett., 36, 301 (1975); D. F. Dever and E. Grunwald (~~J. Chem. Phys. 98, 5055 (1976)~~) ~~also assumed non-randomized excitation~~ to explain their observed results on multiphoton dissociation of CFC_3 .
4. K. L. Kompa and coworkers, see reference 1.
5. J. G. Black, E. Yablonovitch, N. Bloembergen and S. Mukamel, (to be published).
6. M. J. Coggiola, P. A. Schulz, Y. T. Lee and Y. R. Shen, Phys. Rev. Lett. 38, 17 (1977)
7. C. R. Quick, Jr. and C. Wittig, Chem. Phys. Lett. 00, 000 (1977).
8. J. M. Preses, R. E. Weston, Jr. and G. W. Flynn, ibid 00, 000 (1977).

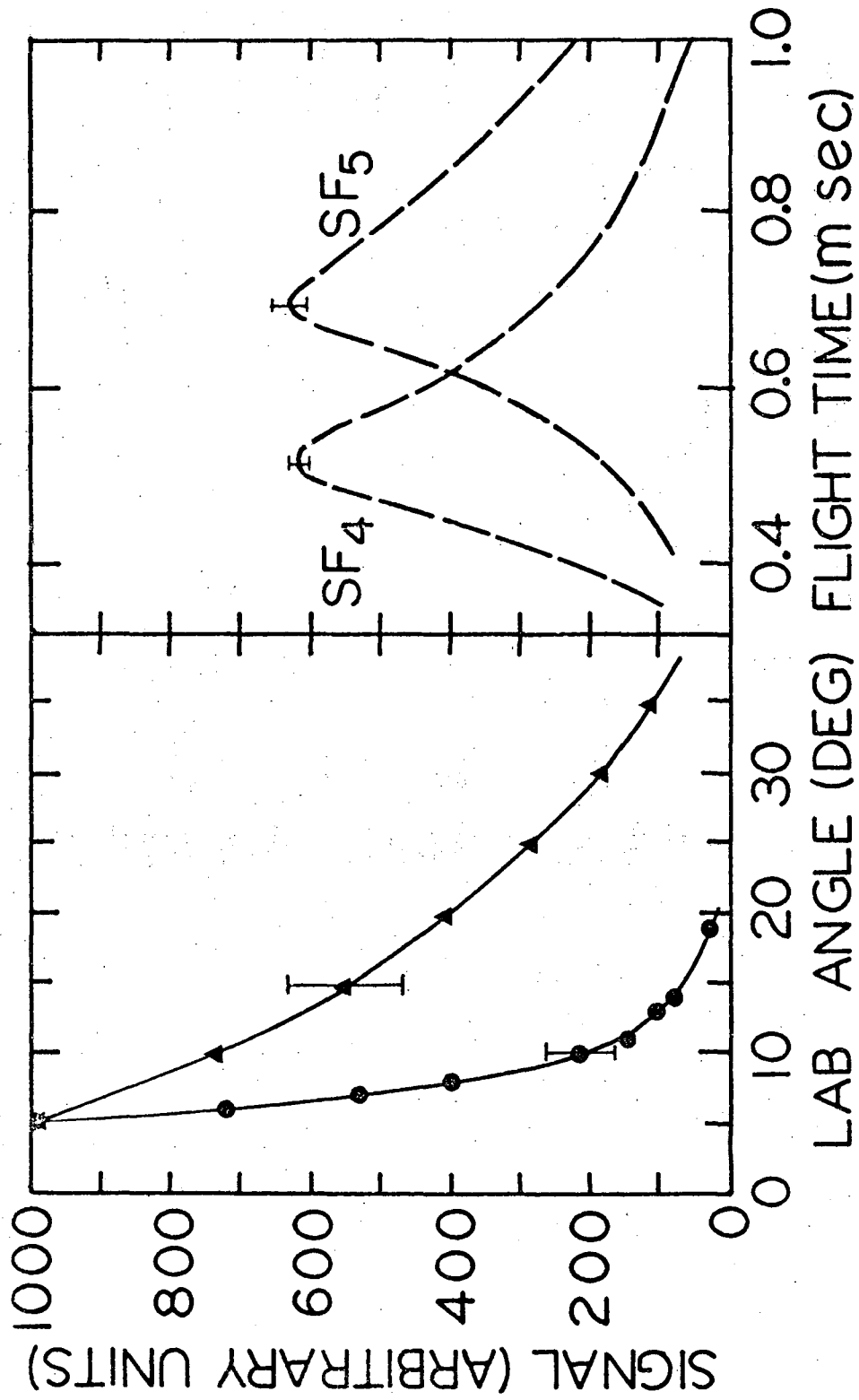
9. See, for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," (J. Wiley, New York, 1972).
10. E. R. Grant, M. J. Coggiola, P. A. Schulz, Y. T. Lee, and Y. R. Shen, (in preparation).

Table I. RRKM Unimolecular Rate Constants and Lifetimes for the Production of SF₅.

Energy (E*-E°) in excess photons	k (E*) a sec ⁻¹	τ nsec
2	7.4 x 10 ³	135,000
3	1.0 x 10 ⁵	10,000
4	7.4 x 10 ⁵	1,351
5	3.6 x 10 ⁶	278
6	1.3 x 10 ⁷	77
7	3.7 x 10 ⁷	27
8	9.8 x 10 ⁷	10
9	2.3 x 10 ⁸	4

FIGURE CAPTIONS

- Fig. 1. Angular and time of flight distributions for products of the multiphoton dissociation of SF_6 : ●, SF_5 product with ~50 nsec laser pulse; ▲, SF_4 product (detected as SF_3^+) with 500 nsec laser pulse (see text).
- Fig. 2. Fragment recoil energy distributions for $\text{SF}_6 \rightarrow \text{SF}_5 + \text{F}$. 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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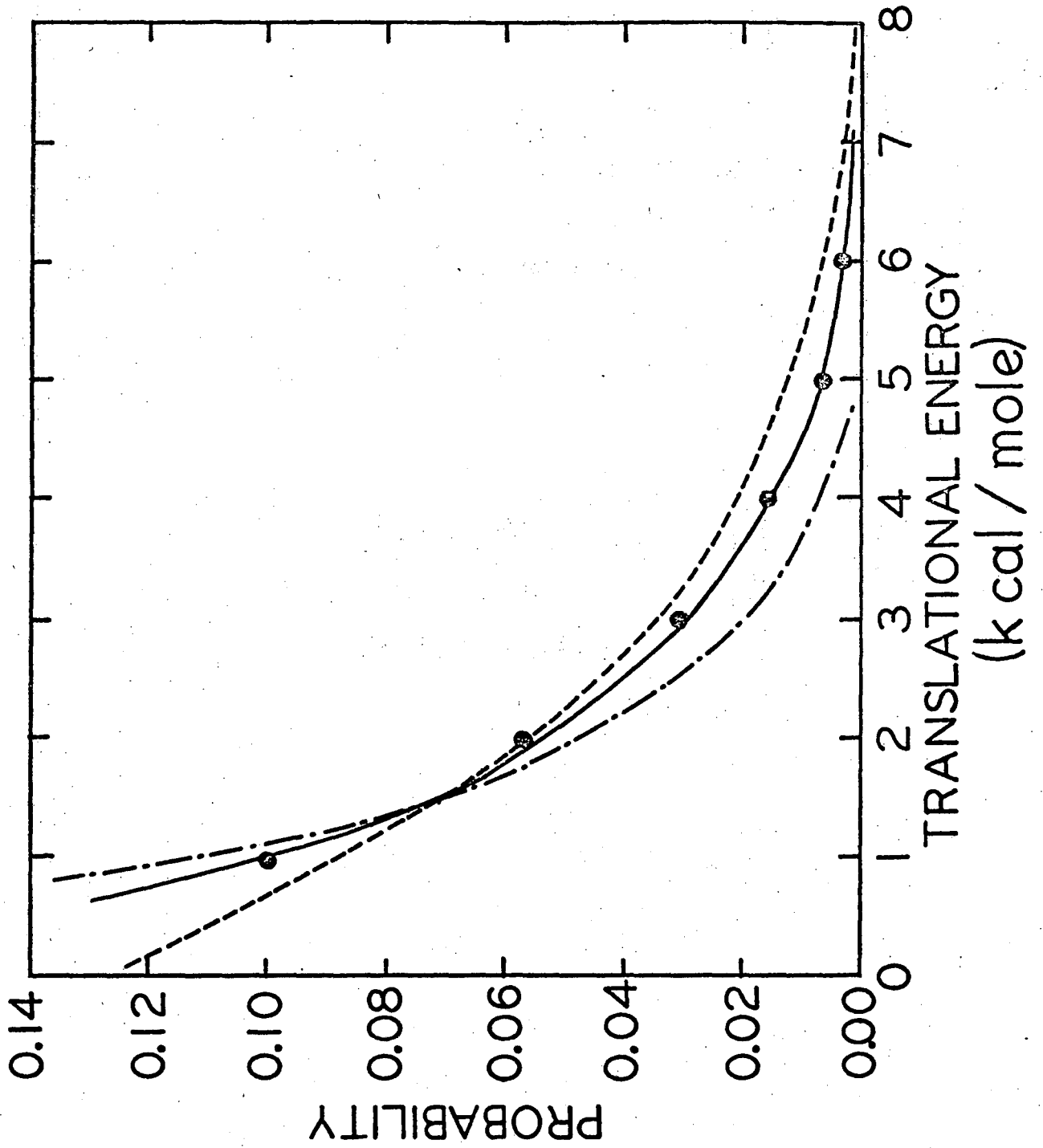


Fig. 2

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