To be presented at the VI International
Symposium on Molecular Beams,
Noordwijkerhout, the Netherlands,
April 18 - 22, 1977

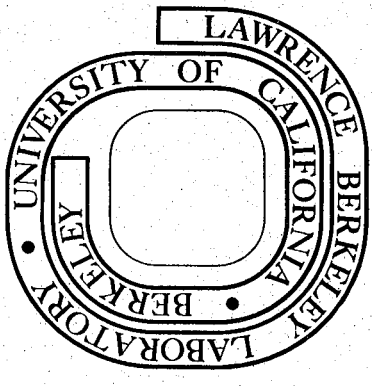
LBL-6035

DYNAMICS OF INFRARED MULTIPHOTON DISSOCIATION OF SF_6 BY MOLECULAR BEAM METHOD

E. R. Grant, M. J. Coggiola, Y. T. Lee,
P. A. Schulz, and Y. R. Shen

January 1977

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48



LBL-6035

LBL-6035

Dynamics of Infrared Multiphoton Dissociation of SF_6 By Molecular Beam Method

E. R. Grant, M. J. Coggiola and Y. T. Lee

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California, Berkeley, CA 94720

P. A. Schulz and Y. R. Shen

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Physics
University of California, Berkeley, CA 94720

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, selective and collisionless.[1] The physical principles which are mainly responsible for the absorption of a large number of photons by an isolated molecule under intense infrared laser radiation have been elucidated through many experimental and theoretical investigations.[1,2] However, one very important question which remains to be answered is the relation between the dynamics of molecular decomposition and the degree of vibrational excitation, i.e., the question of whether the excitation energy is completely randomized before molecular decomposition. The production of electronically excited fragments in the dissociation of halogenated hydrocarbons and the observations of SF_4 fragment in the decomposition of SF_6 without the evidence of the formation of lower energy SF_5 fragment[3] provided some basis of speculation that the excitation energy might not be randomized before the dissociation of excited molecules.[2(g)]

A crossed molecular beam apparatus has been adapted to study the dynamics of excitation and dissociation of polyatomic molecules in intense IR laser fields. Initial experiments have involved the study of the dissociation of SF_6 by CO_2 laser radiation at 10.6 μm. A molecular beam of SF_6 was formed by supersonic expansion using three stages of differential pumping. A grating tuned pulsed CO_2 TEA laser was used as the excitation source. The laser beam was focused by a 25 cm focal length ZnSe lens, and crossed the molecular beam near its focal point. The fragments produced by multiphoton dissociation of SF_6 within the small interaction region were detected as a function of recoil angle and velocity.

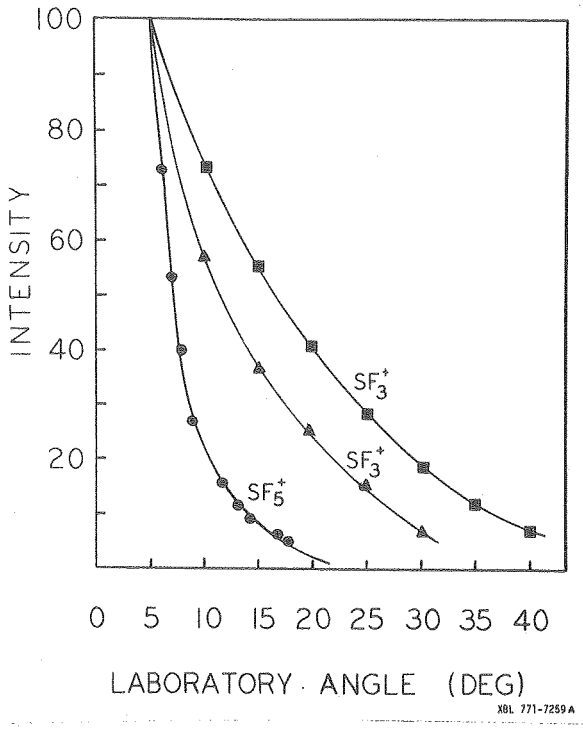


Fig. 1. Angular distributions of the fragment products

SF_5^+ (SF_5); pulse width: 60 ns FWHM. Energy: 30 J/cm^2
SF_3^+ (SF_4); pulse width: 500 ns FWHM. Energy: 5 J/cm^2
SF_3^+ (SF_4); pulse width: 500 ns FWHM. Energy: 15 J/cm^2

Figure 1 shows the measured angular distributions of fragments of SF_6 under various conditions. With an average laser power of 5×10^8 W/cm^2 and a pulse width of 60 nsec FWHM, the major fragments observed in the mass spectrometric detector are SF_5^+, SF_3^+, SF_2^+ and F^+, all with identical angular distribution to that of SF_5^+ shown. The angular distribution of a particular fragment is a very sensitive function of its mass and recoil velocity, and thus the invariance of the fragment angular distributions clearly implies that they all are due to the same parent, SF_5. This result then unambiguously identifies the primary dissociation products at this power density as SF_5 and F. The very narrow angular distribution of SF_5 peaking near the SF_6 beam also indicates that the SF_6 molecules do not dissociate explosively, the average energy released into translation is less than 1.5 kcal/mole and there is no substantial potential energy barrier beyond the dissociation energy of SF_6 into SF_5 and F.[4]

A more detailed profile of the SF_5 fragment recoil energy distribution has been obtained from a kinematic analysis of the angular distribution together with time of flight velocity measurements. Relative probabilities taken from the normalized distribution have been listed in Table I. An RRKM theoretical statistical model has been constructed to represent the multiphoton dissociation of SF_6. Based on this model, predicted recoil energy distributions for five, six and seven photons in excess of the dissociation threshold have been

determined. Representative probabilities from these distributions have been included in Table I for the purpose of comparison with the experimental results. As can be seen from this comparison, an RRKM model for dissociation from a narrow range of energies is consistent with the experimental results, if an average of approximately six excess photons is absorbed beyond the dissociation energy.

The statistical model with the absorption of six excess photons is also consistent with an estimate of the dissociative lifetime of excited SF_6 in our apparatus. As described above, for normal laser pulse lengths of 60 nsec, only fragments associated with the primary product, SF_5, are observed. However, when the laser pulse length is widened to 300 nsec, SF_5^+ is no longer observed; instead, SF_3^+, SF_2^+ and F^+ are seen with the same, broadened angular distributions. The results of these measurements at two different laser powers are also shown in Fig. 1. This indicates that SF_5 is formed during the period of the long laser pulse, and that this incipient SF_5 undergoes secondary absorption and decomposition to SF_4. Thus, the average lifetime for the multiphoton dissociation of SF_6 at a power density of 500 MW/cm^2 is comparable to or longer than 60 nsec, but should be much shorter than 300 nsec. The RRKM lifetimes associated with five, six and seven photons in excess of the dissociation threshold are given in Table I. The agreement of both the recoil energy distribution and lifetime estimate with RRKM prediction suggests that the absorption and decomposition processes involved in the multiphoton dissociation of SF_6 proceed statistically.

Table I. Unimolecular Dissociation Lifetimes and Distributions of Product Recoil Energy

Recoil Energy Kcal $Mole^{-1}$		Relative Probabilities		
	Experimental	Theoretical		
		(5)*	(6)	(7)
1	0.100	0.104	0.100	0.096
2	.057	.052	.053	.055
3	.031	.024	.028	.031
4	.016	.011	.014	.017
5	.006	.004	.006	.009
6	.003	.002	.003	.005
Lifetimes(ns):	60-300	276	75	27

*Number of photons in excess of dissociation threshold.

This work was done with support from the U. S. Energy Research and Development Administration.

References

1. See, for example, papers on the subject presented at the Nordfjord Conference on Tunable Lasers and Applicatons (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. Puretzkii, ZhETF Pis. Red. 23, 26 (1976); (d) S. Mukamel and J. Jortner, Chem. Phys. Lett. 40, 150 (1976) and J. Chem. Phys. (to be published) (e) C. D. Cantrell and H. W. Galbraith, Optics Communications 18, 515 (1976) (f) V. S. Letokov and A. Makarov (to be published); (g) T. P. Cotter (to be published).

3. K. L. Kompa and coworkers, see reference 1.

4. M. J. Coggiola, P. A. Schulz, Y. T. Lee and Y. R. Shen, Phys. Rev. Lett. 38, 17 (1977).