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### Publication Date

1977-08-01

Submitted to Chemical Physics  
Letters

uc-4  
LBL-6201 Rev. c. /  
Preprint

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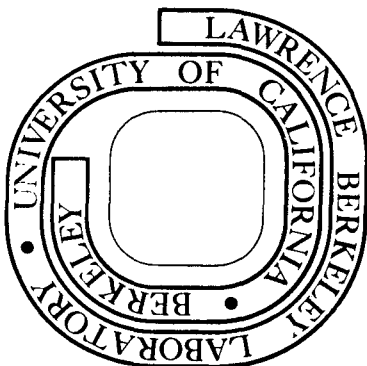
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August 1977

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

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THE EXTENT OF ENERGY RANDOMIZATION IN THE  
INFRARED MULTIPHOTON DISSOCIATION OF SF<sub>6</sub>

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AUGUST 1977

ABSTRACT

Crossed laser and molecular beams were used to obtain the recoil-energy distributions of fragments in the study of multiphoton dissociation of SF<sub>6</sub>. The measured recoil-energy distributions of SF<sub>5</sub> under a laser excitation of  $\sim 10 \text{ J/cm}^2$  are in good agreement with the theoretical prediction of the RRKM model for unimolecular dissociation assuming an average excitation of  $\sim 22 \text{ kcal/mole}$  beyond the dissociation threshold and complete energy randomization in the excited molecule before dissociation. At higher laser energy fluence, it was observed that a secondary dissociation process could occur in which the primary dissociation product, SF<sub>5</sub>, absorbed more photons and further decomposed into SF<sub>4</sub> and F. From the results, we found that the average dissociation lifetime for SF<sub>6</sub> was  $\sim 10 \text{ nsec}$  under our experimental conditions.

## 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.<sup>1</sup> 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.<sup>2</sup> However, one very important question which remains to be answered is the relation between the dynamics of the laser induced unimolecular dissociation and the energy distribution among the 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,<sup>3</sup> the apparent detection of SF<sub>4</sub> and F<sub>2</sub> fragments in the decomposition of SF<sub>6</sub>,<sup>4</sup> and the observation of seemingly mode-controlled multiphoton dissociation of halogenated hydrocarbons,<sup>5</sup> 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.,<sup>6</sup> based on absorption measurements, suggest that multiphoton dissociation is a statistical process.

Recently,<sup>7</sup> we reported the results of a crossed laser - molecule beam experiment that provided the first unambiguous characterization of the primary products of the multiphoton dissociation of SF<sub>6</sub> as SF<sub>5</sub> and F. In addition, this work showed that, on the average, the recoil energy of the products was less than 3 kcal. These results

have been confirmed by the recent findings of Quick and Wittig<sup>8</sup> and Preses et al.<sup>9</sup> that chemiluminescence, characteristic of the reaction of slow fluorine atoms with H<sub>2</sub>, occurs in SF<sub>6</sub> - H<sub>2</sub> 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<sub>5</sub> seen with variations in laser pulse length has provided an estimate of the dissociative lifetime of SF<sub>6</sub>.

The experimental recoil energy distribution and dissociative lifetime have been compared to the corresponding theoretical predictions of a detailed RRKM calculation.<sup>10</sup> 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<sub>6</sub> with an assumed energization of 8-9 photons (22 kcal/mole) above the dissociation threshold.

#### EXPERIMENTAL

The experimental setup was identical to that described previously.<sup>7</sup> A molecular beam of SF<sub>6</sub> was crossed by the 10.6 μm beam from a Tachisto CO<sub>2</sub> TEA laser. The laser beam was focused by a ZnSe lens of 25 cm focal length. For some measurements of SF<sub>6</sub>  $\xrightarrow{nh\nu}$  SF<sub>5</sub> + F, the laser

pulsewidth was shortened by means of a plasma discharge shutter to a 20 nsec full width at half maxima. For long pulse (50 ns) measurements of this primary reaction, the laser energy density at the interaction region was attenuated by ZnSe beam splitters and by defocusing to less than  $10 \text{ J/cm}^2$ . The  $\text{SF}_5$  fragments were identified in our detecting mass spectrometer as follows. Both  $\text{SF}_6$  and  $\text{SF}_4$  are known to decompose completely in the ionization chamber of the mass spectrometer; they yield respectively  $\text{SF}_5^+$  and  $\text{SF}_3^+$  as the major mass peaks. It appears that the radical  $\text{SF}_5$  also decomposes completely in the ionization process, with  $\text{SF}_3^+$  and  $\text{SF}_2^+$  as the prominent mass peaks. In our earlier observation,<sup>7</sup> the  $\text{SF}_5^+$  signal was heavily contaminated by  $\text{SF}_6$  molecules scattered into the detector by molecules released from the walls of the beam apparatus by the laser radiation. With this background scattering eliminated, the laboratory angular distributions of  $\text{SF}_3^+$  and  $\text{SF}_2^+$  were found to be identical as shown in Fig. 1. The ratio of  $\text{SF}_3^+$  to  $\text{SF}_2^+$  was  $\sim 4$  as compared with 6 and 2 given respectively by the fragmentation of  $\text{SF}_6$  and  $\text{SF}_4$ .

At higher laser energy densities, the  $\text{SF}_5$  radical could absorb more photons and further decompose into  $\text{SF}_4 + \text{F}$ . The appearance of this secondary dissociation process could be detected through the observation that the angular distributions of  $\text{SF}_3^+$  and  $\text{SF}_2^+$  started to deviate from each other, owing to the disproportionate production of  $\text{SF}_2^+$  by the  $\text{SF}_4$  dissociation product.

The fragment velocity distributions at various laboratory scattering angles 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 multiscaling the mass spectrometer output signal. Typically, a 10  $\mu$ sec channel width was used in a scan over 2.5 msec.

#### RESULTS AND DISCUSSION

The angular distributions for the  $\text{SF}_3^+$  signal at three laser pulse energy densities are shown in Fig. 1. The narrowest one was taken with the short pulse at c.a. 4  $\text{J}/\text{cm}^2$ . The intermediate and broadest ones were obtained with the longer pulse (50 nsec) at energies of 10 and 30  $\text{J}/\text{cm}^2$  respectively. For the two lower energy densities the  $\text{SF}_3^+/\text{SF}_2^+$  ratio was constant and equal to  $\sim 4$  at all angles. The time-of-flight spectra for both fragments at 10  $\text{J}/\text{cm}^2$  were also identical as shown in Fig. 2. The correspondence between the angular and time-of-flight distributions for the two fragments, together with their ratio, is evidence that the only dissociation product detected at these energies is  $\text{SF}_5\cdot$ . Such angular distribution and time-of-flight data were combined and deconvoluted using the velocity distribution of the molecular beam to obtain the center of mass recoil energy distribution. The result for this  $\text{SF}_5\cdot$  product at 10  $\text{J}/\text{cm}^2$  is shown in Fig. 3. Two qualitative but important conclusions can readily be drawn from these data:

- (1) The average recoil energy is low, approximately 2.5 kcal, indicating that, if  $\text{SF}_6$  absorbs more than one photon above the dissociation threshold, a substantial fraction of that



excess energy must be retained by the SF<sub>5</sub> 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-controlled "explosive" dissociative mechanism for which a velocity distribution skewed to higher energy would be expected.

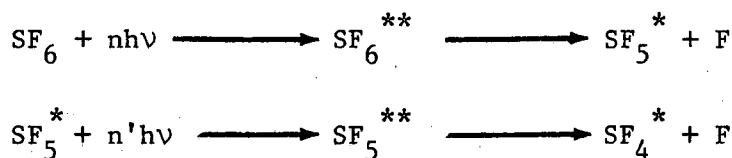
In addition, identical results were seen for laser polarizations both parallel and perpendicular to the detection plane. This indicates that the product recoil direction has no dependence on the polarization of the laser field and/or that the lifetime of the excited molecule is many rotational periods.

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. 3, correspondence between the experimental data and the theoretical curve for an energization by 8-9 photons (22 kcal) in excess of the dissociation threshold is very good. This, and other observations which will be discussed later, strongly suggests the validity of the statistical model for collisionless multiphoton dissociation.

For a low laser pulse energy density ( $< 10 \text{ J/cm}^2$ ), the dissociation products were almost exclusively  $\text{SF}_5$  and  $\text{F}$ . When the laser energy fluence was increased the angular distributions of the observed  $\text{SF}_3^+$  and  $\text{SF}_2^+$  in our mass spectrometer broadened and started to deviate from each other with fractionation ratios ranging from  $\sim 4$  at small angles to  $\sim 2$  at larger angles. Finally, at our highest laser energy density ( $\sim 35 \text{ J/cm}^2$ ), the angular distributions for  $\text{SF}_3^+$  and  $\text{SF}_2^+$  again merged with a fractionation ratio of  $\sim 2$  at all angles.

We can then conclude that  $\text{SF}_4$  had appeared as one of the dissociation products and dominated the signal at large angles for intermediate powers and at all angles for high powers. Since no  $\text{F}_2$  fragment was found in our experiment in spite of an exhaustive search, the  $\text{SF}_4$  fragments must have resulted from dissociation of the radical  $\text{SF}_5$ . This was supported by the recent chemiluminescence experiments of Quick and Wittig<sup>8</sup> and Preses et al.<sup>9</sup> With higher laser energy fluence, the  $\text{SF}_4$  signal was greatly enhanced and a broader angular distribution of  $\text{SF}_4$  was observed.

Apparently, the  $\text{SF}_5$  radicals produced during the laser pulse could absorb more photons and further decompose into  $\text{SF}_4 + \text{F}$  with additional recoil energy



where \* and \*\* denote respectively internal excitations below and above the dissociation threshold. Since most of the excess energy of  $\text{SF}_6^{**}$  is retained by the  $\text{SF}_5^*$  fragment in the dissociation process, the  $\text{SF}_5^*$  produced should already be excited to its quasi-continuum states, and

could therefore readily absorb more laser photons to and beyond the dissociation threshold. In order for this secondary dissociation process to occur,  $SF_6^{**}$  must have a dissociation lifetime shorter than the laser pulse and the laser energy fluence must be sufficiently high so that the  $SF_5^*$  radicals can absorb enough photons to exceed the dissociation threshold for  $SF_5 \rightarrow SF_4 + F$ . In our experiment with an energy density of from 6-10  $J/cm^2$  (Fig. 1) we found essentially no  $SF_4$ . Allowing time for energy deposition into the molecule, this suggests that the average dissociation lifetime of  $SF_6^{**}$  should be around 10 nsec. This value is consistent with our theoretical estimate (4-10 nsec) of the dissociation lifetime for  $SF_6^{**}$  with an excess energy of 8-9 photons (~22 kcal/mole) as shown in Table I.

The above results therefore provide fairly conclusive evidence that under our experimental conditions,  $SF_6$  absorbs on the average 8-9 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  $SF_6$ .<sup>10</sup>

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 8-9 photons beyond the dissociation threshold. The experimentally estimated 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 indicates that the multiphoton absorption and dissociation process in  $SF_6$  proceeds statistically. Recently, we have carried out similar studies on other molecules such as  $CF_3Br$  and  $CFCl_3$ . In all cases, we found that the statistical model for dissociation worked well even though the levels of excitation for different molecules were different.<sup>10</sup> The results now enable us to more or less predict the multiphoton dissociation dynamics for a large number of polyatomic molecules.

#### ACKNOWLEDGMENT

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

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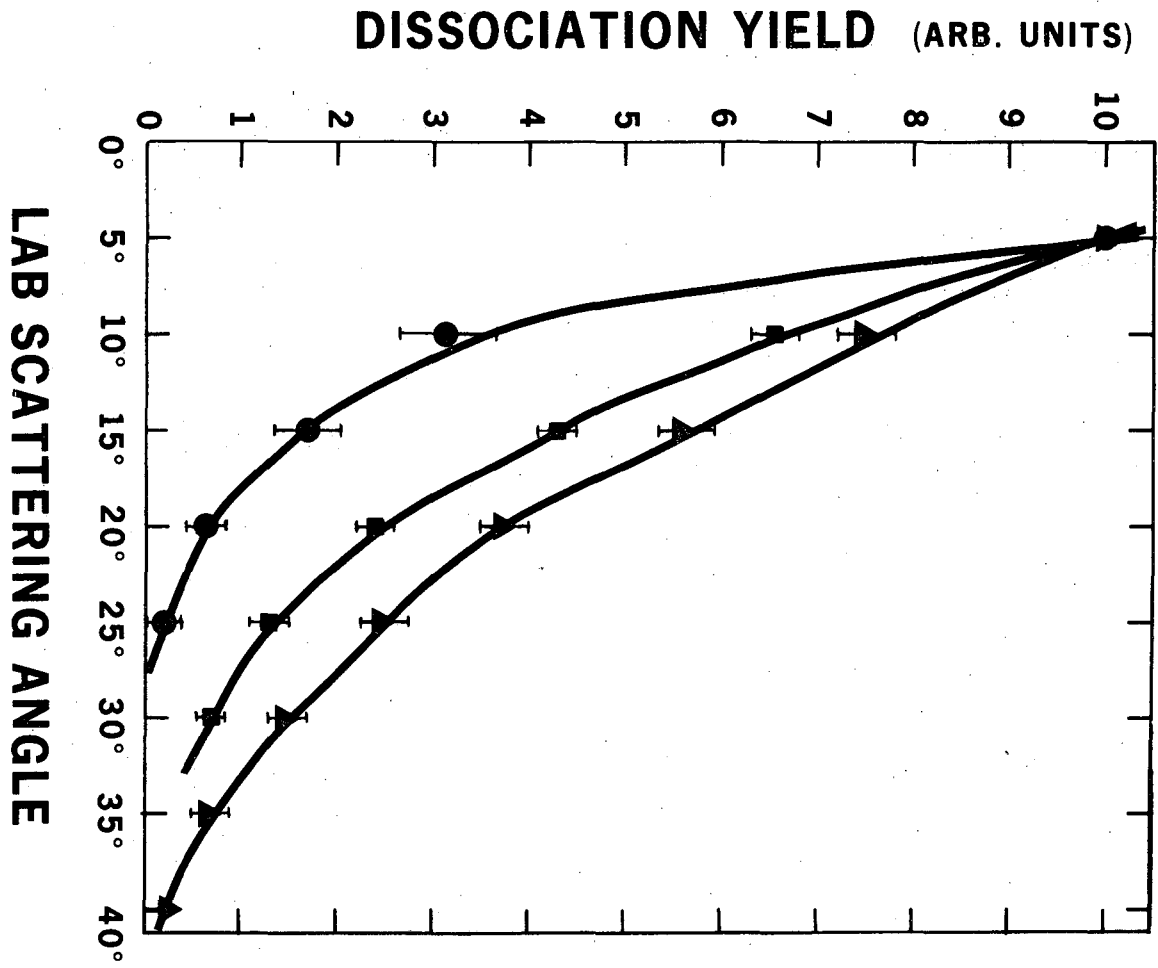
Table I. RRKM Unimolecular Rate Constants and Lifetimes for the Production of SF<sub>5</sub>.

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

FIGURE CAPTIONS

- Fig. 1. Angular distributions of  $SF_3^+$  signal detected from  $SF_5$  product at  $\sim 4 \text{ J/cm}^2$  (short laser pulse),  $\bullet$ ; at  $\sim 10 \text{ J/cm}^2$ ,  $\blacksquare$ ; and from  $SF_4$  product at  $\sim 35 \text{ J/cm}^2$ ,  $\blacktriangle$ .
- Fig. 2. Time-of-flight distribution for  $SF_3^+$  and  $SF_2^+$  produced in the ionizer from  $SF_5$ . Data taken  $10^\circ$  from the beam with a laser pulse energy density of  $10 \text{ J/cm}^2$ .
- Fig. 3. Deconvoluted center of mass recoil energy distribution for  $SF_6 \rightarrow SF_5 + F$  obtained from experiment at  $10 \text{ J/cm}^2$ ; statistical rate theory predictions for seven,  $- - -$ ; nine,  $---$ ; and eleven,  $---$  photons above the dissociation threshold.





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Fig. 1

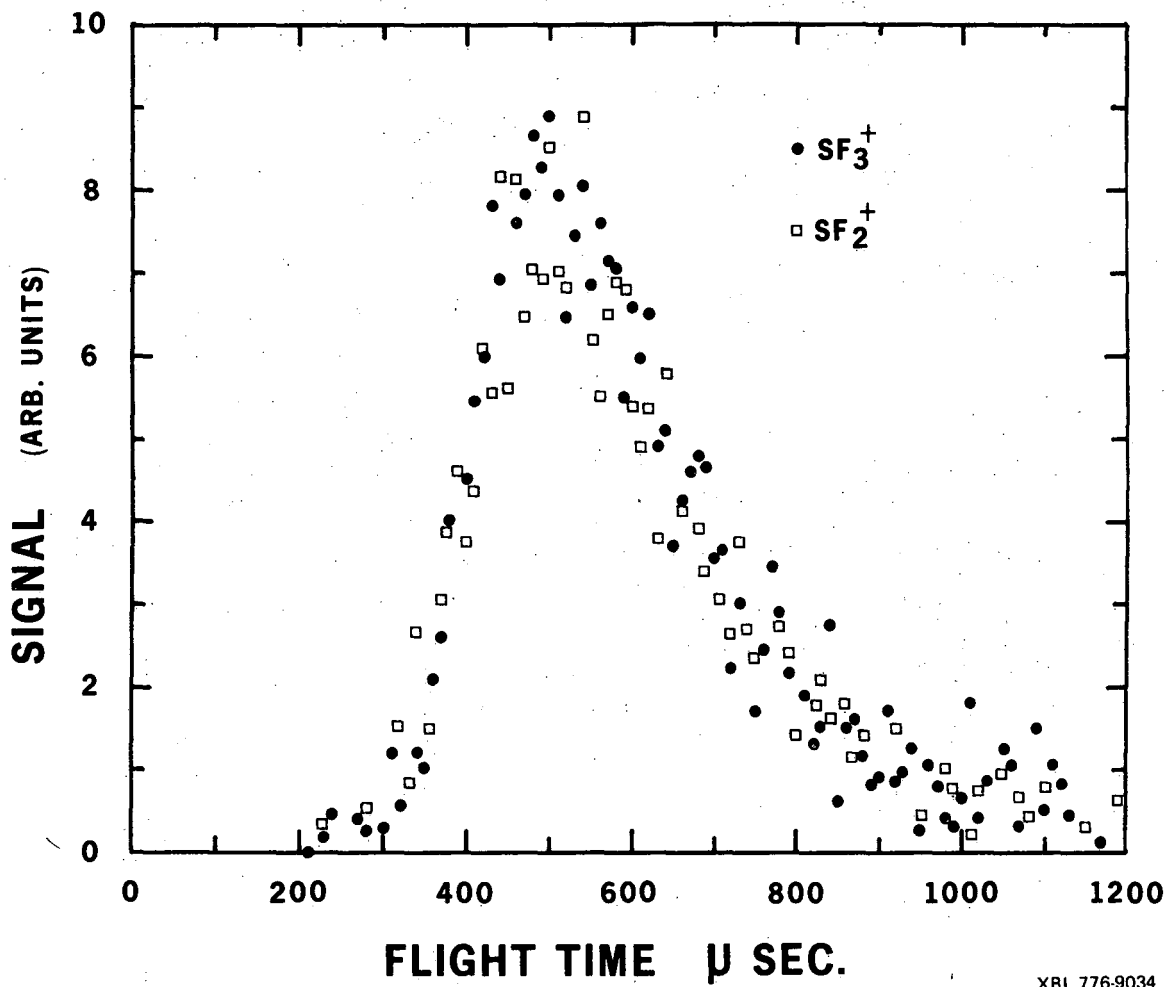


Fig. 2

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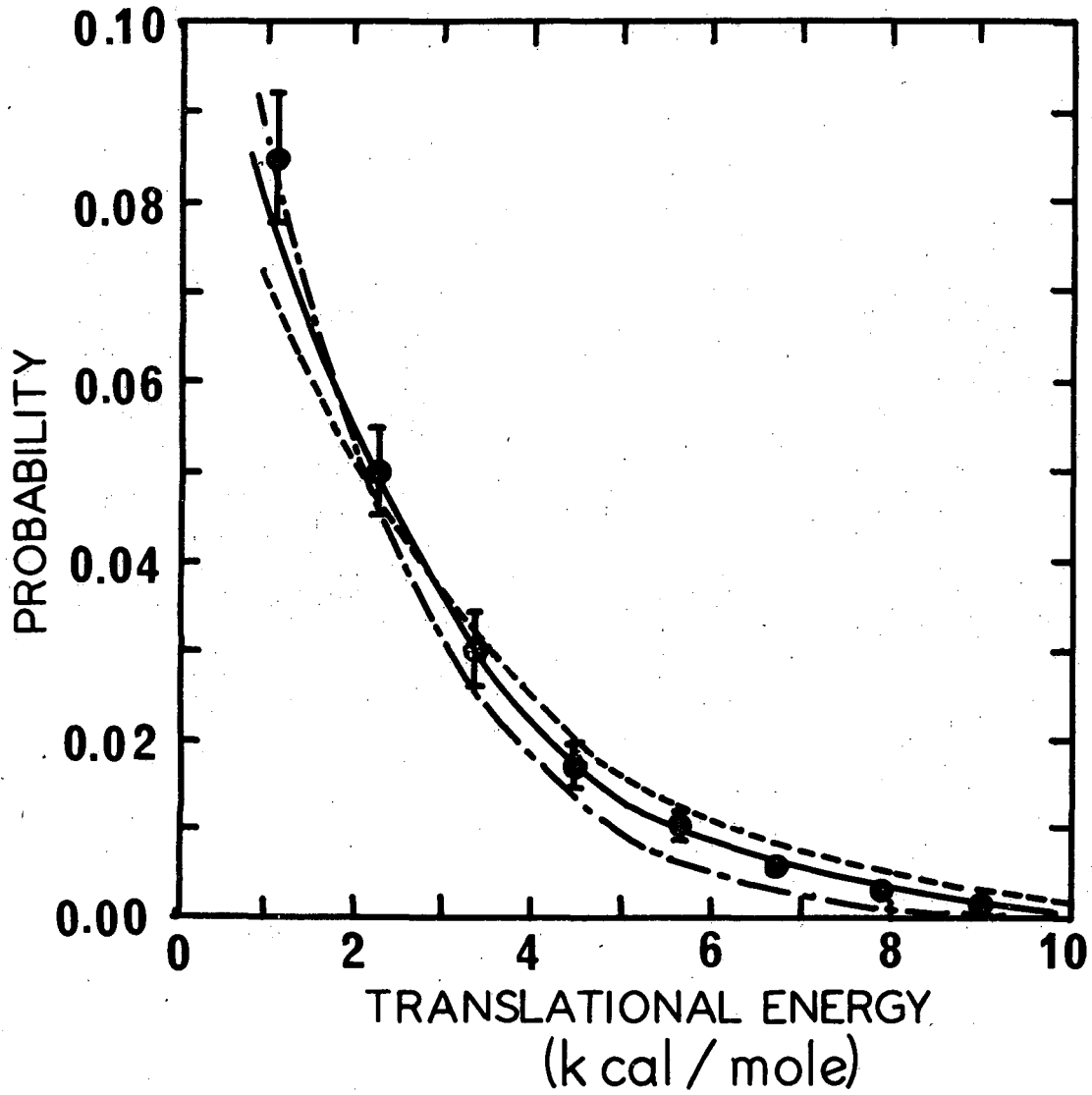


Fig. 3

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This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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