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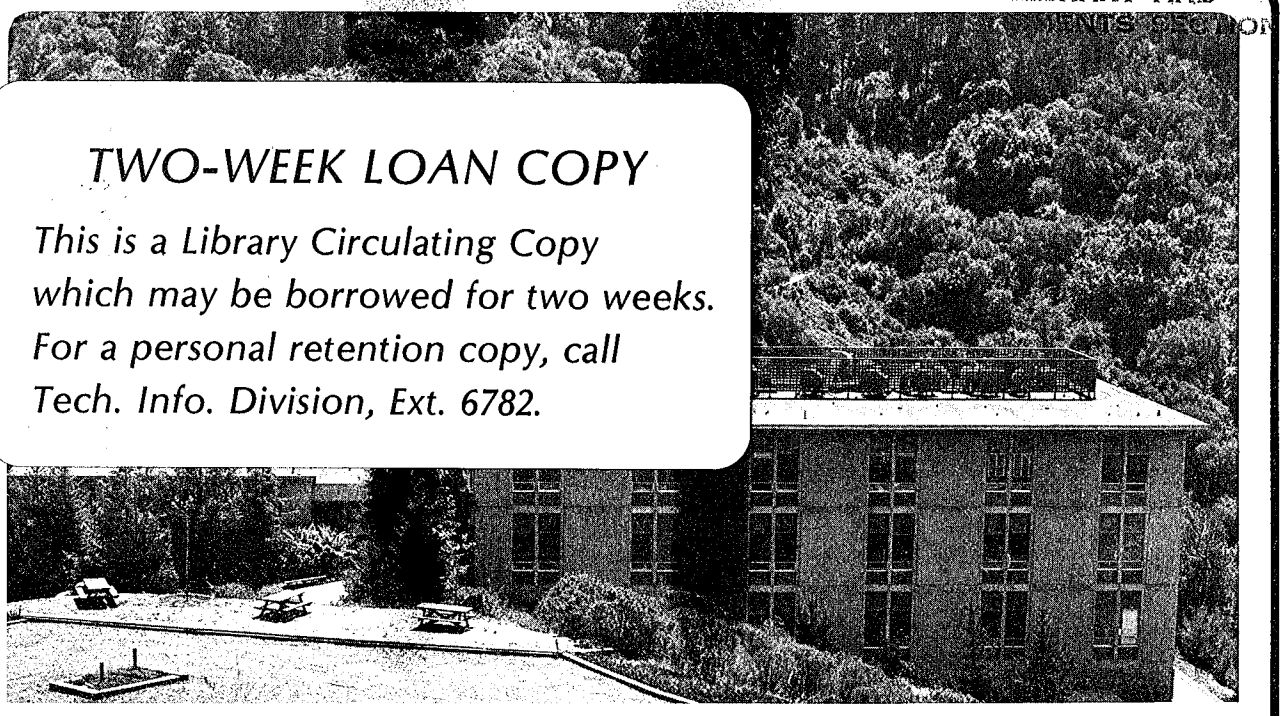

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On the Photodissociation of Nitromethane at 266 nm

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ABSTRACT

In a crossed laser-molecular beam study of nitromethane, it was found that the excitation of nitromethane at 266 nm did not yield dissociation products under collision free conditions. When a small cluster of nitromethane was excited at the same frequency, product was seen only at energies and masses consistent with rupture of the van der Waals bond by vibrational predissociation of the excited state.

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INTRODUCTION

Nitromethane is one of the high yield clean liquid fuels. Its detonation characteristics have been studied quite extensively.[1] Recently, there has also been some interest in the photodissociation of nitromethane because of a possible important role in atmospheric chemistry. The absorption spectrum of nitromethane in the UV region consists of a main band peaking at 190 nm with a relatively large cross section of ~2 x 10^{-17} cm^2 and a much weaker band at around 270 nm with almost a 600 times smaller cross section.[2-4] The transition is believed to be a $n \rightarrow \pi^*$ transition into a NO_2 π orbital. A quantum yield of unity was often assumed for dissociation over this entire absorption range in view of the continuous nature of the absorption spectrum. A recent estimate of the atmospheric photodissociation lifetime of nitromethane was based on this assumption.[2]

However, in an earlier study of the photodissociation of nitromethane in liquid using 266 nm picosecond pulses, it was found that the production of NO_2 seemed to increase linearly in time after an induction period of several nanoseconds after the laser pulse.[5] This apparent abnormal behavior was in line with the suggestion that the photodissociation of CH_3NO_2 at 266 nm is indirect[6] and raised the question of quantum yield and primary dissociation mechanism in the weaker absorption band around 270 nm.

We have performed a study of the photodissociation of nitromethane and nitromethane clusters in a crossed laser-molecular beam apparatus.

Our purpose was to clarify whether the previously reported photodissociation of nitromethane at 266 nm can actually take place under collision free conditions. If the excitation of isolated nitromethane is not a direct photodissociation transition and does not dissociate appreciably under collision free conditions, then it would be interesting to investigate whether the intramolecular dissociation will be facilitated by the presence of other nearby molecules. This possible process was investigated by exciting small (2 or 3 molecules) clusters of CH_3NO_2 produced in a supersonic expansion. The cluster could either decay by perturbation induced fragmentation of the CH_3NO_2 molecules, or by dissociation of the van der Waals bonds holding the clusters together.

EXPERIMENTAL

The crossed laser-molecular beam machine with a rotatable mass spectrometric detector used in this experiment was similar in design to an older machine[7] and has been described in detail elsewhere.[8] Its distinguishing characteristics are a much higher resolution in time-of-flight velocity measurements due to a longer flight path, much lower detector background levels, and a wider angular scanning range. It has been successfully applied to a study of the photodissociation of ozone, in which the vibrational states of the O_2 photofragment product were clearly resolved.[9]

The laser source used in this experiment was the fourth harmonic frequency of the Nd:YAG laser. Typically 50 mJ of energy per pulse at 266 nm was used. The laser pulse duration was about 7 ns and the repetition rate was 10 pps. In order to collect signal for 30,000 laser shots, a typical run lasted for one hour. The central feature of the detection system is a very fast 255 channel scaler triggered by the laser pulse with negligible delay.[8]

The molecular beam of nitromethane was produced by a supersonic expansion of a mixture of nitromethane with a rare gas carrier through a 0.23 mm diameter quartz nozzle. The temperature of the nozzle was controlled externally by a resistive heater. The gas mixture was formed by bubbling the carrier gas, either argon or helium, through a bottle of liquid nitromethane immersed in a constant temperature bath. The temperature of the bath was adjusted to control the partial pressure of the nitromethane.

In the molecular beam photofragmentation experiments where the yield of photodissociation products are expected to be low, it is possible to enhance the detectability of the dissociation products, with the sacrifice of angular and velocity resolution, by increasing the laboratory velocity of the molecular beam. If the velocity of the molecules in the beam could be increased to a value which is substantially larger than the velocity of the product in the center-of-mass coordinate, the product would be confined in a relatively small forward cone in the laboratory frame. We tried to accomplish this by both raising the nozzle temperature and seeding 35 torr of nitromethane in 400 torr of helium gas in the supersonic expansion. At a nozzle temperature of 100°C, excessive formation of molecular clusters was prevented, the velocity of the nitromethane molecules was found to be 1.55×10^5 cm/s. By changing the expansion conditions of the nozzle, namely, seeding 35 torr of nitromethane in 175 torr of argon in a room temperature nozzle, we were able to produce dimers, trimers and some higher polymers of CH_3NO_2 in the molecular beam. The velocity of trimers under this expansion condition was 0.56×10^5 cm/s.

RESULTS AND DISCUSSION

After an intensive search for the most likely photodissociation products; CH_3 and NO_2 at masses 15 (CH_3^+), 46 (NO_2^+), no signal was observed even after accumulating for over 40,000 laser shots. Signals were also checked for less likely dissociation channels at masses 30 (NO^+), 31 (HNO^+) and 45 (CH_3NO^+), but again, no evidence of dissociation was found at any of these mass numbers. Detector angles were set at 20° and 30° from the molecular beam in our search for signal. According to a velocity diagram using the molecular beam velocity and the c.m. translational recoil velocity of the fragment for a given product translational energy, dissociation products should reach these laboratory detector angles, even if a large fraction of excess energy of 45 kcal/mole appears as internal excitation of products. For CH_3 and NO_2, the required product translational energies are only 0.1 and 0.9 kcal/mole respectively at a laboratory angle of 20° and 0.2 and 2.0 kcal/mole respectively at 30°.

According to an estimate of the sensitivity of our detection system, commensurate with the integration time and the intensity of the molecular beam, the minimum detectable dissociation cross section is approximately 10^{-21} cm^2 if the molecule dissociates with a lifetime shorter than 10^{-5} second, which is the transit time of the molecules passing through the viewing zone of the detector. This estimate is also in agreement with the results of ozone and ketene photofragmentation experiments which have been successfully performed using this apparatus.[10] The published absorption cross section for nitromethane is around 3×10^{-20} cm^2 at

266 nm.[2,11] Therefore, the apparent conclusion is that nitromethane excited at 266 nm does not photodissociate directly. Namely, the dissociation lifetime must be much longer than 10^{-5} seconds under collision free conditions.

Crossing the laser (266 nm) with the molecular beam containing small fractions of dimers and trimers of nitromethane, signals due to laser excitation were observed at mass 61 ($CH_3NO_2^+$) and 122 $(CH_3NO_2)_2^+$. These signals were due to the following vibrational predissociation processes of vibronically excited molecular clusters.

$$(CH_3NO_2)_2 + h\nu \rightarrow (CH_3NO_2)_2^* \rightarrow 2CH_3NO_2$$
$$(CH_3NO_2)_3 + h\nu \rightarrow (CH_3NO_2)_3^* \rightarrow (CH_3NO_2)_2 + CH_3NO_2$$

These predissociations occur because the excitation energy in the vibrational degrees of freedom in the cluster is larger than the binding energy between components of the cluster. Similar predissociations have been observed via infrared vibrational excitation in clusters of benzene, ammonia, methanol, water and hydrogen fluoride.[12] Figure 1 and Fig. 2 show the angular and velocity distributions of the product detected as $(CH_3NO_2)_2^+$. The solid lines passing through the data points in both figures represent the result of a theoretical fit calculated using a translational energy distribution shown in Fig. 3. The dotted curve in Fig. 2 represents the velocity distribution of the nitromethane trimers before dissociation. We can see that the extra translational energy in the fragments broadens the velocity distibution considerably.

From Fig. 3, it is clearly seen that the maximum translational energy in the predissociation product is about 1 kcal/mole. However, most of the product fragments prefer to have no excess kinetic energy. This observation is almost identical to the results on the infrared predissociation of benzene clusters.[13]

The observation of strong predissociation signal from the clusters also points to the conclusion that the lack of signal from the photodissociation of CH_3NO_2 experiment is indeed a real indication that CH_3NO_2 excited by 266 nm does not dissociate directly. And, as we have mentioned above, it implies an upper limit of 10^{-21} cm^2 for the direct photodissociation cross section of CH_3NO_2. Since the corresponding absorption cross section is 3×10^{-20} cm^2, this absorption must be due to a bound-bound transition. The observation of NO_2 fragments in all previous bulk experiments on nitromethane must be due to collisional dissociation of the excited molecules. At atmospheric pressure, collisional relaxation and/or collision induced intersystem crossing should compete with collisional dissociation and the assumption of a quantum yield of unity in the weaker absorption band peaking at 270 nm is clearly not justified. Since the excitation energy at 266 nm is much larger than the dissociation energy of $CH_3NO_2 \rightarrow CH_3 + NO_2$, lack of direct dissociation signal implies either an intersystem crossing for the excited singlet state, so that the effect of photoexcitation at 266 nm might result in a bound metastable triplet state with some vibrational excitation, or an extremely long predissociation lifetime.

Collision induced processes cannot be important for monomers in the molecular beam, however, all of them are, in principle, possible processes in the clusters. Apparently, in dimeric or trimeric clusters of nitromethane, "collision induced" chemical dissociation does not seem to compete efficiently with vibrational predissociation processes. The identity of the electronic state from which the system predissociates is not determined by our experiment and certainly presents an interesting question. Also, the predominance of vibrational predissociation in the cluster suggests, but does not necessarily imply, that vibrational relaxation of the excited electronic state will be the major process in room temperature collisions. The very low internal temperature of the cluster requires that it samples a much more restricted region of the interaction potential than would occur in a normal collision. An investigation of the relative importance of vibrational relaxation and collision induced dissociation as a function of collision energy would be very interesting, as would its dependence on the vibrational energy of the excited electronic state.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1. Laboratory angular distributions of $(CH_3NO_2)_2$ from vibrational predissociation of vibronically excited $(CH_3NO_2)_3$ at 266 nm excitation. Dots are experimental results. The solid curve is the calculated angular distribution using the energy distribution of Fig. 3.
XBL-8010-12360

Fig. 2. Laboratory velocity distributions of $(CH_3NO_2)_2$ from $(CH_3NO_2)_3$. Symbols are the same as indicated in Fig. 1. Dashed curve is the velocity distribution of $(CH_3NO_2)_3$.
XBL-8010-12362

Fig. 3. Translational energy distribution of the process $(CH_3NO_2)_3 \xrightarrow{266\ nm} (CH_3NO_2)_2 + CH_3NO_2$ which gives the best fit to the data shown in Fig. 1 and Fig. 2.
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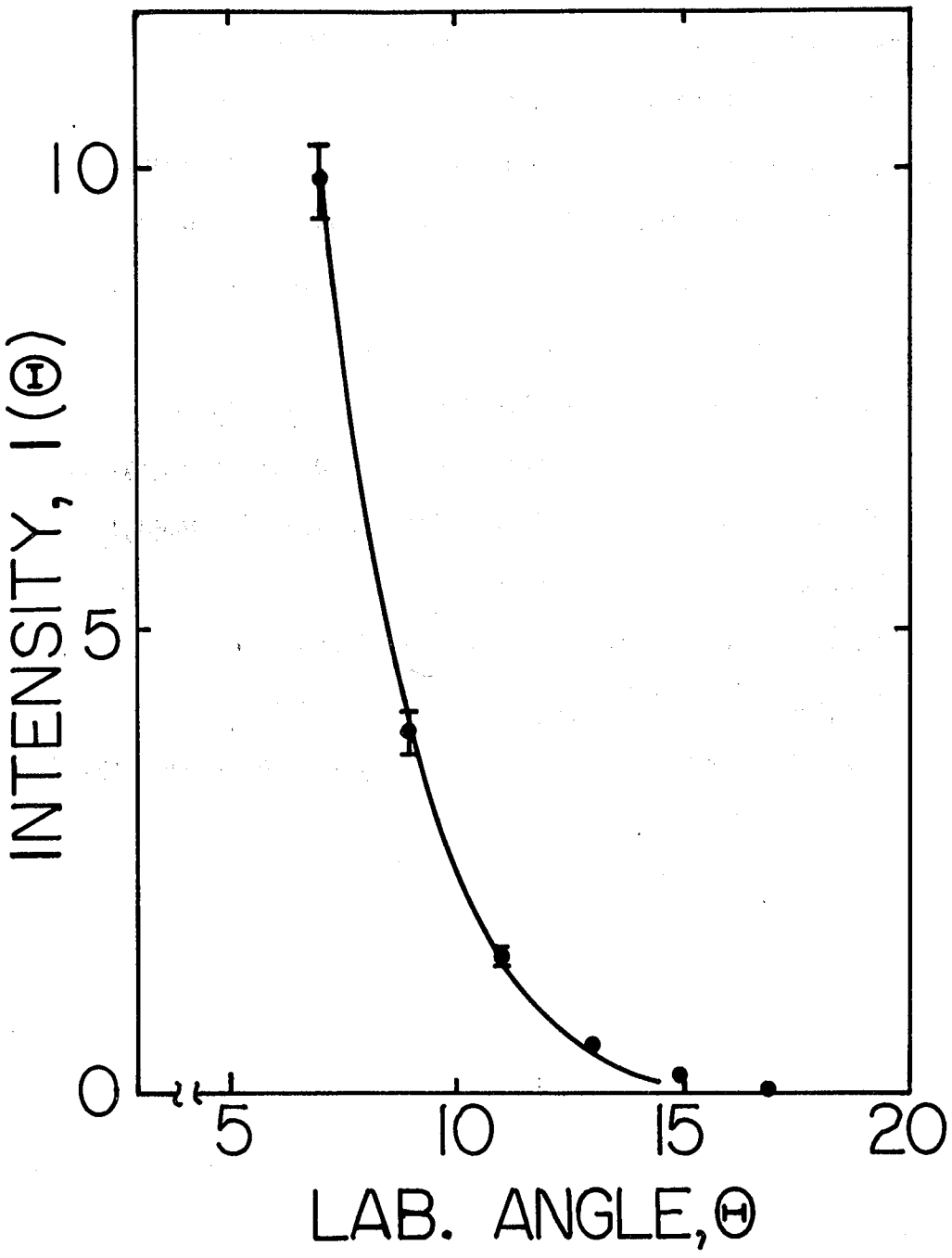

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Fig. 1

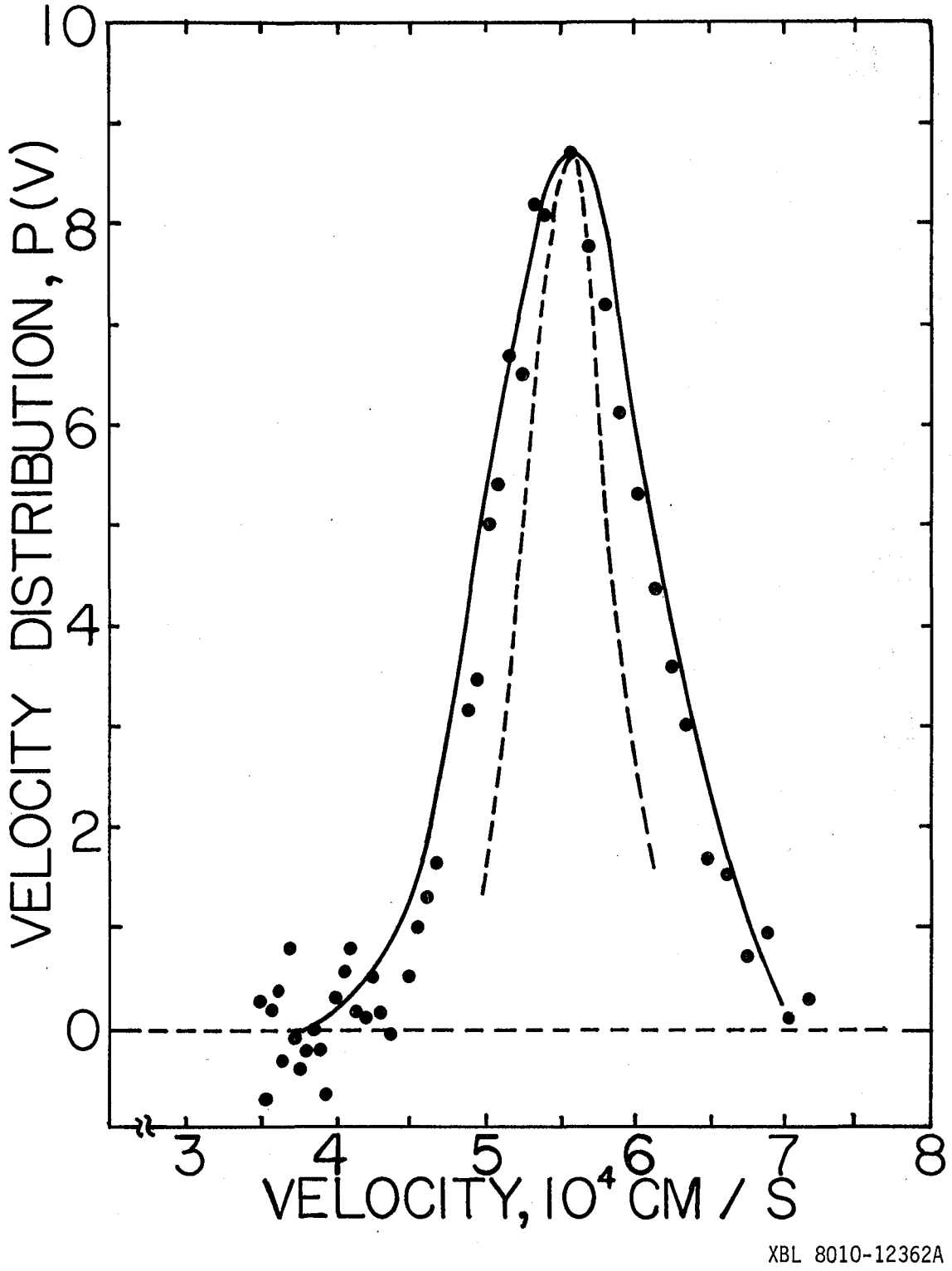
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Fig. 2

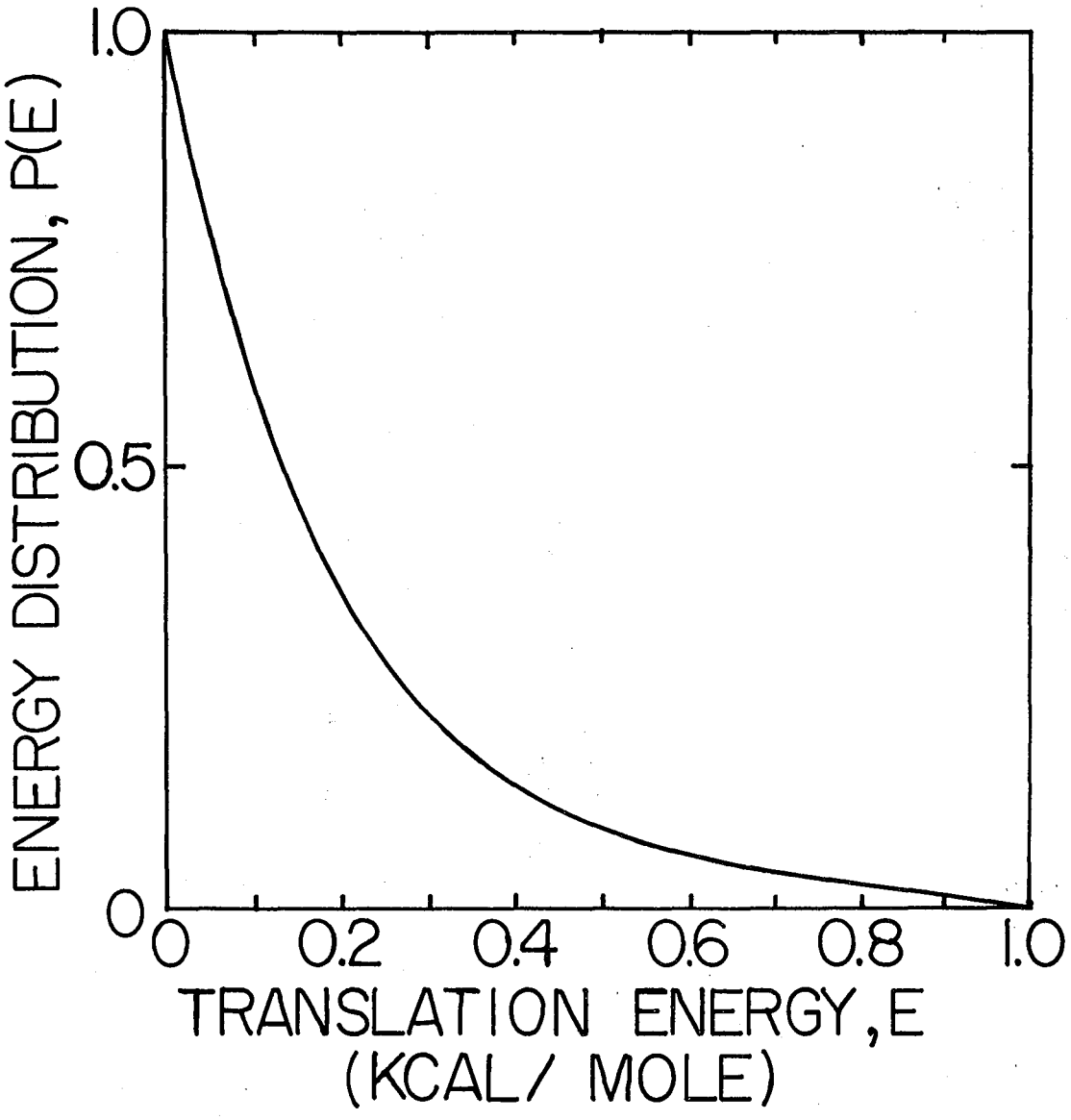

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Fig. 3