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THREE AND FOUR CENTER ELIMINATION OF HCl IN THE MULTIPHOTON DISSOCIATION OF HALOGENATED HYDROCARBONS

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ABSTRACT

Three and four center unimolecular elimination reactions of HCl have been investigated for CHF_2Cl, $CHFCl_2$, CH_3CCl_3, CH_3CF_2Cl and $CHClCF_2$ in a molecular beam experiment using infrared multiphoton absorption to energize the molecule. The translational energy distributions obtained in this work show that the average translational energy released to the fragments is around 8-12 kcal/mole, except for the three center elimination reaction from $CHClCF_2$, which gives a value of 1 kcal/mole. In four center eliminations, the translational energy released is less than 20% of the potential energy barrier of the back reaction. This is somewhat less than previous indications that approximately 30% of the potential energy barrier of the exit channel in four center reactions should be released into translation.

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INTRODUCTION

During the last couple of years, there has been tremendous interest in the process of unimolecular dissociation induced by a strong infrared field through multiphoton excitation.[1] The process has been observed for a variety of molecules, most of which have a strong infrared absorption band coinciding with the output frequencies of the CO_2 laser. In particular, collisionless multiphoton dissociation (MPD) has been investigated for a number of halogenated methanes,[2-4] ethenes,[2,5,6] and ethanes.[2,7] It is now reasonably well established[1,2,8,10] that energy pumped into a molecule by the laser field is more or less randomly distributed in all vibrational degrees of freedom before decomposition if the molecule is excited above the dissociation energy level. Such a highly excited molecule is not qualitatively very different from the energized complexes produced by a collisional excitation or chemical activation. However, the highly selective nature of the MPD process, together with the fact that it can be realized under collisionless conditions, makes it a useful probe for the study of dynamics of unimolecular reactions. This has already been established by a number of workers.[2,5-7]

Most of the experiments reported so far, have been on 2-center atomic elimination reactions, especially those involving halogen atoms. In such reactions, the energy required for dissociation is roughly the same as the difference in the enthalpy of formation of the fragments and the parent molecule, i.e., there is essentially no energy barrier for the back reaction. One can then use a statistical (RRKM[9]) theory of unimolecular reactions to explain the results successfully. In particular, the theory predicts that during dissociation only a relatively small fraction of the excess energy (i.e., the excess amount of energy over the dissociation energy) is released as translational energy in the fragments. This agrees with the observations made in our laboratory.[2,10] However, for 3- and 4-center eliminations, it is known[9,11] that the energy threshold for dissociation may be considerably higher than the difference in enthalpy of formation between the parent molecule and the products. Consequently, the dynamics of dissociation may be quite different from that of a two-center elimination process. It has been the object of several studies to map out the partition of excess energy between translational, rotational and vibrational degrees of freedom in the reactions products. Setser et al.[12] did a series of experiments on hydrogen halide elimination from chemically activated deuterated haloethanes, and obtained information about the vibrational energy distribution in the fragments. Pimentel et al.[13-15] obtained laser emission from highly excited ($v = 4$ at least) hydrogen halides through dissociation of chemically activated halogenated ethanes and ethenes. Using IR multiphoton excitation, Quick and Wittig[6] observed spontaneous emission from vibrationally excited HF in MPD of vinyl fluoride, and King and Stephenson[16] measured rotational and vibrational energy distributions in the CF_2 fragment from MPD of CHF_2Cl via laser-induced fluorescence.

So far, little is known about the amount of excess energy released as translational energy to the fragments in these 3- and 4-center elimination reactions. The translational energy distribution contains information about the nature of the potential energy surface of the reaction, in the region beyond the critical configuration.[9] To address this problem, we have investigated five systems (CH_3CCl_3, CH_3CF_2Cl, $CHClCF_2$, CHF_2Cl and $CHFCl_2$) that exhibit either 3-center or 4-center HCl elimination as a major dissociation channel, using infrared multiphoton excitation to initiate the unimolecular dissocation. To ensure complete elimination of molecular collisions we have used the crossed laser and molecular beam method[5] for the investigation. Thus we can obtain directly the translational energy distribution of the dissociation fragments. In order to have a better understanding of the dynamics of unimolecular dissociation, it is important that we have some knowledge about the level of excitation in the activated molecules before dissociation. In several experiments[2c] we have found that this level is not far above the dissociation threshold. On average, it corresponds to a level from which the up-transition rate induced by the infrared field and the dissociation rate are of comparable magnitudes. The RRKM theory, which predicts the dissociation rate from a given excitation level, together with a simple set of rate equations for the excitation process, has been proven,[2b,17,18] to be quite successful in describing the MPD, and can therefore be used to find the average level of excitation for a given molecule. We will use it to understand and interpret our experimental results.

EXPERIMENTAL METHOD AND DATA ANALYSIS

Our experimental apparatus has been described in detail elsewhere.[10] In short, we had a supersonic nozzle beam of molecules crossed at 90° with the focused beam from a Tachisto CO_2 TEA laser in a vacuum chamber. Dissociation fragments were analyzed and their angular distributions measured by a high-resolution rotatable mass spectrometer detector. Their velocity distributions at various angles were obtained by time-of-flight measurements through multiscaling of the output signal from the mass spectrometer. Typically, a 10 μs channel width was used in a scan over 5 ms. A block diagram of the setup is shown in Fig. 1.

This experimental method has numerous advantages over alternative methods using gas cells. Most importantly, one can be assured that the dissociation is truly collisionless and free from wall effects. A direct identification of the dissociation products and hence the major dissociation channels can be obtained. From the measured angular and velocity distributions of the fragments, the dissociation dynamics can be deduced. Because of the collisionless conditions under which the experiment is done, and because of the high selectivity of both the excitation (the resonant frequency dependence of the MPD) and of the mass spectrometer detector, reactant purity is not of great concern as long as impurities do not affect the molecular beam parameters. Thus, reactants can be used as supplied from the manufacturers. This is in striking contrast to experiments using gas cells, where even trace impurities may have strong effects on the chain reactions following the initial production of free radicals from MPD.

But there are also pitfalls involved with this molecular beam method. There is the problem of van der Waals polymer complex formation in the supersonic expansion of the molecular beam. The complexes will be readily dissociated into monomers by the laser field,[19] and since the mass spectrum of the monomer has components coinciding with those of the dissociation fragments of the molecule, presence of dimers or higher polymers in the beam must be avoided. Then, in detecting the dissociation fragments, there is also the problem of background due to the always present parent molecules. The true signal must be obtained from the difference of measurements with and without the laser excitation. This makes it very time consuming to attain an acceptable signal-to-noise ratio in the experiment when the laser pulse repetition rate is low. To identify the dissociation products, we have to establish mass spectra for the products. These spectra may not be tabulated, because the fragments are chemically unstable or highly vibrationally excited. The tabulated mass spectra usually refer to molecules at room-temperature. Thus, in identifying the fragments, the translational energy distribution of both dissociation products should preferably be measured and checked for consistency. This can only be realized if a component of the mass spectrum of one fragment is not present in the mass spectrum of the other. Further complications we have encountered, in some cases, are competing decomposition channels,[2] and the secondary dissociation of the primary dissociation products.[10] All of the above effects should be either eliminated from the experiment, or accounted for in the data analysis.

All our results correspond to dissociation close to saturation, i.e., more than ~20% of the molecules in the region of highest laser intensity dissociated during the laser pulse. Unless this were the case, the poor statistics of the resulting data would make it prohibitively time consuming to obtain fragment angular and velocity distributions of sufficient quality. For instance, the extent of dissociation of CH_3CCl_3 in our experiments was estimated to be between 50% and 100% at the laser beam center, based on measurement of the depletion of the direct beam by the laser pulse.

The analysis of our experimental results is illustrated in Fig. 2 with a simple example. A similar example is given in Ref 2c. Consider a number of particles travelling with a velocity v_o, and suddenly being supplied with some isotropically distributed translational energy (e.g., through dissociation). The translational energy distribution is chosen as $p(E) \sim \sqrt{E}$ for $\frac{1}{32} mv_o^2 < E < \frac{1}{8} mv_o^2$, so that the velocity distribution is constant between two spheres of radius $\frac{1}{4} v_o$ and $\frac{1}{2} v_o$ in Cartesian velocity space, and zero elsewhere. (Unless explicitly stated otherwise, "translational energy distribution" in this paper refers to the total translational energy in all fragments from the dissociation. In this example we consider only one fragment.) Fig. 2a shows the corresponding Newton diagram. One can then calculate the resulting speed distribution along a given direction. This is shown in Fig. 2b for the direction indicated in Fig. 2a. Figure 2c gives the corresponding time-of-flight spectrum as it would be recorded by our multichannel scaler. Direct transformation to time space would give a t^{-4} dependence, but we have also to take into account the ionization efficiency in the ionization chamber of the mass spectrometer. For small ionization probability, the ionization efficiency is proportional to the time spent by the molecule in the ionizer, i.e., inversely proportional to the speed of the molecule. This results in the t^{-3} dependence of the time-of-flight spectrum. Figure 2d shows the angular distribution which would be obtained in the lab frame.

In analyzing our data, we use computer programs to a) give us a velocity distribution for the molecular beam from the time-of-flight spectrum measured with a chopper wheel; b) transform the multichannel scaler time-of-flight spectra for the fragments obtained at various angles, into a speed distribution of the fragments; and c) calculate the laboratory speed distribution of the fragments from a postulated translational energy distribution and the measured velocity distribution of the primary beam to compare with the experimental angular and velocity distribution obtained under b). The programs take into account all experimental details such as the finite chopper slit width, the finite detector aperture, and the finite ionizer length in the mass spectrometer. Data for rare gas beams, assuming that there is complete relaxation in the nozzle beam expansion (confirmed by the large Mach number), have been used to calibrate the parameters needed in these calculations.

As can be readily inferred from Fig. 2, if the dissociation products are isotropically distributed in the center-of-mass coordinates and the molecular beam has no angular and velocity spread, a time-of-flight spectrum of the fragments in the molecular beam direction gives all information about the energy distribution of the fragments. As soon as the detector is moved away from the molecular beam direction, information about the low energy part of the fragment energy distribution is lost. In reality, however, the molecular beam has a finite angular and velocity spread and produces too strong a background in the mass spectrometer detector if the detector is too close to the direction of the beam. Thus, reliable data can only be obtained along directions sufficiently far away (> 5°) from the beam direction. This limits our knowledge about the very low-energy fragments to what can only be guessed on the basis of extrapolation. An additional uncertainty about low-energy fragments arises from the fact that energized molecules with little excess energy have dissociation lifetimes which may be longer than the flight time across the region monitored by our detector. In addition, this time varies with detection angle. It should also be mentioned that the maximum angle at which we can make observations, is limited by the fact that in order to avoid the laser beam hitting the detector housing, we have to stay within 50° of the molecular beam.

Another point of relevance is that in some cases, most of the fragments produced have recoil velocities greater than the molecular beam velocity. In those cases, for isotropic dissociation, the fragment laboratory angular distribution should look almost constant, at least within the 50° observing angle about the molecular beam. Then, the angular distribution contains very little information, and one must rely solely on the time-of-flight spectrum to obtain information about the translational energy distribution.

RESULTS

We have observed 3-center and 4-center HCl elimination in multiphoton dissociation (MPD) of five compounds: 1,1,1-trichloroethane (CH_3CCl_3, Dow), 1,1-difluoro-1-chloroethane (CH_3CF_2Cl, Matheson), 1-1-difluorochloroethene ($CHClCF_2$, Matheson), dichlorofluoromethane ($CHFCl_2$, Matheson) and chlorodifluoromethane (CHF_2Cl, Matheson). The decomposition of chemically activated CH_3CCl_3 and infrared multiphoton excited CHF_2Cl have been studied quite extensively by others.[11,16] They will thus serve as our prime examples, because comparison with relevant data from different experiments is possible.

The observed dissociations all seem to proceed through the channel with the lowest activation energy for dissociation and agree with those observed in pyrolysis, whenever a comparison can be made. In all cases except that of $CHClCF_2$, the observed translational energy distribution has its peak at a finite energy. This is expected because of the existence of the back reaction barriers for these systems, as it is well known that the potential energy of the exit barrier will transform efficiently into translational and rotational energies of fragments in the dissociation. The observed average translational energy of the fragments is about 8-12 kcal/mole. This is much higher than that seen in halogen atom elimination reactions from halogenated hydrocarbons, but it is appreciably less than the total available energy, especially in the 4-center elimination. The observed translational energy distribution is fairly wide, typically 5-10 kcal/mole, FWHM, in the center-of-mass frame.

3-center Elimination

Our best data showing 3-center elimination was obtained for CHF_2Cl. In this experiment the antisymmetric and possibly the symmetric F-C stretching modes were excited. The two modes are at 1116 cm^{-1} and 1176 cm^{-1} respectively.[20,21] These frequencies are not attainable by a CO_2 laser, so we used a laser frequency of 1082.3 cm^{-1} (the R(26) line of the 9.6 μm band) for excitation, but heated the gas to 280°C so that multiphoton dissociation could occur via the red-shifted hot-band absorption. We focused the laser beam to an energy fluence of 20-30 J/cm^2.

The major ions detected in the mass spectrometer were CF^+, Cl^+ and HCl^+, with the latter two having the same translational energy distribution. From this and the consistency in the balance of linear momentum in the center-of-mass coordinate system as reflected in the angular and velocity distributions of the fragments, we conclude that the primary dissociation products are CF_2 (yielding CF^+) and HCl (yielding HCl^+ and Cl^+ in the ionizer), as was also reported by King and Stephenson.[16] The pyrolysis of CHF_2Cl[11] also yields CF_2 and HCl as the only direct dissociation products. As shown in the level diagram of Fig. 3, this is the lowest energy channel. At the energy fluences we used, there is no possibility that light fragments such as HCl and CF_2 could further dissociate in the laser field - thus the problem of secondary dissociation did not arise in this experiment. Also, with a 0.1 mm diameter nozzle used throughout this experiment and a beam stagnation pressure of 200 torr (corresponding to a Mach number of about 6 and a specific heat ratio $\gamma = 1.3$ in the supersonic expansion), the formation of van der Waals dimers was found to be negligible.

In Fig. 4 we show a typical experimental speed distribution of the fragments at 10° from the CHF_2Cl beam, the speed distribution of the CHF_2Cl beam, and the various fragment speed distributions calculated from the assumed translational energy distributions in the center-of-mass coordinates shown in Fig. 5. One of the translational energy distribution curves in Fig. 5 was calculated from the RRKM theory assuming a dissociation lifetime of 1.5 ns, and assuming that the excess energy due to the back reaction barrier of 6 kcal/mole[22] all appears as the translational energy of the fragments. This distribution peaks at only slightly too high an energy, but is much too narrow to fit the observed speed distribution, owing to the fact that the spread in the excitation energy in multiphoton excitation and the interaction between fragments along the exit channel has not been taken into account. We could fit the observed speed distribution using the fragment translational energy distribution represented by the analytic expression $p(E) \sim E^2 \exp(-3E/\langle E \rangle)$ where $\langle E \rangle$ is the average translational energy in the center-of-mass frame. From Figs. 4 and 5, we can conclude that the average translational energy released is about 8 kcal/mole, with the distribution having a FWHM of about 8 kcal/mole.

For a similar compound, $CHFCl_2$, we were not able to get sufficiently high signal-to-noise ratio in our experiment to allow as detailed an analysis as for CHF_2Cl. The experiments were run under very similar conditions. The gas has an absorption band at 1082 cm^{-1}.[20,21] We heated the gas to 290°C and excited it via the hot-band absorption with the P(10) line of the 9.6 μm CO_2 laser band at 1055.6 cm^{-1}. The ions detected in the mass spectrometer were CF^+, HCl^+ and Cl^+, whereas $CHFCl^+$, $CFCl^+$ and HF^+ could not be observed. Time-of-flight spectra of HCl^+, although with quite a bit poorer signal-to-noise ratio, were very similar to the ones observed with CHF_2Cl. Thus we conclude that the dissociation fragments are CFCl and HCl, and that within a factor of two, the translational energy distribution in the center-of-mass coordinates is similar to the one for the CHF_2Cl dissociation.

The results on $CHClCF_2$, which also showed 3-center HCl elimination, were more complicated. The molecule has a C-Cl stretching frequency[24] of 968 cm^{-1}, and the gas was excited with the 967.7 cm^{-1} R(8) line of the 10.6 μm CO_2 laser band with an energy fluence of 5-10 J/cm^2. The ions observed in the mass spectrometer were Cl^+, HCl^+, CF^+, $C_2HF_2{}^+$ and $C_2F_2{}^+$. No $CHClCF_2{}^+$ signal could be detected, indicating that van der Waals dimer formation in the molecular beam was no problem with a stagnation pressure of 200 torr. Since both HCl^+ and $C_2HF_2{}^+$ were present, we must conclude that two dissociation channels, namely 2-center

Cl elimination and 3-center HCl elimination, must compete with comparable probabilities. However, we do not know quantitatively the ionization patterns of various fragments in the mass spectrometer. Therefore, we cannot determine the relative importance of the two channels, but the Cl^+ and $CHCF_2{}^+$ mass spectrometer signals were so much stronger than the HCl^+ and $C_2F_2{}^+$ signals that the Cl atom elimination appeared to be more probable than the 3-center HCl elimination.

The experimental results for $CHClCF_2$ are presented in Fig. 6, which shows the angular distribution for Cl^+ and HCl^+, and in Fig. 7, which shows a speed distribution for HCl at 10° from the $CHClCF_2$ beam. We assumed that the fragment translational energy distribution has the form $p(E) = \exp(-E/\langle E\rangle)$ (which is quite close to that typically produced by the RRKM theory), and adjusted $\langle E\rangle$ to fit the experimental data. As seen in Figs. 6 and 7, this works very well with the average energy $\langle E\rangle$ anywhere between 1.0 and 1.5 kcal/mole. Fig. 6 indicates that the translational energy in the Cl atom elimination may be slightly higher than in the HCl elimination. The figures also clearly display the fact that the translational energy released in the Cl as well as in the HCl elimination from $CHClCF_2$ is small and peaks within 0.1 kcal/mole of zero energy, just as in the case of the F atom elimination from SF_6.[2,10] This HCl elimination is in striking contrast to what was observed in the other two cases of 3-center elimination we have studied, and indicates that in the present case, there is essentially no translational energy released to the fragments after they pass the critical configuration.

4-center Eliminations

The molecule CH_3CCl_3, which shows 4-center elimination in MPD, is the one we have investigated most extensively. Measurements were made with two different molecular beams, a pure CH_3CCl_3 beam and a seeded beam composed of 4.7 torr of CH_3CCl_3 mixed with 300 torr of helium in order to raise the average speed of CH_3CCl_3 to 1200 m/s with a Mach number of over 12. With the seeded beam, we had the advantage that the recoil velocity of the fragments was smaller than the beam velocity, and hence the signal-to-noise ratio was enhanced. As mentioned earlier, the isotropic center-of-mass angular distribution of the fragments enabled us to deduce information about the fragments' translational energy distributions from their laboratory angular distributions. However, the beam seeding technique also tends to produce more van der Waals polymers in the supersonic expansion. This could be monitored by the observation of $CH_3CCl_3^+$ signal in the mass spectrometer resulting from laser-induced dissociation of the polymers into monomers.[19] The $CH_3CCl_3^+$ signal from polymers, however, only appeared within 5° of the primary beam and went away with reduced helium pressure. So for beam stagnation pressures around 300 torr or less, the interference from the dissociation of van der Waals molecules was not a problem.

We excited the 1075 cm^{-1} C-C stretching and the 1084 cm^{-1} CH_3 rocking vibrations[26,27] with a CO_2 laser pulse at 1073.3 cm^{-1} (the R(12) line of the 9.6 μm band) focused to 5-10 J/cm^2. Our data clearly indicates that HCl elimination is the primary dissociation induced by

IR multiphoton excitation. CH_2CCl_2 was detected in the mass spectrometer as CH_2CCl^+, and HCl as HCl^+, while CH_3^+, $CH_3CCl_2^+$, CH_3CCl^+, and $CH_2CCl_2^+$ were not detectable. The absence of $CH_2CCl_2^+$ can be explained by the fact that the fragment CH_2CCl_2 was so highly vibrationally excited that electron bombardment in the mass spectrometer would readily decompose it, yielding much less $CH_2CCl_2^+$ than one normally observes with CH_2CCl_2 at room temperature.[28] (In addition, we used 200 eV electron energy in our ionizer as compared to 70 eV in Ref 28.) As a further check that CH_2CCl_2 and HCl were indeed the dissociation products, we found that the velocity distributions of HCl and CH_2CCl_2 were correctly related according to the momentum conservation law. This result is in agreement with the result of pyrolysis of CH_3CCl_3, and shows that MPD of CH_3CCl_3 goes through the lowest energy channel, as illustrated in Fig. 8. There was also a weak but broad background in the velocity distribution of HCl, which we attribute to secondary dissociation of CH_2CCl_2. Since this fragment molecule is vibrationally hot, and has an absorption band at 1095 cm^{-1},[29] it should readily dissociate in the presence of the CO_2 laser field to form chloroacetylene and hydrogen chloride. This reaction has been observed previously in flash photolysis.[14] The HCl fragment produced by secondary dissociation should have a rather broad velocity distribution since the distribution of CH_2CCl_2 was already fairly broad. There was also the possibility that CH_2CCl_2 would further decompose into CH_2CCl and Cl. This could also explain the absence of the $CH_2CCl_2^+$ ion in our experiment. However, the translational energy released in halogen atom elimination is usually small[2c,10] so that it would not perturb the CH_2CCl^+ velocity distribution enough for us to determine the presence or absence of this process. Our data is interpreted under the assumption that no Cl elimination from CH_2CCl_2 takes place.

We show in Fig. 9 the experimental speed distribution of CH_2CCl_2 detected as CH_2CCl^+ at various angles, together with the speed distribution of the CH_3CCl_3 beam, and in Fig. 10 the angular distribution of CH_2CCl_2. We used the set of translational energy distributions in Fig. 11 generated by the analytic expression $p(E) = (E - a)^2 \exp(-(E - a)/b)$, with adjustable a and b to fit the experimental data. The quality of the data on CH_3CCl_3 was good enough to permit the independent determination of the width as well as the center of gravity for the translational energy distribution. The results are shown in Figs. 9 and 10. For comparison, we have also included in Fig. 11 a translational energy distribution obtained from the RRKM calculation (see appendix) with a dissociation lifetime of 10 nsec, assuming the peak of the distribution at 5 kcal/mole and no interaction between fragments beyond the critical configuration. All the energy distributions are normalized to the same peak value. In Fig. 10 the distributions are normalized so as to be equal at 10°, and this normalization is carried over without modification to Fig. 9. That is, if one calculates the angular distributions directly from Fig. 9, one gets the plot in Fig. 10. From these results, we conclude that the average translational energy released is about 8 kcal/mole, with a FWHM of about the same value.

The other molecule we have studied that exhibits 4-center elimination is CH_3CF_2Cl. It has a methyl rocking mode at 967 cm^{-1}. We used the P(6) line of the 10.6 μm band of the CO_2 laser at 956.2 cm^{-1} to excite the molecules and again heated the gas to 280°C to enhance the multiphoton absorption. The primary beam was not seeded and the laser beam was focused to an energy fluence of 5-10 J/cm^2. Ions observed were mainly CH_2CF^+ and HCl^+, whereas no HF^+ or $CH_3CF_2^+$ could be detected. Thus we concluded that the primary dissociation products were CH_2CF_2 and HCl. This is in agreement with what is observed for this molecule in UV photolysis[33] and by chemical activation,[34] although HF elimination is a competing reaction with almost the same activation energy[34] as the HCl elimination, namely 69 kcal/mole. The translational energy distribution was again assumed to be of the form $p(E) \sim E^2\exp(-3E/\langle E\rangle)$, and the average translational energy that gives the best fit to the time-of-flight spectrum, in Fig. 12, is $\langle E\rangle = 12$ kcal/mole with a FWHM of about 8 kcal/mole. Thus CH_3CF_2Cl does not seem to be qualitatively different from CH_3CCl_3, and most of the earlier discussion relevant to CH_3CCl_3 should also apply to CH_3CF_2Cl.

The results of our experiments are summarized in Table 1, where parameters of the translational energy distributions are compiled for all five compounds.

DISCUSSION

In order to interpret our experimental results, it is important that we have a clear picture of the laser excitation leading to dissociation. A rate equation approach developed by us[18] and by others,[17] based on experimental studies of SF_6, provides a good description and is quite helpful in the context of the experiments reported here. The results of this model for the case of an exciting laser pulse with total energy fluence sufficient to saturate the dissociation, but not orders of magnitude higher, are as follows: Above the dissociation level, up-excitation and dissociation are the two main competing processes to deplete the population in a given energy level. The molecules are, crudely speaking, pumped to the levels where the net up-pumping rate approximately equals the dissociation rate. For energy fluences around the saturation limit, this rate is of the order of 10 times the inverse pulse duration.[10b,34] Therefore, for typical CO_2 TEA laser pulses of about 50 to 100 nsec duration, the corresponding dissociation lifetimes should be of the order of 5 to 10 ns. Using this estimate for the typical lifetime of the energized molecule, the RRKM theory[9] can be used to predict roughly how much excess energy beyond the dissociation threshold is available for the fragments. For example, our RRKM calculation for CHF_2Cl shows that at the excitation level with an excess energy of about 7 kcal/mole above the dissociation threshold, the dissociation lifetime of CHF_2Cl is around 10 ns. For CH_3CCl_3, which has many more degrees of freedom, one needs 22 kcal/mole of excess energy beyond the dissociation threshold to reach the level with a 10 ns lifetime. For reactions with no back reaction barrier, such as many C-halogen bond rupture reactions[2c] and the HCl elimination from $CHClCF_2$ we have observed, the RRKM theory provides a prescription for calculation of the distribution of translational energy for a given level of energization. The assumption of excitation of the molecules to levels with lifetimes around 10 ns with the dissociation yield near saturation indeed gives translational energy distributions in agreement with our experimental observations.[2c]

However, in the 3-center and 4-center eliminations we have studied (with the exception of HCl from $CHClCF_2$), we do not observe this agreement. For some C-C and C-H bond rupture reactions an appreciable fraction of the potential energy of the exit channel barrier can be converted into translational energy of the fragments.[35] The presence of a barrier for the back reaction, typical of many 3-center and 4-center eliminations, implies that there is considerable interaction between the fragments even after the critical configuration is passed. Thus the partitioning between vibrational, rotational and translational degrees of freedom of the energy available to the fragments cannot be predicted without further modelling of the potential enrgy surface along the exit channel.

According to the RRKM theory, for molecules such as CHF_2Cl and CH_3CCl_3 excited to a level with a dissociation lifetime of about 10 nsec, the translational energy associated with the reaction coordinates in the critical configuration is typically of the order of 2-4 kcal/mole (see Figs. A2 and A3). This is much smaller than the actual translational energy released, as observed in this series of experiments. Clearly, a fair fraction of the potential energy of the back reaction barrier must have been converted into translational energy of the fragments in the dissociation beyond the critical configuration. Thus, the partitioning of excess energy (specifically, into translation) reflects more of the character of the potential energy surface along the dissociation reaction channel than of the intramolecular dynamics of the excited parent molecule.

As we mentioned earlier, the RRKM calculation can give us a fair estimate of the excess energy in the multiphoton excited molecule. In the case of the 3-center elimination of HCl from CHF_2Cl, the average excess energy above the dissociation threshold corresponding to a 10 ns dissociation lifetime is 7 kcal/mole. With a back reaction barrier of 6 kcal/mole, the total average excess energy in the fragments should be 13 kcal/mole. The average translational energy associated with the fragments in the critical configuration of an RRKM calculation is only about 2 kcal/mole while the observed average translational energy of the fragments is about 8 kcal/mole. Thus we must conclude that an appreciable portion, probably more than half of the back reaction barrier, must have been transformed into translational energy in the fragments. This implies that the main effect of the barrier is to provide a repulsive force between the two fragments, and that in the critical configuration, CF_2 and HCl are not much distorted from their equilibrium configurations.

These observations should be compared with the recent measurements of King and Stephenson.[16] They used the laser-induced fluorescence technique on the CF_2 fragment from MPD of CHF_2Cl to deduce both the internal energy and the translational energy distributions of CF_2. Our experiment unfortunately can only give the translational energy distribution of the fragments, King and Stephenson found that the internal energy distribution in CF_2 could be characterized by a vibrational temperature of 1160 K and a rotational temperature of about 2000 K. Their deduced average translational energy of CF_2 from the time dependent reduction of CF_2 concentration in the radiation zone is not expected to be as accurate. Their value of 7 kcal/mole does not agree with our observed value of 3.5 kcal/mole (out of the total translational energy of 8 kcal/mole). However, their results on the internal energy distribution together with our results on the translational energy distribution yield an unprecedented, detailed picture of the partition of energy in a unimolecular dissociation. Note that the rotational temperature of CF_2 is much higher than the vibrational temperature. The high rotational energy contained in CF_2 indicates that along the reaction path in the region of exit barrier, there exists a repulsive non-central force between CF_2 and HCl. This non-central force converts part of the potential energy of the barrier into rotational energy in the fragments.

In the case of 4-center elimination of CH_3CCl_3, the excess energy above the dissociation threshold corresponding to a 10-nsec dissociation lifetime is 22 kcal/mole. Since the back-reaction barrier is 42 kcal/mole, the total excess energy available to the fragments is around 64 kcal/mole. The average translational energy of the fragments deduced from our observed translational energy distribution is only 8 kcal/mole. This is only a rather small fraction, 10-15%, of the total excess energy (or 20% of the excited channel potential energy barrier). Also, the translational energy distribution of the fragments is quite wide compared with that for fragments in the critical configuration as determined from the RRKM calculation. Our results on the average translational energy distributions are somewhat lower than those estimated by Setser and coworkers[12] on similar reactions. In a series of experiments on deuterated halogen derivatives of ethane using the chemical activation method, they tried to map out the energy distribution in 3-center and 4-center elimination of hydrogen halides. They concluded that in the 4-center elimination of a sizeable fraction (> 25%) of the excess energy (or 30% of exit potential energy barrier) is released to the translational degrees of freedom, in agreement with an observation on hydrogen halide elimination from positive alkyl halide ions.[36] Although our experimental results and analysis on CH_3CF_2Cl are less extensive, the close similarity of the results in the two cases indicates that a considerably smaller fraction of the potential energy in four center HX elimination than hitherto believed is converted into translational energy in the fragments.

A couple of important conclusions on 4-center elimination can be readily drawn from our observations. The results on the average translational energy released to fragments suggest that a large fraction (> 85%) of the total excess energy is left as internal excitation of the fragments. This is just the opposite of what we found in 3-center elimination reactions. A large fraction of the internal energy should appear as vibrational energy of the CH_2CCl_2 fragment. Of course, the HCl fragments must also be highly vibrationally excited. In fact, in a similar unimolecular reaction involving elimination of HF from CH_3CF_3, Berry and Pimentel[13] observed laser emission from the vibrationally excited HF. Our results also indicate that in a 4-center elimination, the critical configuration should not be modelled by a HCl molecule loosely coupled to a CH_2CCl_2 molecule, but rather by a distorted CH_3CCl_3 molecule with a lot of stored potential energy and a partial bond formed between a Cl and H atom. This picture resembles closely models for the critical configuration used by Setser et al.[12] for similar reactions.

In our present investigation, a special case is provided by $CHClCF_2$. The 3-center elimination from this molecules does not seem to have any appreciable back reaction barrier in the exit channel, and the translational energy distribution of the fragments is very much like the one observed in halogen atom eliminations. This is a result similar to the conclusion of Kim and Setser[12] about the

3-center elimination of HCl from 1,1,2-trichloroethane. It is, however, not clear whether observations on ethanes and ethenes are comparable.

CONCLUSION

In this work we have successfully applied the method of IR multiphoton excitation to study a number of 3-center and 4-center elimination reactions in a molecular beam. This method of preparing energized molecules promises to be a valuable tool for studies of the dynamics of unimolecular reactions. The molecules one wants to study can be excited, with no interference from collisions, to the interesting range above the dissociation threshold where dissociation lifetimes are in the nanosecond region. Thus, problems involving bimolecular processes, frequently encountered in standard experimental procedures, can be greatly alleviated. The pulsed nature of the method even makes possible time-resolved investigation of some relaxation phenomena such as the secondary reactions of the dissociation products and the thermal equilibration of various degrees of freedom in the fragments.[16] The major problem of the method is on the sensitivity of selective detection of the dissociation fragments.

As demonstrated here, the molecular beam method gives translational energy distribution for the fragments. With the help of the RRKM theory, the excess energy released in the dissociation can also be estimated. However, for more complicated reactions than a simple 2-center atomic elimination, the translational energy distribution alone is not sufficient to characterize the dynamics of the reaction. The experiment cannot give us any information about the internal energy distribution in the fragment in the presence of an appreciable back-reaction barrier. Thus, in order to fully understand the dissociation dynamics, the mass spectrometric detection must be complemented whenever possible by a method which is sensitive to internal excitation of fragment detection, such as the laser induced fluroescence used by King and Stephenson in the observation of CF_2, so that the distribution of internal energy in the fragments can also be determined. Various other spectroscopic techniques, such as spontaneous emission, (from vibrationally or electronically excited fragments), double resonance, and photoionization spectroscopy can also be used. Combined with such techniques, multiphoton dissociation in a molecular beam then promises to be a most useful tool for studies of dynamics of unimolecular reactions.

ACKNOWLEDGEMENT

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Table 1. Total translational energy distributions of the fragments from multiphoton dissociation.

Compound	Average translational energy (kcal/mole)	Average spread (FWHM, kcal/mole)	Energy barrier in the back reaction	Distribution peaks at nonzero energy
$CHF_2Cl \rightarrow CF_2 + HCl$	8	6	6	yes
$CHFCl_2 \rightarrow CFCl + HCl$	?	?	?	yes
$CF_2CHCl \rightarrow C_2F_2 + HCl$	1	1	~0[a]	no
$CH_3CF_2Cl \rightarrow CH_2CF_2 + HCl$	12	8	55[b]	yes
$CH_3CCl_3 \rightarrow CH_2CCl_2 + HCl$	8	8	42[c]	yes

a) Ref. 12

b) Taking the heat formation of CH_3CF_2Cl to be -117 kcal/mole[32], that of CF_2CH_2 to be -81 kcal/mole,[37] that of HCl to be -22 kcal/mole[25], and using an activation energy of 69 kcal/mole[32] for the dissociation.

c) Ref. 11.

Appendix: RRKM Theory

For the two molecules CHF_2Cl and CH_3CCl_3 we performed a standard RRKM calculation of rate constants and translational energy distributions in the critical configuration. The calculations were done with a computer program provided to us by the late Professor D. L. Bunker. A more extensive description of it is given in ref. 2c. For the two systems studied here, a critical configuration was postulated. For CHF_2Cl we used the parameters of ref. 8. For CH_3CCl_3 we used the vibrational frequencies of CH_2CCl_2[29] and HCl, with the remaining four frequencies adjusted to fit the high pressure A-factor for the dissociation rate.[11] For the energized molecule, we assumed one free internal rotation, and thus a reaction path degeneracy of 9. All the parameters used are listed in Table A1, and the results are presented in Figs. A1, A2 and A3. Fig. A1 shows the dissociation lifetimes as a function of excess energy above the dissociation threshold in the activated complex, and Figs. A2 and A3 show the corresponding translational energy distributions for several values of excess energy, corresponding to dissociation lifetimes around 10 ns.

Table A1. RRKM CALCULATION PARAMETERS

	CHF_2Cl		CH_3CCl_3		units
	molecule	complex	molecule	complex	
Vibrational frequencies					
	3025	3025	2954	3035	cm^{-1}
	1311	1500	1383	1627	"
	1178	1178	1069	1400	"
	809	1116	526	603	"
	595	595	344	299	"
	422	500	205*	686	"
	1347	1600	3017(2)	3130	"
	1116	1000	1456	800	"
	365		1427	372	"
			1089(2)	875	"
			725(2)	460	"
			301(2)	2990	"
			241(2)	900(2)	"
				150(2)	"
Moments of inertia					
I_{xx}	-	-	214	177	amuÅ^2
I_{yy}	-	-	214	222	"
I_{zz}	-	-	289	274	"
Other parameters					
log A	12.6	-	14.1	-	-
E_o	56	-	54	-	kcal/mole
L‡	1	-	9	-	-

---

*Internal rotation.

FIGURE CAPTIONS

Fig. 1. Experimental arrangement. The "SF_6 beam source" is the molecular beam source. The pulse generator triggers the laser (which partly dissociates a section of the molecular beam) and the multichannel scaler, opens a gate to scaler 1 a few hundred microseconds later, (to count dissociation product signal and background signal) and a gate to scaler 2 a few milliseconds later (to count background signal).

Fig. 2. Example of a dissociation process: a) Newton diagram: b) Speed distribution of fragments; c) Time-of-flight distribution; and d) Angular distribution.

Fig. 3. Energy levels for the dissociation of CHF_2Cl. The level energy in kcal/mole relative to the ground state CHF_2Cl is written to the right of each level. (Data compiled on the basis of refs. 11, 23, 25, 30.)

Fig. 4. Speed distribution at 10° of HCl fragment from CHF_2Cl

o Experiment

——— $\langle E \rangle = 6$ kcal/mole

— — $\langle E \rangle = 7$ kcal/mole $\quad$ $p(E) \sim E^2 \exp(-\frac{3E}{\langle E \rangle})$

- - - - $\langle E \rangle = 8$ kcal/mole

. . . . RRKM distribution corresponding to a dissociation lifetime of 1.5 ns.

Fig. 5. Energy distributions as used on Fig. 4. The curves are normalized to equal peak values. (Symbols as in Fig. 4.)

Fig. 6. Angular distributions of fragments from $CHClCF_2$, and theoretical distributions. The curves are normalized to give the same value at 10°.

● $H^{35}Cl^+$ ion ▲ $^{35}Cl^+$ ion, from experiment.

$$\left.\begin{array}{lcl} \text{— — —} & \langle E\rangle = & 0.75 \text{ kcal/mole} \\ \text{————} & \langle E\rangle = & 1.0 \text{ kcal/mole} \\ \text{- - - - - -} & \langle E\rangle = & 1.25 \text{ kcal/mole} \end{array}\right\} \quad p(E) = \exp(-\frac{E}{\langle E\rangle})$$

Fig. 7. Speed distribution of HCl fragment from $CHClCF_2$, taken at 10°, compared to theoretical curves as in Fig. 6.

Fig. 8. Energy level diagram for the dissociation of CH_3CCl_3. (Data compiled on the basis of refs. 11, 25, 31).

Fig. 9. Speed distributions at various angles of the fragment CH_2CCl_2. (The curves are all normalized so as to give the same value of the angular distribution at 10°.)

○ Experiment

$$\left.\begin{array}{ll} \text{———} & a = 0 \text{ kcal/mole, } b = 9 \text{ kcal/mole} \\ \cdots\cdot & a = 0 \text{ kcal/mole, } b = 8 \text{ kcal/mole} \\ \text{----} & a = 1 \text{ kcal/mole, } b = 7 \text{ kcal/mole} \end{array}\right\} \quad p(E) \sim (E-a)^2 \, e^{-\frac{3(E-a)}{b}}$$

Fig. 10. Angular distribution of CH_2CCl_2 (symbols as in Fig. 8). All the curves are normalized to the same value at 10°.

Fig. 11. Translational energy distributions for the fragments from CH_3CCl_3 in the center-of-mass frame of the parent molecule (symbols as in Fig. 8, plus — · — · —: RRKM distribution.) The curves are normalized to their peak values.

Fig. 12. Speed distribution at 10° of HCl fragment from CH_3CF_2Cl.

● Experiment

—— Distribution for $p(E) \sim E^2 \exp(-E/4 \text{ kcal/mole})$ in the center of mass

···· CH_3CF_2Cl beam speed distribution

Fig. A1. RRKM rate constants for the HCl elimination from CHF_2Cl and CH_3CCl_3, as a function of excess energy above the dissociation threshold in the critical configuration.

Fig. A2. RRKM translational energy distributions of the fragments (total translational energy in the center-of-mass frame) from the dissociation of CHF_2Cl calculated for different values of excess energy above the dissociation threshold.

— — — 2.7 kcal/mole excess energy

——— 6.9 kcal/mole excess energy

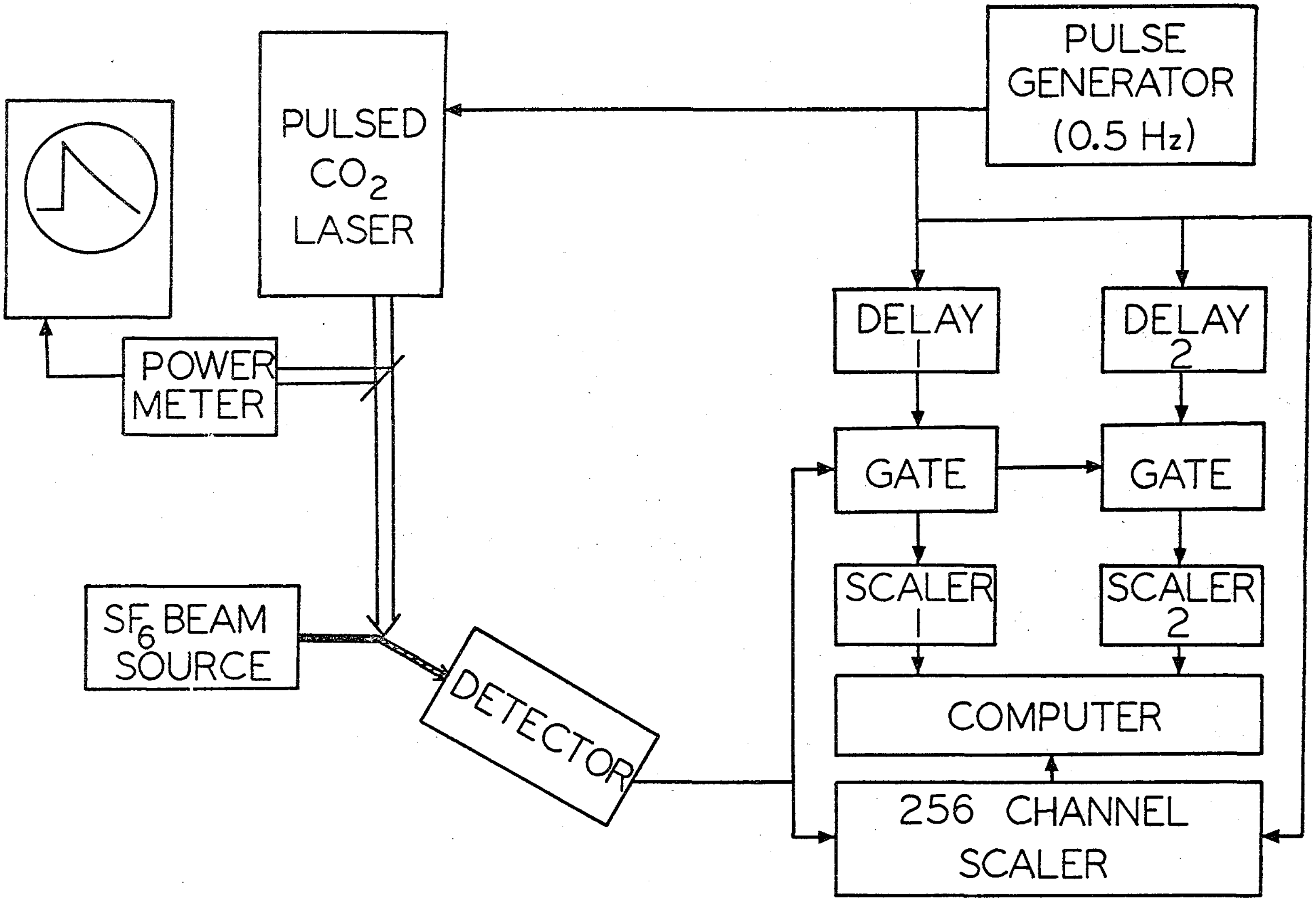
· · · · 13.7 kcal/mole excess energy

Fig. A3. RRKM translational energy distributions of the fragments from the dissociation of CH_3CCl_3 calculated for different values of excess energy above the dissociation threshold.

— — — 10.9 kcal/mole excess energy

——— 16.7 kcal/mole excess energy

· · · · 21.8 kcal/mole excess energy



XBL 768-10159

Fig. 1

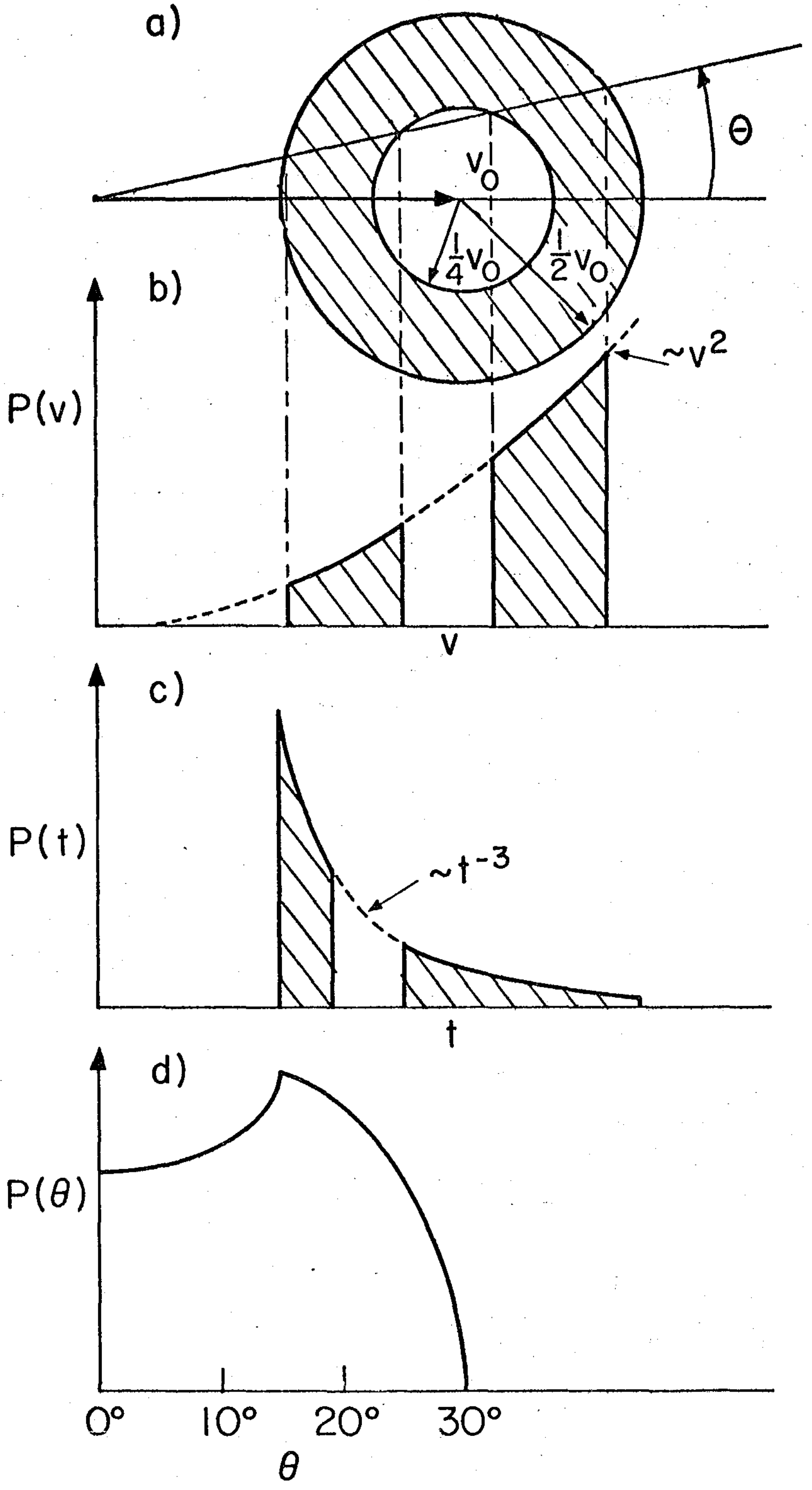


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Fig. 2

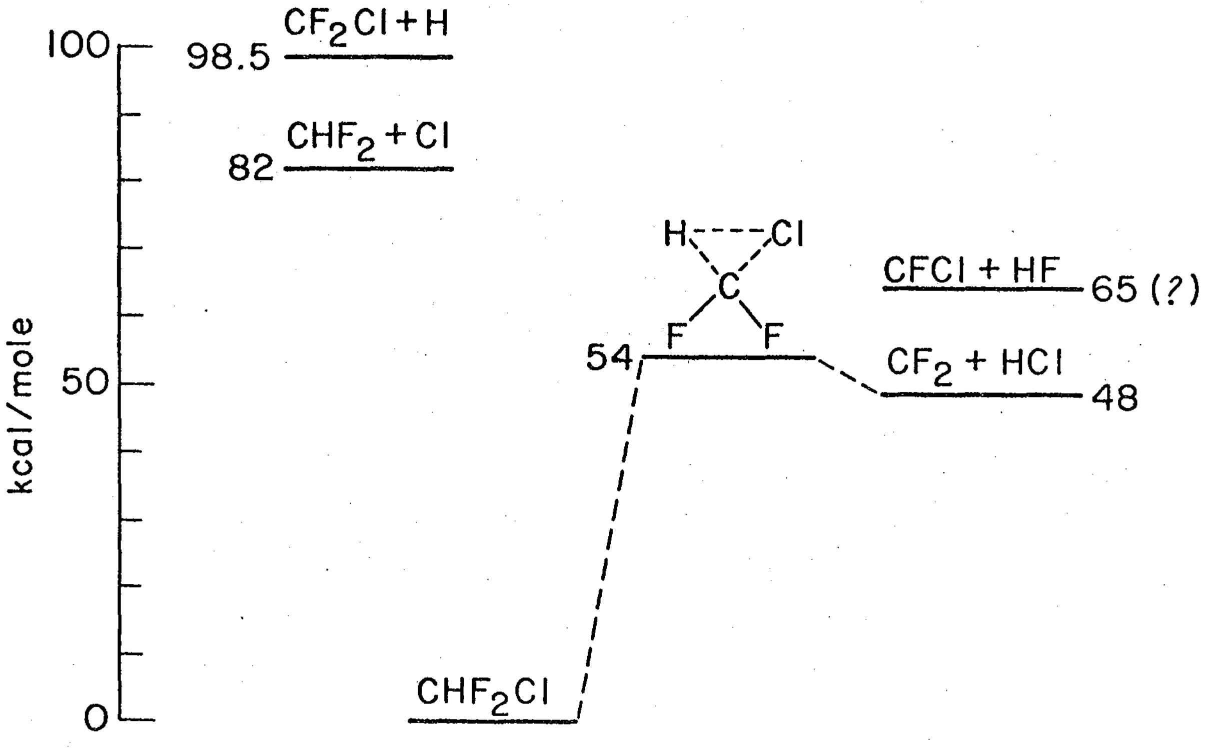

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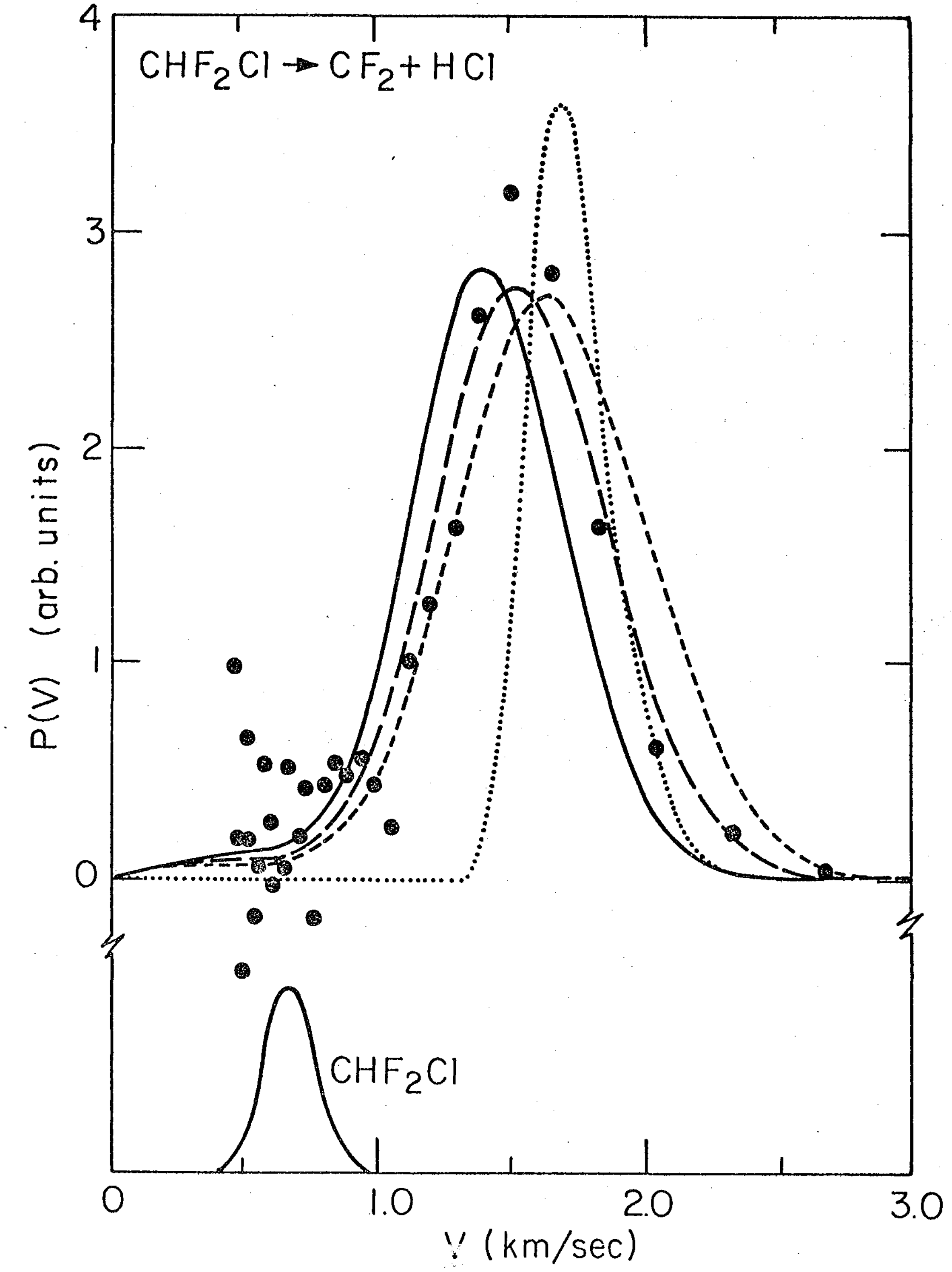
Fig. 3


CHF$_2$Cl → CF$_2$ + HCl
4
3
2
1
0
P(V) (arb. units)
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1.0
2.0
3.0
V (km/sec)
XBL 781-4439

Fig. 4

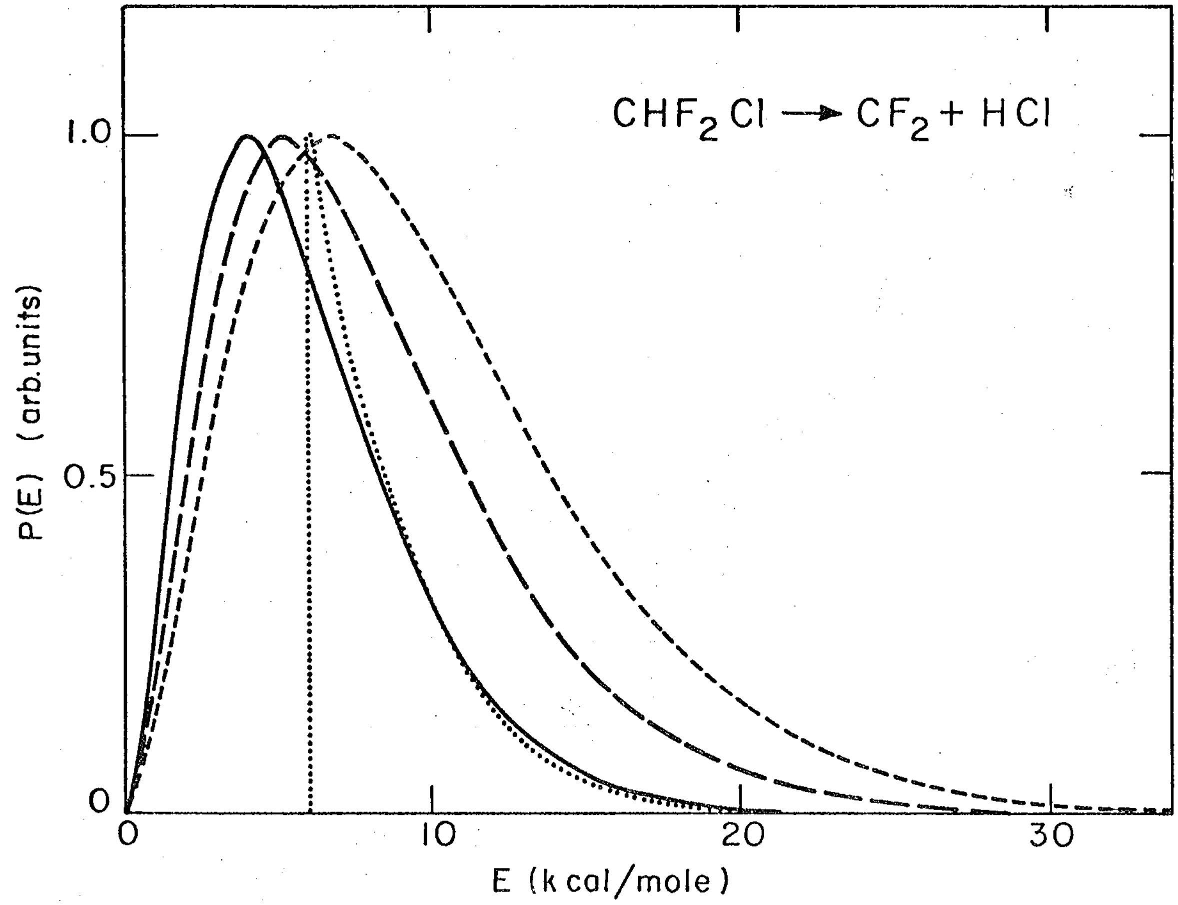

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Fig. 5

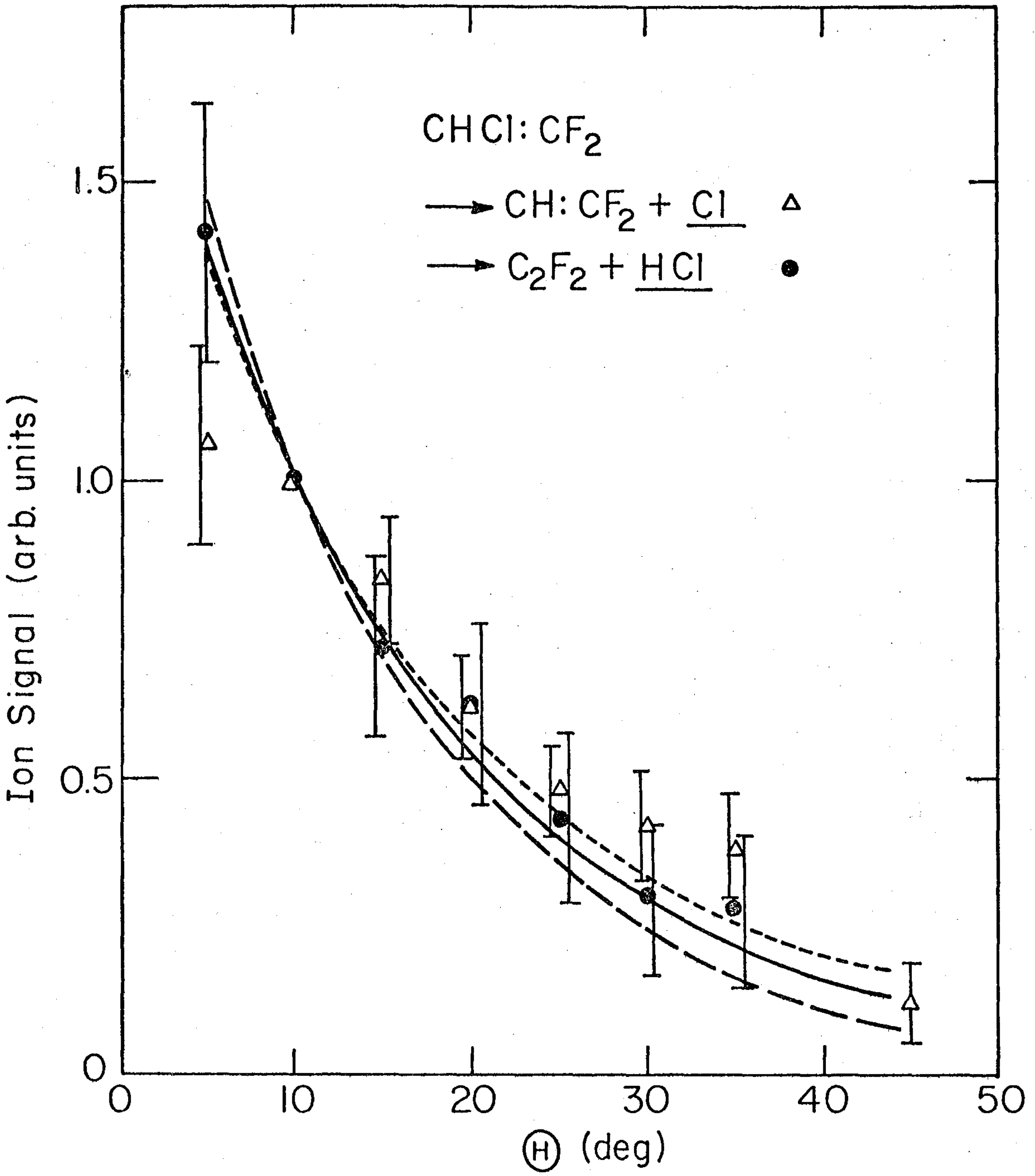

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Fig. 6

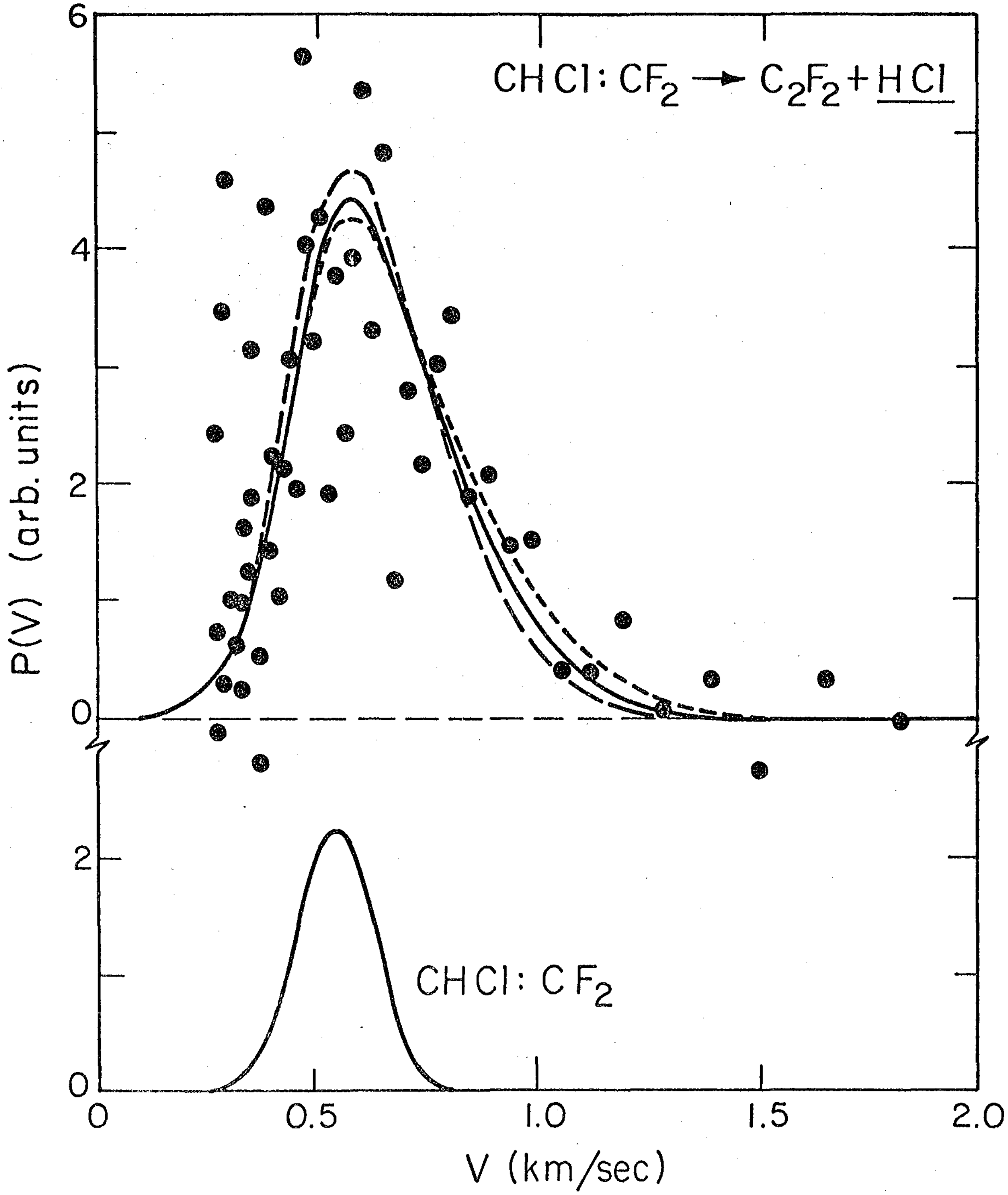

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Fig. 7

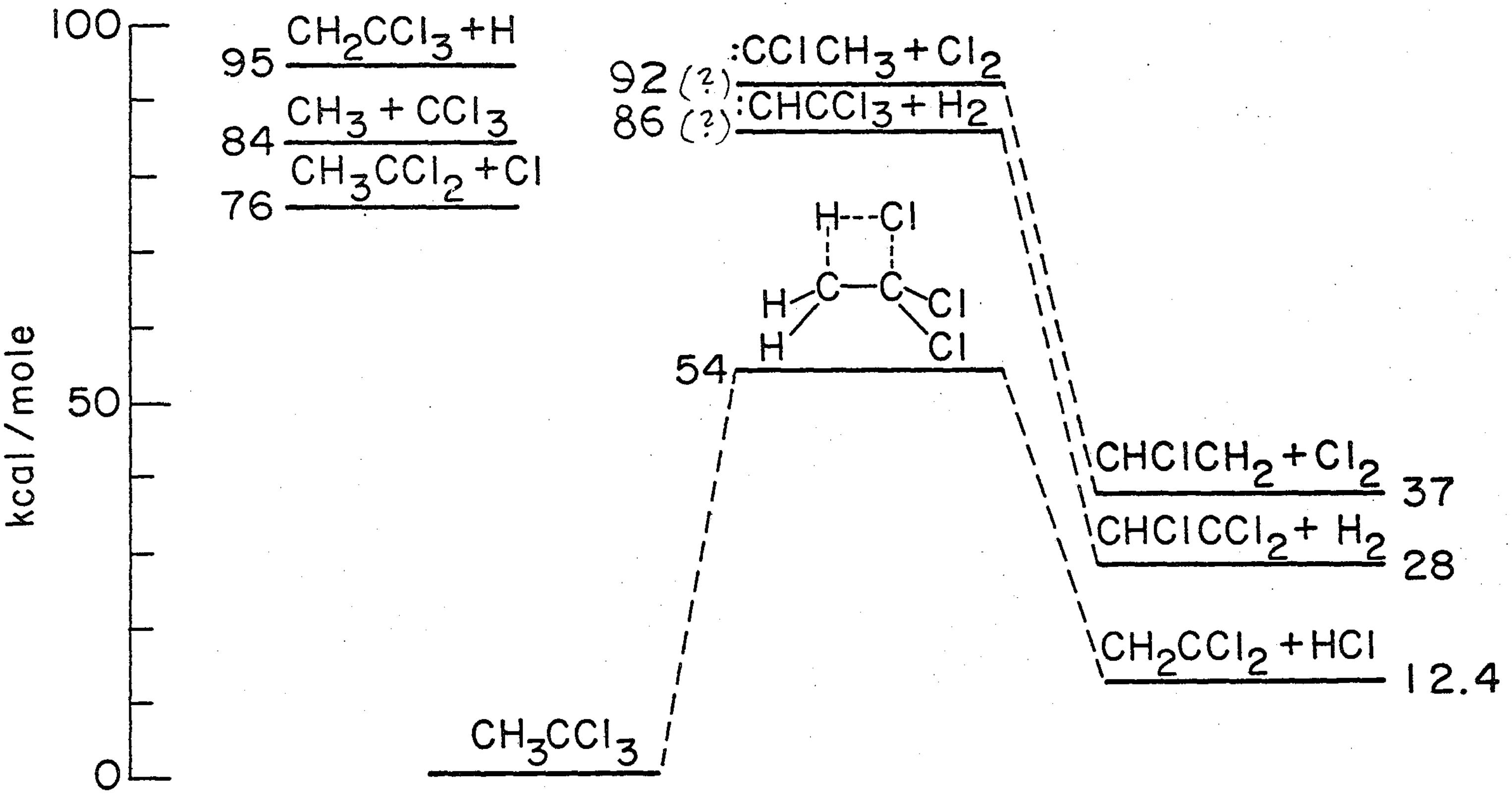

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Fig. 8

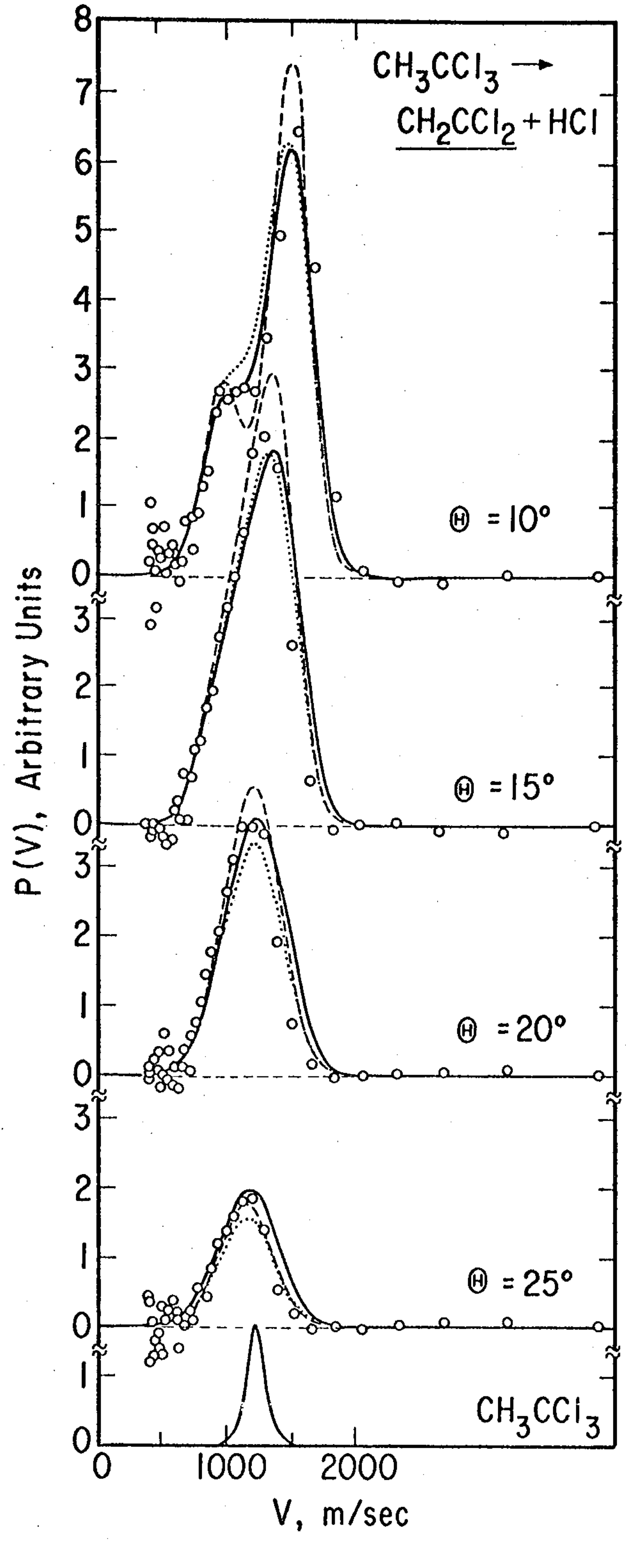

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Fig. 9

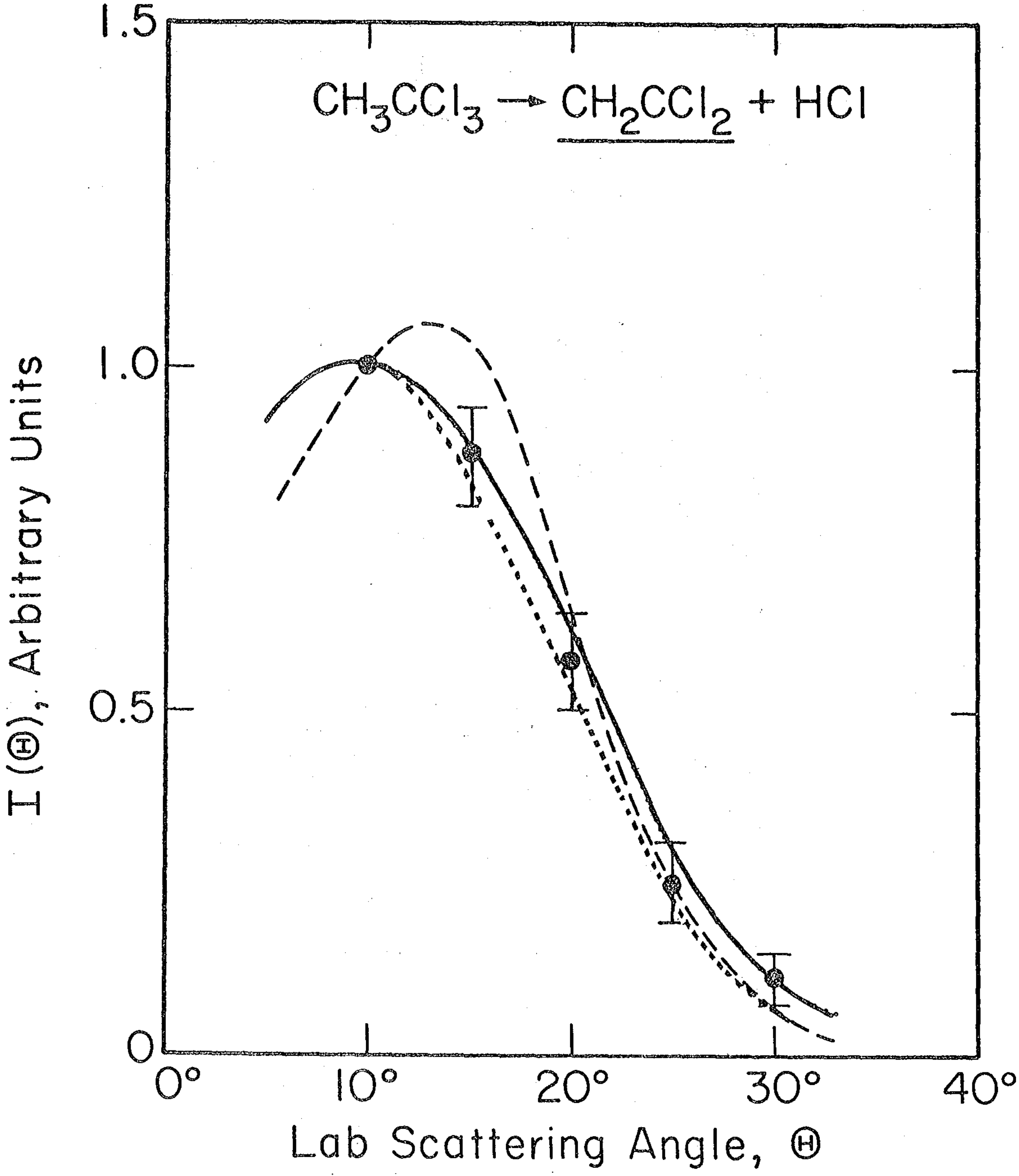

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Fig. 10

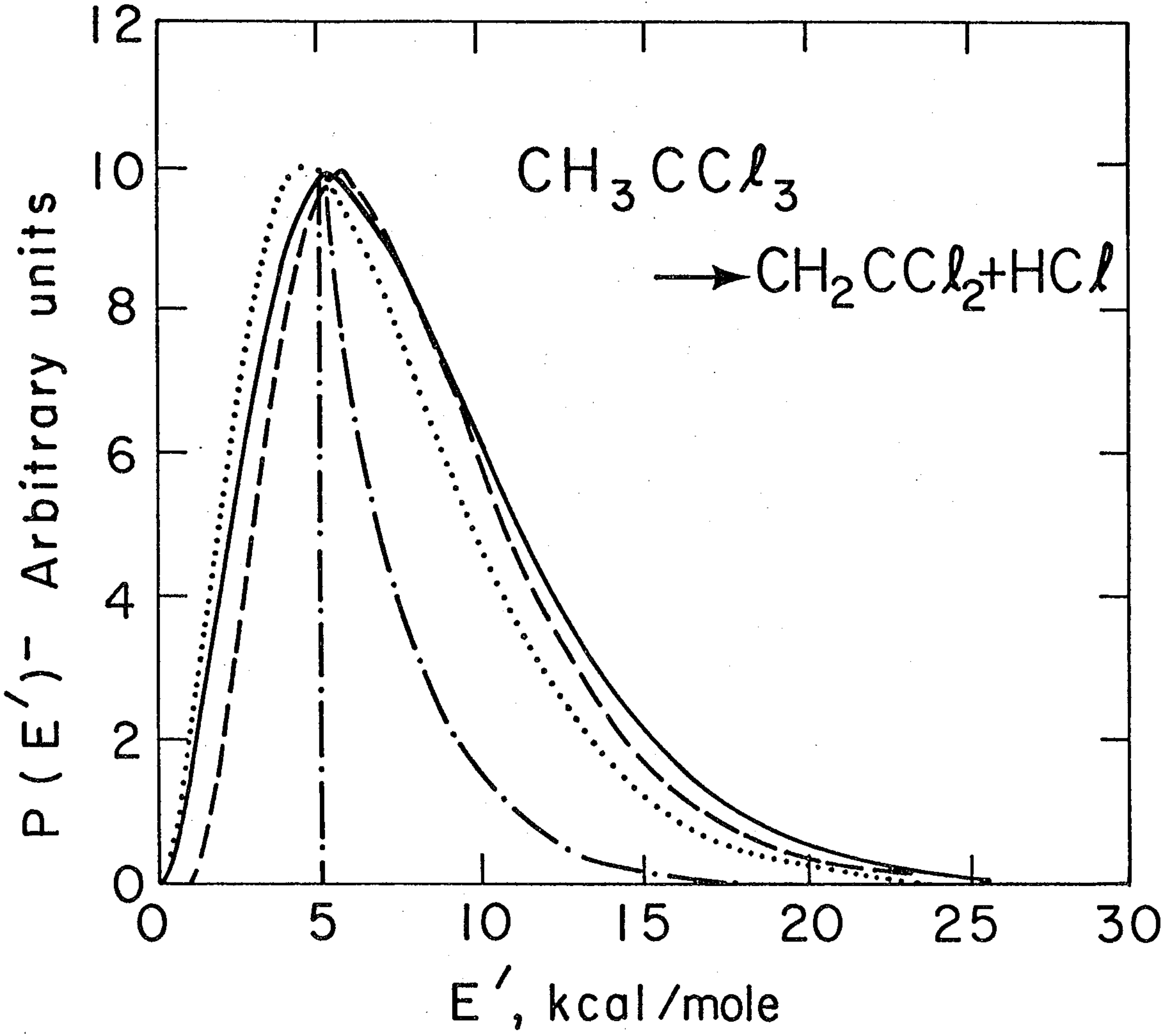

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Fig. 11

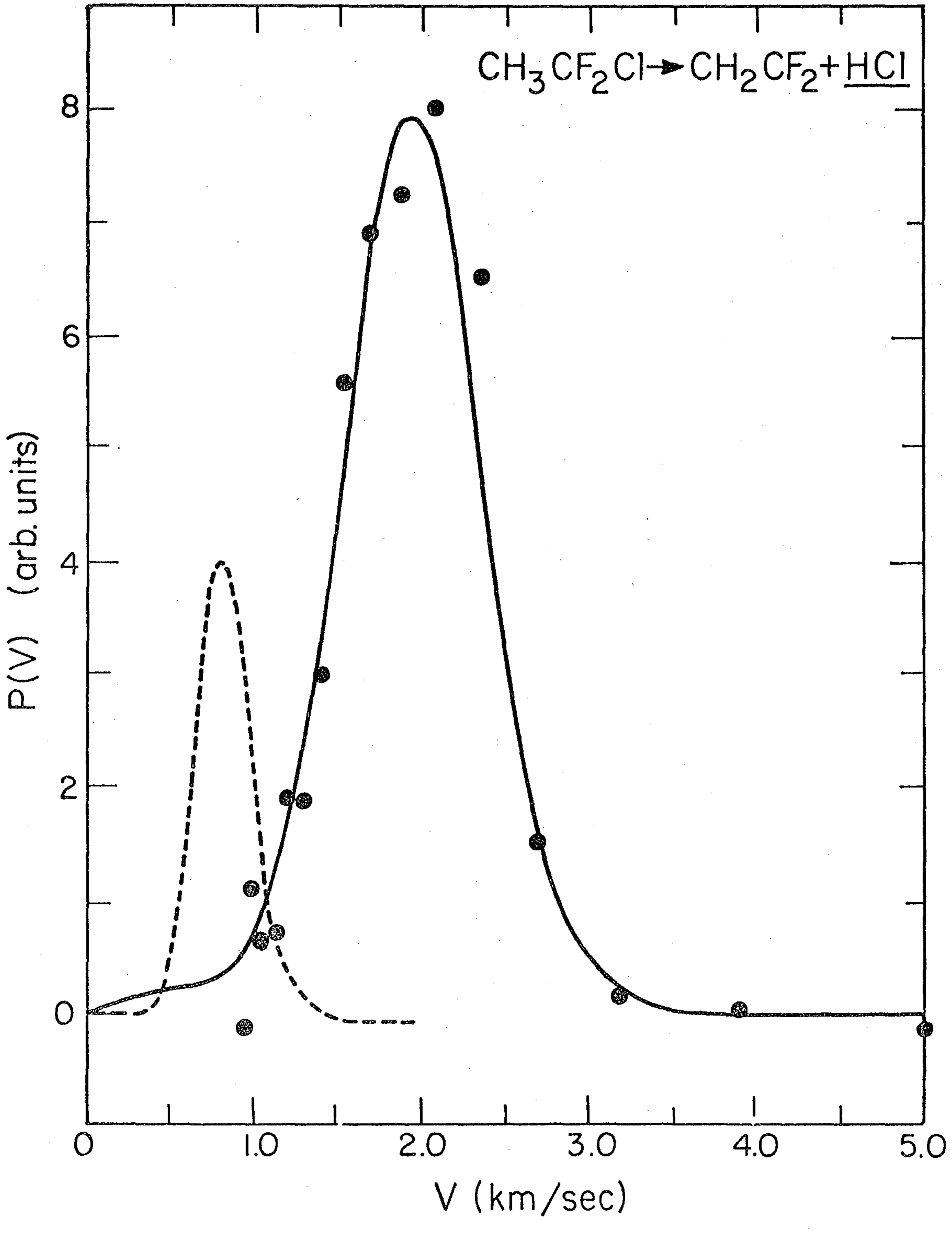

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Fig. 12

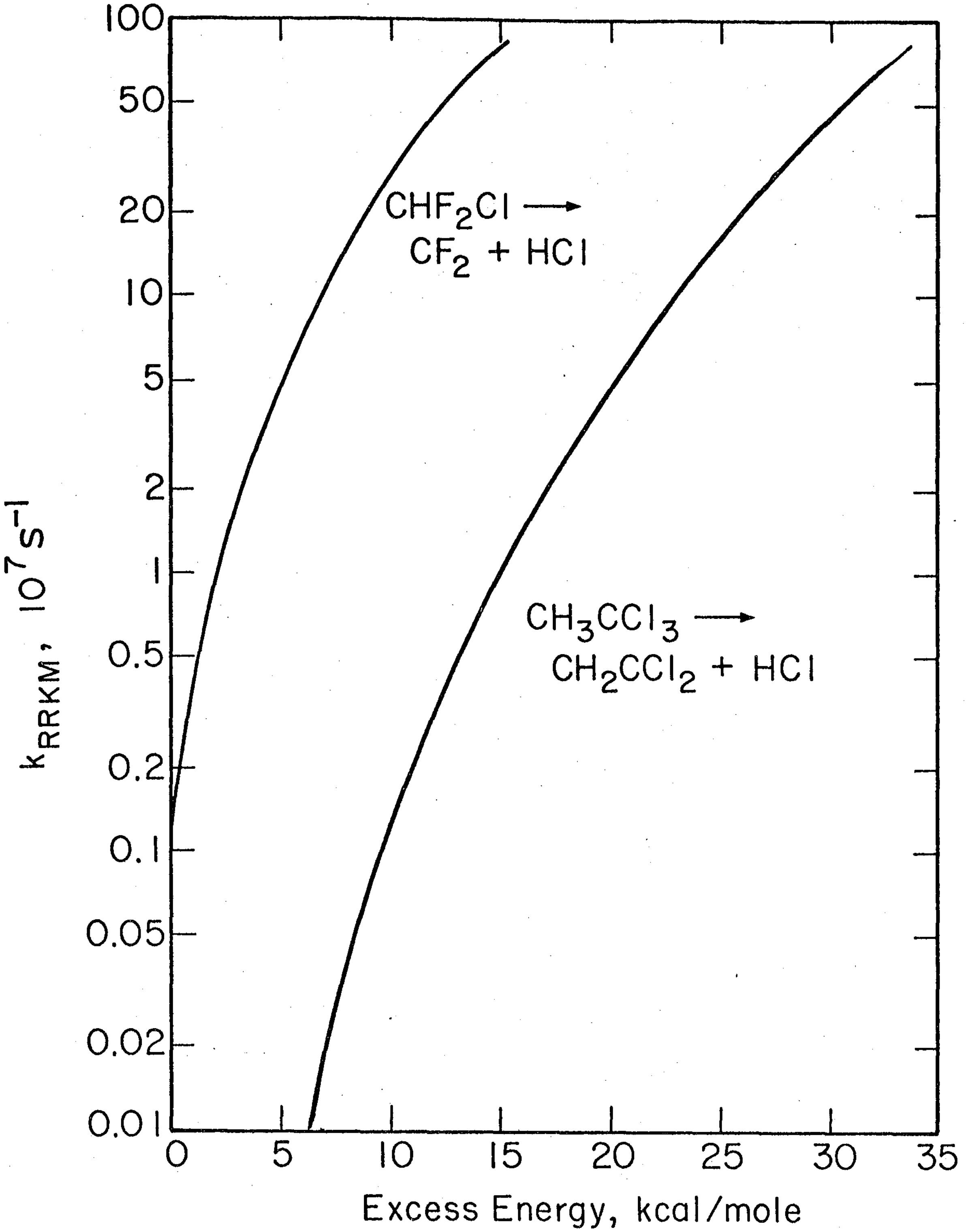

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Fig. A1

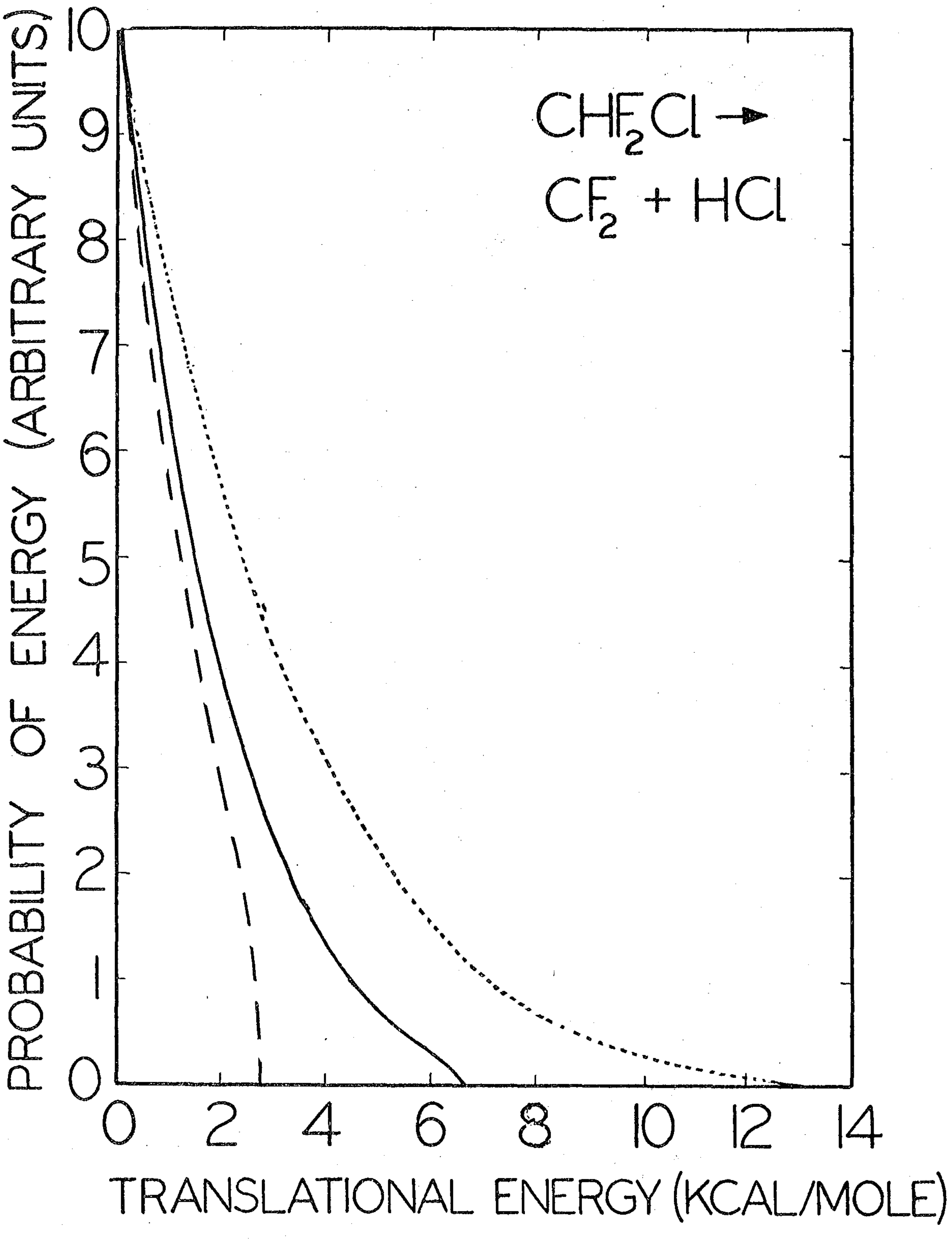

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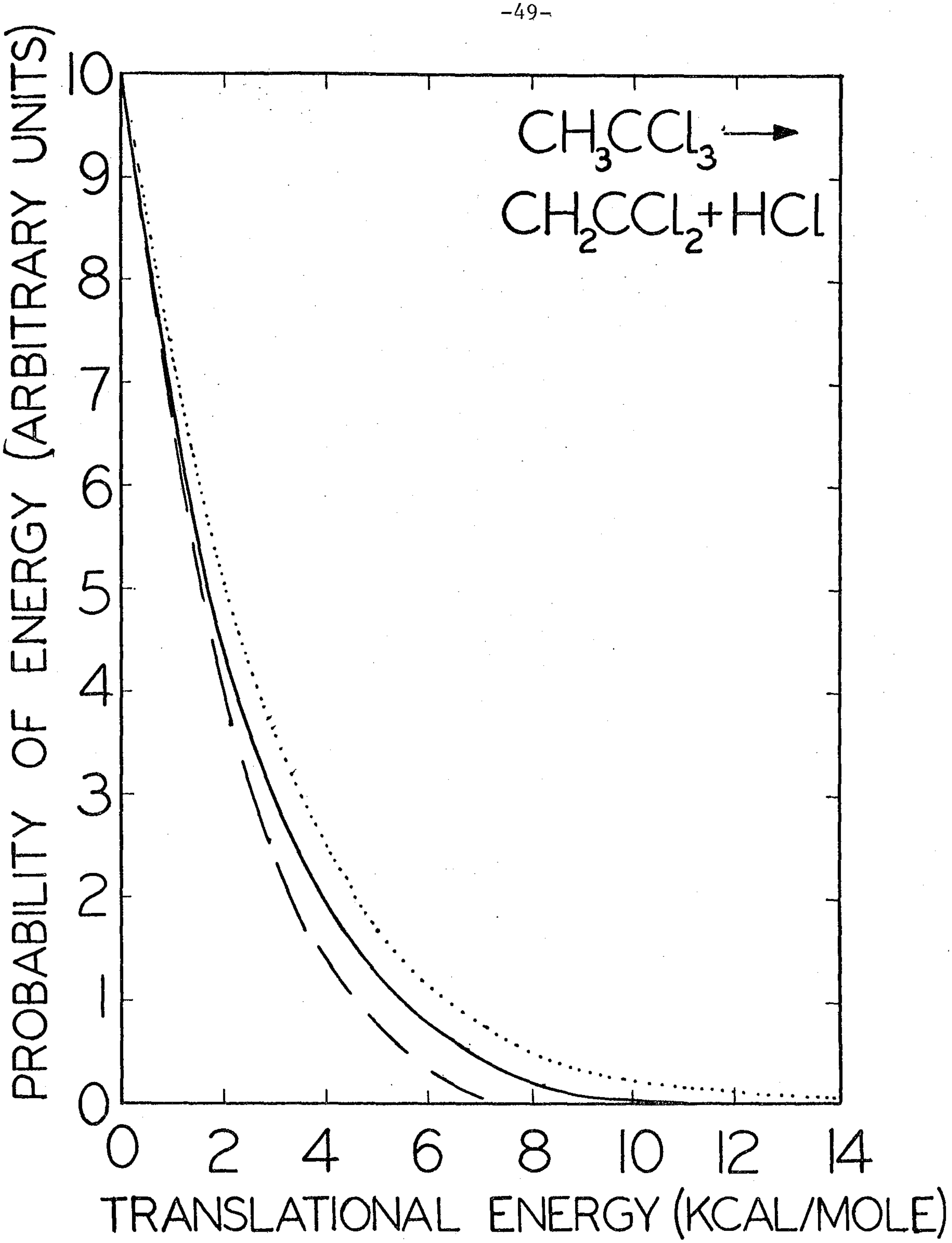
Fig. A2



XBL 782-7328

Fig. A3