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# Photodissociation of Ethylene at 193 nm

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## I. ABSTRACT:

The photodissociation of ethylene at 193 nm was studied by measuring the product translational energy distributions for the $H + C_2H_3$ and $H_2 + C_2H_2$ channels. In agreement with previous workers, it was determined that atomic and molecular elimination occur in relatively equal amounts. Using 1,1 $D_2CCH_2$ and 1,2 cis HDCCDH, it was shown that both acetylene and vinylidene are formed and that the acetylene/vinylidene ratio is approximately 2/3 in the molecular elimination. This $H_2$ elimination channel has a translational energy distribution peaked at around 20 kcal/mole, indicating that it is a concerted process with a substantial exit barrier. Evidence is presented which suggests that limited 1,2 H migration takes place during the formation of acetylene, presumably through an ethylidene type structure. It was found that the H atom elimination channel is best described as a simple bond rupture occurring after the internal conversion process and from the vibrationally excited ground state ethylene. Some of the primary $C_2H_3$ product has sufficient internal energy to spontaneously decompose to H + HCCH. At higher laser intensity a large fraction of the $C_2H_3$, however, absorb another photon and fragment to $H + H_2CC$ ($^1A_1$ and $^3B_2$).

## II. **INTRODUCTION:**

Although, the photochemistry of ethylene has been studied quite extensively since the 1950's, the details of the dissociation processes remain uncertain [1]. A summary of the known energetics for various dissociation channels is given in Figure 1 [2]. The earliest work was mainly concerned with identifying the primary decomposition channels [14-19]. The general consensus was that atomic (ii) and molecular (i) elimination producing H and $H_2$ are of approximately equal importance [17,18,19b]:

$$C_2H_4 \rightarrow HCCH + H_2 \qquad \text{ia}$$

$$\rightarrow H_2CC: + H_2 \qquad \text{ib}$$

$$\rightarrow C_2H_3\cdot + H \qquad \text{iia}$$

$$\rightarrow C_2H_2 + 2H \qquad \text{iib}$$

In the molecular elimination, there appeared to be two different primary products, acetylene (ia) and vinylidene (ib) [14,16]. The elimination of a single H atom (iia) and the simultaneous loss of two H atoms (iib), were difficult to distinguish because the vinyl radicals created with vibrational energy exceeding the dissociation energy of H-CHCH (only 35 ± 3 kcal/mole [2]) are apparently very short-lived with respect to further loss of an H atom [16-19]. Back and Griffiths [18] and Hara and Tanaka [19], however, "detected" stabilized $C_2H_3$ by observing products that could only come from reaction of the vinyl radical, so there is no question that iia occurs.

The use of isotopes in some of these early works provided

additional information about the molecular elimination mechanism. It was shown that the photoexcited $C_2H_4$ has free rotation about the C=C bond and that any pair of H atoms can participate in molecular elimination. No 1,2 H exchange, however, was observed [15,16]. The vinylidene channel is favored over the acetylene by a ratio of approximately 3 to 2 [16]. There is an isotope effect of ≈ 1:1.5:2 with respect to $D_2$:HD:$H_2$ elimination for both channels ia and ib, although Okabe and McNesby noted that there seems to be a slightly smaller isotope effect in (ia) [15,16]. This isotope effect is justified by modeling the elimination as an intramolecular abstraction or as a large vibrational displacement, or by assuming vibrationally excited ethylidene is an intermediate [15].

With the development of laser technology, more detailed measurements on the various channels in ethylene photodissociation have since been possible. Unfortunately, they seem to have raised at least as many questions as they have answered. Using UV flash photolysis along with 137 nm absorption spectroscopy, Fahr and Laufer explored the role of electronically excited triplet vinylidene ($^3B_2$) [20]. They found that this excited radical was a major product with a measured quantum yield of .75 ± .2. Based on appearance times, however, they concluded that neither vinylidene (ground state ($^1A_1$) or $^3B_2$) nor acetylene was the direct product in molecular elimination. They hypothesized that some excited meta-stable precursor must give rise to the $^3B_2$. A gas cell photodissociation study was done

recently at 193 nm that confirmed the general idea that several excited states and intermediates are involved but the authors were unable to identify exactly what these were [21]. The most recent study, by Bersohn and coworkers, concentrated on the H atom elimination channel at 193 nm [22]; the average translational energy of H and D atoms was measured from the Doppler shift observed when the atoms were detected by laser induced fluorescence. Based on the relatively small release of translational energy measured, they concluded that internal conversion of the excited molecule to the vibrationally excited ground electronic state occurred before dissociation.

A limited amount of theoretical work has been done on the primary ethylene photodissociation processes. Evleth and Sevin present a qualitative evaluation of two proposed molecular elimination pathways: three-centered elimination to give vinylidene and dissociation via ethylidene ($CH_3CH$) to form acetylene [23]. The vinylidene and acetylene ground state products can form directly from the $\pi\pi^*$ excited state, the state reached with 193 nm photons, or from the ground state. A later study by Raghavachari et. al. gives a more quantitative description, estimating that the activation energies for the three-centered elimination and the ethylidene channel are ~93.4 and 109.3 kcal/mole, respectively [24]. The atomic elimination is more defined. In Evleth and Sevin's analysis of this channel, they found that to produce ground state vinyl radical, dissociation can only occur from hot ground state ethylene [23].

Applying the photofragment translational spectroscopy technique in which the time-of-flight (TOF) spectra of mass-selected fragments (H or $H_2$) are measured, will provide more detailed information on the dynamics of the ethylene photodissociation. Since the heats of formation of acetylene and vinylidene differ by ~44 kcal/mole [2], the corresponding $H_2$ could have substantially different velocity distributions. In principle, then, the two channels will be clearly identified in the TOF spectra. Similarly, the two atomic elimination pathways will be resolved since channel iib is ~35 kcal/mole more endothermic than iia [2]. The product translational energy distribution, $P(E_T)$, will also reflect whether the dissociation has an exit barrier and will show how the excess energy is partitioned. TOF spectra of the products of the photodissociation of deuterated ethylene (1,1 $D_2CCH_2$ and cis 1,2 HDCCDH) will give additional understanding of the nature of the intermediate states involved; they will also address the question of H atom migration prior to dissociation. This work together with that of other members of this group in which the rovibrational states of $H_2$ produced in the 193 nm photolysis of $C_2H_4$ were detected [25] should provide a fairly clear picture of the concerted elimination of $H_2$ from ethylene.

The experiments described here should help isolate the role of the $\pi\pi^*$ state. Many of the past studies were done at shorter wavelengths where more than one ethylene excited state would be involved. In this study, 193 nm photons are used. Although

ethylene has a small absorption cross-section at this wavelength [$\sigma \approx 2 \times 10^{-20}$ cm$^2$ [26,27]] the excitation is exclusively via a $\pi^* \leftarrow \pi$ transition to the $^1B_{1u}$ (V) excited state. The $^1B_{1u}$ excited state is believed to be twisted with the $CH_2$ groups perpendicular to each other. The changes in geometry from the planar ground state during excitation result in the excitation of the torsional as well as the C-C stretching and $CH_2$ symmetric scissors vibrations [28].

## III. **EXPERIMENT**:

The apparatus used to investigate the 193 nm photodissociation of ethylene is a modified fixed source/rotating detector molecular beam apparatus. The use of this machine in high resolution photodissociation studies has been described previously [29]. Briefly, a 50 hz pulsed ethylene beam is produced by expanding neat ethylene at a stagnation pressure of 50 torr from a piezoelectric pulsed valve with a 1 mm diameter nozzle into a photolysis chamber. The focused output (~3 x 5 mm spot at interaction region) of a Lambda Physik EMG202MSC excimer laser operating at the 193 nm ArF transition enters this chamber and crosses the molecular beam perpendicularly. The nozzle is approximately 3 mm away from the laser beam. The focusing lens tends to accumulate photolysis by-product buildup so the laser power at the interaction region slowly decreases during an experiment. The quoted laser powers are those before the lens

since the actual value inside the chamber during the experiment is not measured. The mass spectrometric detector is kept perpendicular to both the laser and molecular beams. The distance between the photolysis volume and the electron bombardment ionizer is 39.0 cm which contributes to the high resolution of the TOF spectra.

The ethylene (99.99% min stated purity from Matheson) was used neat with no further purification. To fully understand the details of the ethylene photodissociation 1,1 $D_2CCH_2$ (99.1 atom % D from MSD Isotopes) and 1,2 cis HDCCDH (98.2 atom % D from MSD Isotopes) were used.

The experimental protocol is the same as for the previous acetylene photodissociation experiments [29], the only difference being that all TOF spectra were taken without the skimmer. Having the skimmer in place significantly decreased the S/N and did not resolve any additional structure. Using an iterative process, the $P(E_T)$ is calculated from the measured TOF with a forward convolution data analysis procedure that averages over the apparatus function [30]. The detector parameters required in the calculation are established from the photodissociation of HI and DI.

## IV. **RESULTS AND ANALYSIS:**

### A. **Comparison of Atomic and Molecular Channels:**

The relative importance of the atomic and molecular

elimination pathways in $C_2H_4$ photodissociation was studied by integrating the TOF spectra of $H_2$ and H taken close together in time and conditions. The comparison was made at four different laser powers ranging from 120 to 220 mJ/pulse. The molecular to atomic elimination ratio was consistently 1:1 (± .15); no appreciable correlation between laser power and branching ratio was observed.

B. **Molecular Elimination:**

1. $C_2H_4$:

The total accumulated $H_2$ TOF spectrum after the appropriate background corrections were made is shown in Figure 2. The process appears to be free of effects due to multiphoton absorption, at least in the laser intensity range of these experiments; there was no observable change in the spectrum when the laser power was varied from ~80 to ~220 mJ/pulse. The $P(E_T)$ used to fit the data (see Figure 3) is smooth and shows no obvious vibrational structure. This is not surprising since the products that form, $H_2$ and $H_2CC/HCCH$, are expected to be vibrationally and rotationally excited because of the large changes in geometry required to form the products through three- and/or four-centered elimination.

The fast edge of the $P(E_T)$ is where the acetylene products should be separated from the vinylidene product. Assuming ground state vinylidene forms, the maximum translational energy expected is ~64 kcal/mole [2]. If ground state acetylene is produced, the

fastest products should appear at ~108 kcal/mole [2]. The observed highest kinetic energy released, 88 kcal/mole, is between these. Internal thermal excitation of parent $C_2H_4$ could contribute to some increase in the maximum translational energy. However, based on the analogous $C_2H_2$ photodissociation experiments [29,31], this effect should only contribute a maximum of 2 kcal/mole. Since the $P(E_T)$ threshold is much greater than 64 kcal/mole, the fast tail must be attributed to acetylene formation. That the observed maximum kinetic energy is so much less than that predicted for the formation of ground state acetylene and hydrogen implies that these products are formed vibrationally excited. It should be noted that this $H_2$ TOF spectrum does not mean that the acetylene channel is responsible for all the product; in fact, although the $P(E_T)$ is not bimodal, the slope dramatically increases near the maximum kinetic energy limit for vinylidene formation.

2. $C_2H_2D_2$ and $C_2D_4$:

The TOF spectra from the photodissociation of $C_2H_4$ does not show convincingly whether or not vinylidene is formed. To resolve this question, the photodissociation of 1,1 and 1,2 cis deuterated ethylene was studied by measuring the TOF spectra for the $D_2$ and HD products. The pure $H_2$ spectrum could not be obtained because of contamination from D atoms produced in the atomic elimination. Both the comparison between the integrated spectra at each mass and the derived $P(E_T)$'s were used to learn about the relative importance of the acetylene and vinylidene

channels.

Table I gives the relative signal of HD and $D_2$ from each isotopomer. Figure 4 shows the summed spectra used in determining the ratios (normalized to the observed ratios) to give some idea of the degree of uncertainty involved.

Table I. Relative Amounts of Product Formed in the Photolysis of 1,1 $D_2CCH_2$ and 1,2 cis HDCCDH

| Isotopomer | $D_2$ m/e = 4 | HD m/e = 3 |
|---|---|---|
| 1,1 $D_2CCH_2$ | .5 | 1 |
| cis 1,2 HDCCDH | ~.2 | 2 |

The relative HD and $D_2$ ratios from the photodissociation of the isotopomers provide important clues on the molecular elimination mechanism. First, all four H atoms cannot be equivalent, i.e. there is not complete randomization in the excited state. If this were true, equal amounts of HD and $D_2$ would be formed in the photolysis of 1,1 $D_2CCH_2$ and cis 1,2 HDCCDH which is clearly not the case. The ratios also show that four-centered elimination to produce acetylene is not the only process that occurs. Assuming that this is the only channel, one would expect just HD products from 1,1 $D_2$CCH2. However, a significant amount of $D_2$, as much as 50% of the HD product, was observed. The fact that 1,1 $D_2CCH_2$ give more $D_2$ product than cis 1,2 HDCCDH suggests that the three-centered elimination is likely

to be more facile than the four-centered elimination.

The only mechanism that adequately explains the data is one in which both acetylene and vinylidene form from an intermediate with no appreciable H scrambling but with full rotation about the C=C bond. Let $\theta_v$ be proportional to the probability of forming vinylidene via three-centered elimination and $\theta_a$ be proportional to the probability of forming acetylene via four-centered elimination from each possible atomic pair. If the isotope effects for elimination to form vinylidene and acetylene are assumed equal, the following relative yields are expected ($i_{HD}$ and $i_{DD}$ represent the isotope effects):

```
D        H
 \      /
  C = C
 /      \
D        H
```

HD $4\theta_a \cdot i_{HD}$

$D_2$ $1\theta_v \cdot i_{DD}$

```
H        H
 \      /
  C = C
 /      \
D        D
```

HD $2\theta_a \cdot i_{HD} + 2\theta_v \cdot i_{HD}$

$D_2$ $\theta_a \cdot i_{DD}$

Based on the relative amount of HD formed from the two isotopomers, a relationship between $\theta_a$ and $\theta_v$ can be determined:

$$\frac{HD\ 1,1}{HD\ cis\ 1,2} = \frac{4\theta_a \cdot i_{HD}}{2\theta_a \cdot i_{HD} + 2\theta_v \cdot i_{HD}} \approx \frac{1}{2}\ (observed)$$

$$\therefore \quad 3\theta_a = \theta_v$$

Thus, the vinylidene elimination channel is approximately three times as important as the acetylene for each possible atomic pair. Normalizing for the number of ways three-centered and four-centered elimination can occur in $C_2H_4$, the acetylene/vinylidene ratio should be 2:3, exactly the value previously estimated by Okabe and McNesby [16].

The proposed mechanism and the $\theta_v = 3\theta_a$ relationship can also provide a value for $i_{HD}/i_{DD}$. Taking the measured ratio of HD and $D_2$ from 1,1 $D_2CCH_2$,

$$\frac{HD\ 1,1}{D_2\ 1,1} = \frac{4\theta_a \cdot i_{HD}}{\theta_v \cdot i_{DD}} \approx \frac{2}{1} \quad (observed)$$

Substituting $\theta_v = 3\theta_a$, one obtains

$$i_{HD} = \frac{3}{2} i_{DD}$$

The HD to $D_2$ isotope effect ratio of 1.5 is exactly what was previously observed and predicted [15,16]. This gives further credibility to the mechanism.

Using the calculated $\theta_a/\theta_v$ and $i_{HD}/i_{DD}$, the HD/$D_2$ product ratio for the cis 1,2 deuterated ethylene can also be predicted.

$$\frac{HD\ cis\ 1,2}{D_2\ cis\ 1,2} = \frac{2\theta_a \cdot i_{HD} + 2\theta_v \cdot i_{HD}}{\theta_a \cdot i_{DD}} = \frac{8 \cdot 3}{2} = 12$$

The observed ratio, $HD/D_2$ = 10, is close to the calculated value.

The acetylene/vinylidene formation mechanism derived from the $HD/D_2$ product ratios also provides some insight for the interpretation of the TOF spectra from 1,1 and cis 1,2 $C_2H_2D_2$. Figure 4 shows the TOF spectra fit with the $P(E_T)$'s in Figure 5. The gross differences between the $P(E_T)$'s where 100% acetylene (HD from 1,1) and 100% vinylidene ($D_2$ from 1,1) are expected are consistent with the mechanism; the HD $P(E_T)$ has relatively more product at higher translational energies (50 to 80 kcal/mole). The finer details, however, suggest that there may be more to consider. The "100% vinylidene" spectrum has a maximum energy release of ~78 kcal/mole, much greater than the available excess energy for vinylidene formation (64 kcal/mole). The obvious explanation is that some $D_2$ + acetylene is forming by four-centered elimination from 1,2 HDCCDH which is present as an impurity or formed through extensive 1,2 exchange in the excited state before $D_2$ elimination. This, however, is unlikely because the experiments show that photodissociation of the 1,2 compound produces virtually no $D_2$. The most reasonable answer is that the $D_2$ is forming and leaving as the H is transferring from one carbon to the other (an ethylidene type mechanism) as illustrated in Figure 6. The formation of acetylene instead of vinylidene in this three-centered elimination mechanism will have the same available excess energy as four-centered elimination to give acetylene.

C. **Atomic Elimination:**

The shape of the H atom TOF spectra is extremely dependent on laser power. Figure 7 shows the accumulated scans taken at four different average laser powers (40, 90, 140, and 180 mJ/pulse). In fact, it was not possible to average long enough at low enough power to obtain a pure primary distribution; product too fast to be from primary bond dissociation was always found. These secondary photodissociation processes made it impossible to use the fast edges of the H atom TOF spectra to obtain a C-H bond energy. In the further analysis of the results, then, the C-H bond energy was taken as 108 kcal/mole [2].

In fitting the TOF spectra, it was initially assumed that all the H atoms were from the combination of the primary process, $C_2H_4 \rightarrow H + C_2H_3$, and the subsequent photodissociation of the primary product, $C_2H_3 \rightarrow H + C_2H_2$, and that all the vinyl radicals produced had an equal probability of absorbing a photon regardless of the extent of the internal excitation. If this picture were correct, the high power experiments would yield more primary and secondary H atoms and the TOF spectra would have higher signal at all arrival times; the only change in shape would be from a relative increase in secondary H atoms at the higher laser powers. However, as shown in Figure 8, TOF spectra obtained in the high power scans have significantly less slow "primary" product and more fast. There is no secondary $P(E_T)$ such that the TOF spectra at all the different powers will share same primary $P(E_T)$. Since the primary $P(E_T)$ should not change

with laser power, the dissociation process described above must be oversimplified.

Ethylene multiphoton absorption is one possible explanation for the decrease in slow H atoms and increase in fast H atoms at high laser powers. In this scheme, the $C_2H_4$ could absorb more than one photon at higher laser powers producing H atoms with greater translational energy. The observed disappearance of slow H atoms at high laser powers, then, is the result of the photoexcited $C_2H_4$ absorbing a second photon before it eliminates an H atom; the $P(E_T)$ would shift to higher translational energies simply because more energy is available for product translation. This explanation hinges on the fact that ethylene multiphoton absorption occurs at 193 nm. The cross-section for 193 nm absorption by ethylene is so small ($\sigma = 2 \times 10^{-20}$ cm$^2$) that even at 180 mJ/pulse ($2 \times 10^{18}$ photons/pulse·cm$^2$) it is unlikely that saturation is occurring; for this scenario to work, the absorption cross-section for the second photon would have to be much greater than for the first. Not enough is known about the multiphoton absorption of $C_2H_4$ to prove or disprove. The lack of power dependence in the molecular elimination channel, however, suggests that it is not two photon absorption of $C_2H_4$ that gives rise to the observed power dependence in H atom elimination.

Perhaps a better explanation for the change in shape of the primary $P(E_T)$ at higher laser powers would invoke a fast spontaneous decomposition of excited $C_2H_4$, followed by spontaneous decomposition of internally excited $C_2H_3$ and

competitive secondary photodissociation of the $C_2H_3$. This scenario is illustrated in Figure 9. At low laser powers, when the ethylene absorbs a photon at 193 nm, it will be excited by 148 kcal/mole. Since breaking a C-H bond breaks requires ~108 kcal/mole, the resulting vinyl radical could have as much as 40 kcal/mole excess energy, which is greater than the H-CHCH bond energy (35 kcal/mole). Primary $C_2H_3$ products with an internal energy above 35 kcal/mole, i.e. those with $E_T \leq 5$ kcal/mole, can further dissociate, with no additional photon required, producing H + HCCH with 0 to 5 kcal/mole in translation. The net result, then, will be two slow ($E_T \leq 5$ kcal/mole) H atoms from the same ethylene. At higher laser powers, there is a greater chance for the vinyl radicals formed to absorb a photon rather than spontaneously decompose. Those that do absorb a photon will have more internal energy and upon fragmentation will produce faster product. The apparent difference in the low and high power "primary" $P(E_T)$'s, then, is that at the high power fewer slow H atoms will come from spontaneous decomposition of $C_2H_3$ but more fast H atoms will be created from the secondary absorption by the slow $C_2H_3$.

The two mechanisms offered to explain the effects of laser power are essentially the same except that in the latter, the vinyl radical absorbs the second photon rather than the $C_2H_4$. The vinyl radical absorption mechanism is preferred for several reasons. First, no multiphoton effects were seen in the $H_2$ elimination channel which would be expected in excited ethylene

absorbed a second photon. Second it is known that the vinyl radical absorbs at 164.7 and 168.33 nm [32]. Third, if it is assumed that the secondary dissociation of the slow vinyl radicals is similar to the fast, the H + $C_2H_2$ products falls in the right spot.

Because the H atom elimination is so complex, there are not enough breaks in the TOF spectra to uniquely determine the limits of each channel, and the secondary bond energies are not known accurately enough, the fitting procedure cannot be expected to provide the true $P(E_T)$'s. As long as these limitations are recognized, using reasonable assumptions to fit the spectra will provide some information. In the fitting procedure, four channels were considered:

$$(1) \quad C_2H_4 \xrightarrow{h\nu} H + C_2H_3$$

$$(2a) \quad C_2H_3 \ (E_T > 5\ kcal/mole) \xrightarrow{h\nu} H + C_2H_2$$

$$(2b) \quad C_2H_3 \ (E_T \leq 5\ kcal/mole) \xrightarrow{h\nu} H + C_2H_2$$

$$(3) \quad C_2H_3 \ (E_T \leq 5\ kcal/mole) \rightarrow H + HCCH$$

In the secondary dissociation pathways in which a photon was absorbed, it was assumed that all the vinyl radicals had an equal probability of becoming excited. The secondary product from channel (3) could, of course, contain no more than 5 kcal/mole in translation; however, in the $P(E_T)$ a maximum of 8 kcal/mole in translation was considered to account for uncertainty in bond

energies. It was also assumed that the secondary $P(E_T)$ for (2a) was the same as for (2b). A primary, secondary, and spontaneous $P(E_T)$ were derived such that all the TOF spectra could be fit simply by changing the relative contribution of each channel. The final fits to the TOF are shown in Figure 7; Figures 10 to 12 show the primary, secondary, and spontaneous $P(E_T)$'s used.

The photodissociation of 1,1 $D_2CCH_2$ to give H + $HCCD_2$ gives some understanding of the effect that isotopes have on the atomic elimination. The H atom $P(E_T)$ TOF spectrum calculated using the $P(E_T)$ from $C_2H_4$ at similar laser power was compared to the 1,1 $D_2CCH_2$ H atom data. As seen in Figure 13, the H + $HCCD_2$ product seems to have more slow (higher internal energy) product. This is probably a result of the lower frequency C-D vibrations in the transition state [22] which allows more of the excess energy to couple into vibration.

## V. **DISCUSSION:**

### A. **Molecular Elimination:**

The product ratios measured in the photolysis of 1,1 $H_2CCD_2$ and cis 1,2 HDCCDH as well as the TOF spectra support a mechanism in which both acetylene and vinylidene are formed. When the ethylene is excited there appears to be free rotation about the C=C bond but no significant 1,2 H exchange. For each possible pair of hydrogen atoms in $C_2H_4$, the vinylidene formation was found to be three times as likely as the formation of acetylene.

Since there are twice as many possible ways of producing acetylene in $C_2H_4$ as vinylidene, the vinylidene/acetylene product ratio was estimated to be 3/2. In the case where pure vinylidene ($D_2$ from 1,1 $H_2CCD_2$) was expected, fast product that could only have come from acetylene formation was detected. This could be accounted for by 1,2 migration of H at some point during the dissociation. The $E_{act}$ for 1,2 H exchange, ~75.3 kcal/mole [24], is well within the available energy. Although this 1,2 H migration is related to the formation of ethylidene, the lack of extensive isotope scrambling in the photodissociation of partially deuterated ethylene strongly suggests that it might be incorrect to think of the three-centered elimination of $D_2$ from 1,1 $H_2CCD_2$ to form acetylene as occurring through an ethylidene intermediate. The more accurate description, perhaps, is the concerted reaction involving the simultaneous migration of the H atom and the elimination of $D_2$ as shown in Figure 6.

The $P(E_T)$ for $H_2$ elimination from ethylene peaks well away from zero at ~22 kcal/mole which reflects a substantial exit barrier. This is quite typical of concerted elimination dissociation. For example, the $P(E_T)$'s for the concerted reactions, cyclohexene $\rightarrow$ $C_2H_4$ + $H_2CCHCHCH_2$ and cyclohexadiene $\rightarrow$ benzene + $H_2$ both peak at ~20 to 25 kcal/mole [30,33]. In concerted elimination, when the excited molecule reaches the transition state, fast electron rearrangement often leaves the two newly formed product molecules in very close contact. As the old chemical bonds disappear and new bonds form, the interaction

between the products suddenly becomes repulsive. The repulsive separation converts a large fraction of the potential energy associated with the exit barrier into product translation. The fact that the three-centered elimination forming $H_2$ and vinylidene appears to be concerted, clearly shows that the vinylidene does not behave like a diradical in the conventional sense. The repulsive interaction with $H_2$ is more like that of a "stable molecule". The two electrons in vinylidene must be strongly paired. This is, in fact, reflected in the heat of formation of vinylidene. The C-H bond in ethylene is known to be ~108 kcal/mole. However, breaking the C-H bond in the vinyl radical to form vinylidene, in spite of the fact that it does not involve any change in the bond order, only requires ~80 kcal/mole. This is ~28 kcal/mole less than what one expects from the simple bond additivity concept [34]. The additional 28 kcal/mole stability in vinylidene is likely to come from the energy released by the pairing of two electrons in vinylidene.

The $P(E_T)$ obtained for the molecular elimination does not indicate whether dissociation is taking place from an electronically excited ethylene or whether internal conversion to vibrationally hot ground state ethylene precedes the dissociation. However, as will be discussed, the translational energy distribution of the simple C-H bond rupture clearly shows that a very fast internal conversion process takes place before the molecules start to dissociate.

The $H_2$ $P(E_T)$ from $C_2H_4$ photolysis contains more detailed

information about the acetylene and vinylidene channels. the first electronically excited state of $H_2$ is out of the range of 193 nm photons. The lowest electronically excited states of acetylene ($^3B_2$ cis) and vinylidene ($^3B_2$) can form but would only appear at $E_T$ < 29 kcal/mole and < 16 kcal/mole respectively [2]. Since vibrational and rotational excitation of both fragments is expected and a fairly significant amount has been observed in the $H_2$ product (an average of ~12 kcal/mole) [25], the peak of the distribution for these excited states would be expected at even lower $E_T$'s, where the $P(E_T)$ drops off. Thus, only a small percentage of the products could be formed electronically excited. Triplet vinylidene does not appear to be a major product in the molecular elimination channel at 193 nm. This is contrary to what Fahr and Laufer surmise from their flash photolysis studies of the photodissociation at much shorter wavelengths [20].

Because all acetylene + $H_2$ product appears at a translational energy less than 88 kcal/mole, at least 20 kcal/mole internal energy must be partitioned between the acetylene and $H_2$. At the translational energy at which vinylidene can just form ($E_{Int}$ = 0 kcal/mole), the HCCH + $H_2$ products can have $E_{Int}$ = 44 kcal/mole. The peak of the translational energy distribution corresponds to $E_{Int}$ = 43 kcal/mole for the $H_2CC$ + $H_2$ channel and $E_{Int}$ = 87 kcal/mole for the HCCH + $H_2$ channel. This experiment cannot identify how the internal energy is partitioned between hydrogen and the

acetylene/vinylidene. However, the measurements carried out by Cromwell et. al. of this laboratory have shown that although $H_2$ is formed in rovibrational states as high as v=3/j=9, most of the $H_2$ is produced in v=0 and the average internal excitation of $H_2$ is only around 12 kcal/mole [25]. A large fraction of the internal energy, then, must be going into vibrations and rotations of the $H_2CC$ and HCCH since not much electronically excited triplet $H_2CC$ and HCCH are expected to form. For a molecule with so many vibrational degrees of freedom, is not surprising that the vibrational energy is extensively shared by the internal degrees of freedom.

B. **Atomic Elimination**:

The $P(E_T)$ obtained from the fitting process, provides some important information on the dynamics of the primary process. As Figure 10 shows, the $P(E_T)$ peaks very close to 0 kcal/mole suggesting that the H atom elimination is a simple bond rupture with very little exit barrier. It is consistent with dissociation from the ground electronic state, implying that the electronically excited ethylene internally converts to the upper vibrational levels of the electronic ground state before decomposing as has been suggested by theoretical studies [23] and Bersohn's experiments [22]. The other point apparent from the $P(E_T)$ is that most of the vinyl radical and hydrogen atom product forms with $E_{Int}$ = 40 - 37 kcal/mole, not enough to excite the lowest electronic state of $C_2H_3$ (≈ 53 - 57 kcal/mole [2]). The majority of the vinyl radical, then, must be produced in high

vibrational levels of the ground electronic state.

The sharp rise in the fast edge of the H atom TOF spectra with laser power as well as the velocity of the fastest products indicates that secondary photodissociation of primary products is important in the power range studied. The lowest laser intensity for which data is available is 40 mJ/pulse which corresponds to ~200mJ/cm$^2$ at the photolysis region.

As discussed in a previous paper, it is difficult to obtain precise information about the secondary dissociation channels: so much averaging is inherently involved [29,30]. It is also hard to discern the contribution of slow secondary products since they will appear with a velocity in the same range as the primary products. Nevertheless, the H atom TOF spectra taken do give some valuable information about the secondary events. The position of the fast edge, which is the most certain part of the spectrum, gives the maximum translational energy release. Assuming $C_2H_3$ with $E_{Int}$ = 35 kcal/mole absorbs another photon and dissociates to HCCH, the ground state products should have a maximum translational energy of 148 kcal/mole. The observed maximum, however, is closer to 100 kcal/mole. If vinylidene were to form rather than acetylene, the expected maximum translational energy would be approximately 104 kcal/mole, closer to that observed. Most (~95%) of the product, however, does not appear near this threshold; it is much slower, with $E_T$ ~15-30 kcal/mole. The relatively narrow translational energy distribution and peaking at a high value indicates that direct photodissociation

from an electronically excited state is occurring. At the translational energy most of the products were observed at, there is enough internal energy for the triplet states of acetylene and vinylidene to form. The expected maximum translational energy for ground state H + $^3CCH_2$ is ≈ 56 kcal/mole and for H + $^3HCCH$ is ≈ 69 kcal/mole [2]. It seems likely that these excited states are forming in the secondary photodissociation.

The formation of triplet products implied by the secondary $P(E_T)$ is not entirely unexpected. As mentioned, Fahr and Laufer observed a significant amount of nonprimary triplet vinylidene [20]. They, however, attributed this product to the molecular elimination channel, making the assumption that the $C_2H_3$ would decompose to the thermodynamically favored product, HCCH. In this experiment, there was little (if any) triplet vinylidene or acetylene detected from the molecular elimination channel. Since Fahr and Laufer's results do not appear to be inconsistent with the triplet vinylidene forming from the atomic elimination channel, perhaps the metastable state they propose may be the vibrationally excited $C_2H_3$.

## VI. **CONCLUSIONS**:

For the most part, the H and $H_2$ TOF studies agree with the previous work but offer a few more details. The two major channels, the molecular and atomic elimination, were observed and were found to be of approximately equal importance. 1,1 $D_2CCH_2$ and 1,2 cis HDCCDH were photolyzed to understand the details of

the molecular elimination channel. The product ratios and TOF spectra obtained were consistent with a mechanism in which both acetylene and vinylidene were produced in a 2 to 3 ratio for $C_2H_4$, there is free rotation about the C=C bond, and all H's are equally accessible but not equivalent. The $D_2$ TOF spectrum from 1,1 $D_2CCH_2$, where 100% vinylidene is expected, has some products too fast to be vinylidene; this is presumably from acetylene formation but with the elimination of $D_2$ from the same carbon atom. It is proposed that the H is transferring while the $D_2$ is leaving, through an ethylidene type intermediate. The data cannot determine where along the reaction coordinate such a migration takes place and if it is responsible for all acetylene formation.

The $P(E_T)$ for the molecular elimination peaks away from zero and so indicates the presence of an exit barrier. A large fraction of the excess energy goes into internal energy of the $H_2$ + $HCCH/H_2CC$ products which is understandable considering the fast internal conversion of the excited molecules and the geometry changes that are required in the excitation and dissociation. Because vibrational/rotational excitation is expected and experiments done by others in this group show that a significant fraction of this energy is in the rovibrational states of $H_2$ [25], very little of the acetylene and vinylidene can be formed in the lowest excited electronic states ($T_1$).

The studies of the atomic elimination channel were plagued by secondary dissociation even at as low laser intensity as 200

$mJ/cm^2$. Although this meant that the C-H bond energy could not be accurately determined, important features of the secondary photodissociation were explored. The best explanation for the changes in the H atom TOF spectra observed in going from low to high laser power is a competition between spontaneous decomposition and secondary photodissociation of the highly vibrationally excited vinyl radical with the latter becoming more important at high laser powers. The 193 nm dissociation begins with the absorption of a photon by ethylene. The elimination of the H atom peaks at very low translational energies suggesting simple bond rupture from the ground electronic state as theoretically predicted [23] and experimentally inferred by Bersohn's group [22]. The $C_2H_3$ that forms has ~0 - 40 kcal/mole in translation--not enough to go to the first electronic state ($^2A''$). Since the C-H bond energy to form acetylene is only ~35 kcal/mole, many of the $C_2H_3$ molecules have enough energy to spontaneously decompose to form $C_2H_2$ + H with 0 to 5 kcal/mole in translation. To explain the fast H atoms seen, the $C_2H_3$ must also be able to absorb a second photon and decompose to H + $C_2H_2$. With this second photon, enough energy is available to form HCCH and $H_2CC$ in the ground electronic state or in the lowest electronic state, $T_1$. The maximum energy release for the secondary decomposition is closer to that expected for H + $H_2CC$ suggesting that little ground state H + HCCH is produced. Based on the position of the peak in the secondary $P(E_T)$, the production of electronically excited triplet HCCH and/or $H_2CC$ is

apparently the favored pathway. The isomer that forms cannot be identified but since so little ground state acetylene is seen and Fahr and Laufer report detecting $H_2CC(^3B_2)$ as a major product in their flash photolysis studies [20] the $H_2CC(^3B_2)$ is apparently the most likely product in the secondary photodissociation of $C_2H_3$.

## VII. **ACKNOWLEDGEMENTS**:

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## IX. **FIGURE CAPTIONS:**

Figure 1. Heats of reaction (0K) for the various channels in the photodissociation of ethylene. The photolysis energy is 148 kcal/mole. Many of the molecules' heats of formation are not well known; the values this diagram is constructed from are given in reference 2.

Figure 2. $H_2$ TOF spectrum from photolysis of $C_2H_4$; the data was accumulated for 16.1 hrs at an average laser power of 130 mJ/pulse. The solid line is the best fit calculated using the $P(E_T)$ shown in Figure 3.

Figure 3. $P(E_T)$ for $H_2 + C_2H_2$ used to fit the $H_2$ TOF spectrum in Figure 2. The arrows show the maximum translational energy at which the acetylene, vinylidene, excited state acetylene, and excited state vinylidene channels are expected.

Figure 4. TOF spectra from the photolysis of 1,1 $D_2CCH_2$ and 1,2 cis HDCCDH deuterated ethylenes. (a), (b), (c), and (d) show the 1,1 HD and $D_2$ and 1,2 cis HD and $D_2$ scans, respectively. The total accumulation times/average laser power for each are as follows: (a) 14.4 hrs at 105 mJ/pulse, (b) 17.2 hrs at 115 mJ/pulse, (c) 13.8 hrs at 80 mJ/pulse and (d) 6.9 hrs at 70 mJ/pulse. The areas of these spectra have been normalized to reflect the observed relative ratios given in Table I. (a), (b), and (c) have been fit using the appropriate $P(E_T)$ in Figure 5.

Figure 5. $P(E_T)$'s used to fit the deuterated ethylene molecular elimination TOF spectra in Figure 4. These curves have been normalized to the same area. The solid line is for HD + $C_2HD$ from 1,1 $D_2CCH_2$. The dashed line is for $D_2 + C_2H_2$ from 1,1 $D_2CCH_2$; the dotted line is for HD + $C_2HD$ from 1,2 cis HDCCDH.

Figure 6. Diagram showing the ethylidene-type mechanism which can explain why acetylene + $D_2$ is observed in the photolysis of 1,1 $D_2CCH_2$. The excited ethylene (twisted) rearranges to an ethylidene-like intermediate; the 1,2 migration of the H atom occurs while the $D_2$ is leaving to produce $D_2$ + HCCH.

Figure 7. H atom TOF spectra from $C_2H_4$ photolysis. Solid line is the fit using the mechanism/assumptions discussed in the text. The dashed line shows the primary H + $C_2H_3$ product. The dotted line represents H from spontaneous dissociation of $C_2H_3$. The -·- line shows the H from secondary dissociation of $C_2H_3$ in which the $C_2H_3$ radical does not have enough internal energy to undergo spontaneous decomposition. The -···- line is the H from secondary dissociation of $C_2H_3$ that has enough internal energy to undergo spontaneous decomposition but absorbs a photon before falling apart. Scans (a), (b), (c), and (d) were accumulated for 8.9, 7.8, .2, and .2 hrs at an average laser power of 40, 90,

140, and 180 mJ/pulse respectively.

Figure 8. Comparison of the H atom TOF spectra taken at high (X's) and low (open circles) laser power. The solid line is the best fit calculated using the preliminary assumptions discussed in the text. The dashed lines show the primary H + $C_2H_3$ product. The dotted lines represent the H atoms from secondary dissociation of the $C_2H_3$ after absorption of a photon.

Figure 9. Diagram illustrating the spontaneous decomposition explanation for the change in shape of the H atom TOF spectra with laser power. The ethylene absorbs a photon (1) to produce H + $C_2H_3$. Some of the $C_2H_3$ has enough internal energy to fragment to H + HCCH (3). Otherwise, the $C_2H_3$ can absorb a photon (2) and decompose to H + HCCH/$H_2CC$. As the laser power increases, the fraction of molecules undergoing spontaneous decomposition (3) decreases while the fraction that absorb a photon (2) increases.

Figure 10. Primary $P(E_T)$ for $C_2H_4 \rightarrow H + C_2H_3$ used to fit all the H atom TOF spectra in Figure 7.

Figure 11. Secondary $P(E_T)$ for $C_2H_3$ (fast) $\rightarrow$ H + $C_2H_2$ and $C_2H_3$ (slow) $\rightarrow$ H + $C_2H_2$ used to fit all the H atom TOF spectra in Figure 7. The lines show the expected maximum translational energy of the possible products assuming the $E_{Int}$ of the $C_2H_3$ is 35 kcal/mole. The figure shows that most of the $C_2H_2$ product is formed in the lowest triplet state.

Figure 12. Spontaneous decomposition $P(E_T)$ used to fit the H atom TOF spectra in Figure 7. Although from the bond energies used in the paper no H + HCCH product with $E_T > 5$ kcal/mole would be expected, to account for the uncertainty in this value, product with $E_T$ up to 8 kcal/mole was considered.

Figure 13. H atom TOF spectrum from photolysis of 1,1 $D_2CCH_2$. The spectrum is fit with the same $P(E_T)$ used to fit the high power (180 mj/pulse) H atom TOF spectrum from $C_2H_4$ photolysis. The H + $HCCD_2$ product clearly has more slow H atoms being formed than the H + $HCCH_2$.

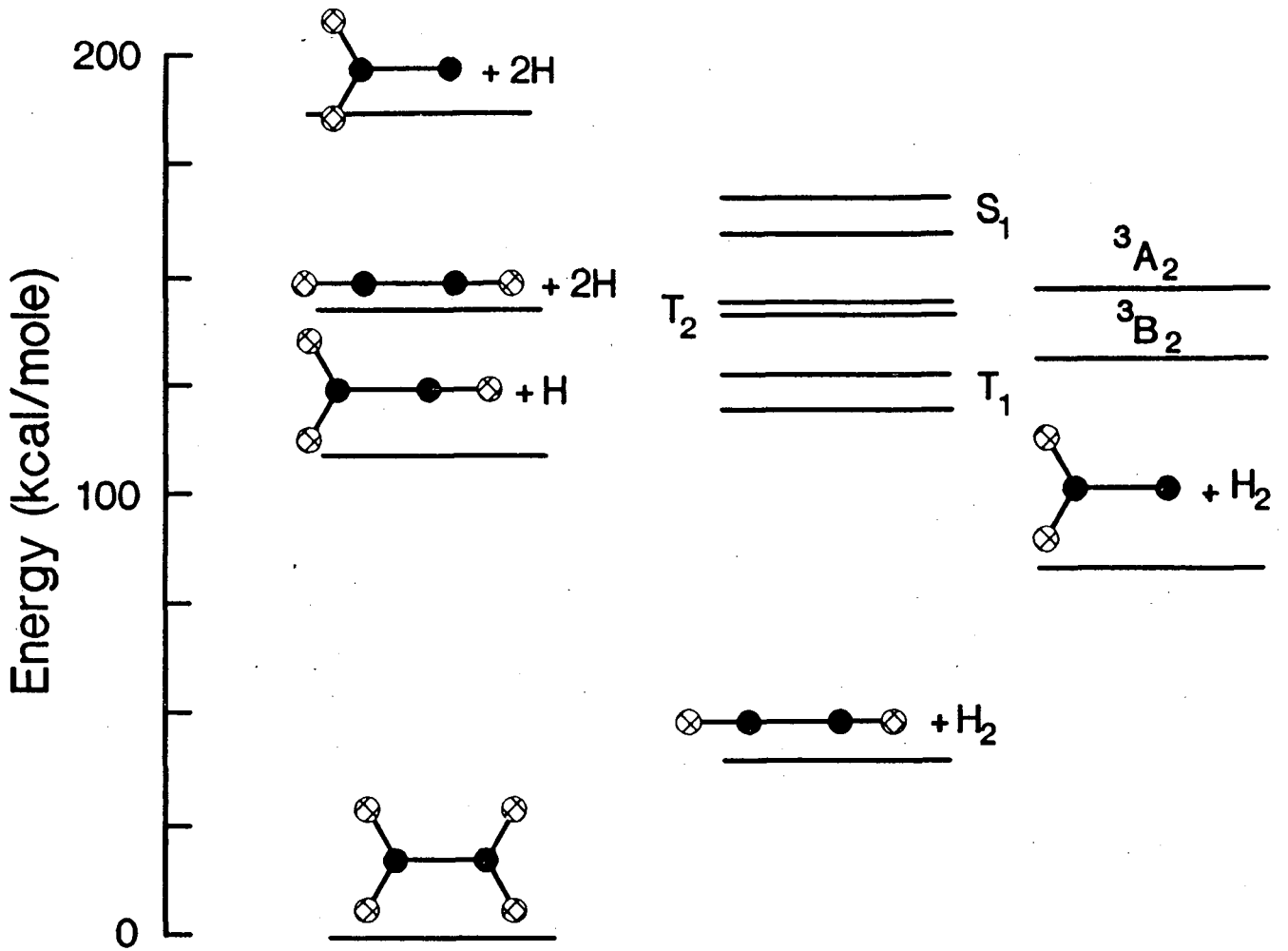
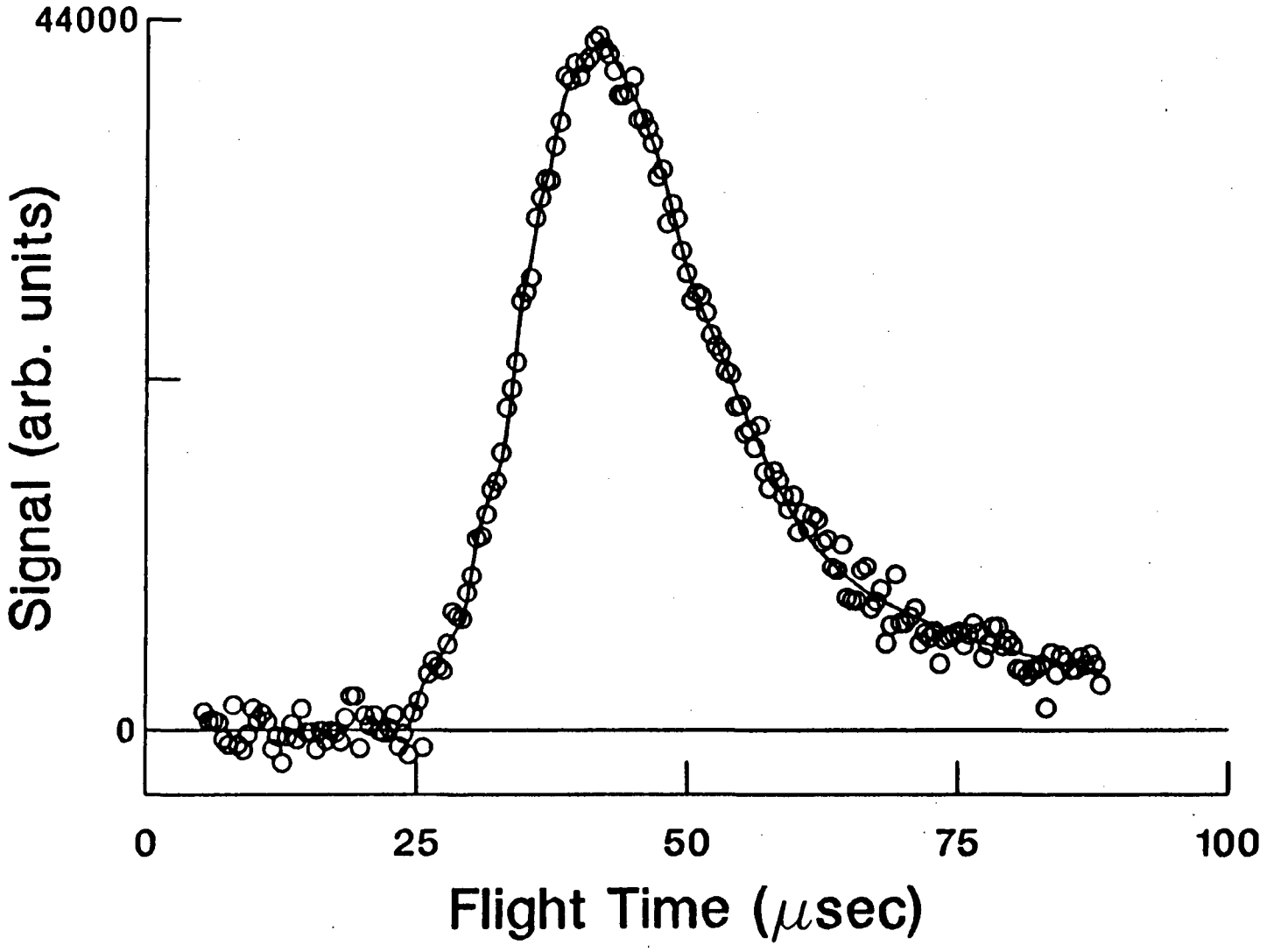



Figure 1

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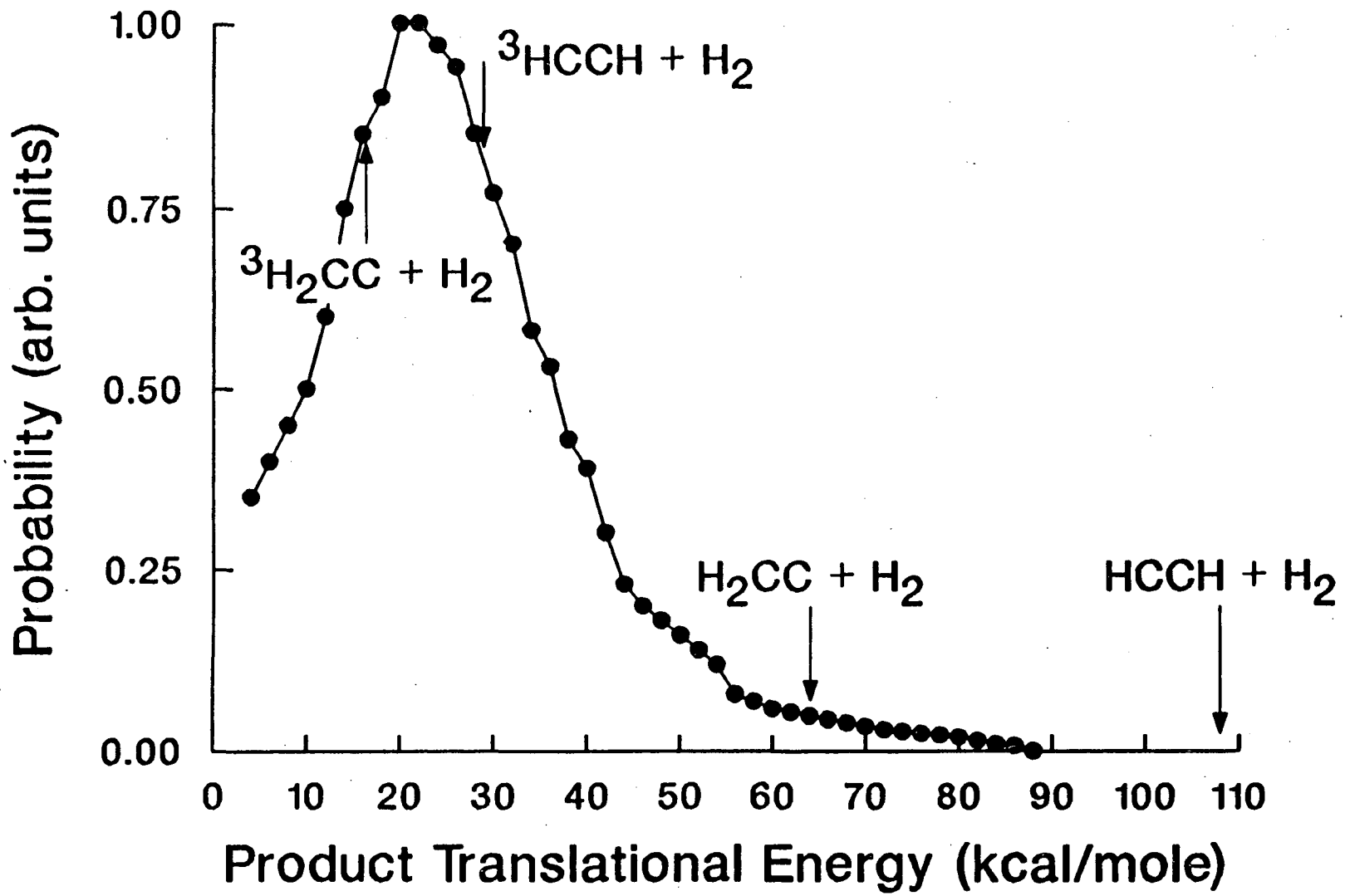
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40
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60
70
80
90
100
110
Product Translational Energy (kcal/mole)
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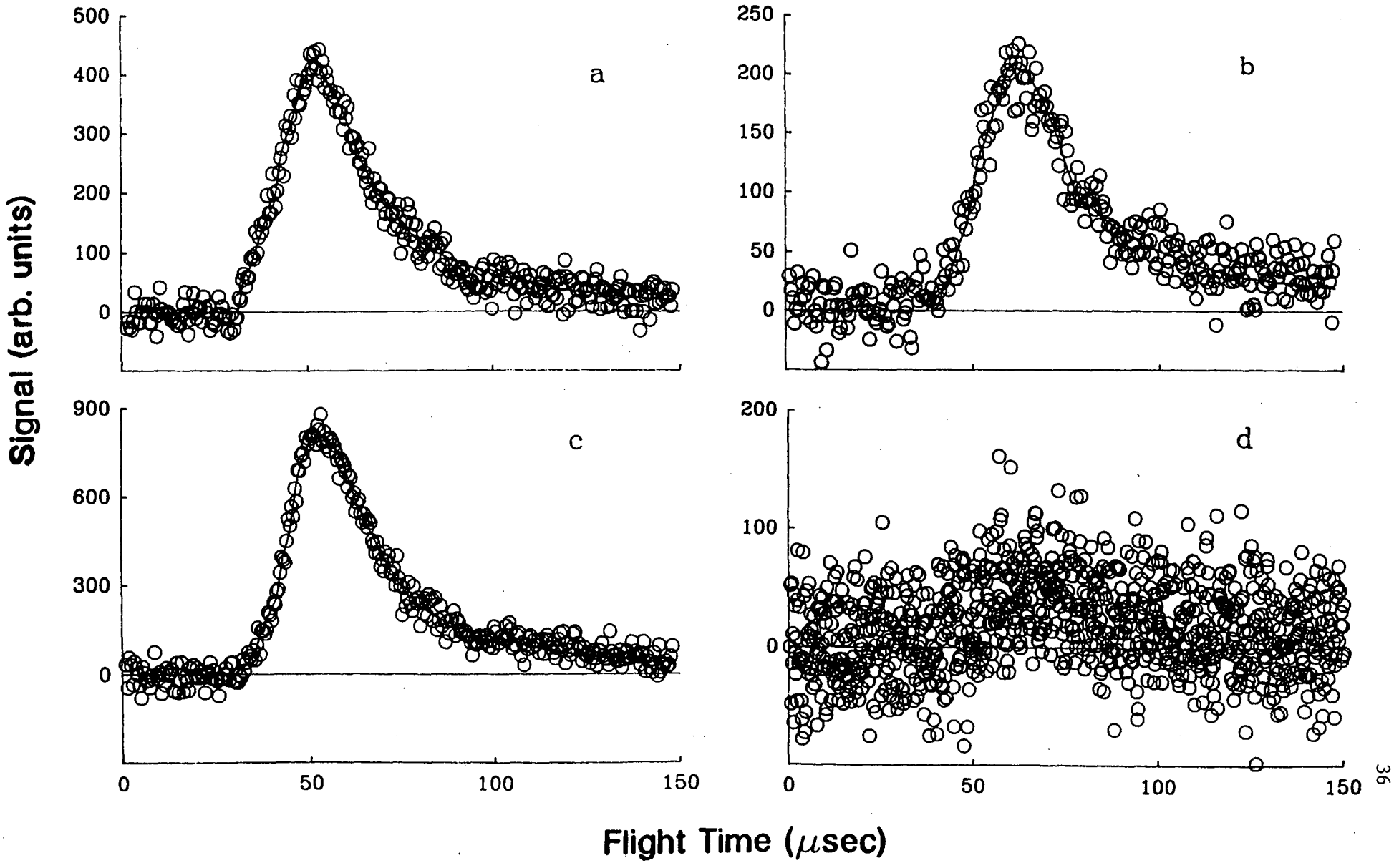
$^3H_2CC + H_2$
$H_2CC + H_2$
$HCCH + H_2$

Figure 3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Flight Time (μsec)
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b
c
d
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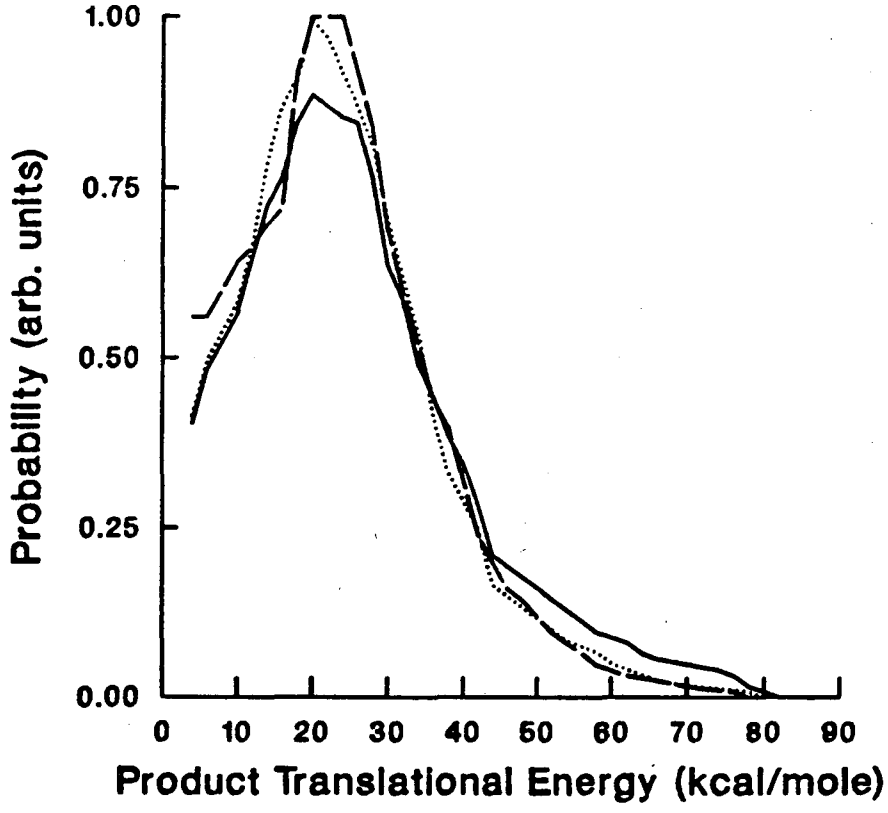
0
50
100
150

Figure 4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90
Product Translational Energy (kcal/mole)

Figure 5

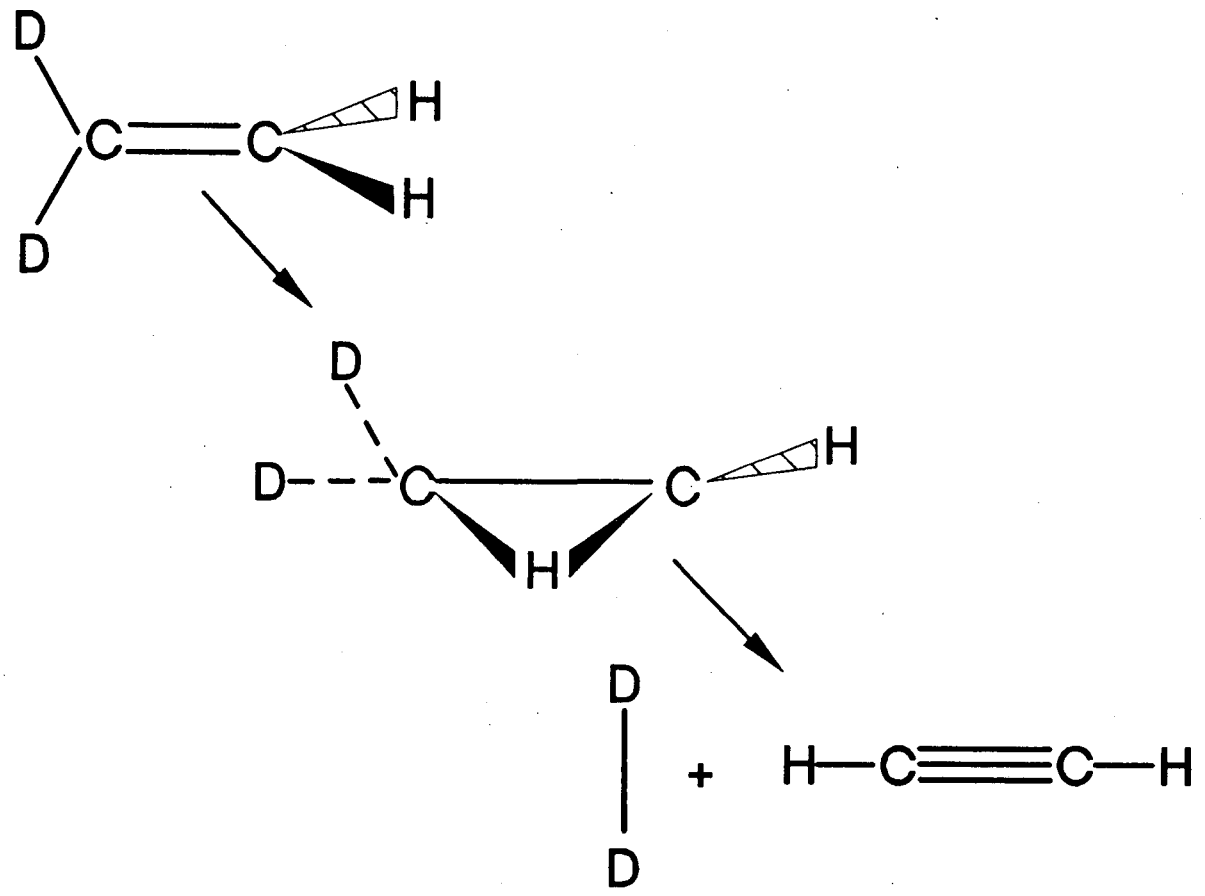
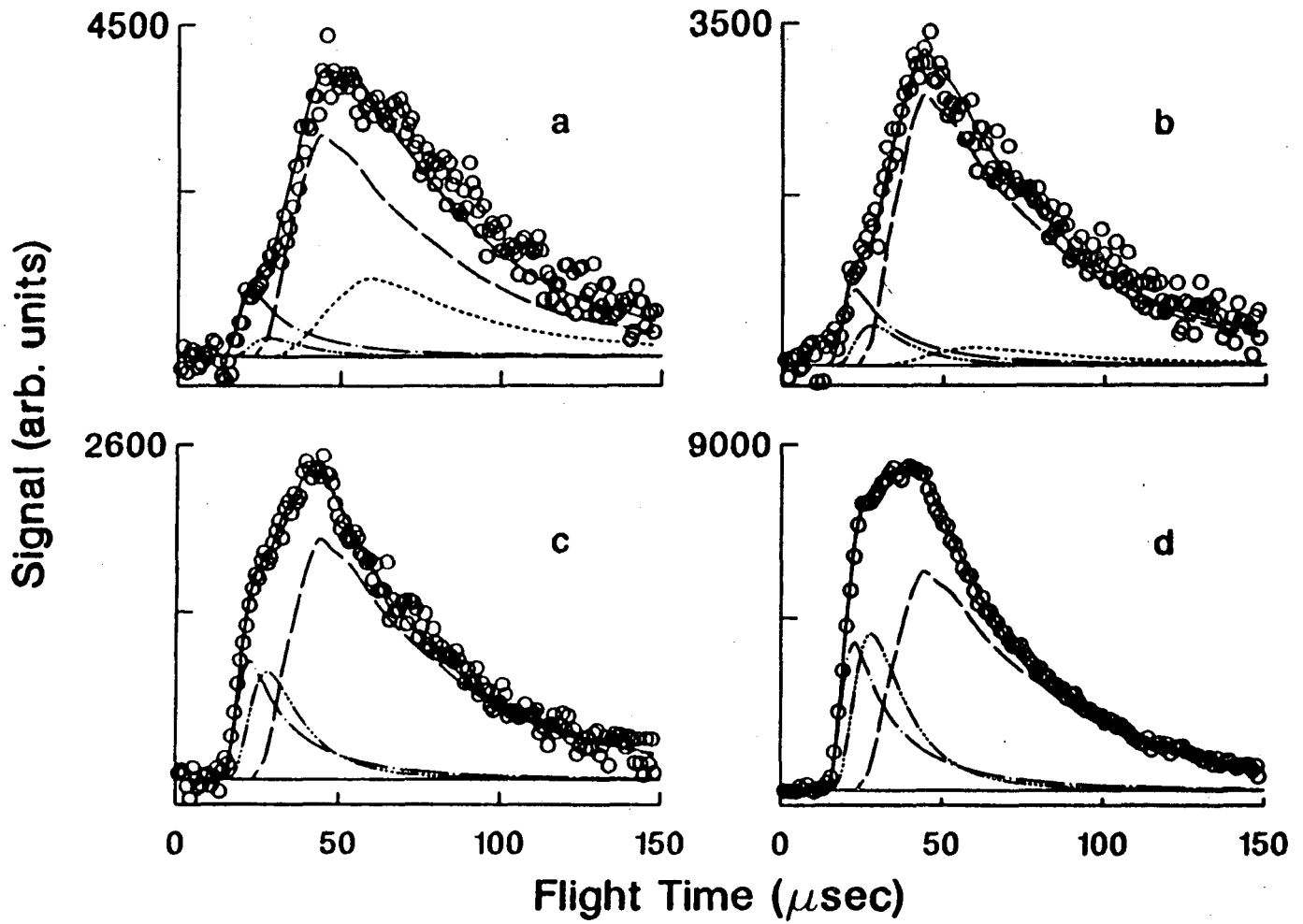



Figure 6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Flight Time (μsec)

Figure 7

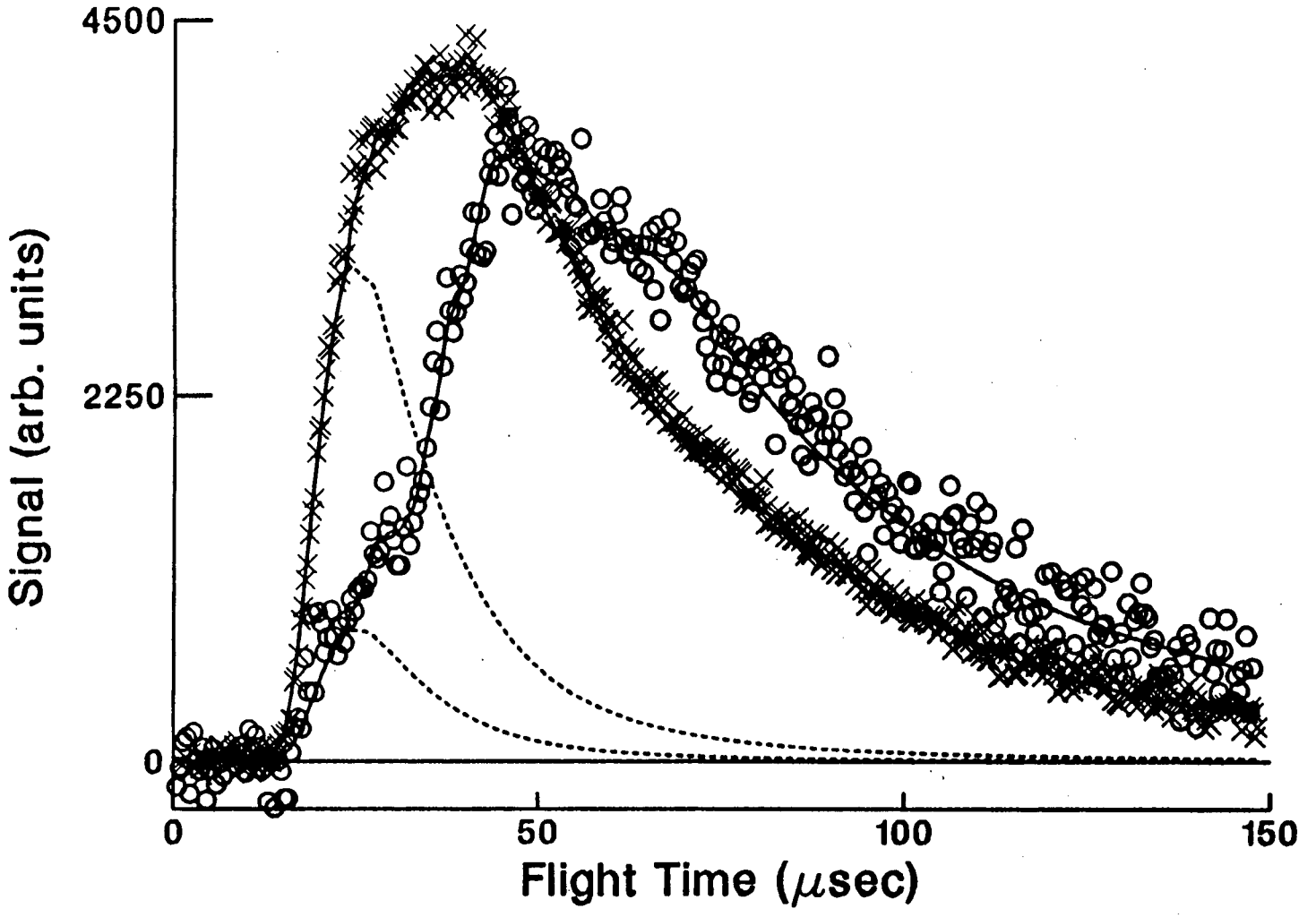



Figure 8

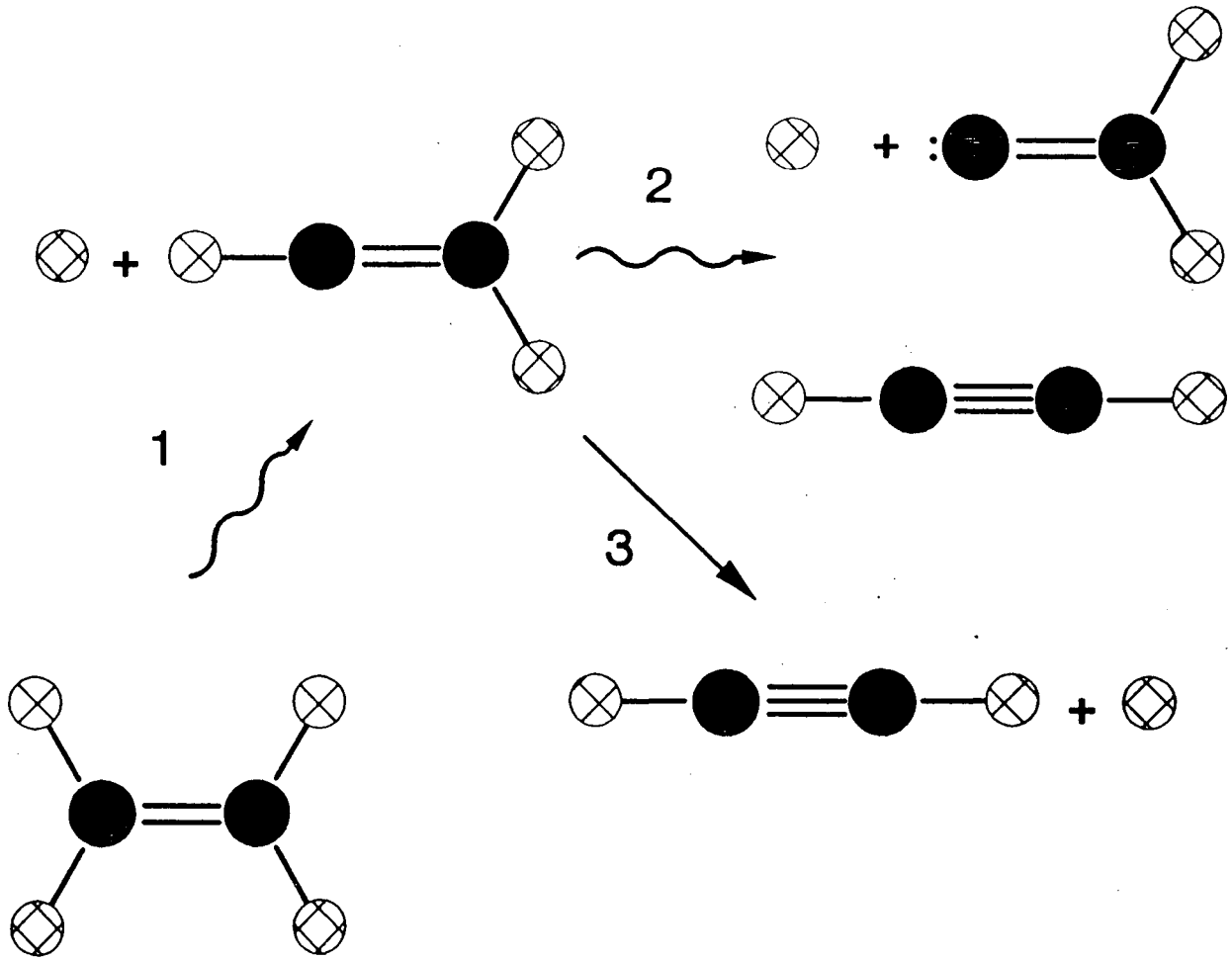
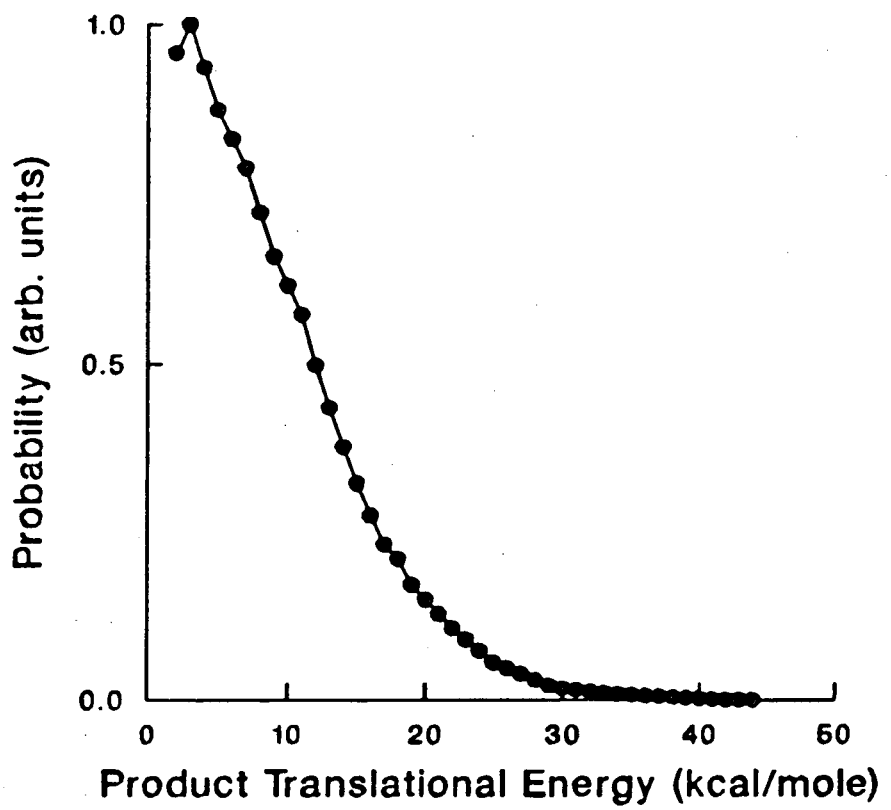



Figure 9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Probability (arb. units)
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30
40
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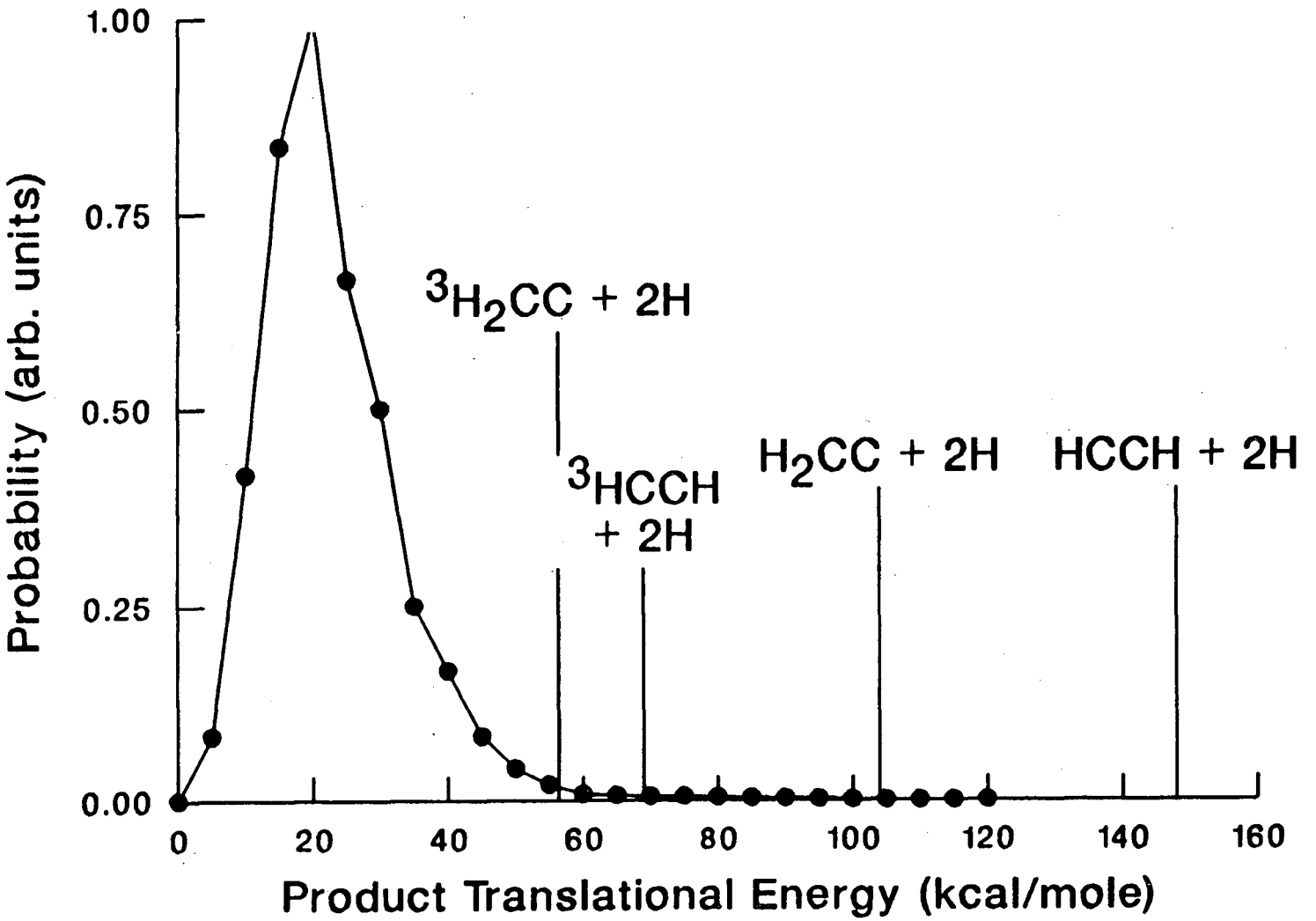
Product Translational Energy (kcal/mole)

Figure 10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Probability (arb. units)
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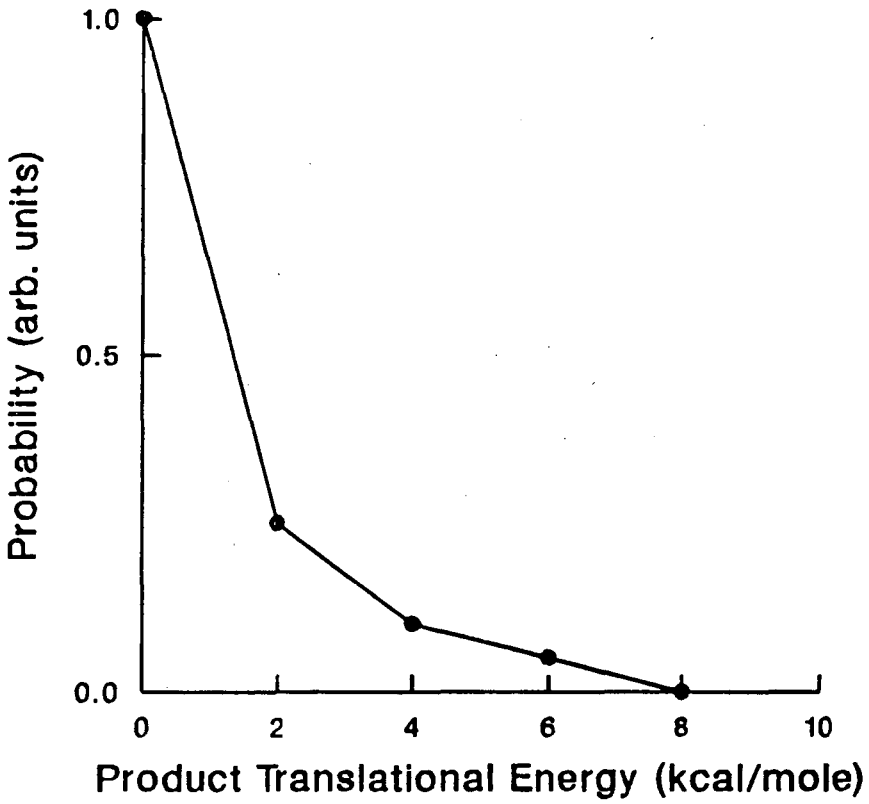
60
80
100
120
140
160
Product Translational Energy (kcal/mole)
$^3H_2CC$ + 2H
$^3HCCH$ + 2H
$H_2CC$ + 2H
HCCH + 2H

Figure 11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Probability (arb. units)
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6
8
10
Product Translational Energy (kcal/mole)

Figure 12

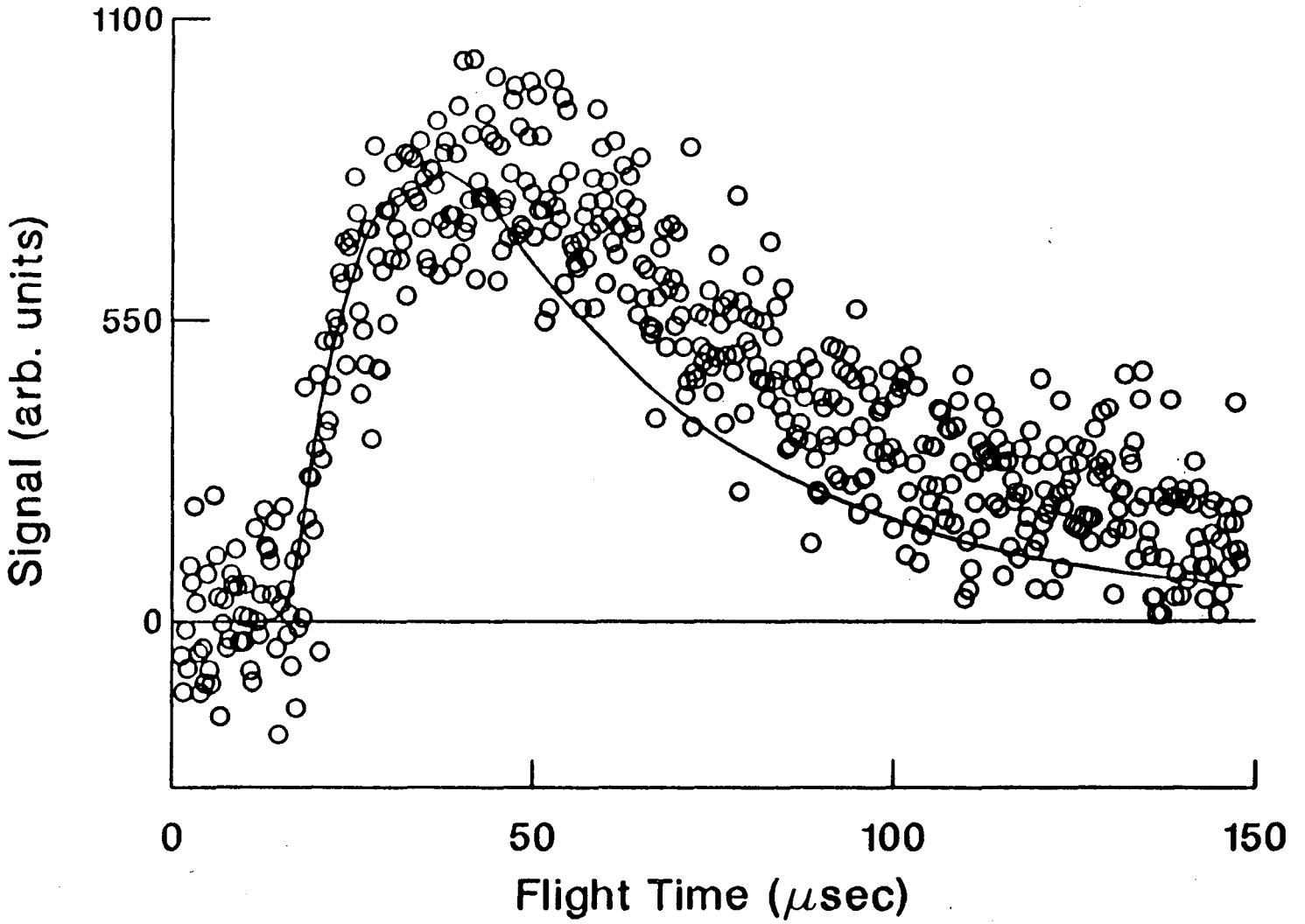


Figure 13

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