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Citation: The Journal of Chemical Physics **97**, 935 (1992); doi: 10.1063/1.463196 View online: http://dx.doi.org/10.1063/1.463196 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/97/2?ver=pdfcov Published by the AIP Publishing

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# Photodissociation of ethylene at 193 nm

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(Received 6 August 1991; accepted 3 April 1992)

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<sub>2</sub>CCH<sub>2</sub> 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<sub>2</sub> elimination channel has a translational energy distribution peaked at around 20 kcal/mol, indicating that it is a concerted process with a substantial exit barrier. It was found that the H atom elimination channel is best described as a simple bond rupture occurring after internal conversion of the electronically excited molecule to the vibrationally excited ground state ethylene. Some of the primary  $C_2H_3$  product has sufficient internal energy to spontaneously decompose to  $H+HC\equiv CH$ . At higher laser intensity a large fraction of the  $C_2H_3$ , however, absorbs another photon and fragments to  $H+H_2C=C$ : (<sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub>).

# **I. INTRODUCTION**

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

$$C_2H_4 \rightarrow HC \equiv CH + H_2, \tag{ia}$$

$$\rightarrow H_2C = C: + H_2, \qquad (ib)$$
  
$$\rightarrow H_2C = CH: + H. \qquad (ija)$$

$$\rightarrow$$
 HC $\equiv$ CH+2H. (iib)

In the molecular elimination, there appeared to be two different primary products, acetylene (ia) and vinylidene (ib).<sup>14,16</sup> 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-CH=CH· [only  $35 \pm 3$  kcal/mol (Ref. 2)] are apparently very short lived with respect to further loss of an H atom.<sup>16-19</sup> Back and Griffiths<sup>18</sup> and Hara and Tanaka,<sup>19</sup> however, "detected" stabilized  $H_2C$ —CH· by observing products that could only come from reaction of the vinyl radical, so there is no question that channel (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.<sup>15,16</sup> The vi-

nylidene channel is favored over the acetylene by a ratio of approximately 3 to 2.16 There is an isotope effect of  $\approx$ 1:1.5:2 with respect to D<sub>2</sub>:HD:H<sub>2</sub> elimination for both channels (ia) and (ib), although Okabe and McNesby noted that there seems to be a slightly smaller isotope effect in channel (ia).<sup>15,16</sup> This isotope effect can be explained by modeling the elimination as an intramolecular abstraction or as a large vibrational displacement, or by assuming vibrationally excited ethylidene is an intermediate.<sup>15</sup>

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  $({}^{3}B_{2})$ .<sup>20</sup> They found that this excited radical was a major product with a measured quantum yield of  $0.75 \pm 0.2$ . Based on appearance times, however, they concluded that neither vinylidene [ground state  $({}^{1}A_{1})$  or  ${}^{3}B_{2}$ ] nor acetylene was the direct product in molecular elimination. They hypothesized that some excited metastable precursor must give rise to the triplet vinylidene. 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.<sup>21</sup> The most recent study, by Bersohn and co-workers, concentrated on the H atom elimination channel at 193 nm;<sup>22</sup> 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

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

and Sevin present a qualitative evaluation of two proposed molecular elimination pathways: three-centered elimination to give vinylidene and dissociation via ethylidene (CH<sub>3</sub>CH:) to form acetylene.<sup>23</sup> 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  $\sim 93.4$  and 109.3 kcal/mol, respectively.<sup>24</sup> Evleth and Sevin have also done some theoretical studies on the other primary dissociation channel, atomic elimination. The ground state of the  $H_2C = CH \cdot + H$  products correlates with the ground state ethylene or singlet ethylidene but there is no direct correlation between excited singlet ethylene and the ground state radical products.23

Applying the photofragment translational spectroscopy technique to obtain translational energy distributions of both H and H<sub>2</sub> fragments will provide more detailed information on the dynamics of the ethylene photodissociation. Since the heats of formation of acetylene and vinylidene differ by  $\sim 44$  kcal/mol<sup>2</sup>, the corresponding H<sub>2</sub> formed could have substantially different velocity distributions. In principle, then, the two channels will be clearly identified in the time-of-flight (TOF) spectra. Similarly, the two atomic elimination pathways could be resolved since channel (iib) is  $\sim 35$  kcal/mol more endothermic than channel (iia).<sup>2</sup> 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 information on the nature of the intermediate states involved. This work together with that of other members of this group, in which the rovibrational states of H<sub>2</sub> produced in the 193 nm photolysis of  $C_2H_4$  were detected,<sup>25</sup> 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 in the dissociation. 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<sup>2</sup> (Refs. 26 and 27)], the excitation is exclusively via a  $\pi^* \leftarrow \pi$  transition to the  ${}^{1}B_{1u}$  (V) excited state. The  ${}^{1}B_{1u}$  excited state is believed to be twisted with the CH<sub>2</sub> 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<sub>2</sub> symmetric scissors vibrations.<sup>28</sup>

### **II. EXPERIMENT**

The apparatus used is a modified fixed source/rotating detector molecular beam apparatus. The use of this machine in high resolution photodissociation studies has been described previously.<sup>29</sup> 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 ( $\sim 3 \times 5$  mm spot at interaction region) of a Lambda Physik EMG202MSC excimer laser 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 region and the ionizer of the mass spectrometer is 39.0 cm which contributes to the high resolution of the TOF spectra.

The ethylene from Matheson (99.99% min stated purity) was used with no further purification. 1,1 D<sub>2</sub>C=CH<sub>2</sub> (99.1 at % D) and 1,2 *cis* HDC=CDH (98.2 at % D) were both obtained from MSD Isotopes.

The experimental protocol is the same as for the previous acetylene photodissociation experiments,<sup>29</sup> the only difference being that all TOF spectra were taken without the skimmer. Photolysis in the free jet rather than a skimmed beam results in somewhat lower resolution in the TOF measurements of product velocity distributions. This is a result of collisional broadening and the larger photolysis volume which is defined by the intersection of the laser and the detector acceptance angle.<sup>29(b)</sup> Less internal cooling of some of the parent molecules is another possible complication when no skimmer is used in the experiments. However, the spread in the internal energy in ethylene is negligible compared to the excess energy available. Aside from the slight differences in the maximum energy available to the products, then, the different degrees of internal



FIG. 2. H<sub>2</sub> time-of-flight spectrum from photolysis of C<sub>2</sub>H<sub>4</sub>; the data was accumulated for 2.9  $\times$  10<sup>6</sup> laser shots at an average laser power of 130 mJ/pulse. The solid line is the best fit calculated using the center-of-mass product translational energy distribution [ $P(E_T)$ ] shown in Fig. 3.

cooling in the parent ethylene due to the lack of a skimmer should not affect the experiment. Having the skimmer in place significantly decreased the S/N without resolving any additional structure in the TOF. Consequently, all the experiments were carried out without a skimmer. The data obtained was analyzed as described in the earlier photodissociation studies.<sup>29</sup> Briefly, the raw data was first corrected for pulsed valve temporal background and rf pickup. Using an iterative process, the  $P(E_T)$  is calculated from the corrected TOF with a forward convolution data analysis procedure that averages over the apparatus function.<sup>30</sup> The detector parameters required in the calculation are established from the measurements of H and D atoms produced in the photodissociation of HI and DI.

#### **III. MOLECULAR ELIMINATION**

# A. Results and analysis

The total accumulated  $H_2$  TOF spectrum after the appropriate background corrections were made is shown in Fig. 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 is shown in Fig. 3.

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/mol.<sup>2</sup> If ground state acetylene is produced, the fastest products could appear with ~108 kcal/mol translational energy.<sup>2</sup> The observed highest kinetic energy released, 88 kcal/mol, is between these. Internal thermal excitation of parent C<sub>2</sub>H<sub>4</sub> could only contribute a maximum of 2 kcal/mol, based on the analogous C<sub>2</sub>H<sub>2</sub> photodissociation experiments.<sup>29,31</sup> Since the  $P(E_T)$  threshold is much greater than 64 kcal/ mol, the fast tail must be attributed to acetylene formation.



FIG. 3.  $P(E_T)$  for  $H_2 + C_2H_2$  used to fit the  $H_2$  time-of-flight spectrum in Fig. 2.

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.

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. The comparison between the integrated spectra at m/e=3 and 4 for the two isotopomers was 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.

The relative HD and  $D_2$  ratios provide important clues on the molecular elimination mechanism. First, all four H atoms cannot be equivalent, i.e., there is not complete randomization of H and D after excitation. 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 fourcentered 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  $D_2CCH_2$ .

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 <sub>2</sub> CCH <sub>2</sub>	0.5	1
cis 1,2 HDCCDH	~0.2	2



FIG. 4. Time-of-flight 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 laser shots/average laser power for each are as follows: (a) 2.6  $\times$  10<sup>6</sup> shots at 105 mJ/pulse, (b) 3.1  $\times$  10<sup>6</sup> shots at 115 mJ/pulse, (c) 2.5  $\times$  10<sup>6</sup> shots at 80 mJ/pulse and (d) 1.2  $\times$  10<sup>6</sup> shots at 70 mJ/pulse. The areas of these spectra have been normalized to reflect the observed relative ratios given in Table I.

However, a significant amount of  $D_2$ , as much as 50% of the HD product, was observed. The fact that 1,1  $D_2CCH_2$  gives more  $D_2$  product than *cis* 1,2 HDC-CDH 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 relative yields shown in the scheme below are expected  $(i_{\rm HD}$  and  $i_{\rm DD}$  represent the isotope effects):

HD  $4\theta_a \cdot i_{\text{HD}}$ D<sub>2</sub>  $1\theta_v \cdot i_{\text{DD}}$ ,



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

$$\frac{HD}{HD} \frac{1,1}{i,1} = \frac{4\theta_a \cdot i_{HD}}{2\theta_a \cdot i_{HD} + 2\theta_v \cdot i_{HD}} \approx \frac{1}{2} \text{ (observed)} \quad \exists \theta_a = \theta_v.$$

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 threecentered 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.<sup>16</sup>

The proposed mechanism and the  $\theta_v = 3\theta_a$  relationship can also provide a value for  $i_{\rm HD}/i_{\rm DD}$ . Taking the measured ratio of HD and D<sub>2</sub> from 1,1 D<sub>2</sub>CCH<sub>2</sub>,

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

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

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

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

Using the calculated  $\theta_a/\theta_v$  and  $i_{\rm HD}/i_{\rm DD}$ , the HD/D<sub>2</sub> product ratio for the *cis* 1,2 deuterated ethylene can also be predicted,

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

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

# **B.** Discussion

The  $P(E_T)$  for H<sub>2</sub> elimination from ethylene peaks well away from zero at ~22 kcal/mol reflecting a substantial exit barrier. This is quite typical of concerted elimination dissociation. For example, the  $P(E_T)$ 's for the concerted reactions, cyclohexene  $\rightarrow$  ethylene + butadiene and cyclohexadiene  $\rightarrow$  benzene + H<sub>2</sub> both peak at ~20 to 25 kcal/mol.<sup>30,32</sup> 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 repulsion between the H<sub>2</sub> and vinylidene products seen in the  $P(E_T)$  indicates that the vinylidene does not behave like a chemically reactive singlet methylene. This is, in fact, reflected in the heat of formation of vinylidene. The C-H bond in ethylene is known to be  $\sim 108$  kcal/mol. However, breaking the C-H bond in the vinyl radical to form vinylidene, even though there is no change in the bond order, only requires  $\sim 80$  kcal/mol. This is  $\sim 28$  kcal/mol less than what one expects from the simple bond additivity concept.<sup>33</sup> The additional 28 kcal/mol stability in vinylidene is likely to come from the energy released by the pairing of two electrons in vinylidene.

The H<sub>2</sub>  $P(E_T)$  from C<sub>2</sub>H<sub>4</sub> 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  $({}^{3}B_{2} cis)$  and vinylidene  $({}^{3}B_{2})$ can form but would only appear at  $E_T < 29$  and < 16 kcal/ mol, respectively.<sup>2</sup> Since vibrational and rotational excitation of both fragments is expected because of the large changes in geometry required to form the products and a fairly significant amount of excitation has been observed in the H<sub>2</sub> product (an average of  $\sim 12$  kcal/mol),<sup>25</sup> the peak of the distribution for these excited states would be expected at even lower translational energies, where the  $P(E_T)$  drops off. Thus, if any, only a small percentage of the products could be formed electronically excited. This observation that triplet vinylidene is not a major primary product is contrary to what Fahr and Laufer surmise from their flash photolysis studies of the photodissociation at much shorter wavelengths.<sup>20</sup>

Because all acetylene + H<sub>2</sub> product appears at a translational energy less than 88 kcal/mol, at least 20 kcal/mol internal energy must be partitioned between the acetylene and H<sub>2</sub>. At the translational energy at which vinylidene can just form ( $E_{Int} = 0 \text{ kcal/mol}$ ), the HC=CH+H<sub>2</sub> products can have  $E_{Int} = 44 \text{ kcal/mol}$ . The peak of the translational energy distribution corresponds to  $E_{Int} = 43 \text{ kcal/}$ mol for the H<sub>2</sub>C=C:+H<sub>2</sub> channel and  $E_{Int} = 87 \text{ kcal/mol}$ for the HC=CH+H<sub>2</sub> 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<sub>2</sub> is formed in rovibrational



FIG. 5. H atom TOF spectra from  $C_2H_4$  photolysis. Solid line is the fit using the mechanism/assumptions discussed in the text. The long 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 short dashed 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  $1.6 \times 10^6$ ,  $1.4 \times 10^6$ ,  $3.6 \times 10^4$ , and  $1.6 \times 10^4$  laser shots at an average laser power of 40, 90, 140, and 180 mJ/pulse, respectively.

states as high as v=3/j=9, most of the H<sub>2</sub> is produced in v=0 and the average internal excitation of H<sub>2</sub> is only around 12 kcal/mol.<sup>25</sup> A large fraction of the internal energy, then, must be going into vibrations and rotations of the H<sub>2</sub>C=C: and HC=CH.

# IV. ATOMIC ELIMINATION

# A. Results and analysis

The shape of the H atom TOF spectra strongly depends on laser power. Figure 5 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





FIG. 6. 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  $H+HC\equiv CH$  (3). Otherwise, the  $C_2H_3$  can absorb a photon (2) and decompose to  $H+HC\equiv CH/H_2C=C$ :. As the laser power increases, the fraction of molecules undergoing spontaneous decomposition (3) decreases while the fraction that absorb a photon (2) increases.

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  $108 \text{ kcal/mol.}^2$ 

#### **B.** Discussion

In interpreting 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. This simple model, however, is unable to fit the data. TOF spectra obtained in the high power scans have significantly less slow product and more fast.

Dissociation of ethylene dominated by two photon absorption is one possible explanation for the decrease in slow H atoms and increase in fast H atoms at high laser powers. 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.

A better explanation for the change in shape of the TOF spectra at higher laser powers invokes a fast fragmentation of excited  $C_2H_4$ , followed by either spontaneous decomposition of internally excited  $C_2H_3$  or secondary photodissociation of the  $C_2H_3$ . This scenario is illustrated in Fig. 6. At low laser powers, when the ethylene absorbs a photon at 193 nm, it will be excited by 148 kcal/mol. Since breaking a C-H bond requires ~ 108 kcal/mol, the resulting vinyl radical could have as much as 40 kcal/mol excess energy, which is greater than the H-CH=CH · bond en-

FIG. 7. Primary  $P(E_T)$  for  $C_2H_4 \rightarrow H + C_2H_3$  used to fit all the H atom time-of-flight spectra in Fig. 5.

ergy (35 kcal/mol). Primary  $C_2H_3$  products with an internal energy above 35 kcal/mol, i.e, those with  $E_T \le 5$  kcal/ mol, can further dissociate, with no additional photon required, producing H+HC=CH with 0 to 5 kcal/mol in translation. The net result, then, will be two slow ( $E_T \le 5$ kcal/mol) H atoms from the same ethylene. At higher laser powers, there is a greater chance for the highly excited vinyl radicals formed to absorb a photon before spontaneous decomposition occurs. The apparent difference in the low and high power TOF spectra 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  $C_2H_3$ .

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,

$$C_2H_4 \rightarrow H + C_2H_3, \tag{1}$$

$$C_2H_3(E_T > 5 \text{ kcal/mol}) \xrightarrow{n\nu} H + C_2H_2, \qquad (2a)$$

$$C_2H_3(E_T \leq 5 \text{ kcal/mol}) \xrightarrow{n} H + C_2H_2,$$
 (2b)

$$C_2H_3(E_T \leq 5 \text{ kcal/mol}) \rightarrow H + HC \equiv CH.$$
 (3)

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 Fig. 5. Figures 7–9 show the primary, secondary, and spontaneous  $P(E_T)$ 's used.

The primary  $P(E_T)$  obtained from the fitting process, provides some important information on the dynamics of the primary process. As Fig. 7 shows, the  $P(E_T)$  peaks very close to 0 kcal/mol suggesting that the H atom elimination is a simple bond rupture with very little exit bar-



FIG. 8. 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 time-of-flight spectra in Fig. 5.

rier. 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<sup>23</sup> and Bersohn's experiments.<sup>22</sup> The other point apparent from the  $P(E_T)$  is that most of the vinyl radical and hydrogen atom product form with  $E_{\text{Int}} = 40\text{--}37$  kcal/mol. Since there is not enough energy to excite the lowest electronic state of C<sub>2</sub>H<sub>3</sub> [ $\approx$ 53-57 kcal/mol (Ref. 2)], the majority of the vinyl radicals, then, are produced in high vibrational levels of the ground electronic state.

Despite the limitations of fitting secondary dissociation, the H atom TOF spectra and secondary  $P(E_T)$  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 transla-



FIG. 9. Spontaneous decomposition  $P(E_T)$  used to fit the H atom timeof-flight spectra in Fig. 5. Although from the bond energies used in the paper no H+HC=CH product with  $E_T > 5$  kcal/mol would be expected, to account for the uncertainty in this value, product with  $E_T$  up to 8 kcal/mol was considered.

tional energy release. Assuming  $C_2H_3$  with  $E_{Int} = 35$  kcal/ mol absorbs another photon and dissociates to HC=CH, the ground state products could have a maximum translational energy of 148 kcal/mol. The observed maximum, however, is closer to 100 kcal/mol. If vinylidene were to form rather than acetylene, the expected maximum translational energy would be approximately 104 kcal/mol, closer to that observed. Most ( $\sim 95\%$ ) of the product, however, does not appear near this threshold; it is much slower, with  $E_T \sim 15-30$  kcal/mol. 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  $H + {}^{3}H_{2}C = C$ : is  $\approx 56$  kcal/mol and for  $H+{}^{3}HC \equiv CH$  is  $\approx 69$  kcal/mol.<sup>2</sup> It is possible that these excited states are forming in the secondary photodissociation.

# V. 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 (±0.15); no appreciable correlation between laser power and branching ratio was observed.

# **VI. CONCLUSIONS**

For the most part, the H and  $H_2$  TOF studies done at 193 nm agree with the previous work done with other excitation schemes. This suggests that the  $\pi\pi^*$  state does not have a critical role in the dissociation, implying that fragmentation occurs after the electronically excited ethylene internally converts to the upper vibrational levels of the ground electronic state. This conclusion could also be inferred from the primary  $P(E_T)$  for the atomic elimination channel which peaks at low translational energy.

The molecular elimination data obtained do give additional details on this dissociation process. Because vibrational/rotational excitation of the H<sub>2</sub> and HC=CH/H<sub>2</sub>C=C: products 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<sub>2</sub>,<sup>25</sup> the  $P(E_T)$  shows that very little of the acetylene and vinylidene can be formed in the lowest excited electronic states  $(T_1)$ , contrary to what Fahr and Laufer see at shorter wavelengths.<sup>20</sup>

The studies of the atomic elimination channel were plagued by secondary dissociation even at as low laser intensity as 200 mJ/cm<sup>2</sup>. Although this meant that the C–H bond energy could not be accurately determined, important features of the secondary photodissociation were revealed. 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 maximum energy release for the secondary decomposition is closer to that expected for  $H+H_2C=C$ : suggesting that little ground state  $H+HC\equiv CH$  is produced. Based on the position of the peak in the secondary  $P(E_T)$ , the production of electronically excited triplet  $HC\equiv CH$  and/or  $H_2C=C$ : could be an important pathway and perhaps explains Fahr and Laufer's detection of  $H_2C=C$ :  $({}^{3}B_2)$ .

#### ACKNOWLEDGMENTS

This work was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-67SF00098.

<sup>1</sup>See review, G. J. Collin, Adv. Photochem. 14, 136 (1988).

<sup>2</sup>The bond energies and heats of formation for molecules involved in the photodissociation of ethylene are not well known. We are using the following values in this paper:  $H_{f}^{0}(C_{2}H_{2}) = 54.68 \text{ kcal/mol};$   $\Delta H_{f}^{0}(C_{2}H_{4}) = 14.58 \text{ kcal/mol};$   $\Delta H_{f}^{0}(C_{2}H_{4}) = 14.58 \text{ kcal/mol};$  $\Delta H_{f}^{0}(H) = 51.6336 \text{ kcal/mol}$  (see Ref. 3 and references therein).  $D_{0}(H-CHCH_{2}) = 108 \pm 3 \text{ kcal/mol}$  (see Refs. 3-5);  $\Delta H_{\text{Isom}}(\text{acetylene} \rightarrow \text{vinyliden}) = 44 \pm 3 \text{ kcal/mol}$  (see Refs. 3, 6-8);  $\Delta H[C_{2}H_{3}(^{2}A'' \leftarrow ^{2}A')] = 53-57 \text{ kcal/mol}$  (see Refs. 9 and 10);  $H_{2}CC(^{3}B_{2} \leftarrow ^{-1}A_{1}) = 47.6 \pm 0.5 \text{ kcal/mol}$  (see Ref. 8);  $H_{2}CC(^{3}A_{2} \leftarrow ^{-1}A_{1}) = 63.4 \pm 0.5 \text{ kcal/mol}$  (see Ref. 8);  $HCCH[^{3}B_{2}(cis) \leftarrow ^{-1}\Sigma_{g}^{+}] = 79.1 \text{ kcal/mol}$ ;  $HCCH[^{3}B_{u}(trans) \leftarrow ^{-1}\Sigma_{g}^{+}] = 101.7 \text{ kcal/mol}$ ;  $HCCH[^{3}A_{2}(cis) \leftarrow ^{-1}\Sigma_{g}^{+}] = 103.8 \text{ kcal/mol}$  (see Ref. 11);  $HCCH[^{1}A_{u}(trans) \leftarrow ^{-1}\Sigma_{g}^{+}] = 122.6 \text{ kcal/mol}$  (see Ref. 12);  $HCCH[^{1}A_{2}(cis) \leftarrow ^{-1}\Sigma_{g}^{+}] = 127.8 \text{ kcal/mol}$  (see Ref. 13).

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