



# Translational energy distributions and angular difference Doppler profiles of the excited hydrogen atom produced in eC2H4 collisions: Dissociation dynamics of ethylene

Nobuaki Yonekura, Keiji Nakashima, and Teiichiro Ogawa

Citation: The Journal of Chemical Physics 97, 6276 (1992); doi: 10.1063/1.463689 View online: http://dx.doi.org/10.1063/1.463689 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/97/9?ver=pdfcov Published by the AIP Publishing

# Articles you may be interested in

Electronimpact dissociation of HCI: Translational energy and angular distributions of excited hydrogen atoms J. Chem. Phys. 101, 3696 (1994); 10.1063/1.467554

Kinetic energy distribution of excited H atoms produced through dissociative photoionization excitation of H2 J. Chem. Phys. 92, 1713 (1990); 10.1063/1.458053

The relative kinetic energy distribution of the hydrogen atoms formed by the dissociation of the electronically excited H2 molecule J. Chem. Phys. 89, 1986 (1988); 10.1063/1.455096

Translational energy distribution and asymmetry parameter of the excited hydrogen atom produced in e C2H2 collisions: Dissociation dynamics of acetylene J. Chem. Phys. 88, 4263 (1988); 10.1063/1.453784

Translational energy distributions of the excited nitrogen atom produced by electronimpact dissociative excitation of nitrogen molecules

J. Chem. Phys. 82, 1920 (1985); 10.1063/1.448947



# Translational energy distributions and angular difference Doppler profiles of the excited hydrogen atom produced in e-C<sub>2</sub>H<sub>4</sub> collisions: Dissociation dynamics of ethylene

Nobuaki Yonekura, Keiji Nakashima, and Teiichiro Ogawa Department of Molecular Science and Technology, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

(Received 21 May 1992; accepted 17 July 1992)

Formation of an excited hydrogen atom (H\*) through electron-impact dissociation of ethylene has been investigated by measuring Doppler profiles of the Balmer- $\beta$  line and their angular dependence at an optical resolution of 0.007 nm. The Doppler profiles show a clear anisotropy. The translational energy distribution (TED) and the angular difference Doppler profile were obtained. There are four major dissociation processes for the formation of  $H^*(n)$ =4). Component 1 has a peak of TED at 1 eV, is produced in a perpendicular distribution, and should be produced by predissociation through the Rydberg states converging to the  $(1b_{1\mu})^{-1}$  state. Component 2 has a peak of TED at 1.8 eV, is produced in a parallel distribution, and should be produced through the Rydberg states converging to the  $(2a_{\sigma})^{-1}$  state. Component 3 has a peak of TED at 2-6 eV and is produced in a parallel distribution. Component 4 has a peak of TED at 5-10 eV. Molecular orientation at the time of excitation was estimated; the molecular plane is perpendicular to the electron beam for component 1, and the C—C bond is perpendicular and the molecular plane is parallel to the electron beam for components 2 and 3. The asymmetry parameters of components 2 and 3 were <0.2; these values were much smaller than anticipated due largely to molecular rotation and deformation at the time of dissociation.

## I. INTRODUCTION

The electron-impact induced molecular dissociation has been widely studied not only for understanding its primary process but also for elucidating chemical events in plasma, atmospheric, and interstellar phenomena. The dynamic aspect of the molecular dissociation can be clarified through analyses of translational and angular distributions of nascent fragments. Detectable fragments, however, have been mostly long-lived ionic and metastable fragments, because the conventional time-of-flight technique is applicable only to them. Meanwhile, the Doppler profile of an emission line of a short-lived fragment exposes the translational and angular distributions of the fragment and thus can provide valuable information on the kinetics of the dissociation process.<sup>1</sup> The translational energy distribution (TED) and the angular dependence of the Doppler profile have provided useful information on major dissociation channels, disposal of the initial excitation energy, and symmetry of the dissociative states.<sup>2-4</sup> A series of studies on dissociation dynamics has been done based on Doppler profile measurements of the excited hydrogen atom (H\*) produced by electron impact;  $H_2$ ,<sup>3,5,6</sup>  $H_2$ O,<sup>7,8</sup>  $H_2$ S,<sup>9</sup> CH<sub>4</sub>,<sup>10,11</sup> C<sub>2</sub>H<sub>2</sub>,<sup>12</sup> and aliphatic hydrocarbons.<sup>13</sup>

Little has been investigated on the dissociation of  $C_2H_4$ through highly excited states and, in particular, through superexcited states. de Heer *et al.*<sup>14-16</sup> measured the excitation function and the emission cross section of  $H^*(n=4)$ produced in *e*-C<sub>2</sub>H<sub>4</sub> collisions and concluded that  $H^*(n$ =4) was produced through superexcited states. Donohue *et al.*<sup>17</sup> measured the excitation function and the threshold energy of  $H^*(n=4,5)$  produced in *e*-C<sub>2</sub>H<sub>4</sub> collisions and concluded that there are three major dissociation processes of  $C_2H_4$  for the formation of H<sup>\*</sup>. Although these measurements are indispensable for understanding the complicated dissociation processes of  $C_2H_4$ , further information on the TED and the angular distribution would be necessary for clarification of the dissociation dynamics.

Dissociation to H\* has been related to dissociation to the high Rydberg (HR) hydrogen atom and to the proton; this is known as the core-ion model.<sup>18</sup> Schiavone *et al.*<sup>18</sup> measured time-of-flight spectra, excitation functions, appearance potentials, and TEDs of H\*(HR) produced in  $e-C_2H_4$  collisions and found seven major dissociation processes of  $C_2H_4$ . Formation of H<sup>+</sup> was investigated with a time-of-flight technique by Kusch *et al.*<sup>19</sup> Ibuki *et al.*<sup>20</sup> have recently reported dissociative photoionization of  $C_2H_4$ . These studies permit useful comparisons on the basis of the core-ion model.

The steric effect is one of the oldest problems in chemical reactivity, and a specific molecular orientation at the time of the collision may favor a certain reaction.<sup>21</sup> However, little has been known about the orientational effect in electron-molecule collisions except for recent studies on water<sup>8</sup> and acetylene.<sup>12</sup>

We have measured the TED and its angular dependence of  $H^*(n=4)$  produced in  $e \cdot C_2 H_4$  collisions and have tried to clarify the dissociation processes through higher excited states of  $C_2 H_4$ . The steric effect of dissociation has been clarified through analyses of angular dependence.

# **II. EXPERIMENT**

The apparatus used in this work was described in detail in the previous publications.<sup>11,22</sup> In brief, the collision chamber has a rotatable electron gun and a gas cell. The



FIG. 1. Doppler profiles of the Balmer- $\beta$  line produced in  $e-C_2H_4$  collisions (left) and TED of H\*(n=4) (right) at various incident electron energies. Two TEDs are shown simultaneously; one of them was obtained from the left side of the Doppler profile and the other from the right side. The ordinates are normalized at the peak.

electron beam current was 20–80  $\mu$ A and its energy resolution was  $\pm 1.5$  eV. The base pressure was  $1 \times 10^{-6}$  Torr and the operating pressure was  $(1-4) \times 10^{-5}$  Torr.

The Balmer- $\beta$  radiation was measured using a Fabry-Pérot interferometer with a typical optical resolution of 0.007 nm. The Balmer line was separated using a DIF-C filter ( $\Delta \lambda_{1/2} = 1.3$  nm). The angular dependence of the Doppler profiles of the Balmer- $\beta$  line was measured at 90° and 125° with respect to the electron beam. Polarization was measured at 90° using a JASCO CT-50 monochromator.

Ethylene of stated purity of 99% was purchased from Sumitomo-Seika and was used without further purification.

# **III. RESULTS**

# A. Translational energy distribution

The emission spectrum of ethylene excited by electrons consists mainly of the Balmer lines of H\* and bands of the excited CH and C<sub>2</sub> radicals.<sup>23</sup> We have measured the Doppler profiles of the Balmer- $\beta$  line at a higher optical resolution at several incident electron energies, as shown in Fig. 1. The shape and width of the Doppler profiles varied as the electron energy increased.



FIG. 2. Differences of the translational energy distributions. The open dots are translational energy distributions and the black dots are their difference. The ordinates are proportional to the absolute scale and indicate the increase in the total emission cross sections at a larger electron energy. (a) Difference between 27 and 35 eV. (b) Difference between 27 and 40 eV. (c) Difference between 40 and 50 eV.

The TED of H\* can be obtained by differentiating the Doppler profiles obtained at 125° with respect to the electron beam; any effect due to anisotropy can be ignored by measuring them at the magic angle (125°). The differentiation was carried out by smoothing the profile curve by a least-squares procedure using a seven-point cubic convolute.<sup>24</sup> The results are also shown in Fig. 1; the ordinate is an arbitrary scale normalized to the peak. The TED of  $H^*(n=4)$  varies according to the electron energy, indicating the existence of more than one dissociation process for the formation of  $H^*(n=4)$ . Donohue *et al.*<sup>17</sup> found three major thresholds for the formation of  $H^*(n=4)$  at 19.2  $\pm 1.0$ , 23.9  $\pm 1.0$ , and 39  $\pm 3$  eV and indicated that there are at least three major dissociation process of  $C_2H_4$ . The TED at an electron energy below 23.9 eV would be very useful for an assignment but was unobservable due to a weak signal.

The TED at 27 eV has a peak at  $\sim 1$  eV and extends up to 7 eV. On increasing the incident electron energy, the peak of the TED shifts to 2 eV at 50 eV and then to 3 eV at 100 eV. There seems to be a weak shoulder at 6–10 eV at 100 eV.

If we subtract the TED at 35 eV from that at 27 eV, a component with a peak at  $\sim 1.8$  eV appears, as shown in Fig. 2 (a); the difference distribution is rather noisy and small peaks such as at 1.2 and 2.4 eV are artifacts. Figure 2(a) indicates that there are two major components in the TED at 35 eV; one has a peak at 1 eV and the other at 1.8 eV. Both of them appear at 27 eV, too. The former is relatively more intense at 27 eV. The latter, however, becomes more intense at higher electron energies and most



FIG. 3. The degree of polarization of the Balmer- $\beta$  line at several electron energies.

intense at 50 eV. Accordingly we can expect that the former has a lower threshold energy than the latter. The difference in the TED at 40 and 27 eV as shown in Fig. 2(b) confirms this assignment.

The difference in the TED at 50 and 40 eV was also calculated as shown in Fig. 2(c) and indicated the existence of a component with a broad peak at 2–6 eV. This component becomes most intense at 100 eV.

By comparing the TED at 40 and 50 eV and at 100 and 300 eV, we can indicate a shoulder in the 5–12 eV region of TED. The peak of this component is somewhere around 6-10 eV.

Thus, we can conclude that there are four major components in the TED and their peaks are  $\sim 1$ , 1.8, 2–6, and 6–10 eV.

#### **B.** Angular dependence

The polarization of the Balmer- $\beta$  line was measured at 90° with respect to the electron beam for electron energies of 27–100 eV, as shown in Fig. 3. Error bars in the figure were drawn based on statistical uncertainty. The degrees of polarization at all electron energies are approximately zero, and we can conclude that the Balmer- $\beta$  line is not polarized.

The spectral line of a moving atom shows the Doppler shift,  $\Delta \lambda = \lambda - \lambda_0$ . The angular difference Doppler profile,  $\Delta F$ , is the difference in two Doppler profiles taken at two different angles with respect to the electron beam. When the two angles are taken as 90° and 125° as in the present case, Eq. (9) of Ref. 4 becomes

$$\Delta F(\Delta \lambda, v) = F(90^{\circ}) - F(125^{\circ})$$
  
= - (3c/32\pi \lambda\_0 v) (J\_{\parallel} + J\_{\pi})  
\times [1 - J\_p(\Delta \lambda c/\lambda\_0 v)^2]\beta P\_2(\Delta \lambda c/\lambda\_0 v), (1)

where  $\beta$  is the asymmetry parameter,  $J_p$  is the degree of polarization on the molecular axis  $[J_p = (J_{\parallel} - J_{\perp})/(J_{\parallel} + J_{\perp})]$ , v is the velocity of H<sup>\*</sup>, and  $P_2$  is the Legendre polynomial of the second order.  $\beta$  and  $J_p$  are two basic parameters;  $\beta$  indicates the angular distribution of the excited atom and  $J_p$  indicates the distribution in its magnetic sublevels. The difference profile can clearly disclose aniso-



FIG. 4. The angular difference Doppler profiles of  $H^*(n=4)$  at electron energies of 27 and 40 eV. The dotted line is the smoothed difference profile and is used for an estimation of  $\beta$ .

tropic parts in the Doppler profile, because isotropic parts are canceled by taking the difference.

Normalization of the emission intensity was carried out using the following equation<sup>25</sup>:

$$I(\theta) = I(90^{\circ})(1 - P\cos^2\theta), \qquad (2)$$

where P is the degree of polarization measured on the laboratory axis and was zero in the present case. Thus, we can equate the emission intensity at 90° with that at 125°.

The angular difference Doppler profiles<sup>4</sup> were calculated from the Doppler profiles obtained at 90° and 125°, and the results at 27 and 40 eV are shown in Fig. 4. They are positive in the center and negative in the wing. This shape of the difference profile indicates that  $\beta$  is positive<sup>4</sup> and that the dissociation is parallel with respect to the electron beam.<sup>1</sup> The central peak is broader at 40 eV than at 27 eV, indicating that both the slower component at 27 eV and the faster component at 40 eV have positive values for  $\beta$ . The relation<sup>11</sup> of  $\beta$ , P, and  $J_p$  indicates that  $J_p$  should be zero, because P=0 and  $\beta > 0$ . Thus,  $H^*(n=4)$  is produced in a parallel distribution with respect to the electron beam and the magnetic sublevels are statistically populated.

In the present case,  $\beta$  is the only parameter which determines the anisotropic distribution, because  $J_p=0$ . Then  $\beta$  can be determined as a function of the translational energy with a least-squares fitting procedure.<sup>8</sup> Because the observed difference profiles (Fig. 4) are very noisy, we have smoothed them using a fast Fourier transform routine<sup>26</sup> in order to remove high frequency noise. The dotted lines in Fig. 4 were thus obtained. We have determined  $\beta$ using a least-squares fitting to these smoothed difference



FIG. 5. The asymmetry parameter,  $\beta$ , and its dependence on the translational energy.

profiles, as shown in Fig. 5. We can conclude that  $\beta$  is positive and tends to be larger at larger translational energies.

# **IV. DISCUSSION**

#### A. Assignments of the dissociation process

The ground state electronic configuration of ethylene is

$$(KK')^4 (2a_g)^2 (1b_{1u})^2 (1b_{2u})^2 (3a_g)^2 (1b_{3g})^2 (1b_{3u})^2$$

in the Mulliken convention,<sup>27</sup> where the molecule lies in the yz plane with the C=C bond along the z-axis. The vertical ionization energies of the six outer orbitals (in reverse order) were determined by photoelectron spectroscopy as  $10.68 \pm 0.02$ ,  $12.8 \pm 0.1$ ,  $14.8 \pm 0.1$ ,  $16.0 \pm 0.1$ ,  $19.1 \pm 0.1$ , and  $23.6 \pm 0.1$  eV.<sup>28</sup>

There are four major components in the TED and three major components<sup>17</sup> in the excitation function. The core-ion model<sup>18</sup> has been successful in qualitative interpretations of dissociation dynamics in various molecules and is used for assignments of these components.

The lowest threshold energies of  $H^*(n=4)$ ,  $H^*(HR)$ , and  $H^+$  produced in  $e - C_2H_4$  collisions were  $19.2 \pm 1.0$ eV,<sup>17</sup>  $18.7 \pm 0.5 eV$ ,<sup>18</sup> and  $18.66 \pm 0.5 eV$ ,<sup>29</sup> respectively. Because these threshold energies are close to the fifth ionization potential of ethylene at  $19.1 \pm 0.1 eV$ , we can conclude on the basis of the core-ion model that dissociation for the formation of  $H^+$ ,  $H^*(HR)$ , and  $H^*(n=4)$  should proceed through the  $(1b_{1u})^{-1}$  ionized state or the Rydberg states converging to this ionized state. The  $(1b_{1u})$  molecular orbital is C–H bonding,<sup>27,30</sup> and ejection of an electron from this orbital weakens the C–H bond. The fifth photoelectron band has an irregular structure,<sup>31</sup> and the  $(1b_{1u})^{-1}$  ionized state is probably long-lived. Then the Rydberg states converging to this ionized state are also longlived, and anisotropy in the formation of this component would be small. We denote this as component 1 hereafter. Component 1 of  $H^*(n=4)$  should correspond to the TED with a peak at 1 eV, because this component has the lowest threshold energy. This component corresponds well with component 1 of  $H^*(HR)$  because the latter has a TED with a peak at 0.6 eV.<sup>18</sup> The TED of component 1 of  $H^*(HR)$  was broad and extended to 5.8 eV.<sup>18</sup> This agrees with the TED of  $H^*(n=4)$  measured at 27 eV, though another component with a peak of translational energy at 1.8 eV, which extends to 10 eV as shown in Fig. 2, overlaps on component 1 at 27 eV.

The dissociation limit of component 1 should be

$$C_2H_4 + e \rightarrow C_2H_4^{**} \rightarrow C_2H_3(X) + H^*(n=4)$$
 17.5 eV.  
(3)

The thermochemical energy of the dissociation limit was calculated from the bond dissociation energy.<sup>32</sup> The difference between the threshold energy  $(19.2\pm1.0)$  and the dissociation limit (17.5 eV), 1.7 eV, should be converted to the translational energy of fragments [mostly of H\*(n = 4)] and the vibrational and rotational energy of C<sub>2</sub>H<sub>3</sub>. However, the excess energy may be smaller than 1.7 eV, because the threshold energy of H\*(n = 4) should be smaller than those of H\*(HR) and H<sup>+</sup> (~18.7 eV) and the fifth ionization potential (19.1 eV). Because the TED peak of component 1 of H\*(n=4) is 1 eV, most of the excess energy would be converted to the translational energy.

The second threshold of  $H^*(n=4)$  was reported to be  $23.9 \pm 1.0 \text{ eV}$ ;<sup>17</sup> we denote this as component 2 hereafter. There were three thresholds of  $H^*(HR)$  in this region at  $21.6 \pm 0.5$ ,  $23.6 \pm 0.5$ , and  $26.0 \pm 0.5 \text{ eV}$ .<sup>18</sup> Those at 21.6 and 26.0 seem to be weak and may not be found for  $H^*(n=4)$ ; component 2 of  $H^*(n=4)$  should correspond to  $H^*(HR)$  with a threshold at 23.6 eV. Judging from the TED in Fig. 1 and from the TED differences in Fig. 2, we can conclude that the TED of component 2 should be the one with a peak at ~1.8 eV. The TED of the corresponding component of  $H^*(HR)$  lay in the region of 0.3-1.9 eV (Ref. 18) and agreed approximately with that of  $H^*(n=4)$ .

The threshold energy of component 2 is close to the sixth ionization potential at  $23.6\pm0.1$  eV. Then the dissociation for the formation of component 2 of  $H^*(n=4)$  proceeds through Rydberg states converging to the  $(2a_g)^{-1}$  ionized state. The dissociation limit should be either of the following processes:

$$C_2H_4 + e \rightarrow C_2H_4^{**} \rightarrow H^*(n=4) + C_2H_2(X)$$
  
+H(n=1) 19.1 eV, (4)

$$\rightarrow \mathbf{H}^*(n=4) + \mathbf{C}_2 \mathbf{H}(X)$$

$$+H_2(X)$$
 19.3 eV, (5)

$$\rightarrow$$
 H\*(n=4)+CH<sub>2</sub>=C+H(n=1). (6)

There is an intense component of  $H^*(n=4)$ , which has a TED peak at ~2-6 eV and becomes a major component at 100 eV and above, as shown in Figs. 1 and 2(c). A similar component can be found in the case of  $H^*(HR)$ ,

is article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to II

TABLE I. The translational energy distributions (TED) and dissociation processes of  $H^*(n=4)$  from  $C_2H_4$  by electron impact.

Component	Threshold energy <sup>a</sup> (eV)	TED peak (eV)	Dissociation process			
			Dissociation limit (eV)	Fragmentation pattern		
1	$19.2 \pm 1.0$	1	17.5	$H^*(n=4) + C_2H_3(X)$		
2	$23.9 \pm 1.0$	1.8	19.1	$H^*(n=4) + H(n=1) + C_2H_2(X)$		
			19.3	$H^*(n=4) + H_2(X) + C_2H$		
				$H^*(n=4) + CH_2 = C + H(n=1)$		
3	(28–29)	26		-		
4	$39 \pm 3$	6-10				

<sup>a</sup>Taken from Ref. 11. The value in parentheses was estimated.

which has a peak of the translational energy distribution at  $\sim 3.8 \text{ eV}$  and a threshold at  $29.2 \pm 1.0 \text{ eV}$ . However, no threshold for  $H^*(n=4)$  has been reported at  $\sim 29 \text{ eV}$ . There is a clear threshold at around this energy for the formation of  $H^+$  by photodissociation.<sup>20</sup> An increase in the value of  $\beta$  as shown in Fig. 5 also indicates the existence of a dissociation process between 27 and 40 eV. Thus, we can conclude that there should be a threshold at 28–29 eV, and we denote this as component 3 hereafter. Component 3 should include an optically-allowed process, because  $H^+$  is produced by photodissociation in a corresponding process. A careful remeasurement of the excitation function may be necessary for its confirmation.

Component 3 is a major component at higher electron energies, and this is consistent with the behavior of process 5 of H(HR).<sup>18</sup> The Fano plot indicated that the major process for the formation of H\* from ethylene should be optically forbidden.<sup>14-16</sup> In all cases so far investigated except water, the major component at higher electron energy is produced through an optically-forbidden process and intermediate states are doubly excited states.<sup>2-13</sup> Thus, we should expect the existence of another optically-forbidden process in component 3. In other words, component 3 consists of two processes; one is optically allowed and has a threshold at  $\sim 29$  eV, and the other is optically forbidden and is responsible for most of the intensity at higher incident electron energies. Both have a peak of TED at 2-6 eV. The threshold energy of the latter is unknown but should be  $\sim 30 \text{ eV}$ .

The TED at higher electron energies has a shoulder at 6-10 eV. We denote this as component 4. Its threshold should be the one at  $39 \pm 3$  eV. A corresponding component of  $H^*(HR)$  has a threshold at  $\sim 40 \pm 5$  eV and a peak of TED at ~6 eV.<sup>18</sup> Another component of H\*(HR) has a threshold at  $\sim 52 \pm 3$  eV and a peak of TED at  $\sim 8$  eV. Our component 4 may consist of two dissociation processes corresponding to the above two components of  $H^*(HR)$ . There are many doubly excited states at above 30 eV. Many stable dications of C2H4 were observed in mass spectroscopy.<sup>33,34</sup> Appell et al.<sup>35</sup> found the double ionization potentials of ethylene at 31.8, 35.0, and 38.5 eV. The Rydberg states converging to some of the double ionized state may be intermediate states for the formation of component 4. Since this component has a large translational energy, its intermediate states should be highly repulsive.

The results of these assignments are summarized in Table I.

#### B. Anisotropy and orientation in dissociation

The asymmetry parameter,  $\beta$ , represents the angular distribution of H<sup>\*</sup>. If the dissociation is rapid, the angular distribution of the excited fragment depends on the orientation of the molecule at the time of excitation and, thus, on the symmetry of the transition to the dissociative excited state.<sup>1</sup>

The angular difference Doppler profiles (Fig. 4) indicate that major dissociation processes proceed in a direction parallel to the electron beam. Dependence of  $\beta$  on the translational energy (Fig. 5) has a positive slope to the right both at 27 and 40 eV. Because  $\beta$  should in principle be constant for a given transition, the slope indicates that there is more than one anisotropic dissociation process.  $\beta$ may be dependent on the dissociation lifetime and thus on the translational energy because the lifetime can vary with it; this dependence is, however, negligibly small for discussions described below. It should be kept in mind that an isotropic process does not contribute to  $\beta$ , because such a process has been canceled on the difference profile.

 $\beta$  at 27 eV indicates that the major anisotropic component should have the TED extended to 7 eV and has a positive value of  $\beta$ . This component should be component 2, because it has a threshold at 23.9 eV and its TED extends up to 8 eV [Fig. 2(a)].  $\beta$  decreases toward 0 at lower translational energy and this finding indicates that component 1 should have a negative value of  $\beta$ , although the absolute value would be small.

 $\beta$  at 40 eV is larger than that at 27 eV.  $\beta$  of a component should decrease at higher electron energy, because the direction of the momentum transfer vector becomes unclear at higher electron energies and a directional property is always blurred.<sup>36</sup> Thus, increases in  $\beta$  indicate that another component with a higher positive value of  $\beta$  contributes to the dissociation process, and its positive slope indicates that the other component has a large translational energy. Then this component should be component 3. Thus, we can conclude that  $\beta$  is negative for component 1 and positive for components 2 and 3.

There are three plausible orientations of the ethylene molecule at the time of excitation, as shown in Fig. 6. The



FIG. 6. Three possible orientations of the ethylene molecule with respect to the direction of the electron beam near threshold.

large arrow indicates the direction of the transition moment, which is parallel to the electron beam at threshold. At the electron energies used in the present study, the direction of the transition moment is expected to be approximately parallel to the direction of the electron beam. If the dissociation is rapid and axial, that is, if the molecule neither deforms nor rotates before dissociation,  $\beta$  can be estimated for each orientation.  $\beta$  is 2.0 when the dissociating C-H bond is parallel to the direction of the transition moment (the electron beam) and is -1.0 when it is perpendicular. When the excited fragment recoils at angle  $\psi$ with respect to the transition moment,  $\beta$  reduces to  $2P_2(\psi)$ , where  $P_2$  is the Legendre polynomial of the second order.<sup>37,38</sup> The calculated values of  $\beta$  for three orientations are summarized in Table II.

Dunn<sup>39</sup> showed a selection rule for electron impact excitation for diatomic molecules based on group theory. There are selection rules for the identification of the symmetry of the dissociative excited state.<sup>6,40</sup> We have extended these results to the case of the  $D_{2h}$  point group, as shown in Table III for the three orientations of C<sub>2</sub>H<sub>4</sub>. Rules were obtained for transitions connected with the ground state and were straightforward due to lack of any degenerate representation.

Component 1 has a negative value of  $\beta$  and thus the intermediate states are either in orientation 1 or 3; orientation 1 represents an out-of-plane excitation and orientation 3 represents an in-plane excitation. One of the electrons in the  $(1b_{1u})$  orbital is excited to a highly excited orbital in its formation, as is described in the previous section, and the excitation from this orbital should be inplane due to symmetry. Thus, we can conclude that component 1 is produced when the molecule lies in orientation 3 and that the symmetry of the intermediate excited state is  $a_g$  if the transition is optically allowed.

Components 2 and 3 have a positive value of  $\beta$  and thus the intermediate states are in orientation 2. One of the

TABLE II. The value of  $\beta$  for the three configurations of the ethylene molecule assuming axial recoil and rapid dissociation.

Orientation	1	2	3
β	-1.0	1.25	-0.25

TABLE III. The selection rule for transitions for a molecule with  $D_{2k}$  symmetry.

6281

Config- uration	Ag	A <sub>u</sub>	B <sub>1g</sub>	Biu	B <sub>2g</sub>	B <sub>2u</sub>	B <sub>3g</sub>	B <sub>3u</sub>
(1)	Eb	0°	0	0	0	0	0	V
(2)	E	0	0	0	0	V	0	0
(3)	E	0	0	Vª	0	0	0	0

<sup>a</sup>V, allowed both for electron and photon excitation.

<sup>b</sup>E, allowed only for electron excitation.

°0, forbidden.

electrons in the  $(2a_g)$  orbital is excited to a highly excited orbital in the formation of component 2. In this case, the symmetry of intermediate excited state should be  $b_{2u}$  if the transition is optically allowed.

# C. Asymmetry parameter

The observed values of  $\beta$  are, however, much smaller than those described in Table II. Naturally, a positive value of component 2 and a negative value of component 1 cancel each other. Judging from the TED at 27 eV, however,  $\beta$  at above 4 eV of TED should represent  $\beta$  of component 2, and thus  $\beta$  of component 2 would be ~0.15, as is indicated in Fig. 5. This value is much smaller than the expected value (1.25). There are three possible reasons for the smaller observed value; indefinite direction of the momentum transfer vector, rotation of the intermediate excited states, and deformation of the intermediate excited states.

Zare calculated the angular distribution  $[I(\theta)]$  of the fragment atom averaged over all directions and magnitudes of the momentum transfer vector K.<sup>36</sup> In the dipole limit

$$I(\theta) \propto \int_{k_0-k_n}^{k_0+k_n} \{ [I_c(\theta)\cos^2\theta' + I_s(\theta)\sin^2\theta']/k^2K^3(4 + K^2)^4 \} dK,$$
(7)

$$I_c(\theta) = 1 + 2P_2(\cos \psi)P_2(\cos \theta), \qquad (8)$$

$$I_s(\theta) = 1 - P_2(\cos \psi) P_2(\cos \theta), \qquad (9)$$

$$\cos \theta' = (K^2 - k_0^2 - k_n^2)/2k_0 K, \tag{10}$$

where  $k_0$  and  $k_n$  are the initial and final momentum of the electron, and  $\theta$  and  $\theta'$  are angles between the electron beam axis and fragment recoil axis and between the former and the momentum transfer axis, respectively. For components 1 and 2 at an incident electron energy of 27 eV and at the scattered electron energy of 8 and 3 eV, Eq. (7) gives

$$I(\theta) \propto 1 - 0.19 P_2(\cos \theta), \tag{11}$$

$$I(\theta) \propto 1 + 1.13 P_2(\cos \theta), \tag{12}$$

respectively. Accordingly, the estimated value -0.25 of  $\beta$  for component 1 is reduced to -0.19, and 1.25 for component 2 is reduced to 1.13. The value of component 1 would be compatible with the observed results, but the value of component 2 is still too large. Thus, the indefinite

direction of the momentum transfer vector plays a small role in the small value of  $\beta$  of component 2, but not a major role.

When the lifetime of the intermediate excited state is large and the molecule rotates before dissociation, the value of  $\beta$  apparently decreases.<sup>41-44</sup> This effect would be important at least for component 1 because of predissociation. In the limit of very slow dissociation compared to the rotational period, the anisotropy is reduced by a factor of 4.<sup>43</sup> If the dissociation is very slow in the present case,  $\beta$ of component 1 is reduced to below -0.19/4 = -0.05 and that of component 2 to 1.13/4 = 0.28. The latter is still larger than the observed value, even though dissociation for component 2 would be very slow.

The effect of molecular deformation in the intermediate excited states on the asymmetry parameter has not been investigated. An electron is excited from the  $2a_g$  orbital for the formation of component 2. According to Walsh's rule for an XH<sub>2</sub> molecule,<sup>45</sup> this orbital is correlated to the  $a_1$ orbital of CH<sub>2</sub> and removal of an electron from this orbital will increase the CH bond length and reduce the HCH bond angle. In other words, ethylene is expected to deform in the intermediate excited state for the formation of component 2.

If the dissociation of component 2 is rapid, the HCH angle will decrease at the time of dissociation, and the dissociation direction of H\* will be moved in a way to increase  $\psi$ , that is, to decrease  $\beta$ . The wave number of the HCH scissors vibration is ~1400 cm<sup>-1</sup>, and thus its zero point vibrational energy is ~0.043 eV. If the dissociating hydrogen atom carries this energy as the translational energy to a direction perpendicular to the C-H bond,  $\psi$  will increase from 30° to 38.5° and  $\beta$  will decrease from 1.13 to 0.75. This is still much larger than the observed value of 0.15.

If the dissociation of component 2 is very slow, there is enough time for the intermediate excited state to rearrange itself at the new equilibrium position. We do not know the molecular structure at the intermediate excited state except that the HCH angle would be smaller than it is in the ground state. If the angle would be  $100^{\circ}$ ,  $\beta$  would be reduced to 0.69 from 1.13. If the dissociation is very slow,  $\beta$ should be divided by 4 due to the molecular rotation and it would become 0.17, which agrees approximately with the observed value.

The above discussion includes several assumptions, and further spectroscopic evidence is needed to obtain a conclusive picture of anisotropic dissociation of the ethylene molecule.

## ACKNOWLEDGMENTS

This work was partially supported by Grant-In-Aids for Scientific Research on Priority Areas (01632517, 02214220) from the Ministry of Education, Science, and Culture.

- <sup>1</sup>R. N. Zare and D. R. Herschbach, Proc. IEEE 51, 173 (1963).
- <sup>2</sup>T. Ogawa, Eng. Sci. Rept. Kyushu Univ. 7, 231 (1986).
- <sup>3</sup>T. Ogawa and M. Higo, Chem. Phys. Lett. 65, 610 (1979).
- <sup>4</sup>K. Nakashima and T. Ogawa, J. Chem. Phys. 83, 4920 (1985).
- <sup>5</sup>M. Higo, S. Kamata, and T. Ogawa, Chem. Phys. 66, 243 (1982).
- <sup>6</sup>K. Nakashima, H. Tomura, and T. Ogawa, Chem. Phys. Lett. 138, 575 (1987).
- <sup>7</sup>J. Kurawaki, K. Ueki, M. Higo, and T. Ogawa, J. Chem. Phys. **78**, 3071 (1983).
- <sup>8</sup>T. Ogawa, N. Yonekura, M. Tsukada, S. Ihara, T. Yasuda, H. Tomura,
- K. Nakashima, and H. Kawazumi, J. Phys. Chem. 95, 2788 (1991).
   <sup>9</sup>T. Ogawa, M. Tsukada, and K. Nakashima, Chem. Phys. 156, 473 (1991).
- <sup>10</sup>T. Ogawa, J. Kurawaki, and M. Higo, Chem. Phys. **61**, 181 (1981).
- <sup>11</sup>T. Ogawa, H. Tomura, K. Nakashima, and H. Kawazumi, Chem. Phys.
- 113, 65 (1987). <sup>12</sup>T. Ogawa, H. Tomura, K. Nakashima, and H. Kawazumi, J. Chem. Phys. 88, 4263 (1988).
- <sup>13</sup>T. Ogawa, T. Tsuboi, and K. Nakashima, Chem. Phys. 156, 465 (1991).
- <sup>14</sup>J. F. M. Aarts, C. I. M. Beenakker, and F. J. de Heer, Physica 53, 32 (1971).
- <sup>15</sup>C. I. M. Beenakker and F. J. de Heer, Chem. Phys. 7, 130 (1975).
- <sup>16</sup>G. R. Möhlmann and F. J. de Heer, Chem. Phys. 19, 233 (1977).
- <sup>17</sup>D. E. Donohue, J. A. Schiavone, and R. S. Freund, J. Chem. Phys. 67, 769 (1977).
- <sup>18</sup> J. A. Schiavone, D. E. Donohue, and R. S. Freund, J. Chem. Phys. 67, 759 (1977).
- <sup>19</sup>P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. 52, 843 (1937).
- <sup>20</sup>T. Ibuki, G. Cooper, and C. E. Brion, Chem. Phys. 129, 295 (1989).
- <sup>21</sup> D. H. Parker and R. B. Bernstein, Annu. Rev. Phys. Chem. 40, 561 (1989).
- <sup>22</sup>T. Ogawa, H. Tomura, K. Nakashima, J. Kurawaki, and H. Kawazumi, J. Spectrosc. Soc. Jpn. 35, 303 (1986).
- <sup>23</sup>T. Ogawa, Y. Ueda, and M. Higo, Bull. Chem. Soc. Jpn. 56, 3033 (1983).
- <sup>24</sup>A. Savitzky and M. J. E. Golay, Anal. Chem. 36, 1627 (1964).
- <sup>25</sup>R. H. McFarland and E. A. Soltysik, Phys. Rev. 129, 2581 (1963).
- <sup>26</sup>W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Cambridge, 1986), Chap. 12, p. 435.
- <sup>27</sup>A. J. Merer and R. S. Mulliken, Chem. Rev. A 6, 2181 (1972).
- <sup>28</sup>G. Bieri and L. Åsbrink, J. Electron Spectrosc. 20, 149 (1980).
- <sup>29</sup> H. Shiromaru, Y. Achiba, K. Kimura, and Y. T. Lee, J. Phys. Chem. **91**, 17 (1987).
- <sup>30</sup>K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, Handbook of HeI Photoelectron spectra of Fundamental Organic Molecules (Japan Science Society, Tokyo, 1981), p. 57.
- <sup>31</sup> J. E. Pollard, D. J. Trevor, J. E. Reutt, Y. T. Lee, and D. A. Shirley, J. Chem. Phys. 81, 5302 (1984).
- <sup>32</sup> Handbook on Chemistry-Basic Chemistry, 3rd ed. (Maruzen, Tokyo, 1984), Vol. 2, p. 324.
- <sup>33</sup> Rabrenovic and J. H. Beynon, Int. J. Mass Spectrom. Ion Processes 54, 79 (1983).
- <sup>34</sup>B. Brehm, U. Frobe, and H. P. Neitzke, Int. J. Mass Spectrom. Ion Processes 57, 91 (1984).
- <sup>35</sup> J. Appell, J. Durup, F. C. Fehsenfeld, and P. G. Fournier, J. Phys. B 7, 406 (1974).
- <sup>36</sup>R. N. Zare, J. Chem. Phys. 47, 204 (1967).
- <sup>37</sup>R. N. Zare, *Angular Momentum* (Wiley-Interscience, New York, 1988), p. 120.
- <sup>38</sup> R. Bersohn and S. H. Lin, Adv. Chem. Phys. 16, 67 (1969).
- <sup>39</sup>G. H. Dunn, Phys. Rev. Lett. 8, 62 (1962).
- <sup>40</sup>S. Ohshima, T. Kondow, T. Fukuyama, and K. Kuchitsu, Chem. Phys. 85, 403 (1984).
- <sup>41</sup>C. Jonah, J. Chem. Phys. 55, 1915 (1971).
- <sup>42</sup>G. E. Busch and K. R. Wilson, J. Chem. Phys. 56, 3638 (1972).
- <sup>43</sup>S. C. Yang and R. Bersohn, J. Chem. Phys. 61, 4400 (1974).
- <sup>44</sup>R. J. van Brunt, J. Chem. Phys. 60, 3064 (1974).
- <sup>45</sup>G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand-Reinhold, New York, 1966), p. 319.