Photoion-pair formation and photoelectron-induced dissociative attachment in C_2H_2: D_0(HCC–H)

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The formation of C_2H^- is observed in two broad resonance bands when C_2H_2 is irradiated with vuv light. The higher-energy band has partially resolved structure, approximately linear pressure dependence, and a threshold at $16.33_5 \pm 0.02_1$ eV. It is attributed to photoion-pair formation ($C_2H^- + H^+$) consequent upon predissociation of one or more Rydberg states. This threshold, together with IP(H) and EA(C_2H), gives D_0(HCC–H) $\leqslant 5.70_6 \pm 0.02_2$ eV $\equiv 131.6 \pm 0.5$ kcal/mol, or ΔH^0_{f0} (C_2H) $\leqslant 134.5 \pm 0.5$ kcal/mol. The lower-energy band has an approximately quadratic pressure dependence and curved step-like structure. It is attributed to photoelectron-induced dissociative attachment mediated by a π_g shape resonance. The threshold, at 878.5 ± 2.0 Å, corresponds to a photoelectron energy of $2.71_5 \pm 0.03_2$ eV. This threshold combined with EA(C_2H) = 2.969 ± 0.010 eV, yields D_0(HCC–H) $\leqslant 5.68_4 \pm 0.03_3$ eV $\equiv 131.1 \pm 0.7$ kcal/mol, or ΔH^0_{f0} (C_2H) = 134.0 ± 0.7 kcal/mol.

I. INTRODUCTION

The C–H bond energies of alkanes, alkenes, and alkynes tend to be characteristic of a homologous series, and to differ between series. The prototypical alkanes are CH_4 and C_2H_6. The C–H bond energies in these systems (0 K) are now known to be 103.3 ± 0.2 kcal/mol (Ref. 1) and 99.6 ± 0.6 kcal/mol (Ref. 2), respectively. In 1987, Shiromaru *et al.*[3] generated renewed interest in the C–H bond energies of C_2H_4 and C_2H_2 (the prototypical alkene and alkyne) by reporting the photodissociative ionization thresholds for the processes

$$C_2H_4 + h\nu \rightarrow C_2H_3 + H^+ + e \qquad (1)$$

and

$$C_2H_2 + h\nu \rightarrow C_2H + H^+ + e. \qquad (2)$$
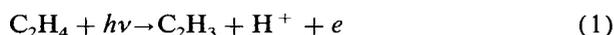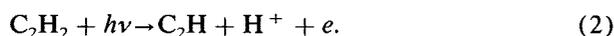
The advantage of examining the thresholds for H^+ is that the bond energy may be extracted from the measured threshold value by subtracting the well-known ionization potential of hydrogen atom, 13.598 eV.[4] The disadvantage is that the H^+ threshold in these systems lies considerably higher than the lowest-energy dissociative ionization thresholds. For example, the H^+ (C_2H_4) threshold reported by Shiromaru *et al.* is 18.66 ± 0.05 eV, whereas the threshold for $C_2H_3^+$ (C_2H_4) is 13.22 ± 0.02 eV.[5] For acetylene, the H^+ threshold reported is 19.35 ± 0.05 eV,[3] whereas that for C_2H^+ is 17.33–17.36 eV.[6,7] Higher-energy thresholds often suffer a "kinetic shift," i.e., their appearance energies are retarded; consequently, such a threshold can be correlated with an upper limit to the bond dissociation energy, but this upper limit may be several kcal/mol above the true threshold.

Clearly, the more problematic case in this regard is ethylene, where the gap between the $C_3H_3^+$ and H^+ thresholds is 5.44 eV. In order to test for possible errors such as a kinetic shift in the experiments of Shiromaru *et al.*,[3] we[8] performed an experiment to measure the adiabatic ionization potential of C_2H_3. The value we obtained for this quantity, 8.59 ± 0.03 eV, could be combined with the threshold for

$C_2H_3^+$ (C_2H_4) to yield a C–H bond energy of 107 kcal/mol. Since the photoion yield curve for $C_2H_3^+$ (C_2H_3) approached the background level gradually, indicating poor Franck–Condon factors and hence a large geometry change accompanying photoionization, we allowed for the possibility of an additional vibrational quantum, which could conceivably increase this bond energy to $\sim$110 kcal/mol. By contrast, the H^+ (C_2H_4) threshold obtained by Shiromaru *et al.*[3] corresponds to D_0(C_2H_3–H) = 117 kcal/mol. Hence, we inferred that a kinetic shift of 7–10 kcal/mol could be plaguing the C_2H_4 experiment of Shiromaru *et al.* Subsequently, other experiments[9,10] have clustered around 106–109 kcal/mol for the C_2H_3–H bond energy, corroborating our result.

This raises some question about the accuracy of the C–H bond energy in acetylene obtained by Shiromaru *et al.* Here, the gap between the thresholds for C_2H^+ and H^+ from C_2H_2 is only $\sim$2 eV. There may be a smaller kinetic shift in this instance, or perhaps none at all.

A possible approach, analogous to that in C_2H_4, is to measure the adiabatic ionization potential of C_2H. We have attempted this, so far without success. It has been measured directly by electron impact,[11] but the resulting value (11.6 ± 0.5 eV) is rather crude. An indirect approach, measuring the difference between the photodissociative ionization thresholds of C_2H^+ and Br^+ from C_2HBr, yields 11.51 eV.[12] Even if an accurate IP(C_2H) were available, the determination of the C–H bond energy hinges upon the appearance potential of C_2H^+ (C_2H_2), about which there has been some controversy.[6,7,13,14] If we accept the photodissociative ionization threshold for C_2H^+ (17.33-17.36 eV) at face value, and take IP(C_2H) = 11.51–11.6 eV, the C–H bond energy in C_2H_2 is 5.73–5.85 eV = 132.1–134.9 kcal/mol, close to the value obtained by Shiromaru *et al.*, 5.75 ± 0.05 eV $\equiv 132.6 \pm 1.2$ kcal/mol.

Two photon impact methods have been reported[15,16] which aim to directly measure D_0(HCC–H). Both investigate the process

$$C_2H_2 + h\nu(193 \text{ nm}) \rightarrow C_2H + H. \qquad (3)$$

Wodtke and Lee[15] measured the time-of-flight velocity distribution (and hence kinetic-energy distribution) of the C_2H product. The highest kinetic energy is correlated to $D_0(HCC-H)$. Segall et al.[16] detected H atoms by using laser-generated Lyman-α radiation to excite to $H(^2P)$, then ionizing $H(^2P)$ with a 346.7 nm photon. The velocity of the H atoms could be obtained from the Doppler effect, since the laser-generated Lyman-α radiation had sub-Doppler width. Both methods depend upon the determination (and interpretation) of a threshold. Wodtke and Lee[15] obtained 132 ± 2 kcal/mol for $D_0(HCC-H)$, although a higher threshold (and hence lower D_0) could be observed. They performed some additional tests, and concluded that the higher threshold was attributable to a hot band. Segall et al.[16] used supersonic expansion to produce their C_2H_2 beam. They picked the highest threshold (corresponding to $D_0(HCC-H) = 127 \pm 1.5$ kcal/mol), arguing that vibrational internal energy would be relaxed (cooled) in the supersonic expansion.

Other, nonimpact methods have been directed at this problem. Green, Kinsey, and Field[17] observed a decrease in the fluorescence lifetimes of certain rovibronic levels of the S_1 ($\tilde{A}^1A_u$) state of C_2H_2 upon application of a Stark field. They attributed this decrease to the onset of predissociation. From the lowest-energy rovibronic state displaying this effect, they inferred $D_0(HCC-H) \leqslant 5.4920$ eV $\equiv 126.647$ kcal/mol. Ervin et al.[9] determined the gas-phase acidity, i.e., the enthalpy for the reaction

$$C_2H_2 \rightarrow C_2H^- + H^+ \tag{4}$$

by taking the gas-phase acidity of HF as a known standard, and measuring the forward and backward rate of the reaction

$$F^- + C_2H_2 \rightarrow HF + C_2H^-. \tag{5}$$

The ratio of forward and backward rates provided an equilibrium constant, and hence ΔF. By using known and estimated entropies, they could arrive at ΔH_{298}, and eventually ΔH_0.

They[9] also determined an accurate value for the electron affinity of C_2H (2.969 ± 0.010 eV) by photodetachment spectroscopy. When combined with IP(H) = 13.598 eV, they obtained $D_0(HCC-H) = 131.3 \pm 0.7$ kcal/mol. Thus, the recent measurements, some based on impact methods and others on spectroscopic or kinetic measurements, cluster around 131–132 kcal/mol or 126–127 kcal/mol. An earlier high-temperature equilibrium study[11] using Knudsen cell mass spectrometry arrived at 124 ± 3 kcal/mol. Bond energies based on pyrolysis kinetics[18,19] yield significantly lower values, 118–124 kcal/mol.

Bond energies based on impact methods are always upper bounds. There may be selection rules preventing the lowest-energy state of the products from being accessed. Even if one could establish the maximum product kinetic-energy threshold for reaction (3), the C_2H may be internally excited. The same criticism could be directed at the photodissociative ionization experiment. It is unlikely, however, for impact methods which measure different products to be displaced from the true threshold by about the same increment in energy.

Our initial goal was to directly determine the threshold for reaction (4) by photoion-pair formation. This was successfully achieved[20] in the isoelectronic process

$$HCN + h\nu \rightarrow CN^- + H^+. \tag{6}$$

Unfortunately, the magnitude of the photoion-pair formation process is unpredictable. With our conventional "low" resolution [0.28 Å full width at half maximum (FWHM)] and sample pressure ($\sim 10^{-4}$ torr), we failed to see clear evidence for this process, at the expected wavelengths (<770–755 Å). With still lower resolution (~ 1.0 Å) and higher sample pressure (several mtorr), we observed C_2H^- at the expected wavelengths, and also at much longer wavelengths (>850 Å). The C_2H^- spectrum consisted of two broad bands, with maxima at ~ 660 and ~ 830 Å. The results of these experiments could be related to $D_0(HCC-H)$.

II. EXPERIMENTAL ARRANGEMENT

The basic photoionization mass spectrometric apparatus consists essentially of a light source, a 3 m vacuum ultraviolet monochromator, a vacuum chamber containing the sample cell, a quadrupole mass filter, and detectors for measuring the intensity of the wavelength-selected light and the mass-selected ions. The light source utilized in these experiments was the Hopfield continuum of helium,[21] providing a smooth continuum between ~ 600 and 1000 Å. Wavelength resolution (and light intensity) could be altered with various choices of fixed entrance and exit slits on the monochromator. The light leaving the exit slit passed through the sample cell. Ions generated by the vuv radiation were directed toward the focusing elements and the quadrupole mass filter (normal to the light path) by a repeller potential. "Tight" sample cells were employed, where the apertures (light entrance and exit, ion exit) were minimized, thereby permitting higher sample pressures to be used. This enhanced the probability of bimolecular processes. One of the sample cells had provision for cooling the incoming gas. Measurements were made at room temperature and ~ 150 K, as measured by an iron–Constantan thermocouple.

In order to enhance the observed C_2H^- signal, relatively large slits (500 or 300 μm entrance and 300 μm exit) were employed. This resulted in a photon bandwidth (and hence a photoelectron bandwidth) of 0.03 and 0.014 eV (FWHM), respectively. Pressures in the sample chamber were measured by an MKS Baratron gauge, and also by a Beer's law analysis of photoabsorption in the cell. When it was established that the lower-energy band was attributable to a second-order process involving photoelectrons, the repeller within the sample chamber was maintained barely negative, to minimize additional broadening of the kinetic energy of the photoelectrons. The nominal field (apart from patch effects) was <0.05 V/cm. In all experiments, acetylene was passed through a dry-ice/i-propanol bath prior to introduction into the instrument, in order to trap residual acetone.

III. EXPERIMENTAL RESULTS

The spectrum of C_2H^- obtained at a pressure of ~ 30 mtorr (as determined by the fractional absorption of light in the ionization cell) and room temperature is shown in Fig. 1.
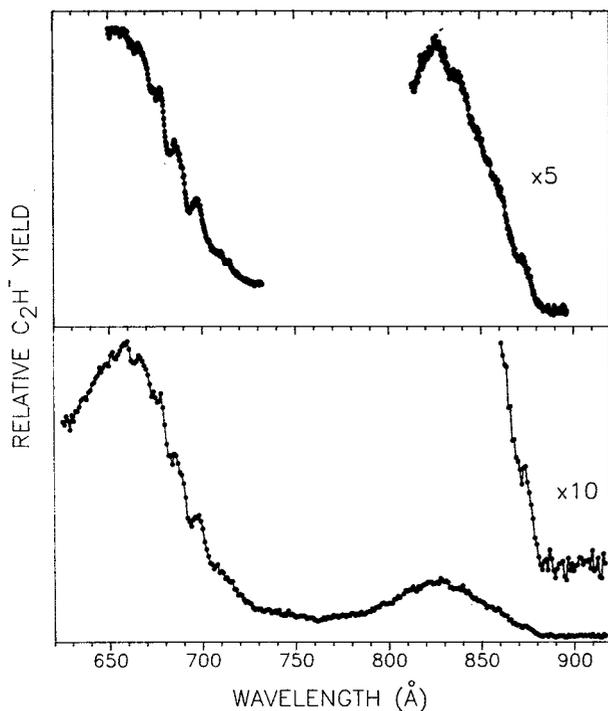
FIG. 2. Same as Fig. 1(a), but with a sample pressure of ~5 mTorr. Note the diminution of the 830 Å band, compared to the 660 Å band. The threshold for the latter band, attributed to ion-pair formation, is now clearly seen.

FIG. 1. (a) Photoion yield curve of C_2H^- (C_2H_2), obtained at room temperature, with a resolution of 1.4 Å (FWHM), equivalent to ~0.03 eV, and a sample pressure of 30 mtorr. The shorter-wavelength band ($\lambda_{max} \approx 660$ Å) increases linearly with pressure, the longer-wavelength band ($\lambda_{max} \approx 830$ Å) increases quadratically with pressure. The interpretation of the 830 Å band involves photoelectron-induced dissociative attachment. (b) Same as (a), but with the resolution of 0.84 Å (FWHM), equivalent to ~0.014 eV. The longer-wavelength band shows rounded step structure, while the shorter-wavelength band shows partially resolved peak structure.

The lower panel is a manual scan, with a wavelength resolution of ~1.4 Å; the upper panel is a computer-controlled scan, with a wavelength resolution of 0.84 Å (FWHM) and a higher density of points. Two broad bands with some partially resolved structure are seen, with maxima at ~660 and ~830 Å. Pressure dependence studies were performed at selected wavelengths on both bands. The intensity of the longer-wavelength band increased as ~$P^{1.8}$; that of the shorter-wavelength band increased as ~$P^{1.1}$. Within experimental uncertainty, this observation was interpreted as quadratic and linear pressure dependence, respectively.

The 830 Å band was also studied using a cell cooled to ~150 K. There was no appreciable difference in the shape of the band, nor in its approach to threshold. The observed onset of the first band, apparently independent of temperature, is 878.5 ± 2 Å.

We show below that the quadratic dependence is a consequence of photoionization, followed by photoelectron-induced dissociative attachment. If we assume that the photoelectron energy is the difference between the incident photon energy and the adiabatic ionization potential of C_2H_2, the onset of the first band occurs at a photoelectron energy of $2.71_5 \pm 0.03_2$ eV.

Various means of normalizing the C_2H^- intensity were employed, including incident light intensity, electron intensity (as measured at the zero mass position of the quadrupole mass spectrometer), or $C_2H_2^+$ intensity, each as a function
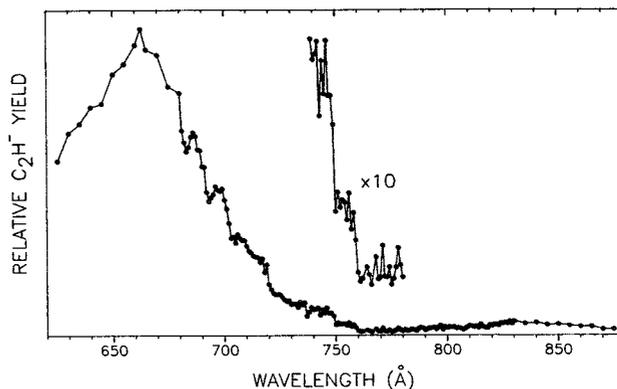
of wavelength. The effect on the yield curve of C_2H^- was slight. In order to determine more accurately the onset of the second band, it was necessary to operate at lower sample pressure which diminishes the intensity of the first band more than the second. However, the resulting signal was quite weak. To partially compensate for this loss of intensity, the monochromator entrance slit was increased to 500 μm, thereby diminishing the photon resolution to ~1.4 Å ≡ 0.03 eV (FWHM). The spectrum obtained under these conditions (sample pressure reduced by approximately a factor 5) is shown in Fig. 2. The first band is indeed diminished relative to the second. A relatively abrupt onset for the second band is now apparent, at 759 ± 1 Å ≡ $16.33_5 \pm 0.02_1$ eV.

A crude estimate of the cross section for photoion-pair formation was obtained by comparing the intensity of the C_2H^- signal at ~662 Å with the intensity of $C_2H_2^+$ at this wavelength ($C_2H_2^+$ undergoes rapid ion–molecule reactions at these high pressures; the $C_4H_n^+$ product intensities were added to the $C_2H_2^+$ intensity to determine the total ionization). From the ratio of intensities (~2×10^{-4}) and the photoionization cross section[22] (~30 Mb), we obtain $\sigma_{ion\ pair} \approx 6 \times 10^{-21}$ cm². The cross section for dissociative attachment was estimated by comparing the C_2H^- intensity at ~830 Å (~30 c/s) with the incident photoelectron current (~10^5 c/s) at a path length of ~0.5 cm and a pressure of ~25 mtorr. With these values, $\sigma_{diss\ att} \approx 5^{+5}_{-2.5} \times 10^{-19}$ cm².

Some fine structure can be discerned within each band. For the lower-energy band, the fine structure appears as curved steps, while for the higher-energy band, partially resolved peak structure is apparent.

IV. INTERPRETATION OF RESULTS

The C_2H_2 molecule is particularly favorable for observing a photoelectron-induced dissociative attachment process. At the adiabatic ionization potential of C_2H_2 the Franck–Condon region for this ionization process is compact; the 0–0 process dominates.[23(a)] As the photon energy is increased, the energy in excess of the ionization threshold becomes increased kinetic energy of the photoelectron. This process continues until the photon energy is sufficient to ac-
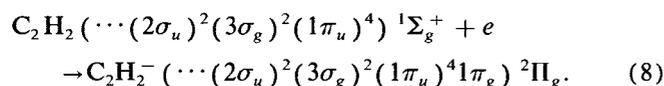
cess the first excited state of $C_2H_2^+$, at 16.36 eV.[23(b)] There is some weak autoionizing structure between 11.40 and 16.36 eV which could result in less-well-defined electron kinetic energies, but the dominant process is direct ionization. Even at 21.2 eV, the 0–0 transition of the first band is the dominant peak.[23(b)] Hence the kinetic energy of the photoelectrons is controlled by the incident photon energy. This provides a smoothly tunable, high-resolution source of electrons, built into the experiment.

Dissociative attachment experiments are usually performed utilizing a hot filament as an electron source, and controlling the kinetic energy of the electron beam with a suitable extraction potential. The negative ion of interest is selected with a mass spectrometer. In fact, such an experiment was reported[24,25] for acetylene. The process

$$C_2H_2 + e \rightarrow C_2H^- + H \tag{7}$$

was studied. The reaction was reported to have a threshold at 2.8 ± 0.2 eV, and to have a relatively large cross section[24] ($\sim 10^{-18}$ cm^2). A second band was also observed,[24] weaker in intensity, and having a threshold at 6.0 ± 0.3 eV. Azria and Fiquet-Fayard[26] performed a more indirect experiment. They monitored negatively charged species formed in the collision chamber, which could be trapped and detected. They assumed that these negatively charged species were negative ions (not slow electrons). In a separate experiment, alluded to but not described in detail, mass spectrometric identification was performed. Azria and Fiquet-Fayard[26] observed four bands. The band at lowest energy was attributed to the formation of C_2H^-, had an appearance potential of 2.3 ± 0.1 eV and a cross section at its peak of only $2.2 \pm 0.3 \times 10^{-20}$ cm^2. The second band, attributed to H^-, C_2^-, and C_2H^-, had an estimated onset of 6.5–6.7 eV, with a peak cross section of $3.1 \pm 0.4 \times 10^{-20}$ cm^2. There is a significant discrepancy between the results of von Trepka and Neuert[24] and Azria and Fiquet-Fayard[26] regarding the threshold of the first band, and the maximum cross section.

One implication from the above-cited studies is that there may be several quasibound states of $C_2H_2^-$. Such resonances can also manifest themselves in electron-scattering experiments. Bowman and Miller[27] first observed peaks in the electron excitation spectrum of acetylene, using the trapped-electron method. Their spectrum displayed peaks at ~ 2 eV, ~ 6 eV, and also higher energies. Later, Dance and Walker[28] obtained a similar spectrum, with somewhat better resolution. Van Veen and Plantenga[29] also obtained such a spectrum, and began to observe some fine structure, but in a higher energy band (centered at ~ 8 eV). The peak of the first band was given as 1.7 eV (Ref. 28) and 1.85 eV (Ref. 29). It was described as a shape resonance, corresponding to the transition

$$C_2H_2 (\cdots (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4) \ ^1\Sigma_g^+ + e$$
$$\rightarrow C_2H_2^- (\cdots (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 1\pi_g) \ ^2\Pi_g. \tag{8}$$

Tronc and Malegat[30] and Kochum et al.[31] have examined electron-impact-induced vibrational excitation of C_2H_2 in the energy region of this $^2\Pi_g$ resonance. Both direct (dipole allowed) and resonance-induced vibrational excitation occur, which skews the low-energy peak observed by the

trapping method[27–29] or by elastic scattering[31] to lower energy. By analyzing the interference between direct and resonance-induced vibrational excitation, it is possible to extract the parameters of the resonance. In particular, the ν_2 mode (C–C stretch) is excited only by the resonance. Both Tronc and Malegat[30] and Kochum et al.[31] concur that the center of the resonance is 2.6 eV, whereas the electron-trapping method[27–29] yields a peak at ~ 2 eV. The width of the resonance is given[30] as 1.2 eV. A rough estimate of the cross section of the resonance at 2.6 eV can be obtained by converting the differential cross section[30] for ν_2 at 2.6 eV (5×10^{-17} cm^2 sr$^-$) into a total cross section. This estimate ignores the contribution from other modes excited by the resonance, but presumably does include the elastic-scattering component, since Kochum et al. give $\sim 0.5 \times 10^{-17}$ cm^2 sr^{-1} for excitation of the *fundamental* of ν_2 at the resonance. From these considerations, a rough estimate of the total cross section of the resonance (probably on the low side) is $\sim 6 \times 10^{-16}$ cm^2.

In Fig. 3, we have simulated this resonance, using $\sigma_{max} \sim 6 \times 10^{-16}$ cm^2, $\Gamma = 1.2$ eV, and assuming a Lorentzian shape. Also shown in this figure is the experimental dissociative attachment excitation function, on the same electron energy scale. One can see that the dissociative attachment threshold occurs near the maximum of the resonance. This fulfills one of the requirements for observing a true thermochemical onset. The other is the relative probability of dissociative attachment to autodetachment at the threshold.

The dissociative attachment cross section σ_{da} is sometimes written[32] in the form $\sigma_{da} = \sigma_{cp} e^{-\rho}$, where σ_{cp} is the cross section for capture of the electron by the molecule (our $^2\Pi_g$ resonance cross section) and $e^{-\rho}$ is called the survival factor. The parameter $\rho = \tau_d/\tau_a$ is the ratio of mean lifetimes for dissociative attachment (τ_d) and autodetachment (τ_a). If we plot σ_{da}/σ_{cp} as a function of electron energy, we have a measure of the dependence of the survival factor $e^{-\rho}$ on excess energy. Such a plot is shown in Fig. 4, using the
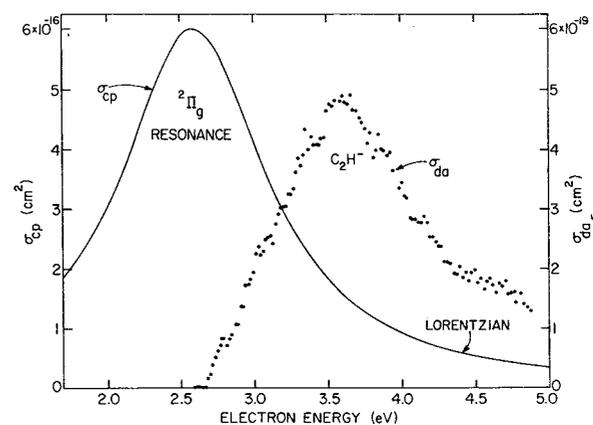

FIG. 3. Juxtaposition of the cross section for electron capture to the $^2\Pi_g$ shape resonance (σ_{cp}) and the experimentally deduced cross section for dissociative attachment (σ_{da}), both as functions of electron energy. The σ_{cp} curve has been simulated by taking $\sigma_{max} \approx 6 \times 10^{-16}$ cm^2, estimated from Refs. 30 and 31, the location of σ_{max} at 2.6 eV (Refs. 30 and 31), a half-width of 1.2 eV (Ref. 30) and a Lorentzian shape. The estimate of the absolute cross section of σ_{da} is given in the text.
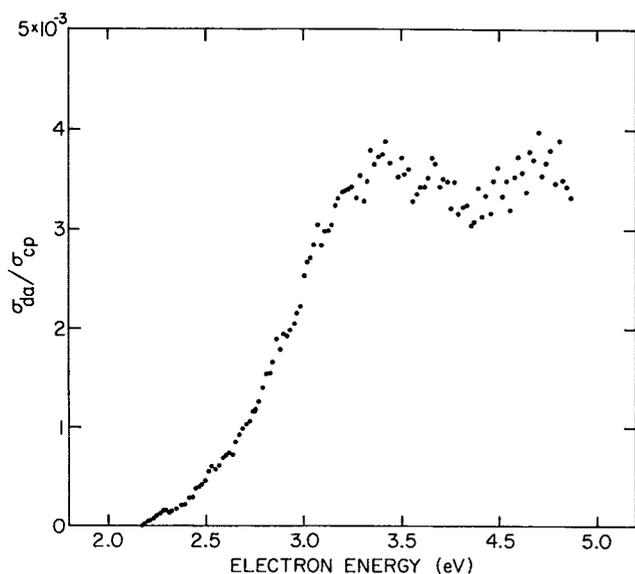
FIG. 4. The ratio of σ_{da} to σ_{cp} as a function of energy. The assumptions entering into the determination of σ_{da} and σ_{cp} are the same as in Fig. 3.

same assumptions described in constructing Fig. 3. The survival factor is seen to grow more than linearly near threshold. About 1 eV above threshold, the survival factor becomes roughly constant.

O'Malley[33] has discussed the case of dissociative attachment when the electron-capture resonance corresponds to an attractive potential curve. His analysis refers to a diatomic molecule. He concludes that the vertical onset approximation should be quite good for this case. In this approximation, the thermochemical threshold for dissociative attachment occurs somewhere within the energy range of the electron-capture resonance. At this thermochemical threshold, the dissociative attachment cross section rises abruptly. Examples are the 9.7 eV onset of O^- from CO,[34] the 3.73 eV peak,[35] and possibly the 13.9 eV peak[33] in H_2.

The curves in Fig. 3 imply a situation similar to that described by O'Malley, except that here we are dealing with a polyatomic molecule, and the C_2H^- cross section does not conform to the behavior expected by the vertical onset approximation. Instead, it increases gradually from a threshold at 2.69 eV to a maximum at ~ 3.6 eV. We believe that this differing threshold behavior is characteristic of polyatomic vs diatomic molecules. Within the electron-capture state, several vibrational modes may be excited in a polyatomic molecule. At the thermochemical threshold for dissociative attachment, a limited range of configurations can lead to the products $C_2H^- + H$ before autodetachment occurs. As the internal energy of the negative-ion complex increases, the dissociation lifetime τ_d, and hence the parameter ρ, should decrease, and the survival factor $e^{-\rho}$ should increase. The high-energy limit of $e^{-\rho}$ can be estimated as follows.

A typical lifetime for a shape resonance is 10^{-14}–10^{-15} s, and is not expected to vary greatly with energy. (In the present case, an energy width of 1.2 eV implies $\Delta t \approx 10^{-15}$ s.) The lifetime for dissociative attachment in a diatomic molecule is often estimated as the classical traversal time

from r_e (the equilibrium internuclear distance in the neutral molecule, projected onto the negative-ion potential curve by Franck–Condon considerations) to a critical internuclear distance r_c, beyond which autodetachment is negligible. For a diatomic hydride, this time would be of order 10^{-14} s. For a polyatomic molecule, one must consider the contour diagram of a potential-energy surface characterizing the resonant state. The motion of the separating particles, especially in a bent resonance state (see below) will likely execute bending motions as well as C–H stretching. The effect would be to increase the lifetime for dissociative attachment. In Fig. 4, the high-energy limit of $e^{-\rho}$ is $(\sim 3$–$4) \times 10^{-3}$, or $\rho \approx 5.8$. If we assume that this high-energy limit corresponds to the most rapid dissociation of a quasidiatomic hydride, i.e., take $\tau_d \approx 10^{-14}$, then $\tau_a \approx 1.7 \times 10^{-15}$ s, which is consistent with the expected lifetime of a shape resonance. Near threshold, $e^{-\rho}$ is $\sim 10^{-4}$, or $\rho \approx 9.2$. Since τ_a is expected to vary slowly with energy, the larger value of ρ can be related to a slightly slower dissociation time, $\sim 1.6 \times 10^{-14}$ s. Unlike the decomposition of cations, the dissociation of resonant-state anions must be very rapid in order to compete favorably with autodetachment. We note parenthetically that the C–H stretching wave numbers in C_2H_2 are ~ 3300 cm^{-1}, which correspond to a frequency of $\sim 10^{14}$ s^{-1}. Although the shape of the curve in Fig. 4 hinges on the assumed Lorentzian form of the resonance, the above discussion implies that the result is plausible.

Both the dissociative attachment and the electron excitation processes involving the lowest-energy band may be rationalized with the aid of ab initio calculations. Chu and Goodman[36] have calculated the energy and structure of the $^2\Pi_g$ anion state. They find that the vertical excitation energy corresponding to transition (8) is 2.7 eV, and the adiabatic value is 1.3 eV (which would be the negative electron affinity of C_2H_2). Furthermore, the most stable equilibrium structure of $^2\Pi_g$ is no longer linear, but transbent, with a C–C–H bending angle of $\sim 52°$. This behavior has been explained[36] as a manifestation of Walsh's rule, the π_g orbital being stabilized by bending. It can also be described[37] as an example of Renner–Teller splitting. Thus, between ~ 1.3 and ~ 2.7 eV, the incident electron is temporarily trapped in the π_g orbital by a centrifugal barrier, and then autodetaches. At 2.71_5 eV (according to our measurements) a new channel becomes accessible from this resonance—the dissociative attachment process creating $C_2H^- + H$. These products correlate with a $^2\Sigma$ state of $C_2H_2^-$, whereas we have been discussing a $^2\Pi_g$ resonance ($^2A'$ in the bent geometry). However, as pointed out by Jordan and Barrow,[37] a $^2\Sigma_u$ anion state is expected in the same energy range for which vertical attachment occurs to give the $^2\Pi_g$ state. "These two anion states will undergo avoided crossings for appropriate bent structures,"[37] thus enabling the dissociative attachment process to occur.

The fine structure in the first band of Fig. 1 has been described as rounded step structure. This can be ascribed to Franck–Condon structure in the transition from C_2H_2 to $C_2H_2^-$ (in which case the C–C stretch and bending modes should be excited[30]) or it can be viewed as structure induced as the C_2H^- and H depart from the collision zone. We focus on the latter process first. Wigner[38] has shown that the

threshold law appropriate to the present case is

$$\sigma_J \propto K^{2J+1} \equiv E^{(2J+1)/2}, \qquad (9)$$

where σ_J is the cross section for a given rotational state J, K is the relative momentum of the departing particles, and E is the corresponding energy. When $J = 0$, one obtains $\sigma_J \propto E^{1/2}$, which is a kind of rounded step structure. However, O'Malley[33] has considered the applicability of Wigner's threshold law to dissociative attachment, and concluded that the region of applicability "... will always be negligibly small except for enormous values of the rotational quantum number J...".

Nevertheless, if we accept this threshold behavior as a trial model, we can extract a "true" threshold from the experimental data. Convolution of the function in Eq. (9) ($l = J = 0$) with a Gaussian function representing the photon resolution (111 cm^{-1}, FWHM) yields a curve which rises more rapidly from the apparent threshold than does the experimental curve. There are two other possible sources of broadening—the Maxwellian distribution of velocities, which could introduce some Doppler width, and the weak repeller field, which could modify the distribution of electron velocities. Since there was an imperceptible change in the experimental curve between 300 and ~150 K, Doppler broadening is not likely to be a major contributor.[39] A pragmatic approach was adopted to simulate additional broadening, by varying the half-width of the Gaussian until a simulation approximated the experimental curve. With a Gaussian of 300 cm^{-1} FWHM, a plausible fit was obtained, which resulted in a threshold of 881 Å $\equiv$ 113 495 cm^{-1} $\equiv$ 14.072 eV. This corresponds to a photoelectron energy of 2.672 eV as the threshold for the dissociative attachment reaction, Eq. (7), which we regard as a lower limit. When combined with the electron affinity of C$_2$H,[9] we obtain D_0(HCC–H) = 5.641 eV $\equiv$ 130.1 kcal/mol from this convolutional fit.

An alternative interpretation is that the structure in the first band is governed by the Franck–Condon factors in the excitation process

$$C_2H_2(\widetilde{X}\,^1\Sigma_g^+) + e \rightarrow C_2H_2^-\,(^2A'). $$
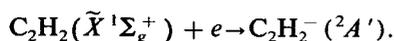
The anticipated peak structure is broadened by (a) its natural lifetime, (b) the photon resolution, and (c) the weak residual electric field in the chamber. According to Khvostenko and Tolstikov,[32] a typical lifetime for a shape resonance is 10^{-14}–10^{-15} s. Even if we take the longer time estimate, the uncertainty principle broadening amounts to ~500 cm^{-1}, or ~4 Å. This is much larger than the experimental resolution, and very likely larger than the broadening due to the weak repeller field.

A rather good fit to the threshold region is obtained if we assume that the rounded step structure corresponds to excitation of a vibrational progression ($\omega \sim 1870$ cm^{-1}) which is lifetime broadened (represented by a Gaussian convolution, with a half width of ~1750 cm^{-1}). This analysis implies that a 1.2 eV half-width of the $^2\Pi_g$ resonance is composed of several sharper resonances (of half-width ~0.2 eV) superimposed. The lifetime of these sharper resonances would be ~3$\times$10^{-15} s, which would be consistent with our previous analysis of lifetimes.

If we focus our attention on the initial ascent from threshold, it may be described as a linear segment, or possibly an S-shaped curve. If it is truly linear in the absence of an electric field, we estimate that the influence of an electric field of ~0.1 V/cm will be to preserve the linearity, but to lower the threshold by ~0.03 eV. Thus, the extrapolated threshold, 880.5 Å $\equiv$ 14.081 eV, corresponding to a photoelectron energy of 2.683 eV, is shifted upwards in energy to 2.713 eV. This estimate is based on the view that some of the photoelectrons in the collision region will have been accelerated by the field before scattering from C$_2$H$_2$ molecules. If, alternatively, the true threshold function in the absence of a field were a step function (recalling the vertical onset approximation discussed by O'Malley), than the influence of the field would be to smooth the step into an S-like shape, in which case the proper threshold would be the half-rise point, 876.5 Å $\equiv$ 14.145 eV, or a photoelectron energy of 2.747 eV. We regard this latter value as an upper limit. Thus, choosing the threshold as 878.5 $\pm$ 2 Å would appear to nearly encompass both extreme values. This choice corresponds to a photoelectron energy of 2.71$_5$ $\pm$ 0.03$_2$ eV, or D_0(HCCH) = 131.1 $\pm$ 0.7 kcal/mol.

The partially resolved peak structure in the second band implies a slightly longer lifetime for this resonance. It is attributed to predissociation of one or more Rydberg states by the repulsive portion of the ion-pair state. In this energy region (17.2–19.1 eV), the Rydberg states are likely to be those converging to the third photoelectron band,[23(b)] for which the expected configuration would be

$$...(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4 n\sigma_g, \,^1\Sigma_u$$

or

$$...(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4 n\pi_g, \,^1\Pi_u. \qquad (10)$$

The photoelectron spectrum of the third band[23(b)] displays vibrational structure attributed to a symmetrical C–H stretch (~1900 cm^{-1}) and possibly another vibration, with $\omega = 2510$ cm^{-1}. In our second band, the separation between peaks is not regular, but several differences imply a vibrational progression with $\omega \sim 2630$ cm^{-1} (which we attribute to a C–H stretch) and also one with $\omega \sim 1600$ cm^{-1} (perhaps a C–C stretch).

The onset of the second band (759 $\pm$ 1 Å $\equiv$ 16.33$_5$ $\pm$ 0.02$_1$ eV) is an upper limit for the thermochemical threshold of the ion-pair process [Eq. (4)]. Since the ion-pair state can be expected to cross several Rydberg states in this vicinity, the upper limit should not be far from the true thermochemical threshold. Combining with IP(H) and EA(C$_2$H) as in Ref. 9, we obtain D_0(HCCH) $\leqslant$ 5.70$_6$ $\pm$ 0.02$_2$ eV $\equiv$ 131.6 $\pm$ 0.5 kcal/mol.

Thus, the results of the analyses on the first and second bands yield values for D_0(HCC–H) which are very close to one another. In both cases, however, the electron affinity of C$_2$H enters in the same fashion. Hence, the final result is critically dependent upon EA(C$_2$H). Ervin *et al.*[9] have displayed their photodetachment electron spectrum of C$_2$H$^-$. In generating this spectrum, they initially found evidence for vibrationally excited C$_2$H$^-$ (up to 15% in the C–C stretch), but were able to quench this vibration substantially by several methods. In their published spectrum, this hot band

amounts to $\lesssim 1\%$. The dominant peak in their spectrum is labeled as the 0–0 transition, with the 0–1 (C–C stretch) amounting to $\sim 7.5\%$. A simple quasidiatomic calculation, taking $\omega \cong 1800$ cm^{-1} for the C–C stretch, implies a change in the C–C distance (anion to neutral) of ~ 0.02 Å. *Ab initio* calculations[40] have concluded that the C–C distance in the anion is 0.039 Å larger than in the neutral species, in fair agreement with this simplified Franck–Condon analysis. In their spectrum, Ervin *et al.* observe a weak peak which they assign to a hot band of the C–C stretch, from which we estimate $\omega_{C-C}(C_2H^-) \cong 1816$ cm^{-1}, whereas from their 0–1 transition we estimate $\omega_{C-C}(C_2H) \cong 1854$ cm^{-1}. Such a small change in ω_{C-C} also implies that the 0–0 transition should be dominant. Hence, the assignment of the relatively simple photodetachment electron spectrum of C₂H⁻ seems well established.

With the deductions from the various experiments and the *ab initio* calculations in mind, we have constructed a schematic, quasidiatomic potential-energy diagram of some relevant C₂H₂ and C₂H₂⁻ states (see Fig. 5). The $^2\Pi_g$ shape resonance is displayed with a minimum about 1.4 eV above that of the C₂H₂ ground state, along the C–H coordinate; this internuclear distance remains virtually unchanged in the transition.[36] However, the C–C distance increases substantially (1.203 to 1.282 Å, according to Ref. 36), which shifts the vertical transition to ~ 2.6 eV. The asymptote for C₂H⁻ ($^1\Sigma$) + H(^2S) occurs at ~ 2.72 eV, but these asymptotic products must correlate with a $^2\Sigma$ state of C₂H₂⁻. This is presumably the state anticipated by Jordan and Barrow,[37] which interacts with the "$^2\Pi_g$" bent resonance state, giving rise to avoided crossings and thereby enabling the products C₂H⁻ ($^1\Sigma$) + H(^2S) to be formed.

The observed onset for these products is an upper limit. The probability of observing the true thermochemical limit will depend upon the initial excitation probability to the "$^2\Pi_g$" resonance at about 2.6 eV, and the location of the avoided crossing. The transition to the $^2\Sigma$ surface must compete with the autodetachment probability. Although the excitation probability to the "$^2\Sigma_g$" resonance should be higher (the maximum probability occurs at ~ 2.6 eV), we cannot at this time be certain about the other factors. However, the relatively abrupt onset of the C₂H⁻ signal provides some support for the view that this is the true threshold.

With the introduction of a $^2\Sigma_u$ state which correlates with C₂H⁻ ($^1\Sigma$) + H(^1S), one might plausibly inquire about the direct excitation to this state, ignoring the $^2\Pi_g$ resonance state. O'Malley[33] has considered this case for a diatomic molecule, and concluded that "... the smallness of the overlap integral ... should make the cross section too small to be of much interest." The shape of the dissociative attachment curve should also be different, waning exponentially toward threshold. The relatively abrupt onset observed tends to argue against direct excitation as a major contributor to the dissociative attachment process near threshold.

V. CONCLUSIONS

In attempting to determine D_0(HCC–H) by an alternative impact method, we have searched for evidence of ion-pair formation (C₂H⁻ + H⁺) in the photoionization of
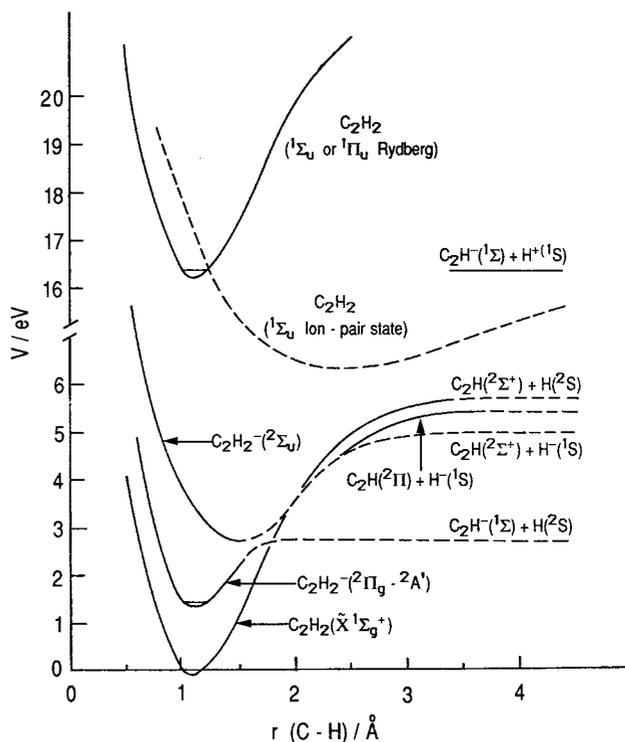

FIG. 5. A schematic, quasidiatomic potential-energy diagram denoting the ground state of neutral C₂H₂, some resonance states of (C₂H₂⁻)*, and the asymptotic products C₂H⁻ + H, C₂H + H⁻, and C₂H + H.

acetylene. Evidence was indeed found for this process, apparently induced by predissociation, with a maximum probability at ~ 660 Å (~ 18.8 eV). The process was weak, and declined gradually in intensity toward threshold. Nevertheless, a distinct threshold was observed at 759 ± 1 Å $\equiv 16.33_5 \pm 0.02_1$ eV, setting an upper limit of $5.70_6 \pm 0.02_2$ eV $\equiv 131.6 \pm 0.5$ kcal/mol for D_0(HCC–H). At higher pressures, a new process generating C₂H⁻ was observed, and assigned to the second-order reactions

$$C_2H_2 + h\nu \rightarrow C_2H_2^+ + e,$$

$$e + C_2H_2 \rightarrow C_2H^- + H.$$
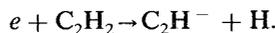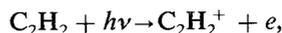
The higher-energy portion of this band (corresponding to the dissociation attachment process) extended to just about the onset of the ion-pair band. For the dissociative attachment process, the kinetic energy of the electrons could be tuned from zero at the photoionization threshold to values as high as ~ 8 eV, by varying the photon energy. A threshold was chosen at $2.71_5 \pm 0.03_2$ eV. When combined with EA(C₂H) = 2.969 ± 0.010 eV,[9] this yields D^0(HCC–H) = $5.68_4 \pm 0.03_3$ eV $\equiv 131.1 \pm 0.7$ kcal/mol. Since ΔH_{f0}^0 (C₂H₂) and ΔH_{f0}^0(H) are well established, ΔH_{f0}^0 (C₂H) = D_0(HCC–H) + 2.85 kcal/mol. Thus, the present results lead to ΔH_{f0}^0(C₂H) $\leqslant 134.5 \pm 0.5$ kcal/mol (from ion-pair formation) and ΔH_{f0}^0(C₂H) = 134.0 ± 0.7 kcal/mol (from dissociative attachment). Baldwin and co-workers[41] have recently measured the velocity of H atoms consequent upon photodissociation of C₂H₂ at 193 nm and other wavelengths, and deduce D_0(HCC–H) between 130 and 132 kcal/mol. They infer that Segall *et al.*[16] were observing fas-

ter H atoms from other photodissociative processes. Hence, the various impact methods appear to be converging on the "higher" value. In particular, the photodissociative ionization threshold for H^+ does not appear to have a serious kinetic shift, in this case.[3] The present experiments yield similar results to those of some earlier electron impact studies,[24,25] but with considerably better resolution.

ACKNOWLEDGMENT

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