An experimental and theoretical determination of the electron affinity of the ethynyl radical, HC₂.

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The cross section for electron photodetachment has been measured for the acetylide anion (HC_2^-) using an ion cyclotron resonance spectrometer in conjunction with a xenon arc lamp. Calculation of the photodetachment behavior near threshold and an estimate of the Franck–Condon factors for the anion→neutral transition allow us to determine $EA(HC_2 \cdot) = 2.94 \pm 0.10$ eV. A theoretical determination using eighth-order perturbation theory gives an adiabatic electron affinity of 3.18 ± 0.25 eV, in good agreement with the experimental result. The use of a thermochemical cycle with the experimental electron affinity and gas-phase acidity data gives a C–H bond dissociation energy in acetylene of 132 ± 5 kcal/mol.

I. INTRODUCTION

Acetylene, one of the simplest organic molecules, is a remarkably strong acid both in the gas phase[1] and in solution.[2] This great acidity must be a consequence of the electron affinity (EA) of the ethynyl radical ($HC_2 \cdot$), since the bond dissociation energy[3] in acetylene is quite large $[DH°(HC_2-H) \cong 120$ kcal/mol]. Although it is obviously important, the EA of the ethynyl radical is not known except for a limiting value[4] $[EA(HC_2 \cdot) \lesssim 3.78$ eV]. Consequently, we have undertaken an experimental photodetachment study and theoretical studies in order to determine its value.

The acetylide anion (HC_2^-) is sufficiently small to be tractable in a sophisticated theoretical treatment, and the experimental results can be compared with the theoretical EA. A recent theoretical determination[5] employing extensive configuration interaction gives $EA(HC_2 \cdot) = 2.14$ eV.

The large bond dissociation energy in acetylene has precluded its direct determination and has led to some confusion regarding the thermochemistry of the ethynyl radical. The best estimates of $\Delta H_f°(HC_2 \cdot)$, by photon impact[6] (5.5 eV) and mass spectrometric methods[7,8] (5.6 eV) give $DH°(HC_2-H)$ of 125 and 127 kcal/mol, respectively,[9] both higher than the accepted value.[3] An alternative method of deriving accurate bond strengths uses a thermochemical cycle to combine electron affinity and gas-phase acidity data.[10] Since the gas-phase acidity of acetylene is known,[11] the key to determining $DH°(HC_2-H)$ is the electron affinity of the ethynyl radical, $EA(HC_2 \cdot)$.

In this paper we present a determination of $EA(HC_2 \cdot)$ by the direct method of photodetachment spectroscopy.[12] We also present a theoretical determination by the many-body perturbation theory method and comment on the validity of the theoretical model employed. Finally, we

derive a value for $DH°(HC_2-H)$ based on the gas-phase acidity of acetylene.

II. EXPERIMENTAL

The acetylide anions were generated and trapped in a modified V-5900 ion cyclotron resonance spectrometer[13] using cell plate potentials similar to those previously described.[14] The cell pressure was 2×10^{-7} Torr, allowing the ions to be trapped for ~ 0.5 s. The acetylide anion was generated via proton transfer from acetylene (Liquid Carbonic) to F⁻ which was formed from NF_3 by dissociative electron impact at 1.7 eV (electron energy minus trapping voltage). Although the proton transfer from acetylene to F⁻ is slightly unfavorable[15] ($\Delta G_{298}° = +1.5$ kcal/mol) this reaction proved to be a good source of acetylide anion.

The light source used for the photodetachment experiments consisted of a 1000-W xenon arc lamp used in conjunction with a grating monochromator. The spectral bandwidth of the monochromator was 58.1 nm (fwhm). Maximum photodestruction of the acetylide anion was 1.8%. The method of data collection and analysis has been previously described.[13b]

III. THRESHOLD SHAPES

The interpretation of experimental photodetachment cross sections is aided greatly with the *a priori* knowledge of the cross section behavior near threshold. A method for treating the photodetachment cross sections of molecular anions[16] has been useful in interpreting data on both localized[10] and delocalized[17] systems. This theory extends the Wigner law[18] to molecular systems by expanding $\sigma(E)$, the photodetachment cross section as a function of energy, in terms of partial cross sections, $\sigma_l(E)$. The partial cross section represents photodetachment into a final state in which the electron and neutral have a relative effective angular momentum of $l\hbar$. This expansion gives

$$\sigma(E) = A_l * k^{2l*+1} [1 + O(k^2)] , \qquad (1)$$

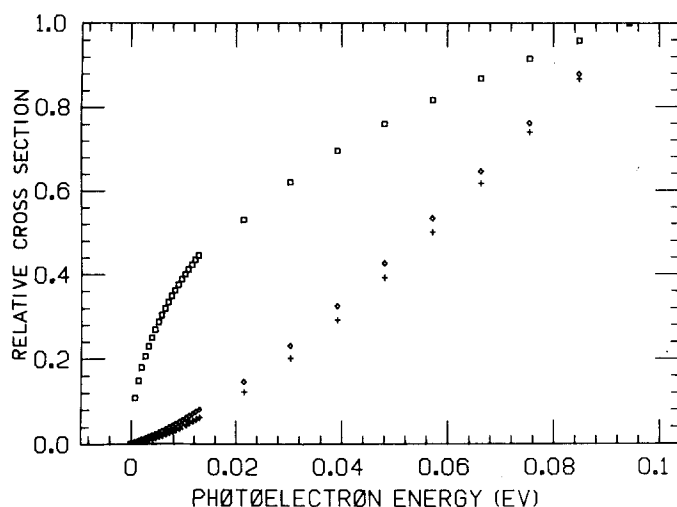where k is the magnitude of the reduced linear momen-

FIG. 1. Calculated photodetachment cross sections for CN^- ($\square$), HC_2^- ($\Diamond$), and C_2^- (+).

tum of the photoelectron $[k = (2m\Delta E)^{1/2}/\hbar]$ and l^* is the *smallest* value of l for which $\sigma_l(E)$ is not identically zero for symmetry reasons. The value of l^* can be determined from group theory and is used to predict the slope of the cross section at threshold.

Applying this formalism to C_2^-, we note that in $D_{\infty h}$, the highest occupied molecular orbital (HOMO) of C_2^- is σ_g^+ which transforms as $l = 0, 2$ giving $l^* = 1$ by the selection rule $\Delta l = \pm 1$. Thus, for C_2^- we predict a p wave behavior, i.e., a cross section which rises with zero slope at threshold $(\sigma \propto E^{3/2})$. By comparison, we next consider CN^- and HC_2^- where the molecular symmetry has been lowered to $C_{\infty v}$. The HOMO for both of these anions (σ^+) leads to $l^* = 0$ and we predict an s wave at threshold $(\sigma \propto E^{1/2})$.

To obtain an analytical description of the C_2^-, CN^-, and HC_2^- photodetachment cross sections, $\sigma(E)$ can be calculated by the one-electron formalism developed by Reed *et al.*[16] By first-order time-dependent perturbation theory, the cross section is proportional to the square of the dipole matrix element

$$\sigma \propto |\langle \psi_i | \mathbf{r} | \psi_f \rangle|^2 \ . \qquad (2)$$

The initial state is taken to be the HOMO of the anion and is determined by an LCAO calculation; the final state is approximated as a plane wave orthogonalized to this HOMO (partially orthogonalized plane wave). The Slater exponents in the HOMO expansion are adjusted to fit atomic photodetachment cross sections; this takes into account the diffuseness of anionic atomic orbitals. The HOMO's from CNDO/2 are

$$\Psi_{C_2^-} = 0.2872 \ \phi_s(C_1) - 0.6462 \ \phi_{p_x}(C_1) + 0.2872 \ \phi_s(C_2)$$
$$+ 0.6462 \ \phi_{p_x}(C_2) \ ,$$

$$\Psi_{CN^-} = 0.1639 \ \phi_s(N) - 0.5616 \ \phi_{p_x}(N) + 0.4550 \ \phi_s(C)$$
$$+ 0.6714 \ \phi_{p_x}(C) \ ,$$

$$\Psi_{HC_2^-} = 0.2320 \ \phi_s(H) - 0.1657 \ \phi_s(C_1) - 0.2486 \ \phi_{p_x}(C_1)$$
$$+ 0.5739 \ \phi_s(C_2) + 0.7263 \ \phi_{p_x}(C_2) \ ,$$

where the molecules lie along the x axis and the hydrogen atom is bonded to C_1 in HC_2^-. Figure 1 shows the calculated photodetachment cross section for these three anions. The calculated cross section for HC_2^- is essentially the same if we use the HOMO from a many-body perturbation theory calculation (see below). The CN^- cross section rises more rapidly than the HC_2^- cross section indicating that the s-wave contribution to the CN^- cross section is much stronger than that in HC_2^-. This is because the σ^+ orbital in CN^- is much more unsymmetrical than that in HC_2^- giving a better s-wave overlap. Thus, by making the σ MO more symmetrical, the s-wave contribution is decreased until in the limiting case (C_2^-) it vanishes completely.

IV. EXPERIMENTAL DETERMINATION OF ELECTRON AFFINITY

The experimental relative photodetachment cross section of HC_2^- is shown in Fig. 2. The theoretical prediction of the acetylide ion photodetachment cross section enables us to choose an accurate photodetachment threshold from the experimental cross section. To accomplish this, we find the theoretical cross section (after convolution with the monochromator slit function) which best describes the experimental data. In Fig. 2 we see that the convoluted theoretical cross section with threshold energy of 2.94 eV provides a very good fit to the data. This analysis works only within the following context: (1) the neglect of rotational broadening, (2) the absence of hot bands, and (3) the absence of a superposition of transitions over the energy range studied. The rotational effects can be ignored since they will be very small (~ 2 nm) compared to the resolution of the experiment. The second assumption is reasonable since the ions are formed via a thermoneutral reaction and thermal excited vibrational populations are negligible (the lowest frequency in HCN, for example, is[19] 712 cm^{-1} and will be populated 3% relative to the ground vibrational state at 300 K). Finally, transitions to excited vibrational levels of the ethynyl radical will be very
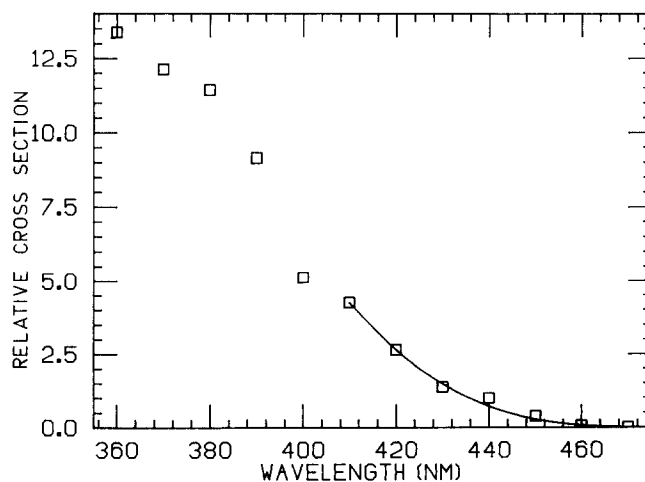

FIG. 2. Experimental photodetachement cross section for HC_2^- ($\square$). Theoretical cross section (threshold energy = 2.94 eV) convoluted with monochromator slit function (—).

TABLE I. Calculated Franck–Condon factors for C–C stretch.

Transition	Franck–Condon factor
$v'' = 0 \rightarrow v' = 0$	0.972
$v'' = 0 \rightarrow v' = 1$	2.76×10^{-2}
$v'' = 0 \rightarrow v' = 2$	8.95×10^{-5}

weak and should not be observed in our spectrum (see below).

The determination of the threshold photodetachment energy only sets an upper limit to the ethynyl radical electron affinity; to determine if the threshold energy corresponds to the adiabatic electron affinity, an estimate of the Franck–Condon factors for the anion → neutral transition must be made. Theoretical work[20] has established that both the anion and radical are linear and that $R_{C-H}(HC_2^-) \approx R_{C-H}(HC_2)$. This leaves the C–C bond length as the remaining degree of freedom to be analyzed. SCF–CI level potential curves for HC_2^- and $HC_2 \cdot$ along the C–C coordinate give[5] $R_{C-C}(HC_2^-) = 1.273$ Å and $R_{C-C}(HC_2 \cdot) = 1.242$ Å. Within the one-dimensional harmonic oscillator assumption[21] we obtain the Franck–Condon factors shown in Table I. Since the adiabatic transition is by far the strongest we conclude that the observed photodetachment threshold corresponds to the adiabatic electron affinity and that $EA(HC_2 \cdot) = 2.94 \pm 0.10$ eV.

V. THEORETICAL DETERMINATION OF THE ELECTRON AFFINITY

The vertical electron affinity of the ethynyl radical was computed at its equilibrium geometry ($R_{CC} = 1.24$ Å) within the Koopmans' theorem[22] (KT), self-consistent field (SCF), approximate all double-excitation configuration interaction[23] (CI), and many-body perturbation theory[24] (PT) approximations. Combining this information with the CI-level potential curves for HC_2^- and HC_2 given in Ref. (5), an adiabatic electron affinity of 3.18 ± 0.25 eV is obtained.

The atomic orbital basis sets used in these calculations were formed by augmenting Dunning's $[9s\,5p/3s\,2p]$ contracted Gaussian (CGTO) basis[25] for carbon. The s, p, and d functions added to Dunning's original set of functions were chosen to yield the lowest possible (SCF) energies for ($^1\Sigma$) HC_2^- and ($^2\Sigma$) HC_2. As a result of this procedure, the terminal carbon atom was augmented with two s-, two sets of p-, and one set of d-type primitive Gaussian orbitals having exponents of 0.07, 0.01, 0.07, 0.01, and 0.068, respectively. The central carbon atom basis consisted of Dunning's functions plus one s-, one p-, and one d-type Gaussian with exponents of 0.05, 0.05, and 0.068, respectively. The hydrogen atom was described within a $[4s/2s]$ contracted GTO basis. The resultant SCF-level energy for H_2C^- obtained within this basis (-76.21150 a.u.) is considerably lower than that computed recently by Grein et al.[5] (-76.19780 a.u.) using a reasonably large set of Gaussian orbitals plus Gaussian bond functions (off-nucleus

orbitals). Because our SCF-level description of the $H_2C \cdot$ radical is given within the spin unrestricted SCF approximation while that reported in Ref. 5 involves a spin restricted approximation, it is not possible to compare the SCF calculations on the radical.

The vertical EA's calculated with the above described basis set within several levels of approximation are listed in Table II. The KT EA, which is given by minus the energy of the HOMO of H_2C^-, is seen to be considerably larger than either the experimental EA (2.94 eV) cited in the present work or the presumably quite accurate PT estimate. As is well known, this is due to the fact that the KT approximation neglects both the orbital relaxation which accompanies electron detachment as well as the dynamical interactions (correlations) among the electrons which serve to differentially stabilize the molecular anion. Both of the SCF-level values reported in Table II tend to underestimate the EA because they incorporate orbital relaxation but still ignore the electron correlation effects which are larger for the anion than for the radical. Both our approximate CI and high-order PT predictions seem to be in reasonably good agreement with the experimental results (2.94 eV) quoted in the present work. Our CI result is a simple Rayleigh–Schrödinger approximation[23] to the true all-doubles CI value. Hence, we believe our eighth-order many-body perturbation theory value (3.13 eV) to be the most accurate of the theoretical predictions and to have a maximum error (due to basis set size primarily) in the EA of ± 0.25 eV.

The fact that our correlated (CI and PT) EA's are considerably different from those of Grein et al. is, in our opinion, most likely a reflection of the not entirely adequate basis set used in Ref. 5. In support of this, we point out that our HC_2^- SCF energy is 0.37 eV lower than that of Ref. 5. In addition, our CI energies for H_2C^- and H_2C are, respectively, 1.1 eV and 0.27 eV lower than those of Ref. 5 (although in Ref. 5 the CI energy for H_2C^- was computed at $R_{CC} = 1.273$ Å). Moreover, the basis used by Grein et al. had no d-type basis functions and contained only diffuse s- and p-type functions located at the center of the carbon–carbon bond. It is our experience in developing the basis used in the present calculations, that the incorporation of diffuse s- and p-type

TABLE II. Vertical electron affinity of $H_2C \cdot$ in eV at $R_{CC} = 1.24$ Å.

Method	EA
Koopmans' theorem	3.44
Self-consistent field[a]	1.57
Approximate configuration interaction	2.88
Eighth-order perturbation theory	3.13
Grein et al. SCF[b]	1.96
Grein et al. CI[b]	2.09

[a]This value involves the spin-unrestricted SCF calculation on $H_2C \cdot$ and is, therefore, not rigorously comparable to the SCF result listed for Ref. 5.
[b]K. Vasudevan and F. Grein, Ref. 5. These authors report the CI value at $R = 1.242$ Å and the SCF value at 1.203 Å.
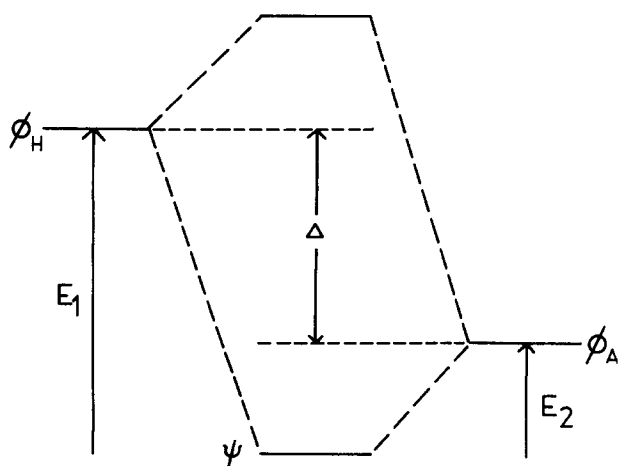
FIG. 3. Perturbation model which shows the relationship between increasing EA and increasing bond dissociation energy.

functions centered on the terminal carbon atom is crucial. The $5\sigma(sp$-hybrid) orbital is highly localized on the terminal carbon; it is primarily this orbital which is involved in the $^1\Sigma \rightarrow \Sigma^2$ detachment process. Hence, the most likely explanation of the discrepancy between our correlated EA and that of Ref. 5 is the inadequacy of the latter basis in describing the lone-pair 5σ orbital of the HC_2^- anion. If this is in fact the case, it is quite likely that accurate Franck–Condon factors could be obtained from Grein's CI-level H_2C^- and $H_2C \cdot$ potential curves. We feel that the anion curve of Ref. 5 may be quite accurate in shape (because of the use of a good bonding basis set) but is likely to be shifted to higher total energy because of errors in treating the nonbonding, 5σ orbital.

Due to the cost involved in computing the highly correlated EA's reported here, we were not able to obtain CI or PT potential energy curves for the anion and radical using our basis set. Instead, we have used Grein's CI-level potential curves for both HC_2^- and $HC_2 \cdot$ to estimate the difference between the vertical EA at $R_{CC} = 1.24$ Å and the adiabatic electron affinity. According to the Grein curves, the increase in the equilibrium C–C bond length in going from the radical to the anion results in a stabilization of 0.25 eV in the anion. Therefore, this value is added to our best vertical EA (3.13 eV) to give an adiabatic EA of 3.18 ± 0.25 eV which is in good agreement with the experimental value of 2.94 ± 0.10 eV.

VI. THERMOCHEMISTRY

The use of a thermochemical cycle with electron affinity and gas phase acidity data provides a means of deriving accurate bond strengths.[10] The most recent determination of the gas phase acidity of acetylene[26] gives $\Delta H^\circ_{298}(C_2H_2 \rightarrow H^+ + HC_2^-) = 378 \pm 3$ kcal/mol which, when combined with our experimental electron affinity, gives a C–H bond dissociation energy in acetylene of 132 ± 5 kcal/mol (5.72 ± 0.23 eV). With this number and[9] $\Delta H_f^\circ(C_2H_2)$ we also obtain $\Delta H_f^\circ(HC_2 \cdot) = 134 \pm 5$ kcal/mol (5.82 ± 0.23 eV). This value is in good agreement with the most direct experimental determinations[6-8] of $\Delta H_f^\circ(HC_2 \cdot)$.

The magnitude of both the C–H bond strength in acetylene and the electron affinity of the ethynyl radical is larger than the corresponding values in ethylene and ethane. The C–H bond strength in ethylene is ≥ 108 kcal/mol and in ethane[27] 93 kcal/mol, and the electron affinity of the ethyl radical, although unknown, if positive must be close to zero. These trends can be best understood in terms of a simple perturbation approach which has been used to explain the trends in bond dissociation energies and electron affinities for simple hydride systems.[28] In this model, an A–H bond MO, ψ, is constructed from atomic orbitals ϕ_A and ϕ_H (Fig. 3). The A–H bond dissociation energy is then given by the energy required to remove the bonding electrons from ψ and put one each in ϕ_A and ϕ_H; this energy is given by $E_1 + E_2$. As the unsaturation increases in the series C_2H_6, C_2H_4, C_2H_2, and amount of s character in the ϕ_A hybrid orbital increases. This *decreases* the energy of ϕ_A and increases the A–H bond dissociation energy $(E_1 + E_2)$. Also, if the magnitude of the perturbation remains constant,[29] any increase in the bond dissociation energy must be paralleled by an increase in $\Delta = E_1 - E_2$. The energy spacing Δ represents the electron affinity of A relative to that of H if Koopmans' theorem[22] is assumed. This follows the expected trend of electron affinities for the series EA (alkynyl) > EA (alkenyl) > EA (alkyl).

VII. CONCLUSIONS

The measurement of the electron photodetachment cross section for the acetylide anion (HC_2^-) has allowed us to determine EA $(HC_2 \cdot) = 2.94 \pm 0.10$ eV. This is in good agreement with a theoretical determination of 3.18 ± 0.25 eV using eighth-order perturbation theory. The experimental result not only provides important thermochemical information but serves as an excellent test of the validity of the theoretical model being employed to calculate the electron affinity. Using the experimental value combined with the gas phase acidity of acetylene, the C–H bond energy in acetylene is estimated to be 132 ± 5 kcal/mol

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