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Photodissociation of acetylene: Determination of $D_0^\infty$(HCC–H) by photofragment imaging

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Acetylene cooled in a He supersonic expansion is photodissociated by excitation in the 201–216 nm region of the $A^1A_u - X^1\Sigma^+_g$ transition. Subsequent ionization of the H-atom fragments by 2 + 1 (243 nm) REMPI, and mass-selected ion imaging allows analysis of the velocity distribution of H-atoms from the HCC $\rightarrow$ C$_2$H + H process. Measurement of the maximum velocity for H atoms from this channel produced by photodissociation of acetylene through the $A^1A_u - X^1\Sigma^+_g$ $V_0^2K_0^0$, $V_1^2K_0^0$, $V_0^2K^0_1$ and $V_0^2K^1_0$ vibronic transitions gives a value for $D_0^\infty$(HCC–H) of 131 ± 1 kcal/mol. Other channels producing hydrogen atoms (including HC$_3$H, C$_2$H + and HCC$_2$H$\rightarrow$HC$_2$H$^+$ C$_2$H$^+$ + H) are detected at all photon fluxes used. These multiphoton channels produce hydrogen atoms with higher translational energy and therefore obscure measurement of the maximum velocity of H atoms produced by single-photon dissociation of acetylene. Reduction of photon flux by more than two orders of magnitude to $\sim 5 \times 10^6$ J/cm$^2$ gives a background, multiphoton, H-atom intensity of <7% of the peak primary dissociation intensity. Because this multiphoton background limits the detectability of fast H atoms from single-photon dissociation of acetylene, the dissociation energy reported here is an upper limit. Calculations of potential rovibronic excitation of the C$_2$H fragment are discussed.

I. INTRODUCTION

The HCC–H bond dissociation energy of acetylene is of considerable interest for the modelling of combustion kinetics. This bond energy may also be used to calculate the heat of formation of C$_2$H, another species of interest in combustion kinetics. Recently a variety of experimental techniques have been employed to measure $D_0^\infty$(HCC–H) and have yielded values ranging from 132 to 126.6 kcal/mol. All of these experiments except Ref. 6 give upper limits to $D_0^\infty$(HCC–H), subject to interpretation of some observed threshold behavior in acetylene. Angularly resolved time-of-flight detection of the C$_2$H heavy fragment by Wodtke and Lee$^2$ yielded a value of 132 ± 2 kcal/mol with some resolution of the C$_2$H internal structure. These experiments were performed using an ArF excimer photolysis laser (193.3 nm). The velocity aligned Doppler spectroscopy (VADS) experiment of Segall, et al.$^3$ involved the measurement of the Doppler width of the Lyman-$\alpha$ hydrogen transition following 193.3 nm photodissociation of acetylene. Segall et al. report a value of $D_0^\infty$(HCC–H) = 127 ± 1 kcal/mol from their experiment. Two separate experiments by Field et al. gave different values for upper limits to $D_0^\infty$(HCC–H). The Zeeman anti-crossing spectroscopy (ZACS) experiment gave a value of 132.290 ± 0.001 (Ref. 4) while the Stark anti-crossing spectroscopy (SACS) experiment gave 126.647 ± 0.003 kcal/mol.$^5$ The work by Ervin et al.$^6$ used photoelectron spectroscopy of the C$_2$H radical and gas phase acidities to calculate a value of $D_0^\infty$(HCC–H) = 131.3 ± 0.7 kcal/mole. Studies of the ionization mechanisms of C$_2$H$_2$ and C$_2$H by Berkowitz and Ruscic give a value of 131.1 ± 0.7 kcal/mole.$^7$ Recent ab initio calculations of this bond energy give values of 130.1 ± 1.0 kcal/mol$^8$ and 131.1 ± 1 kcal/mole.$^9$

The work presented here involves the imaging of the ionized H-atom fragment following dissociation of jet-cooled acetylene. The photofragment imaging technique has been applied to other molecules$^{10}$ and offers many advantages for C$_2$H$_2$. Detection of the H-atom rather than the C$_2$H fragment required a much shorter time-of-flight to spatially resolve the dissociation threshold. Also, the detection of H atoms spatially rather than by arrival time or by Doppler shift permitted collection of angularly resolved data for all angles simultaneously, without convolution due to laser linewidth. This technique probes an entire velocity distribution for each laser shot. In the present study, several rovibronic bands of the acetylene $\tilde{A}^1A_u - \tilde{X}^1\Sigma^+_g$ transition are excited, leading to photodissociation via different combinations of excited state CH bend ($v_3^e$, $v_5^e$ trans-bend denoted $V_0^e$+) and CC ($v_2^e$) or CH stretches ($v_1^e$, symmetric stretch). The angular momentum about the $a$-axis is denoted by $K_0^e$ as in Ref. 11. The selection of a variety of rovibronically analyzed intermediate states$^{12}$ decreased the probability of selective production of vibrationally excited C$_2$H.

II. EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Fig. 1. Acetylene, dissolved in acetone, is purified by cooling in a cold...
finger immersed in a dry ice–isopropyl alcohol bath. An approximately 1-liter reservoir is filled with 200 Torr of the purified acetylene and 800 Torr of helium. This mixture is introduced into the chamber through a General Valve Corp., series 9 molecular beam valve, pulsed at 10 Hz for a duration of 350 μs/pulse. This pulsed jet enters a region evacuated to approximately 10⁻⁴⁻¹⁰⁻⁵ Torr by a turbomolecular pump. A collimated beam is formed by skimming the jet. The beam passes into the scattering chamber evacuated to 4 x 10⁻⁷ Torr by a second turbomolecular pump. The acetylene is photodissociated by a tunable ultraviolet laser (201–216 nm) and the H atoms are ionized by a second laser (243 nm).

The photodissociation laser is a Quanta Ray PDL-2 pulsed dye laser, operated in fourth order of the grating, with no intracavity etalon (0.2 cm⁻¹ resolution), pumped by the second harmonic of an injection-seeded DCR-2A Nd:YAG laser operated at 10 Hz. The dye laser output is frequency doubled in a KD*P crystal and the doubled light is mixed with the fundamental in a BBO crystal. This system produces 1–2 mJ/pulse of light tunable between 201 and 216 nm. This light is focussed onto the molecular beam perpendicular to the direction of the molecular beam propagation. The linear polarization of this laser is oriented either perpendicular or parallel to the molecular beam using a Soleil–Babinet rotator. A second, counter-propagating laser beam (~243 nm) is focussed onto the molecular beam overlapped with the photodissociating laser beam. This light is produced by frequency doubling the output of a second Nd:YAG pumped dye laser and mixing the doubled light with the fundamental of the Nd:YAG laser at 1064 nm. This produces ~2 mJ/pulse of 243 nm light, one half the hydrogen-atom Lyman-α transition frequency. The 243 nm light resonantly excites the ground-state H atoms with two photons to the n = 2 level of hydrogen, and a third photon ionizes the atom. This laser is operated in first order of its grating with no intracavity etalon. Because of the large Doppler width of the H-atom fragments (calculated value of 5 cm⁻¹ for v_H = 9000 m/s), this dye laser is deliberately operated with a large linewidth so that an entire velocity distribution is ionized and imaged during each laser pulse. The linewidth of the doubled and mixed light source is ~3 cm⁻¹ producing an effective linewidth for the two-photon atomic hydrogen transition of ~6 cm⁻¹. The two lasers are temporally overlapped (~1 ns) at the molecular beam. Variation of the time delay between the photodissociation and ionization laser pulses from 0 to 10 ns produces no changes in signal levels or the shape or size of the images. However, images recorded with time delays as large as 50 ns show considerable reduction in sensitivity to H atoms with large velocities perpendicular to the laser propagation axis. This loss of signal is due to fast H-atom fragments moving outside the focal volume of the laser beams prior to the arrival of the ionization laser pulse. All of the images used in the determination of the dissociation energy of acetylene are recorded with less than 10 ns delay between the laser pulses. Images recorded with an unfocussed photodissociation laser beam and a focussed ionization laser beam produce velocity distributions identical to those with both beams focussed and time delays of less than 10 ns. Therefore, we are confident that there is no loss of sensitivity to fast H atoms in these experiments.

Photodissociation studies of the A-X 2Σ⁺ 3Σ⁺ band are
performed using a Coherent 699-29 ring dye laser, pulse dye amplified in three transversely pumped dye cells and a final longitudinally pumped dye cell. The output of this system is doubled and mixed with its fundamental as before to produce a photodissociation laser source with much higher resolution ($\sim 150$ MHz for the fundamental) and frequency stability than the pulsed dye laser. This improvement allows the excitation of single, assigned, rovibronic transitions in the $R$ and $Q$ branches of the $2^3 \Sigma_g^+$ band. It also allows measurement of the linewidths for several lines in the $R$ branch of this band leading to a calculation of a lifetime for this state.

The $H^+$ ions are accelerated into a time-of-flight tube by the electric field between the $+1$ kV repeller plate and the grounded extractor screen at the opening of the time-of-flight tube. The ionized fragments travel down a 5 cm time-of-flight tube and strike the front plate of a Galileo electronics chevron-type microchannel plate (MCP). The front plate is normally at ground potential; however, fragments of a single desired mass are gated for image detection by operating the MCP below threshold voltage across the first plate and pulsing the front of the first plate to $-650$ V at the arrival of the desired mass fragments. During this 100 ns pulse, the MCP voltages are above threshold values. The MCP (gain = $10^6 - 10^7$) is coupled to a phosphor screen at the output of the fiber-optic bundle onto a Peltier-cooled, Photometrics CC200 $384 \times 576$ CCD array. Images are collected and summed over 10 000 laser shots for a typical peak signal level of 150 to 200 events/pixel. By timing the molecular beam to arrive after the laser pulses, we obtain a background image which is subtracted from the photodissociation image to remove the effects of ambient light.

By operating the MCP above threshold voltage, replacing the CCD camera with a Hamamatsu R955 photomultiplier tube, and placing the gates of a pair of Stanford Research Systems SR250 boxcar averagers on the $H^+$ and HCCH$^+$ mass peaks, we simultaneously obtain $H^+$ production and acetylene $1 + 1$ resonance-enhanced multiphoton ionization (REMPI) spectra by scanning the photodissociation laser. In this manner, we are able to locate assigned vibronic transitions in the $A + 14_A - \tilde{X} + + 12_g^+$ band of acetylene for our dissociation experiments.

Images sizes are calibrated by substituting HI for acetylene in the He beam (1:10). HI has a well known dissociation energy [$D^0(\text{HI}) = 3.054 \pm 0.002$ eV] with this calibration, the H-atom velocity uncertainty is limited by the pixel resolution of the CCD detector. The resolution of the detector gives a typical velocity uncertainty of $\sim 2\%$. Initial attempts at calibration using $\text{H}_2S$ in He (1:200) showed significant internal excitation in the HS fragment as well as a separate fast hydrogen atom channel which appears to correspond to removal of $H$ atoms from the HS product. The need for a standard with a narrow H-atom product distribution with only simple, well-resolved structure (corresponding to production of I in both $^2P_{3/2}$ and $^2P_{1/2}$) makes HI an excellent standard.

**III. RESULTS AND ANALYSIS**

Assignments of vibronic features observed in both the acetylene REMPI and $H^+$ production spectra are made by comparison to transition frequencies from Watson, et al. and Van Craen, et al. and by extrapolation to higher energies using the vibrational constants provided in these references. The $V^0_0K^0_0$ and $2^0_0V^0_0K^0_0$ bands of the $A - \tilde{X}$ transition were rovibronically analyzed by Van Craen, et al. while the $V^2_0K^2_0$ and $1^2_0V^2_0K^2_0$ bands are vibrationally assigned here by extrapolation. The rotational temperature of the $C_2H_2$ is obtained by comparison of the rotational distribution in the REMPI spectrum of the $2^0_0V^0_0K^0_0$ band to a calculated spectrum (see Fig. 2). This calculation is based upon the ground state term energies from Watson, the excited state term values of Van Craen, rotational strengths and degeneracies from Herzberg, with a Boltzmann distribution of population in the ground state. The best match of relative line strengths in the unblended $R$ branch of this red degraded band is obtained for a rotational temperature between 35 and 40 K. The $Q$ and $P$ branches are obscured by unassigned transitions in the REMPI spectrum and are therefore not used for this comparison.

Images recorded using the photofragment imaging technique are two dimensional projections of the three dimensional photofragmentation velocity distribution. The cylindrical symmetry of the velocities around the polarization axis of the photodissociation laser allows one to reconstruct the entire three dimensional velocity distribution by performing an inverse Abel transformation. The transformation is not necessary to analyze our data because this experiment requires the measurement of the speed of only the fastest $H$ atoms formed by the HCC--$H^+\cdot C_2H$ + $H$ mech-
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It is possible to measure the speed of the fastest H atom by taking a cross section of the recorded image and measuring the width of the distribution.

Images of the ionized H-atom photodissociation product from the $1 \bar{b} P_0^0 K_0^0$ band with $\sim 2 \text{ mJ}$ of focussed photodissociation laser light give the diffuse image seen in Fig. 3(b). The change in slope at approximately half maximum of the intensity in the cross section of this image [Fig. 3(a)] as well as the large size of this image (approximately twice the width and four times the expected available translational energy at threshold/maximum velocity) suggests the possibility of more than one H atom producing mechanism. The $\text{C}_2\text{H}^+ \text{C}_2(n,v,J) + \text{H}(^2S_{1/2})$ process for H-atom production was studied extensively by Wodtke and Lee. They observed this mechanism for H-atom production over a large range of incident laser powers. Reduction of laser power to 200 $\mu$J [Fig. 3(c) and (d)], 60 $\mu$J [Fig. 3(e) and (f)], and 20 $\mu$J [Fig. 3(g) and (h)] by the insertion of neutral density filters in the laser beam confirms the presence of at least two sources of hydrogen atoms. There is a strong source of relatively slow H atoms with nearly linear dependence on laser power [presumably HCC-H$^+\text{HC}_2(n,v,J) + \text{H}(^2S_{1/2})$]. Along with this primary dissociative channel, there is a secondary source of H atoms with a higher order dependence on incident laser power. This other channel produces a much faster and wider distribution of H-atom velocities.

In order to determine the dissociation energy, $D_0^0$ (HCC-H), from the primary H-atom distribution, it is necessary to measure the velocity of the fastest H atoms, those corresponding to all available energy in translation with no internal excitation of the C$_2$H fragment. This may normally be done by measuring the diameter of the image where the intensity cross section intersects the baseline. However, in these experiments, the intersection of the primary H-atom signal with the baseline is obscured by the H-atom signal from the multiphoton mechanisms. If this background were to lead us to mistakenly select a maximum velocity for the primary channel which were too large, our reported value for the dissociation energy would be low. Likewise if we were to select a velocity which was too small, if for instance the outer edge were hidden under the secondary channel signal, our reported value for the dissociation energy would be too large. At 20 $\mu$J incident power, the residual secondary signal, at velocities corresponding to a dissociation energy less than 131 kcal/mole, is $<8\%$ of the peak intensity for the primary photodissociation channel. This background of secondary H atoms gives a lower limit of detectability for primary photodissociation. The higher spectral density of the narrow linewidth laser used for excitation of the $2 \bar{b} P_0^0 K_0^0$ band gives more single photon dissociation of acetylene (the primary dissociative source of H atoms) at all observed incident laser intensities. This results in a lower background secondary H-atom intensity and lowers our threshold for outer edge detection to $<7\%$ at these higher velocities. Since the edges of the distributions are steep, the measurements of maximum velocities are obtained by linearly extrapolating these edges to the baseline (see Fig. 4).

The results of this extrapolation for the four excitation bands in the $A-X$ transition are presented in Table I. The dissociation energies obtained by this method ranged from 131.0 to 130.4 kcal/mole with an estimated uncertainty in this extrapolation of $\pm 1$ kcal/mole. Therefore, we report a value of $D_0^0$ (HCC-H) = 131 $\pm$ 1 kcal/mole.

Images are taken using both vertically and horizontally (parallel and perpendicular to the detection plane) polarized light for the photodissociation. All of the images show completely isotropic distributions of the H-atom product. Since the images are obtained by excitation via well characterized perpendicular transitions, we would expect to see an isotropic (purely $\sin^2 \Theta$) photofragment distributions about the polarization axis of the photodissociation laser beam if the dissociation were prompt. The observation of an isotropic distribution indicates that the dissociation mech-

![FIG. 3. Cross sections and CCD images for the H atom fragment from photodissociation of acetylene at 203.5 nm ($1 \bar{b} P_0^0 K_0^0$). The incident laser intensity is varied over two orders of magnitude. The H atoms with the largest velocity are seen to have a higher order dependence on laser intensity than the slower atoms. This indicates the presence of at least two different H atom production mechanisms. At the lowest power used [(g) and (h)], the fast atom mechanism is suppressed to $\sim 5\%$ of the peak signal at the velocity corresponding to 127 kcal/mole.](image-url)
nism occurs via a pathway which is slow enough for the orientation of the dissociation axis with respect to the laser polarization to be randomized by molecular rotation. In the REMPI (C$_2$H$_2^+$ detection) spectrum of the $\tilde{A} \rightarrow \tilde{X}$ $^2 \Sigma^+_g$ band of acetylene the use of a high resolution photodissociation source allows the measurement of linewidths for several assigned rovibronic transitions. Linewidths in this band (0.3 to 0.6 cm$^{-1}$) indicate a predissociative lifetime of 10 to 20 ps. Other sources of line broadening such as laser power saturation and Doppler shift (a negligible source of broadening in the molecular beam expansion) could only make our measurement of the lifetime shorter than the actual dissociative lifetime. Appreciable power broadening is unlikely since no apparent change in linewidth is observed over an order of magnitude change in incident laser intensity. Therefore, we conclude that the observed transition linewidth and isotropic distribution of dissociation fragments are the result of a relatively long lifetime ($>10$ ps) for the excited acetylene prior to dissociation.

IV. DISCUSSION

The secondary H-atom background discussed in the previous section presents a limitation to the accuracy of this experiment. It allows the possibility that the photodissociation mechanism selectively produces C$_2$H in some rovibronically excited state, with < 7% of the C$_2$H being produced in the nonrotating, lowest vibronic state. We will discuss here the amount of rotational excitation of the C$_2$H fragment predicted by a simple, purely impulsive model. We will also discuss the possibility of vibrational or electronic excitation in the C$_2$H fragment.

A calculation of the expected rotational excitation imparted to the C$_2$H fragment by the dissociation of the acetylene C-H bond is given here in a treatment similar to that of Tuck and Spiglanin et al. $^{15}$ This purely classical impulsive model depends upon $E^*$, the available energy during dissociation (as much as 10.1 kcal/mole for the $V_0^+$ band), and the transition-state geometry. The amount of rotational excitation is given by

$$E_r = \frac{\mu r_c^2 \sin^2 \gamma_{HCC}}{I_{HCC}} E^*,$$

where $\mu$ is the reduced mass of the departing H and the C atom on which it is pushing, $r_c$ is the distance of that C atom from the center of mass of the C$_2$H fragment, $\gamma_{HCC}$ is the angle of the departing H atom with the CC bond, and $I_{HCC}$ is the moment of inertia of the C$_2$H fragment. We use the geometry of acetylene in the trans-bent $\tilde{A}$ $^1 \Delta_u$ state from So, et al. $^{16}$ for the transition-state geometry although the ground-state C$_2$H fragment is linear with slightly different bond distances. Using the acetylene $\tilde{A}$ $^1 \Delta_u$ values of $\gamma_{HCC} = 121.7^\circ$, $\mu = 0.923$ amu, $r_c = 0.75$ Å, and $I_{HCC} = 14.0$ amu Å$^2$, we obtain a value of $E_r = 0.214$ kcal/mole (74.8 cm$^{-1}$). Decreasing $\gamma_{HCC}$ to 90° gives a maximum value of 0.295 kcal/mole (103 cm$^{-1}$). Changing the geometry of the C$_2$H fragment in this calculation toward the equilibrium $\tilde{X} \tilde{\Sigma}^+$ geometry $^{17}$ will tend to decrease the value of $I_{HCC}$ toward the equilibrium value, 11.7 amu Å$^2$. However, this effect should be more than offset by the increase in $\gamma_{HCC}$, having the net effect of reducing $E_r$. At the equilibrium geometry the bond is linear ($\gamma_{HCC} = 180^\circ$) and $E_r = 0$. This calculation shows the intuitive effect, that a light atom pushing on a heavy fragment, even at a large (~1 Å) distance from the center of mass, imparts only a small torque on the heavier fragment. This small amount of C$_2$H fragment rotation (~2% of the available translational energy) is much smaller than the estimated ± 1 kcal/mole error quoted here, and may therefore be considered a negligible effect in the measurement of the dissociation energy.

Although the mechanism for the dissociation of acetylene is unknown, and therefore the C$_2$H product vibrational state distribution is not easily ascertained, a variety of means are used to minimize the probability that our experiments produce only vibrationally excited fragments. The images recorded in this experiment are produced by excitation of

![Figure 4](image-url)
four different vibrational states of the acetylene \( \tilde{A}^1A_u \) state. If excitation of the \( 2^1V^5 \) vibronic state were to result in vibrationally adiabatic dissociation to the \( \text{C}_2\text{H} \) fragment, retaining one quanta of CC stretch, excitation of the \( V^5 \) state should show an image with 5.3 kcal/mole \( (v_2 = 1840 \text{ cm}^{-1}) \) more translational energy. However, these two states result in images which extrapolate to the same dissociation energy. Similarly, if the \( V^5 \) state were to dissociate adiabatically, retaining five quanta of CCH bend, excitation of the \( V^5 \) vibronic state of acetylene should result in a significantly different measurement of the dissociation energy. Since all of these images extrapolate to the same value of \( D_0^5(\text{HCC-H}) \), we can conclude that the dissociation is vibrationally nonadiabatic.

A second consequence of using several different excitation features to obtain images is that the dissociation is sampled over a range of 5.6 kcal/mole \( (2025 \text{ cm}^{-1}) \). This range of energy is large enough that exclusive production of a single excited fragment vibrational state due to some energy degeneracy is unlikely.

Finally, although the lifetime of \( >10 \text{ ps} \) measured here indicates that the electronically excited acetylene has a relatively long lifetime, if dissociation of the C–H bond were rapid compared to the relaxation of the other nuclei, the difference in CC bond distances between excited acetylene and ground-state, vibrationless \( \text{C}_2\text{H} \) could result in the preferential production of \( \text{C}_2\text{H} \) in an excited vibrational state. In order to estimate the fraction of \( \text{C}_2\text{H} \) fragments produced in the lowest vibrational state, we perform a calculation of Franck-Condon overlap \( (Q_v) \) between acetylene in the \( \tilde{A}^1A_u \) \( (2^6)V^5 \) and \( 2^1V^5 \) vibrational states and \( \text{C}_2\text{H} \) in the \( \tilde{X}^2\Sigma^+ \) \( 3^0 \) and \( 3^1 \) \( (v_3 = \text{the CC stretch in } \text{C}_2\text{H}) \) vibrational states. Harmonic RKR potentials are calculated as in Refs. 18 and 19 using \( v_2 \) and the rotational constant, \( B \), for acetylene from Ref. 11, and for \( v_3 \) and \( B \) for \( \text{C}_2\text{H} \) from Ref. 17. In these calculations, only the CC stretching mode is calculated. The calculation is performed assuming the pseudo diatomic structures \( \text{HC–CH} \) and \( \text{C–CH} \). From the calculated values of the Franck-Condon overlap, we estimate the fraction of \( \text{C}_2\text{H} \) produced in the lowest vibrational state. Following excitation of the \( V^5 \) band (no excitation of \( v_2 \)), we predict the fragment ground-state \( (v_3 = 0) \) population to be \( 30\% \) \( (Q_0/Q_1 = 0.0315/0.105) \) of the excited vibrational state population \( (v_3 = 1) \). If the measured threshold for this band \( (130.7 \text{ kcal/mole}) \) were due to an excited vibrational state, the fraction of lowest vibrational \( \text{C}_2\text{H} \) fragments would be well above the 8% detection limit for the experiment in this sequence (see experimental section). Furthermore, the calculation for vibrationally excited fragments from the \( 2^1V^5 \) band predicts a fractional signal of 59% \( (Q_0/Q_1 = 0.111/0.188) \) for the lowest vibrational state. The detection limit in this experiment is only 7%. From this calculation, we expect population in the lowest vibrational state fragments to be well above the detection limit in both of these experiments.

Excitation of features as low in energy as the \( V^5K^1 \) band at 135.2 kcal/mole show the strong primary H-atom signal. The extrapolation to baseline for the \( V^5K^1 \) band shows 4.5 kcal/mole of translational energy, giving a value of \( D_0^5 = 130.7 \text{ kcal/mole} \). If the photodissociation of acetylene in this experiment were selectively producing \( \text{C}_2\text{H} \) in the \( \tilde{A}^1\text{II} \) state, \( \sim 10 \text{ kcal/mole} \) above the ground state,\(^{2,20} \) these experiments would indicate a value of \( D_0^5 \approx 121 \text{ kcal/mole} \). This result is well outside the range of calculated and observed values discussed in the introduction to this work and therefore seems unreasonably low. We therefore conclude that the \( \text{C}_2\text{H} \) fragments are produced in the ground electronic state. Furthermore, at this excitation energy there is insufficient energy available to populate the \( \text{C}_2\text{H} \) fragment \( \tilde{A}^1\text{II} \) state unless the dissociation energy is smaller than 125 kcal/mole. The electronic assignment of the \( \text{C}_2\text{H} \) fragment is to some extent uncertain; however, we base our analysis on the experimental work of Carrick et al.\(^ {20} \) Our analysis of the vibronic distribution of products could be affected should the presently accepted assignment be proved incorrect.

V. CONCLUSION

The technique of photofragment imaging has unique advantages in the analysis of photofragmentation processes. Unfortunately, the high sensitivity to H atoms in a system as complicated as the photodissociation of acetylene leads to the detection of more than one channel for the production of H atoms. By varying the power and linewidth of the photodissociation laser and selectively exciting several assigned rovibronic transitions, we are able to reduce the higher order channels, relative to the primary \( \text{HCC-H}^\text{n+HCC} \) reaction, to 7% of the peak signal. The main criterion for measuring the dissociation energy of acetylene by this technique is to measure H-atom velocities corresponding to rovibronicless, ground electronic state \( \text{C}_2\text{H} \). Our calculations of rotational and vibronic excitation in the \( \text{C}_2\text{H} \) fragment suggest that the fraction of population in the lowest rovibronic state would be easily detectable if any were produced in the lowest electronic state. Exclusive production of the \( \text{C}_2\text{H} \) fragment in an excited electronic state would lead to an unreasonably low value for the dissociation energy of acetylene, well outside the range of calculated and observed threshold values.\(^{2,9} \) The same secondary H-atom background that limits our sensitivity at high velocities also causes an uncertainty in our extrapolation to baseline. As a result, we report a value of \( D_0^5 (\text{HCC-H}) = 131 \pm 1 \text{ kcal/mole} \). The use of a narrow band laser in some of our experiments allows us to measure a dissociative lifetime in the \( \tilde{A}^1A_u \) \( 2^1V^5 \) state of \( >10 \text{ ps} \).

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9. R. J. Harrison (personal communication).