

Propensities toward $C_2H(\tilde{A}^2\Pi)$ in acetylene photodissociation

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When expansion-cooled acetylene is excited to the $\nu_1''+3\nu_3''$ vibrational level (4 quanta of CH-stretch) and then photodissociated at 248.3 nm, the dominant product channel is $C_2H(\tilde{A}^2\Pi)$. This differs markedly from one-photon 193.3 nm photodissociation, which provides 1200 cm^{-1} less energy and yields $C_2H(\tilde{X}^2\Sigma^+)$ as the primary product. Photodissociation at 121.6 nm yields $C_2H(\tilde{A}^2\Pi)$ exclusively. © 1995 American Institute of Physics.

Although acetylene figures prominently in many areas of chemistry, the dissociation mechanisms and dynamics of its lowest electronically excited states are not well understood. For example, despite the fact that nonadiabatic processes are known to be present and are expected to play a significant role,¹⁻⁷ no detailed model has been put forth for couplings between the excited potential surfaces, and even the surfaces themselves are not established for bond extensions far from equilibrium.⁸ This situation is attributable in part to experimental difficulties involving product detection. Namely, there are few benchmarks against which high-level calculations can be judged. In this Communication we report the vibrationally mediated photodissociation of acetylene brought about by sequential infrared-ultraviolet excitation. Specifically, vibrationally excited acetylene molecules containing 4 quanta of CH-stretch are photodissociated at 248.3 nm. Vacuum ultraviolet (vuv) photodissociation at 121.6 nm is also reported. In both cases, the dominant channel is $C_2H(\tilde{A}^2\Pi)+H$, i.e., the lowest energy channel [$C_2H(\tilde{X}^2\Sigma^+)+H$] is minor.

Early spectroscopic studies indicated that absorption in the region 190–240 nm is due to the $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition.⁹ Progressions of the excited state ν_3' *trans*-bend and ν_2' C–C stretch modes are consistent with a transition from linear $\tilde{X}^1\Sigma_g^+$ to *trans*-bent \tilde{A}^1A_u . Recently, a normal mode analysis for the \tilde{A}^1A_u state has been carried out by Crim and co-workers¹⁰ based on their double resonance studies and other spectroscopic investigations.

Photodissociation via the \tilde{A}^1A_u surface has been studied experimentally at 193.3 nm by using the method of photofragment translational energy spectroscopy. Specifically, Wodtke and Lee showed that the $C_2H(\tilde{X}^2\Sigma^+)$ and $C_2H(\tilde{A}^2\Pi)$ channels (differing by 3692 cm^{-1}) are both present, and that $\tilde{X}^2\Sigma^+$ is dominant.¹ These results were confirmed by other similar studies.^{11,12} It is not surprising that $\tilde{A}^2\Pi$ is observed, since it correlates adiabatically with the \tilde{A}^1A_u state to which ground state C_2H_2 is excited at 193.3 nm and it is believed that $C_2H(\tilde{X}^2\Sigma^+)$ is formed via nonadiabatic predissociative processes.^{1,5}

Dissociation following excitation of \tilde{A}^1A_u also occurs at lower energies. Laser induced fluorescence (LIF) of C_2H_2 has been examined in the 215–240 nm region,^{2-5,7(b),13} i.e., at energies up to and slightly above the $C_2H(\tilde{X}^2\Sigma^+)$ threshold (217 nm). Fluorescence ceased below 215.8 nm, confirming that a predissociation mechanism yields ground elec-

tronic state products.⁵ Furthermore, high-resolution LIF studies^{3,4,7(b)} and quantum beat measurements^{6,7} indicated that coupling between \tilde{A}^1A_u and a low-lying triplet state(s) is involved in predissociation, at least near D_0 . Dissociation at energies between the $C_2H(\tilde{X}^2\Sigma^+)$ and $\tilde{A}^2\Pi$ thresholds was also examined with photofragment translational energy spectroscopy.^{14,15} Ashfold and co-workers reported $C_2H(\tilde{X}^2\Sigma^+)$ *V,R* excitations for $h\nu - D_0 = 1200\text{ cm}^{-1}$;¹⁴ they appear to be in accord with a predissociation mechanism and a very low exit barrier.

From the available data, it appears that photodissociation mechanisms depend on excess energy, changing qualitatively between 217 nm (the $\tilde{X}^2\Sigma^+$ threshold region) and 193.3 nm.

In the present study, the high-*n* Rydberg time-of-flight (HRTOF) technique has been applied to the H atom product to obtain center-of-mass (c.m.) translational energy distributions.¹⁶ H atoms generated from photodissociation of C_2H_2 molecules in a pulsed molecular beam are excited to high-*n* Rydberg states by sequential absorption of 121.6 nm and 366 nm photons. A small percentage of these excited atoms drift with their nascent velocities to a multichannel plate (MCP) detector, where they are detected as ions after being field-ionized in front of the MCP. The flight path is 110.6 cm. Photodissociation was also carried out at 193.3 nm (with improved resolution relative to an earlier report)¹¹ for comparison with the ir+uv experiment. In the latter, C_2H_2 in the pulsed molecular beam was excited to a single $\nu_1''+3\nu_3''$ rotational level, where ν_1'' is the symmetric CH-stretch and ν_3'' is the antisymmetric CH-stretch.^{17,18} The $\nu_1''+3\nu_3''$ vibrational level corresponds to 4 quanta of the CH-stretch local mode (i.e., 004⁻).¹⁹ This excitation step was achieved by using a pulsed Ti:sapphire laser (STI, HRL100Z, 788.6 nm, 30 mJ, 500 MHz linewidth). Vibrationally excited molecules were further excited with 248.3 nm radiation from a KrF excimer laser. The ir radiation is polarized along the flight path while the uv radiation is unpolarized. Photoacoustic spectra and a pulsed wavemeter (Burleigh, WA-4500) were used to match the Ti:sapphire laser frequency to the overtone transitions.¹⁷ Survey scans of acetylene overtone spectra from the molecular beam were carried out as well, and it was found that *R*(1) and *R*(3) transitions yielded the largest signals. TOF spectra for ir+uv photodissociation required averaging results from $\sim 2 \times 10^5$ laser firings.

Figure 1 shows the c.m. translational energy distribution for 193.3 nm photolysis, including tentative assignments.²⁰

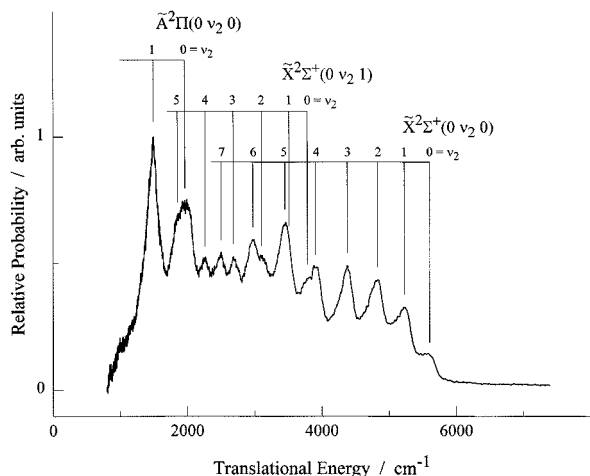


FIG. 1. c.m. translational energy distribution for 193.3 nm photodissociation and tentative assignments of C_2H product states. Note that comb lines indicate peaks in rotational distributions, not vibrational origins.

Rotational excitation of C_2H is modest, so low frequency bending states are resolved in the spectrum. The average C_2H rotational energy is estimated to be $\sim 200 \text{ cm}^{-1}$ after deconvoluting the contributions from the excimer laser linewidth ($\sim 150 \text{ cm}^{-1}$) and the TOF spectrometer. It is clear that C_2H bend and C–C stretch vibrations are excited, in accord with \tilde{A}^1A_u vibrational excitation of the levels $10\nu'_3$ and/or $\nu'_2+8\nu'_3$ by 193.3 nm photoexcitation. It is also clear that ground state $C_2H(\tilde{X}^2\Sigma^+)$ is dominant. An isotropic product angular distribution^{15,21} was confirmed when using polarized photolysis radiation, consistent with an excited state lifetime longer than a rotational period.

Figure 2(a) shows the TOF spectrum for 248.3 nm photodissociation of the level $\nu'_1+3\nu'_3$, $j''=2$. Note that a single 248.3 nm photon has insufficient energy to dissociate C_2H_2 . The thin line is the experimental data (obtained as the difference between spectra recorded with the ir laser on and off) while the thicker line represents the fitted TOF spectrum using a forward convolution program²² with a slight modification. In the fitting procedure, a trial c.m. translational energy distribution, $P(E)$, was used to calculate the TOF distribution convoluted with the spectrometer function. $P(E)$ was optimized by iterative comparison between the calculated and experimental spectra. Figure 2(b) shows the optimized $P(E)$ and tentative assignments. The prominent slow peaks at energies corresponding to $C_2H(\tilde{A}^2\Pi)$ can be assigned to a bending progression. Though the $C_2H(\tilde{X}^2\Sigma^+)$ features suffer from low S/N (signal-to-noise ratio) the peak positions agree with those from 193.3 nm excitation. Moreover, the fitted c.m. translational energy distribution is similar to that obtained from direct conversion of the TOF spectrum, though the latter is much noisier. Figure 2(c) shows the smoothed c.m. translational energy distribution obtained from direct conversion of the TOF spectrum in Fig. 2(a).

Figure 2 indicates that $C_2H(\tilde{A}^2\Pi)$ is favored strongly over $C_2H(\tilde{X}^2\Sigma^+)$ for ir+uv excitation, in contrast with the 193.3 nm result at 1220 cm^{-1} lower energy. $C_2H(\tilde{A}^2\Pi)$ bending levels up to $v_2=3$ are observed. As with 193.3 nm, C_2H rotational excitation is small ($\sim 160 \text{ cm}^{-1}$), which is

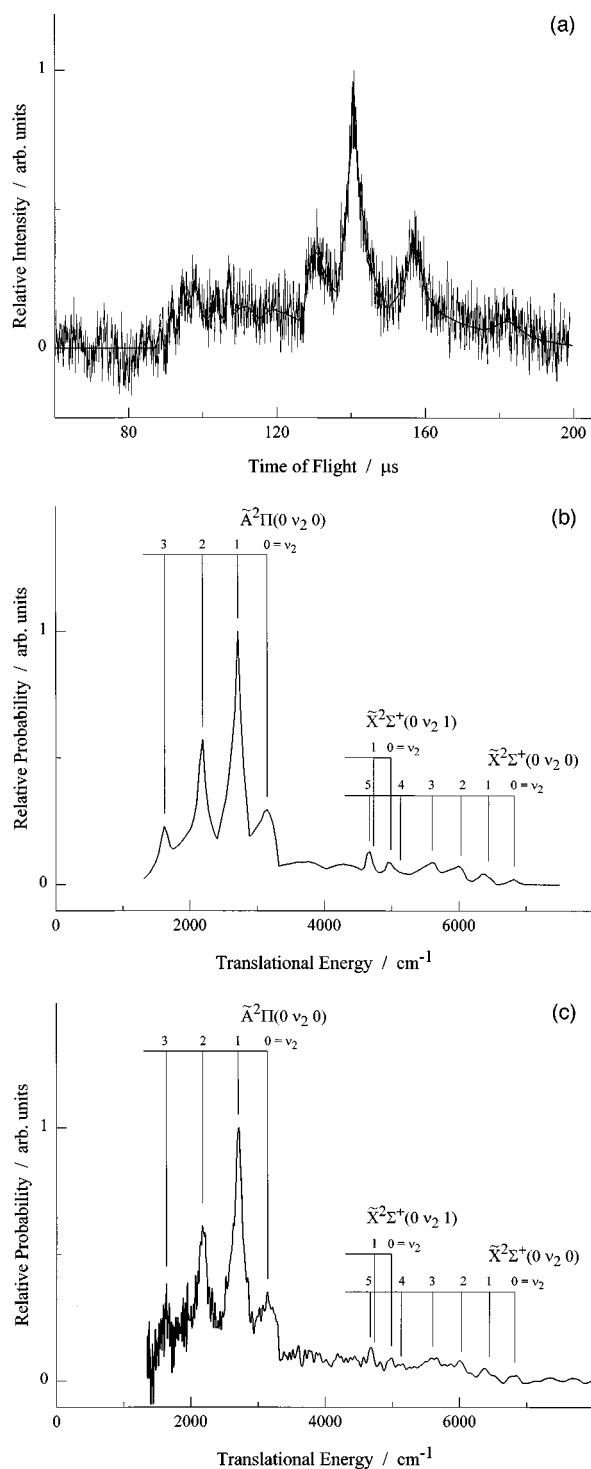


FIG. 2. (a) H atom TOF distribution for double resonance photodissociation; the solid line is the forward convolution fit; (b) c.m. translational energy distribution obtained from the forward convolution; (c) smoothed c.m. translational energy distribution obtained from direct conversion of the H atom TOF distribution in Fig. 2(a).

reasonable on the basis of the modest exit channel recoil imparted by the departing H atom, e.g., with the maximum relative velocity and an impact parameter of $\sim 0.6 \text{ \AA}$, the angular momentum is $\sim 11\hbar$, corresponding to a C_2H rotational energy of $\sim 160 \text{ cm}^{-1}$.

Dissociation for the ir+uv experiment involves

$C_2H(\tilde{A}^1A_u)$. The trans-bent B^1B_u state^{8,9(c)} is inaccessible at the present excitation energies, which are centered around $52\,950\text{ cm}^{-1}$. ir-uv excitation to cis-bent excited states is also unlikely. Detailed information about $C_2H_2(\tilde{A}^1A_u)$ near the energies accessed here is unavailable. However, the normal mode analysis by Crim and co-workers¹⁰ and an ir-uv double-resonance study by Ito and co-workers²³ offer guidance. Since the initially prepared $C_2H_2(\tilde{X}^1\Sigma_g^+)$ vibrational state ($\nu_1''+3\nu_3''$) has b_u symmetry in the C_{2h} point group, the \tilde{A}^1A_u vibrational levels should have b_u symmetry. Note that two-photon excitation leads to \tilde{A}^1A_u ungerade vibrations instead of the *gerade* vibrations accessed by one-photon excitation.^{10,23}

In an ir-uv double resonance study, Ito and co-workers²³ explored the \tilde{A}^1A_u state above the dissociation threshold, i.e., with total energies from $49\,500$ to $\sim 52\,500\text{ cm}^{-1}$. C_2H_2 was prepared initially in $\nu_1''+\nu_3''$, leading to \tilde{A}^1A_u vibrational levels having b_u symmetry. Three bands were assigned to $5\nu_3'+\nu_5'$, $6\nu_3'+\nu_5'$, and $7\nu_3'+\nu_5'$ (or $\nu_1'+\nu_2'+2\nu_3'+\nu_5'$), where ν_1' and ν_5' are symmetric and antisymmetric CH-stretch modes, respectively. Note that the third band coincides with the 193.3 nm photon energy. Vibronic interactions are seen in the spectra, and predissociation appears to be accelerated above $51\,744\text{ cm}^{-1}$. By using the spectroscopic parameters provided by Crim and co-workers,¹⁰ the \tilde{A}^1A_u vibrational levels with b_u symmetry whose energies are closest to our ir+uv energy are found to be $8\nu_3'+\nu_5'$, $\nu_1'+2\nu_2'+2\nu_3'+\nu_5'$, and $2\nu_2'+5\nu_3'+\nu_5'$. The first two states seem to be extensions of the $n\nu_3'+\nu_5'$ and/or $\nu_1'+n\nu_2'+2\nu_3'+\nu_5'$ vibrational progressions observed by Ito and co-workers, though predissociation may be faster in our energy region of $\sim 52\,950\text{ cm}^{-1}$, which is $\sim 1200\text{ cm}^{-1}$ above $7\nu_3'+\nu_5'$ (or $\nu_1'+\nu_2'+2\nu_3'+\nu_5'$). Because of the broad uv laser linewidth ($\sim 70\text{ cm}^{-1}$) and the vibronic coupling it is difficult to assess contributions of different vibrational levels. Furthermore, if the \tilde{A}^1A_u surface is distorted significantly by an avoided crossing in this energy region, assigning vibrational levels is difficult. Symmetry requires that the ir+uv optically accessed \tilde{A}^1A_u vibrations have b_u symmetry, and of the two b_u modes [ν_5' and ν_6' (*cis*-bend)], ν_5' and its combination bands seem the more likely for an initially prepared $C_2H_2(\tilde{X}^1\Sigma_g^+)$ $\nu_1''+\nu_3''$ or $\nu_1''+3\nu_3''$ level.²³ Therefore, it is reasonable that in our ir+uv experiment in the CH-stretch in \tilde{A}^1A_u is excited. Note that 193.3 nm excitation ($\pi-\pi^*$) does not efficiently excite the CH-stretch.

The qualitative mechanism put forward by Wodtke and Lee for 193.3 nm photodissociation starts with initial excitation to high bending levels of \tilde{A}^1A_u . The adiabatic connection of this surface to $C_2H(\tilde{A}^2\Pi)$ involves a barrier which inhibits the efficient production of $\tilde{A}^2\Pi$, and consequently nonadiabatic processes are responsible for the dominant $\tilde{X}^2\Sigma^+$ channel. These arguments were based on intuitive reasoning and theoretical studies of isoelectronic HCN,²⁴ though energies differ significantly, some important features were expected to carry over. Furthermore, it has been shown that triplet surfaces can also be involved in predissociation.^{4,6,7}

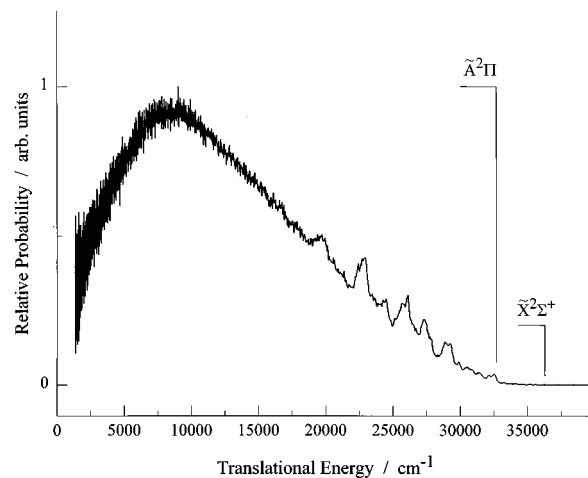


FIG. 3. c.m. translational energy distribution for 121.6 nm photodissociation. Thresholds for $C_2H\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states are labeled.

One possible interpretation of the result shown in Fig. 2 is that the additional 1200 cm^{-1} (relative to 193.3 nm excitation) overcomes a barrier on $\tilde{A}^1A_u(1^1A''$ in C_s symmetry), leading to efficient $\tilde{A}^2\Pi$ production. Alternatively, 4 quanta of CH-stretch moves the Franck-Condon region and may affect nonadiabatic processes. For example, the avoided crossing that accounts for $C_2H(\tilde{X}^2\Sigma^+)$ at 193.3 nm occurs only for significantly bent $C_2H_2(\tilde{A}^1A_u)$, and therefore CH-stretch excitation in the ir+uv experiment may suppress the $C_2H(\tilde{X}^2\Sigma^+)$ channel. In either case, the change in product branching reflects a delicate interplay between the excited potential surfaces.

It was also possible to photodissociate acetylene at 121.6 nm , where a number of C_2H_2 electronic states are energetically accessible²⁵ and where the accessible C_2H doublets are $\tilde{X}^2\Sigma^+$, $\tilde{A}^2\Pi$, and possibly $\tilde{B}^2\Sigma^+$.^{25,26} If C_2H_2 electronic excitation in which an electron is removed from the π system is biased against producing C_2H in the $\tilde{X}^2\Sigma^+$ state, $\tilde{A}^2\Pi$ may dominate. A similar situation was noted for isoelectronic HCN.²⁷

Figure 3 shows the translational energy distribution obtained at 121.6 nm , corresponding to an excess energy of $36\,180\text{ cm}^{-1}$. There is no discernible signal in the energy region between the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ thresholds, suggesting that $\tilde{X}^2\Sigma^+$ is a minor channel. Note that there are no pure $\tilde{A}^2\Pi$ levels, since the zeroth-order $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ levels are coupled by vibronic interaction.²⁸ However, if the excited state dynamics occur on a timescale short compared to the inverse of the coupling matrix elements, $\tilde{A}^2\Pi$ character can dominate. The fact that the distribution peaks $\sim 8000\text{ cm}^{-1}$ indicates that the C_2H product is highly excited (the 121.6 nm photon energy is below the C_2+H+H channel). The fast, structured portion of the spectrum may provide more information about C_2H vibrational levels, and it appears that both bend and C-C stretch are populated. To unravel the dynamics of this system is a task of some proportions.

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