

Autodetachment from Vibrationally Excited Vinylidene Anions

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S Supporting Information

ABSTRACT: Slow electron velocity-map imaging of the cryogenically cooled H₂CC⁻ anion reveals a strong dependence of its high-resolution photoelectron spectrum on detachment photon energy in two specific ranges, from 4000 to 4125 cm⁻¹ and near 5020 cm⁻¹. This effect is attributed to vibrational excitation of the anion followed by autodetachment to $H_2CC + e^{-}$. In the lower energy range, the electron kinetic energy (eKE) distributions are dominated by two features that occur at constant eKEs of 114(3) and 151.9(14) cm⁻¹ rather than constant electron binding energies, as is typically seen for direct photodetachment. These features are attributed to $\Delta J = \Delta K = 0$ autodetachment transitions from two vibrationally excited anion states. The higher energy resonance autodetaches to neutral eigenstates with amplitude in the theoretically predicted shallow well lying along the vinylidene-acetylene isomerization coordinate. Calculations provide assignments of all autodetaching anion states and show that the observed autodetachment is facilitated by an intersection of the anion and neutral surfaces.



Winylidene (H₂CC) is the simplest unsaturated carbene,¹ a key reactive intermediate,^{2–4} and a high-energy isomer of acetylene (HCCH).^{5–7} The potential energy surface (PES) for the benchmark 1,2-hydrogen shift⁸ from vinylidene to acetylene has a small barrier $(\sim 0.1 \text{ eV})$,⁹ allowing for tunneling-induced coupling between vinylidene and vibrationally excited acetylene. While HCCH does not support a bound anion, vinylidene anions are relatively easy to generate in the gas phase, enabling experiments in which photodetachment of H₂CC⁻ is used to characterize the neutral vinylidene isomer and the extent of its coupling to acetylene.^{11–16} Most of this prior work has focused on direct photodetachment of H₂CC⁻ to the neutral + electron continuum. In the current Letter, we consider autodetachment of the anion following vibrational excitation. Such an experiment explores novel aspects of coupling between anionic and neutral vinylidene and probes otherwise inaccessible regions of the H₂CC PES. The experimental results are interpreted with the aid of quantum chemistry and dynamics calculations, a combined approach that has proved fruitful in gaining insights into complex molecular photodetachment processes.

The photoelectron spectrum of the vinylidene anion was first measured by Lineberger and coworkers in 1983.^{11,12} Vibrationally resolved transitions to several electronic states of neutral vinylidene were observed, and comparison of line widths between ground and excited state bands revealed that the ground-state transitions were uniformly broader than those in the excited state spectra.¹² This broadening was attributed to

detachment to a short-lived neutral vinylidene configuration that isomerized to acetylene on a subpicosecond time scale. However, subsequent Coulomb explosion imaging (CEI) measurements¹³ indicated that neutral H₂CC formed by photodetachment is stable on a microsecond time scale, a result consistent with several theoretical studies of vinylidene isomerization dynamics.^{6,19}

Recent work using slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) at Berkeley and highresolution photoelectron imaging at Australian National University^{15,16} has yielded a series of high-resolution vinylidene photoelectron spectra covering electron binding energies (eBEs) from ~0.5 to 5 eV; these spectra include transitions to the singlet ground state and several electronically excited singlet and triplet states of neutral H₂CC. Detachment to the singlet ground state did not show the broadening reported by Ervin et al.¹² With the assistance of quantum dynamics calculations, it was determined that coupling to acetylene only occurs for vinylidene vibrational levels with excitation along the CH₂ in-plane rocking mode (ν_6). This work is consistent with the conclusion of the CEI experiments that neutral vinylidene is (for the most part) stable with respect to isomerization, although the state-specific information obtained

Received: January 15, 2018 Accepted: February 13, 2018 Published: February 13, 2018 from cryo-SEVI reveals that vinylidene–acetylene mixing is indeed promoted by excitation along v_6 . The origin of the broadening in the earlier photoelectron spectrum¹² is unclear. It may reflect higher rotational or vibrational excitation of the anions in that experiment owing to warmer ion source temperatures; photodetachment could then produce internally excited H₂CC that is more strongly coupled to acetylene.

In the process of acquiring the cryo-SEVI spectrum of H_2CC^- , it was observed that the photoelectron kinetic energy (eKE) distribution depended nontrivially on photon energy (*hv*) over narrow energy regions near the adiabatic electron affinity (EA) of H_2CC , 0.4866(8) eV.¹⁶ Such a result is not consistent with direct detachment to the neutral + electron continuum (eq 1), in which intensities are determined primarily by Franck–Condon (FC) factors involving the anion and neutral vibrational levels.

$$H_2CC^- + h\nu \to H_2CC + e^-$$
(1)

In direct detachment, the observed eKEs for each transition simply track the photon energy according to eKE = hv - eBE. The more complex dependence on photon energy observed with cryo-SEVI is a signature of autodetachment (eq 2 and



Figure 1. Schematic energy diagrams showing the detachment mechanisms used to describe the current results for detachment from vinylidene anions. (a) Direct detachment as well as autodetachment to a FC forbidden state (gray neutral energy level) neglecting the rotational manifolds of all three states. (b) Mechanism used to describe the constant-eKE autodetachment structure arising from $\Delta J_{2,3} = \Delta K_{2,3} = 0$ rotational transitions within a single vibrational resonance (see eq 3 for definition of notation). Direct detachment has been omitted from this panel for clarity.

Figure 1a), wherein an initially excited anion state subsequently detaches an electron via a nonadiabatic transition.^{20–22}

$$H_2CC^- + h\nu \to H_2CC^{-*} \to H_2CC + e^-$$
(2)

In this process, the intermediate state can be a vibrationally excited anion in its ground electronic state²³ or an electronically excited anion.^{24–27} As illustrated in the energy diagram of Figure 1a, autodetachment occurs only when hv is resonant with a transition in the anion and can result in the observation of otherwise inaccessible neutral states or eKE distributions that deviate from a FC profile.

Autodetachment from vibrationally excited vinylidene anions has been previously detected by Gerardi et al.,¹⁴ who sought to measure the infrared spectrum of the vinylidene anion using predissociation spectroscopy of messenger-tagged H₂CC⁻. In that work, autodetachment resonances of bare H₂CC⁻ were reported for photon energies just above the EA of H₂CC, and the photon energies at which these transitions occurred were found to correspond to features in the predissociation spectrum of Ar-tagged H_2CC^- . This correspondence indicates that a vibrationally mediated autodetachment process is in play, wherein the anion undergoes vibrational (rather than electronic) excitation and subsequently detaches to the neutral + free electron continuum.

The likelihood of an anion undergoing autodetachment is strongly dependent on the PESs of the relevant anion and neutral states.²¹ There has been much effort to map out global PESs describing both isomers of the neutral vinylidene/ acetylene system,^{9,28,29} although a spectroscopically accurate, full-dimensional PES has only become available somewhat recently.³⁰ The PES for anionic vinylidene has also been developed and successfully used to simulate the spectrum for direct detachment.³¹ Interestingly, the neutral PES possesses a shallow intermediate well between the vinylidene and acetylene isomers that supports bound, delocalized vibrational levels.³¹ Several eigenstates of neutral H2CC were found to be welldescribed as linear combinations of these intermediate-well states with the v_6 fundamental. These states have little or no FC overlap with the anion ground state and are thus unlikely to be observed by direct photodetachment. However, the work presented herein shows that they are accessible via autodetachment.

Details of the cryo-SEVI method and apparatus are provided in Section S1 of the Supporting Information (SI). Figure 2a,b shows the complex structure observed in the H₂CC⁻ cryo-SEVI spectra using photon energies ranging from 4000 to 4125 cm⁻¹ plotted versus eBE and eKE, respectively. Individual scans are provided in Figures S1 and S2 of the SI. This range of photon energies is sufficient to reach only the ground vibrational state of H₂CC by direct detachment, and the trace at hv = 4040 cm⁻¹ in Figure 2a was presented as the high-resolution scan of the vibrational origin in the previously reported cryo-SEVI spectrum of H₂CC⁻¹⁶ Other spectra from 4000 to 4050 cm^{-1} are similarly dominated by a single peak at the vibrational origin, highlighted in gray in Figure 2a, whose eBE is independent of photon energy, as expected for direct detachment. In addition to this structure, there are two features that (in eBE) appear to pass through the vibrational origin as the photon energy is increased, in some cases dominating over the contribution from direct detachment. These shifting peaks are seen over two partially overlapping ranges of hv, 4000-4075 and 4050-4100 cm-

Figure 2b provides an alternate view of the same data, showing that many of the peaks appear at one of two values of constant eKE as the photon energy is varied, as indicated by the shaded regions A and B. This trend is shown more explicitly in Figure 2c, in which the eKEs of major spectral features are plotted versus photon energy and compared with the expected eKE for the vibrational origin (solid line) given the EA of H₂CC. Averaging the data in Figure 2c gives constant eKEs of 114(3) and 151.9(14) cm⁻¹ for features A and B, respectively.

The results in Figure 2a–c indicate that there are significant contributions from processes other than direct photodetachment in the photoelectron spectrum of H_2CC^- for this range of photon energies. Figure 2c shows that the spectral regions of the two constant eKE features are centered around 4050 and 4070 cm⁻¹; these energies line up reasonably well with two of the autodetachment peaks in the infrared photodetachment spectrum obtained by Gerardi et al.,¹⁴ displayed in Figure 2d. The peaks in that spectrum correspond to excitation of vibrationally excited states of H_2CC^- that are embedded in the



Figure 2. (a) H_2CC^- cryo-SEVI data for photon energies ranging from 4000 to 4125 cm⁻¹ plotted versus electron binding energy (eBE). The position of the vibrational origin is highlighted in gray. Individual traces may be found in Figure S1 of the SI. (b) Same cryo-SEVI data as in panel a plotted versus electron kinetic energy (eKE). The constant-eKE features A and B are highlighted in gray. Individual traces are provided in Figure S2 of the SI. (c) Summary of the eKEs of the major structure highlighted in panels a and b, where error bars correspond to 2σ and σ is the width parameter obtained from a Gaussian fit to the experimental feature. The solid line shows the expected eKE for direct detachment to the ground vibrational state of neutral H₂CC. (d) Relevant portion of the photodetachment spectrum previously measured by Gerardi et al.¹⁴ (black) as well as the position of the EA of neutral H₂CC (blue dashed line). The red sticks show the corresponding portion of the simulated infrared spectrum calculated in this work (red, arbitrarily scaled). See the SI (Section S3a and Table S1) for the details of the assignments of features K, L, and M.

neutral continuum and decay by autodetachment, that is, eq 2. We thus attribute the constant eKE features observed with cryo-SEVI to photoelectrons produced by the autodetachment transitions reported in the work of Gerardi et al. One must then elucidate the nature of the anion excitation and formulate a mechanism for autodetachment that explains the constant eKE features.

To assign the anion excitations, we turn to the calculated infrared spectrum of the vinylidene anion, shown fully in the top panel of Figure S3. Details regarding the current theoretical work are provided in Sections S2 and S3 of the SI. The portion of the theoretical spectrum that is relevant to the current discussion is shown in Figure 2d overlaid with the previously reported detachment spectrum.¹⁴ Inspection of the relative oscillator strengths (which have been arbitrarily scaled in Figure 2d) reveals two vibrational transitions (K and M, Table S1) with elevated intensities. These transitions terminate in the 2_15_1 and 1_12_1 vibrational levels of the anion, with calculated frequencies of 4075 and 4116 cm⁻¹, respectively. (Here we adapt a convention in which a vibrational state is represented by its normal-mode numerals with superscripts (subscripts) to denote the corresponding quantum numbers of the neutral (anion).) If the calculated frequencies are each red-shifted by 30-40 cm⁻¹, then they line up well with the first two experimental peaks in Figure 2d, suggesting that those peaks should be assigned as excitations to the 2_15_1 and 1_12_1 anion

states. Given their energies, these levels can autodetach only to the 0^0 level of neutral H₂CC.

To explain the constant eKE features, we consider the full autodetachment process as a vibrational excitation of the anion and subsequent relaxation to the neutral ground state, where each of these states has an associated rotational manifold. Using quantum numbers J and K to specify the rotational state of the near-prolate asymmetric top, the autodetachment process is expressed as

$$H_2CC^{-}(\mathbf{v}_1 = 0, J_1, K_1) + h\nu \to H_2CC^{-}(\mathbf{v}_2, J_2, K_2)$$

$$\to H_2CC(\mathbf{v}_3 = 0, J_3, K_3) + e^{-}$$
(3)

where \mathbf{v}_i represents the full set of vibrational quantum numbers for state *i*. In this labeling convention, state 1 is the anion ground state, state 2 is the anion excited state, and state 3 is the final neutral state. The eKE depends only on the energy difference between states 2 and 3 and can be written as

$$eKE = E_{vib} - EA - \Delta E_{rot}$$
(4)

where $E_{\rm vib}$ is the (rotationless) vibrational energy of the anion excited state, EA = 0.4866 eV is the neutral electron affinity,¹⁶ and $\Delta E_{\rm rot} = E_{\rm rot,3} - E_{\rm rot,2}$ is the change in rotational energy upon detachment.

Our experimental results show that as the detachment laser is tuned across the rotational manifold associated with each vibrational resonance, the eKE given by eq 4 remains constant. Vinylidene ions prepared by cryo-SEVI are rotationally cold, with rotational temperatures of ~ 17 K, as determined by fitting a rotational model to the line shape of the experimental band origin.¹⁶ At this temperature, the $K_1 = 1$ and 0 levels are populated in a 1:3 ratio according to nuclear spin statistics, and there is a small population (~2%) of anions with $K_1 > 1$. Hence, as discussed in more detail in Section S4 of the SI, we expect a range of K_2 levels to be populated as we scan across each resonance. The eKE is constant under these circumstances if ΔE_{rot} is close to 0, which can be satisfied if (a) $\Delta J_{2,3} = \Delta K_{2,3} =$ 0 and (b) the rotational constants of the vibrationally excited anion are similar to those of the 0^0 neutral. On the basis of previous electronic structure calculations of the anion and neutral geometries,^{7,15,16} the latter condition is satisfied insofar as rovibrational coupling is negligible, so we attribute the constant-eKE nature of detachment features A and B to $\Delta J =$ $\Delta K = 0$ transitions between the excited anion and neutral ground vibrational states. This photophysical mechanism is illustrated schematically in Figure 1b for the 2_15_1 resonance, for which $\Delta K_{1,2} = \pm 1$; the three transitions shown in Figure 1b have different excitation energies, but the electrons produced by autodetachment have the same eKE. As $\Delta E_{\rm rot} \approx 0$, the energies of the autodetaching anion states (E_{vib}) in eq 4 are given by $E_{\rm vib}$ = EA + eKE, providing vibrational energies of 4039(7) and 4077(7) cm⁻¹ for the 2_15_1 and 1_12_1 anion states that autodetach to yield features A and B, respectively.

Increasing the photon energy past the range covered in Figure 2 reveals an additional set of autodetaching resonances of the vinylidene anion over a narrower range of photon energies centered around 5020 cm⁻¹ (Figure 3a), resulting in the appearance of three features labeled a, b, and c. This photon energy is higher than those used in the work of Gerardi et al., so these resonances are reported here for the first time. The oscillator strengths in the calculated anion infrared spectrum (Figure S3) are quite small in the $hv \approx 5020 \text{ cm}^{-1}$ vicinity, but two transitions (P and Q) have elevated intensities relative to the other transitions in this region. These terminate in the 5_2 and 1_15_1 vibrational levels of the vinylidene anion (Table S1), with calculated excitation energies of 5066 and 5094 cm⁻¹, respectively. Of these two transitions, the 5_2 feature (P) has higher intensity and is closer to the \sim 5020 cm⁻¹ excitation energy estimated from experiment. Thus the autodetachment transitions which give rise to peaks a, b, and c are assigned to detachment from the 52 state of H2CC⁻ to three vibrational levels of neutral H₂CC.

The binding energies and assignments of these features in the $hv = 5020 \text{ cm}^{-1}$ scan are summarized in Table 1; as discussed further in Section S3 of the SI, the observed peak positions of a-c match well with the relative energies of the neutral eigenstates identified as possessing intermediate-well character $(0^{u}, 0^{g}, 6^{1})$.³¹ (The notation used to label the states containing intermediate-well character is borrowed from ref 31, where the g and u superscripts refer to symmetric and antisymmetric linear combinations of the left- (L) and right-well (R) vibrational states.) The shape of the neutral PES giving rise to these states is shown in Figure 3b along the minimum energy path for isomerization. Thus the autodetachment behavior observed in Figure 3a provides direct observation of the intermediate-well states described by eq S5 in the SI, confirming the multi-well shape of the vinylidene/acetylene PES identified in previous work.³¹



Figure 3. (a) H_2CC^- cryo-SEVI scans showing the autodetachment structure observed for photon energies of ~5020 cm⁻¹. (b) Minimum energy path for the vinylidene–acetylene isomerization and the zeroth-order states in the vinylidene and intermediate wells. The anion potential and its ground vibrational state are also included for comparison.

Table 1. Binding Energies and Shifts from the Vibrational Origin for Autodetachment Features Observed in the cryo-SEVI Spectrum of H_2CC^- Obtained with a Photon Energy of 5020 cm^{-1a,b}

peak	eBE (cm ⁻¹)	shift (cm^{-1})	assn.	theo. $(cm^{-1})^{31}$
a	4119(13)	184	0 ^{<i>u</i>}	183.9
b	4159(10)	224	0 ^g	208.8
с	4206(13)	271	61	283.2

^{*a*}Neutral states involved in the autodetachment transitions are assigned (assn.) and the theoretical energies of these levels with respect to the vinylidene vibrational origin (theo.) are provided for comparison. ^{*b*}eBE uncertainties correspond to one standard deviation of a Gaussian fit to the experimental peak.

The observation of autodetachment transitions requires coupling between the initial anion and final neutral + e⁻ states, which permits the conversion of nuclear kinetic energy (vibrational and rotational) into electronic energy (eKE). The interpretation of the constant eKE features in Figure 2 in terms of $\Delta J = \Delta K = 0$ transitions implies that in the present case the autodetachment transitions are purely driven by vibrational coupling of the anion and neutral electronic states through the nuclear kinetic energy operator. The electronic structure effects that favor such vibrationally induced autodetachment from molecular anions have been explored extensively by Simons, who has used both perturbative and semiclassical approaches to derive explicit expressions for the state-to-state autodetachment transitions are most likely to occur in regions of nuclear configuration (*Q*) space where the anion and neutral PESs are close in energy, resulting in detachment of electrons with relatively low kinetic energies. In particular, if the anion and neutral PESs cross for some intermediate value Q_{0} , then autodetachment (or the reverse process, resonant electron attachment³⁵) is likely to occur between anion and neutral states provided that they have relatively large amplitudes in the vicinity of Q_{0} .

Further exploration of the anion and neutral PESs for the purposes of the current work has revealed such a crossing for the vinylidene system. This crossing seam is characterized in Section S3 and Figure S4 in the SI. The minimum crossing point is very close to the neutral H_2CC equilibrium, lying merely 0.04 eV higher in energy. A first-principles characterization of the nonadiabatic autodetachment dynamics is beyond the scope of this work as it requires treatment of the derivative coupling between the two electronic states. However, the identification of such an anion/neutral surface crossing provides an explanation for the extensive involvement of H_2CC^- for photon energies near the neutral electron affinity.

To conclude, resonant autodetachment from vinylidene anions has been observed in two photon energy windows. All resonances reported here occur at energies sufficiently high that the anion excitation corresponds to a combination or overtone band, and the resultant eKEs indicate conversion of multiple quanta of vibrational excitation into electronic energy. Constant-eKE transitions were observed over a relatively wide range of photon energies and were assigned as $\Delta I = \Delta K = 0$ detachment transitions from the 2_15_1 and 1_12_1 anion states to the 0° neutral state. Additional anion resonances were seen over a narrower range of photon energies centered around 5020 cm⁻¹. These detachment transitions were identified as terminating in neutral vibrational levels with intermediate-well character, confirming the multi-well structure of the neutral H₂CC-HCCH isomerization PES. The nonadiabatic coupling between anion and neutral states that facilitates all of the observed autodetachment transitions is likely due to a crossing of these PESs, which has been reported here for the first time. This set of vinylidene cryo-SEVI data and the accompanying theoretical analysis reveal new subtleties in this benchmark system, highlighting the unexpected complexity of the tetraatomic C₂H₂ molecule.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b00144.

Experimental methods, theoretical methods and results, considerations of constant-eKE autodetachment, Tables S1 and S2, Figures S1–S5. (PDF)

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Notes

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