Photoelectron Imaging of Cyanovinylidene and Cyanoacetylene Anions

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Photoelectron spectroscopy of negative ions has been used extensively to study reactive intermediates that shape the composition of our planet and the Universe. A classic example is the chemistry of vinylidene, :C=CH2, which undergoes a rapid 1,2-hydrogen atom shift to the more stable acetylene structure, HC≡CH, with only a small (2 ± 1 kcal/mol) potential barrier.1−7 In contrast to the neutral, the ground state of the C2H2− anion corresponds to the vinylidene geometry, CCH2−, while the acetylene anion, HCCCN−, is unstable. Thus, photodetachment of C2H2− provides access to the reactive (vinylidene) part of the neutral potential energy surface, where the CCH2− → HCCCN rearrangement ensues on a time scale ≤0.2 ps.1,2

In the present work, we use negative-ion photoelectron imaging to examine cyano-substituted vinylidene and acetylene, :C=CHCN and HC≡CCN, respectively. The relative energetics of the two neutral structures are qualitatively similar to those of vinylidene and acetylene, and so one might expect the behavior of cyanovinylidene to be comparable to that of vinylidene. Namely, CCHCN is expected to undergo rearrangement to the more stable HCCCN structure, with only a small (2.2 kcal/mol) barrier predicted by calculations.8 Small rearrangement barriers are also found for other substituted vinylidenes, such as fluoro-, tert-butyl-, and vinylvinylidenes, which have been studied by both photoelectron spectroscopy9−11 and theory.12,13 Qualitative analysis suggests that the properties of cyanovinylidene should be similar to those of fluorovinylidene, since the CN substituent acts as a pseudohalogen. On the other hand, the conjugated π system with the CN substituent might also result in similarities to vinylvinylidene.

Due to the electron affinity of the CN group, the cyanovinylidene and cyanoacetylene anion structures are affected by the substitution to a greater extent than the corresponding neutrals. In stark contrast to acetylene, the cyanoacetylene anion, HCCCN−, is in fact a stable species.14,15 The large dipole moment and the unsaturated π system of HCCCN are responsible for the predicted existence of dipole-bound and valence anionic states.14 These states have attracted attention not only because of their exotic fundamental properties, including the possible coupling between the dipole-bound and valence states of the anion,14 but also because of the dissociative electron attachment to cyanoacetylene (involving these states) that may play a role in the formation of carbon-rich and CN-containing negative ions in extraterrestrial environments.15−20 However, until recently15 HCCCN− had eluded definitive experimental detection—not only in space but also in the laboratory. Despite the general interest in reactive intermediates, cyanovinylidene has also not been studied by anion photoelectron spectroscopy.

We demonstrate the simultaneous formation of CCHCN− and HCCCN−, providing access (via photodetachment) to both the cyanovinylidene and cyanoacetylene sides of the CCHCN → HCCCN rearrangement reaction. The two isomeric forms of the anion are generated via the competing channels of O− reaction with acrylonitrile, H2C=CHCN. The vinylidene form of the anion is formed via the 1,1-H2− abstraction pathway, while the valence anions of cyanoacetylene are formed via the cis- and/or trans-1,2-H2− abstraction channel(s).15

The cyanovinylidene anion was indicated in a previous study of the reaction of O− with 2-deuterioacrylonitrile (H2C=CDCN),21 but no evidence for the simultaneous formation of the cyanoacetylene anion had been reported. However, HCCCN− was once proposed in electron attachment to acrylonitrile, but that assignment has also not been confirmed.22 The key to the formation of the elusive anion of HCCCN− in the present work is the bent −C≡C−C≡ skeleton of the reactant acrylonitrile, contrasting the corresponding linear arrangement in neutral HCCCN.15 High-level ab initio calculations by Sommerfeld and Knecht predicted a roughly w-shaped equilibrium geometry of valence HCCCN−, which is adiabatically stable with respect to electron detachment by only 50 meV.14

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However, the large geometry difference between HCCCN and HCCCN results in a sizable vertical detachment energy (VDE) of the anion, VDE = 1.04 eV, as determined by photoelectron spectroscopy. This experimental determination is compared to the theoretical prediction of 1.25 eV.

In this work, we characterize the stable valence anions of cyanovinylidene and cyanoacetylene by means of photoelectron imaging spectroscopy at 532 and 355 nm. The two anion isomers show drastically different photoelectron spectra: a broad, unstructured band with no identifiable origin for HCCCN and a resolved vibrational progression assigned to CCHCN. We examine the energetics of the two anion species revealed by their photoelectron spectra and model the vibrational progression in CCHCN using a Franck–Condon simulation based on the parallel-mode approximation and the Duschinsky algorithm.

2. Experimental Arrangement

The experiments were performed using a pulsed time-of-flight mass spectrometer with a velocity-map imaging detector that has been described previously. Anions were generated by the reaction of O− with acrylonitrile. Acrylonitrile vapor was entrained in neat N2O carrier gas with a backing pressure of 20 psi and expanded into high vacuum through a pulsed supersonic nozzle (General Valve, Inc., series 99) operating at a 50 Hz repetition rate. The expanding gas was crossed with a 1 keV electron beam, which produced slow secondary electrons by collisions with the neutral gas molecules. Dissociative electron attachment to N2O generated O−, which in turn reacted with acrylonitrile via the 1,1- or 1,2-H2+ abstraction channels to form the cyanovinylidene and cyanoacetylene anions, respectively.

Thus formed negatively charged ions were extracted into a pulsed time-of-flight mass spectrometer and after acceleration to 3 keV entered a field-free region of the instrument, where the mass-segregated m/z = 51 ions were irradiated with a linearly polarized output of a Nd:YAG laser (Spectra Physics, Inc., model Lab-50). The laser output was frequency doubled or tripled to produce 532 or 355 nm pulses, with a pulse width of ~8 ns and pulse energies of 30 and 10 mJ, respectively. Static electric fields within a velocity-map imaging assembly projected the photodetached electrons onto a position sensitive detector, and the resulting images were captured with a 1 megapixel camera. In all measurements, the laser polarization axis was set parallel to the detector plane. A typical data set included ~10^5 experimental cycles. The final images reported here are the compositions of three to four such data sets.

The nascent three-dimensional photoelectron distributions, which are cylindrically symmetric with respect to the laser polarization axis (z), were reconstructed from the photoelectron images using the inverse Abel transformation implemented in the BASEX program. The electron kinetic energy (eKE) scale was calibrated using the known detachment energy of O−. The photoelectron spectra were obtained by integrating Abel-inverted photoelectron images with respect to the angular coordinate, while integration over a radial range yielded the photoelectron angular distributions (PADs) for the corresponding transitions. The PADs were analyzed to determine the values of the photoelectron anisotropy parameter β, which uniquely describes the angular distribution in a one-photon photodetachment transition.

3. Electronic Structure and Franck–Condon Simulations

Electronic structure calculations were carried out on the B3LYP/aug-cc-pVDZ, MP2/aug-cc-pVDZ, and CCSD(T)/6-311++G** levels of theory using the Gaussian 03 program package. The geometries for the anion and neutral ground and excited states were optimized with normal-mode analysis to confirm the structures corresponded to true potential minima. The energies of the neutral ground and excited states were also calculated at the optimized anion geometry to obtain estimates of the vertical detachment energies.

To simulate photoelectron spectra from the results of ab initio or density-functional theory calculations, we developed a program for calculating Franck–Condon factors of polyatomic molecules, which adopts the general procedure described by Duschinsky. In this approach, the normal modes for the anion are expressed in generalized coordinates Q*, while the coordinates for the neutral are expressed as Q. The two sets of coordinates are related by the Duschinsky rotation matrix J and a displacement vector K.

\[
Q^* = J \cdot Q + K
\]

We calculate J and K from normal coordinates and geometries using the methods outlined by Chen and co-workers for converting Gaussian output from Cartesian coordinates to the generalized coordinates in a home-written LabView program. Evaluation of the multidimensional overlap integrals is a well-known, but generally complicated, problem. We simplify it by making the parallel mode approximation, where J is set equal to the identity matrix I. The Franck–Condon factors then simplify to a set of one-dimensional integrals:

\[
\langle \nu_1' \nu_2' ... \nu_n' | \nu_1 \nu_2 ... \nu_n \rangle^2 = \prod_{i=1}^{n} \langle \nu_i' | \nu_i \rangle^2
\]
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4. Experimental Results and Spectroscopic Assignments

The 532 and 355 nm photoelectron images and the corresponding photoelectron spectra for the $m//z = 51$ anions (CCHCN$^-$ and HCCCN$^-$) are shown in Figure 1. While the 532 nm data were included in our preliminary report, the 355 nm results are presented here for the first time. Both images show two distinct features. In the 532 nm image, the outer band, A, peaks in the direction parallel to the laser polarization axis, while the inner feature, B, consisting of several well-resolved vibrational bands, peaks in the perpendicular direction. In the 355 nm image, the bands are shifted to higher eKE and, owing to the decrease in absolute energy resolution with increasing wavelength, are in excellent agreement. The origin transition, B(0), is centered at eBE = 1.85 eV in the 532 nm spectrum and 1.83 eV in the 355 nm spectrum. The origin transition corresponds to the most intense peak in the vibrational progression. Its energy, therefore, corresponds to both the adiabatic electron affinity of the neutral and the vertical detachment energy (VDE) of the anion.

The above experimentally determined value agrees with the VDE = 1.85 eV predicted at a high level of theory for the cyanovinylidene anion. We therefore assign band B to the photodetachment of CCHCN$^-$.

The energetics and the anisotropy parameters determined for the different spectral features are summarized in Table 1. The anisotropies are average values; uncertainties are standard deviations.

5. Discussion

5.1. Cyanovinylidene and Cyanoacetylene Structures and Energetics

The geometry of cyanovinylidene (S) shown in Figure 2 is very similar to the structure determined using a combination of the Brueckner coupled cluster and DFT methods, BCCSD(T)/cc-pVTZ and B3LYP/aug-cc-pVTZ. The cyanoacetylene anion structure is qualitatively similar to that predicted at the CCSD(T)/aug-cc-pVDZ level of theory, although some of the bond angles are not reproduced very well by the DFT.

The relative energies for the different cyanovinylidene and cyanoacetylene structures obtained using various levels of theory are summarized in Table 2. The diagram is intended as a survey of the relevant structures and energetics. The deficiencies of the inexpensive DFT calculations should not mask the important qualitative features of the potential energy landscape, as the quantitative details can be adjusted whenever higher-level ab initio results are available.

All energies in Table 2 and Figure 3 are in electronvolts relative to the HCCCN (S) ground state. The black and red lines in Figures 1 and 2 correspond to the ground and excited states of cyanovinylidene anions, respectively. The red line is displaced by 0.05 eV.

TABLE 1: Photoelectron Band Energies and Anisotropy Parameter ($\beta$) Values Determined from the CCHCN$^-$ / HCCCN$^-$ Photoelectron Images Shown in Figure 1$^a$

<table>
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<th>band</th>
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<th>eBE (eV)</th>
<th>eKE (eV)</th>
<th>$\beta$</th>
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<td>A</td>
<td>532</td>
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<td>1.29</td>
<td>0.32 ± 0.04</td>
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<tr>
<td></td>
<td>355</td>
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<td>0.06 ± 0.04</td>
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<tr>
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<tr>
<td></td>
<td>355</td>
<td>2.03</td>
<td>1.46</td>
<td>-0.10 ± 0.13</td>
</tr>
</tbody>
</table>

$^a$The anisotropies are average values; uncertainties are standard deviations.
The adiabatic electron affinity of HCCCN cannot be determined from the photoelectron spectra of HCCCN\(^-\), since the corresponding band in Figure 1, band A, shows no identifiable origin. This is due to the large geometry difference between the equilibrium HCCCN\(^-\) and HCCCN structures (Figure 2). However, the above theoretical values for the anion VDE compare reasonably well with the experimental result of 1.04 ± 0.05 eV, especially considering that the electronic structures of weakly bound anions are notoriously difficult to model theoretically.

The purple dashed lines in Figure 3 correspond to the CCHCN\(^-\), trans-HCCCN\(^-\), and cis-HCCCN\(^-\) anion structures obtained from acrylonitrile via the vertical 1,1-H\(_2\)\(^+\), trans-1,2-H\(_2\)\(^+\), and cis-1,2-H\(_2\)\(^+\) abstraction processes (so labeled in the figure), respectively. These structures, referred to as the vertical abstraction geometries, are derived from the equilibrium structure of acrylonitrile with the two indicated hydrogen atoms, plus a charge, removed without changes to other bond lengths or angles (see also Figure 1 in ref 15). Unstable with respect to geometry relaxation, the vertical abstraction structures correspond to the sudden limit of anion formation by H\(_2\)\(^+\) abstraction from acrylonitrile. Although the sudden approximation is admittedly crude, it provides useful guides for estimating the nascent CCHCN\(^-\) and \(^-\) excitations.

The trans-1,2-H\(_2\)\(^+\) vertical abstraction geometry of HCCCN\(^-\) is rather similar to the equilibrium trans structure of HCCCN\(^-\). This structural similarity is the key to the formation of the HCCCN\(^-\) anion.\(^{15}\) The vertical cis-1,2-H\(_2\)\(^+\) abstraction process, on the other hand, yields the anion in the initial cis configuration. The DFT calculations did not locate a local HCCCN\(^-\) minimum corresponding to a cis geometry. That is, while cis-HCCCN\(^-\) is vertically stable with respect to electron detachment, we expect it to be unstable with respect to rearrangement to the trans form of the anion. Therefore, regardless of the mechanistic details, the 1,2-H\(_2\)\(^+\) abstraction reaction should ultimately yield HCCCN\(^-\) anions in their equilibrium trans configuration.

On the other hand, the nascent energies of CCHCN\(^-\) and HCCCN\(^-\) formed by vertical 1,1-H\(_2\)\(^+\) and 1,2-H\(_2\)\(^+\) abstraction from acrylonitrile are estimated to be significantly lower than the barrier separating the cyanovinylidine and cyanoacetylene minimum energy forms of the anion (Figure 3). We therefore predict that the CCHCN\(^-\) and HCCCN\(^-\) products of the O\(^+\) + H\(_2\)CCHCN reaction do not interconvert into one another.

**5.2. Analysis of the CCHCN\(^-\) Spectrum.** Calculations (summarized in Table 2) predict the adiabatic electron binding energy of the cyanovinylidine anion, CCHCN\(^-\), in the range 1.65–2.06 eV. These predictions are in good agreement with the origin of band B in the photoelectron spectra in Figure 1 observed at 1.84 ± 0.01 eV. A comparison with the previously reported spectra of other substituted vinylidenes provides further support for this band’s assignment. Table 3 gives a summary of the eBEs and photoelectron anisotropy parameters determined for the anions of vinylidene, fluorovinylidene, vinylvinylidene, and cyanovinylidene. Since the cyano group acts as a pseudohalogen, we might expect the electron affinity of singlet cyanovinylidene (1.84 ± 0.01 eV) to be comparable to that of the X\(^1\)A\(^\prime\) state of fluorovinylidene. The latter was determined to be 1.718 eV.\(^{15}\)

Since no higher-energy bands are observed in the photoelectron spectra in Figure 1, the first excited state of cyanovinylidene (a\(^1\)A\(^\prime\)) must lie outside the experiment’s energy range. The 3.49 eV energy of 355 nm photons combined with the 1.84 eV electron affinity of the ground singlet state gives a 1.65 eV lower bound for the singlet–triplet splitting. The theoretical results summarized in Table 2 support this conclusion.

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**Figure 2.** Optimized structures of CCHCN\(^-\) and HCCCN\(^-\), CCHCN and HCCCN ground state singlets (S), and the excited state triplet (T) of CCHCN. The inset in the top right shows the predicted geometry of the transition state (TS) on the singlet potential energy surface for the cyanoacetylene rearrangement. All structures shown are from the B3LYP/aug-cc-pVDZ calculations. The bond lengths are indicated in Angstroms. The corresponding state energies are summarized in Table 2.

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**Figure 3.** The adiabatic electron affinity (aBE) of HCCCN cannot be determined from the photoelectron spectra of HCCCN\(^-\), since the corresponding band in Figure 1, band A, shows no identifiable origin. This is due to the large geometry difference between the equilibrium HCCCN\(^-\) and HCCCN structures (Figure 2). However, the above theoretical values for the anion VDE compare reasonably well with the experimental result of 1.04 ± 0.05 eV, especially considering that the electronic structures of weakly bound anions are notoriously difficult to model theoretically.

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**Figure 4.** The adiabatic electron affinity (aBE) of HCCCN cannot be determined from the photoelectron spectra of HCCCN\(^-\), since the corresponding band in Figure 1, band A, shows no identifiable origin. This is due to the large geometry difference between the equilibrium HCCCN\(^-\) and HCCCN structures (Figure 2). However, the above theoretical values for the anion VDE compare reasonably well with the experimental result of 1.04 ± 0.05 eV, especially considering that the electronic structures of weakly bound anions are notoriously difficult to model theoretically.
The results of the B3LYP/aug-cc-pVDZ calculations for CCHCN simulations in the parallel-mode approximation. We used this change expected in the photodetachment of HCCCN and unstructured band A, which corresponds to a large geometry vibrational progression. These properties contrast with the broad width of band B and the appearance of a defined CCHCN(S) structure makes this system suitable for Franck–Condon treatment.

Figure 3. Schematic diagram (not to scale) showing the relative energies of different cyanovinylidene and cyanoacetylene neutral and anion structures. Geometric details of most structures are found in Figure 2. The diagram is based on the results of the B3LYP/aug-cc-pVDZ calculations, supplemented by the relevant experimentally determined values (marked “exp”) and the G3(MP2) and CCSD(T)/aug-cc-pVDZ results from ref 14 (marked with asterisks). The energies are indicated in electronvolts, relative to the ground state of HCCCN. The black and red lines correspond to the neutral and anion structures, respectively. The purple dashed lines correspond to the CCHCN(S), trans-HCCCN*, and cis-HCCCN* anion structures obtained from acrylonitrile via the vertical (sudden) 1,1-H₂⁺, trans-1,2-H₂⁺, and cis-1,2-H₂⁺ abstraction processes, respectively.

The features of band B in Figure 1 support its assignment to the cyanovinylidene anion. The optimized CCHCN⁻ and CCHCN (S) structures shown in Figure 2 are not considerably different. In fact, the optimized geometries of both singlet and triplet cyanovinylidene resemble the corresponding anion structure. The most noticeable change upon anion photodetachment to the singlet occurs in the CCH bond angle, which decreases by 13°. The predicted structural similarity is consistent with the sharp onset of band B and the appearance of a defined vibrational progression. These properties contrast with the broad and unstructured band A, which corresponds to a large geometry change expected in the photodetachment of HCCCN⁻.

The predicted similarity of the optimized CCHCN⁻ and CCHCN (S) structures makes this system suitable for Franck–Condon simulations in the parallel-mode approximation. We used this approach, as described in section 3, in conjunction with the results of the B3LYP/aug-cc-pVDZ calculations for CCHCN⁻ and CCHCN (S) to simulate the photoelectron spectrum of the cyanovinylidene anion. The simulated stick spectrum was convoluted with a Gaussian function to reproduce the observed peak widths and shifted to overlap the band origin in the experimental spectrum. The simulated spectrum is shown in Figure 4, where it is compared to the 532 nm experimental spectrum (band B, reproduced from Figure 1).

The two spectra are in good overall agreement, confirming the validity of the spectral assignment, although the intensities of the higher-order vibrational peaks are not well reproduced. As the simulated spectrum does not involve any fitting parameters, other than a shift of the transition’s origin, an instrumental peak broadening factor, and a scaling factor for frequencies, an exact agreement cannot be expected. The discrepancies are most likely due to the use of the parallel mode approximation used instead of calculating the full multidimensional overlap integrals. Although the full Franck–Condon treatment would likely result in a better fit, our simulation procedure is adequate for assigning the vibrational progression of band B to the X¹A’ state of cyanovinylidene.

The major progression in the simulated spectrum in Figure 4 corresponds to the calculated (unscaled) CCH bend frequency of 924 cm⁻¹. By comparing the optimized geometries in Figure 2, we see the CCH bond angle decreases noticeably upon electron detachment from CCHCN⁻ to the X¹A’ state of CCHCN. The average peak spacing in both the 355 and 532 nm spectra in Figure 1 is in agreement with the calculated frequency. All vibrational modes were included in the simulation, but only the CCH bend shows appreciable intensity in our spectrum.

The lifetimes of reactive intermediates can be estimated by line shape analysis. In the previous studies of vinylidenes,2,9,11 this is done by first modeling the line shapes corresponding to the triplet state to determine the rotational temperature of the ions and then using the result to simulate the rotational profile for the singlet state. The remaining peak width, unaccounted for by the rotational contribution, is attributed to lifetime broadening. In the present experiment, the triplet state is not observed and the rotational temperature of the ions is not known. If we assume that the full width at half-maximum of the B(0) peak in the 532 nm photoelectron spectrum in Figure 1 (∼45 meV) is due to lifetime broadening, the lower limit for the lifetime of cyanovinylidene is estimated to be ∼30 fs.

This limit is consistent with the previous studies of vinylidene, which found lifetimes of 20–200 fs.2  However, it does not take into account the instrumental response and the rotational envelope of the transitions. In the studies of other ions with similar energetics under similar experimental conditions, we found line widths of about 20–25 meV. As a very crude estimate, it can be assumed that a similar line shape accounts for the rotational broadening, the lower limit for the rotational temperature of the ions is not known. If we assume that the full width at half-maximum of the B(0) peak in the 532 nm photoelectron spectrum in Figure 1 (∼45 meV) is due to lifetime broadening, the lower limit for the lifetime of cyanovinylidene is estimated to be ∼30 fs.

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5.3. Photoelectron Angular Distributions. The photoelectron angular distributions may serve as additional indicators of the nature of the initial anion and final neutral electronic states. The PADs reflect the symmetry of the parent orbitals from which the electrons are ejected. Both CCHCN$^-$ and HCCCN$^-$ have planar equilibrium geometries, corresponding to the $C_3v$ symmetry point group and in both cases the highest-occupied molecular orbitals (HOMO) transform under the $a'$ irreducible representation. In general, parallel PADs are usually expected in the photodetachment from totally symmetric orbitals. Among the $C_3v$ point group examples, in the previous study of vinoxide, detachment from the $a'$ orbitals yielded parallel PADs ($\beta > 0$), while detachment from the $a''$ orbitals yielded perpendicular distributions ($\beta < 0$). The same trend was recently demonstrated for the nitromethane anion.37

In the present work, the positive $\beta$ values observed for band A (Table 1) are consistent with the above arguments, considering the $a'$ symmetry HOMO of HCCCN$^-$. However, the PADs for band B (CCHCN$^-$) are predominantly perpendicular in character ($\beta < 0$), even though the band is also assigned to electron detachment from the $a'$ symmetry HOMO. The apparent discrepancy is due to the low symmetry of the $C_1$ point group, where two of the three orthogonal coordinate vectors transform as the nondegenerate representation $a'$. The limitation of the symmetry-based approach can be heightened to the extreme, if one considers an asymmetric molecule ($C_1$ point group), in which all orbitals transform under the same, nominally “totally symmetric” representation. Photodetachment transitions in such anions may still produce PADs of different characters and perpendicular ($\beta < 0$) transitions are not forbidden by any means, while the symmetry analysis becomes trivial and obsolete in such a case. Hence, the strict symmetry-based PAD analysis, proven to be quite powerful for $C_2v$ and higher-symmetry species,38–40 is less useful in systems of reduced symmetry. Even though its utility has been demonstrated in some $C_1$ symmetry cases,36,37 the present contradictory examples of CCHCN$^-$ and HCCCCN$^-$ emphasize the need for other approaches.

The perpendicular PADs observed for CCHCN$^-$ (band B, Table 1) are not surprising, if we compare the reported $\beta$ values with those obtained for other vinylidenes. Table 3 lists the anisotropy parameters reported for the photodetachment of the vinylidene,2 fluorovinylidene,9 and vinylvinylidene10 anions, in comparison to cyanovinylidene. In all available cases, photodetachment to the ground neutral state displays perpendicular PADs ($\beta < 0$). Both fluorovinylidene and vinylvinylidene have $C_2v$ symmetry structures with $a'$ symmetry HOMOs, consistent with the present case of cyanovinylidene. The vinylidene anion has $C_2v$ symmetry, and the lowest photodetachment transition originates from a $b_2$ orbital. Group symmetry analysis for the $C_2v$ point group correctly predicts the perpendicular nature of the PAD in this case.38

Finally, for all vinylidene anions in Table 3, the HOMOs are qualitatively described as carbon $\pi^*$ or $2\pi$ orbitals in the plane of the molecule, which are similar in character to the $\pi^*_g$ ($d_z$-like) HOMO of $O_2^-$. The photodetachment of superoxide is known to yield predominantly perpendicular angular distributions,41–43 lending additional support for the interpretation of the present cyanovinylidene results.

6. Conclusions

The cyanoacetylene and cyanovinylidene anions are generated simultaneously via the competing 1,1-H$_2^+$ and 1,2-H$_2^+$ abstraction channels of O$^-$ reaction with acrylonitrile. Via photodetachment, the two isomeric forms of the anion, separated by a large (~2 eV) potential energy barrier, provide access to both the reactant and the product sides of the neutral cyanovinylidene $\rightarrow$ cyanoacetylene rearrangement reaction.

Using photoelectron imaging spectroscopy at 532 and 355 nm, the adiabatic electron affinity of cyanovinylidene (X$^1\text{A}'$) is

<table>
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<th>neutral molecule electronic state</th>
<th>wavelength (nm)</th>
<th>electron binding parameter, $\beta$</th>
<th>source</th>
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<tr>
<td>$X^1\text{A}_1$</td>
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<td>$X^1\text{A}'$</td>
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<td>-0.399</td>
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The cyanoacetylene and cyanovinylidene anions are generated simultaneously via the competing 1,1-H$_2^+$ and 1,2-H$_2^+$ abstraction channels of O$^-$ reaction with acrylonitrile. Via photodetachment, the two isomeric forms of the anion, separated by a large (~2 eV) potential energy barrier, provide access to both the reactant and the product sides of the neutral cyanovinylidene $\rightarrow$ cyanoacetylene rearrangement reaction.

Using photoelectron imaging spectroscopy at 532 and 355 nm, the adiabatic electron affinity of cyanovinylidene (X$^1\text{A}'$) is
determined to be $1.84 \pm 0.01$ eV, while the first excited state ($a^1A'$) lies at least 1.65 eV higher. Using electronic structure calculations, the equilibrium geometry of CCHCN$^-$ is predicted to be rather similar to that of neutral cyanovinylidene. The major vibrational progression in the $X^1A' \rightarrow X^2A'$ photoelectron spectrum of CCHCN$^-$ is attributed to the excitation of the CCH bending mode. The spectral features are reproduced reasonably well using a Franck-Condon simulation under the parallel-mode approximation, while a crude line shape analysis gives a lower bound for the cyanovinylidene rearrangement lifetime of $\sim$30–35 fs.

In contrast to unsubstituted acetylene, cyanoacetylene has a stable anionic state. The valence HCCCN$^-$ structure, which had until recently eluded experimental detection, is adiabatically weakly bound with respect to electron detachment but has an experimentally determined vertical detachment energy of $1.04 \pm 0.05$ eV.

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References and Notes