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Photoelectron spectroscopy of HC₄N

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We report the 364-nm photoelectron spectrum of HC₄N⁻. We observe electron photodetachment from the bent \(^{2} \Sigma^+\) state of HC₄N⁻ to both the near-linear \(^{1} \Sigma^+\) and the bent \(^{1} \Pi\) states of neutral HC₄N. We observe an extended, unresolved vibrational progression corresponding to \(^{2} \Sigma^+\) \rightleftharpoons \(^{2} \Sigma^+\) photodetachment, and we measure the electron affinity (EA) of the \(^{2} \Sigma^+\) state of HC₄N to be 2.05(8) eV. Photodetachment to the bent \(^{1} \Pi\) state results in a single intense origin peak at a binding energy of 2.809(4) eV, from which we determine the singlet-triplet splitting (ΔEST) of HC₄N: 0.76(8) eV. For comparison and to aid in the interpretation of the HC₄N⁻ spectrum, we also report the 364-nm photoelectron spectra of HCCN⁻ and DCCN⁻. Improved signal-to-noise over the previous HCCN⁻ and DCCN⁻ photoelectron spectra allows for a more precise determination of the EAs and ΔEST of HCCN and DCCN. The EAs of HCCN and DCCN are measured to be 2.001(15) eV and 1.998(15) eV, respectively; ΔEST(HCCN) is 0.510(15) eV and ΔEST(DCCN) is 0.508(15) eV. These results are discussed in the context of other organic carbene chains. © 2011 American Institute of Physics. [doi:10.1063/1.3663617]

I. INTRODUCTION

The cyanopolyne (HCₙN) HC₄N is a carbene (:CXY), as it contains a neutral divalent carbon atom with two electrons occupying two orbitals that lie close in energy. Carbены are highly reactive and serve as important intermediates in chemical reactions, and their reactivity is affected by whether the carbene exists as a singlet or a triplet. The carbene’s substituents determine the electronic ground state of the molecule, as well as the difference in energy between the singlet and triplet states, known as the singlet-triplet splitting (ΔEST).¹ The simplest carbene, methylene (CH₂), possesses a triplet ground state because the energy separation between the σ and π orbitals is less than the electron correlation energy.² The donation of π electrons, e.g., by halogen atoms, tends to increase the separation between the σ and π orbitals, leading to a singlet ground state.³,⁴ Although CN is considered a “pseudohalogen,” it does not donate π electrons. Previous experiments have shown that HCCN has a triplet ground state with a relatively large ΔEST.⁵

In addition to their fundamental importance as carbены, cyanopolyyenes have attracted interest because of their significance in astrophysics. These species are abundant in circumstellar environments of carbon-rich stars and dense molecular clouds; because nitrogen is a major component of interstellar dust, cyanopolyyenes are also important constituents of molecular clouds.⁶ Odd cyanopolyyene chains (HCₙN where n = odd) up to HC₁₁N have been detected in space,⁷ and microwave rotational spectra of odd cyanopolyyenes up to n = 17 have been recorded.⁸ These studies have established that, like the isoelectronic polycylenes HC₂nH, odd cyanopolyyenes possess a linear singlet ground state. The chain has alternating single and triple bonds, giving rise to alternating bond lengths.⁹

There have been many reports of the observation of odd cyanopolyyenes in circumstellar and laboratory environments; however, the same do not exist for the even cyanopolyyenes, implying that odd cyanopolyyenes are more stable than even species.⁶ In fact, McCarthy and Thaddeus report a factor of 10–100 lower abundance of the even cyanopolyyenes HC₄N, HC₆N, and HC₈N as compared to odd cyanopolyyenes of similar length.¹⁰ They attribute this discrepancy to the greater stability of the closed-shell singlet odd cyanopolyyenes as compared to the reactive triplet even cyanopolyyenes, and to the fact that the mechanisms of carbon chain formation¹¹ favor the formation of odd cyanopolyyenes. Furthermore, while the geometry of odd cyanopolyyenes has been characterized, the geometry of the lowest energy isomers of even cyanopolyyenes is not as well understood.

HC₄N is of particular interest to experimental and theoretical groups alike because it is one of the smallest systems calculated to possess multiple low-lying, highly polar carbene isomers.¹² McCarthy and co-workers generated two singlet isomers of HC₄N in a supersonic molecular beam and detected them with Fourier transform microwave (FTM) spectroscopy: a cyanoxyldene carbene structure, NC(H)C≡C≡C:,¹³ and a ring-chain structure.¹⁴ A number of theoretical works have been aimed at understanding the relative stability of various isomers and electronic states;⁶,¹²,¹⁵–¹⁸ for the most part, these studies found that the ring-chain (cyclopropenyldene) singlet isomer of HC₄N is lower in energy.
than the linear chain triplet isomer, but the results were dependent upon the method employed.

There is also question as to whether the structure of the triplet ground state of the chain isomer of HC₄N is linear or bent; it is useful to compare HCC–C–CN with several other triplet carbenes (Scheme 1). In the case of triplet HCC–C–CCH, experiment and theory agree that the triplet is axially symmetric.19 Sanov et al. concluded that triplet NC–C–CN is linear or quasilinear.20 Tang et al. reported the first observation of the triplet ground state of the chain isomer of HCC–C–CN in the laboratory using FTM spectroscopy; with the aid of calculations, they concluded that triplet HC₄N has a very small barrier to linearity (25 cm⁻¹ at CCSD(T)/6-311G(d,p)) and thus can be considered a linear molecule.21 Aoki et al., also using CCSD(T), predict a linear triplet.16 Later, Cer- nicharo et al. reported the observation of the linear triplet form of HC₄N in the carbon-rich IRC + 10216 envelope.22

Here, we present a photoelectron spectroscopy study of the HC₄N⁻ anion. From the 364-nm photoelectron spectrum of HC₄N⁻, we obtain the first experimental measurement of the electron affinity (EA) and ΔE_ST of the chain isomer of HC₄N. For comparison and to aid in our understanding of the HC₄N⁻ spectrum, we also report the 364-nm photoelectron spectra of HCCN⁻ and DCCN⁻ with improved signal-to-noise over the previously published spectrum.5 The improvement in the HCCN⁻ and DCCN⁻ photoelectron spectra allows for better resolution of the vibrational progressions and a more precise determination of the EAs and ΔE_STs of HCCN and DCCN. We compare the HC₄N⁻ and HCCN⁻ (DCCN⁻) spectra and consider them in the context of a broader set of carbene carbon chains.

II. EXPERIMENTAL METHOD

The negative ion photoelectron spectrometer used in this experiment has been described in detail in Refs. 23–25. The apparatus consists of four main sections: an ion source, a mass filter, an interaction region with crossed laser and ion beams, and an electrostatic electron kinetic energy analyzer. Negative ions are formed in a flowing afterglow ion source. A microwave discharge containing trace amounts of O₂ gas in He buffer gas (~0.4 Torr) generates atomic oxygen radical anion, O⁻. To generate HC₄N⁻ anions, tetrolonitrile (H₃C₄N) is added downstream of O⁻ (Scheme 2). Synthetic details for the preparation of tetrolonitrile are presented in supplementary material.26 To make HCCN⁻ anions, acetonitrile (H₂CCN) is added downstream of O⁻: O⁻ + H₂CCN → HCCN⁻ + H₂O. We produce DCCN⁻ using the analogous reaction and beginning with D₂CCN.

Collisions with He buffer gas cool the ions to ~300 K. The flow tube can be further cooled with a liquid nitrogen jacket to obtain a “cold spectrum” of ions with temperatures near 150 K. Anions are extracted into a differentially pumped region and are accelerated to 735 eV before entering a Wien velocity filter with a mass resolution of m/Δm ~ 60.27 With this resolution, we cannot cleanly resolve HC₄N⁻ and H₂C₄N⁻, both of which are produced in the flowing afterglow ion source; however, we select the low-mass side of the m/z ~ 63–64 peak to obtain the spectrum of HC₄N⁻. We also obtained the photoelectron spectrum of neat H₂C₄N⁻ (generated by first reacting O⁻ with CH₄ to produce OH⁻, which then reacts with H₂C₄N to produce H₂C₄N⁻⁻) to ensure that there was no contribution from H₂C₄N⁻ in the HC₄N⁻ spectra. The photoelectron spectrum of H₂C₄N⁻ is a broad, featureless progression that appears at lower binding energy than HC₄N⁻, as shown in Fig. S1.26

The mass-selected ion beam (typically 70 pA) is decelerated to 35 eV and focused into the laser interaction region. Here, the 1 W output from a single-mode continuous-wave argon ion laser operating at 364 nm (3.40814 eV) is built up to ~100 W of circulating power in an optical buildup cavity located within the vacuum system. Photodetachment of an electron yields the neutral species, as depicted for HC₄N⁻ photodetachment in Scheme 3. Photoelectrons ejected in the direction orthogonal to both the laser and ion beams enter a hemispherical energy analyzer. The photoelectron signal is recorded as a function of electron kinetic energy with a position-sensitive detector. The energy analyzer has a resolution of ~11 meV under the conditions used for the present experiments.

The electron kinetic energy (eKE) can be converted to electron binding energy (eBE) through the relationship
eBE = hν - eKE. The absolute kinetic energy scale is calibrated\textsuperscript{23,24,28} before and after each experiment using the well-known EA of atomic oxygen.\textsuperscript{29} Additionally, the energy scale is corrected for a slight linear compression (<1\%)\textsuperscript{23} using the photoelectron spectrum of O\textsubscript{2}\textsuperscript{−}, which provides a number of known transitions spanning the photoelectron energy range.\textsuperscript{30,31} After making these corrections and accounting for the resolution of the spectrometer and rotational peak profiles, absolute electron binding energies can be determined with an accuracy of better than 5 meV.

A rotatable half-wave plate positioned outside the buildup cavity varies the polarization of the photodetachment radiation in order to control the angle \(\theta\) between the electric field vector of the laser beam and the photoelectron collection axis. The photoelectron angular distribution is described by the equation\textsuperscript{32}

\[
I(\theta) = \frac{\sigma_0}{4\pi} (1 + \beta P_2(\cos \theta)),
\]

where \(\sigma_0\) is the total photodetachment cross section, \(\beta\) is the anisotropy parameter, and \(P_2(\cos \theta)\) is the second Legendre polynomial. We measure the anisotropy parameter explicitly by recording the photoelectron signal at the kinetic energy of one suitable intense peak in the photoelectron spectrum as a function of \(\theta\) (between \(\theta = 0^\circ\) and \(\theta = 360^\circ\) in steps of \(10^\circ\)). The photoelectron angular distribution is fit with Eq. (1), and full spectra collected at \(\theta = 0^\circ\) and \(\theta = 90^\circ\) are scaled to match \(\beta\) at the energy at which it was measured. Separately, we collect a photoelectron spectrum at \(\theta = 54.7^\circ\) (the so-called magic angle), where the photoelectron intensity is independent of \(\beta\) and directly reflects the relative photodetachment cross section.

III. THEORETICAL METHODS

All electronic structure calculations were performed using the Gaussian 03 program package.\textsuperscript{33} Optimized geometries, harmonic vibrational frequencies, and normal mode coordinates were calculated at the ROMP2 level of theory\textsuperscript{34} with the 6-311++G(d,p) basis set\textsuperscript{35} for the \(X^2\)\(A''\) states of HC\textsubscript{4}N\textsuperscript{−} and HCCN\textsuperscript{−} (DCCN\textsuperscript{−}) as well as for the \(X^3\)\(A''\) and \(\tilde{\sigma}^1\)\(A'\) states of the neutrals HC\textsubscript{4}N and HCCN (DCCN). All molecules were constrained to \(C_3\) symmetry. For the reported scans along the CCC (HC\textsubscript{4}N) or HCC (HCCN) angle, Figs. 3 and S4 (Ref. 26), the geometries were further constrained so that all but the scanned angles were 180\(^{\circ}\), and the bond lengths were constrained to their optimized values on the anion surface when all but one of the angles was 180\(^{\circ}\).

We employ a Franck-Condon analysis of the vibrational structure in the photoelectron spectra to identify the active vibrational modes and the geometry change upon photodetachment. The Franck-Condon profiles of the photoelectron spectra are simulated with the PESCAL program,\textsuperscript{33} using the calculated geometries, normal mode vectors, and vibrational frequencies of the anion and neutral states. The normal modes and the Duschinsky \(J'\) matrix and \(K''\) displacements are calculated. The Franck-Condon factors are computed in the harmonic oscillator approximation including Duschinsky rotation using the Sharp-Rosenstock-Chen method.\textsuperscript{36} The individual vibronic peak contours are simulated by a Gaussian function with a full-width half-maximum of 11 meV, consistent with instrumental resolution.

Activity of a large-amplitude bending vibration upon photodetachment of the bent HC\textsubscript{4}N\textsuperscript{−} anion to the quasi-linear \(\tilde{X}^3\)\(A''\) state of HC\textsubscript{4}N renders our standard independent harmonic oscillator approximation unsuitable for simulating \(\tilde{X}^3\)\(A''\) \rightarrow \(\tilde{X}^2\)\(A''\) photodetachment of HC\textsubscript{4}N\textsuperscript{−}. A more appropriate treatment of \(\tilde{X}^3\)\(A''\) \rightarrow \(\tilde{X}^2\)\(A''\) photodetachment would utilize a curvilinear HCC–C–CN bending coordinate and a vibration-rotation Hamiltonian that allows for large displacements of the bending coordinate.\textsuperscript{37} However, this more sophisticated treatment is beyond the scope of this work. In our standard Franck-Condon analysis using the Sharp-Rosenstock-Chen method, nonphysical \(K''\) displacements are computed that result in an inadequate simulation of \(\tilde{X}^3\)\(A''\) \rightarrow \(\tilde{X}^2\)\(A''\) photodetachment. For this reason, we will only present partial simulations of the HC\textsubscript{4}N\textsuperscript{−} and HCCN\textsuperscript{−} (DCCN\textsuperscript{−}) photoelectron spectra; full simulations are included in Figs. S3 and S5.\textsuperscript{26}

IV. RESULTS

A. HC\textsubscript{4}N\textsuperscript{−}

1. Photoelectron spectra of HC\textsubscript{4}N\textsuperscript{−}

It is instructive to first consider the valence electronic structure of HC\textsubscript{4}N (Fig. 1) and its implications for the photoelectron spectrum of HC\textsubscript{4}N\textsuperscript{−}. Like HCCN\textsuperscript{−},\textsuperscript{5} the ground state of HC\textsubscript{4}N\textsuperscript{−} is \(\tilde{X}^2\)\(A''\). The excess charge resides primarily on the third carbon atom, and the anion is bent. If an electron is photodetached from the in-plane \(\pi\) orbital to form the \(\tilde{X}^3\)\(A''\) ground state of HC\textsubscript{4}N, the molecule straightens to become quasi-linear. However, if an electron is removed from the out-of-plane \(\pi\) orbital to form the \(\tilde{\sigma}^1\)\(A'\) excited state of HC\textsubscript{4}N, the molecule remains bent in much the same geometry as the anion. Intuitively, we expect the large geometry change upon photodetachment of the bent anion to the quasi-linear triplet ground state to result in an extended vibrational progression at low binding energy in the photoelectron spectrum of HC\textsubscript{4}N\textsuperscript{−}. We expect multiple vibrational modes—especially bending modes involving the carbene center—to
be active upon photodetachment and to contribute intensity to the triplet manifold. Since both the anion and the neutral singlet are bent, we expect significant Franck-Condon overlap between the ground vibrational state of HC \(_4\)N\(^-\) and the singlet state of HC \(_4\)N. This will result in an intense “origin” peak corresponding to the 0-0 transition, and it will appear higher in energy than the triplet state.

The 364-nm, magic angle photoelectron spectrum of HC \(_4\)N\(^-\) is shown in Fig. 2. The spectrum was collected at both room temperature (300 K, blue trace) and at 150 K (black trace). As anticipated, we observe a broad progression at low binding energy, corresponding to photodetachment to the \(X^3\) \(A'\) ground state of HC \(_4\)N. The large geometry change that occurs upon \(X^3\) \(A'\) \(\leftrightarrow X^3\) \(A''\) photodetachment precludes the observation of the origin peak. Additionally, because there are multiple active modes upon photodetachment—particularly the low frequency HCC—C-CN bend—we observe a congested spectrum and are unable to resolve individual vibronic peaks in the triplet envelope. Therefore, we cannot measure vibrational frequencies of the \(X^3\) \(A''\) ground state of HC \(_4\)N. Though we do not resolve an origin peak from which we can determine the EA, comparison of the 300 K and 150 K spectra shows that the EA of HC \(_4\)N is 2.05(8) eV (Table I). The 300 K spectrum displays a sharp onset at 2.00 eV; in the 150 K spectrum, the intensity between 2.00 and 2.05 eV is suppressed. This indicates that the intensity observed between 2.00 and 2.05 eV in the 300 K spectrum results from hot bands or vibronic transitions arising from vibrationally excited anions. In the 150 K spectrum, we observe intensity above the baseline beginning at \(\sim\)2.05 eV, and we begin to resolve two features between 2.00 and 2.15 eV (see inset of Fig. 2). Unfortunately, the substantial geometry change in coupled modes means that the independent mode Franck-Condon simulation is not even qualitatively reliable\(^4\),\(^{38}\) and cannot help in estimating a lower bound for the origin (EA) of the triplet state. Because the features in the origin region are not well resolved, we assign the EA of HC \(_4\)N to be 2.05 eV—where we see appreciable intensity above the baseline in the cooled spectrum—with an uncertainty that encompasses both the shelf in the 300 K spectrum and the two small features in the 150 K spectrum. Thus, the EA of HC \(_4\)N is measured to be 2.05(8) eV.

At higher binding energy, a sharp feature appears at eBE \(= 2.809(4)\) eV. The polarization dependence of the photoelectron spectrum of HC \(_4\)N\(^-\) is given in Table I and is shown in Fig. S2;\(^{26}\) the difference in the \(\beta\) anisotropy parameters between the broad progression beginning at 2.05(8) eV and the sharp feature at eBE \(= 2.809(4)\) eV indicates that these features result from two different electronic states of HC \(_4\)N. The peak at eBE \(= 2.809(4)\) eV corresponds to the origin of the \(\tilde{a}^1\) \(A'\) excited state of HC \(_4\)N. Because the geometry of the \(X^2\) \(A''\) state of HC \(_4\)N\(^-\) and the \(\tilde{a}^1\) \(A'\) excited state of HC \(_4\)N
are both bent, we observe a very prominent \( \beta \) origin peak. We measure the singlet-triplet splitting (\( \Delta E_{0\Sigma} \)) of HC\( \text{4N} \) to be 0.76(8) eV (Table I).

The most striking—and most curious—difference between the 300 K and 150 K HC\( \text{4N} \) spectra shown in Fig. 2 is the appearance of an additional sharp feature at 3.106(4) eV in the 150 K spectrum. The intensity of this peak, which is separated from the \( \tilde{\alpha}^{1}A' \) origin by 2395 cm\(^{-1} \), fluctuated with respect to the \( \tilde{\chi}^{3}A'' \) and \( \tilde{\alpha}^{1}A' \) features throughout the day and from day to day, and it was never observed at room temperature. The eBE of this feature suggests that it is a CN stretch.

### 2. Electronic structure calculations for HC\( \text{4N} \)

As discussed in Sec. III, our standard Franck-Condon analysis of the HC\( \text{4N} \) photoelectron spectrum is inadequate for modeling \( \tilde{\chi}^{3}A'' \leftarrow \tilde{\chi}^{2}A'' \) photodetachment. Using ROMP2/6-311++G\((d,p)\), we calculate the EA(HC\( \text{4N} \)) to be significantly greater than the measured EA of 2.05(8) eV (Table I); Kalcher’s ACPF calculation (using the averaged coupled pair functional in conjunction with the ROHF wave function for the anion and triplet state of the neutral, and the CAS(2,2) wave function for the singlet state of the

### TABLE III. Calculated (ROMP2/6-311++G\((d,p)\)) unscaled, harmonic frequencies of \( \tilde{\chi}^{3}A'' \) HC\( \text{4N} \) and the \( \tilde{\chi}^{3}A'' \) and \( \tilde{\alpha}^{1}A' \) states of HC\( \text{4N} \). The measured CN stretch frequency is listed in italics below the calculated value. Computed \( K'' \) displacements (PESCAL) are also listed. The computed \( \tilde{\chi}^{3}A'' \leftarrow \tilde{\chi}^{3}A'' \) \( K'' \) displacements do not accurately represent the geometry change that takes place upon photodetachment and result in a Franck-Condon simulation that does not reproduce the observed triplet progression (Fig. S3) (Ref. 26).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>HC( \text{4N} )</th>
<th>( \tilde{\chi}^{3}A'' \leftarrow \tilde{\chi}^{2}A'' )</th>
<th>( \tilde{\alpha}^{1}A' \leftarrow \tilde{\chi}^{3}A'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{1} )</td>
<td>CH stretch</td>
<td>3521.5</td>
<td>(-0.0093727 )</td>
<td>3494.4</td>
</tr>
<tr>
<td>( \nu_{2} )</td>
<td>CN stretch</td>
<td>2159.8</td>
<td>(-0.12460 )</td>
<td>2309.5</td>
</tr>
<tr>
<td>( \nu_{3} )</td>
<td>CCC asym stretch</td>
<td>1937.7</td>
<td>(-0.052916 )</td>
<td>1714.3</td>
</tr>
<tr>
<td>( \nu_{4} )</td>
<td>CCC asym stretch</td>
<td>1215.3</td>
<td>(-0.044035 )</td>
<td>1308.1</td>
</tr>
<tr>
<td>( \nu_{5} )</td>
<td>CCC sym stretch</td>
<td>812.1</td>
<td>(-0.48678 )</td>
<td>651.6</td>
</tr>
<tr>
<td>( \nu_{6} )</td>
<td>HCC–C–CN bend</td>
<td>580.3</td>
<td>0.48465</td>
<td>353.7</td>
</tr>
<tr>
<td>( \nu_{7} )</td>
<td>HCC–C–CN rocking</td>
<td>407.6</td>
<td>0.23376</td>
<td>214.0</td>
</tr>
<tr>
<td>( \nu_{8} )</td>
<td>H wag</td>
<td>283.2</td>
<td>0.29055</td>
<td>589.1</td>
</tr>
<tr>
<td>( \nu_{9} )</td>
<td>HCCC–C–N bend</td>
<td>153.6</td>
<td>1.7090</td>
<td>286.0</td>
</tr>
<tr>
<td>( \nu_{10} )</td>
<td>H wag</td>
<td>403.4</td>
<td>0</td>
<td>491.8</td>
</tr>
<tr>
<td>( \nu_{11} )</td>
<td>N–C–C bend</td>
<td>336.3</td>
<td>0</td>
<td>177.7</td>
</tr>
<tr>
<td>( \nu_{12} )</td>
<td>NCC–C–CH bend</td>
<td>155.7</td>
<td>0</td>
<td>297.2</td>
</tr>
</tbody>
</table>

\( ^{a} \)Experiment, this work.
neutral) also overestimates the EA by ~250 meV. The calculated geometry change upon photodetachment is illustrated in Table II, and the calculated vibrational frequencies are listed in Table III. As expected, a large geometry change is calculated to occur upon $\tilde{X}^3A'' \rightarrow \tilde{X}^2A''$ photodetachment, which results in the observed extended vibrational progression. Specifically, the C2–C3 bond length decreases by 0.059 Å, while the $\angle$C2–C3–C4 increases by 28.2° as the molecule becomes nearly linear. Previous studies seem to favor a linear $\tilde{X}^3A''$ structure, while our calculations predict a slightly bent equilibrium geometry. Though we calculate the minimum to occur at a $\angle$C2–C3–C4 of 147.8° (Table II), a one-dimensional potential cut along the $\angle$C2–C3–C4 bending coordinate (Fig. 3) reveals that the $\tilde{X}^3A''$ state of HC$_4$N is extremely floppy with a barrier to linearity of only ~24 meV. The one-dimensional cuts also reveal that as C2–C3–C4 becomes more bent, the triplet and singlet states cross. The unresolved nature of the triplet vibrational progression prevents us from determining the geometry of the $\tilde{X}^3A''$ state from the photoelectron spectrum. Activity of this large-amplitude bending motion is the source of the breakdown of the independent harmonic oscillator analysis (see Fig. S3 for the $\tilde{X}^3A'' \rightarrow \tilde{X}^2A''$ photodetachment spectrum). Such failure of the harmonic, normal mode analysis has been observed in other floppy systems undergoing large amplitude geometry changes upon photodetachment.

The partial simulated HC$_4$N$^-$ spectrum, which shows only those features arising from $\tilde{a}^1A' \leftarrow \tilde{X}^2A''$ photodetachment, is shown in Fig. 2 in purple, with gray sticks representing individual calculated vibronic transitions. The simulation uses the calculated geometries, $\mathbf{K}$ displacements, and vibrational frequencies (Tables II and III). The calculated $\tilde{a}^1A'$ origin, using either ROMP2 or ACPF, is lower than the measured value of 2.809(4) eV (Table I); therefore, we use the observed $\tilde{a}^1A'$ origin in the simulation. The simulation of $\tilde{a}^1A' \leftarrow \tilde{X}^2A''$ photodetachment is very successful. Both the HC$_4$N$^-$ anion and the $\tilde{a}^1A'$ excited state of HC$_4$N are bent ($\angle$C2–C3–C4 ~ 120°). None of the internal coordinates of HC$_4$N$^-$ undergo a significant change upon photodetachment to the $\tilde{a}^1A'$ state, resulting in a very prominent origin peak and a modest vibrational progression. The simulation reproduces the temperature-dependent peak that appears at 3.106(4) eV. The simulation confirms that this feature arises primarily from activation of the $v_2$ CN stretch as well as activity of $v_3$ (C1–C2 asymmetric stretch).

We find no evidence of an open-shell singlet state in our spectra. In the case of NCCCN, Sanov et al. calculate the open-shell $^1\Delta_g$ to lie 0.1–0.3 eV higher in energy than the closed-shell $^1A_1$, depending on the level of theory. The two singlet states are degenerate at the linear NCCCN geometry, but upon distortion Renner-Teller coupling results in energy splitting to make the closed-shell singlet more stable. In the case of the oxayllyl diradical, the open-shell $^1\text{B}_2$ is calculated to lie 1.346 eV higher in adiabatic energy than the closed-shell $\tilde{X}^1\text{A}_1$. To our knowledge, the energy of the open-shell singlet of HC$_4$N has not been computed. There is no indication of the open-shell singlet state in our spectra, though it is possible that it lies close in energy to the closed-shell $^1A'$.

**FIG. 3.** One-dimensional potential cut along the HCC–C–CN bend coordinate. Energies are relative to the minimum on the anion surface. All internal angles except $\angle$C2–C3–C4 are constrained to be linear, while the remaining internal coordinates are set to the values that minimize the energy of the anion under these constraints. All curves were calculated using ROMP2/6-311++G(d,p) level of theory/basis set.

**B. HCCN$^-$ and DCCN$^-$**

The new 364-nm, magic angle photoelectron spectra of HCCN$^-$ and DCCN$^-$ are shown in Fig. 4. The data shown in Fig. 4 display significantly improved signal-to-noise over the previous data. As a result, we more clearly resolve transitions within the vibrational progressions. As briefly mentioned in connection with HC$_4$N$^-$, it is extremely difficult to obtain a precise, reliable measurement of the EA of a molecule exhibiting an extended vibrational progression. In such cases, the intensity of the origin peak is weak or even unobservable. Furthermore, normal mode analysis often fails to accurately represent the photoelectron spectrum, and we therefore cannot use calculated Franck-Condon factors to help assign the origin or to anticipate its relative intensity. Like HC$_4$N$^-$, the photoelectron spectra of HCCN$^-$ and DCCN$^-$ display extended vibrational progressions in the ground state. Through comparison of the HCCN$^-$ and DCCN$^-$ spectra, we assign the origins of HCCN$^-$ and DCCN$^-$ to the peaks marked with arrows in Fig. 4. We measure the EA of HCCN to be 2.001(15) eV and of DCCN to be 1.998(15) eV, in accord with the measurements of the previous work (Table I). We measure the $\Delta E_{ST}$ of HCCN as 0.510(15) eV and the $\Delta E_{ST}$ of DCCN to be 0.508(15) eV.
uncertainties assume that the origin peaks have been assigned correctly. However, it is notoriously difficult to assign the origin of an extended progression, and the uncertainties given in the previous study were definitely optimistic.

The photoelectron spectra of HCCN\(^{-}\) and DCCN\(^{-}\) exhibit several similarities to the HC\(_4\)N\(^{-}\) spectrum. Both HC\(_4\)N\(^{-}\) and HCCN (DCCN) possess a \(X^3\)A\(^{\prime}\) ground state that is significantly less bent than the anion. Upon \(\tilde{X}^3\)A\(^{\prime}\) \(\rightarrow\) \(\tilde{X}^2\)A\(^{\prime}\) photodetachment, the \(\tilde{\chi}\)H–C1–C2 increases by 35.0\(^{\circ}\), and the C1–C2 bond decreases by 0.050 Å (Table S1).\(^{26}\) The large geometry change from the bent anion to the quasilinear triplet\(^{42}\) results in an extended vibrational progression beginning at 2.0 eV (Table I). The peaks in the \(\tilde{X}^3\)A\(^{\prime}\) HCCN progression are spaced by roughly 400 cm\(^{-1}\), corresponding to activity of the \(\nu_2\) HCC bending mode.\(^{5}\)

As in the case of HC\(_4\)N\(^{-}\), the large geometry change leads to the failure of the harmonic normal mode analysis to adequately model the \(\tilde{X}^3\)A\(^{\prime}\) \(\rightarrow\) \(\tilde{X}^2\)A\(^{\prime}\) photodetachment photoelectron spectrum. One-dimensional potential cuts along the H–C–CN bend coordinate are presented in Fig. S4.\(^{26}\) The simulated \(\tilde{X}^3\)A\(^{\prime}\) \(\rightarrow\) \(\tilde{X}^2\)A\(^{\prime}\) spectra of HCCN\(^{-}\) and DCCN\(^{-}\) are shown in Fig. S5; the calculated geometries, \(K^{\prime\prime}\) displacements, and vibrational frequencies are given in Tables S1–S3.\(^{26}\) In the HCCN\(^{-}\) (DCCN\(^{-}\)) case, the large change in the \(\tilde{\chi}\)H–C1–C2 is represented in the harmonic normal mode analysis in Cartesian coordinates by a nonphysical change in the H–C1 bond length.\(^{38}\) This is manifested in the appearance of a CH (CD) stretch progression in the predicted spectrum.

Like HC\(_4\)N, the origin of the excited \(\tilde{a}^1\)A\(^{\prime}\) state is the most prominent feature in the spectrum of HCCN. The \(\tilde{\chi}\)H–C1–C2 of both HCCN\(^{-}\) and the \(\tilde{a}^1\)A\(^{\prime}\) state of HCCN are strongly bent (\(~110^{\circ}\)), resulting in an intense origin peak and a short vibrational progression. At higher binding energy, we observe an additional sharp feature at eBE = 2.747 eV, or 1903 cm\(^{-1}\) higher in energy than the \(\tilde{a}^1\)A\(^{\prime}\) HCCN origin. As in the case of HC\(_4\)N\(^{-}\), the eBE of this peak suggests it is a CN stretch of the \(\tilde{a}^1\)A\(^{\prime}\) state. In the HCCN\(^{-}\) and DCCN\(^{-}\) spectra, this feature does not display the same strong temperature dependence as the analogous peak in the HC\(_4\)N\(^{-}\) 150 K spectrum; however, the intensity of the peak does vary with time with respect to the \(\tilde{a}^1\)A\(^{\prime}\) origin peak and the \(\tilde{X}^3\)A\(^{\prime}\) progression. The photoelectron spectra shown in Fig. 4 indicate the average intensity of the eBE \(\sim\) 2.75 eV peak over the data-sets collected.

In the previous anion photoelectron spectroscopy study of HCCN\(^{-}\) and DCCN\(^{-}\), Nimlos et al. also report the appearance of a peak at eBE \(\sim\) 2.75 eV.\(^{3}\) In contrast to our findings, however, they observe this peak in the cold HCCN\(^{-}\) spectrum but not at room temperature. Furthermore, they do not report the appearance of this peak in either the cold or room temperature DCCN\(^{-}\) spectra. The photoelectron spectrum of the isomer HCNC\(^{-}\) is also shown in the 2002 work. There is no indication of a peak at eBE \(\sim\) 2.75 eV due to the HCNC isomer, confirming that the eBE \(\sim\) 2.75 eV peak is indeed due to HCCN\(^{-}\) (DCCN\(^{-}\)). In the 2002 study, the peak is left unassigned.

One important outcome of our reexamination of the HCCN\(^{-}\) and DCCN\(^{-}\) spectra is the identification of the eBE \(\sim\) 2.75 eV peak, which was previously left unassigned. The harmonic normal mode analysis successfully predicts the \(\tilde{a}^1\)A\(^{\prime}\) \(\rightarrow\) \(\tilde{X}^2\)A\(^{\prime}\) photodetachment photoelectron spectra of HCCN\(^{-}\) and DCCN\(^{-}\) (Fig. 4) to verify the identity of the eBE \(\sim\) 2.75 eV peak. The simulation shows a peak at eBE = 2.77 eV resulting from excitation of CN stretch in the \(\tilde{a}^1\)A\(^{\prime}\) state of HCCN. From our photoelectron spectra, we measure the frequency of the \(\nu_2\) CN stretch in the \(\tilde{a}^1\)A\(^{\prime}\) state of HCCN to be 1903(40) cm\(^{-1}\) (Table S2),\(^{26}\) and in DCCN to be 1936(40) cm\(^{-1}\) (Table S3).\(^{26}\) We resolve additional features in the DCCN\(^{-}\) 150 K spectrum (Fig. 4(a)) between 2.55 and 2.65 eV that are reproduced in the simulation, giving us further confidence in the Franck-Condon simulations of the \(\tilde{a}^1\)A\(^{\prime}\) \(\rightarrow\) \(\tilde{X}^2\)A\(^{\prime}\) photoelectron spectra of these species.

The fact that this condition-dependent peak appears at a similar energy relative to the \(\tilde{a}^1\)A\(^{\prime}\) origin in both the HC\(_4\)N\(^{-}\) and HCCN\(^{-}\) (DCCN\(^{-}\)) spectra (2395 and \(\sim\) 1920 cm\(^{-1}\), respectively) and that there is no significant isotope shift upon deuteration of HCCN\(^{-}\) confirms that these peaks result from CN stretch excitation of the \(\tilde{a}^1\)A\(^{\prime}\) state of the neutral.
V. DISCUSSION

We observe several similarities between the HC₄N and HCCN (DCCN) systems, but it is useful to also examine them in the context of a broader series of molecules.

First, we observe that the EAs of HCCN and HC₄N are similar, but they are very different from the EA of HC₃N. The EAs of HCCN and HC₄N are both ~2.0 eV, whereas the EA of HC₃N is considerably lower: ~0.5 eV. This is perhaps not surprising, as trends in abundance, structure, and reactivity that depend on whether n is even or odd have been noted among HCₙN cyanopolyynes. This difference may be due in part to the carbene nature of the even cyanopolyynes as compared to the closed-shell singlet odd cyanopolyynes. The neutral n = odd cyanopolyyne molecules are considered to be more stable than the even ones; thus, the greater EA of the even cyanopolyynes implies that—unlike their neutral counterparts—the odd cyanopolyne anions are not more stable than the even cyanopolyne anions.

We also observe that exchanging an alkynyl group for a nitrile increases the vertical detachment energy (VDE) by ~1 eV, which is clearly a result of the CN group shifting the spectrum to higher eBE. The VDE is the energy at which the maximum of the vibrational progression. The VDE of the triplet ground state of HCCCH is 1.714 eV, of HCCN is 2.05(8) eV. At 2.809(4) eV, we observe the origin peak. The adiabatic EA of HC₄N is measured to be 2.05(8) eV, which is very similar but not more accurate than the EA(HC₄N). The ∆EST of HC₄N is measured to be 0.76(8) eV, with an uncertainty primarily due to our inability to resolve the origin of the triplet state.

For comparison, we also report the photoelectron spectra of HCCN⁻ and DCCN⁻. The photoelectron spectra of HCCN⁻ and DCCN⁻ also exhibit an extended progression corresponding to X³Σ⁺ ← X²Π photodetachment. In this case, however, the origin transition can be resolved, giving EA(HCCN) = 2.001(15) eV, which is very similar but more accurate than the EA(HC₄N). The △¹A' origin of HCCN appears at 2.511(4) eV, yielding a ∆EST of HCCN of 0.510(15) eV. Like HC₄N⁻, the photoelectron spectra of HCCN⁻ and DCCN⁻ reveal peaks ~2000 cm⁻¹ higher in energy than the singlet origin that vary in intensity depending on experimental conditions. In each case, these peaks result from CN stretch excitation of the △¹A' state of the neutral.

The HC₄N and HCCN (DCCN) systems display several similarities, but through comparison with other organic chains, we gain insight into how they relate to a broader series of molecules. While the EA of HC₄N is essentially the same as that of HCCN, the EA of HC₃N is much lower. In addition, exchanging an alkynyl group for a nitrile raises the VDE by ~1 eV.

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26See supplementary material at http://dx.doi.org/10.1063/1.3663617 for details of the synthesis of H₃C₄N; the photoelectron spectrum of H₂C₅N⁻ (Fig. S1); the polarization dependence of the photoelectron spectrum of HCN⁻ (Fig. S2); the full simulated photoelectron spectrum of HCN⁻.
(Fig. S3); one-dimensional potential cuts along the H–C–CN bend coordinate of HCCN (Fig. S4); the full simulated photoelectron spectra of DCCN− and HCCN− (Fig. S5); and for tables of the calculated equilibrium geometries of HCCN− (DCCN−) and HCCN (DCCN) (Table S1) and frequencies of HCCN (Table S2) and DCCN (Table S3).


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