A Joint Experimental and Computational Study of the Negative Ion Photoelectron Spectroscopy of the 1-Phospha-2,3,4-Triazolate Anion, HCPN$_3$#

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Citation: Hou, Gao-Lei et al. “A Joint Experimental and Computational Study of the Negative Ion Photoelectron Spectroscopy of the 1-Phospha-2,3,4-Triazolate Anion, HCPN$_3$#.” The Journal of Physical Chemistry A 120, 31 (August 2016): 6228–6235 © 2016 American Chemical Society

As Published: http://dx.doi.org/10.1021/acs.jpca.6b06343

Publisher: American Chemical Society

Persistent URL: http://hdl.handle.net/1721.1/111573

Version: Author’s final manuscript: final author’s manuscript post peer review, without publisher’s formatting or copy editing

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DOI: 10.1021/acs.jpca.6b06343

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A Joint Experimental and Computational Study of the Negative Ion Photoelectron Spectroscopy of the 1-Phospha-2,3,4-triazolate Anion, HCPN₃⁻

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*Supporting Information

ABSTRACT: We report here the results of a combined experimental and computational study of the negative ion photoelectron spectroscopy (NIPES) of the recently synthesized, planar, aromatic, HCPN₃⁻ ion. The adiabatic electron detachment energy of HCPN₃⁻ (electron affinity of HCPN₃•) was measured to be 3.555 ± 0.010 eV, a value that is intermediate between the electron detachment energies of the closely related (CH)₂N₃⁻ and P₂N₃⁻ ions. High level electronic structure calculations and Franck-Condon factor (FCF) simulations reveal that transitions from the ground state of the anion to two nearly degenerate, low-lying, electronic states, of the neutral HCPN₃• radical are responsible for the congested peaks at low binding energies in the NIPES spectrum. The best fit of the simulated NIPES spectrum to the experimental spectrum indicates that the ground state of HCPN₃• is a 5π-electron 2A″ π radical state, with a 6π-electron, 2A′, σ radical state being at most 1.0 kcal/mol higher in energy.

1. INTRODUCTION

Until recently, the cyclo-pentaphosphorus anion (P₅⁻) represented the only all-pnictogen analogue of cyclopentadienide anion (C₅H₅⁻)¹−⁶ that could be synthesized and isolated in bulk quantities.⁷−⁹ Although the cyclo-pentazolate anion (N₅⁻) was observed in the gas phase more than a decade ago¹⁰ and has been calculated to be a stable species,¹¹ attempts to synthesize it in large quantities have, at least thus far, been futile.¹² Consequently, the recent synthesis of P₂N₅⁻ represents important progress in the study of all-pnictogen analogues of C₅H₅⁻.¹³−¹⁷

Formal replacement of both phosphorus atoms in P₂N₅⁻ by CH groups yields the 1,2,3-triazolide anion, (CH)₂N₃⁻ (Figure 1). In 2008, Lineberger and co-workers reported the 335 nm negative ion photoelectron (NIP) imaging spectrum of (CH)₂N₃⁻ and measured the adiabatic electron detachment energy [i.e., ionization energy (IE)] of this anion.¹⁸ Later, Dillon et al. simulated the NIPES spectrum of (CH)₂N₃⁻ using a quasidiabatic Hamiltonian to study the vibronic energy levels of the neutral 1,2,3-triazolyl radical (CH)₂N₃•.¹⁹

Figure 1. Schematic depictions of the (CH)₂nPₙN₃⁻ series (n = 0−2).

The IE of (CH)₂N₃⁻ [3.447(4) eV]¹⁸ is significantly larger than that of C₅H₅⁻ [IE = 1.808(6) eV]², but only slightly smaller than that of P₂N₅⁻ [IE = 3.765(10) eV].²⁰ Comparisons of the (CH)₂N₃ anion and radical with the previously studied (CH)₄N²¹ and (CH)₃N₂²²,²³ species found that substitution of each CH group in C₅H₅⁻• by an isoelectronic N atom has a significant effect on the chemistry and thermodynamic properties, such as the C−H bond dissociation energies and gas-phase acidities, of these three nitrogen-containing analogues of C₅H₅⁻.

Received: June 22, 2016
Revised: July 19, 2016

DOI: 10.1021/acs.jpca.6b06343
J. Phys. Chem. A XXXX, XXX, XXX−−XXX
In a recent Communication, Transue et al. reported the synthesis of the 1-phospha-2,3,4-triazolate anion, HCPN$_3^{-}$.

This anion can be viewed as the $n = 1$ member of the series, (CH)$_2$P$_n$N$_3^{-}$ ($n = 0$–2). Nucleus-independent chemical shift (NICS) and quantum theory of atoms in molecules (QTAIM) calculations showed that HCPN$_3^{-}$ is aromatic, with its aromaticity being intermediate between that of the $n = 0$ [(CH)$_2$N$_3^{-}$] and the $n = 2$ (P$_2$N$_3^{-}$) members of this series.

In this paper we report the detailed results of NIPE spectroscopy and electronic structure calculations on HCPN$_3^{-}$ and the neutral radical formed from it. Our experimental and computational results are compared with those for (CH)$_2$N$_3^{-}$ and P$_2$N$_3^{-}$ as well as the neutral radicals formed from them.

2. EXPERIMENTAL METHODS

The NIPEs experiment was performed with an apparatus consisting of an electrospray ionization source (ESI), a cryogenic ion trap, and a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer.  

An acetonitrile solution synthesis was recently reported by Transue et al., was of the tetrabutylammonium (TBA) salt of HCPN$_3$.

In this case the solution was transferred immediately into the electrospray ionization source, which was purged with N$_2$, in order to minimize the O$_2$ and moisture content of the solution.

The electrospray ionization conditions were optimized, to make sure there was only one dominant peak at $m/z = 86$ (i.e., the mass of HCPN$_3^{-}$) in the mass spectrum (Figure S1 in the Supporting Information). The anions generated by ESI were guided by quadrupole ion guides into an ion trap, where they were accumulated and cooled for 20–100 ms by collisions with cold buffer gas at 20 K, before being transferred into the extraction zone of a TOF mass spectrometer. The cooling of the anions to 20 K eliminated the possibility of the appearance of peaks in the NIPE spectra due to hot bands. The HCPN$_3^{-}$ anions were then mass selected, and maximally decelerated before being photodetached with 266 nm ($4.661$ eV) photons from a Nd:YAG laser or with 193 nm ($6.424$ eV) photons from a ArF excimer laser. Both lasers were operated at a 20 Hz repetition rate, with the ion beam off at alternating laser shots, in order to enable shot-to-shot background subtraction to be carried out.

Photoelectrons were collected with ca. 100% efficiency with the magnetic bottle and analyzed in a 5.2 m long electron flight tube. The recorded TOF photoelectron spectrum was converted into an electron kinetic energy spectrum by calibration with the known NIPE spectra of I$^-$, OsCl$_3^{2-}$, and/or Cu(CN)$_2^{-}$. The electron binding energy spectrum was obtained by subtracting the electron kinetic energy spectrum from the energy of the detaching photons. The energy resolution was about 2%, i.e., $\sim20$ meV for 1 eV kinetic energy electrons.

3. COMPUTATIONAL DETAILS

In order to help analyze the NIPE spectra of HCPN$_3^{-}$, three different types of electronic structure calculations were performed: B3LYP density functional theory (DFT) calculations, CASPT2 many body perturbation methods, and CCSD(T) coupled-cluster ab initio calculations. The aug-cc-pVTZ basis set was employed in all three types of calculations, although the smaller aug-cc-pVDZ basis set was used for some of the initial CASPT2 calculations.

A (14/9)CASSCF active space was used for HCPN$_3^{-}$ in the CASPT2 calculations. The (14/9) active space consisted of four, highest, doubly occupied $\sigma$ MOs, which are mainly in-plane, lone pair orbitals on the P and three N atoms, plus all five valence $\pi$ and $\pi^*$ MOs, three of which are doubly occupied in the lowest electronic configuration. The active space used for HCPN$_3^{+}$ was (13/9), since the radical has one less active electron than the anion.

The B3LYP geometry optimizations and harmonic vibrational analyses were performed using the Gaussian09 suite of programs. The CASPT2 calculations were carried out with the Molcas program (version 8). The CCSD(T) geometry optimizations and vibrational analyses were performed using the Molpro 10 program. The program ezSpectrum was used to compute the Franck–Condon factors (FCFs) that were necessary in order to simulate the vibrational progressions in the NIPE spectra of HCPN$_3^{-}$.

A temperature of 20 K was used in the simulations of the NIPE spectra. As expected, no vibrational hot bands were seen in the simulations. In carrying out the simulations, the imaginary frequencies of some vibrations in the electronic states of the radical were treated as real frequencies; but the FCFs for these modes were calculated to be zero.

4. RESULTS AND DISCUSSION

4.1. The NIPE Spectra of HCPN$_3^{-}$. Figure 2 presents the 20 K NIPE spectra of HCPN$_3^{-}$ at 266 and 193 nm. It can be seen that the 193 nm NIPE spectrum contains three main broad spectral features in the electron binding energy ranges of EBE = 3.5–4.4, 4.5–5.2, and 5.4–5.9 eV.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** The 20 K NIPE spectra of HCPN$_3^{-}$ at 266 (4.661 eV) and 193 nm (6.424 eV), respectively. The origin of the band for what appears to be the first electronic state of HCPN$_3^{+}$ is labeled X in the 266 nm spectrum.
In the 266 nm spectrum of HCPN$_3^-$, the intrinsic energy resolution of the instrument is better than in the 193 nm spectrum, due to the reduced detachment photon energy. As a result, the broad spectral features in the EBE range of 3.5 – 4.4 eV that is observed in the 193 nm spectrum become narrower and better resolved. However, the 266 nm spectrum still contains at least six closely spaced peaks. As in our recent NIPES study of P$_2$N$_3^-$, these closely spaced peaks suggest that this region of the spectrum may contain transitions to more than one state of the HCPN$_3^*$ radical and the vibrational progressions that are associated with these transitions. The adiabatic IE of HCPN$_3^-$ (i.e., the electron affinity (EA) of HCPN$_3^*$) is determined from the 0 – 0 transition (X) in the 266 nm NIPE spectrum in Figure 2 to be $EA = 3.555 \pm 0.010$ eV.

The value $EA = 3.555 \pm 0.010$ eV of HCPN$_3^*$ is only slightly smaller than that of P$_2$N$_3^*$, which was recently measured to have $EA = 3.765 \pm 0.010$ eV, but the EA of HCPN$_3^*$ is slightly larger than that of (CH)$_2$N$_3^*$, which was previously measured by Lineberger and co-workers to be $3.447 \pm 0.004$ eV, and which we remeasured as $EA = 3.445 \pm 0.010$ eV. (See Figure S2 in the Supporting Information.)

The similar EA values for the $n = 0$ – 2 members of the (CH)$_n$P$_n$N$_3$ series of molecules may be viewed as a consequence of the fact that carbon and phosphorus have very similar electronegativities. However, the electronegativity of nitrogen is substantially larger than those of both carbon and phosphorus. Therefore, the presence of three nitrogen atoms in each of the members of this series is the reason why all of these EA values are much larger than that of C$_5$H$_5^*$, which has $EA = 1.808 \pm 0.006$ eV.

### 4.2. The Electronic Structures of HCPN$_3^-$ and HCPN$_3^*$. In order to help interpret the NIPE spectra of HCPN$_3^-$, we carried out electronic structure calculations on both the HCPN$_3^-$ anion and the neutral HCPN$_3^*$ radical. Table 1 shows the comparison of the optimized geometries of HCPN$_3^-$ calculated at B3LYP/aug-cc-pVTZ, (14/9)CASPT2/aug-cc-pVTZ, and CCSD(T)/aug-cc-pVTZ levels of theory, with the X-ray structure in the solid tris(dimethylamino)sulfonium (TAS) salt. The calculated bond lengths and bond angles are respectively within 0.021 Å and 1.1° of those determined by X-ray diffraction. This good agreement is indicative of the accuracy of all three theoretical methods employed in this work, at least for providing optimized geometries.

<table>
<thead>
<tr>
<th></th>
<th>r$_1$</th>
<th>r$_2$</th>
<th>r$_3$</th>
<th>r$_4$</th>
<th>r$_5$</th>
<th>a$_1$</th>
<th>a$_2$</th>
<th>a$_3$</th>
<th>a$_4$</th>
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<tr>
<td>X-ray structure</td>
<td>1.347</td>
<td>1.328</td>
<td>1.684</td>
<td>1.722</td>
<td>1.340</td>
<td>114.9</td>
<td>112.0</td>
<td>89.5</td>
<td>112.0</td>
<td>111.6</td>
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<td>B3LYP/aug-cc-pVTZ</td>
<td>1.344</td>
<td>1.310</td>
<td>1.705</td>
<td>1.742</td>
<td>1.338</td>
<td>115.5</td>
<td>112.4</td>
<td>88.4</td>
<td>112.1</td>
<td>111.6</td>
</tr>
<tr>
<td>(14/9)CASPT2/aug-cc-pVTZ</td>
<td>1.334</td>
<td>1.339</td>
<td>1.691</td>
<td>1.729</td>
<td>1.359</td>
<td>115.5</td>
<td>111.7</td>
<td>89.6</td>
<td>111.7</td>
<td>111.6</td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ</td>
<td>1.351</td>
<td>1.324</td>
<td>1.709</td>
<td>1.743</td>
<td>1.349</td>
<td>115.5</td>
<td>112.2</td>
<td>88.6</td>
<td>112.4</td>
<td>111.3</td>
</tr>
</tbody>
</table>

*Bond distances (r$_1$–r$_5$) are in angstroms (Å) and bond angles (a$_1$–a$_5$) are in degrees (°).*

Figure 3 shows the eight highest occupied molecular orbitals (HOMOs) and the two virtual MOs in the lowest electronic configuration of HCPN$_3^-$, and the two lowest unoccupied molecular orbitals (LUMOs) of HCPN$_3^*$ at a C$_s$ geometry, and their orbital energies (in eV), calculated at the B3LYP/aug-cc-pVTZ level of theory. Of the virtual MOs, only the valence π* MOs (LUMO+2 and LUMO+7) are shown. The other low-lying virtual MOs, for example, the LUMO (2.80 eV) and the LUMO+1 (3.50 eV), are Rydberg MOs, formed from diffuse functions in the aug-cc-pVTZ basis set. The Rydberg MOs are not shown here.
Table 2. Energies, with Zero-Point Energy (ZPE) Corrections in Parentheses, of the \( ^2\text{A}'' \), \( ^2\text{A}' \), \( ^2\text{A}'' \), and \( ^2\text{A}' \) States of HCPN\(_3\)\(^{-}\), Relative to the \( ^1\text{A} ' \) State of HCPN\(_3\)\(^{-}\), Computed at (U)B3LYP/aug-cc-pVTZ, (14/9)CASPT2/aug-cc-pVTZ, and (U)CCSD(T)/aug-cc-pVTZ Levels of Theory

<table>
<thead>
<tr>
<th>molecule</th>
<th>electronic state</th>
<th>singly occupied MO</th>
<th>( \text{(U)B3LYP/aug-cc-pVTZ energies} )</th>
<th>( \text{(14/9)CASPT2/aug-cc-pVTZ energies} )</th>
<th>( \text{(U)CCSD(T)/aug-cc-pVTZ energies} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>\text{in kcal/mol}</td>
<td>\text{in eV}</td>
<td>\text{in kcal/mol}</td>
</tr>
<tr>
<td>HCPN(_3)(^{-})</td>
<td>( ^1\text{A} ' ) (6( \pi ))</td>
<td>none</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>HCPN(_3)(^{+})</td>
<td>( ^2\text{A} '' ) (5( \pi ))</td>
<td>HOMO</td>
<td>81.7 (80.1)</td>
<td>3.54 (3.47) ( ^a )</td>
<td>86.9</td>
</tr>
<tr>
<td></td>
<td>( ^2\text{A} ' ) (6( \pi ))</td>
<td>HOMO-1</td>
<td>81.5 (80.6)</td>
<td>3.53 (3.49)</td>
<td>84.6</td>
</tr>
<tr>
<td></td>
<td>( ^2\text{A} '' ) (5( \pi ))</td>
<td>HOMO-2</td>
<td>98.1'</td>
<td>4.25'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^2\text{A} '' ) (5( \pi ))</td>
<td>HOMO-3</td>
<td>108.0'</td>
<td>4.68'</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \)UB3LYP predicts an imaginary frequency (i104.6 cm\(^{-1}\)) for an out-of-plane vibration of the central N (N2, see Table 1) for the \( ^2\text{A}'' \) state. 
\( ^b \)UCCSD(T) predicts an imaginary frequency (i51.1 cm\(^{-1}\)) for an out-of-plane vibration of the central N (N2 in Table 1) for the \( ^2\text{A}' \) state.  
\( ^c \)The geometry is optimized at the (14/9)CASPT2/aug-cc-pVDZ level.

Figure 4. Simulated vibrational progressions (stick spectra) at 20 K for the formation of the two low-lying states of HCPN\(_3\)\(^{+}\) from the \( ^1\text{A} ' \) ground state of HCPN\(_3\)\(^{-}\), using (U)B3LYP geometries, frequencies, and FCFs. The 0–0 peak for each state is positioned at the (U)B3LYP calculated EA. Geometry changes (the most significant changes are highlighted in red) from the initial state of the anion to the target state of the radical and the active modes (with frequencies) for both transitions are also shown. The assignments of the major peaks in the stick spectra are given.

On the basis of the small difference between the B3LYP energies of the HOMO and HOMO−1 of HCPN\(_3\)\(^{-}\), one would expect that the IE of an electron from each of these two MOs should be very similar. Therefore, the two lowest states of neutral HCPN\(_3\)\(^{+}\)—the \( ^1\text{A} ' \) state in which the unpaired electron occupies a \( \pi \) MO and the \( ^2\text{A}' \) state in which the unpaired electron occupies a \( \sigma \) MO—are likely to be very close in energy.

Table 2 shows the energies of four electronic states of HCPN\(_3\)\(^{+}\), relative to the \( ^1\text{A} ' \) ground state of HCPN\(_3\)\(^{-}\). These are, by definition, the EAs of the lowest energy electronic states of HCPN\(_3\)\(^{+}\). The MOs of HCPN\(_3\)\(^{-}\) in Figure 3, from which the singly occupied MOs in the radical originate, are indicated in Table 2.

The \( ^2\text{A}' \) and \( ^2\text{A}'' \) states of HCPN\(_3\) have almost the same energies (within 0.02 eV) at the UB3LYP/aug-cc-pVTZ level of
theory. The CASPT2/aug-cc-pVTZ calculations favor the \( ^2A' \) state by 2.3 kcal/mol (0.10 eV). However, at the UCCSD(T)/aug-cc-pVTZ level, the \( ^2A'' \) state is predicted to be the ground state and to be 3.7 kcal/mol (0.16 eV) lower than the \( ^2A' \) state. Although these methods do not agree on whether the unpaired electron occupies a \( \sigma \) or a \( \pi \) MO in the ground state of HCPN\(_3\)^+, the methods do agree that the \( ^2A' \) and \( ^2A'' \) states are close in energy and that the EA of the ground state of the radical is 3.5–3.8 eV. The EA computed for the ground state of the radical is in very good agreement with the experimental value of EA = 3.555 ± 0.010 eV.

Of the \( ^2A' \) and \( ^2A'' \) states, the one with the higher electronic energy is calculated, by the UB3LYP and UCCSD(T) methods, to have an imaginary frequency, corresponding to an out-of-plane vibration of the central N atom (footnotes a and b of Table 2). Loss of the symmetry element that distinguishes between \( \sigma \) and \( \pi \) means that a geometry optimization continues on the potential energy surface for the excited state after such a symmetry-breaking molecular distortion.

We also performed CASPT2 calculations on the second lowest \( ^2A' \) and \( ^2A'' \) states of HCPN\(_3\)^+. As shown in Table 2, the calculations show that the unpaired electron in the \( ^2A' \) and \( ^2A'' \) states occupies a MO that originates from, respectively, HOMO–2 and HOMO–3 of HCPN\(_3\)^+. The \( ^2A' \) and \( ^2A'' \) states are much higher in energy than the lowest \( ^2A' \) and \( ^2A'' \) states, and they are likely to be responsible for the spectral features in the higher EBE region (4.2–5.2 eV) in the 193 nm NIPE spectrum in Figure 2.

### 4.3. Simulation of the Vibrational Progressions in the NIPE Spectra

A potentially useful method for determining whether the ground state of HCPN\(_3\)^− is \( ^2A' \) or \( ^2A'' \) is to simulate the NIPE spectra for formation of each of these states from the \( ^1A' \) state of HCPN\(_3\)^− and to see which of these simulations provides a better fit to the low energy region of the experimental NIPE spectrum. We simulated the vibrational progressions in the transition from the \( ^1A' \) ground state of HCPN\(_3\)^− to each of the two lowest-lying electronic states of HCPN\(_3\)^+, \( ^2A' \) and \( ^2A'' \), based on the calculated Franck–Condon factors (FCFs) for different vibrations in each of these two transitions.

Figure 4 shows the vibrational progressions, simulated using the (U)B3LYP geometries, frequencies, and FCFs. The geometry changes and the active vibrational modes that yield the vibrational progressions for each transition are also shown in Figure 4. Simulations using (U)CCSD(T) geometries, frequencies, and FCFs gave vibrational progression patterns that are very similar to (U)B3LYP, and the (U)CCSD(T) stick spectra are provided in Figure S4 of the Supporting Information.

As shown in Figure 4, the electronic transitions from the \( ^1A' \) ground state of HCPN\(_3\)^− to the two lowest-lying states of HCPN\(_3\)^+, both feature relatively strong 0–0 peaks and long vibrational progressions. The vibrational progressions associated with the \( ^2A'' \) state are more complex and attenuate less slowly than those associated with the \( ^2A' \) state. The long vibrational progressions for both states are due to significant geometry changes from the anion to the radical. These geometry changes can be understood based on the MOs in Figure 3.

For example, in the \( ^1A' \rightarrow ^2A'' \) transition (Figure 4), an electron is removed from the B3LYP HOMO, which is a \( \pi \) MO, of HCPN\(_3\)^−. As shown in Figure 3, this MO is \( \pi \) bonding between three pairs of nearest-neighbor atoms (N1–N2, N3–P, and P–C), but \( \pi \) antibonding between the N2–N3 and N1–C bonds. Removing one electron from this orbital should lead to lengthening of the N1–N2, N3–P, and P–C bonds, and shortening of the N2–N3 and N1–C bonds, which is found to be the case when the calculated geometries of the \( ^2A' \) and \( ^2A'' \) states are compared. The most significant geometrical change is the lengthening of the N1–N2 bond, from 1.344 to 1.478 Å.

One quantum of the N1–N2 stretching vibration (\( \nu_1 = 574.6 \text{ cm}^{-1} \)), which is associated with this geometry change, is calculated to give rise to the strongest peak in the simulated spectrum for the \( ^1A' \rightarrow ^2A'' \) transition. The other two active modes in the \( ^1A' \rightarrow ^2A'' \) transition are \( \nu_2 = 585.6 \text{ and } \nu_3 = 809.0 \text{ cm}^{-1} \). The motions of the atoms in each of these vibrations are shown in Figure 4.

In the \( ^1A' \rightarrow ^2A' \) transition, the electron is detached from HOMO–1 in Figure 3, which is a \( \sigma \) MO and mainly N2–N3 antibonding. Therefore, there is a shortening of the N2–N3 bond distance, from 1.310 to 1.221 Å, associated with this transition.

Consequently, long and strong vibrational progressions due to N2–N3 stretching (\( \nu_1 = 1508.6 \text{ cm}^{-1} \)) appear in the simulation. In fact, the most intense peak in the simulation is due to one quantum of the N2–N3 stretching vibration. Two more vibrations, \( \nu_1 = 790.1 \text{ and } \nu_2 = 903.3 \text{ cm}^{-1} \) are also calculated to be active in the \( ^1A' \rightarrow ^2A' \) transition. The motions of the atoms in each of these vibrations are depicted in Figure 4.

The spacing between the first two peaks in the 266 nm spectrum is 85 meV = 685 cm\(^{-1}\); whereas, the calculated spacings between the first two major peaks in the simulated spectra are, respectively, 574.6 cm\(^{-1}\) for \( ^2A' \) and 790.1 cm\(^{-1}\) for \( ^2A'' \). Therefore, the simulated spectrum for neither \( ^2A' \) nor \( ^2A'' \) provides a good fit to the separation between the first two peaks in the 266 nm spectrum.

However, the average of the spacing between the first two peaks in the two states [(574 + 790)/2 = 682 cm\(^{-1}\)] matches the experimental value reasonably well. This suggests that the first two peaks in the 266 nm experimental spectrum may both have contributions from the first two peaks for both the \( ^2A' \) and \( ^2A'' \) states, but this would be the case only if the 0–0 peaks for both states appear at almost the same energy.

### 4.4. Simulation of the NIPE Spectra of HCPN\(_3\)^−

We simulated the experimental 266 nm NIPE spectrum of HCPN\(_3\)^− by convoluting the (U)B3LYP calculated stick spectrum with Gaussian functions having full widths at half maxima for each stick. As shown in Figure 5a and b, after small adjustments of the (U)B3LYP calculated energies of the 0–0 bands for the two lowest electronic states of HCPN\(_3\)^+ (\( +0.09 \text{ eV for } ^2A' \text{ and } +0.07 \text{ eV for } ^2A'' \), which yield EA = 3.56 eV for both the \( ^2A' \) and \( ^2A'' \) states of HCPN\(_3\)^+), the peak positions in the simulated NIPE spectrum of HCPN\(_3\)^− match those in the experimental 266 nm spectrum reasonably well.

Alternatively, we found that if we adjust the 0–0 bands for \( ^2A' \) and \( ^2A'' \) states by \( +0.09 \) and \( +0.11 \) eV, respectively, the simulated (U)B3LYP NIPE spectrum matches the experimental 266 nm spectrum reasonably well in terms of the peak intensities, but slightly less well in terms of peak positions. (Figure S5 in the Supporting Information) This latter pair of adjustments yields EA = 3.56 eV for the \( ^2A'' \) state and EA = 3.60 eV for the \( ^2A' \) state of HCPN\(_3\)^+.
placed the 0 band of the 2A state is the ground state of HCPN3, and P2N3.20

5. CONCLUSIONS
B3LYP calculations find that the two highest occupied MOs of HCPN3, a σ MO and a π MO, have very similar orbital energies. This near energetic degeneracy of two occupied MOs leads to the expectation that the 2A′ σ and 2A′ π states of the HCPN3 radical are close in energy. This conjecture is supported by the results of (U)B3LYP, CASPT2, and (U)CCSD(T) calculations, which all find that these two electronic states of the radical do, indeed, have very similar energies.

We have calculated the FCFs for the vibrations associated with both a 2A′ → 2A′ transition in the NIPE spectrum of HCPN3, and we have used the computed vibrational progressions to simulate the NIPE spectrum. The best fit to the experimental spectrum is obtained when the 2A′ σ state is assumed to be equal to or 1.0 kcal/mol lower than the energy of the 2A′ π state in the HCPN3 radical that is formed by photodetachment of an electron from HCPN3. This assignment contrasts with our recent finding that the ground state of P2N3 is a 6σ-electron, σ radical state.20

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b06343.

We have also simulated the 266 nm NIPE spectra of HCPN3 with other possible adjustments of the calculated energies of the 0–0 bands of 2A′ and 2A′. In one simulation, we placed the 0–0 band of the 2A′ state 0.1 eV higher than that of the 2A′ state; in another simulation we placed the 0–0 peak of 2A′ at an energy lower than that of 2A′, thus assuming that 2A′ is the ground state of HCPN3. These additional simulations are presented in Figures S6 and S7 of the Supporting Information. However, these simulated spectra agree less well with the experimental 266 nm NIPE spectrum than the simulated spectra in Figures 5 and S5 do. Therefore, we tentatively assign the 2A′ state, in which the unpaired electron occupies a π MO, as the ground state of HCPN3, but with the 2A′ σ state being nearly degenerate and higher in energy by less than ~1.0 kcal/mol.36

It is worth mentioning that starting with EBE > 4.0 eV, the bands in the 266 nm experimental NIPE spectrum seem to sit on top of a background, which makes the spectral features in this region appear more intense than they would be if only direct detachment processes were involved. Resonant photodetachment via some excited state of HCPN3, may give rise to an underlying band in this region, which could account for the differences between the experimental and simulated NIPE spectra at EBE > 4.0 eV. Resonant photodetachment was also suggested to occur in our previous NIPES studies of the 1,2,4,5-tetraoxatetramethylenebenzene (TOTMB) radical anion38 and P2N3.20

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The NIPES research done at PNNL was supported by U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, the Division of Chemical Sciences, Geosciences, and Biosciences, and performed using EMSL, a national scientific user facility sponsored by DOE’s Office of

Figure 5. (a) Convoluted spectra (Gaussian line shapes with 45 meV full widths at half maxima), using the (U)B3LYP/aug-cc-pVTZ stick spectra, for the 2A′ (in blue) and 2A′ (in green) states of HCPN3, superimposed onto the experimental 266 nm NIPE spectrum (red). The (U)B3LYP predicted 0–0 band positions of 2A′ and 2A′ have been slightly adjusted, by +0.09 (3.47 → 3.56 eV) for 2A′ and by +0.07 eV (3.49 → 3.56 eV) for 2A′. (b) The spectrum with contributions from the 2A′ and 2A′ states summed (in gray), superimposed on the experimental 266 nm spectrum (in red).

DOI: 10.1021/acs.jpca.6b06343
Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle Memorial Institute for the DOE. The theoretical calculations at UNT were supported by Grant B0027 from the Robert A. Welch Foundation. The synthesis work of [TBA][HCPN]− was supported by the National Science Foundation under Grant No. CHE-1362118. G.-L.H. thanks Dr. Shaoguang Zhang from PNNL for providing the dry and degassed acetonitrile.

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(33) Simulations using (U)CASSCF(T) geometries, frequencies and FCFs gave similar vibrational patterns to the (U)B3LYP simulations in Figure 5. The (U)CASSCF(T) stick spectra are provided in Figure S4. In addition, we also simulated two sets of 266 nm spectra, by convoluting the (U)B3LYP calculated stick spectrum with Gaussian functions having full widths of 40 and 50 meV at half maxima for each stick,
respectively, to account for the variation of energy resolution of our TOF type photoelectron spectrometer in the observed photoelectron energy range (E_BE = 3.5–4.3 eV). These two simulated spectra (Figures S8 and S9) gave similar fits to the experimental spectrum as the simulated spectra with the 45 meV energy resolution in Figure 5.
