Probing the Electronic Structure and Aromaticity of Pentapnictogen Cluster Anions Pn$_5^-$ (Pn = P, As, Sb, and Bi) Using Photoelectron Spectroscopy and ab Initio Calculations

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The electronic structure and chemical bonding of the pentapnictogen cluster anions, Pn$_5^-$ (Pn = P, As, Sb, and Bi), were investigated using both photoelectron spectroscopy and ab initio calculations. Well-resolved photoelectron spectra were obtained for the anions at several photon energies and were analyzed according to the theoretical calculations. The ground state of all the Pn$_5^-$ species was found to be the aromatic cyclic $D_{5h}$ structure with a $C_{2v}$ low-lying isomer. We found that the $C_{2v}$ isomer gains stability from P$_5^-$ to Sb$_5^-$, consistent with the experimental observation of the coexistence of both isomers in the spectra of Sb$_5^-$.

The valence molecular orbitals (MOs) of the $D_{5h}$ Pn$_5^-$ were analyzed and compared to those of the aromatic C$_5H$_5$^-$ hydrocarbon. The same set of $\pi$-MOs is shown to be occupied in the $D_{5h}$ Pn$_5^-$ and C$_5H$_5$^-$ species, except that the MO ordering is slightly different. Whereas the three $\pi$-MOs in C$_5H$_5$^-$ all lie above the $\sigma$-MOs, the third $\pi$ orbital (1a$''$ in Pn$_5^-$) lies below the $\sigma$-MOs. The stabilization of the $\pi$-MO relative to the $\sigma$-MOs seems to be common in inorganic aromatic molecules and distinguishes them from the organic analogues.

1. Introduction

The structural and electronic properties of clusters of the pnictogens (Pn) have been of continuing interest. Since the pioneering works done by the groups of Dahl,$^1$ Ginsberg,$^2$ and Sacconi$^3$ in the field of coordinatively stabilized Pn ligands (Pn = P, As), rapid developments have taken place in phosphorus and arsenic chemistry.$^{4-7}$ Among the various Pn ligands, the pentapnictogen anions, Pn$_5^-$, are particularly interesting.$^{6,7}$ The planar cyclic P$_5^-$ anion, isovalent with the cyclopentadienyl anion C$_5H$_5$^-$, has been prepared in the form of MP$_5$ salts (M = Li, Na, and Cu).$^6$ It has also been coordinatively stabilized in the form of a stable CpFe($\eta_5$-P$_5$) sandwich complex.$^10$ Very recently, a carbon-free metallocene [($\eta_5$-P$_5$)$_2$-Ti]$^{2-}$ has been synthesized.$^{11}$

Gas-phase pnictogen clusters have also been the subject of intensive investigation both theoretically$^{12-43}$ and experimentally.$^{16,32,44-60}$ In particular, photoelectron spectroscopy (PES) has been performed on the pnictogen clusters,$^{16,32,44-52,57,58}$ When combined with high level theoretical calculations,$^{12-16,24-26,28,33,37-39,44}$ PES of anions could provide a wealth of information on the geometries, electronic structure, vibrational frequencies, and electron affinities of the neutral clusters. A number of previous experimental and theoretical works have been devoted to the Pn$_5^-$ clusters.$^{16,24-26,32,52,58}$ However, the structures and chemical bonding of these important inorganic species are still not completely understood. In the current work, we report a systematic characterization of the series of pentapnictogen cluster anions Pn$_5^-$ (Pn = P, As, Sb, and Bi) by a combined PES and ab initio study with a special interest of their aromaticity. The rich and well-resolved PES features and the excellent agreement between the experiment and theory allow the structural and chemical bonding properties of the Pn$_5^-$ species to be thoroughly elucidated. The aromaticity in the Pn$_5^-$ clusters was compared to that in the isovalent and classical aromatic molecule, C$_5H$_5$^-$.

We have been interested in exploring and characterizing gaseous nonstoichiometric molecules,$^{61}$ where novel chemical bonding exists in contradiction to classical stoichiometry. As a serendipitous discovery, we observed all-metal aromatic Al$_4^2-$ in bimetallic clusters MAl$_4^-$ (M = Li, Na, and Cu).$^{62}$ We also prepared the analogous aromatic NaGa$_4^-$ and NaIn$_4^-$ species.$^{63}$ We further observed aromaticity in heteroclusters MAL$_5^-$ (M = Si, Ge, Sn, and Pb)$^{64}$ and explored the aromaticity in Hg$_4^{2-}$,$^{65}$ which are all isoelectronic to Al$_2^{2-}$. The present work represents our continuing interest in exploring aromaticity in inorganic systems.

2. Experimental Method

The experiments were carried out using a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer coupled with a laser vaporization supersonic cluster source, details of which have been described previously.$^{66,67}$ The Pn$_5^-$ (Pn = P, As, Sb, and Bi) clusters were produced by laser vaporization of the corresponding Pn targets in the presence of a pure helium carrier gas. Various clusters were formed in the source and were mass-selected and decelerated before being photodetached. Three detachment photon energies were used in the current study, 355 nm (3.496 eV), 266 nm (4.661 eV), and 193 nm.
nm (6.424 eV). The higher photon energy (6.424 eV) used in the current work allowed much more neutral excited states to be accessed. The higher spectral resolution afforded by the low photon energies (355 and 266 nm) allowed the accessible electronic transitions to be better resolved, yielding more accurate electron affinities and electron binding energies. The photoelectron spectra were calibrated using the known spectrum of Rh$^{68}$ and the resolution of the apparatus was better than 30 meV for 1 eV electrons.

3. Theoretical Methods

We performed ab initio calculations on a wide variety of structures for Pn$^-$ to search for the global minimum. We initially optimized geometries and calculated frequencies of Pn$^-$ (Pn = P, As, and Sb) using analytical gradients with polarized split-valence basis sets (6-311+$\text{G}^*$)\textsuperscript{69-71} for P and As and analytical gradients with polarized split-valence basis sets (3-21G*\textsuperscript{71-77}) extended by a set of 2s, 2p, and 1d diffuse functions (3-21G*+2s2p1d; $\alpha_{2s}=0.0289$, $\alpha_{2p}=0.0096$; $\alpha_{1d}=0.0703$) for Sb and a hybrid method known in the literature as B3LYP.\textsuperscript{78-80} Two of the most stable structures of P$^-$ and one of As$^-$ were further optimized using the coupled-cluster method [CCSD(T)]\textsuperscript{81-83} with the 6-311+$\text{G}^*$ basis sets. Then the energies of the most stable structures were refined using the CCSD(T) method and the more extended 6-311+G(2df) basis sets. Two of the most stable structures of Sb$^-$ were calculated using the coupled-cluster method [CCSD(T)] with the 3-21G*+2s2p1d basis sets. The vertical electron detachment energies (VDEs) were determined from the peak maxima and are given in Table 1 for all four species. These data are compared with the Pn$^-$ anions to the various states of the Pn$^-$ neutrals. The spectra of P$^-$ (Figure 1) revealed four well-resolved features (X, A, B, and C) with very high electron binding energies. Six well-resolved features were observed for As$^-$ (X, X', A−D, Figure 2). The weak feature observable in the 193 nm spectrum of As$^-$ around 2.6 eV (Figure 2b) was shown to be due to a fragmentation process of the parent anion, as discussed later. The spectra of the two heavier Pn$^-$ species (Pn = Sb and Bi) showed many more features, which were all well resolved and relatively sharp. As will be shown later by comparing the experimental data with theoretical results, two isomers were in fact present for Sb$^-$.

4. Experimental Results

Figures 1–4 show the PES spectra of Pn$^-$ (Pn = P, As, Sb, and Bi), respectively. Numerous well-resolved PES features were observed for each species, representing transitions from the Pn$^-$ anions to the various states of the Pn$^-$ neutrals.
5. Theoretical Results

We found that the most stable structure for Pn5− (Pn = P, As, and Sb) is the cyclic D3h structure, as shown in Figure 5. All the Pn5− species were also found to possess a C2h bridged-roof low-lying singlet isomer. The optimized geometries and relative energies agreed well at the B3LYP and CCSD(T) levels of theory for P5− and As5−. Thus, we decided to limit the Sb5− calculations only to the B3LYP/3-21G* level of theory. At our highest level of theory, the global minimum D3h planar cyclic Pn5− structure is more stable than the C2h, bridged-roof structure by 33.4, 20.0, and 8.2 kcal/mol for Pn = P, As, and Sb, respectively.

We also calculated the energies of the following reactions

\[ \text{Pn}_5^{-} (D_{3h}, \mathbf{A}_1') \rightarrow \text{Pn}_4 (T_d', \mathbf{A}_1) + \text{Pn}^{-} (3\mathbf{P}) \]  

\[ \text{Pn}_5^{-} (D_{3h}, \mathbf{A}_1') \rightarrow \text{Pn}_3^{-} (D_{3h}, \mathbf{A}_1') + \text{Pn}_2^{-} (\Sigma_g^+) \]  

for Pn = P, As, and Sb at the CCSD(T)/6-311+G(2df) level of theory for P and As and at the CCSD(T)/3-21G*+2s2p1d level of theory for Sb in order to evaluate the stability of the anions toward dissociation. The calculated energies for the first reaction were found to be: 121.4 kcal/mol for P, 106.6 kcal/mol for As, and 91.0 kcal/mol for Sb; the calculated energies for the second reaction were: 75.8 kcal/mol for P, 68.2 kcal/mol for As, and 70.6 kcal/mol for Sb.

6. Interpretation of the Experimental Spectra

Theoretical calculations of the first five detachment processes for the D3h global minimum structures and the first eight detachment channels for the C2h isomers were performed for Pn5− (Pn = P, As, Sb) and are compared with the experimental VDEs in Table 1. The pole strengths, given in the parentheses in Table 1, are larger than 0.8 for all the calculated detachment channels, implying that the OVGF method is valid and all the electron detachment channels can be considered as primarily one-electron processes. Excellent overall agreement between the experimental photoelectron spectra and the theoretical calculations make the interpretation of the PES data straightforward.

### Table 1: Experimental and Theoretical Adiabatic (ADE) and Vertical (VDE) Detachment Energies in eV for P5−, As5−, Sb5−, and Bi5−

<table>
<thead>
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<th>Species</th>
<th>exptl ADE</th>
<th>theor ADE</th>
<th>exptl VDE</th>
<th>theor VDE</th>
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<td>4.15</td>
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<tr>
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<tr>
<td>D</td>
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*The numbers in the parentheses represent the experimental uncertainty in the last digit.* The VDEs were calculated at the OVGF/6-311+G(2df)/CCSD(T)/6-311+G* level of theory for P5− and As5− structures and at the OVGF/3-21G*+2s2p1d/B3LYP/3-21G*+2s2p1d level of theory for Sb5− structures. The numbers in the parentheses indicate the pole strength, which characterizes the validity of the one-electron detachment picture.
yielded the ADE of 3.88 eV for P$_5$. The electron binding with the binding energy axis to take into account the instrumental resolution and a finite thermal effect. This procedure yielded the ADE of 3.88 eV for P$_5$. The electron binding energies of P$_5$ is much higher than its neighbors P$_4$ and P$_6$ (not shown), whose ground-state PES features have VDEs of ~1.4 and ~2.2 eV, respectively, indicating that P$_5$ is an unusually unstable cluster species, consistent with its aromatic nature. The width of feature X is much broader than the theoretical one-electron detachment channels from the ground state. Indeed, the calculated VDEs for the isomer of Sb$_5$ is only 8.2 kcal/mol higher in energy, much closer to the ground state. This isomer was not fit our PES data, suggesting that this isomer was not populated in our beam. This is consistent with the high energy of this isomer (20.0 kcal/mol) relative to the D$_{3h}$ ground state. The weak feature around 2.6 eV observable in the 193 nm (Figure 2b) was not due to the C$_2v$ isomer. This feature was likely due to photofragmentation of the parent As$_5^-$, consistent with the calculated dissociation energy (2.95 eV). Similar spectral features were observed previously in PES spectra of P$_5$.\textsuperscript{16}

6.2. As$_5^-$. The observed PES features for As$_5^-$ are in good agreement with the first five one-electron detachment channels calculated for the D$_{3h}$ ground-state structure, as shown in Figure 2b (vertical bars) and Table 1. The first two adjacent features (X and X') were probably due to the Jahn–Teller splitting because of the doubly degenerate nature of the HOMO (1e') of As$_5^-$. The ground-state feature X defined an ADE of ~3.5 eV for As$_5$ and a VDE of 3.75 eV. We found that As$_5^-$ has a significantly enhanced stability relative to its neighbors As$_4^-$ (with a ground-state VDE of ~1.45 eV, PES data not shown) and As$_6^-$ (with a ground-state VDE of ~2.05 eV, PES data not shown), similar to P$_5^-$. The excellent agreement between the experimental and theoretical VDEs confirmed unequivocally the D$_{3h}$ ground-state structure of As$_5^-$ and its aromatic character.

Similar to the case of P$_5^-$, the calculated VDEs for the C$_{2v}$ isomer of As$_5^-$ did not fit our PES data, suggesting that this isomer was not populated in our beam. This is consistent with the high energy of this isomer (20.0 kcal/mol) relative to the D$_{3h}$ ground state. The weak feature around 2.6 eV observable in the 193 nm (Figure 2b) was not due to the C$_2v$ isomer. This feature was likely due to photofragmentation of the parent As$_5^-$, consistent with the calculated dissociation energy (2.95 eV). Similar spectral features were observed previously in PES spectra of P$_5^-$.\textsuperscript{16}

6.3. Sb$_5^-$. The PES spectra of Sb$_5^-$ (Figure 3), measured at three wavelengths (355, 266, and 193 nm), appeared much more complicated, compared with those of P$_5^-$ and As$_5^-$. As shown in Figure 3, fourteen PES features could be identified, with all the VDEs given in Table 1. The complexity and dissimilarity between the Sb$_5^-$ spectra to those of the lighter P$_n^-$ clusters suggested the existence of isomers. Our theoretical calculations showed that the ground state of Sb$_5^-$ is the D$_{3h}$ structure, similar to those of P$_5^-$ and As$_5^-$. However, the C$_2v$ isomer of Sb$_5^-$ (Figure 5f) is only 8.2 kcal/mol higher in energy, much closer to the ground state. Indeed, the calculated VDEs for the D$_{3h}$ Sb$_5^-$ and C$_2v$ Sb$_5^-$ can account for all the PES features and the theoretical VDEs are in excellent agreement with experimental data, as shown in Figure 3c and Table 1. The six “main” features, labeled as X, X', A, B, C, and D, were pretty similar to those of As$_5^-$, and agree well with the five theoretical one-electron detachment channels from the D$_{3h}$ species. The well-resolved and well-separated features X and X' were again attributed to the Jahn–Teller splitting, similar to those in the spectra of As$_5^-$, as discussed above. Feature X defined a VDE of 3.46 eV for the ground state of the D$_{3h}$ Sb$_5^-$ anion, and an ADE of 3.46 eV for Sb$_5$. The eight “minor” features (x, a, b, c, d, e, f, and g) in Figure 3 were attributed to the eight theoretical one-electron detachment channels from the C$_2v$ species. The overall agreement between the theory and experiment for both the D$_{3h}$ and C$_2v$ isomers was excellent, giving considerable credence to the spectral assignments and the theoretical results.

6.4. Bi$_5^-$. The PES spectra of Bi$_5^-$ at 355, 266, and 193 nm were shown in Figure 4. A total of nine well-resolved and quite sharp features were observed, with their VDEs given in Table 1. We did not carry out ab initio calculations on Bi$_5^-$, because we could not include the relativistic effect in our current level of theory. However, we suspect that the ground-state structure of Bi$_5^-$ is likely to be D$_{3h}$, similar to the lighter Pn$^-$ clusters. The spectral patterns of Bi$_5^-$ bear some similarities to those of P$_5^-$ and As$_5^-$, consistent with the suggestion that they all should present in our cluster beam, in agreement with the high relative energy (33.4 kcal/mol) of the C$_{2v}$ isomer.
have similar structures. Relativistic effects are important in Bi atom and clusters, as well documented by the theoretical works of Balasuramanian and co-workers. The rich spectral features presented here for Bi$_5^-$ suggest that it would be interesting to perform further theoretical calculations on this system with the relativistic effects explicitly included.
7. Characterization of the Aromaticity in the D_{5h} Pn_{5}^- Clusters

The excellent agreement between the observed PES features and the ab initio calculations presented herein firmly established that the D_{5h} cyclic structure is the global minimum for all the Pn_{5}^- anions investigated here. These cluster anions were found to be unusually stable electronically, as indicated by their high electron binding energies. This unusual electronic stability derives from both the closed shell nature of the Pn_{5}^- clusters and their aromaticity, which will be discussed next.

The D_{5h} Pn_{5}^- anions are isovalent to the classical aromatic cyclopentadienyl C_{5}H_{5}^- anion. Figure 6 displays the thirteen valence molecular orbitals of the D_{5h} AsS_{5}^-, compared to those of the D_{5h} C_{5}H_{5}^- . The similarity between the MOs of the two anions is obvious. The MO pictures show clearly six delocalized π electrons for AsS_{5}^- in the 1e_{v}'' and 1a_{v}'' orbitals, which fulfill the (4n + 2) Hückel rule for classical aromaticity. The order of the MOs for the two species corresponds to the ones given by the OVGF method, at the OVGF/6-311+G(2df) level of theory for AsS_{5}^- and the OVGF/6-311+G(2df,2p,d) level of theory for C_{5}H_{5}^- species. The three aromatic π-MOs are identical in both anions, except that their orders differ. In C_{5}H_{5}^-, the π-aromatic 1a_{v}'' MO is 0.67 eV higher in energy than the highest degenerate σ-MO (2e_{v}), while in AsS_{5}^- the analogous 1a_{v}'' MO is 1.54 eV lower in energy than the highest degenerate σ-MO (2e'). Thus, in the case of the aromatic hydrocarbon C_{5}H_{5}^-, the σ-MOs are filled before the π-MOs. But in the case of AsS_{5}^-, the π-aromatic 1a_{v}'' MO (HOMO-2) is lower in energy than the 2e' (HOMO-1) σ-MOs, and thus the π-MO is filled before the σ-MOs. Similar situations were found in P_{5}^- and Sb_{5}^- (Table 1). In the case of P_{5}^-, the π-aromatic 1a_{v}'' MO is lower in energy even more: it becomes separated from the 1e_{v}' π-MOs by two degenerate σ-MOs. Such behavior makes inorganic aromatic compounds different from the organic analogues. The same tendency to fill π-aromatic MOs before the σ-MOs have also been seen in other inorganic aromatic clusters studied in our previous works, for example, in C_{4}H_{4}NaGa^{+}, D_{3h}Na_{2}Ga_{4}^{2-}, and C_{4}H_{4}NaGa_{3}^{-}, as well as in C_{2}R SiAl_{3}^- and GeAl_{3}^{-}.64

Both the energy difference between the global minimum D_{5h} structure and the C_{2v} isomer and the energies of reactions 1 and 2 decrease from P_{5}^- to Sb_{5}^-, implying that the stability of the D_{5h} structure relative to the C_{2v} structure is reduced for the heavier Pn_{5}^- clusters. This is due to the fact that the aromatic stabilization is weakened for the heavier species as a result of the poorer overlap between the np, atomic orbitals.

The pentagonal structures of the Pn_{5}^- clusters and their aromaticity were established previously.91-94 In this work we were able to probe deeper MOs in Pn_{5}^- because of the use of high detachment energies and the electron propagator theory. Detailed comparison between the MOs of Pn_{5}^- and C_{5}H_{5}^- reveals that while both species are aromatic, their order of the valence MOs is different. In the case of the aromatic hydrocarbon C_{5}H_{5}^-, the σ-MOs are filled before the π-MOs, but in the case of Pn_{5}^-, the lowest π-aromatic MO is lower in energy than the σ-MOs, and thus the π-MO is filled before the σ-MOs. This observation may be responsible for the inactivity of pentanitrogen to form large polycyclic planar aromatic systems, analogous to naphthalene and anthracene. This question will be addressed in the future using large pentanitrogen clusters.

8. Conclusions

We have carried out a combined photoelectron spectroscopy and ab initio study of the pentanitrogen Pn_{5}^- (Pn = P, As, Sb, and Bi) species to elucidate their structure, bonding, and aromaticity. Well resolved photoelectron spectra were obtained for all the anions at several photon energies. Ab initio calculations showed that all the Pn_{5}^- species have the aromatic cyclic D_{5h} singlet structure as their ground state with a C_{2v} bridged-bridge low-lying singlet isomer. We found that the stability of the aromatic planar cyclic structure relative to the C_{2v} bridged-bridge low-lying isomer decreases from P_{5}^- to Sb_{5}^-, for which both isomers were observed experimentally. Molecular orbital analyses showed that the occupied orbitals in the Pn_{5}^- clusters are similar to those of the isovalent C_{5}H_{5}^- with the same set of π-orbitals. However, we found that the 1a_{v}'' orbital (the most stable π orbital) is lower in energy than the upper σ-orbitals in the cyclic Pn_{5}^- species, which is different from the valence isoelectronic hydrocarbon C_{5}H_{5}^-, where all the π-orbitals are higher in energy and well separated from the σ-orbitals. This behavior makes inorganic aromatic compounds different from the organic ones.

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References and Notes
