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Probing the Electronic Structure and Aromaticity of Pentapnictogen Cluster Anions Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{and Bi}$) Using Photoelectron Spectroscopy and *ab Initio* Calculations

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The electronic structure and chemical bonding of the pentapnictogen cluster anions, Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{and Bi}$), 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 π -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 π -MOs in C_5H_5^- all lie above the σ -MOs, the third π orbital ($1a_2''$ in Pn_5^-) lies below the σ -MOs. The stabilization of the π -MO relative to the σ -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 Sacconi³ in the field of coordinatively stabilized Pn ligands ($\text{Pn} = \text{P}, \text{As}$), 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 ($\text{M} = \text{Li}, \text{Na}$) by Baudler et al.^{8,9} It has also been coordinatively stabilized in the form of a stable $\text{CpFe}(\eta^5\text{-P}_5)$ sandwich complex.¹⁰ Very recently, a carbon-free metallocene $[(\eta^5\text{-P}_5)_2\text{-Ti}]^{2-}$ 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.^{16,32,44,52,57,58,60} 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^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb},$

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^- ($\text{M} = \text{Li}, \text{Na}, \text{and Cu}$).⁶² We also prepared the analogous aromatic NaGa_4^- and NaIn_4^- species.⁶³ We further observed aromaticity in heteroclusters MAL_3^- ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$)⁶⁴ and explored the aromaticity in Hg_4^{6-} ,⁶⁵ which are all isoelectronic to Al_4^{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^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{and Bi}$) 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 analyzed using a TOF mass spectrometer. The Pn_5^- species of interest 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

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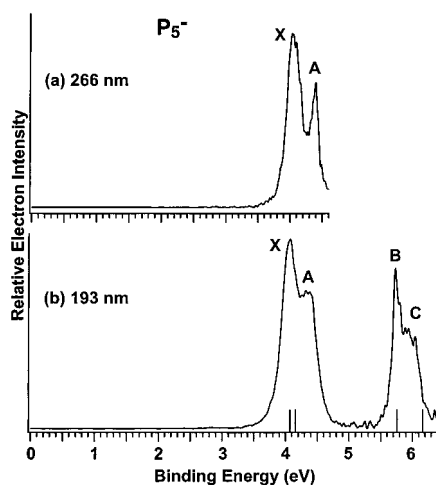


Figure 1. Photoelectron spectra of P_5^- at (a) 266 nm, and (b) 193 nm. The vertical bars mark the calculated vertical electron detachment energies from the D_{5h} ground state of P_5^- .

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_5^- to search for the global minimum. We initially optimized geometries and calculated frequencies of Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{and Sb}$) using analytical gradients with polarized split-valence basis sets (6-311+G*)^{69–71} for P and As and analytical gradients with polarized split-valence basis sets (3-21G*)^{71–77} extended by a set of 2s, 2p, and 1d diffuse functions (3-21G*+2s2p1d; $\alpha_{1sp} = 0.0289$, $\alpha_{2sp} = 0.0096$; $\alpha_{1d} = 0.0703$) for Sb and a hybrid method known in the literature as B3LYP.^{78–80} Two of the most stable structures of P_5^- and one of As_5^- were further optimized using the coupled-cluster method [CCSD(T)]^{81–83} with the 6-311+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_5^- were calculated using the coupled-cluster method [CCSD(T)] with the 3-21G*+2s2p1d basis sets. The vertical electron detachment energies (VDEs) were calculated using the outer valence Green Function method^{84–88} [OVGF/6-311+G(2df)] and CCSD(T)/6-311+G* geometries for Pn_5^- ($\text{Pn} = \text{P}$ and As) and [OVGF/3-21G*+2s2p1d] and B3LYP/3-21G*+2s2p1d geometries for Sb_5^- . Core electrons were kept frozen in treating the electron correlation at the CCSD(T), and the OVGF levels of theory. All calculations were performed using the Gaussian 98 program.⁸⁹ Molecular orbitals (MOs) for C_5H_5^- and As_5^- were calculated at the RHF/6-311+G* level of theory. All MO pictures were made using the MOLDEN 3.4 program.⁹⁰

4. Experimental Results

Figures 1–4 show the PES spectra of Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{and Bi}$), respectively. Numerous well-resolved PES features were observed for each species, representing transitions from

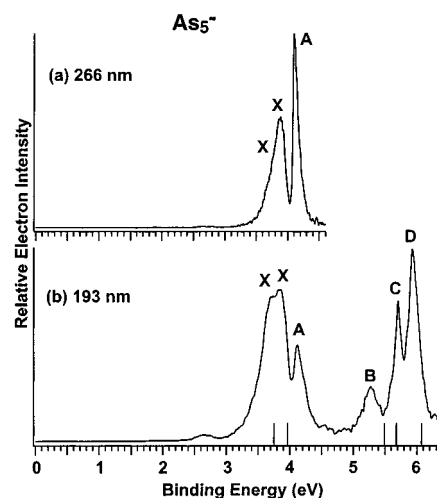


Figure 2. Photoelectron spectra of As_5^- at (a) 266 nm, and (b) 193 nm. The vertical bars mark the calculated vertical electron detachment energies from the D_{5h} ground state of As_5^- .

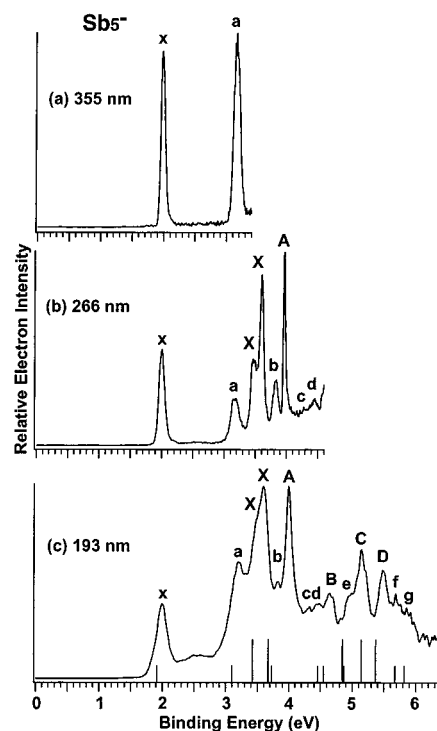


Figure 3. Photoelectron spectra of Sb_5^- at (a) 355 nm, (b) 266 nm, and (c) 193 nm. The longer vertical bars mark the calculated vertical electron detachment energies from the D_{5h} ground state of Sb_5^- , and the shorter vertical bars mark those from the C_{2v} low-lying isomer.

the Pn_5^- anions to the various states of the Pn_5 neutrals. The spectra of P_5^- (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_5^- (X, X', A–D, Figure 2). The weak feature observable in the 193 nm spectrum of As_5^- 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_5^- species ($\text{Pn} = \text{Sb}$ 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_5^- . The VDEs of all the observed spectral features were determined from the peak maxima and are given in Table 1 for all four species. These data are compared with

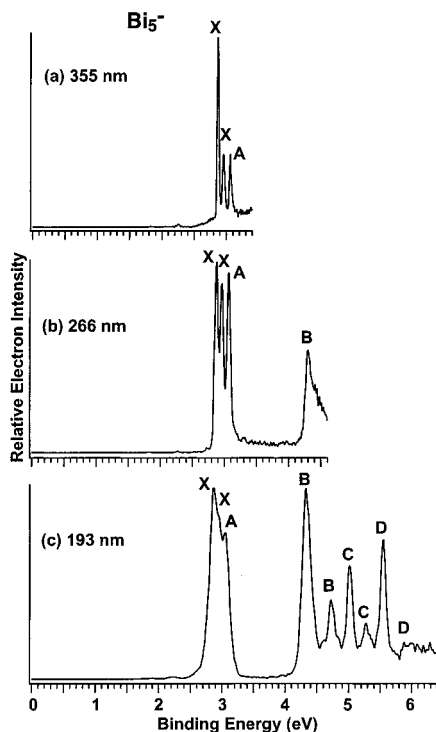


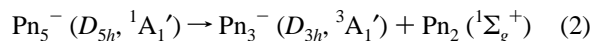
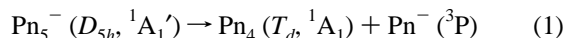
Figure 4. Photoelectron spectra of Bi_5^- at (a) 355 nm, (b) 266 nm, and (c) 193 nm.

the results of the ab initio calculations (also shown in Table 1), which will be discussed later.

5. Theoretical Results

We found that the most stable structure for Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{and Sb}$) is the cyclic D_{5h} structure, as shown in Figure 5. All the Pn_5^- species were also found to possess a C_{2v} bridged-roof low-lying singlet isomer. The optimized geometries and relative energies agreed well at the B3LYP and CCSD(T) levels of theory for P_5^- and As_5^- . Thus, we decided to limit the Sb_5^- calculations only to the B3LYP/3-21G*+2s2p1d level of theory. At our highest level of theory, the global minimum D_{5h} planar cyclic Pn_5^- structure is more stable than the C_{2v} bridged-roof structure by 33.4, 20.0, and 8.2 kcal/mol for $\text{Pn} = \text{P}, \text{As}, \text{and Sb}$, respectively.

We also calculated the energies of the following reactions



for $\text{Pn} = \text{P}, \text{As}, \text{and Sb}$ 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 D_{5h} global minimum structures and the first eight detachment channels for the C_{2v} isomers were performed for Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$) and are compared with the experimental VDEs in Table 1. The pole strengths, given in the parentheses

TABLE 1: Experimental and Theoretical Adiabatic (ADE) and Vertical (VDE) Detachment Energies in eV for P_5^- , As_5^- , Sb_5^- , and Bi_5^-

exptl feature	exptl ADE ^a	exptl VDE ^a	<i>D</i> _{5h}		<i>C</i> _{2v}	
			MO	theor VDE ^b	MO	theor VDE ^b
<i>P</i> ₅ [−]						
X	3.88 (3)	4.05 (3)	1e ₁ ^{−−}	4.07 (0.87)	3b ₁	1.87 (0.89)
A		4.39 (2)	2e ₁ [−]	4.15 (0.88)	3b ₂	3.23 (0.89)
B		5.72 (4)	2e ₂ [−]	5.76 (0.87)	6a ₁	4.15 (0.88)
C		5.95 (8)	1a ₂ ^{−−}	6.16 (0.80)	1a ₂	5.33 (0.88)
			2a ₁ [−]	6.87 (0.83)	2b ₁	5.41 (0.86)
					5a ₁	5.74 (0.87)
					4a ₁	6.99 (0.85)
					2b ₂	7.21 (0.87)
<i>As</i> ₅ [−]						
X	~ 3.5 (1)	3.75 (5)	1e ₁ ^{−−}	3.75 (0.87)	3b ₁	1.86 (0.89)
X′		3.88 (2)			3b ₂	3.27 (0.88)
A		4.12 (2)	2e ₁ [−]	3.96 (0.88)	5a ₁	3.95 (0.88)
B		5.28 (4)	1a ₂ ^{−−}	5.50 (0.79)	1a ₂	4.86 (0.88)
C		5.70 (3)	2e ₂ [−]	5.69 (0.88)	2b ₁	4.98 (0.86)
D		5.92 (3)	2a ₁ [−]	6.07 (0.83)	4a ₁	5.35 (0.87)
					2b ₂	6.50 (0.87)
					3a ₁	6.37 (0.85)
<i>Sb</i> ₅ [−]						
X	3.46 (3)	3.46 (3)	1e ₁ ^{−−}	3.42 (0.87)		
X′		3.60 (3)				
A		3.97 (2)	2e ₁ [−]	3.68 (0.88)		
B		4.65 (5)	1a ₂ ^{−−}	4.84 (0.78)		
C		5.14 (4)	2e ₂ [−]	5.15 (0.88)		
D		5.48 (4)	2a ₁ [−]	5.37 (0.83)		
x	1.99 (3)	1.99 (3)			3b ₁	1.90 (0.88)
a		3.17 (2)			3b ₂	3.08 (0.89)
b		3.82 (2)			6a ₁	3.72 (0.88)
c		4.32 (5)			1a ₂	4.45 (0.89)
d		4.44 (5)			2b ₁	4.55 (0.86)
e		4.95 (5)			5a ₁	4.86 (0.87)
f		5.70 (5)			4a ₁	5.69(0.86)
g		5.87 (5)			2b ₂	5.81 (0.93)
<i>Bi</i> ₅ [−]						
X	2.87 (2)	2.87 (2)				
X′		2.96 (2)				
A		3.06 (2)				
B		4.33 (2)				
B′		4.72 (4)				
C		5.02 (4)				
C′		5.27 (4)				
D		5.55 (4)				
D′		5.95 (5)				

^a The numbers in the parentheses represent the experimental uncertainty in the last digit. ^b The VDEs were calculated at the OVGF/6-311+G(2df)//CCSD(T)/6-311+G* level of theory for P_5^- and As_5^- structures and at the OVGF/3-21G*+2s2p1d//B3LYP/3-21G*+2s2p1d level of theory for Sb_5^- structures. The numbers in the parentheses indicate the pole strength, which characterizes the validity of the one-electron detachment picture.

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. The D_{5h} species were responsible for all the observed PES features for P_5^- and As_5^- , whereas both the D_{5h} and C_{2v} isomers were shown to exist in the spectra of Sb_5^- . Jahn–Teller effect and spin–orbit effect are responsible for the fine features observed. More detailed interpretation of the PES data is given below.

6.1. P_5^- . The four observed PES features (X, A, B, and C) for P_5^- were in excellent agreement with the four lowest-lying

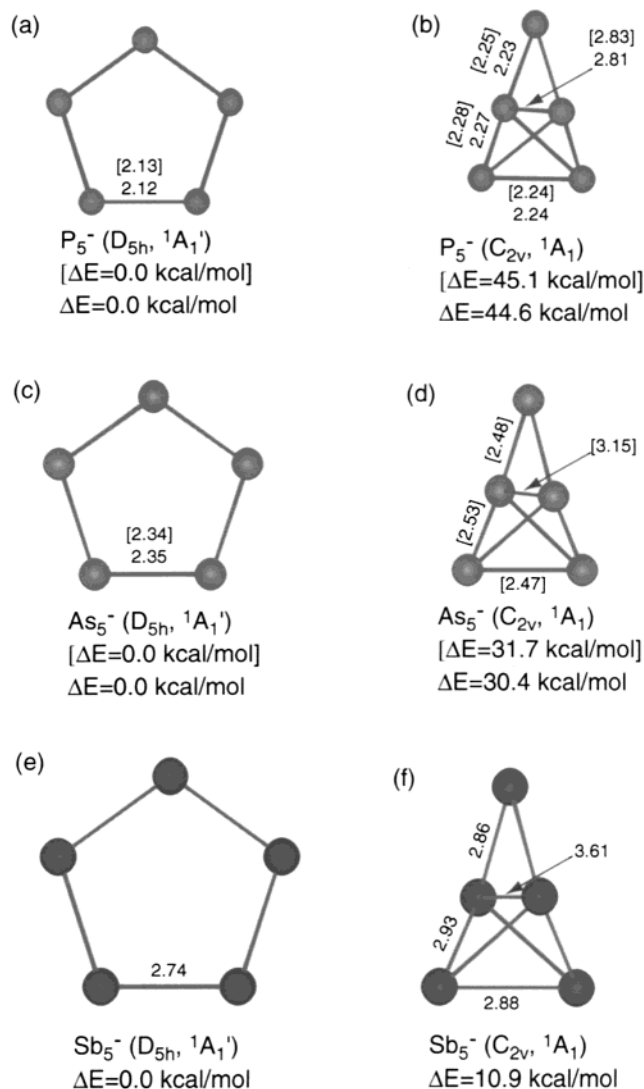


Figure 5. Optimized structures of (a) P_5^- (D_{5h} , $1A_1'$) and (b) P_5^- (C_{2v} , $1A_1$), (c) As_5^- (D_{5h} , $1A_1'$) and (d) As_5^- (C_{2v} , $1A_1$) at the B3LYP/6-311+G* and CCSD(T)/6-311+G* levels of theory, and (e) Sb_5^- (D_{5h} , $1A_1'$) and (f) Sb_5^- (C_{2v} , $1A_1$) at the B3LYP/3-21G*+2s2p1d level of theory. Data at the B3LYP/6-311+G* level of theory are given in brackets. Bond lengths are given in Å.

one-electron detachment channels calculated for the D_{5h} structure (Figure 1b and Table 1). The fifth theoretical one-electron detachment channel (6.87 eV) is beyond our highest photon energy range (6.424 eV). Since no vibrational structures were resolved for the X band, the adiabatic detachment energy (ADE) of P_5^- was evaluated by drawing a straight line at the leading edge of the X band and adding a constant to the intersection 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),¹⁶ whose ground-state PES features have VDEs of ~ 1.4 and ~ 2.2 eV, respectively, indicating that P_5^- is an unusually stable cluster species, consistent with its aromatic nature. The width of feature X is much broader than the instrumental resolution, indicating a structural change from the anion to the neutral state. This is indeed the case: while the anion ground state is D_{5h} , the neutral state is of C_{2v} symmetry, mainly due to the Jahn–Teller effect.¹³

The C_{2v} isomer gave much lower binding energies, according to the theoretical calculations (Table 1). This isomer was not

present in our cluster beam, in agreement with the high relative energy (33.4 kcal/mol) of the C_{2v} isomer.

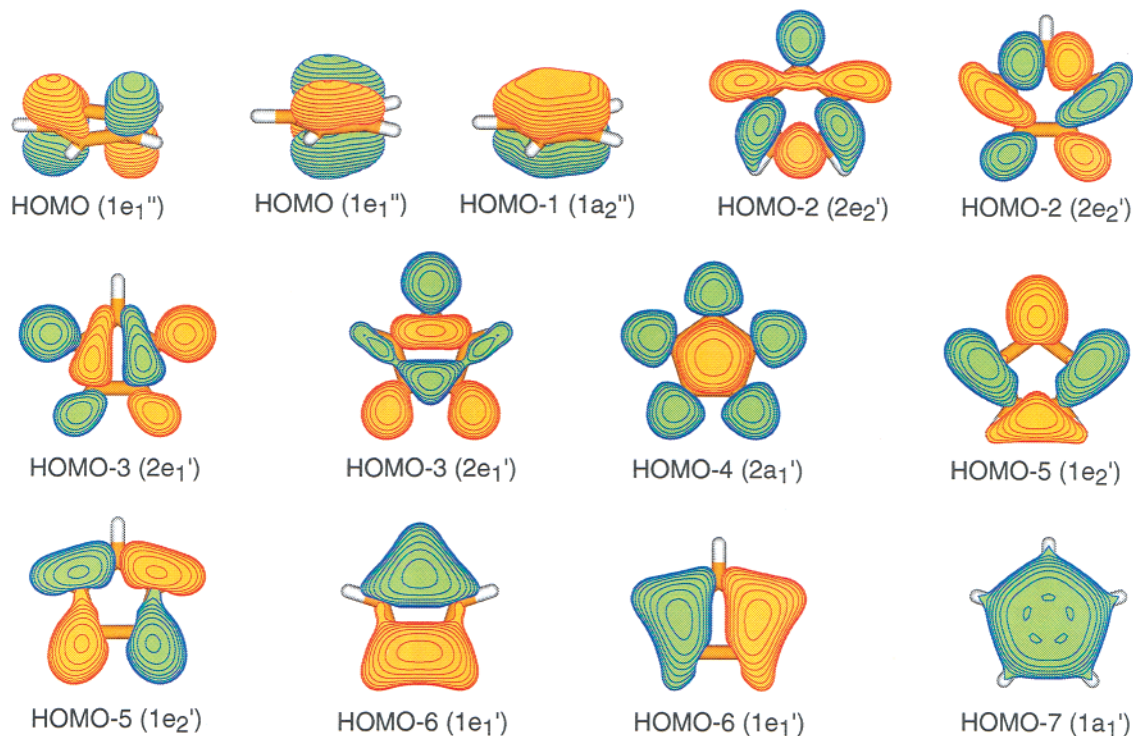
6.2. As_5^- . The observed PES features for As_5^- are in good agreement with the first five one-electron detachment channels calculated for the D_{5h} ground-state structure, as shown in Figure 2b (vertical bars) and Table 1. The first two adjacent features (X and X') were probably due to the Jahn–Teller 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_{5h} 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_{5h} 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^- .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 Pn_5^- clusters suggested the existence of isomers. Our theoretical calculations showed that the ground state of Sb_5^- is the D_{5h} 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_{5h} 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_{5h} 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_{5h} 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_{5h} 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_{5h} , similar to the lighter Pn_5^- 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

Molecular Orbitals of the C_5H_5^- Species (D_{5h} , $^1A_1'$)



Molecular Orbitals of the As_5^- Species (D_{5h} , $^1A_1'$)

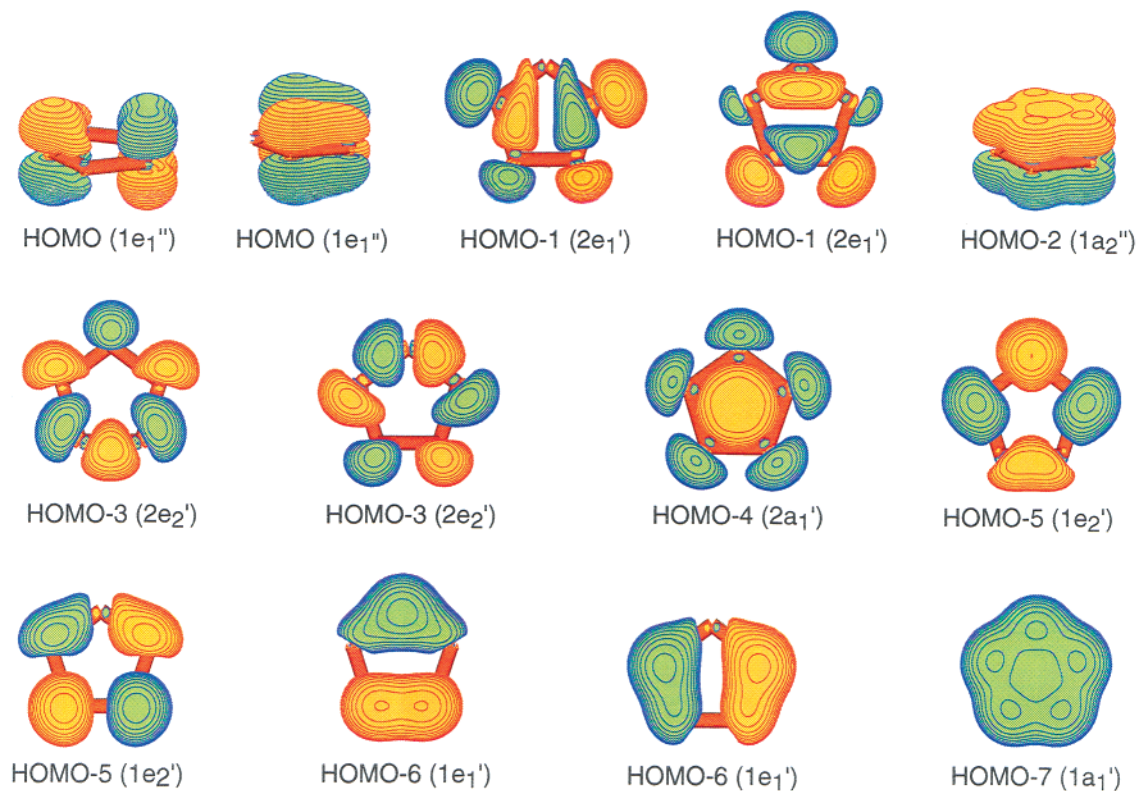


Figure 6. Molecular orbital pictures of C_5H_5^- (D_{5h} , $^1A_1'$) and As_5^- (D_{5h} , $^1A_1'$) species.

have similar structures. Relativistic effects are important in Bi atom and clusters, as well documented by the theoretical works of Balasuramanian and co-workers.^{37–39} 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_5H_5^- anion. Figure 6 displays the thirteen valence molecular orbitals of the D_{5h} As_5^- , compared to those of the D_{5h} C_5H_5^- . The similarity between the MOs of the two anions is obvious. The MO pictures show clearly six delocalized π electrons for As_5^- in the $1e_1''$ and $1a_2''$ 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 As_5^- and the OVGf/6-311++G(2df,2pd) level of theory for C_5H_5^- species. The three aromatic π -MOs are identical in both anions, except that their orders differ. In C_5H_5^- , the π -aromatic $1a_2''$ MO is 0.67 eV higher in energy than the highest degenerate σ -MO ($2e_2'$), while in As_5^- the analogous $1a_2''$ MO is 1.54 eV lower in energy than the highest degenerate σ -MO ($2e_1'$). Thus, in the case of the aromatic hydrocarbon C_5H_5^- , the σ -MOs are filled before the π -MOs. But in the case of As_5^- , the π -aromatic $1a_2''$ MO (HOMO-2) is lower in energy than the $2e_1'$ (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 $1a_2''$ MO is lower in energy even more: it becomes separated from the $1e_1''$ 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_{4v} NaGa_4^- , D_{4h} Na_2Ga_4 , and C_s Na_2Ga_4 ,⁶³ as well as in C_{2v} 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_z 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_5H_5^- reveals that while both species are aromatic, their order of the valence MOs is different. In the case of the aromatic hydrocarbon C_5H_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 inability of pentapnictogens to form large polycyclic planar aromatic systems, analogous to naphthalene and anthracene. This question will be addressed in the future using large pentapnictogen clusters.

8. Conclusions

We have carried out a combined photoelectron spectroscopy and ab initio study of the pentapnictogen Pn_5^- ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{and Bi}$) 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-roof low-lying singlet isomer. We found that the stability of the aromatic planar cyclic structure relative to the C_{2v} bridged-roof 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_5H_5^- with the same set of π -orbitals. However, we found that the $1a_2''$ 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_5H_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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