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Photoelectron spectroscopy of boron aluminum hydride cluster anions

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Boron aluminum hydride clusters are studied through a synergetic combination of anion photoelectron spectroscopy and density functional theory based calculations. Boron aluminum hydride cluster anions, $B_xAl_yH_z^-$, were generated in a pulsed arc cluster ionization source and identified by time-of-flight mass spectrometry. After mass selection, their photoelectron spectra were measured by a magnetic bottle-type electron energy analyzer. The resultant photoelectron spectra as well as calculations on a selected series of stoichiometries reveal significant geometrical changes upon substitution of aluminum atoms by boron atoms. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871884>]

I. INTRODUCTION

Even though aluminum and boron belong to the same group in the periodic table, they show great differences in their hydride chemistry. Boron is known for its rich chemistry with hydrogen.^{1,2} Boron hydrides (boranes), with a broad diversity of stoichiometries^{1–4} have been studied since 1912 when the first boranes were prepared and characterized. On the other hand, aluminum is known to only exhibit the oxidation state of 0 or +3. Only a few aluminum hydrides (alanes) have been reported earlier.⁵ For example, AlH_3 and Al_2H_6 molecules exist in cryogenic matrices,^{6,7} in gas phase,⁸ and on surfaces.⁹ Polymeric alanes were also characterized as AlH_4^- and AlH_6^{3-} in their alkali metal salts.¹⁰

In recent years, there has been a considerable interest in energetic materials and in substances associated with the hydrogen economy. Decades ago, boranes were believed to be promising energetic materials.^{11–15} However, the highly exothermic reaction of boranes oxidation¹⁶ cannot be completed due to the formation of stable hydrogen-containing species such as HBO, HOBO, and $H_2B_2O_3$,¹³ which prevent further oxidation to release all the energy. Very recently, more than 200 new aluminum hydride cluster anions have been discovered by mass spectrometry.^{17–20} Some of these aluminum hydrides were recognized as magic species in the mass spectra,^{18,20} and further confirmed by photoelectron spectroscopy and theoretical calculations.^{17–19} Although there is no direct evidence that these aluminum hydrides exist in condense phase, Henke *et al.* were able to synthesize and characterize bulk material of $Al_4(P^tBu_2)_6$, a derivative of the Al_4H_6 .²¹ A baby-crystal of solid $\gamma-AlH_3$, Al_6H_{18} , was also predicted by theoretical calculations.²² Similar to boranes, aluminum hydrides (alanes) are also believed to be excellent energetic materials.^{23–25} More importantly, alanes are shown

to follow a different combustion mechanism where hydrogens are released at relatively low temperature followed by complete energy release.²⁵ This was also confirmed in our mass spectrometric studies on aluminum hydride oxidation.²⁶

Considering the different behavior of alanes and boranes, it is interesting to study their mixed hydrides, i.e., boron aluminum hydrides (or aluminum boron hydrides). Theoretical studies^{27,28} confirmed a dramatic structural diversity among B_3H_3 , B_2AlH_3 , BAl_2H_3 , and Al_3H_3 . Similar electronic and geometric structural changes were also reported in mass spectrometric²⁹ and photoelectron spectroscopic studies³⁰ on $B_mAl_n^-$ cluster anions. Thus, when boron atoms within boranes are substituted by aluminum atoms (or aluminum atoms within alanes are substituted by boron atoms), it might be possible to manipulate the properties of the complex by controlling the ratio between aluminum and boron atoms. More importantly, boron aluminum hydrides might bypass the formation of HOBO species and release all the energy from the complex, and thus lead to a new category of energetic materials.

Here, we report the identification and characterization of a series of boron aluminum hydride clusters, $B_xAl_yH_z$, by mass spectrometry and anion photoelectron spectroscopy. To better understand the properties of these boron aluminum hydride clusters, density functional theory (DFT) based calculations were carried out on selected $B_xAl_yH_z$ cluster anions and their corresponding neutrals. The computational focus of this study was on neutral and negatively charged Al_6H_2 and $B_xAl_yH_2$ ($x + y = 6$) clusters. Al_6H_2 cluster was shown to be a stable magic cluster, following 20-electron shell closing.^{17,31} Moreover, it has been shown that the neutral and anionic Al_6H_2 clusters prefer to form an octahedral structure with the hydrogen atoms either bonding radially or bridging the Al atoms.¹⁷ Note that Al_6H_2 and $B_xAl_yH_2$ ($x + y = 6$) are isoelectronic clusters. The choice of Al_6H_2 and $B_xAl_yH_2$ ($x + y = 6$) clusters for our computational calculations is thus motivated by the stability of Al_6H_2 cluster and to investigate

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how this stable 20 electron system responds to a sequential substitution of aluminum atom with boron atoms.

II. METHODS

A. Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a beam of mass selected anions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Our apparatus has been described in detail in Ref. 32. In brief, the apparatus consists of an ion source, a linear time-of-flight (TOF) mass spectrometer, a Nd:YAG photodetachment laser, and a magnetic bottle photoelectron spectrometer (MB-PES). The instrumental resolution of the MB-PES is ~ 35 meV at 1 eV EKE. The fourth harmonic (266 nm, 4.661 eV/photon) of a Nd:YAG was used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the well-known atomic lines of Cu^- .³³

In the present work, both aluminum hydride and boron aluminum hydride cluster anions were generated in a pulsed arc cluster ionization source (PACIS), which has been described in detail in Ref. 19. In brief, a discharge is triggered between a copper anode and a sample cathode and vaporizes sample from the cathode. For aluminum hydride clusters, an aluminum rod was used as the cathode. For boron aluminum hydride clusters, the cathode was prepared by mixing and pressing aluminum and isotopic boron powder (^{11}B) into a well drilled on the top of an aluminum rod. About 10-bar of UHP (ultrahigh purity) hydrogen gas is back-filled into the discharging region between the anode and the cathode. Then, a ~ 30 μs long 150 V pulse is applied to the anode causing the discharge between the electrodes where the hydrogen gas partially dissociates (generating a momentarily high concentration of H atoms) and aluminum (or boron and aluminum) atoms are vaporized. About 10-bar of helium gas flushes the aluminum-(boron)-hydrogen plasma mix down a 20 cm flow tube, where it reacts, cools and forms clusters. The source was operated at 10 Hz repetition rate.

B. Computational

Electronic structure calculations based on density functional theory (DFT) were carried out on neutral and negatively charged Al_6H_2 and $\text{B}_x\text{Al}_y\text{H}_z$ ($x + y = 6$; $x = 1-3$) clusters using the Gaussian 09 program.³⁴ The Becke's three parameter hybrid exchange functional³⁵ with Lee, Yang, and Parr correlation functional³⁶ (B3LYP) form, along with 6-311+G** basis set was used for all calculations. In the geometry optimization, the convergence criterion for energy was set to 10^{-9} hartree, while the gradient was converged to 10^{-4} hartree/Å. Vibrational frequency calculations were carried out to verify the stability of these clusters and all the isomers were found to have positive frequencies.

The vertical detachment energies (VDEs) and the adiabatic detachment energies (ADE) are calculated for the lowest energy isomers and compared with the measured values to verify the reliability of the predicted structures. The VDE is the energy difference between the ground state anion and its neutral counterpart at the geometry of the anion. The ADE is calculated to be the energy difference between the lowest energy anion and its corresponding neutral with the neutral relaxed into its nearest local minimum. If both the anion and neutral are in their ground states, the ADE of the anion equals the electron affinity (EA) of the neutral.

III. RESULTS AND DISCUSSION

Boron aluminum hydride cluster anions, $\text{B}_x\text{Al}_y\text{H}_z^-$, were generated in the PACIS and analyzed by the TOF mass spectrometer. Isotopic boron powder, ^{11}B , was used in the experiment to avoid possible mass coincidence. Figure 1 shows a typical mass spectrum obtained under low B:Al ratio conditions. Several envelopes of peaks showing bare Al_yH_z^- , BAl_yH_z^- , and $\text{B}_2\text{Al}_y\text{H}_z^-$ cluster anions are identified. The zoomed in region (inset of Figure 1) shows several cluster anions with multiple hydrogen atoms. It should be noted that the mass of $\text{B}_x\text{Al}_y\text{H}_z$ will be the same as that of $\text{B}_{x-3}\text{Al}_{y+1}\text{H}_{z+6}$, and $\text{B}_{x-2}\text{Al}_{y+1}\text{H}_{z-5}$. Extreme care was taken when collecting photoelectron spectrum of mass selected clusters. For example, the photoelectron spectrum of the mass peak at 88 amu, which could be Al_4H_7^- or $\text{B}_3\text{Al}_3\text{H}^-$, is significantly different from the previously reported photoelectron spectrum of Al_4H_7^- ,¹⁸ confirming the species observed in current study was indeed $\text{B}_3\text{Al}_3\text{H}^-$.

Photoelectron spectra of relatively intense $\text{B}_x\text{Al}_y\text{H}_z$ cluster anions were collected and are presented in Figure 2. The spectra are organized based on the total number of boron and aluminum atoms (in each block) and the number of

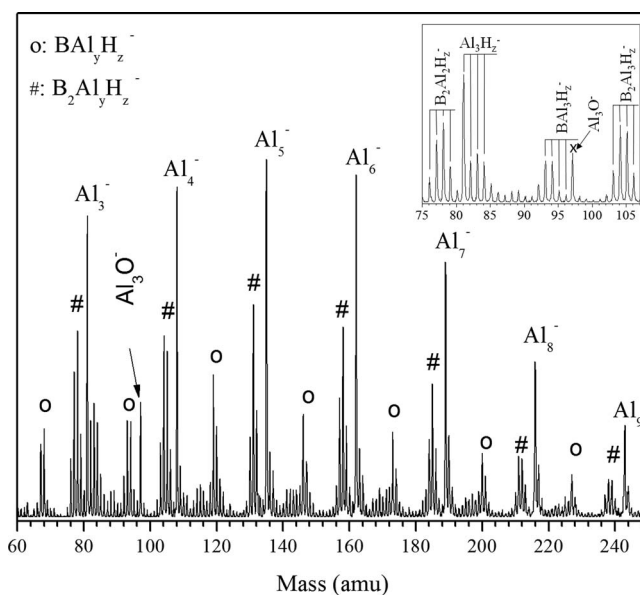


FIG. 1. Mass spectrum of boron aluminum hydride cluster anions, $\text{B}_x\text{Al}_y\text{H}_z^-$. Al_y^- cluster anions are indicated in the spectrum. BAl_yH_z^- cluster anions are marked with an “o,” while $\text{B}_2\text{Al}_y\text{H}_z^-$ cluster anions are marked with a “#.” The inset shows cluster anion peaks with multiple hydrogen atoms. (The Al_3O^- cluster anion is observed as an impurity.)

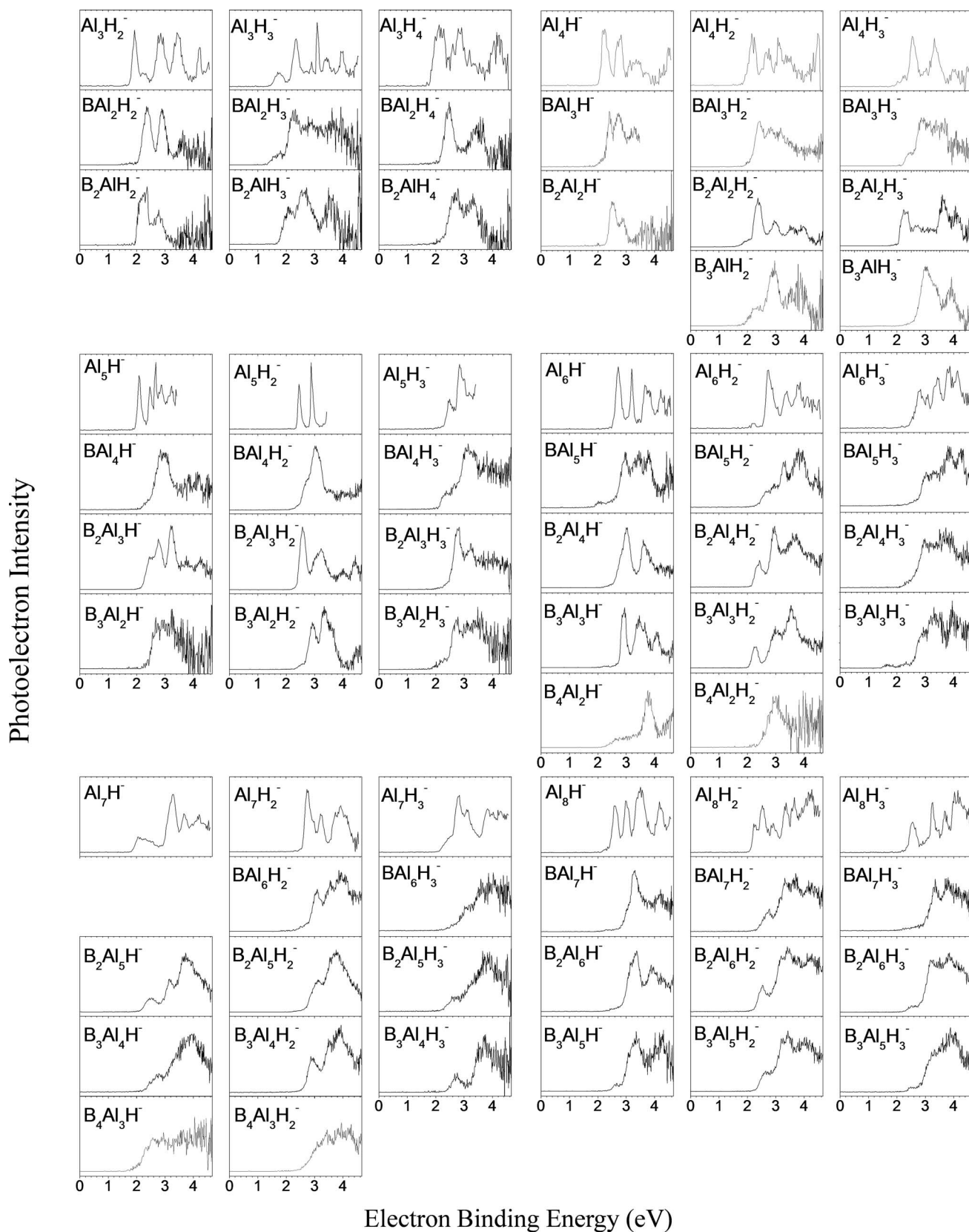


FIG. 2. Photoelectron spectra of boron aluminum hydride cluster anions, $B_xAl_yH_z^-$, where $x = 0-4$, $y = 3-8$, and $z = 1-4$.

hydrogen atoms (in each column within a block). Overall, multiple peaks (features) are observed in most of the spectra. The positions of the peaks in each spectrum measure the electron binding energies (EBE) of the photodetachment transi-

tions from the ground electronic state of the particular cluster anion to the ground and excited electronic states of the cluster anion's neutral counterpart. The electron affinity (EA) of the neutral and the vertical detachment energy (VDE) of the

TABLE I. Experimental EA and VDE values extracted from the photoelectron spectra of $B_xAl_yH_z^-$ cluster anions.

| $B_xAl_yH_z$ | $z = 1$ | | $z = 2$ | | $z = 3$ | | $z = 4$ | |
|--------------|---------|------|---------|------|---------|------|---------|------|
| | EA | VDE | EA | VDE | EA | VDE | EA | VDE |
| $x + y = 3$ | | | | | | | | |
| Al_3H_z | | | 1.7 | 1.92 | 1.5 | 1.73 | 1.8 | 2.12 |
| BAI_2H_z | | | 2.1 | 2.34 | 1.4 | 1.73 | 2.1 | 2.47 |
| B_2AlH_z | | | 1.9 | 2.23 | 1.7 | 2.06 | 2.2 | 2.66 |
| $x + y = 4$ | | | | | | | | |
| Al_4H_z | 2.0 | 2.21 | 1.9 | 2.18 | 2.2 | 2.53 | | |
| BAI_3H_z | 2.1 | 2.40 | 2.1 | 2.41 | 2.4 | 2.87 | | |
| $B_2Al_2H_z$ | 2.3 | 2.53 | 2.0 | 2.37 | 2.1 | 2.28 | | |
| B_3AlH_z | | | 1.9 | 2.34 | 2.6 | 2.99 | | |
| $x + y = 5$ | | | | | | | | |
| Al_5H_z | 2.0 | 2.08 | 2.4 | 2.45 | 2.3 | 2.49 | | |
| BAI_4H_z | 2.3 | 2.84 | 2.4 | 2.74 | 2.1 | 2.43 | | |
| $B_2Al_3H_z$ | 2.2 | 2.47 | 2.3 | 2.57 | 2.5 | 2.78 | | |
| $B_3Al_2H_z$ | 2.3 | 2.76 | 2.5 | 2.91 | 2.3 | 2.69 | | |
| $x + y = 6$ | | | | | | | | |
| Al_6H_z | 2.5 | 2.72 | 2.0 | 2.22 | 2.4 | 2.81 | | |
| BAI_5H_z | 2.6 | 2.96 | 2.4 | 2.71 | 2.8 | 3.01 | | |
| $B_2Al_4H_z$ | 2.5 | 3.01 | 2.1 | 2.43 | 2.6 | 2.94 | | |
| $B_3Al_3H_z$ | 2.7 | 2.94 | 2.1 | 2.30 | 2.5 | 2.97 | | |
| $B_4Al_2H_z$ | 2.3 | 2.64 | 2.4 | 2.94 | | | | |
| $x + y = 7$ | | | | | | | | |
| Al_7H_z | 1.8 | 2.07 | 2.6 | 2.73 | 2.1 | 2.50 | | |
| BAI_6H_z | | | 2.7 | 3.07 | 2.7 | 3.09 | | |
| $B_2Al_5H_z$ | 2.1 | 2.49 | 2.7 | 3.09 | 2.3 | 2.60 | | |
| $B_3Al_4H_z$ | 2.3 | 2.76 | 2.6 | 2.87 | 2.4 | 2.73 | | |
| $B_4Al_3H_z$ | 1.8 | 2.34 | 2.6 | 3.08 | | | | |
| $x + y = 8$ | | | | | | | | |
| Al_8H_z | 2.3 | 2.60 | 2.1 | 2.27 | 2.3 | 2.55 | | |
| BAI_7H_z | 2.8 | 3.29 | 2.4 | 2.74 | 2.9 | 3.33 | | |
| $B_2Al_6H_z$ | 2.8 | 3.19 | 2.3 | 2.51 | 2.8 | 3.19 | | |
| $B_3Al_5H_z$ | 2.7 | 3.06 | 2.3 | 2.66 | 2.7 | 3.22 | | |

anion are estimated from the EBE values at the onset (threshold) region and at the intensity maximum, respectively, in the lowest EBE band in the spectrum. The EA is the energy difference between the ground states of the anion and its neutral cluster, while the VDE is the energy difference between the anion and its neutral counterpart at the geometry of the anion. If the ground state structures of anion and neutral clusters differ significantly, the onset (threshold) region of the lowest EBE peak is compared to the calculated ADE of the anionic cluster. If the structure of the neutral is similar to that of the anion, the VDE will be close to EA, as indicated by sharper peaks. The experimental EA and VDE values of all $B_xAl_yH_z$ clusters are extracted from the spectra and tabulated in Table I.

As shown in Figure 2, in general, relatively sharp peaks are observed in the photoelectron spectra of clusters with no boron atoms, indicating less structural change between the neutrals and corresponding anions. In addition to peak broadening, within the same column in Figure 2 (species with same number of hydrogen atoms), addition of boron atoms also results in fewer peaks in the spectra. For example, the spectra of $B_4Al_yH_z^-$ ($y = 2, 3; z = 1, 2$) only show one broad peak, while the spectra of corresponding $Al_{y+4}H_z^-$ clusters feature multiple sharp peaks. This phenomenon can be attributed to the smaller covalent radii (0.84 Å for boron vs. 1.21 Å for aluminum) and higher electronegativity (2.04 for boron vs. 1.61 for aluminum on Pauling scale) of boron. In addition, boron clusters and some boron hydride clusters prefer to form pla-

nar structures,^{37–40} while aluminum and aluminum hydrides favor 3D structures, especially for large sizes.^{18,41} These different properties of boron can lead to strong perturbation to the aluminum structures, which resulted in differences in EA values (Table I) and the general spectral patterns (Figure 2) between the $B_xAl_yH_z^-$ and $Al_{x+y}H_z^-$ anions. Their structures are quite different.

In addition, among the series of species varying in only number of hydrogen atoms, the EA values (see Table I) vary in a Zig-Zag pattern as the number of hydrogen atoms increases. For example, the EA of BAI_2H_2 is measured to be 2.1 eV, while that of BAI_2H_3 drops to 1.4 eV, and that of BAI_2H_4 increases back to 2.1 eV. Similar variations in electron affinities were reported in previous studies on $Al_yH_z^-$ clusters.¹⁸ Since the B-H interaction is different than the Al-H interaction,^{27,28} additional hydrogen atoms could lead to significantly different geometries. It should also be mentioned that no clear patterns are observed comparing the spectra of species varying only in number of boron atoms or aluminum atoms.

Because Al_6H_2 cluster was shown to be a stable magic cluster,^{17,31} both experimental and theoretical studies were carried out on Al_6^{2-} and B_6^{2-} dianion clusters,^{42–44} and also because $B_xAl_yH_2$ ($x + y = 6$) clusters are isoelectric to Al_6H_2 clusters, we carried out a comprehensive study on $B_xAl_yH_2$ ($x + y = 6, x = 1–3$) clusters. The photoelectron spectra of $Al_6H_2^-$ and $B_xAl_yH_2^-$ ($x + y = 6; x = 1–3$) are extracted and presented in Figure 3. In order to identify the ground

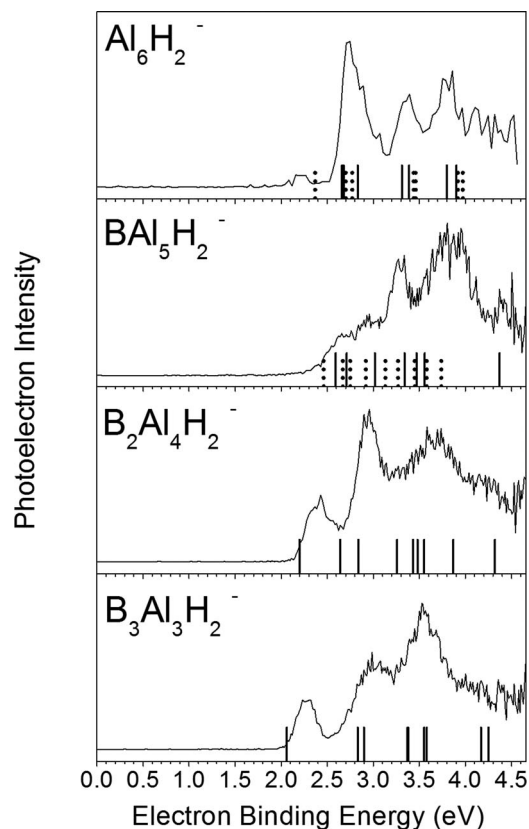


FIG. 3. Photoelectron spectra of $Al_6H_2^-$ and $B_xAl_{6-x}H_2^-$ ($x = 0–3$) along with calculated transitions. The solid sticks denote transitions from lowest energy anion to the corresponding neutral. The dotted sticks denote transitions from the second lowest anion isomers (isomer II for $Al_6H_2^-$ and isomer 2 for $BAI_5H_2^-$).

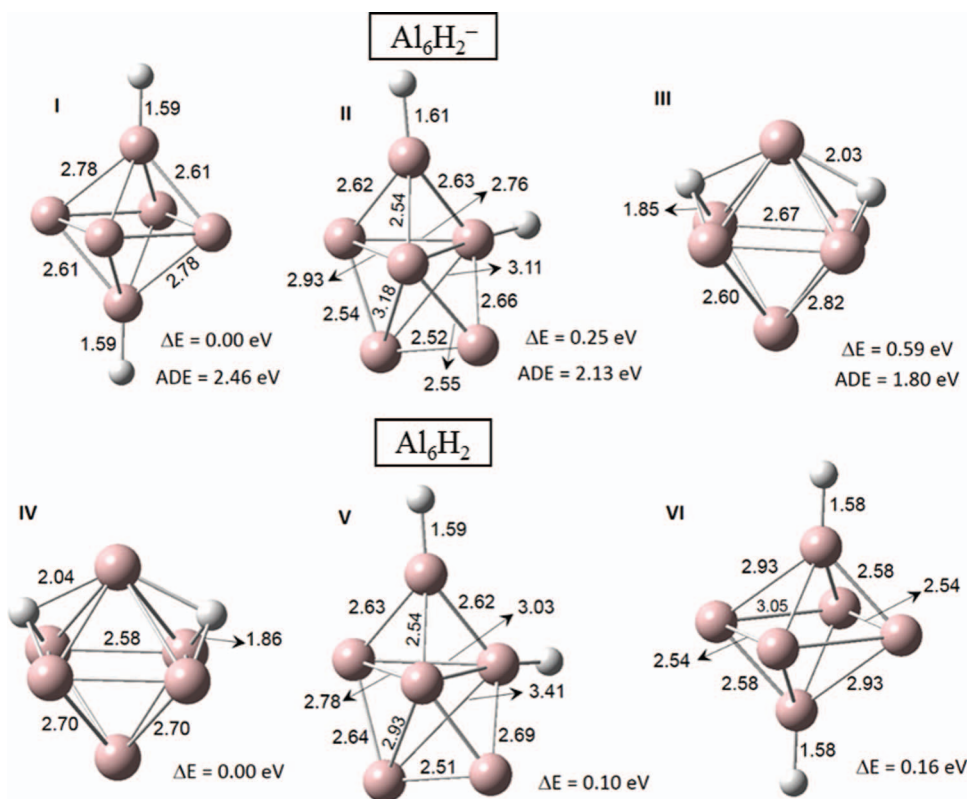


FIG. 4. Calculated geometries of low energy isomers of anionic and neutral Al_6H_2 clusters. **I–III** present the structures of the isomers of the Al_6H_2^- anion, whereas **IV–VI** present the structures of the isomers of the neutral Al_6H_2 cluster. The bond lengths are given in Å. The calculated adiabatic detachment energies (ADEs) are shown in eV.

state geometries of $\text{B}_x\text{Al}_y\text{H}_2$ ($x + y = 6$; $x = 1-3$) clusters and to check if the sequential substitution of aluminum atoms with boron atoms is indeed resulting in a significant structural change as hypothesized from the PES spectra results above, DFT based calculations were carried out on neutral and negatively charged Al_6H_2 and $\text{B}_x\text{Al}_y\text{H}_2$ ($x + y = 6$; $x = 1-3$) clusters.

It should be noted that the EA of Al_6H_2 estimated from our experiment (2.0 eV) is different from previous reported value (1.66 eV).³¹ This inconsistency could be attributed to the difference in experimental conditions which lead to the observation of different isomers. The ground state and other higher energy isomers of these clusters are given in Figure 4. The ground state geometry (**I**) of the Al_6H_2^- cluster anion is an octahedral structure in which the two hydrogen atoms are bonded terminally to the two opposite aluminum atoms. A face-capped trigonal bi-pyramidal structure (**II**), with two radially bonded hydrogen atoms, was found to be 0.25 eV higher in energy than isomer **I**. The octahedral structure in which both the hydrogen atoms cap the face-sites of the octahedron (**III**) was found to be 0.59 eV higher in energy than the lowest energy structure (**I**). The calculated VDE of isomer **I** (2.66 eV) is in agreement with the second EBE peak (2.75 eV), while the VDE of isomer **II** (2.37 eV) is in good agreement with the lowest EBE peak (2.22 eV) of the Al_6H_2^- spectrum (see Figure 3), indicating that both these isomers were produced in the cluster beam. In addition, the calculated transitions from the ground electronic state of the isomers **I** and **II** to the ground and excited electronic states of the cor-

responding neutral clusters are presented as stick spectra in Figure 3. Although not each transition can be identified in the spectrum due to the spectral resolution, the calculated transitions for both isomers **I** and **II** match well with the spectral features. In the neutral Al_6H_2 cluster, the octahedral structure with the hydrogen atoms capping the face-sites (**IV**) was found to be ground state geometry, while the neutral Al_6H_2 isomer (**VI**), having the same structure as the lowest energy isomer of the anion (**I**), is 0.16 eV higher in energy than the ground state of the neutral cluster (**IV**). The face-capped trigonal bi-pyramidal structure (**V**) was 0.10 eV higher in energy than isomer **IV**. Thus, Al_6H_2 cluster, both in its neutral and anionic states, prefers to form a compact octahedron or a face capped trigonal bi-pyramidal structure. The lowest energy structures of neutral and anionic Al_6H_2 clusters are consistent with our previously reported theoretical results.¹⁷ However, in the previous study the possibility of face-capped trigonal bi-pyramidal structure was not considered.

We now compare the geometrical structures and the energetics of Al_6H_2 clusters to those of the $\text{B}_x\text{Al}_y\text{H}_2$ ($x + y = 6$) clusters. First, we start by substituting a single aluminum atom in the Al_6H_2^- with a boron atom resulting in BAI_5H_2^- cluster. The ground state and energetically low lying isomers of negatively charged and neutral BAI_5H_2^- clusters are given in Figure 5. The lowest energy isomer (**I**) of BAI_5H_2^- anion is a quasi-planar structure, in which a planar BAI_4 moiety, with the boron atom in the middle of the AI_4 ring, is bound to an AIH_2 unit. The planarity of the BAI_5H_2^- anion is in contrast with the ground state structure of Al_6H_2^-

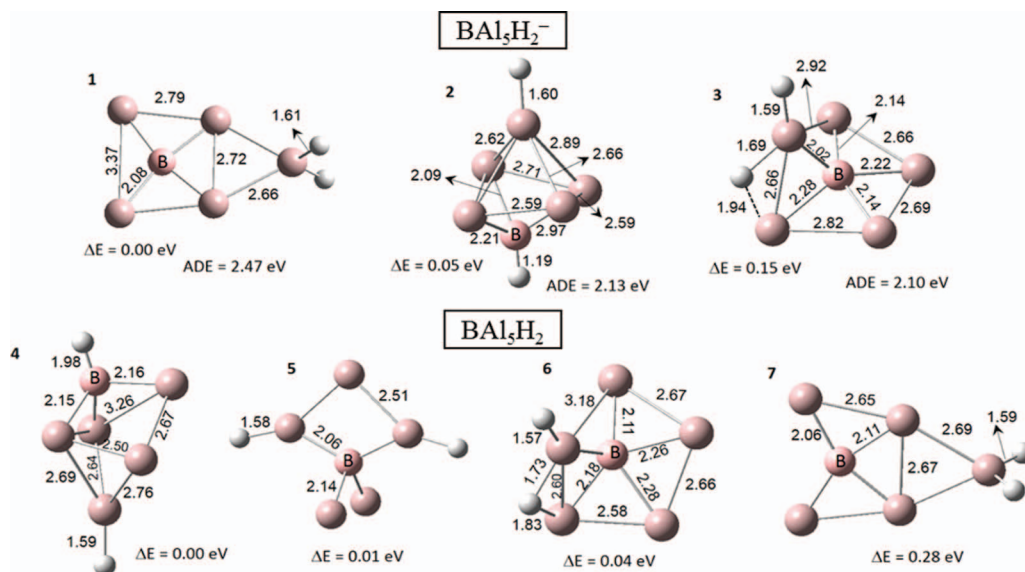


FIG. 5. Calculated geometries of low energy isomers of anionic and neutral $\text{BA}_5\text{H}_2^{-/0}$ clusters. **1–3** present the structures of the isomers of the $\text{BA}_5\text{H}_2^{-}$ cluster anion, whereas **4–7** present the structures of the isomers of the BA_5H_2 neutral cluster. The bond lengths are given in Å. The calculated adiabatic detachment energies (ADEs) are shown in eV.

cluster anion that was discussed above and reported in previous studies.^{17,31,41} Interestingly, a distorted octahedron-like structure (**2**) was found to be only 0.05 eV higher in energy than isomer **1**. Isomer **2** is similar to the ground state structure of $\text{Al}_6\text{H}_2^{-}$ with the aluminum atom on the vertex substituted by a boron atom. Since, boron atom is smaller in size and more electronegative than aluminum atom, it capped only three aluminum atoms in the octahedron, thereby leading to a distorted structure. A quasi-planar isomer (**3**), in which Al_5 forms a pentagonal ring, with the B atom at the center and the hydrogen atoms binding radially to one of the aluminum atoms, is found to be 0.15 eV higher in energy than isomer **1**.

In the case of neutral BA_5H_2 cluster, we found three energetically degenerate isomers, **4**, **5**, and **6** with three different boron atom bonding patterns. Isomer **4** is a highly distorted octahedron-like structure, with one of the hydrogen atoms bonded to boron atom and the other bonded to aluminum atom. This 3D isomer is similar to the second lowest energy isomer (**2**) of the anionic $\text{BA}_5\text{H}_2^{-}$ cluster and the ground state structure of $\text{Al}_6\text{H}_2^{-}$ cluster. In Isomer **5**, boron atom prefers to have a tetrahedral coordination, while isomer **6** is a quasi-planar with one of the aluminum atoms out of the plane. In these two isomers, the H atoms are bound to Al atom radially or to two Al atoms on the bridge site. Interestingly, the planar structure (**7**), similar to the lowest energy structure (**1**) of anionic $\text{BA}_5\text{H}_2^{-}$ cluster, is found to be 0.28 eV higher in energy than the lowest energy octahedral structure (isomer **4**). Thus, the substitution of a single aluminum atom with a boron atom in $\text{Al}_6\text{H}_2^{-/0}$ clusters leads to a competition between planar (or quasi-planar) and compact three-dimensional structures in the resultant $\text{BA}_5\text{H}_2^{-/0}$ clusters.

Since the energy difference between the three anionic isomers is small, we have calculated the VDE values of all three isomers (**1–3**). The VDE values of 2.59 eV (isomer **1**) and 2.46 eV (isomer **2**) compare well with the experimental value

of 2.71 eV. However, the calculated VDE value of isomer **3**, which is 2.31 eV, is much lower than the experimental value. Thus it is unlikely that isomer **3** is present in cluster beam. In order to further verify this, we have calculated the higher energy transitions of the lowest energy isomers (**1** and **2**) of anionic $\text{BA}_5\text{H}_2^{-}$ clusters, shown as stick spectra in Figure 3. Note that some of the transitions are very close to each other in energy, resulting in broad peak observed in the photoelectron spectrum. Transitions corresponding to both isomers **1** and **2** match well with the spectral features. Thus, it is likely that both isomer **1** and **2** are present in the cluster beam. Further understanding of the nature of these transitions comes from analyzing the corresponding molecular orbitals (MOs). The four highest occupied MOs for the isomers **1** and **2** are given in Figure 7. Despite the structural dissimilarities between **1** (quasi planar) and **2** (three-dimensional), the frontier orbitals reveal that the electrons are localized on aluminum atoms and contributions from the boron is minimal. This partially explains the close proximity of the transition energies of **1** and **2**.

Although there is a competition between planar (or quasi-planar) and octahedron-like structures in neutral and anionic BA_5H_2 clusters, as we increase the number of boron atoms, the resulting clusters clearly prefer to form planar structures. In Figure 6, we present the lowest energy isomers of neutral and anionic $\text{B}_x\text{Al}_y\text{H}_2$ ($x + y = 6$; $x = 1-3$) clusters, along with those of Al_6H_2 cluster for comparison. As one moves from BA_5H_2 to $\text{B}_2\text{Al}_4\text{H}_2$ and finally to $\text{B}_3\text{Al}_3\text{H}_2$ cluster, by sequentially replacing aluminum with boron atoms, two distinct structural changes, apart from the planarity of the clusters, were observed. First, the boron atoms bond together and appear as a B_2 unit in $\text{B}_2\text{Al}_4\text{H}_2$ cluster and as B_3 unit in $\text{B}_3\text{Al}_3\text{H}_2$ cluster, while the remaining aluminum atoms adjust around the boron group. Second, the hydrogen atoms bond to the boron atoms rather than to the aluminum atoms. Preference for these structural changes can be traced back

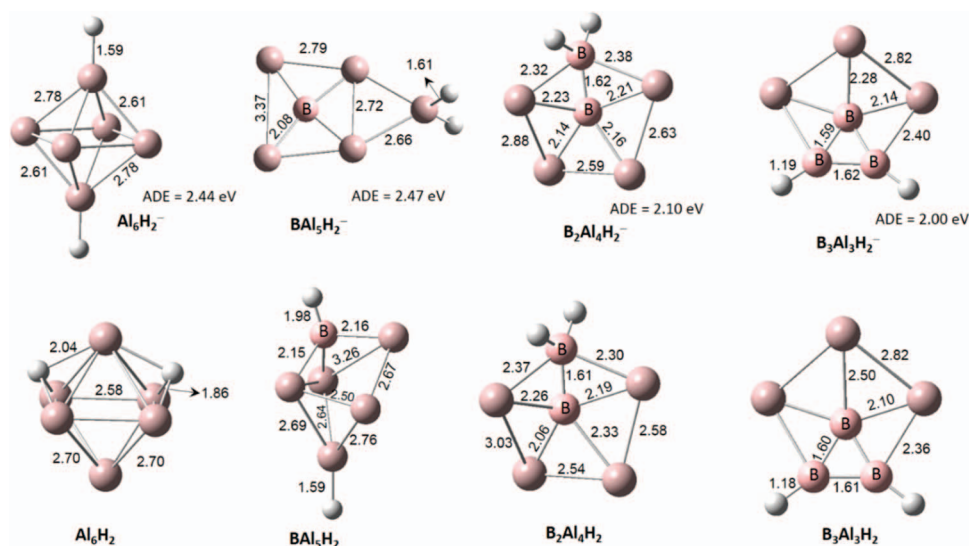


FIG. 6. Calculated geometries of ground state $B_xAl_{6-x}H_2^-$ ($x = 0-3$) cluster anions and neutral $B_xAl_{6-x}H_2$ clusters. The bond lengths are given in Å, and the calculated ADEs are shown in eV.

to the bond-strengths. Both B-B and B-H bonds are stronger than the corresponding Al-Al and Al-H bonds. The calculated VDE/ADE values of $B_2Al_4H_2^-$ cluster is 2.20/2.10 eV, which are in reasonable agreement with the measured VDE/EA values of 2.43/2.10 eV. Similarly, the calculated VDE (2.06 eV) and ADE (2.00 eV) values of $B_3Al_3H_2^-$ cluster are in agreement with experimental VDE (2.30 eV) and EA (2.1 eV) values, respectively. In addition, the higher energy transitions for $B_2Al_4H_2^-$ and $B_3Al_3H_2^-$ cluster were also calculated and shown as solid sticks in Figure 3. These calculated transitions match well with the features in the photoelectron spectra, and thus validate the calculated geometries. When the ground state structures of anion and neutral are similar, the VDE and ADE values are very close to each other. This is indeed reflected in our calculated VDE and ADE values of $B_2Al_4H_2^-$ (2.20 and 2.10 eV) and $B_3Al_3H_2^-$ (2.06 and 2.00 eV) clusters. Note that in the photoelectron spectra of

these clusters, however, broad peaks are observed due to multiple transitions, with similar energies, contributing towards a single peak in the spectra.

Furthermore, the MOs of these clusters (Figure 7) show that as the number of boron atoms increase from one to three the tendency for the electron localization on aluminum atoms increases, thus, lowering the binding energy. This can be understood from the corresponding VDEs which continuously move towards smaller value (Table I). Thus, the current calculations reveal that addition of one boron atom does not affect the compact structural skeleton of neutral Al_6H_2 cluster other than through minor distortion. However, as the number of boron atoms increase in mixed clusters, the structures tend to open-up and form planar (or quasi-planar) structures with B_n units. Planar structure was also predicted for B_6H_2 clusters.⁴⁰ Based on these results, one could predict that in $B_xAl_yH_z$ clusters with high boron content, all the boron atoms will bond together, while the aluminum atoms surround the resulting boron unit.

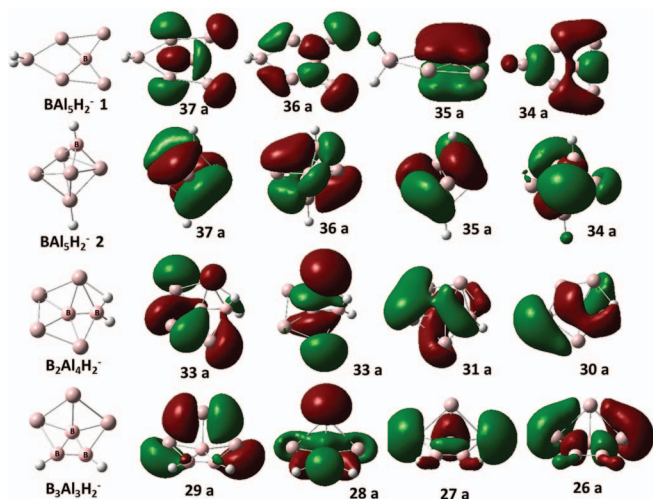


FIG. 7. The four highest occupied molecular orbitals of $BA15H_2^-$ (1 and 2), $B_2Al_4H_2^-$ and $B_3Al_3H_2^-$ clusters.

IV. SUMMARY

Series of boron aluminum hydride cluster anions are generated in the PACIS source and identified by TOF mass spectrometer. Photoelectron spectra are collected for the relatively abundant $B_xAl_yH_z^-$ cluster anions. Comparisons between the photoelectron spectra of $B_xAl_yH_z^-$ and $Al_{x+y}H_z^-$ reflect geometric changes upon substitution of aluminum atoms with boron atoms. Density functional theory based calculations on $Al_6H_2^{-/0}$ and $B_xAl_yH_2^{-/0}$ ($x + y = 6$, $x = 1-3$) clusters further confirm the structural differences between the aluminum hydride clusters and boron aluminum hydride clusters. As candidates for energetic materials, boranes have a checkered history because of the stable hydrogen-containing species such as HBO, HOBO and $H_2B_2O_3$.¹³ The boron aluminum hydrides might be able to release all of their energy, thus serving as improved energetic materials.

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