A Combined Theoretical and Photoelectron Spectroscopy Study of Al$_3$H$_n^-$ ($n=1$–9) clusters


Combined photoelectron spectroscopic experiments and computational studies have been performed on Al$_3$H$_n^-$ ($n=1$–9) clusters. Three modes of hydrogen bonding to the Al$_3$ moiety have been observed: terminal, bridging, and capping. Among various hydrides, Al$_3$H$_5^-$ and Al$_3$H$_6^-$ clusters have highest HOMO-LUMO gap and largest electron affinity, respectively. Our studies indicate that as the number of hydrogen atoms increase the presence of AlH$_2$ groups, representing the tetrahedral coordination of the Al atom, which in turn led to the stoichiometric ring structure.

Introduction

The hydrides of Group 13 elements, especially B and Al, have received a great attention due to their promising potential as hydrogen-storage species and high-energy density materials.[1,2] So far, boron hydrides have been extensively studied, resulting in the fruitful borane chemistry.[3–5] However, knowledge of the aluminum hydrides is still very limited.[6] The absence of reliable experimental data can partially be ascribed to the highly reactive bonds formed between Al and H elements, which have rendered great challenge in synthesis and characterizations. At present, only small alanes AlH$_3$ and AlH$_5$ have been identified in both cryogenic matrices and the gas phase.[6–8] The AlH$_3$ compound, which has 10.1 wt% of hydrogen and a density of 0.148 g/ml, can grow into ring or chain polymeric structures through hydrogen bridges, similar to the ways how AlH$_4^-$, AlH$_4^{2-}$ and AlH$_5^{2-}$ aggregate in alkali metal salts.[9] Unlike the above examples where H bridges were observed, an unprecedented aluminum chain was observed in the Li$_4$AlH$_6^-$ cluster, where the Al$_3$H$_5^-$ kernel mimics the propane molecule.[10] State-of-the-art gas phase techniques facilitate the study of these highly reactive compounds; more than two hundred new aluminum hydride cluster anions were discovered in the gas phase and characterized by anion photoelectron spectroscopy,[11–17] thus becoming a major source of the knowledge on aluminum hydrides.

Small alanes Al$_{m}$H$_n$ ($m<4$) are important intermediates in producing larger alanes. Yet, they don’t follow the well-known Wade-Mingos rule.[1,4,18] Moreover, in these simple systems, the bonding associated with H-atoms might compete with the Al–Al bonding, different from the situation in larger alanes where the electron counting in Al$_m$-cluster plays an important role.[11,12,13] Therefore, despite the simplicity, the inherent bonding complexity has resulted a lot of low-lying isomers. Calculations on Al$_3$H$_n$, $n=1$, 2, 5, 7, 9 have already been reported,[19–38] but their ground state structures are inconclusive. For example, the ground state structure of Al$_3$H$_5$ was suggested to be the consequence of adding two single H bridge to AlH$_3$[25,26] but also considered to have a double bridge.[24,27] We should note that most of the theoretical work on Al$_3$H$_n$ (except ref. 22, 25, 28–30) were carried out at the density functional theory (DFT) level with no higher-level energy corrections.

In this paper, with combined photoelectron spectroscopic experiments and DFT based computations, we carried out a systematic investigation of the structures and the bonding patterns of Al$_3$H$_n^-$ ($n=1$–9) clusters.

Methods

Experimental

Aluminum hydrides were generated in pulsed arc cluster ionization source (PACIS)[31] which has been described in detail previously.[31] In brief, a ~30 μs long 150 V electrical pulse were applied at 10 Hz across a copper anode and an aluminum cathode of the discharging chamber vaporizing aluminum atoms and forming plasma. At the same time, ~200 psi of ultrahigh purity hydrogen gas was also introduced into the discharge region, where it was dissociated into hydrogen...
atoms. The resulting mixture of atoms, ions, and electrons then reacted and cooled as it flowed along a 20 cm tube before exiting into high vacuum. The resulting anions were then extracted and mass-selected prior to photodetachment.

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fix-frequency photon beam and energy-analyzing the resultant photodetached electrons. This process is governed by the energy-conserving relationship,\(^{\text{14}}\)\(^{\text{15}}\)\(^{\text{19}}\)\(^{\text{28}}\)\(^{\text{32}}\) \(h \nu = E_{\text{BE}} + E_{\text{KE}}\), where \(h \nu\) is the photon energy, \(E_{\text{BE}}\) is the electron binding energy, and \(E_{\text{KE}}\) is the electron kinetic energy. Our apparatus, which has been described in detail elsewhere,\(^{\text{32}}\) consists of an ion source, a time-of-flight mass spectrometer, a Nd:YAG photodetachment laser, and a magnetic bottle photoelectron spectrometer (MB-PES). The instrumental resolution of the MB-PES is \(\approx 35\) meV at 1 eV EKE. The fourth harmonic (266 nm, 4.661 eV/photon) of a Nd:YAG was used for photodetachment of anions of interest. Photoelectron spectra were calibrated against the well-known atomic lines of Cu\(^{+}\).\(^{\text{33}}\)

**Computational**

We performed isomeric search for \(\text{Al}_3\text{H}_n^+\) \((q = 0, -1; n = 1–11)\) through the “topology strategies”, followed by vibrational frequency confirmation to ensure that a local minimum isomer has all real frequencies. As shown in Figure 1, the initial configurations were established based on the following considerations: i) cyclic and open \(\text{Al}_3\)-skeleton, ii) terminal (\(-\text{AlH}, -\text{AlH}_2\)) and bridge (i.e., side mono-bridge \(-\text{Al(H)}\text{Al}\), side di-bridge \(-\text{Al(H)}_2\text{Al}\), face bridge \(\Delta(\text{H})\)) hydrogen bonds. Note that the \(\Delta(\text{H})\) bond is only associated with the close structure. In this way, we totally obtained nearly three thousand initial structures. The initial geometrical optimization of various structures was performed at the B3PW91/3-21G(d) level. Excluding the structures with \(\text{H}_2\)-extrusion or \(\text{Al}\)-extrusion, the remaining structures had been optimized at the higher B3PW91/TZVP level. Finally, we obtained 285 structures with all positive frequencies, and the CCSD(T)/cc-pVTZ single-point calculations were performed on the isomers with the energy differences less than 10 kcal/mol to get reliable energetics of these alanes. For the isomers with close energies, computationally more expensive CCSD(T)/aug-cc-pVTZ (energy less than 5 kcal/mol) single-point calculations were performed to ensure the exact ground structures. The vertical electron detachment energy (VDE), the adiabatic detachment energies (ADE), and HOMO-LUMO gap were calculated at both the B3PW91/TZVP and CCSD(T)/aug-cc-pVTZ//B3PW91/TZVP levels. All calculations were carried out using Gaussian 09 program package.\(^{\text{34}}\)

**Results and discussion**

The photoelectron spectra of \(\text{Al}_3\text{H}_n^+\) \((n = 1–9)\) cluster anions are presented in Figure 2. Multiple peaks (features) are observed in the spectra, except for \(\text{Al}_3\text{H}_8^+\) and \(\text{Al}_3\text{H}_9^+\). The position of the peaks in each spectrum measures the electron binding energies (EBE) of the photo-detachment transitions from the ground electronic state of the particular cluster anion to the ground and excited states of the neutral counterpart. The electron affinity (EA) of the neutral can be estimated from the EBE values at the onset region in the lowest EBE band in the spectrum. By definition, the EA is the energy difference between the ground states of the anion and the neutral. The calculated ADE is defined as the energy difference between the ground state structure of the anion and the neutral cluster relaxed to a local minimum near the anionic structure. If the ground state structures of anion and neutral clusters are similar, ADE and EA should be the same value. If multiple peaks are observed in the spectra, the intensity maxima of these peaks represent

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** The initial configurations based on cyclic and open Al3-skeleton, terminal (–AlH, –AlH\(_2\)) and bridge (i.e., side mono-bridge –Al(H)Al, side di-bridge –Al(H)\(_2\)Al, face bridge \(\Delta(\text{H})\)) hydrogen bonds.
transitions from the ground state of anion to the excited states of the neutral counterpart. Among these transitions, the lowest transition is the vertical detachment energy (VDE) of the anion, which is the energy difference between the ground state anion and its neutral counterpart at the geometry of the anion. Estimated EA and transition energies are listed in Table 1 for comparison with computational results. The calculated VDE and ADE values at the DFT level of theory are not only comparable to the corresponding CCSD(T) values but also at times closer to the experimental results. Therefore, we have primarily used DFT results throughout the manuscript.

To better understand the Al$_3$H$_q$\(^{-}\) (q = −1; n = 1–9) clusters, we first focus on the bonding in the bare Al$_3$\(^{-}\) cluster. The Al$_3$\(^{-}\) forms a perfect triangle (D$_{3h}$) with an Al–Al bond length of 2.54 Å. The distribution of the ten valence electrons is shown as molecular orbital diagram in Figure 3. The HOMO (2a’$_1$) consists of three in plane Al 3p orbitals pointing towards the center. This type of σ-bonding is typical for three-membered rings observed in both C$_3$H$_3$\(^+\) and C$_3$H$_6$. The next orbital, HOMO-1 (1a’$_2$) is a π-bonding orbital from the out-of-plane combination of Al 3p orbitals. Note that HOMO and HOMO-1 are very close in energy. The next three orbitals (1e’ and 1a’$_1$), significantly lower in

Figure 2. Photoelectron spectra of Al$_3$H$_{n}^{-}$ (n = 1–9) cluster anions.
energy, are primarily from the Al 3s orbitals with a small (<9%) contribution from the Al 3p. As Wang and coworkers had observed, small Alₙ (n < 5) clusters do not have significant s-p hybridization, and thus in these clusters aluminum atoms essentially behave like one-electron systems. To sum up, Alₙ⁻ is a 4-electron system, displaying both σ- (HOMO) and π- (HOMO-1) aromaticity (double aromatic). The double aromaticity was also observed in the La₃⁻ cluster.[34]

Addition of hydrogen atoms to the Alₙ can occur in at least three ways; terminal (Al-H), bridging (Al-H-Al) and capping (n-H-H). Therefore, in all of the AlₙHₙ⁻ clusters, hydrogens may adopt a combination of these bonding modes depending on the number of hydrogens and charge of the system. In the following we will discuss each AlₙHₙ⁻ cluster in detail. The calculated geometries of the two lowest energy isomers of AlₙHₙ⁻ (n = 1–9) are given in Figure 4, while the frontier molecular orbitals of the lowest energy isomers are shown in Figure 5.

The most stable structure of Al₃⁻ is the one where hydrogen forms terminal bonding (1a¹) with one of the aluminum atoms, and the H-capped isomer (1b¹) is 0.27 eV higher in energy (Figure 4). The calculated VDE and ADE of the terminal isomer are 1.78 eV and 1.66 eV, respectively, which are in decent agreement with the corresponding experimental values of 1.70 (VDE) and 1.45 eV (EA). The calculated VDE for the capped (1.47 eV) isomer is significantly different from the experiments, indicating that only one isomer, i.e., the terminal one, has been observed in the experiments. The first vertical detachment comes from an Al–Al bonding orbital (Figure 5, 5a¹). The second detachment, which is calculated to be 1.94 eV, is due to the out-of-plane pi-bonding orbital (1a²) and matches with the experimental value of (~2.00 eV). The final detachment is from in-plane Al–Al bonding orbital (4a¹) and here as well there is a good agreement between the calculations (3.28 eV) and experiments (~3.14 eV). The common bonding feature between Alₙ⁻ and AlₙHₙ⁻ is the out-of-plane pi-bonding orbital rendering them both to be pi-aromatic, however, the in-plane sigma-bonding observed in Alₙ⁻ has been lost due to the presence of terminal H-attachment.

Adding one more hydrogen atom to Al₃⁻, it leads to two distinct lowest energy isomers of Al₃H⁻ (2a¹ and 2b¹; Figure 4). The isomer with two terminal hydrogens, 2a¹, is more stable than 2b¹ (one terminal and one bridge) by 0.23 eV. The

<table>
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<th>System</th>
<th>Isomer</th>
<th>VDE</th>
<th>CCSD(T)</th>
<th>Expt.</th>
<th>ADE</th>
<th>Expt.</th>
<th>DFT</th>
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<td>2.5</td>
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Figure 3. Molecular Orbital diagram of Al₃⁻.
calculated VDE/ADE values for structure 2a are 1.87/1.81 eV compares very well to the experimental values 1.92/1.76 eV.

Note that the HOMO is again an out-of-plane π-bonding orbital (1b, Figure 5) similar to the one observed in both Al$_3^-$ and Al$_3$H$^-$ and all of these transitions occur around 1.80 eV. Furthermore, the measured high-energy transitions at 2.85 eV and 3.42 eV, from Al–Al bonding orbitals (1b and 2a) matches with the computed values of 2.76 eV and 3.33 eV respectively. On the other hand, the VDE (ADE) and other high-energy transitions of isomer 2b do not match with the experiments very well.

Two lowest energy isomers of Al$_3$H$_n^-$ (n = 1–9) which have markedly different arrangement of hydrogen atoms also found to be isoenergetic (0.06 eV). The calculated VDE/ADE of 4a and 4b are 2.20/1.98 eV and 1.93/1.74 eV, respectively. The corresponding experimental numbers are 2.12/1.79 eV, which match well with the calculation. In addition, the higher transition energies from 4a (4b) and are 2.66 (3.06) and 4.71 (3.68) eV, respectively, and also match the experiments (2.85, 4.14 eV). Therefore, both isomers are present in the experiments. It is noteworthy here that the energy gap between HOMO and HOMO-1 of 4a and 4b is 1.80 eV and 0.63 eV, respectively. This significant difference can be understood from the nature of bonding in these clusters. The HOMO (4a$^-$, Figure 5) of 4a$^-$ is a distorted π-bonding-orbital akin to the one observed for 3a$^-$ which is followed by an Al–Al bonding orbital (2a$^-$). Since both are bonding orbitals their energy difference is relatively small (0.57 eV). On the other hand, the HOMO (4a, Figure 5) of 4b$^-$ is a lone pair orbital on aluminum atoms followed by a bonding orbital between AlH$_2$ and Al–(H)$_2$–Al unit (3a, Figure 5). As a result, the energy difference between these two orbitals is quite large (1.80 eV).
The photoelectron spectrum of Al$_3$H$_5$ is unique among Al$_3$H$_n$ species as the spectra shows largest HOMO-LUMO gap (1.86 eV). The two lowest energy isomers are given in Figure 4. The most stable isomer, 5a' is the one where one AlH$_2$ group interacting with HAl-(H)$_2$-Al and the second isomer, 5b', which is 0.32 eV higher in energy has a linear arrangement of aluminum atoms in which two hydrogen atoms make terminal bonds with the edge aluminum and a triple hydrogen bridge between the remaining two Al atoms. The calculated VDE/ADE of 5a'(1.75/1.56 eV) and 5b'(1.96/1.71 eV). Hence, only the VDE/ADE values of 5a' are in good agreement with the experimentally determined value (1.60/1.39 eV). The high HOMO-LUMO gap in 5a' can be understood as follows: bridged AlH$_2$ is a one-electron donor isoelectronic to H atom and the AlH group is a two-electron donor and Al atom is one electron donor. This leaves total number of available electrons '6', which forms three '3c–2e' Al−H-Al bonds. As a result, the first electron transition from 6a' and second transition for 5b'(3.30 eV) occur nearly at the same energy, providing further proof to the electronic structure.

As the number of hydrogens increases the occurrence of AlH$_2$ groups, which helps to form tetrahedral coordination, also increases. The two lowest energy isomers of Al$_3$H$_7$ are given in Figure 4 as 7a' and 7b'. The calculated VDE/ADE of 7a'(2.71/2.23 eV) and 7b'(2.53/2.00 eV) matches with the experimental values (2.57/2.15 eV). Therefore, we conclude that both isomers are present in the cluster beam.

Al$_3$H$_8$ is also unique among the Al$_3$H$_n$ clusters in the current study. The observed VDE/EA (4.05/3.3 eV) are largest in the series for Al$_3$H$_8$. Two lowest energy structures of Al$_3$H$_8$, 8a' and 8b' are given in Figure 4. The calculated VDE/ADE of...
(3.97/3.08 eV) and 8b$^-$ (3.96/2.81 eV) are in agreement with the experimental value (4.05/3.3 eV). Since the VDE and ADE values of both these isomers are in agreement with the measured values, we cannot rule out the possibility of both these isomers contributing towards the photoelectron spectrum. In isomer 8a, each AlH$_2$ group and H atom provides 1e, which gives total of six valence electrons including one negative charge. This leads to two Al-H-Al &3c-2e' bonds and one Al-Al bond making the system electron sufficient. As a result, the electron affinity of isomer 8a is very high. On the other hand, isomer 8b achieves high electron affinity in a different way. Isomer 8b can be considered as a derivative of well-known Al$_2$H$_6$ with one terminal H is replaced by AlH$_3$, resulting in very stable structure. Finally, the most stable structure of Al$_3$H$_{9}$ (isomer 9a) is shown in Figure 4. As expected, and in accordance with our earlier studies, the neutral clusters are not discussed here.

To understand the energetics involved in the addition of hydrogens we have considered two equations:

$$\text{Al}_3q^+ + \left(\frac{n}{2}\right)\text{H}_2 = \text{Al}_3\text{H}_{n}^q$$  (1)

$$\text{Al}_3\text{H}_{n}^q + \left(\frac{1}{2}\right)\text{H}_2 = \text{Al}_3\text{H}_{n+1}^q$$  (2)

in both cases q (charge) is either 0 or $-1$ and $n$ is from 1 to 11.

There are no new structural motifs or new bonding patterns observed in the neutral Al$_3$H$_n$ clusters. As anticipated several isomers are close in energy since the energy difference between Al-H$_2$ and Al-H is similar, unless of course aided by strong electronic structural effects. Hence, the neutral clusters are not discussed here.

The first equation estimates the energy released by the simultaneous addition of ‘$n$’ number of hydrogens to the Al$_3$ cluster. The calculated values for $n=1$ to 11 is shown in the Figure 6. Obviously, all energies are exothermic. The energy values also show strong even-odd oscillations, which get more pronounced as $n$ increases. Interestingly, there is a strong drop in exothermicity on going from $n=9$ to 10 for neutral and $n=10$ to 11 for anion. These trends are consistent with the fact that for neutral systems $n=9$, Al$_3$H$_9$ is stochiometric unit and very stable. Addition of hydrogen is not expected to be stable. Similarly for the anion, Al$_3$H$_{10}^-$, which is formed by the addition of H$^-$ to the stochiometric Al$_3$H$_9$, is most stable. Equation 2, on the other hand, describes the energy released by successive addition of hydrogens. This equation provides an opportunity

![Figure 6]( Journal of Inorgan ic and General Chemistry Zeitschrift für anorganische und allgemeine Chemie Z. Anorg. Allg. Chem. 2021, 1 – 10 www.zaac.wiley-vch.de © 2021 Wiley-VCH GmbH)

Figure 6. The variation in the amount of energy released due to simultaneous addition of ‘$n$’ number of hydrogen atoms to an Al$_3$ moiety as the value of $n$ increases from 1 to 11.
to unmask stable structures. Once again, the odd-even trend is more pronounced at larger \( n \) and shows enhanced stability for \( n = 9 \) neutral and \( n = 10 \) for anion as shown in Figure 7.

**Concluding remarks**

In conclusion, a systematic anion photoelectron spectroscopy and density functional theory-based study on \( \text{Al}_3\text{H}_n^- \) \((n = 1–9)\) clusters has revealed that the hydrogen atoms attach in three different bonding modes and exothermically to the aluminum clusters. Among the \( \text{Al}_3\text{H}_n^- \) \((n = 1–9)\) clusters, \( \text{Al}_3\text{H}_8^- \) was observed to have the largest VDE and ADE values. Energetics and bonding analysis have revealed that two isomers exist for this cluster and both of them attain their unusually large electron affinity values in two different ways. Our calculated results have also shown that as the number of hydrogens increases the coordination around the aluminum atoms tend towards tetrahedral geometries.

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**Conflict of Interest**

The authors declare no conflict of interest.


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