Alanate Anion, AlH$_4^-$: Photoelectron Spectrum and Computations

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ABSTRACT: The alanate anion, AlH$_4^-$, was generated in the gas phase using a pulsed arc cluster ionization source. Its photoelectron spectrum was then measured with 193 nm photons. The spectrum consists of a broad feature, spanning electron binding energies from 3.8 eV to over 5.3 eV. This band reflects the photodetachment transitions between the ground state of the AlH$_4^-$ anion and the ground state of its thermodynamically unstable neutral counterpart, AlH$_4$. The vertical detachment energy (VDE) of AlH$_4^-$ was measured to be 4.4 eV. Additionally, VDE values were also computed in a comprehensive theoretical study and compared both with the previously computed value and with our experimentally determined value.

INTRODUCTION

The AlH$_4^-$ anion is perhaps the best known aluminum hydride in chemistry. The AlH$_4^-$ anion is the anionic moiety in alkali alanate salts, such as LiAlH$_4$ and NaAlH$_4$, these being powerful reducing agents.\(^1\) AlH$_4^-$ is also of interest as a candidate for hydrogen storage, e.g., as in Mg(AlH$_4$)$_2$, owing to its high hydrogen gravimetric density.

The AlH$_4^-$ anion has been observed and studied in cryogenic matrices\(^2\)\(^\text{−}\)\(^5\) and has been found to be relatively unreactive during gas phase thermochemical measurements.\(^6\) Calculations by Boldyrev and co-workers\(^7\),\(^8\) showed that the high stability of this anion arises from its excess electron occupying a bonding molecular orbital spread over each of its Al−H bonds. They also found the vertical detachment energy (VDE) of this anion to be 4.83 eV and that AlH$_4^-$ is stable against dissociation into AlH$_3$ + H$_2$ and into AlH$_3$ + H$^+$ by 3.0 and 3.3 eV, respectively. Additionally, other computations have found neutral AlH$_4$ to be unstable, dissociating along a barrier-free potential surface into AlH$_3$ and H$_2$.\(^9\)

Although we had previously observed the AlH$_4^-$ anion along with other aluminum hydride anionic species in mass spectra,\(^10\) here we report the measurement of its anion photoelectron spectrum for the first time. Additionally, we have expanded on previous theoretical work by calculating the vertical detachment energy of the AlH$_4^-$ anion at various higher levels of theory. We also computed the energetic differences between AlH$_4^-$ and its decomposition products, AlH$_3^-$ and H$_2$, and between the unbound neutral AlH$_4$ and its decay products, AlH$_3$ and H$_2$.

EXPERIMENTAL METHODS

AlH$_4^-$ ions were generated in the gas phase using a pulsed arc cluster ionization source (PACIS). A detailed description of the PACIS can be found elsewhere,\(^11\) but a brief overview is given here. During operation, a pulsed valve backed by 200 psi of UHP hydrogen is opened for about 200 microseconds and fills a region between a copper anode and grounded aluminum cathode. A 30 microsecond long, 100 V pulse is applied to the copper anode that discharges through the hydrogen gas and subsequently vaporizes the aluminum cathode. The combination of free atomic hydrogen and vaporized aluminum is entrained with the remaining molecular hydrogen and carried along a 20 cm flow tube where it reacts, cools, and forms AlH$_4^-$ along with other aluminum hydrides. AlH$_4^-$ is then extracted and mass-selected before photodetachment.

Anion photoelectron spectroscopy is conducted by crossing a beam of mass-selected negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy-conserving relationship, $h\nu = E_{BE} + E_{KE}$, where $h\nu$ is the photon energy, $E_{BE}$ is the electron binding energy, and $E_{KE}$ is the electron kinetic energy. Our instrument consists of a PACIS, a time-of-flight mass spectrometer, a magnetic bottle electron energy analyzer, and an excimer laser. The ArF excimer laser detaches photoelectrons with 193 nm (6.42 eV) photons. The magnetic bottle has an energy resolution of better than 50
meV at EKE = 1 eV, and photoelectron spectra are calibrated against well-known transitions of atomic Cu$^-$.

## COMPUTATIONAL METHODS

Our calculations of AlH$_4^-$, AlH$_3^-$, AlH$_2^-$, and H$_2$ have been carried out using a number of different methods, which include density functional theory (DFT), hybrid Hartree–Fock–DFT, and post-HF methods combined with basis sets whose quality ranges from triple-$\xi$ to penta-$\xi$. The methods applied are the BPW91 (DFT),$^{12,13}$ B3LYP,$^{14,15}$ and M06$^{16}$ (HF-DFT), second-order Møller–Plesset perturbation theory (MP2),$^{17}$ coupled-cluster with single and doubles (CCSD) and noniterative triples CCSD(T),$^{18}$ and the outer valence Green’s function (OVGF).$^{19–21}$ The OVGF computations were performed with the geometry optimized at the B3LYP level of theory. The basis sets used for Al and H atoms are 6-311+G($^\ast$),$^{22}$ 6-311++G(3df,3pd),$^{22}$ cc-pVQZ, cc-pV5Z, and aug-cc-pV5Z,$^{23,24}$ as implemented in Gaussian03$^{25}$ and Gaussian09 codes.$^{26}$

## EXPERIMENTAL RESULTS

The photoelectron spectrum of AlH$_4^-$ is presented in Figure 1. The spectrum consists of a broad feature, spanning electron binding energies from 3.8 eV to over 5.3 eV. This feature corresponds to transitions between the ground electronic state of the anion and the ground state of the thermodynamically unstable neutral species. The vertical detachment energy (VDE) of AlH$_4^-$ was measured to be 4.4 eV. Since 6.42 eV photons are energetic enough to dissociate AlH$_4^-$ into AlH$_2^-$ + H$_2$ or AlH$_3$ + H$^+$, it is possible that these products could have also been formed and subsequently photodetached in the ion–photon interaction region of our spectrometer. Nevertheless, we saw no evidence for either AlH$_2^-$ at EBE = 1.5 eV (its VDE value) or for H$^+$ at EBE = 0.75 eV (its electron affinity value).

## COMPUTATIONAL RESULTS

We began our optimizations without imposing symmetry constraints, followed by reoptimization of the structures obtained within the actual symmetry of their nuclei. All optimizations have been followed by harmonic vibrational frequency calculations in order to confirm that the structure obtained corresponds to a minimum on the potential energy surface. The convergence threshold in total energy and force was $1 \times 10^{-8}$ eV and $1 \times 10^{-3}$ eV/Å, respectively.

The AlH$_4^-$ anion geometry converged to a geometry of $T_d$ symmetry and its ground state is $^1A_1$. Figure 2a shows the geometrical structure of the AlH$_4^-$ ground state optimized at the B3LYP/6-311++G(3df,3pd) level, along with the charges on its atoms obtained from the natural atomic orbital (NAO)$^{27}$ population analysis. In the AlH$_4^-$ anion, the charge of the central atom is +0.63e, which means that the extra electron is delocalized over hydrogen atoms, each carrying a negative charge of $-0.41e$. The AlH$_4^-$ anion satisfies the superhalogen$^{28,29}$ formula, MX$^{k+1}$ for monovalent ligands, X, where k is the maximal formal valence of the central atom, M. This is because the maximal formal valence of an aluminum atom with the electronic configuration of [Ne]$3s^23p^1$ is three. Formally, the extra electron in AlH$_4^-$ serves as the fourth valence electron of aluminum, which forms single bonds of the 30%(Al) + 70%(H) type with each hydrogen atom in AlH$_4^-$.

The vertical detachment energy (VDE) of the anion is computed at the anion equilibrium geometry according to the following expression:

$$\text{VDE} (\text{AlH}_4^-) = E(\text{AlH}_4^- \text{ at anion’s equilibrium geometry}) - E(\text{AlH}_4^- \text{ at equilibrium geometry})$$

(1)
where \( E \) is the electronic energy. The values obtained from this equation using different methods and basis sets are listed in Table 1 alongside the value measured from the experimental spectrum.

It was found previously\(^3\) and confirmed by the results of our computations that the neutral AlH\(_4\) geometry optimization, beginning with the anion \( T_d \) geometry, leads to a transition state of \( C_{2v} \) symmetry. We performed an extensive search for a stable state of AlH\(_4\) and found an isomer of the \( H_2 \otimes AlH_2 \) adduct type of \( C_{s} \) symmetry with all real harmonic vibrational frequencies. This AlH\(_4\) isomer is stable with respect to the sum of total electronic energies of both AlH\(_2\) and \( H_2 \) and AlH\(_3\) and \( H \) (see Figure 3). This neutral isomer is also shown in Figure 2b, and as is seen from the charges on atoms, the positive charge on the aluminum atom is nearly balanced by the negative charges in the chemically bound hydrogen atoms. The hydrogen atoms in the quasi-molecularly bound \( H_2 \) molecule carry negligible charge and bind weakly to the AlH\(_3\) complex through the charge polarization mechanism.\(^3\) This weak interaction is evident from the differences in total electronic energies, \( \Delta E \), computed according to equation

\[
\Delta E(N ISO) = E(AlH_4) + E(H_2) - E(AlH_3 + H) - E(AlH_2 + H_2)
\]

where \( N \) and ISO indicate \( \Delta E \) is for the neutral AlH\(_4\) isomer. This value is listed in Table 1 and varies between +0.04 and +0.19 eV depending on the method and basis set used.

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**Table 1. Energetic Difference between AlH\(_4^-\) Anion and the Unbound Neutral AlH\(_4\) Decay Products, AlH\(_2\) and \( H_2 \) (\( \omega \text{asym} \)), Vertical Electron Detachment Energy (VDE) of the AlH\(_4^-\) Anion, Interatomic Distances and Harmonic Vibrational Frequency of the \( H - H \) Vibration (\( \omega_e \)) in the AlH\(_4^+\) Isomer Given in Figure 2b, and the Differences in Total Electronic (\( \Delta E \)) Energy and Total Energy (\( \Delta E_{\text{tot}} \)) for the Neutral Isomer Channels (\( N \ ISO \)) \text{AlH}_4 \rightarrow \text{AlH}_2 + H_2 \) and (\( A \ ISO \)) \text{AlH}_4^- \rightarrow \text{AlH}_2^- + H_2\)

<table>
<thead>
<tr>
<th>method</th>
<th>basis set</th>
<th>( E_{\text{asym}} ) (eV)</th>
<th>VDE (eV)</th>
<th>R(H−H) (Å)</th>
<th>R(Al−H(_2)) (Å)</th>
<th>( \omega_e ) (eV)</th>
<th>( \Delta E ) (eV)</th>
<th>( \Delta E_{\text{tot}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPW91</td>
<td>6-311+G(3df,3pd)</td>
<td>2.97</td>
<td>4.14</td>
<td>0.76</td>
<td>2.21</td>
<td>0.50</td>
<td>( \Delta E_{\text{tot}}(N ISO) ) = +0.06</td>
<td>( \Delta E_{\text{tot}}(A ISO) ) = −0.04</td>
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<tr>
<td></td>
<td>cc-pVQZ</td>
<td>2.87</td>
<td>4.14</td>
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<td>2.12</td>
<td>0.49</td>
<td>( \Delta E(N ISO) ) = +0.04</td>
<td>( \Delta E(A ISO) ) = −0.04</td>
</tr>
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<td>cc-pVSZ</td>
<td>2.89</td>
<td>4.13</td>
<td>0.77</td>
<td>2.12</td>
<td>0.49</td>
<td>( \Delta E(N ISO) ) = +0.04</td>
<td>( \Delta E(A ISO) ) = −0.04</td>
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<tr>
<td>B3LYP</td>
<td>6-311+G(^*)</td>
<td>3.14</td>
<td>4.69</td>
<td>0.75</td>
<td>2.53</td>
<td>0.53</td>
<td>( \Delta E(N ISO) ) = +0.06</td>
<td>( \Delta E(A ISO) ) = −0.04</td>
</tr>
<tr>
<td></td>
<td>6-311++G(3df,3pd)</td>
<td>3.17</td>
<td>4.69</td>
<td>0.75</td>
<td>2.41</td>
<td>0.52</td>
<td>( \Delta E(N ISO) ) = +0.06</td>
<td>( \Delta E(A ISO) ) = −0.04</td>
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<td></td>
<td>aug-cc-pVSZ</td>
<td>3.09</td>
<td>4.47</td>
<td>0.75</td>
<td>2.23</td>
<td>0.52</td>
<td>( \Delta E_{\text{tot}}(N ISO) ) = −0.03</td>
<td>( \Delta E_{\text{tot}}(A ISO) ) = −0.03</td>
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<tr>
<td>M06</td>
<td>6-311+G(3df,3pd)</td>
<td>3.11</td>
<td>4.43</td>
<td>0.75</td>
<td>2.29</td>
<td>0.50</td>
<td>( \Delta E(N ISO) ) = +0.07</td>
<td>( \Delta E(A ISO) ) = −0.07</td>
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<td>4.40</td>
<td>0.76</td>
<td>2.22</td>
<td>0.51</td>
<td>( \Delta E(N ISO) ) = +0.19</td>
<td>( \Delta E(A ISO) ) = −0.19</td>
</tr>
<tr>
<td>MP2</td>
<td>6-311+G(^*)</td>
<td>2.59</td>
<td>4.50</td>
<td>0.74</td>
<td>3.06</td>
<td>0.56</td>
<td>( \Delta E(N ISO) ) = −0.09</td>
<td>( \Delta E(A ISO) ) = −0.09</td>
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<tr>
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<td>6-311++G(3df,3pd)</td>
<td>2.84</td>
<td>4.61</td>
<td>0.74</td>
<td>2.48</td>
<td>0.54</td>
<td>( \Delta E_{\text{tot}}(N ISO) ) = −0.06</td>
<td>( \Delta E_{\text{tot}}(A ISO) ) = −0.06</td>
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<tr>
<td></td>
<td>cc-pVQZ</td>
<td>2.95</td>
<td>4.83</td>
<td>0.75</td>
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<td>( \Delta E_{\text{tot}}(N ISO) ) = −0.06</td>
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<td>CCSD</td>
<td>6-311+G(^*)</td>
<td>2.62</td>
<td>4.39</td>
<td>0.75</td>
<td>3.17</td>
<td>0.51</td>
<td>( \Delta E(N ISO) ) = +0.04</td>
<td>( \Delta E(A ISO) ) = +0.04</td>
</tr>
<tr>
<td></td>
<td>6-311++G(3df,3pd)</td>
<td>2.91</td>
<td>4.52</td>
<td>0.75</td>
<td>2.51</td>
<td>0.50</td>
<td>( \Delta E_{\text{tot}}(N ISO) ) = −0.12</td>
<td>( \Delta E_{\text{tot}}(A ISO) ) = −0.12</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>6-311+G(^*)</td>
<td>2.63</td>
<td>4.39</td>
<td>0.75</td>
<td>3.14</td>
<td>0.51</td>
<td>( \Delta E(N ISO) ) = +0.04</td>
<td>( \Delta E(A ISO) ) = +0.04</td>
</tr>
<tr>
<td></td>
<td>6-311++G(3df,3pd)</td>
<td>2.94</td>
<td>4.52</td>
<td>0.75</td>
<td>2.46</td>
<td>0.50</td>
<td>( \Delta E_{\text{tot}}(N ISO) ) = −0.12</td>
<td>( \Delta E_{\text{tot}}(A ISO) ) = −0.12</td>
</tr>
<tr>
<td>OVG(_F)</td>
<td>6-311+G(^*)</td>
<td>4.61</td>
<td>4.61</td>
<td>4.74</td>
<td>0.54(^a)</td>
<td>0.54(^b)</td>
<td>( \Delta E_{\text{tot}}(N ISO) ) = −0.12</td>
<td>( \Delta E_{\text{tot}}(A ISO) ) = −0.12</td>
</tr>
</tbody>
</table>

\(^a\) This work. \(^b\) Experimental value of \( \omega_e \) for the gas-phase \( H_2 \) is 0.547 eV (see ref 31).

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\[ \Delta E(N ISO) = E(\text{AlH}_4^-) + E(\text{H}_2) - E(\text{AlH}_3 + \text{H}) - E(\text{AlH}_2 + \text{H}_2) \]
However, the neutral isomer becomes thermodynamically unstable with respect to the AlH4 → AlH2 + H2 decay channel when the zero-point vibrational energies (ZPVE) are added to the total electronic energies of the AlH4, AlH2, and H2 species. Adding the zero-point vibrational energies to the total electronic energies, we compute the differences in total energies for the neutral isomer as

$$\Delta E_{\text{tot}}(N \text{ ISO}) = E_{\text{tot}}(\text{AlH}_4) + E_{\text{tot}}(\text{H}_2)$$

$$- E_{\text{tot}}(\text{AlH}_4 \text{ isomer})$$

where $E_{\text{tot}}$ is the sum of the total electronic energy of a given species and the corresponding ZPVE. The $\Delta E_{\text{tot}}$(N ISO) values computed according to eq 3 are negative (see Table 1), which means that the neutral isomer is thermodynamically unstable.

As there is no stable neutral AlH4, species, contrary, the neutral AlH4 is thermodynamically unstable and dissociates to AlH2 and H2. The temporary AlH4 radical presents a case of when a species is electronically stable within the Born-Oppenheimer approximation but is unstable with respect to nuclear motions. The energy of the vertical dissociation$^{*}$ (VD$E$) is then computed according to eq 3 are negative (see Table 1), which means that the anionic isomer is thermodynamically unstable.

$$\Delta E_{\text{VD}}(N \text{ ISO}) = E(\text{AlH}_4^{-}) + E(\text{H}_2) - E(\text{AlH}_4 \text{ isomer}^{-})$$

The computed $\Delta E_{\text{VD}}$(N ISO) values are listed in Table 1. Additionally, a stable anionic isomer was found and is shown in Figure 2c. The anionic isomer shows similar behavior to the neutral isomer and is weakly bound at the BPW91, B3LYP, and CCSD(T) levels with the 6-311++G(3df,3pd) basis. In a similar manner as the neutral isomer, the $\Delta E$ value for the anion isomer was computed according to the equation

$$\Delta E(A \text{ ISO}) = E(\text{AlH}_4^{-}) + E(\text{H}_2) - E(\text{AlH}_4 \text{ isomer}^{-})$$

where A and ISO indicate $\Delta E$ is for the anionic AlH4− isomer. Again, as with the neutral isomer, including zero-point vibrational energy to the energy of each component yields

$$\Delta E_{\text{tot}}(A \text{ ISO}) = E_{\text{tot}}(\text{AlH}_4^{-}) + E_{\text{tot}}(\text{H}_2)$$

$$- E_{\text{tot}}(\text{AlH}_4 \text{ isomer}^{-})$$

The computed $\Delta E_{\text{tot}}$(A ISO) values are negative, which indicates that the anion isomer is thermodynamically unstable. The decay channels for the ground-state AlH4− anion calculated at the BPW91/6-311++G(3df,3pd) level are shown in Figure 3.

**DISCUSSION**

Using several computational methods belonging to the density functional theory (DFT), hybrid DFT, second-order perturbation theory, and couple-cluster groups, we studied the geometrical and electronic structure of AlH4 and AlH4−. The AlH4− anion is thermodynamically stable by 1.98 eV with respect to the AlH4− → AlH4− + H2 decay channel according to our BPW91/6-311++G(3df,3pd) computations. On the contrary, the neutral AlH4 is thermodynamically unstable and dissociates to AlH2 and H2. The temporary AlH4 radical presents a case of when a species is electronically stable within the Born-Oppenheimer approximation but is unstable with respect to nuclear motions. The energy of the vertical detachment of an electron strongly depends on the method and basis used and is enclosed in the range from 4.13 to 4.83 eV according to the results of our computations by different methods. The broad width of the photoelectron spectrum of the AlH4− anion is consistent with the instability of neutral AlH4. Our experimental VDE value of 4.4 eV for the AlH4− anion is within the range of our theoretical estimates.

The closest to experimental values are obtained at the B3LYP/aug-cc-pVSZ (4.47 eV), M06/aug-cc-pV5Z (4.40 eV), CCSD/6-311+G* (4.39 eV), and CCSD(T)/6-311+G* (4.39 eV) levels. The values obtained using the BPW91 method are somewhat underestimated, whereas the OVGF values are somewhat overestimated compared to the experimental value. Since agreement between experiment and theory is quite reasonable, one can conclude that the theoretical results are reliable.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**