

Alanate Anion, AlH_4^- : Photoelectron Spectrum and Computations

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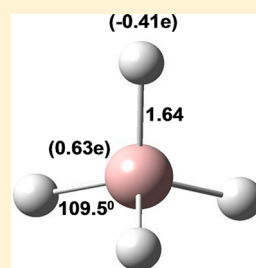
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ABSTRACT: The alanate anion, AlH_4^- , was generated in the gas phase using a pulsed arc cluster ionization source. Its photoelectron spectrum was then measured with 193 nm photons. The spectrum consists of a broad feature, spanning electron binding 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 $\text{Mg}(\text{AlH}_4)_2$, owing to its high hydrogen gravimetric density.

The AlH_4^- anion has been observed and studied in cryogenic matrices^{2–5} 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 $\text{AlH}_2^- + \text{H}_2$ and into $\text{AlH}_3 + \text{H}^-$ 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_2 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_2^- and H_2 , and between the unbound neutral AlH_4 and its decay products, AlH_2 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, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Our 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

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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_4^- , AlH_2 , 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- ξ to penta- ξ . The methods applied are the BPW91 (DFT),^{12,13} B3LYP,^{14,15} and M06¹⁶ (HF/DFT), second-order Moller–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*, 6-311++G(3df,3pd),²² cc-pVQZ, cc-pVSZ, and aug-cc-pVSZ,^{23,24} as implemented in Gaussian03²⁵ and Gaussian09²⁶ codes.

EXPERIMENTAL RESULTS

The photoelectron spectrum of AlH_4^- is presented in Figure 1. The spectrum consists of a broad feature, spanning electron

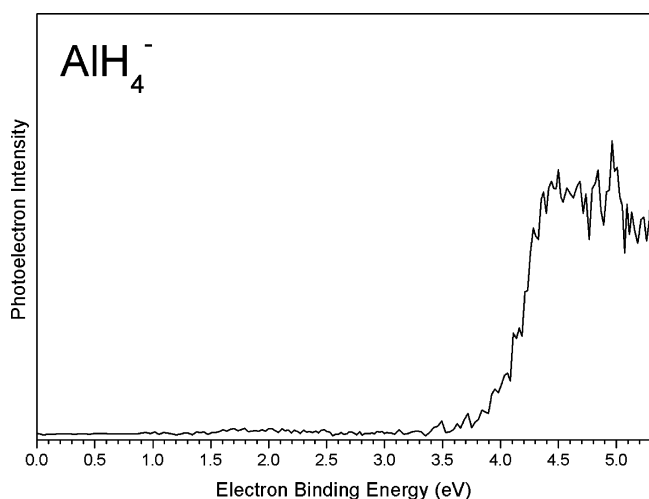


Figure 1. Photoelectron spectrum of the AlH_4^- anion.

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 1×10^{-8} eV and 1×10^{-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:

$$\begin{aligned} \text{VDE}(AlH_4^-) &= E(AlH_4 \text{ at its anion's equilibrium geometry}) \\ &\quad - E(AlH_4^- \text{ at equilibrium geometry}) \end{aligned} \quad (1)$$

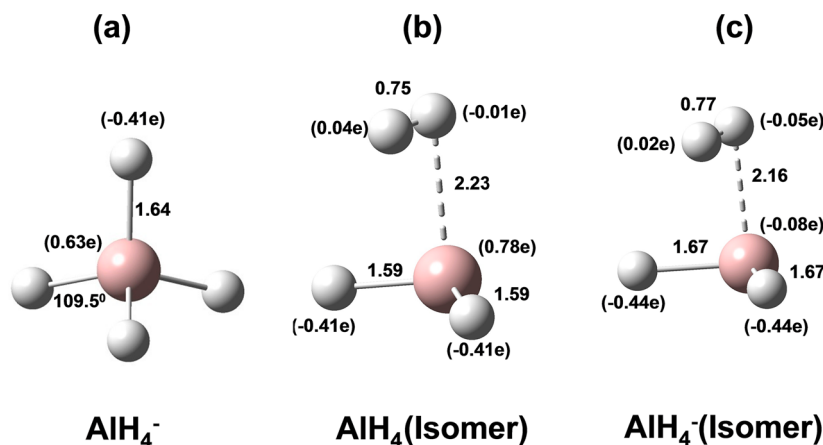


Figure 2. Geometrical structures of the AlH_4^- ground state (a) and electronically stable states of the neutral (b) and anion (c) isomers as optimized at the B3LYP/6-311++G(3df,3pd) level. Bond lengths are in Å and charges on atoms are in units of electronic charge.

Table 1. Energetic Difference between AlH_4^- Anion and the Unbound Neutral AlH_4 Decay Products, AlH_2 and H_2 (E_{asym}), Vertical Electron Detachment Energy (VDE) of the AlH_4^- Anion, Interatomic Distances and Harmonic Vibrational Frequency of the H – H Vibration (ω_e) in the AlH_4 Isomer Given in Figure 2b, and the Differences in Total Electronic (ΔE) Energy and Total Energy (ΔE_{tot}) for the Neutral Isomer Channels (N ISO) $\text{AlH}_4 \rightarrow \text{AlH}_2 + \text{H}_2$ and (A ISO) $\text{AlH}_4^- \rightarrow \text{AlH}_2^- + \text{H}_2$ Computed Using Different Methods and Basis sets

method	basis set	E_{asym} (eV)	VDE (eV)	R(H–H) (Å)	R(Al–H ₂) (Å)	$\omega_e(\text{H–H})$ (eV)	ΔE (eV)
BPW91	6-311++G(3df,3pd)	2.97	4.14	0.76	2.21	0.50	$\Delta E(\text{N ISO}) = +0.04$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.06$ $\Delta E(\text{A ISO}) = +0.08$ $\Delta E_{\text{tot}}(\text{A ISO}) = -0.04$
	cc-pVQZ	2.87	4.14	0.77	2.12	0.49	$\Delta E(\text{N ISO}) = +0.08$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.04$
	cc-pVSZ	2.89	4.13	0.77	2.12	0.49	$\Delta E(\text{N ISO}) = +0.08$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.03$
B3LYP	6-311+G*	3.14	4.69	0.75	2.53	0.53	$\Delta E(\text{N ISO}) = +0.06$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.05$ $\Delta E(\text{A ISO}) = +0.03$ $\Delta E_{\text{tot}}(\text{A ISO}) = -0.06$
	6-311++G(3df,3pd)	3.17	4.69	0.75	2.41	0.52	$\Delta E(\text{N ISO}) = +0.07$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.04$
	aug-cc-pVSZ	3.09	4.47	0.75	2.23	0.52	$\Delta E(\text{N ISO}) = +0.07$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.04$
M06	6-311++G(3df,3pd)	3.11	4.43	0.75	2.29	0.50	
	aug-cc-pVSZ	3.02	4.40	0.76	2.22	0.51	$\Delta E(\text{N ISO}) = +0.19$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.16$
MP2	6-311+G*	2.59	4.50	0.74	3.06	0.56	
	6-311++G(3df,3pd)	2.84	4.61	0.74	2.48	0.54	
	cc-pVQZ	2.95	4.83	0.75	2.27	0.54	$\Delta E(\text{N ISO}) = +0.09$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.02$
CCSD	6-311+G*	2.62	4.39	0.75	3.17	0.51	
	6-311++G(3df,3pd)	2.91	4.52	0.75	2.51	0.50	
CCSD(T)	6-311+G*	2.63	4.39	0.75	3.14	0.51	
	6-311++G(3df,3pd)	2.94	4.52	0.75	2.46	0.50	$\Delta E(\text{N ISO}) = +0.04$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.05$ $\Delta E(\text{A ISO}) = +0.04$ $\Delta E_{\text{tot}}(\text{A ISO}) = -0.12$
OVGF	6-311+G*		4.61				
	6-311++G(3df,3pd)		4.74				
exptl			4.4 ^a			0.547 ^b	

^aThis work. ^bExperimental value of ω_e for the gas-phase H_2 is 0.547 eV (see ref 31).

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 previously³ 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 $\text{H}_2 \otimes \text{AlH}_2$ 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_2 complex through the charge polarization mechanism.³⁰ This weak interaction is evident from the differences in total electronic energies, ΔE , computed according to equation

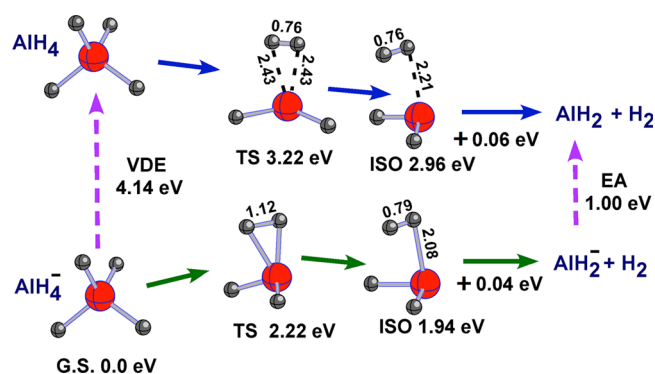


Figure 3. Decay channels of the AlH_4^- anion (in its ground state) and of the AlH_4 neutral, both computed at the BPW91/6-311++G(3df) level of theory. Ground state is abbreviated G.S., transition state is abbreviated TS, and isomer is abbreviated ISO. Bond lengths are in Å.

$$\Delta E(\text{N ISO}) = E(\text{AlH}_2) + E(\text{H}_2) - E(\text{AlH}_4 \text{ isomer}) \quad (2)$$

where N and ISO indicate ΔE 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.

However, the neutral isomer becomes thermodynamically unstable with respect to the $\text{AlH}_4 \rightarrow \text{AlH}_2 + \text{H}_2$ decay channel when the zero-point vibrational energies (ZPVE) are added to the total electronic energies of the AlH_4 , AlH_2 , and H_2 species. Adding the zero-point vibrational energies to the total electronic energies, we compute the differences in total energies for the neutral isomer as

$$\Delta E_{\text{tot}}(\text{N ISO}) = E_{\text{tot}}(\text{AlH}_2) + E_{\text{tot}}(\text{H}_2) - E_{\text{tot}}(\text{AlH}_4 \text{ isomer}) \quad (3)$$

where E_{tot} is the sum of the total electronic energy of a given species and the corresponding ZPVE. The $\Delta E_{\text{tot}}(\text{N ISO})$ 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 AlH_4 species, in place of an adiabatic electron affinity, we define E_{asym} as the energetic difference between AlH_4^- and the unbound neutral AlH_4 decay products, AlH_2 and H_2 , as

$$E_{\text{asym}} = E_{\text{tot}}(\text{AlH}_2) + E_{\text{tot}}(\text{H}_2) - E_{\text{tot}}(\text{AlH}_4^-) \quad (4)$$

The computed E_{asym} values are listed in Table 1.

Additionally, a stable anion isomer was found and is shown in Figure 2c. The anion 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 ΔE value for the anion isomer was computed according to the equation

$$\Delta E(\text{A ISO}) = E(\text{AlH}_2^-) + E(\text{H}_2) - E(\text{AlH}_4^- \text{ isomer}) \quad (5)$$

where A and ISO indicate ΔE is for the anionic AlH_4^- isomer. Again, as with the neutral isomer, including zero-point vibrational energy to the energy of each component yields

$$\Delta E_{\text{tot}}(\text{A ISO}) = E_{\text{tot}}(\text{AlH}_2^-) + E_{\text{tot}}(\text{H}_2) - E_{\text{tot}}(\text{AlH}_4^- \text{ isomer}) \quad (6)$$

The computed $\Delta E_{\text{tot}}(\text{A ISO})$ values are negative, which indicates that the anion isomer is thermodynamically unstable. The decay channels for the ground-state AlH_4^- 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 AlH_4 and AlH_4^- . The AlH_4^- anion is thermodynamically stable by 1.98 eV with respect to the $\text{AlH}_4^- \rightarrow \text{AlH}_2^- + \text{H}_2$ decay channel according to our BPW91/6-111++G(3df,3pd) computations. On the contrary, the neutral AlH_4 is thermodynamically unstable and dissociates to AlH_2 and H_2 . The temporary AlH_4 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 extra 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 AlH_4^- anion is consistent with the instability of neutral AlH_4 . Our experimental VDE value of 4.4 eV for the AlH_4^- anion is within the range of our theoretical estimates.

The closest to experimental values are obtained at the B3LYP/aug-cc-pV5Z (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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