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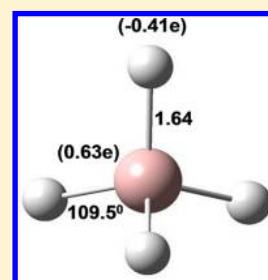
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Alanate Anion,  $\text{AlH}_4^-$ : Photoelectron Spectrum and ComputationsJ. D. Graham,<sup>†</sup> A. M. Buytendyk,<sup>†</sup> X. Zhang,<sup>†</sup> E. L. Collins,<sup>†</sup> B. Kiran,<sup>‡</sup> G. Gantefer,<sup>§</sup> B. W. Eichhorn,<sup>||</sup> G. L. Gutsev,<sup>\*,†</sup> S. Behera,<sup>○</sup> P. Jena,<sup>\*,○</sup> and K. H. Bowen<sup>\*,†</sup><sup>†</sup>Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States<sup>‡</sup>Department of Chemistry, McNeese State University, Lake Charles, Louisiana 70609, United States<sup>§</sup>Department of Physics, Konstanz University, 78457 Konstanz, Germany<sup>||</sup>Department of Chemistry, University of Maryland, College Park, Maryland 20742, United States<sup>†</sup>Department of Physics, Florida A&M University, Tallahassee, Florida 32307, United States<sup>○</sup>Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, United States

**ABSTRACT:** The alanate anion,  $\text{AlH}_4^-$ , 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  $\text{AlH}_4^-$  anion and the ground state of its thermodynamically unstable neutral counterpart,  $\text{AlH}_4$ . The vertical detachment energy (VDE) of  $\text{AlH}_4^-$  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  $\text{AlH}_4^-$  anion is perhaps the best known aluminum hydride in chemistry. The  $\text{AlH}_4^-$  anion is the anionic moiety in alkali alanate salts, such as  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$ , these being powerful reducing agents.<sup>1</sup>  $\text{AlH}_4^-$  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  $\text{AlH}_4^-$  anion has been observed and studied in cryogenic matrices<sup>2–5</sup> and has been found to be relatively unreactive during gas phase thermochemical measurements.<sup>6</sup> Calculations by Boldyrev and co-workers<sup>7,8</sup> 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  $\text{AlH}_4^-$  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  $\text{AlH}_4$  to be unstable, dissociating along a barrier-free potential surface into  $\text{AlH}_2$  and  $\text{H}_2$ .<sup>9</sup>

Although we had previously observed the  $\text{AlH}_4^-$  anion along with other aluminum hydride anionic species in mass spectra,<sup>10</sup> 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  $\text{AlH}_4^-$  anion at various higher levels of theory. We also computed the energetic differences between  $\text{AlH}_4^-$  and its decomposition products,  $\text{AlH}_2^-$  and  $\text{H}_2$ , and between the unbound neutral  $\text{AlH}_4$  and its decay products,  $\text{AlH}_2$  and  $\text{H}_2$ .

## ■ EXPERIMENTAL METHODS

$\text{AlH}_4^-$  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,<sup>11</sup> 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  $\text{AlH}_4^-$  along with other aluminum hydrides.  $\text{AlH}_4^-$  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<sup>+</sup>.

## COMPUTATIONAL METHODS

Our calculations of AlH<sub>4</sub>, AlH<sub>4</sub><sup>−</sup>, AlH<sub>2</sub>, AlH<sub>2</sub><sup>−</sup>, and H<sub>2</sub> 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),<sup>12,13</sup> B3LYP,<sup>14,15</sup> and M06<sup>16</sup> (HF/DFT), second-order Moller–Plesset perturbation theory (MP2),<sup>17</sup> coupled-cluster with single and doubles (CCSD) and noniterative triples CCSD(T),<sup>18</sup> and the outer valence Green's function (OVGF).<sup>19–21</sup> 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),<sup>22</sup> cc-pVQZ, cc-pVSZ, and aug-cc-pVSZ,<sup>23,24</sup> as implemented in Gaussian03<sup>25</sup> and Gaussian09<sup>26</sup> codes.

## EXPERIMENTAL RESULTS

The photoelectron spectrum of AlH<sub>4</sub><sup>−</sup> is presented in Figure 1. The spectrum consists of a broad feature, spanning electron

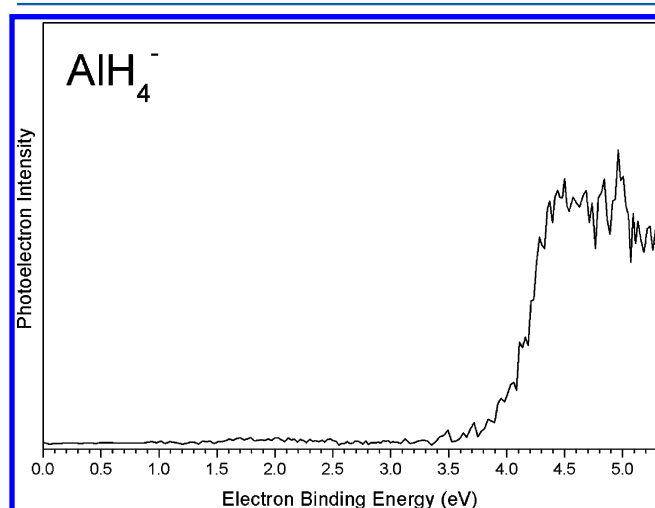


Figure 1. Photoelectron spectrum of the AlH<sub>4</sub><sup>−</sup> anion.

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<sub>4</sub><sup>−</sup> was measured to be 4.4 eV. Since 6.42 eV photons are energetic enough to dissociate AlH<sub>4</sub><sup>−</sup> into AlH<sub>2</sub><sup>−</sup> + H<sub>2</sub> or AlH<sub>3</sub> + H<sup>−</sup>, 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<sub>2</sub><sup>−</sup> at EBE = 1.5 eV (its VDE value) or for H<sup>−</sup> 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<sub>4</sub><sup>−</sup> anion geometry converged to a geometry of *T<sub>d</sub>* symmetry and its ground state is <sup>1</sup>A<sub>1</sub>. Figure 2a shows the geometrical structure of the AlH<sub>4</sub><sup>−</sup> 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)<sup>27</sup> population analysis. In the AlH<sub>4</sub><sup>−</sup> 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<sub>4</sub><sup>−</sup> anion satisfies the superhalogen<sup>28,29</sup> formula, MX<sub>k+1</sub> 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<sup>2</sup>3p<sup>1</sup> is three. Formally, the extra electron in AlH<sub>4</sub><sup>−</sup> 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<sub>4</sub><sup>−</sup>. The vertical detachment energy (VDE) of the anion is computed at the anion equilibrium geometry according to the following expression:

$$\text{VDE}(\text{AlH}_4^-) = E(\text{AlH}_4 \text{ at its anion's equilibrium geometry}) - E(\text{AlH}_4^- \text{ at equilibrium geometry}) \quad (1)$$

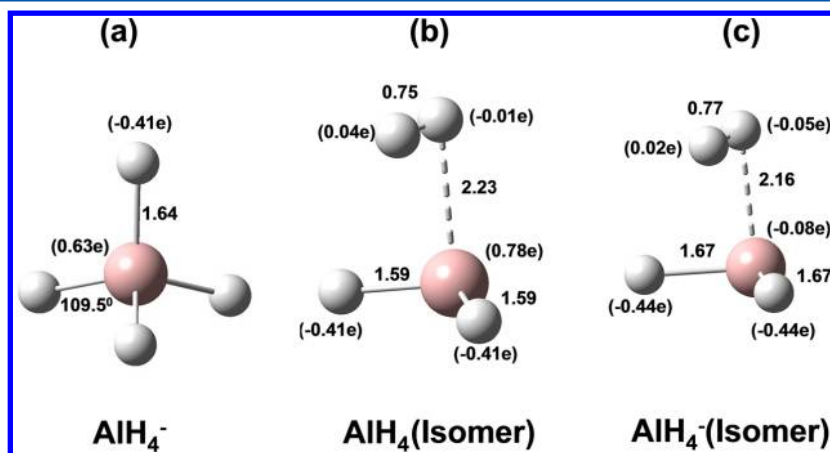


Figure 2. Geometrical structures of the AlH<sub>4</sub><sup>−</sup> ground state (a) and electronically stable states of the neutral (b) and anion (c) isomers as optimized at the B3LYP/6-311++G(3df,3pd) level. Bond lengths are in Å and charges on atoms are in units of electronic charge.

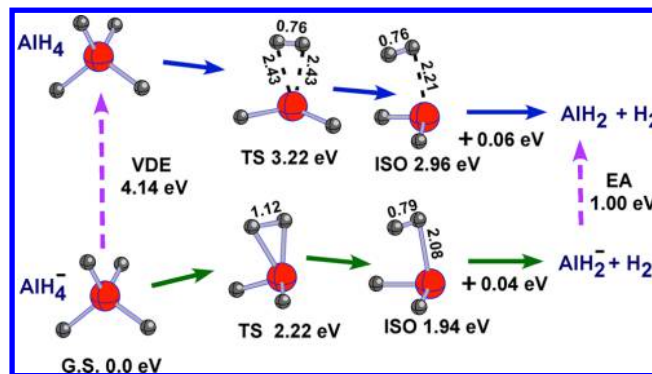
**Table 1.** Energetic Difference between  $\text{AlH}_4^-$  Anion and the Unbound Neutral  $\text{AlH}_4$  Decay Products,  $\text{AlH}_2$  and  $\text{H}_2$  ( $E_{\text{asym}}$ ), Vertical Electron Detachment Energy (VDE) of the  $\text{AlH}_4^-$  Anion, Interatomic Distances and Harmonic Vibrational Frequency of the H – H Vibration ( $\omega_e$ ) in the  $\text{AlH}_4$  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)  $\text{AlH}_4 \rightarrow \text{AlH}_2 + \text{H}_2$  and (A ISO)  $\text{AlH}_4^- \rightarrow \text{AlH}_2^- + \text{H}_2$  Computed Using Different Methods and Basis sets

method	basis set	$E_{\text{asym}}$ (eV)	VDE (eV)	R(H–H) (Å)	R(Al–H <sub>2</sub> ) (Å)	$\omega_e(\text{H–H})$ (eV)	$\Delta E$ (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	$\Delta E(\text{N ISO}) = +0.08$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.04$ $\Delta E(\text{A ISO}) = +0.08$ $\Delta E_{\text{tot}}(\text{A ISO}) = -0.03$
	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	$\Delta E(\text{N ISO}) = +0.19$ $\Delta E_{\text{tot}}(\text{N ISO}) = -0.16$
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	
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 <sup>a</sup>			0.547 <sup>b</sup>	

<sup>a</sup>This work. <sup>b</sup>Experimental value of  $\omega_e$  for the gas-phase  $\text{H}_2$  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 previously<sup>3</sup> and confirmed by the results of our computations that the neutral  $\text{AlH}_4$  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  $\text{AlH}_4$  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  $\text{AlH}_4$  isomer is stable with respect to the sum of total electronic energies of both  $\text{AlH}_2$  and  $\text{H}_2$  and  $\text{AlH}_3$  and  $\text{H}$  (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  $\text{H}_2$  molecule carry negligible charge and bind weakly to the  $\text{AlH}_2$  complex through the charge polarization mechanism.<sup>30</sup> This weak interaction is evident from the differences in total electronic energies,  $\Delta E$ , computed according to equation



**Figure 3.** Decay channels of the  $\text{AlH}_4^-$  anion (in its ground state) and of the  $\text{AlH}_4$  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  $\Delta E$  is for the neutral  $\text{AlH}_4$  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  $\text{AlH}_4$ ,  $\text{AlH}_2$ , and  $\text{H}_2$  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  $E_{\text{tot}}$  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  $\text{AlH}_4$  species, in place of an adiabatic electron affinity, we define  $E_{\text{asym}}$  as the energetic difference between  $\text{AlH}_4^-$  and the unbound neutral  $\text{AlH}_4$  decay products,  $\text{AlH}_2$  and  $\text{H}_2$ , 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  $E_{\text{asym}}$  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  $\Delta E$  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  $\Delta E$  is for the anionic  $\text{AlH}_4^-$  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  $\text{AlH}_4^-$  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  $\text{AlH}_4$  and  $\text{AlH}_4^-$ . The  $\text{AlH}_4^-$  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 BPW91/6-311++G(3df,3pd) computations. On the contrary, the neutral  $\text{AlH}_4$  is thermodynamically unstable and dissociates to  $\text{AlH}_2$  and  $\text{H}_2$ . The temporary  $\text{AlH}_4$  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  $\text{AlH}_4^-$  anion is consistent with the instability of neutral  $\text{AlH}_4$ . Our experimental VDE value of 4.4 eV for the  $\text{AlH}_4^-$  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-pVSZ (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

- (1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Interscience: New York, 1996.
- (2) Pullumbi, P.; Bouteiller, Y.; Manceron, L. The Vibrational Spectrum of Isolated  $\text{AlH}_4^-$ : An Infrared Matrix Isolation and ab Initio Study. *J. Chem. Phys.* **1994**, *101*, 3610–3617.
- (3) Andrews, L.; Wang, X. Infrared Spectra of Dialanes in Solid Hydrogen. *J. Phys. Chem. A* **2004**, *108*, 4202–4210.
- (4) Wang, X.; Andrews, L.; Tam, S.; DeRose, M.; Fajardo, M. Infrared Spectra of Aluminum Hydrides in Solid Hydrogen:  $\text{Al}_2\text{H}_4$  and  $\text{Al}_2\text{H}_6$ . *J. Am. Chem. Soc.* **2003**, *125*, 9218–9228.
- (5) Andrews, L.; Wang, X. The Infrared Spectrum of  $\text{Al}_2\text{H}_6$  in Solid Hydrogen. *Science* **2003**, *299*, 2049–2052.
- (6) Goebbert, D.; Hernandez, H.; Francisco, J.; Wenthold, P. The Binding Energy and Bonding in Dialane. *J. Am. Chem. Soc.* **2005**, *127*, 11684–11689.
- (7) Boldyrev, A. I.; Simons, J. Vertical and Adiabatic Ionization Potentials of  $\text{MH}_{k+1}^-$  Anions. Ab Initio Study of the Structure and Stability of Hypervalent  $\text{MH}_{k+1}$  Molecules. *J. Chem. Phys.* **1993**, *99*, 4628–4637.
- (8) Boldyrev, A. I.; von Niessen, W. The First Ionization Potentials of Some  $\text{MH}_{k+1}^-$  and  $\text{M}_2\text{H}_{2k+1}^-$  Anions Calculated by a Green's Function Method. *Chem. Phys.* **1991**, *155*, 71–78.
- (9) Wong, S.; Li, W.; Paddon-Row, M. On the Structure and Stability of the  $\text{AlH}_4$  Radical and Its Potential Energy Surface for Rearrangement and Dissociation: An ab Initio MO Study. *J. Mol. Struct.* **1991**, *226*, 285–301.
- (10) Zhang, X.; Wang, H.; Collins, E.; Lim, A.; Ganteför, G.; Kiran, B.; Schnöckel, H.; Eichorn, B.; Bowen, K. Photoelectron Spectroscopy of the Aluminum Hydride Anions:  $\text{AlH}_2^-$ ,  $\text{AlH}_3^-$ ,  $\text{Al}_2\text{H}_6^-$ ,  $\text{Al}_3\text{H}_9^-$ , and  $\text{Al}_4\text{H}_{12}^-$ . *J. Chem. Phys.* **2013**, *138*, 124303.

- (11) Cha, G.; Ganteför, G.; Eberhardt, W. New Experimental Setup for Photoelectron Spectroscopy on Cluster Anions. *Rev. Sci. Instrum.* **1992**, *63*, 5661–5666.
- (12) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (13) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. *Phys. Rev. B* **1992**, *45*, 13244–13249.
- (14) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *97*, 5648–5652.
- (15) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (16) Zhao, Y.; Truhlar, D. G. Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States. *J. Phys. Chem. A* **2006**, *110*, 13126–13130.
- (17) Head-Gordon, M.; Pople, J. A.; Frisch, M. MP2 Energy Evaluation by Direct Methods. *J. Chem. Phys. Lett.* **1998**, *153*, 503–506.
- (18) Bartlett, R. J.; Musial, M. Coupled-Cluster Theory in Quantum Chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291–352.
- (19) Cederbaum, L. S. One-Body Green's Function for Atoms and Molecules: Theory and Application. *J. Phys. B* **1975**, *8*, 290–303.
- (20) Ortiz, J. V. Partial Third-Order Quasiparticle Theory: Comparisons for Closed-Shell Ionization Energies and an Application to the Borazine Photoelectron Spectrum. *J. Chem. Phys.* **1996**, *104*, 7599–7605.
- (21) Zakrzewski, V. G.; von Niessen, W. Vectorizable Algorithm for Green Function and Many-Body Perturbation Methods. *J. Comput. Chem.* **1993**, *14*, 13–18.
- (22) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (23) Woon, D. E.; Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum Through Argon. *J. Chem. Phys.* **1993**, *98*, 1358–1371.
- (24) Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (27) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular Interactions from a Natural Bond Orbital, Donor–Acceptor Viewpoint. *Chem. Rev.* **1988**, *88*, 899–926.
- (28) Gustev, G. L.; Boldyrev, A. I. DVM- $X\alpha$  Calculations on the Ionization Potentials of  $MX_{k+1}^-$  Complex Anions and the Electron Affinities of  $MX_{k+1}$  Superhalogens. *Chem. Phys.* **1981**, *56*, 277–283.
- (29) Gustev, G. L.; Boldyrev, A. I. The Theoretical Investigation of the Electron Affinity of Chemical Compounds. *Adv. Chem. Phys.* **1985**, *61*, 169.
- (30) Niu, J.; Rao, B.; Jena, P. Binding of Hydrogen Molecules by a Transition-Metal Ion. *Phys. Rev. Lett.* **1992**, *68*, 2277–2280.
- (31) Hotop, H.; Lineberger, W. C. Binding Energies in Atomic Negative Ions: II. *J. Phys. Chem. Ref. Data.* **1985**, *14*, 731–750.