Does \( \text{Al}_4\text{H}_{14}^- \) cluster anion exist? High-level \textit{ab initio} study

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Abstract A comprehensive \textit{ab initio} investigation using coupled cluster theory with the aug-cc-pVnZ, \( n=D,T \) basis sets is carried out to identify distinct structures of the \( \text{Al}_4\text{H}_{14}^- \) cluster anion and to evaluate its fragmentation stability. Both thermodynamic and mechanistic aspects of the fragmentation reactions are studied. The observation of this so far the most hydrogenated aluminum tetramer was reported in the recent mass spectrometry study of Li et al. (2010) J Chem Phys 132:241103–241104. The four \( \text{Al}_4\text{H}_{14}^- \) anion structures found are chain-like with the multiple-coordinate Al center and can be viewed approximately as comprising \( \text{Al}_2\text{H}_7^- \) and \( \text{Al}_2\text{H}_7 \) moieties. Locating computationally some of the \( \text{Al}_4\text{H}_{14}^- \) minima on the correlated \textit{ab initio} potential energy surfaces required the triple-zeta quality basis set to describe adequately the Al multi-coordinate bonding. For the two most stable \( \text{Al}_4\text{H}_{14}^- \) isomers, the mechanism of their low-barrier interconversion is described. The dissociation of \( \text{Al}_4\text{H}_{14}^- \) into the \( \text{Al}_2\text{H}_7^- \) and \( \text{Al}_2\text{H}_7 \) units is predicted to require 20-22 (10-13) kcal mol\(^{-1}\) in terms of \( \Delta H \) (\( \Delta G \)) estimated at \( T=298.15 \) K and \( p=1 \) atm. However, \( \text{Al}_4\text{H}_{14}^- \) is found to be a metastable species in the gas phase: the \( \text{H}_2 \) loss from the radical moiety of its most favorable isomer is exothermic by 18 kcal mol\(^{-1}\) in terms of \( \Delta H \) (\( \Delta G \)) estimated at \( T=298.15 \) K and by 25 kcal mol\(^{-1}\) in terms of \( \Delta G(298.15 \text{ K}) \), with the enthalpic/free energy barrier involved being less than 1 kcal mol\(^{-1}\). By contrast with alane \( \text{Al}_4\text{H}_{14}^- \), only a weakly bound complex between \( \text{Ga}_2\text{H}_{12}^- \) and \( \text{H}_2 \) has been identified for the gallium analogue using the relativistic effective core potential.

Keywords \( \text{Al}_4\text{H}_{14}^- \) and \( \text{Ga}_4\text{H}_{14}^- \) hydrogen-rich clusters - Coupled cluster calculations - Potential energy surfaces - Thermodynamic and kinetic stability

Introduction

Aluminum-hydrides, or alanes, have been proposed to be potential hydrogen storage media, building blocks for new cluster assemblies and high-energy-density materials [1–6]. During the last three years, several novel alanes, both neutral and anionic, have been made and characterized. The emerging structural and electronic properties of alanes and their derivatives involving a small \( \text{Al}_4 \) cluster core have been notably the focus of the widespread interest [1, 2, 5, 6].

The new hydrogenated \( \text{Al}_4\text{H}_6 \) neutral cluster was reported to be a stable species in the gas phase based on the results of the photoelectron study of the corresponding anion \( \text{Al}_4\text{H}_6^- \) and density functional theory (DFT) electronic structure calculations for the neutral [1]. Furthermore, the \( \text{Al}_4\text{H}_6 \) cluster was suggested to be a high-energy density molecule, with the estimated heat of combustion (giving the \( \text{Al}_2\text{O}_3 \) and water products) to be about 2.5 times greater than that for methane [1]. Various \( \text{Al}_4\text{R}_6 \) and \( \text{Al}_4\text{R}_5\text{X} \) derivatives of \( \text{Al}_4\text{H}_6 \) with the hydrogen atoms substituted by the bulky \( \text{R} \) groups and halogens \( \text{X} \) \((\text{R}^\text{Bu}_2; \text{X}=\text{Br,Cl})\) were subsequently prepared and structurally characterized [5].

The whole series of novel aluminum-hydride cluster anions \( \text{Al}_4\text{H}_n^- \) were generated using the laser-induced plasma technique and characterized by mass spectrometry [2]. The most hydrogenated anionic aluminum tetramer reported in Ref. [2] was \( \text{Al}_4\text{H}_{13}^- \). In the related study published recently, the new gas phase \( \text{Al}_m\text{H}_n^- \) clusters were produced with a pulsed arc discharge source and identified using mass spectrometry [6]. The latter investigation reported the
Fig. 1 S1, S2, S3 and S3' structures of the Al$_4$H$_{14}$ anion (distances in Ångstroms) calculated with the correlated \textit{ab initio} and density functional methods using the aug-cc-pVnZ, n=D,T basis sets. Note that S2 minimum has not been located on the UCCSD/aug-cc-pVDZ and UMP2/aug-cc-pVDZ potential energy surfaces, whereas S3(S3') minima have not been identified on the UMP2/aug-cc-pVDZ energy surface (see the text).
aluminum hydride clusters having an extraordinary hydrogen content, with the hydrogen atom number \(m\)-aluminum atom number \(n\) ratio exceeding 3: for \(n = 0 \ldots 5\), the clusters with \(m = 3n+1\) hydrogen atoms were detected. Most notably, for \(n = 4\), the cluster having \(m = 3n+2\) hydrogens, or \(\text{Al}_4 \text{H}_{14}^-\), was observed according to the authors [6], although the actual structure of this cluster anion with an open electronic shell was not reported.

Previously, using density functional and correlated ab initio methods we compared the structures, thermodynamic stabilities and bonding of the multiply hydrogenated aluminum and gallium neutral clusters \(\text{M}_3\text{H}_9\) and \(\text{M}_4\text{H}_{12}\) (\(\text{M} = \text{Al}, \text{Ga}\)) [7]. The distinct difference found between the corresponding clusters with \(\text{M} = \text{Al}\) and \(\text{Ga}\) was the stability of the open type structures called by us “hypervalent”, involving the five- or six-coordinate \(\text{M}\) atom (in terms of the \(\text{M-H}\) bonds). We showed specifically that, for \(\text{M} = \text{Al}\), such a structure was relatively stable, lying within 2 kcal mol\(^{-1}\) of the cyclic global minimum, whereas for \(\text{M} = \text{Ga}\), the “hypervalent” isomer appeared to be destabilized relative to the lowest energy cyclic species, especially for \(\text{M}_4\text{H}_{12}\) [7].

Herein we present extensive high-level ab initio calculations of the structures and fragmentation stability of \(\text{Al}_4\text{H}_{14}^-\) as well as of the reaction paths for interconversion and decomposition of the anion. Notably, for this novel species, we have carefully studied the dependence of the calculated results on the level of theory used. As described below, we have identified four different chain-like structures of \(\text{Al}_4\text{H}_{14}^-\) which involve the multiple-coordinate \(\text{Al}\) center, reminiscent of the structural motif seen in the “hypervalent” isomer of the \(\text{Al}_4\text{H}_{12}\) cluster [7]. In order to assist in the future assignment of the actual isomer of the \(\text{Al}_4\text{H}_{14}^-\) anion present in the experimental mass spectrum [6], we have calculated vertical electron detachment energies (VDEs) for the distinct structures. We also show that by contrast to the aluminum hydride \(\text{Al}_4\text{H}_{14}^-\), only a weakly bound complex between the \(\text{Ga}_4\text{H}_{12}^-\) anion and \(\text{H}_2\) has been identified for the gallium counterpart \(\text{Ga}_4\text{H}_{14}^-\).

Computational methods

Coupled cluster theory with single and double excitations (CCSD) [8] and second-order Møller-Plesset perturbation theory (MP2) [9] were used in conjunction with the augmented correlation consistent aug-cc-pVnZ, \(n=D,T\) basis sets [10, 11]. All the geometries were optimized and characterized as minima or relevant transition states at each computational level. The MP2 vibrational frequencies were calculated using the analytical Hessians, whereas the CCSD frequencies were computed with the analytical gradients and numerical Hessians. For comparison, optimizations and frequency calculations were also carried out using the same basis sets with the B3LYP density functional [12, 13]. Spin-unrestricted (U) version of each method was used for the open-shell species. To establish accurate energetics, single-point energy calculations were performed at the MP2/aug-cc-pVTZ geometries using CCSD with perturbatively included triples (CCSD(T)) [8] with the aug-cc-pVTZ basis.
In addition, the structures and stability of \( \text{Al}_4\text{H}_{14}^- \) were studied using the multi-level G4 scheme [14]. Enthalpies and Gibbs free energies were calculated at \( T=298.15 \text{ K} \) and \( p=1 \text{ atm} \). For the gallium analogue, \( \text{Ga}_4\text{H}_{14}^- \), the energy-consistent effective core potential (ECP), ECP10MDF [15], which replaces the \( 1s^22s^22p^6 \) core of Ga by the pseudopotential was used (in addition to the all-electron calculations) to take into account relativistic effects of this atom. The explicitly treated Ga electrons \( (3s^23p^63d^{10}4s^24p^1) \) were described by the associated \( (1s^22s^22p^6)\)/[6s6p5d2f] basis set [16], augmented by diffuse functions (aug-cc-pVTZ-PP). The latter basis was employed in conjunction with the all-electron aug-cc-pVTZ basis sets for H [10, 11, 17]. The relevant computational methods using the ECP10MDF will be referred to as MP2/ECP and B3LYP/ECP. Calculations in the current work were performed employing Gaussian 09 program [18].

Fig. 3 A structure of the transition state \( \text{S}3\text{-S}3' \text{ TS} \) (distances in Ångstroms) calculated with the correlated \textit{ab initio} and density functional methods using the aug-cc-pVnZ, \( n=D,T \) basis sets. \( \text{S}3\text{-S}3' \text{ TS} \) is a saddle point for the \( \text{Al}_4\text{H}_{14}^- \text{(S}3) \rightarrow \text{Al}_4\text{H}_{14}^- \text{(S}3') \) interconversion (cf. Fig. 4); the associated imaginary frequency is given at each computational level.

**Interconversion barrier**

\[
\begin{align*}
\text{(kcal/mol)} & \\
1.8/1.6 \quad [2.1/1.6] \\
\{-0.3/-0.4\} & 0.4/0.0
\end{align*}
\]

Fig. 4 Illustration of the \( \text{Al}_4\text{H}_{14}^- \text{(S}3) \rightarrow \text{Al}_4\text{H}_{14}^- \text{(S}3') \) interconversion occurring through the transition state \( \text{S}3\text{-S}3' \text{ TS} \). The interconversion barrier values shown have been corrected for the zero-point vibrational energies; the value before (after) slash is for the \text{S}3\text{--S}3' (S3'--S3) rearrangement.
Table 2: Energies of unimolecular fragmentation reactions (kcal mol$^{-1}$) of Al$_4$H$_{14}^-$ from the various theoretical methods$^a$

| Fragmentation channel | aug-cc-pVDZ$^b$ |  |  |
|-----------------------|-----------------|-----------------|-----------------|
|                       | UB3LYP          | UMP2            | UCCSD           |
| S1$^-$→Al$_2$H$_7^+$ + Al$_2$H$_7^-$ | 15.4            | 12.7            | 18.1            |
| S2$^-$→Al$_2$H$_7^+$ + Al$_2$H$_7^-$ | 16.5            | d               | d               |
| S3$^-$→Al$_2$H$_7^+$ + Al$_2$H$_7^-$ | 18.8            | d               | 22.1            |
| S3$'$→Al$_2$H$_7^+$ + Al$_2$H$_7^-$ | 18.7            | d               | 22.2            |
| S1$^-$→Al$_4$H$_{13}^-$ + H | -0.7            | -8.5            | -6.5            |
| S2$^-$→Al$_4$H$_{13}^-$ + H | 0.4             | d               | d               |
| S3$^-$→Al$_4$H$_{13}^-$ + H | 2.7             | d               | -2.5            |
| S3$'$→Al$_4$H$_{13}^-$ + H | 2.5             | d               | -2.5            |
| S1$^-$→Al$_4$H$_{12}^-$ + H$_2$ | -20.0           | -23.5           | -24.0           |
| S2$^-$→Al$_4$H$_{12}^-$ + H$_2$ | -18.9           | d               | d               |
| S3$^-$→Al$_4$H$_{12}^-$ + H$_2$ | -16.6           | d               | -20.1           |
| S3$'$→Al$_4$H$_{12}^-$ + H$_2$ | -16.7           | d               | -20.0           |

$^a$All values have been corrected for the zero-point vibrational energies. A positive (negative) sign indicates that Al$_4$H$_{14}^-$ is thermodynamically stable (unstable) relative to the fragmentation products

$^b$At the geometries calculated with each method

$^c$At the geometries calculated with each method, except for the UCCSD(T) value calculated at the UMP2/aug-cc-pVTZ optimized structures

$^d$The Al$_4$H$_{14}^-$ structure has not been found at this level (see the text)

$^e$In parentheses, G(0 K) results are given

Results and discussion

Al$_4$H$_{14}^-$ structures - method dependence

Figure 1 illustrates the optimization level dependence of the four distinct structures of the Al$_4$H$_{14}^-$ cluster anion, S1(2A), S2(2A), S3(2A') and S3'(2A). These doublet structures are chain-like with the bridging hydrogens. Attempts to locate a cyclic Al$_4$H$_{14}^-$ isomer were unsuccessful. Computations show that S1 exists on the potential energy surfaces calculated at the five levels (with all positive force constants predicted at each level). By contrast, the identification of S2 appeared to be method dependent: this structure has been located on the UB3LYP/aug-cc-pVDZ, UB3LYP/aug-cc-pVTZ and UMP2/aug-cc-pVTZ potential energy surfaces, but not on the UMP2/aug-cc-pVDZ and UCCSD/aug-cc-pVDZ surfaces. In turn, S3 and S3' structures are potential minima at all the levels, but UMP2/aug-cc-pVDZ. These results indicate that with the correlated methods, the triple-zeta flexibility basis set is required to describe adequately the bonding situation for Al$_4$H$_{14}^-$. As seen in Fig. 1, the unique features of the Al$_4$H$_{14}^-$ species are the involvement of the multi-coordinate (Al1 or Al2) atom, the presence of not symmetrical Al-H-Al bridges with the H atoms not shared equally with the Al atoms as well as the presence of the significantly elongated terminal Al(Al2)-H bonds. It is relevant to note here that multi-coordinate Al centers (participating in the six Al-H-Al bridges) were first observed in the solid state structure of AlH$_3$ polymer in 1969 [19].

Figure 1 also shows that the use of the correlated methods, especially in conjunction with the aug-cc-pVTZ basis set, causes a significant shortening of most of the Al-Al distances (up to 0.3 Å) along with a major decrease of the Al2-H
bridging bond of S1 (relative to the UB3LYP results). As the energy calculations indicate (see Table 1), the four Al4H14− species are of similar stability, lying within 2.2 and 2.4 kcal mol⁻¹ at the most comprehensive UCCSD(T)/aug-cc-pVTZ/UMP2/aug-cc-pVTZ and G4 (0 K) levels, respectively, with S3 being the most stable of the four, followed by S3'.

We suggest that the simplest description of the Al4H14− anion structure would involve the ‘Al2H7−’ and ‘Al2H7’ units. To support this model we report in Fig. 2 the optimized geometries of the isolated Al2H7− anion and Al2H7 radical (both structures in Fig. 2 show positive force constants at each computational level). We find further support from the Mulliken spin populations, which indicate that the ‘Al2H7’ fragment of S1 and S3(S3') is a sole carrier of the spin density. For S2, although its neutral fragment differs most from the isolated Al2H7 geometry (the former matches rather the higher energy Al2H7− isomer [20]), similar to the cases of S1 and S3(S3'), this moiety holds the spin density.

The results in Fig. 2 further show that an appreciable bending occurs for isolated Al2H7− at the correlated levels compared to the UB3LYP results. Earlier computational studies of Al2H7− established this anion to be thermodynamically stable with respect to both the AlH3+AlH4− and Al2H6+H− [21, 22] fragmentations. For isolated Al2H7−(C₃), we predicted the lowest energy structure to be double-bridged, in agreement with the recent density functional work [20] (note that with UB3LYP/aug-cc-pVTZ, Al2H7 has higher C₃ (2A”) symmetry). This radical species also features two lengthened terminal Al-H bonds, to 1.66 and 1.76 Å, with a relatively short Al-Al distance of 2.62 Å (the UMP2/aug-cc-pVTZ results), and it bears resemblance with the radical moiety of Al4H14−, especially for S1. The adiabatic
electron detachment energy of the Al₂H₇⁻ anion, or the adiabatic electron affinity of the Al₂H₇ neutral was computed to be relatively high at 4.14 (4.20) eV with the UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ (G4 (0 K)) calculations, pointing to the appreciable electronic stability of the anion.

Interconversion of Al₄H₁₄⁻ isomers

We found that the lowest-energy isomers of Al₄H₁₄⁻, S₃ and S₃', are connected by the transition state S₃-S₃'TS, shown in Fig. 3. During this interconversion, H₆ and H₇ of S₃ move in the opposite directions, breaking C₃v symmetry.

Fig. 6 A structure of the transition state H₂el.TS for H₂ elimination from Al₄H₁₄⁻ (S₃) (distances in Ångstroms), calculated with the correlated ab initio and density functional methods using the aug-cc-pVnZ, n=D,T basis sets; the associated imaginary frequency is given at each computational level.

Fig. 7 Schematic profiles of ΔH (298.15 K) for the three fragmentation channels of the Al₄H₁₄⁻ (S₃) anion (in kcal mol⁻¹); the corresponding ΔG (298.15 K) values are given in parentheses (G4 results). Note that the Al₄H₁₂⁻…H₂ post-reaction complex (shown in Fig. 8) has been omitted in the H₂ elimination path.
(see Fig. 4). Past the S3-S3′ TS, Hb keeps moving toward Hc, whereas Hα moves away from Al2. In the resulting S3’ structure of very similar stability to S3 (Table 1), the new longest terminal Al-H links are those involving Hα and Hb of 1.67 and 1.87 Å (the UMP2/aug-cc-pVTZ results), with Hα forming “normal” terminal bond, similar to Hb. The S3 → S3-S3′ TS → S3’ reaction path is confirmed by the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier for the intrinsic reaction coordinate (IRC) computation. At the UCCSD(T)/aug-cc-pVTZ level, only a tiny barrier.
The post-reaction van der Waals complex between Al$_4$H$_{12}^-$ and H$_2$ has also been identified as reported in Fig. 8. This complex, denoted Al$_4$H$_{12}^-$...H$_2$, was optimized at all five computational levels. Figure 8 shows that both the actual position of the H$_2$ subsystem within the complex and interaction distance(s) are method dependent. With UMP2/aug-cc-pVTZ, describing best long-range dispersion (at the optimization level), the complex has a structure in which the hydride fragment (Al$_2$-H) of Al$_4$H$_{12}^-$ interacts with the slightly polarized H-H bond (based on the Mulliken charges). Furthermore, the UMP2/aug-cc-pVTZ calculated interacting distance of 2.53 Å is distinctly reduced relative to those predicted with the other methods. The UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ binding energy ($D_e$) of...
Al4H12−...H2 amounts to 0.7 kcal mol−1. Note that this value coincides with the UMP2/aug-cc-pVTZ result indicating the adequate description of dispersion already at the latter level (for comparison of the six D6 values of Al4H12−...H2, see lower panel in Fig. 8).

VDE energies

The VDE energies of the four hydride structures of the Al4H14− anion computed at the UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ level are compared in Table 5. For the S1, S2, S3 and S3′ species the respective values are 4.83, 5.23, 4.72 and 4.77 eV. These VDEs are found to be even larger than the (adiabatic) electron detachment energy of the Al2H7− anion discussed above. On the other hand, except for the S2 result, the remaining three VDEs are quite similar and might not help to assist in the future assignment of the actual isomer of the Al4H14− anion.

Table 5 The VDE energies (eV) of the S1, S2, S3 and S3′ structures of Al4H14− calculated at the UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ level

|   | S1   | S2   | S3   | S3′  |
|---|------|------|------|------|
|   | 4.83 | 5.23 | 4.72 | 4.77 |

*The vertical detachment energy (VDE) was computed as the energy difference between the Al4H14 neutral and Al4H14− anion at the anion optimized geometry.

Does Ga4H14− galane exist?

Following the earlier work on comparing the structures, stabilities and bonding of the hydrogenated aluminum and gallium clusters [7], we next studied computationally Ga4H14− cluster anion. Although at the all-electron DFT UB3LYP/aug-cc-pVTZ level we located the Ga4H14− minimum analogue of Al4H14− (S3) (Fig. 9), neither our UB3LYP/ECP optimization nor that using the correlated UMP2/ECP method confirmed this result (the last two approaches employed the relativistic effective core potential ECP10MDF, see the footnote under Fig. 9). Similarly, our attempts to optimize the Ga4H14− counterparts of S1 and S2 led instead to the van der Waals complex Ga4H12−...H2, depicted in Fig. 10. As in Al4H12−...H2, the location of H2 unit within Ga4H12−...H2 and intermolecular separation are method dependent. Expectedly, the shortest separation between Ga4H12− and H2 is calculated with UMP2/aug-cc-pVDZ and UMP2/ECP (the highest correlated optimization levels used for the complex). At the former geometry, the UCCSD(T)/aug-cc-pVTZ binding energy (D6) of Ga4H12−...H2 is 1.3 kcal mol−1 (see the lower panel in Fig. 10). As Fig. 10 shows additionally, the use of the relativistic ECP resulted in a significant shortening of the terminal Ga-H bonds compared to the all-electron results (this is actually a joint ECP/basis set effect).

The differences noticed here between the Al4H14− and Ga4H14− cluster anions are consistent with our recent symmetry-adapted perturbation theory (SAPT) analysis of the aluminum and gallium species pointing out to much stronger “hydride” character of the former [24]. The larger propensity of Al atom for hypercoordinate bonding situations compared to Ga [25] is a relevant qualitative explanation.

Conclusions

For the first time, distinct minima structures of the hydrogen-rich alane Al4H14−, experimental observation of which was recently reported [6], have been identified at the correlated ab
Fig. 10 A structure (distances in Ångstroms) and binding energy ($D_e$, kcal mol$^{-1}$) of the complex $\text{Ga}_4\text{H}_{12}\cdots\text{H}_2$ calculated at the all-electron and ECP levels; $D_e$ has been calculated as $[E(\text{Ga}_4\text{H}_{12}\cdots\text{H}_2)] - E(\text{Ga}_4\text{H}_{12}) - E(\text{H}_2)$ - note that the UCCSD(T)/aug-cc-pVTZ value of $D_e$ has been computed at the UMP2/aug-cc-pVDZ optimized structures.

\[
\begin{align*}
D_e \text{(Ga}_4\text{H}_{12}\cdots\text{H}_2) \text{(kcal/mol)} & \\
\text{UB3LYP/aug-cc-pVDZ} & 0.4 \\
\text{UMP2/aug-cc-pVDZ} & 1.5 \\
[\text{UB3LYP/aug-cc-pVTZ}] & [0.5] \\
(\text{UMP2/ECP}) & (2.0) \\
\text{UCCSD(T)/aug-cc-pVTZ} & 1.3
\end{align*}
\]
initio levels, and thermodynamic and kinetic stability of this species was assessed at T=0 K and T=298.15 K. The structures found are chain-like, contain the multiple-coordinate Al center and approximately comprise the Al$_2$H$_7^-$ and Al$_2$H$_7$ moieties. Locating computationally some of the Al$_4$H$_{14}^-$ minima on the UCCSD and UMP2 potential energy surfaces required the triple-zeta quality basis set to describe adequately the Al multi-coordinate bonding. The dissociation of Al$_4$H$_{14}^-$ into the Al$_2$H$_7^-$ and Al$_2$H$_7$ units is predicted to require 20-22 (10-13) kcal mol$^{-1}$ with $\Delta H(298.15 \text{ K})$ ($\Delta G(298.15 \text{ K})$). However, Al$_4$H$_{14}^-$ is predicted to be metastable, because H$_2$ loss from its most favorable S3 isomer is exothermic by 18 kcal mol$^{-1}$ in terms of $\Delta H(298.15 \text{ K})$ and by 25 kcal mol$^{-1}$ in terms of $\Delta G(298.15 \text{ K})$, with the enthalpic/free energy barrier involved being less than 1 kcal mol$^{-1}$. The global minimum on the Al$_4$H$_{14}^-$ anion energy surface corresponds to the weakly bound complex Al$_4$H$_{12}^-$...H$_2$. This kind of complex appeared to be the only minimum structure identified for the gallium counterpart Ga$_4$H$_{14}^-$, when Ga relativistic effective core potential was used.

In the original experimental study, Li et al. [6] reported that they could observe strong Al$_n$H$_m^-$ intensities for m$>3n$ “under some source conditions”. Our current thermodynamic and kinetic (fragmentation reaction barrier) considerations suggest that due to the predicted Al$_4$H$_{14}^-$ metastability in the gas phase, this ion would in fact be detected only under the special experimental conditions.

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