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ABSTRACT

Ever since our first experimental and computational identification of $\text{Al}_3\text{H}_6$ as a boron analog [X. Li et al., Science 315, 356 (2007)], studies on aluminum hydrides unveiled a richer pattern of structural motifs. These include aluminum-rich hydrides, which follow shell closing electron counting models; stoichiometric clusters (called baby crystals), which structurally correspond to the bulk alane; and more. In this regard, a mass spectral identification of unusually high intense peak of $\text{Al}_4\text{H}_{14}^−$, which has two hydrogen atoms beyond stoichiometry, has remained mostly unresolved [X. Li et al., J. Chem. Phys. 132, 241103 (2010)]. In this Communication, with the help of global minima methods and density functional theory-based calculations, we identify the lowest energy $\text{bound }$ structure with a unique $\text{Al}−\text{H}−\text{H}−\text{Al}$ bonding. Our electronic structural analysis reveals that two $\text{Al}_2\text{H}_6$ units trap a transient, metastable $\text{H}_2^−$. In other words, three stable molecules, two $\text{Al}_2\text{H}_6$ and an $\text{H}_2$, are held together by a single electron. Our studies provide a pathway to stabilize transient species by making them part of a more extensive system.

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Hydrogen anion ($\text{H}_2^−$), the simplest of all molecular anions, is considered to play an important role in several collision processes, which is, however, metastable with a short lifetime. Despite being very transient in nature, several ingenious experiments had been devised to verify the existence of the molecule. After several attempts by various groups, Gosler et al. provided the first unambiguous experimental evidence of rotationally excited $\text{H}_2^−$ and $\text{D}_2^−$. Recently, Rudnev et al. provided the first photo-detachment spectrum of $\text{H}_2^−$, further cementing the evidence on the existence of $\text{H}_2^−$. Note that the hydrogen molecule has negative electron affinity (∼1.03 eV), which implies that the addition of an electron to the ground state of $\text{H}_2$ is endothermic. This is understandable as the additional electron occupies the anti-bonding orbital, and it explains the elusive nature.

One way to stabilize $\text{H}_2^−$ is to reduce the destabilizing nature of the anti-bonding orbital. This can be accomplished by making the anion a part of a larger molecular system. Aluminum hydrides provide such an opportunity. Over the last decade or so, we have identified several aluminum hydrides ($\text{Al}_n\text{H}_m$), including aluminum rich hydrides ($n > m$) (jellium clusters), analogs of boron hydrides ($n \sim m$), and stoichiometric clusters ($m = 3n$), which form baby crystals. In addition, we have shown that negatively charged aluminum hydrides can expand beyond stoichiometric $\text{Al}_n\text{H}_{3n}^−$ by taking additional hydrogen atoms ($\text{Al}_n\text{H}_{3n+1}^−$) to form long chain-like structures and cyclic ring structures. It was identified that the ion intensities for $\text{Al}_n\text{H}_{3n+1}^−$ species were significantly stronger than the ion intensities of $\text{Al}_n\text{H}_{3n}^−$, suggesting enhanced stabilities of $\text{Al}_n\text{H}_{3n+1}^−$ species. Interestingly, a new species, $\text{Al}_4\text{H}_{14}^−$, which has one extra hydrogen than the expected $\text{Al}_4\text{H}_{13}^−$, was also observed in these experiments. More strikingly, in the mass spectrum, the ion intensity of $\text{Al}_4\text{H}_{14}^−$ was double that of $\text{Al}_4\text{H}_{13}^−$, thus indicating an unusually (thermodynamically) stable $\text{Al}_4\text{H}_{14}^−$. Despite these interesting features and the geometrical structure, a satisfactory explanation for the high intense mass peak of $\text{Al}_4\text{H}_{14}^−$ has remained largely unresolved. In this Communication, we will show that the lowest energy bound isomer of $\text{Al}_4\text{H}_{14}^−$ is where the $\text{H}_2^−$ is trapped between two $\text{Al}_2\text{H}_6$ units. This unprecedented arrangement ushers in a new bonding scheme.

We have employed an unbiased systematic structure search based on the genetic algorithm (GA) method as implemented in TURBOMOLE along with several other isomers based on our past knowledge of aluminum hydride clusters to identify the lowest and other higher energy isomers of $\text{Al}_4\text{H}_{14}^−$ species. Both the initial population and the subsequent generations were fully optimized with the BP/def2-SV(p) level of theory. The validity of this approach was tested and established in our earlier work on aluminum hydride...
clusters. The lowest energy and several other higher energy isomers from the GA were reoptimized using the Gaussian09 program suite. In this step, the B3LYP functional form, along with the augmented CC-pVTZ basis set, was employed. We have also carried out coupled-cluster single double triple (CCSD(T)) calculations with the CC-pVTZ basis set on B3LYP/aug-CC-PVTZ optimized geometries to determine the relative energies between various low energy isomers. In addition, we have carried out potential energy scan of the lowest energy structure at different H–H distances at both B3LYP and CCSD(T) levels using the CC-pVDZ basis set. Vibrational frequency calculations were done for all the reported isomers, and they are found to be minima on the potential energy surface.

Our calculations resulted in two classes of isomers: (1) structures in which Al$_4$H$_{14}^-$ exists as a complex, such as an Al$_2$H$_{12}^-$ moiety weakly interacting with H$_2$, and (2) bound structures, wherein every atom is chemically bonded to another atom in the cluster. Among these two classes of isomers, the complex(or an adduct)-like structures can be ruled out based on two reasons. First, it is worth reminding here that among the reported mass peaks of Al$_4$H$_m^-$ ($m = 12, 13, and 14$), the ion intensity corresponding to Al$_4$H$_{14}^-$ was the strongest, indicating an enhanced stability of Al$_4$H$_{14}^-$. Such a high intensity in the mass spectrum indicates that the experimentally observed Al$_4$H$_{14}^-$ is highly unlikely to have a complex-like structure, wherein an Al$_2$H$_{12}^-$ moiety weakly interacts with H$_2$. Next, the neutral Al$_4$H$_{12}$ is a highly stable cluster. It is well known that if a neutral cluster of a specific size is highly stable, then its anionic counterpart does not usually result in a high intense mass peak. So, it is again unlikely that the high intense peak of Al$_4$H$_{14}^-$ is a result of complex-like structures containing Al$_4$H$_{12}^-$. We, thus, conclude that only the bound structures (in which all the atoms were bonded to each other in one way or the other) are responsible for the experimentally observed Al$_4$H$_{14}^-$. So, rest of our discussion is focused only on the bound structures of Al$_4$H$_{14}^-$ obtained from our GA and density functional theory (DFT)-based calculations.

Figure 1 displays the most stable bound structures that we have identified in our calculations. They reveal several polymer-like chain structures in which the aluminum atoms have either fourfold or fivefold coordination. However, unlike in the case of Al$_n$H$_{3n+1}^+$ species, the cyclic (ring-like) bound structures were found to be very high in energy ($\Delta E \geq 0.4$ eV) for Al$_4$H$_{14}^-$. The lowest energy isomer, structure 1a, can be considered as two Al$_2$H$_6$ units connected by an H$_2$ unit. The next higher energy isomer, structure 1b, is reminiscent of our previously reported lowest energy chain-like structure of Al$_4$H$_{13}^-$, with the additional hydrogen atom bound to one of the terminal aluminum atoms, resulting in a fivefold coordination for that terminal metal atom. This structure can be considered as a combination of Al$_2$H$_7$ and Al$_2$H$_7^-$ units. It is to be noted here that structure 1b was reported as the lowest energy

FIG. 1. The lowest energy bound isomers of Al$_4$H$_{14}^-$ and their relative energies. Also shown are the selected bond lengths.
isomer in an earlier computational study. In that study, the structure and stability of \( \text{Al}_3\text{H}_4^{−} \) were studied at B3LYP/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels. To have a fair comparison between our results and the previously reported results, we have carried out CCSD(T) energy calculations on the B3LYP optimized structures. Our reported structure 1a was found to be lower in energy than the previously reported isomer (structure 1b) at the CCSD(T) level of calculation as well, thereby confirming the energy ordering obtained at the B3LYP level of calculations. Thus, the relative energies in Fig. 1 and in the discussion of the remainder of this work are calculated at the B3LYP/aug-cc-pVTZ level, unless otherwise stated. It is noteworthy here that even though the stabilization of \( \text{H}_2^− \) using molecular traps, such as between two LiCN molecules, has been reported in the past, as to our knowledge, this is the first time trapping of \( \text{H}_2^− \) is reported using aluminum hydrides. Structures 1a and 1b are followed by two more chain-like structures, 1c and 1d (see Fig. 1). Isomer 1c can also be seen as a combination of \( \text{Al}_2\text{H}_2^− \) and \( \text{Al}_4\text{H}_7^− \) units. However, unlike in the case of isomer 1b, in the case of isomer 1c, neither of the terminal aluminum atoms have a fivefold coordination, but an inner aluminum atom has a sixfold coordination. Finally, there is a cyclic (ring-like) structure, isomer 1e, in which two non-adjacent aluminum atoms are bridged by two hydrogen atoms. This structure can be seen as an extension of the double-ring polymeric structure of \( \text{Al}_4\text{H}_{13}^− \), reported in our previous study, with the additional hydrogen atom forming another bridge between the same set of non-adjacent aluminum atoms. Thus, in this isomer, the two di-hydrogen bridged aluminum atoms exhibit hexa-coordination. This ring-like isomer with two hexa-coordinated aluminum atoms (isomer 1e) can also be considered as a part of the ground state structure of \( \text{Al}_6\text{H}_{12} \) (baby crystal), reported previously.

The NPA charge analysis of structure 1a revealed that there exist three distinct units making up the lowest energy bound structure of \( \text{Al}_3\text{H}_4^{−} \): the left-side \( \text{Al}_2\text{H}_4 \) unit with a charge of \( −0.3 \text{e} \), the \( \text{H}_2 \) unit in the middle with a charge of \( −0.28 \text{e} \), and the \( \text{Al}_4\text{H}_4 \) unit on the right side with a charge of \( −0.42 \text{e} \). The stability of structure 1a against dissociation into smaller aluminum-hydride units was studied by calculating the fragmentation energies along two different pathways using the following equations:

\[
E_1 = [E(\text{Al}_4\text{H}_4^{−}) − E(\text{Al}_2\text{H}_2^{−}) − E(\text{Al}_2\text{H}_7^{−})],
\]

\[
E_2 = [E(\text{Al}_4\text{H}_4^{−}) − E(\text{Al}_2\text{H}_6^{−}) − E(\text{Al}_2\text{H}_6^{−}) − E(\text{Al}_2\text{H}_2^{−})].
\]

These fragmentation pathways are all found to be exothermic, with the calculated fragmentation energies of \( E_1 = −1.11 \text{ eV} \) and \( E_2 = −0.37 \text{ eV} \). Fragmentation into \( \text{Al}_3\text{H}_{12}^− \) and \( \text{H}_2 \) units and fragmentation into \( \text{Al}_4\text{H}_{13}^− \) and H are not considered here since there is no direct pathway for structure 1a to fragment into the lowest energy structures of corresponding fragmented units.

To further estimate the energy required to break the central H–H bond in structure 1a, we have scanned the potential energy surface at various H...H distances (the first fragmentation pathway) both at B3LYP and CCSD(T) levels, and the results are depicted in Fig. 2. At each point on the potential energy surface, the entire cluster was completely optimized with a fixed H–H distance at the B3LYP level. Furthermore, IR spectra for isomer 1a reveal an IR active H–H unscaled stretching frequency at 1879 cm\(^−1\), which strongly complements the existence of an elongated H–H bond. All these methods reflect significant energy barriers to break the H–H bond. This further confirms that the anion is kinetically stable toward dissociation along the selected pathway.

The nature of chemical bonding in isomer 1a is studied by analyzing how the total number of electrons is distributed and the nature of frontier molecular orbitals. The total number of valence electrons in \( \text{Al}_3\text{H}_4^{−} \) is 27, 3 from each Al atom [3 × 4 (Al)] and 1 from each H atom [1 × 12 (H)] plus the negative charge. How were these 27 electrons distributed? To understand that, we recall that there are two major types of bonds in aluminum hydrides, namely, 2c-2e Al–H terminal bonds and 3c-2e Al–H–Al bridge bonds. In the most stable structure, 1a, there are nine Al–H terminal bonds, which account for 9 × 2 (18) electrons and six electrons from three Al–Al bonds counting to 24 electrons (18 + 6). This leaves three electrons, which should be distributed, between Al–H–Al atoms. Although it is tempting to associate two electrons to the bonding
and one electron to the antibonding between Al–H–H–Al atoms, it is an oversimplification. To get a clear picture of how H$_2$ interacts with aluminum atoms, we have carried out the Fragment Molecular Orbital (FMO) analysis$^{15}$ on structure 1a. The FMO calculations are done at the PW91/TZVP level, by utilizing the isomer (structure 1a, here) optimized at B3LYP/cc-PVTZ, using the ADF suite of program.$^{16-18}$ Structure 1a can be viewed as H$_2$ is sandwiched between two Al$_2$H$_6$ units. The interaction diagram between H$_2^-$ and Al$_4$H$_{12}$ is given in Fig. 3. This diagram depicts the fragment contributions to each MO of Al$_4$H$_{14}^-$ (central panel) from H$_2^-$ (left panel) and Al$_4$H$_{12}$ (right panel). These contributions depend on the symmetry as well as the energy separation between the fragment MOs. As can be seen from the diagram, the major interactions between H$_2^-$ and Al$_4$H$_{12}$ are as follows. The sigma bonding orbital of H$_2^-$ strongly interacts with the low-lying Al$_4$H$_{12}$ orbitals, giving rise to lowest MOs (1A–3A) of Al$_4$H$_{14}^-$. Pictures of these MOs (Fig. 3) show that these interactions are mainly driven by symmetry considerations rather than a strong overlap between Al atoms with H$_2^-$.

However, there is a minor bonding interaction (6%) between H$_2$ (1A) and Al$_4$H$_{12}$ (13A), which contributes to the Al–H–H–Al bonding. The second major interaction is between H$_2$ sigma$^+$ (2A) with 14A of Al$_4$H$_{12}$ to form SOMO of Al$_4$H$_{14}^-$. This single interaction provides the bulk of the bonding between H$_2$ with the two Al$_2$H$_6$ units. This is as if the two Al$_2$H$_6$ units are trapping H$_2^-$; if this is true, then removing that one electron should make the units fall apart. This is indeed true. Optimization of the neutral Al$_4$H$_{14}$ dissociates the molecule into three units: two Al$_2$H$_6$ and H$_2$. There is not even a stationary point on the potential energy surface holding all these units together. Note that both Al$_2$H$_6$ and H$_2$ are very stable molecules and all these stable units are held together by one single electron. This unusual bonding has not been observed in any other hydrides.

In this Communication, we report a unique structure of Al$_4$H$_{14}^-$, wherein an H$_2^-$ unit is trapped between two Al$_2$H$_6$ units, contributing toward the high intense peak of Al$_4$H$_{14}^-$ in the mass spectrum of aluminum hydrides. To our knowledge, this is the first time a molecular trap using aluminum hydride clusters to stabilize H$_2^-$ is reported, thus further extending our knowledge of aluminum hydride clusters. The electron counting and fragment molecular orbital analysis have revealed a unique bonding pattern in this bound structure (isomer 1a) of Al$_4$H$_{14}^-$, in which a single electron holds the three units, H$_2^-$ and two Al$_2$H$_6$ units, together.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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