

AlH₃ and Al₂H₆: Magic Clusters with Unmagical Properties

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Enhanced stability, low electron affinity, and high ionization potential are the hallmarks of a “magic” cluster. With an electron affinity of 0.28 eV, ionization potential of 11.43 eV, and a large binding energy, AlH₃ satisfies these criteria. However, unlike other magic clusters that interact only weakly with each other, two AlH₃ clusters bind to each other with an energy of 1.54 eV. The resulting Al₂H₆, while also a magic cluster in its own right, possesses the most unusual property that the difference between its adiabatic and vertical detachment energy is about 2 eV—the largest of any known cluster. These results, based on density functional theory, are verified experimentally through photodetachment spectroscopy.

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One of the most exciting discoveries in atomic clusters in the past two decades is that their mass spectra exhibit pronounced peaks suggesting the existence of very stable clusters with a specific size. In alkali metals, the peaks correspond to clusters having 2, 8, 20, . . . atoms [1], while in carbon it is the 60-atom cluster [2] that is among the most stable ones. These clusters, commonly referred to as “magic” clusters, are characterized by low electron affinity and high ionization potential (i.e., large HOMO-LUMO gap), and enhanced stability. Their unwillingness to either accept or donate an electron make them relatively inert, and two magic clusters are expected to interact weakly [3] via a van der Waals-like mechanism.

In this Letter we show that AlH₃ and Al₂H₆ not only deviate from this rule but also exhibit other unusual properties. The results are based on *ab initio* calculations and photodetachment spectroscopy experiments. Al₂H₆ is formed by the coalescence of two AlH₃ clusters in spite of the fact that the latter has all the attributes of a magic cluster. AlH₃ (alane) is the most stable cluster in the AlH_n series. It has low electron affinity (0.28 eV) and very high ionization potential (11.43 eV). In spite of a large barrier separating the two AlH₃ species, the binding energy of Al₂H₆ against dissociation into two AlH₃ units is 1.54 eV. This binding occurs as two hydrogen atoms form bridging sites for the two Al atoms and render Al₂H₆ a structure similar to that of di-borane, B₂H₆. This is particularly interesting as the properties of Al and B clusters are very different. Furthermore, Al₂H₆, with small electron affinity (0.44 eV) and high ionization potential (10.14 eV), also possesses the characteristics of a magic cluster. The most unusual property of Al₂H₆, however, is that its vertical detachment energy (which measures the difference in energy between Al₂H₆⁻ in its ground state and neutral Al₂H₆ having the anion geometry) is almost 2 eV higher than the

adiabatic electron affinity (the difference in energy between the ground states of the neutral and the anionic clusters). Such a large difference between adiabatic and vertical electron affinities is unusual among clusters and signals large changes in geometry and electronic structure between the neutral and anionic species. While we are unable to measure the adiabatic electron affinity of Al₂H₆ due to very small photoelectron intensity, the measured vertical detachment energy of 2.4 eV agrees completely with the predicted value of 2.4 eV. In addition, the broad photodetachment spectra confirm the predicted geometry changes between the ground states of the anion and the neutral. In the following we give details of our theoretical calculations and experimental methods.

The calculations of the equilibrium structure of neutral and anionic AlH_n ($n \leq 4$) and Al₂H₆ clusters and corresponding total energies were carried out using density functional theory (DFT) in which the cluster wave function was expressed as a linear combination of atomic orbitals. We have used linear combination of Gaussians (6-311G^{**}) to represent the orbitals of the constituent atoms. The exchange correlation potential was evaluated using the generalized gradient approximation due to Becke, Perdew, and Wang [4] (BPW91 in GAUSSIAN 94 code). The geometries of the clusters were globally optimized without symmetry constraint using the GAUSSIAN 94 code [5].

We begin with the calculations of AlH_n ($n \leq 4$) clusters. The geometries corresponding to the ground state spin multiplicities are given in Fig. 1. Also listed in parentheses in this figure are the Mulliken charges at Al and H sites. The bond length of Al-H in Fig. 1(a) is 1.68 Å and the net charge on H is slightly negative. This is consistent with the nature of H interacting with metal atoms where hydrogen tends to be “anionic.” However, the amount of charge transfer is too small to classify the Al-H bond as “ionic.”

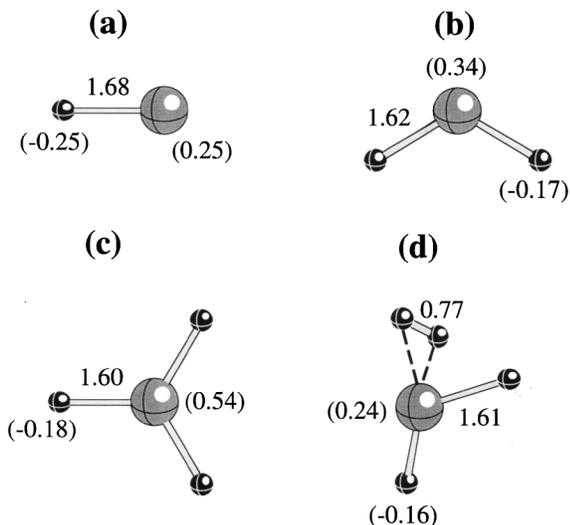


FIG. 1. Geometries of AlH_n ($n \leq 4$) clusters. The bond lengths are given in Å and the Mulliken populations are given in parentheses.

The bonding is rather of covalent character and remains such as more hydrogen atoms decorate the Al atom. The structure of AlH_2 has C_{2v} symmetry with the Al-H bond only marginally reduced from that in the AlH dimer. There is no H-H bond; i.e., hydrogen atoms bind dissociatively and the H-Al-H bond angle is 118.1° . The charge on H in AlH_2 is less negative than that in AlH and remains unchanged as we proceed to AlH_3 . The structure of AlH_3 has C_{3v} symmetry with an Al-H bond length that has saturated at 1.60 Å. The structure of AlH_4 is quite different. Here two hydrogen atoms are bound dissociatively while the other two remain nearly molecular. Note that the bond length of molecular H_2 is 0.74 Å. The consequence of molecular physisorption on the energetics of AlH_4 will be discussed in the following.

The energy gain in adding a hydrogen atom to AlH_{n-1} cluster, namely,

$$\Delta E_n(\text{H}) = -[E(\text{AlH}_n) - E(\text{AlH}_{n-1}) - E(\text{H})], \quad (1)$$

is plotted in Fig. 2(a). Note that AlH gains 3.08 eV as Al attaches to a H atom. However, the energy gain in going from AlH to AlH_2 drops, but is considerably enhanced in the transition from AlH_2 to AlH_3 . This is clearly due to the trivalent character of Al. Although Al behaves as a monovalent atom in small Al_n clusters [6,7] ($n < 7$), it behaves as a trivalent atom while interacting with gas atoms such as H, N, and O. The relative stability of AlH_4 is considerably less than AlH_n ($n \leq 3$) clusters. This is due to the fact that two of the hydrogen atoms in AlH_4 remain molecular and bind only weakly with the remaining AlH_2 .

The vertical ionization potential and electron affinity of AlH_n ($n \leq 4$) are given in Figs. 2(b) and 2(c), respectively. Note that the ionization potential of AlH_3 is the highest in the AlH_n series while its electron affinity is

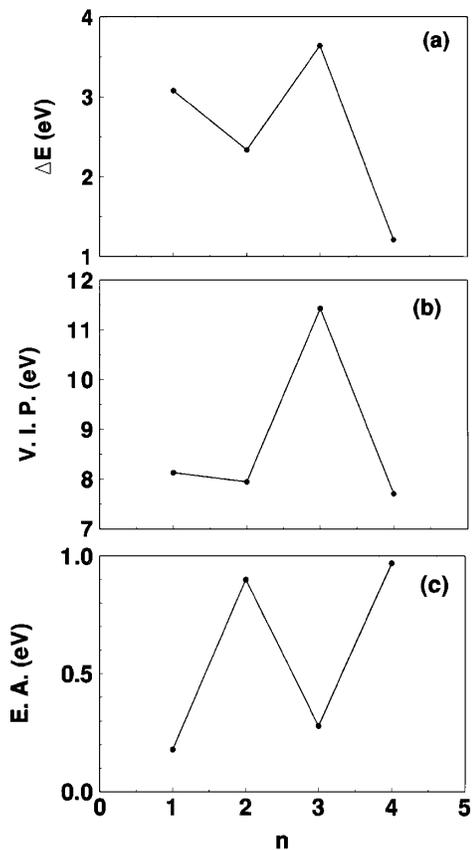


FIG. 2. (a) Energy gain in adding a hydrogen atom to AlH_{n-1} cluster, (b) vertical ionization potential of AlH_n cluster, and (c) adiabatic electron affinity of AlH_n cluster as a function of n .

lower than that of AlH_2 or AlH_4 . These properties coupled with the unusual stability of AlH_3 in Fig. 2(a) make AlH_3 a magic cluster. One would normally expect two AlH_3 clusters to interact weakly, and Al_2H_6 , if formed at all, should be a weakly bound cluster. This proved not to be the case.

Optimization of the geometries of Al_2H_6 to arrive at the ground state structure proved to be a challenging task. The potential energy landscape was marked by many local minima. The optimization procedure was performed starting with several initial configurations. These included (i) two AlH_3 clusters on-top configuration separated by a distance d , (ii) one AlH_3 rotated with respect to the other by 60° , but placed a distance d above, and (iii) two AlH_3 clusters lying in the same plane. The ground state structure of Al_2H_6 is given in Fig. 3(a). This structure is formed as two hydrogen atoms (one in each AlH_3) form bridge sites with respect to the two Al atoms. Since an Al-H bond is quite strong, namely, 3.08 eV [see Fig. 2(a)], this bridging stabilizes the structure of Al_2H_6 . Furthermore, the Al-Al bond distance in Al_2H_6 is 2.62 Å. This has to be compared with the Al_2 dimer bond length of 2.86 Å. Thus, the stability of the neutral Al_2H_6 is derived not only from the hydrogen bridging, but also from the Al-Al bond. Consequently, Al_2H_6 is 1.54 eV more stable than the dissociated AlH_3 units in spite of the fact that AlH_3 is a magic cluster.

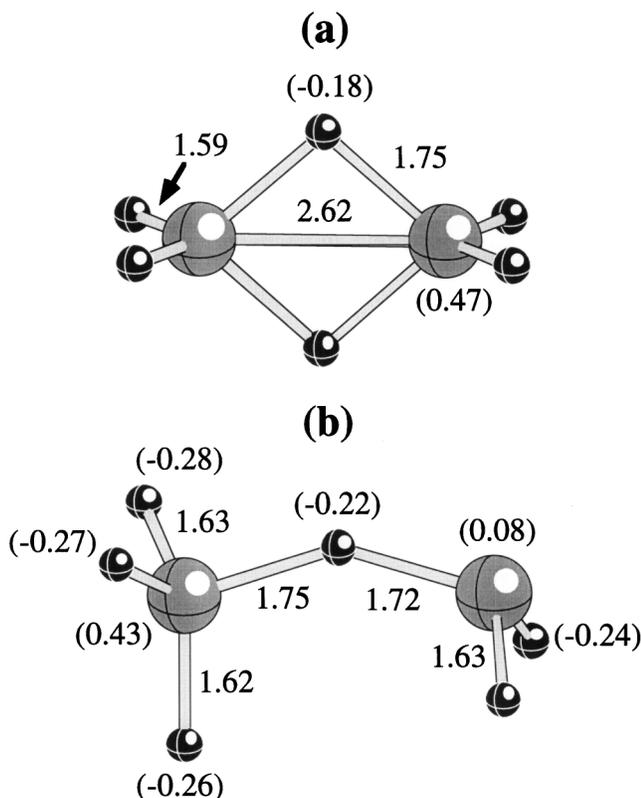


FIG. 3. Geometry of (a) Al_2H_6 and (b) Al_2H_6^- . The bond lengths are given in Å and the Mulliken populations are given in parentheses.

The bridging H atoms are at a distance of 1.75 Å from the Al atoms while the terminal ones maintain the same distance (1.59 Å) as in AlH_n ($n \geq 2$) clusters. The Mulliken charge on H atoms has the same characteristics as those bound dissociatively to Al in AlH_n ($n \leq 4$) clusters.

A number of theoretical investigations [8–10] of the equilibrium geometry, harmonic vibrational frequencies, and binding energy of AlH_3 and Al_2H_6 , as well as those where Al is replaced by isovalent B and Ga, have been performed using different levels of theory and basis functions. These include post-Hartree-Fock methods with correlation treated either perturbatively or through single and double excitation coupled cluster (CCSD) method as well as density functional studies with exchange correlation accounted for through various hybrid functionals [10]. While we refer the reader to these papers for details, we want to point out that our results agree well with the highest level of theory (CCSD) employed by Shen and Schaefer [9] who used double-zeta plus polarization basis sets. For example, our computed dimerization energy, 1.54 eV of Al_2H_6 , agrees well with the 1.55 eV calculated by Shen and Schaefer. Similarly, the Al-Al, Al-H (bridging), and Al-H (terminal) bonds of 2.624, 1.754, and 1.588 Å given in Fig. 3(a) agree well with the corresponding results of 2.5892, 1.7168, and 1.5621 Å calculated by Shen and Schaefer. No experimen-

tal results are available for comparison. To further test the accuracy of the current level of theory, we have optimized the structures of B_2H_6 . The B-B, B-H (bridge), and B-H (terminal) bonds in B_2H_6 obtained here are 1.765, 1.324, and 1.195 Å. The corresponding results obtained by Shen and Schaefer [9] are 1.785, 1.324, and 1.189 Å. Note that these compare well with the experimental values [11] of 1.743, 1.314, and 1.189 Å. No authors, to our knowledge, have calculated the ionization potentials or electron affinities to determine if AlH_3 and Al_2H_6 possess the characteristics of magic clusters. Our calculated vertical ionization potential (i.e., energy needed to remove an electron from the neutral cluster without changing its geometry) of Al_2H_6 and B_2H_6 are, respectively, 10.14 and 11.33 eV.

The structure of Al_2H_6 undergoes a drastic modification as an electron is attached [see Fig. 3(b)]. The bridging seen in neutral Al_2H_6 partially disappears and only one hydrogen atom forms a bridge between two Al atoms and maintains a distance of 1.75 Å as in neutral Al_2H_6 . The Al-Al distance in Al_2H_6 is 2.62 Å, indicating that the bond is broken [see Fig. 3(a)]. The extra electron is shared almost equally among the six hydrogen atoms and is thus delocalized. The adiabatic electron affinity of Al_2H_6 is small, namely, 0.44 eV. However, the vertical electron detachment energy (i.e., the energy difference between the ground state of the anion and the neutral having the ground state geometry of the anion) of Al_2H_6 is 2.42 eV. This large difference between the adiabatic electron affinity and vertical detachment energy is rather unusual, but results from very different ground state geometries of the neutral and the anion [Figs. 3(a) and 3(b)] as well as accompanying changes in the electronic structure. It is important to emphasize that the adiabatic electron affinity of AlH_3 differs from its vertical detachment energy by only 0.01 eV. Thus, while the small electron affinity (0.44 eV) and large ionization potential (10.14 eV) of Al_2H_6 permits its classification as a “magic cluster,” its large geometry changes between the neutral and anionic ground states certainly make it an unusual magic cluster.

We also performed a simulation of the Al_2H_6 dissociation into two AlH_3 units. It was done with a density functional based tight binding method [12,13]. This method gives the geometries of the Al_nH_m clusters studied here in good agreement with those from full DFT calculations. Also the energetics is described quite well; e.g., the dissociation energy of Al_2H_6 into two AlH_3 clusters is 1.28 eV, compared with the 1.54 eV in the full DFT calculation. The simulation was performed within a constant energy molecular dynamics (MD), starting with about 5 eV initial kinetic energy. The activation energy from this MD simulation for the Al_2H_6 dissociation is 4.4 eV. This will certainly be an overestimation for the thermal dissociation of Al_2H_6 , but it gives an estimate for this barrier.

We now describe our experimental investigation. The electron affinity has been determined by photoelectron

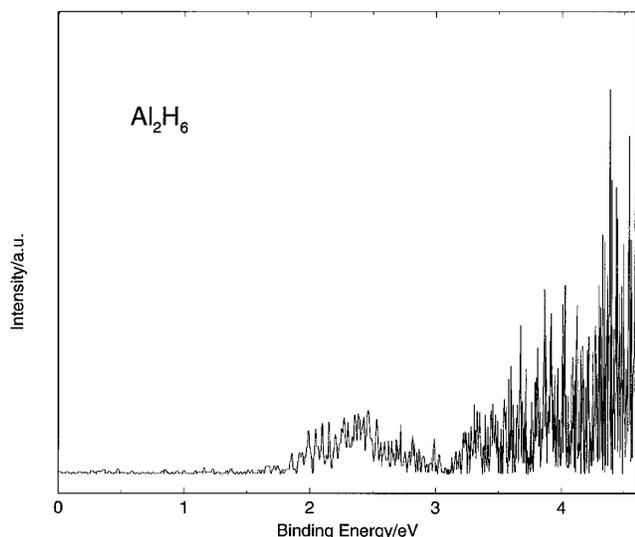


FIG. 4. Photodetachment spectrum for Al_2H_6^- .

spectroscopy of cluster anions [14]. The Al clusters are generated using a pulsed arc cluster ion source [15] and cooled in a 15 cm long extender with a diameter of 3 mm. For the generation of Al_nH_m clusters, hydrogen is introduced into the extender and some of the H_2 molecules are dissociated in the electric arc. As a result, various different Al_nH_m clusters are formed [16,17]. The negatively charged clusters produced directly by the source are mass separated in a time-of-flight mass spectrometer. A selected bunch of anions of defined size is irradiated by a UV laser pulse (photon energy 4.66 eV, intensity about 10 mJ/cm^2), and the kinetic energy of the detached electrons is determined with a “magnetic bottle”-type time-of-flight electron spectrometer. The energy resolution is about 20 meV. The resulting photodetachment spectrum of Al_2H_6^- is plotted in Fig. 4. Note that a broad peak at a kinetic energy of $2.26 \pm 0.15 \text{ eV}$ corresponding to a vertical detachment energy of $2.4 \pm 0.15 \text{ eV}$ appears. This agrees very well with the theoretical value of 2.42 eV discussed earlier. The large width of this transition suggests that the ground state structures of the neutral and anionic Al_2H_6 are different as is evidenced from the theoretical results in Figs. 3(a) and 3(b).

In conclusion, our combined *ab initio* calculations and photodetachment experiments reveal many unusual properties of Al_2H_6 . (1) Al_2H_6 cluster, with low electron affinity and high ionization potential, is formed by the coalescence of two AlH_3 clusters in spite of the fact that AlH_3 itself is a magic cluster and a large barrier separates the two. (2) The geometry of Al_2H_6 is stabilized by bridging hydrogen

atoms and bears strong resemblance to that of di-borane (B_2H_6). (3) Attachment of an electron leads to the rupture of one of these bridging sites, and the geometry of the anion is significantly modified from that of the neutral clusters. (4) This leads to a large difference (2 eV) between the vertical and the adiabatic photodetachment energy of any known cluster.

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