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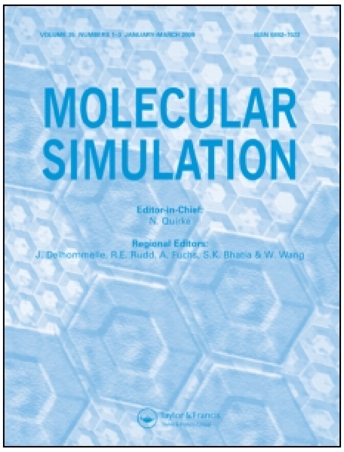

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DFT study of hydrogen adsorption on Al_{13} clusters

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DFT study of hydrogen adsorption on Al_{13} clusters

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In this work, adsorption of hydrogen on Al_{13} clusters has been investigated theoretically using the density functional theory (DFT) approach. We have performed geometry optimization of atomic and molecular hydrogen in the proximity of Al_{13} and calculated the binding energy and electronic properties of the stable $Al_{13} + H_n$ assemblies. We have also calculated the energy barrier for the hydrogen atom transition between different adsorption sites on Al_{13} cluster as well as the activation energy for the dissociation and adsorption of molecular hydrogen. We found that the hydrogen atom adsorbs on the surface of Al_{13} cluster, without an energy barrier onto atop, bridge and hollow sites. A small barrier for H atom transition from one adsorption site to another together with the minor energy difference between the most stable isomers points towards high mobility of the hydrogen atom on the surface. The calculated dissociation–adsorption barrier for the hydrogen molecule of ~14 kcal/mol and a desorption barrier of ~19 kcal/mol together with a high theoretical storage capacity of Al_{13} clusters suggest further investigations of Al nanostructures for application in hydrogen storage.

Keywords: Hydrogen adsorption; Aluminum clusters; Hydrogen storage; Density functional theory

1. Introduction

Metal clusters and nano-structures have attracted attention of many researchers [1–4] since metal clusters with closed electronic shells are extremely stable and can be used as building blocks for new materials. Nano-assemblies of light metal clusters can potentially have applications in a hydrogen energy production technology where a safe, compact and inexpensive system able to store a large amount of hydrogen is of crucial importance.

Metal clusters are usually prepared by molecular beam techniques or matrix isolation and their property measurements are limited due to high reactivity. Stabilization of clusters can be achieved using techniques such as slight oxidation with bulky protecting ligands, but this also raises some problems. Jarrold *et al.* [5] showed that structural transitions can be measured based on the ionized clusters' mobility through a gas under the influence of a weak electric field. However, due to the inherent difficulties associated with experimental characterization of metal clusters, a number of theoretical approaches to describe and explain their properties have been developed.

The so-called jellium model [6–8] was initially found appropriate to describe metal clusters. The basic idea behind this model is that the valence electrons move in a uniformly positively charged background where the electron energy levels are quantized by angular momentum, analogous to the nuclear shell model. According to the jellium model, clusters are particularly stable when their electronic shell is closed. This model predicts that clusters with closed-shell electronic configurations are spherical, whereas those with open-shell electron levels should permit spheroid and ellipsoid distortions and, hence, closed-shell clusters should have higher mobility than those with open-shell electronic structure. In the case of Aluminum clusters, Al_7 and Al_{13} have been identified as particularly stable [9] because their electronic configuration is approaching the closed-shell configurations characterized by the magic numbers within the jellium model [8]. It has been shown [10] that adding a hydrogen atom to the Al_{13} cluster can further stabilize the structure, because the additional electron completes the electronic shell. Jarrold *et al.* [5] also found that substantial geometry change appears to be associated with at least one of the shell closings. They showed that maxima in the measured mobility correspond to 20 and 40 valence electrons for the Al_7^+ and Al_{13}^-/Al_{14}^{++}, respectively. However, they failed to reproduce the "magic" numbers for larger clusters.

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More recently, computer simulations based on density functional theory (DFT) have become a powerful tool for investigating properties of clusters that are difficult to determine from experiment. An extensive theoretical study of Al_n clusters up to $n = 150$ was reported by Ahlrichs and Elliott [9] who argued that for Al_n, the spherical model is valid only for cases with up to 40 or fewer electrons. For larger clusters, the spacing between electronic shells vanishes and geometric effects are dominated by orbital energies near the Fermi level. So, only 20 and 40 appear to be "magic" electron numbers for Al_n cluster stability and for larger clusters the spherical model cannot be applied. The above reasoning is in agreement with the conclusions of later papers of Jarrold based on experimental results summarized in [1–4] and [12–14].

Interestingly, high stability of Al_{13}^- can serve as a core framework for creating stable $Al_{13}I^-$ species. [15]. One of the significant finding of this work is that Al_{13}^- keeps the electron when interacting with the iodine atom. This charge localization suggests the superhalogen analogy and a possibility of synthesizing even larger "polyhalides" featuring Al_{13}^- as the central "halide". Fowler and Ugalde [16] considered Al_{13}^- cluster as a core for bigger Al_{77} clusters and found a remarkable geometric agreement with the experimental results of Ecker [17] where Al_{13}^- has also been considered as a core of a bigger cluster.

Previous studies indicate that Al_7 and Al_{13} deserve special attention as they both show enhanced binding energy. As discussed earlier, based on the jellium model, Al_{13} is just one electron short of a complete outer electron shell. The chemical inertness of Al_{13}^- was demonstrated both experimentally [18,19] and theoretically [11,20]. It can be suggested that passivation through Hydrogen or Alkali metals donating one electron to Al_{13} to complete the electron shell can lead to stable structures. Moreover, the idea of an ionic crystal with the formula $K^+Al_{13}^-$, or $Al_{13}H$ was put forward recently [11,21–23].

Burkart *et al.* [20] demonstrated that other stable structures such as Al_nH_m and $Al_nH_m^-$ with $n = 12–14$ and $m = 0–2$ can serve as building blocks for solids. They studied structures with various n and m numbers, both experimentally and theoretically. For the experimental investigation, they used photoelectron spectroscopy, while for the calculations the DFT was used. In contrast to other work, it was found that the stability of $Al_{13}H^-$ clusters is the same as that of neutral clusters. The icosahedral symmetry of the Al_{13}^- anion, which is highly stable and slightly perturbed by hydrogen adsorption, was confirmed. It was also confirmed that the open-shell species are unstable. Again, the main conclusion of this work was that the $Al_{13}H$ cluster is a promising candidate as a building block for nano-materials.

Alonso *et al.* [11] made an attempt to construct the dimer $(Al_{13}H)_2$ using computer simulations to provide an insight into the assembling of such clusters. In this work, a favorable orientation of the clusters for self-assembling was found. Their stable dimer had a tubular-like structure that suggested that nanowires could be synthesized. It was also suggested that crystalline $Al_{13}H$ should have a simple cubic lattice. The crystal with lattice constant of 24.2 au appeared to be the most stable and had metallic character. Cluster crystals with FCC lattices did not retain their individual character and coalesced. One of the points that therefore need to be addressed is why FCC self-arrangement is not stable [11].

To further investigate a possibility of using Al_{13} as a building block in hydrogen storage devices in this paper we address the basic issues of the structural stability of Al_{13} clusters, their adsorption capacity and reactivity for atomic and molecular hydrogen using the DFT approach.

2. Computational details

All calculations reported in this paper were performed with the DFT program DMol^3 that uses the numerical basis sets [24,25]. In the present study, double numerical polarized (DNP) basis set was employed that includes all occupied atomic orbitals plus a second set of valence atomic orbitals plus polarized *d*-valence orbitals. For exchange, the Becke (B88) [26] in conjunction with correlation Lee-Yang-Parr [27] nonlocal functional (BLYP) was used. Spin unrestricted approach was applied with all electron being considered explicitly.

Our choice of BLYP functional was based on the preliminary calculations for the AlH molecule. This molecule was chosen to establish the most appropriate method as we consider the correct representation of the Al–H interaction crucial in modeling $Al_{13}H_n$ clusters. We calculated the binding energy, the equilibrium distance between Al and H atoms and the HOMO–LUMO energy gap. The BLYP calculated binding energy was 2.94 eV in good agreement with the experimental value of 3.06 eV [28]. Our calculated Al–H distance of 1.68 Å compares well with 1.67 Å reported by Kawamura *et al.* [29]. HOMO–LUMO energy gap of 2.35 eV calculated in the same study [29] also agrees with our calculated value of 2.37 eV. Thus, we considered the BLYP functional to provide sufficient accuracy for our further studies of Al–H assemblies.

In all calculations, atom centered grids were used for the numerical integration with "Fine" option in DMol^3 that includes about 2000 grid points for each atom. The real space cut-off of 5.5 Å was imposed for numerical integration [30].

Self-consistent-field (SCF) convergence criterion was set to the root-mean-square change in the electronic density to be less than 1×10^{-6} Ha. Geometries were optimized using an efficient algorithm which takes advantage of delocalized internal coordinates [31]. Although the time per iteration spent during the optimization in Cartesian and delocalized coordinates is almost the same, the number of iterations using delocalized orbitals is much less. The convergence criteria applied for geometry optimization were 1×10^{-5} Ha for energy, 0.002 Ha/Å for force and 0.005 Å for displacement [30]. For all the optimized structures, we performed frequency analysis to check whether the obtained structure was a true minimum. For transition state (TS) search we applied LST/QST Halgren, Libscomb method [32]. TS optimization procedure was also followed by the frequency analysis where we checked for one negative frequency to confirm the correctly located TS.

In all calculations, the icosahedral structure of Al_{13} cluster was used since it was reported [9] as the most stable.

3. Results and discussion

3.1 Al_{13} cluster

Aluminum is a typical metal with deficient metallic bonding which should lead to the structure with large average number of first nearest neighbors and high symmetry. Indeed, the highest possible Al_{13} cluster symmetry is icosahedral (I_h) that was shown by Ahlrichs *et al.* [9] to have the lowest energy (figure 1).

Icosahedral Al_{13} has an almost spherical compact structure and with its 39 valence electrons is lacking just one electron to complete its outer electronic shell [33]. A closed shell structure should have a large HOMO–LUMO gap, the electron affinity of the Al_{13} has to be low and the Al_{13}^- anion should, in principle, be more stable than the neutral cluster. In agreement with this, our calculations showed that the anion cluster is 2.58 eV lower in energy than the neutral one, as has also been shown by Ahlrichs *et al.* [9]. Although they reported even a larger difference of 3.5 eV (which can be attributed to different exchange correlation functionals and all electron treatment employed here) both calculations confirmed the jellium model idea that the closure of the electronic shall results in increased cluster stability.

As part of our validation studies, we have also calculated the HOMO–LUMO gaps for Al_{13} anion and $Al_{13}H$ cluster and compared our results with previously reported experimental and theoretical studies summarized in table 1, including data published by Burkart *et al.* [20], Khanna *et al.* [34] and Alonso *et al.* [11]. It can be seen that our results show good agreement with the available experimental and theoretical evidence.

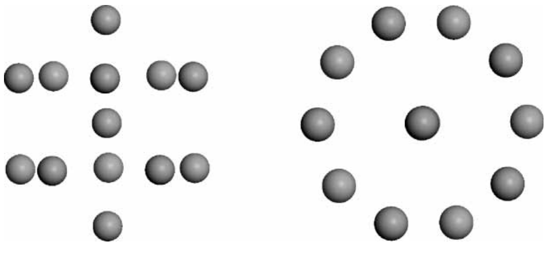

Figure 1. Al_{13} cluster with ideal I_h symmetry, two views are shown.

Table 1. Comparison of the HOMO–LUMO gap for Al_{13} clusters obtained in this work with published experimental and theoretical results.

	HOMO—LUMO gap (eV)		
	Theory	*This work*	*Experiment*
Al_{13}^-	1.9 [20]	1.73	1.8 [34]
$Al_{13}H$	1.77 [11]	1.53	1.4 [20]

3.2 Adsorption of atomic hydrogen on Al_{13}

We have found that the hydrogen atom adsorbs on the surface of Al_{13} cluster without an energy barrier. Three stable positions of atomic hydrogen on the cluster surface obtained by the DFT calculations are shown in figure 2. Hydrogen can be adsorbed in (a) “atop” position, i.e. directly on top of an Al atom on the cluster surface, (b) “bridge” position, i.e. between two Al atoms on the cluster surface and (c) “hollow” position, i.e. between three Al atoms on the cluster surface.

The lowest energy adsorption site on Al_{13} cluster is the atop position where hydrogen atom is attached to one Al atom (figure 2a). It can be seen that the most stable isomer is also the most geometrically distorted. The energy difference between the lowest energy isomers (a) and (b) is only 0.42 kcal/mol. The isomer (c) has the 4.66 kcal/mol higher energy than the most stable isomer (a). This energy difference is rather large and makes the population of isomer (c) at room temperature negligibly small, as follows from the Boltzmann probability distribution. The small energy difference between the most stable isomers (a) and (b) signifies that both isomers will be present at room temperature, although the isomer (a) would have twice as high population compared to isomer (b).

It can be seen from figure 2 that adsorption of hydrogen atom onto the atop site induces distortion of the Al_{13} cluster while only minor geometry changes can be seen in the vicinity of the hydrogen atom for the bridge and hollow sites adsorption. As expected, Al–H distance is shortest for the atop site (1.59 Å). For the bridge site, the Al–H distances are about 1.8 Å for the two nearest Al atoms.

We also obtained TS structure between the isomers (a) and (b) of $Al_{13}H$ cluster and found the transition barrier between the most stable adsorption positions to be ~5 kcal/mol. This relatively small barrier together with the minor energy difference between the most stable isomers points towards high mobility of the hydrogen atom on the cluster surface.

The binding energy of hydrogen to the Al_{13} cluster was calculated according to the expression

$$E_B = \frac{E_{Al_{13}H_n} - E_{Al_{13}} - nE_H}{n}$$

where $E_{Al_{13}}H_n$ is the energy of the cluster Al_{13} with n hydrogen atoms adsorbed, $E_{Al_{13}}$ is the energy of the cluster without hydrogen atoms, E_H is the energy of the hydrogen atom.

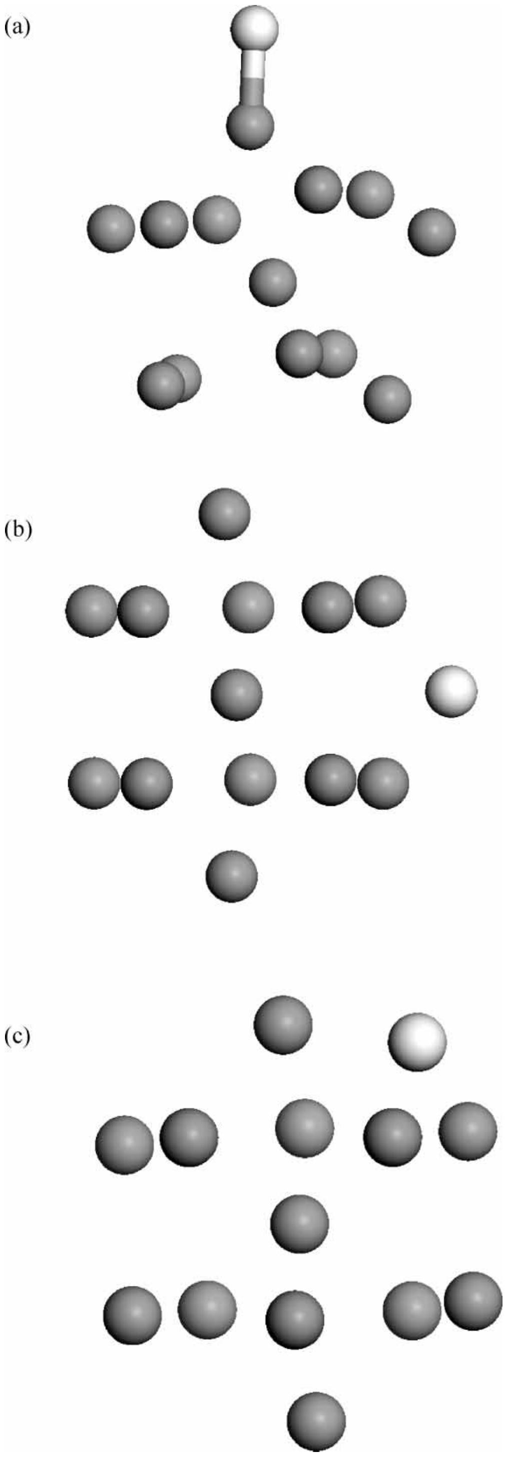

Figure 2. Predicted stable H atom adsorption sites on Al_{13} cluster: (a) atop; (b) bridge; (c) hollow. Here and in all following figures dark circles represent Al atoms; light circles—H atoms.

For the considered $Al_{13}H$ isomers ($n = 1$), the binding energy of hydrogen to the Al_{13} surface was found to be between ~2.4 and 2.5 eV.

3.3 Adsorption of molecular hydrogen on Al_{13} cluster

The H_2 molecule was found to be repelled from the Al_{13} when initially positioned in proximity of the cluster, indicating the physisorption is not likely to occur and the dissociative chemisorption can only be achieved with an additional supply of energy. Although, the dissociation energy of the hydrogen molecule (4.5 eV) is most likely to be reduced due to the proximity of the Al_{13} cluster, there should still be a potential barrier for H_2 dissociative adsorption.

We have performed a series of calculations to gain a further insight into the dissociative chemisorption of H_2 on Al_{13} cluster surface that we present here. Specifically, we have calculated the activation energy for the dissociation and adsorption of molecular hydrogen by calculating the energy of the geometry optimized ($Al_{13} + H_2$) assembly as a function of the separation distance between the H_2 molecule and the Al_{13} cluster used as a reaction coordinate. The resultant energy plot is shown in figure 3 and the reaction coordinate is indicated in figure 4. It can be seen from figure 3 that the potential barrier for dissociative chemisorption of the H_2 molecule is located at ~1.85 Å with the activation energy of ~14.2 kcal/mol while the desorption energy is estimated to be ~18.6 kcal/mol. These values demonstrate that the adsorption–desorption of molecular hydrogen on Al_{13} clusters can be achieved with a moderate supply of additional energy. A small shoulder at ~2.5 Å is indicative of a physisorption barrier of ~3.60 kcal/mol which explains why the H_2 molecule is repelled from the cluster surface during a simple geometry optimization experiment.

The TS for H_2 dissociation on Al_{13} surface located at 1.85 Å is shown in figure 4(b) together with the initial structure (figure 4(a)) and the optimized adsorbed structure (figure 4(c)). A number of geometric parameters describing the systems are summarized in table 2 in order to further illustrate the dissociative chemisorption process as the mechanism for adsorption of H_2 on the Al_{13} cluster. The cluster distortion caused by the chemisorption is also evident from the increased Al1–Al2 distance.

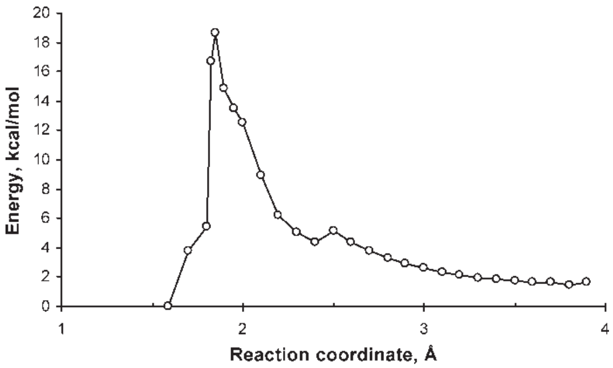

Figure 3. Dissociation–adsorption energy of H_2 on the Al_{13} surface as a function of the reaction coordinate. Energy normalised by the minimum energy value of the optimized adsorbed system with Al1–H1 distance equal to 1.59 Å (shown in figure 4(c)).

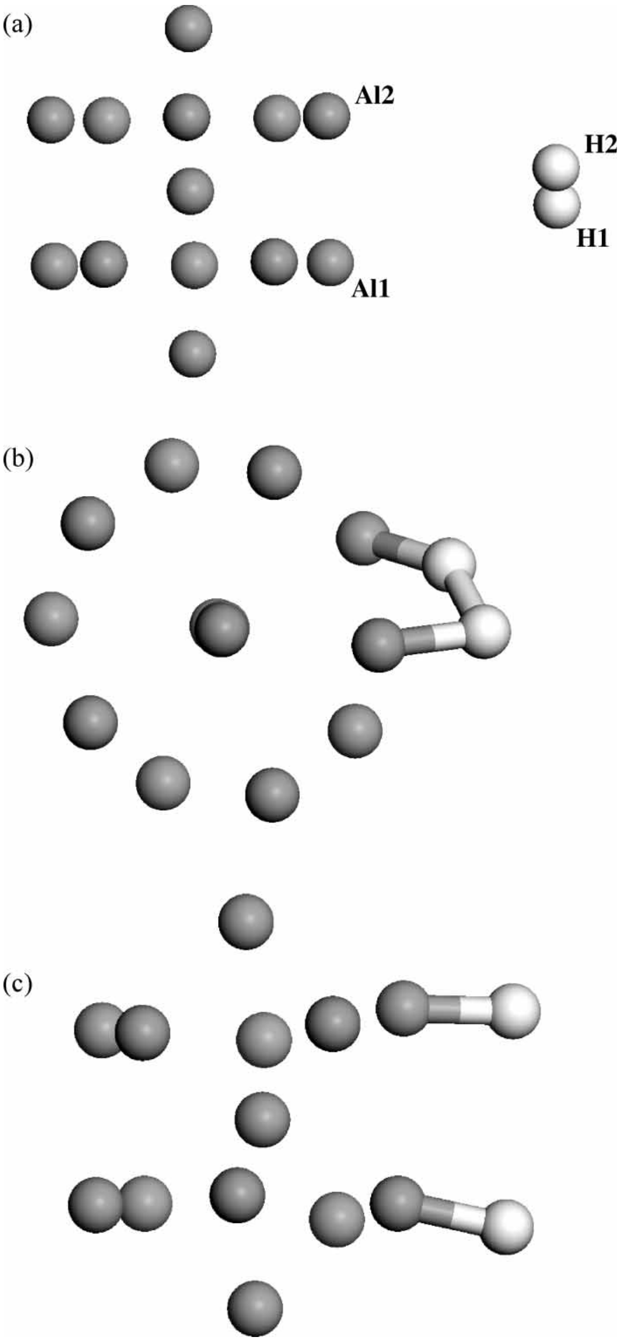

Figure 4. $Al_{13} + H_2$ dissociative adsorption system: (a) initial state; (b) transition state; (c) adsorbed state. The distance between Al1 and H1 atoms was employed as a reaction coordinate.

3.4 *Adsorption of two or more hydrogen atoms on Al_{13} cluster*

Three identified stable isomers of $Al_{13}H$ cluster can result in different combinations of adsorption positions when two or more hydrogen atoms adsorb onto the Al_{13} cluster surface. For two simultaneously adsorbed hydrogen atoms, the lowest energy isomers are shown in figure 5. We found that the most stable isomer has one hydrogen atom in the atop position with the other being placed between two adjacent Al atoms with one Al atom shared (figure 5(a)). This adsorption configuration represents a combination of $Al_{13}H$ isomers (a) and (b). The second lowest energy isomer with two hydrogen atoms attached in the atop geometry to two adjacent Al atoms has about 1.5 kcal/mol higher energy than the first one (figure 5(b)) which will result in the predominant population at room temperature of the isomer (a) (Boltzmann population ratio of the two isomers is ~92:8). This finding suggests that the Al_{13} cluster can potentially adsorb a large number of hydrogen atoms on its surface via the identified adsorption sites.

Table 2. Characteristic interatomic distances (Å) of $Al_{13} + H_2$ adsorption process (atoms are labeled as shown in figure 4)

Distance	*Initial state*	*TS*	*Adsorbed state*
Al1–H1	4.00	1.85	1.59
Al2–H2	4.00	1.81	1.59
H1–H2	0.74	1.59	3.59
Al1–Al2	2.89	3.07	3.38

For any practical application of the Al clusters in hydrogen storage devices there is a need to meet stringent requirements for use in transport applications. The US Department of Energy's Office of Energy Efficiency and Renewable Energy indicated specific performance targets for the coming decade for a successful transition to hydrogen fueled transportation [35]. In this document, the target storage capacity for a workable device was defined as 4.5, 6 and 9% by weight for the years 2005, 2010 and 2015, respectively. We, therefore, have undertaken a series of calculations with increased number of hydrogen atoms, n, on Al_{13} surface, to determine the theoretically possible adsorption capacity. In addition to the adsorption systems with $n = 1$ and 2 reported above, the geometry optimization calculations were performed for $n = 3$, 4, 12, all resulting in stable adsorbed geometries and consistent binding energies. The largest so far optimized adsorption system $Al_{13}H_{12}$ is shown in figure 6. Interestingly, it can be seen from figures 2, 5 and 6, that with increased number of adsorbed hydrogen atoms, the Al_{13} showed increased geometric stability, being perfectly symmetric for $n = 12$. Our calculations also indicated that the binding energy for the optimised $Al_{13}H_n$ systems up to 12 hydrogen atoms falls within the range of 2.3–2.5 eV. However, the hydrogen storage capacity for $Al_{13}H_{12}$ cluster is only 3.41% and we need to consider a possibility of higher loadings, albeit theoretically.

In principle, the icosahedral structure comprises 20 triangles with 30 edges and 12 vertices, i.e. 62 hydrogen

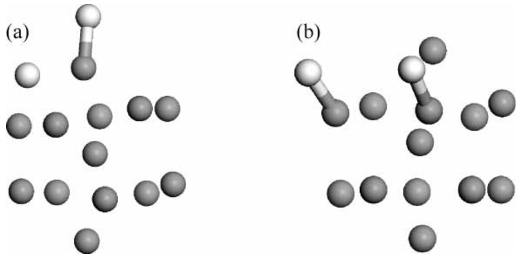

Figure 5. Two lowest energy isomers of $Al_{13}H_2$ cluster.

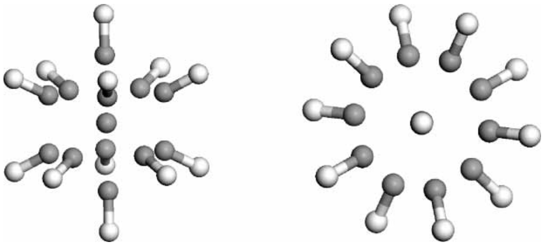

Figure 6. Optimized geometry of $Al_{13}H_{12}$ cluster, two views are shown.

atoms can be positioned for a complete coverage in all theoretically available adsorption sites, including the atop, bridge and hollow sites identified above. However, the hollow sites were found to be of relatively high energy compared to the bridge and atop sites, therefore, we have constructed a hypothetical system with 42 hydrogen atoms occupying only vertices and edges of Al_{13} cluster (figure 7). Such a system would reach a highly desirable target of almost 10.5% hydrogen loading by weight. The studies of the higher capacity systems, including the $Al_{13}H_{42}$ system, are currently underway in our group and will be published elsewhere.

4. Conclusions

We have used the DFT calculations to theoretically demonstrate a strong potential for exploring Al_{13} clusters for hydrogen storage. It has been found that:

- Hydrogen atom can adsorb on the Al_{13} cluster surface without crossing a potential barrier;
- $Al_{13}H$ adsorption system has three stable minima corresponding to the atop, bridge and hollow configurations of hydrogen atom on the cluster surface, with the most stable isomer being that of the atop position;
- Hydrogen atom adsorbed on the surface of Al_{13} cluster induces distortion which diminishes with the larger amount of adsorbed hydrogen;
- Molecular hydrogen H_2 has a potential barrier for physisorption on Al_{13} surface and is repelled from the surface without additional energy supply;
- The activation energy for dissociative chemisorption of molecular hydrogen on Al_{13} is not very high and can be overcome with a relatively modest supply of thermal energy or by adding a catalyst;
- Theoretically high hydrogen storage capacities can be achieved by adsorption into the Al_{13} surface sites identified in our work, however this needs further investigation.

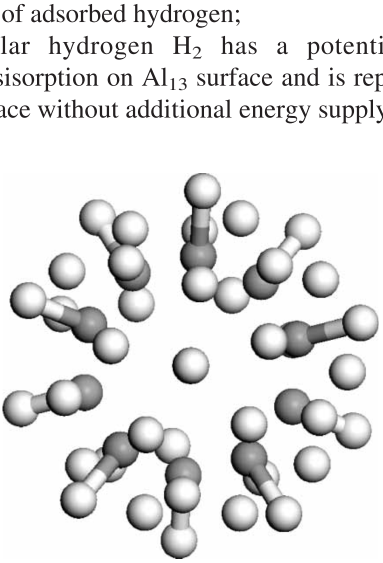

Figure 7. A hypothetical $Al_{13}H_{42}$ cluster.

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