Dissociation of multiple hydrogen molecules on the non-planar aluminium cluster: stationary points on the Al$_6$ + nH$_2$ potential energy surface

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Abstract. Compared to clusters of transition metal atoms, H-H bond activation by main Group metal clusters is much less known. Here, we have examined a potential new way of obtaining a novel alane Al$_6$H$_8$ through addition of multiple H$_2$ molecules to the aluminium hexamer, i.e., Al$_6$ + nH$_2$ (n=1-4) reactions. To this end, systematic high level quantum chemical modeling calculations using density functional theory (DFT) and coupled-cluster singles-doubles-perturbative triples (CCSD(T)) method in conjunction with the aug-cc-pVTZ basis set were performed to identify the lowest energy barrier paths for the consecutive dissociation of several hydrogen molecules on Al$_6$, the smallest aluminium cluster with a three-dimensional ground-state structure. These computational results are relevant to the issues of hydrogen storage and novel stable alanes.

1. Introduction
Although studying the processes of adsorption and dissociation of molecular hydrogen on the surface of transition metal clusters has been an active area of research for the last twenty years [1-3], such reactions involving main group metal clusters have been investigated on a much smaller scale. For the light metals like aluminium this type of reactions is of potential technological importance for hydrogen storage. In the early gas phase experimental studies of the reactions of aluminium clusters with molecular hydrogen of Cox et al [4], it was observed that the onset of reactivity of Al$_n$ towards H$_2$ occurred for hexamer Al$_6$ (n=6). Recently, by using mass spectrometry and photoelectron spectroscopy (PE) techniques, Li et al. [5-6] studied the series of new aluminium hydride anions Al$_n$H$_{n+2}$ (4≤n≤8) and, by analyzing the recorded PE spectra, they drew conclusions on the electronic properties and stability of the corresponding neutral alanes Al$_n$H$_n$. These authors in particular suggested Al$_6$H$_8$ species to have an increased stability relative to that of the other Al$_n$H$_m$ hydrogenated clusters. In other words, Li et al. proposed the former species to be a novel stable “hydrogen rich” alane. Importantly, Al$_6$ hexamer is the smallest aluminium cluster whose ground state structure is three-dimensional, with the octahedron- and prism-like geometries lying close in energy [7]. If one models multiple H$_2$ dissociation reactions on the relatively big cluster like Al$_6$, a systematic exploration of the respective potential energy surfaces (PESs) is crucial. This will ensure that the low-lying transition states (TSs)

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for H-H bond dissociation are located. Identifying the “right” H-H dissociation transition states will have implications, e.g., for the kinetic modelling of these processes.

Below, we will briefly describe the results of the high-level quantum chemical calculations of the reaction paths for the consecutive dissociation of multiple H$_2$ on the aluminium hexamer Al$_6$. The Al$_6$H$_8$ hydrogenated cluster is intended to be the “final” hydrogenation product, consistent with the PE results for the Al$_n$H$_m$ species with n=6 mentioned above. We note that in the experimental studies of Li et al. [5-6], the anion clusters were made by the reactions of the Al$_n^-$ clusters with H atoms (not H$_2$ molecules). The present theoretical results are relevant to the issues of hydrogen storage and novel stable alanes.

2. Computational methods
The correlation consistent triple-zeta quality aug-cc-pVTZ basis set [8] was used throughout. All the structures were optimized and verified as minima or transition states on the respective potential energy surfaces using density functional theory (DFT) with the hybrid B3LYP functional [9-10], and the improved energetics were subsequently obtained via the single-point calculations at the B3LYP/aug-cc-pVTZ structures using the coupled-cluster singles, doubles and perturbative triples (CCSD(T)) method [11]. Connectivity of the transition states for H-H bond dissociation with the hydrogenated products was confirmed by determining the intrinsic reaction coordinates [12]. The harmonic vibrational frequencies computed at the B3LYP/aug-cc-pVTZ level were used to estimate the zero-point energy (ZPE) and thermal and entropic corrections. All the computations were performed using the Gaussian 09 program [13].

3. Outline of results
3.1. The scope and labelling of the stationary points
In the subsections below, the low energy barrier paths computed for the hydrogenation reactions Al$_n$H$_{2n-2}$ + H$_2$ \(\rightarrow\) Al$_n$H$_{2n}$ with n=1-4 will be summarized. The dissociation of the first H$_2$ on Al$_6$ (n=1) was recently discussed in detail [7], thus only a brief account is given below. The bulk of this presentation is devoted to the n=2-4 hydrogenation steps. Transition states involved in the dissociation of the second (S) (n=2), third (T) (n=3) and fourth (F) (n=4) H$_2$ are denoted as TSH-H$_Sj$, TSH-H$_Tj$ and TSH-H$_Fj$, respectively, with \(j=1,2,3,...\) indicating the TS number for each dissociation type. The respective hydrogenated clusters are termed S$_j$, T$_j$ and F$_j$. In order to save space, for each n, only the energetically most favourable structures of the transition states and corresponding hydrogenated clusters are shown, although all the calculated H-H dissociation TSs/hydrogenated clusters are included in the respective enthalpy and free energy profiles.

3.2. n=1
The hydrogenation of the octahedral-based Al$_6$ to form Al$_6$H$_6$(1) dihydride (Figure 1) is thermodynamically favourable, both in terms of enthalpy, \(\Delta H(298K)=-25.3\) kcal/mol, and Gibbs free energy, \(\Delta G(298K)=-25.3\) kcal/mol (Figure 2) [7]. Relative to the ground state reactants Al$_6$(D$_{3d}$,A$_{1g}$) + H$_2$ [7], no enthalpic barrier \(\Delta H(298K)\) is predicted to be involved in the path that passes through the octahedral-like transition state TSH-H (Figure 1), with the corresponding free energy barrier \(\Delta G(298K)\) being 5.3 kcal/mol (Figure 2).

3.3. n=2
Among the three low-lying transition states located on the Al$_6$H$_2$ + H$_2$ potential energy surface, the energetically most preferred one is the four-centered TSH-HS3, where the H-H bond is broken on the Al-Al edge of the Al$_6$ prism (Figure 1). Upon dissociating the second H$_2$ via TSH-HS3, the new terminal and new bridging Al-H bonds are formed in the Al$_6$H$_4$S$_3$ hydrogenated cluster. TSH-HS3 competes energetically with the octahedral-like TSH-HS1 transition state, bearing a strong
resemblance (the “active site”) to TSH-H (n=1). The enthalpic and free energy profiles in Figure 2 show that for n=2 there are indeed two kinetically competitive hydrogenation paths, via TSH-HS3 and TSH-HS1 at 8.9 (17.1) and 9.5 (18.0) kcal/mol, in terms of $\Delta H(298K)$ ($\Delta G(298K)$), relative to the $\text{Al}_6\text{H}_2(1) + \text{H}_2$ asymptote. The lower-energy path via TSH-HS3 affords exothermically the $\text{Al}_6\text{H}_4$ cluster $\text{S}_3$, with the enthalpy (free energy change) of $-18.0$ (-9.7) kcal/mol (Figure 2).

Figure 1. The lowest lying transition states for the hydrogenation reactions $\text{Al}_6\text{H}_{2n-2} + \text{H}_2 \rightarrow \text{Al}_6\text{H}_{2n}$ with n=1-4 along with the resulting hydrogenated $\text{Al}_6$ clusters.

Figure 2. Schematic enthalpic and free energy profiles (kcal/mol) for the hydrogenation reactions $\text{Al}_6\text{H}_{2n-2} + \text{H}_2 \rightarrow \text{Al}_6\text{H}_{2n}$ with n=1,2 calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ
n=3
For the n=3 hydrogenation step, we have identified five transition states for the H-H bond dissociation, with the octahedral-based TSH-HT5 (Figure 1) lying significantly lower in energy compared to the other TSs (cf. Figure 3). All he transition states relevant to the third H2 dissociation are either of the octahedral- or prism-like type. The lowest energy H2 hydrogenation path, via TSH-HT5, leads to the Al6H6(T5) cluster of C2 symmetry, which features four hydrogens in the terminal sites and two Hs occupying the three-fold bridged positions of the Al6 octahedron (Figure 1). The current hydrogenation step via TSH-HT5 requires overcoming the energy barrier comparable to that encountered for the n=2 case, i.e. 7.9 (ΔH(298K)) kcal/mol and 16.6 kcal/mol (ΔG(298K)), with respect to the Al6H6(S3) + H2 asymptote (Figure 3). Relative to this asymptote, the third H2 dissociation is exothermic as indicated by the computed enthalpy (free energy change) of -22.5 (-13.6) kcal/mol (Figure 3).

n=4
Among the three transition states calculated for the fourth H2 dissociation, the lowest lying is the four-centered TSH-HF2 one with the H-H bond being broken on the Al-Al edge of the distorted Al6 octahedron (Figure 1). Upon dissociating the fourth H2 via TSH-HF2, the new terminal and new
bridging Al-H bonds are formed in the resulting Al₆H₈ F₂ hydrogenated cluster. The energy barriers corresponding to the fourth H₂ hydrogenation step via TSH-HF₂ are 14.7 and 22.8 kcal/mol in terms of ΔH(298K) and ΔG(298K), respectively, relative to the Al₆H₆(T₅) + H₂ asymptote (Figure 3). The kinetically most preferred hydrogenation path for n=4 does not lead however to the thermodynamically most favourable Al₆H₈ product. This is because the thermodynamically most favourable Al₆H₈ isomer is F₅ (Figure 1). The latter species of C₂ᵥ symmetry contains six terminal and two three-fold bridged hydrogens. Relative to the Al₆H₆(T₅) + H₂ asymptote, the fourth H₂ dissociation step is again exothermic, with the computed enthalpy (free energy change) of −27.5 (−19.9) kcal/mol (Figure 3).

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