



Probing the structural and electronic properties of small aluminum dideuteride clusters



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ABSTRACT

Adsorption of deuterium on the neutral and anionic Al_n^λ ($n=1-9, 13$; $\lambda=0, -1$) clusters has been investigated systematically using density functional theory. The comparisons between the Franck–Condon factor simulated spectra and the measured photoelectron spectroscopy (PES) of Cui and co-workers help to search for the ground-state structures. The results showed that D_2 molecule tends to be dissociated on aluminum clusters and forms the radial Al–D bond with one aluminum atom. By studying the evolution of the binding energies, second difference energies and HOMO–LUMO gaps as a function of cluster size, we found Al_2D_2 , Al_6D_2 and $Al_7D_2^-$ clusters have the stronger relative stability and enhanced chemical stability. Also, considering the larger adsorption energies of these three clusters, we surmised that Al_2 , Al_6 and Al_7^- may be the better candidates for dissociative adsorption of D_2 molecule among the clusters we studied. Furthermore, the natural population analysis (NPA) and difference electron density were performed and discussed to probe into the localization of the charges and reliable charge-transfer information in Al_nD_2 and $Al_nD_2^-$ clusters.

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1. Introduction

Molecular, semiconductor and atomic clusters in the nanometer size range are a current topic of research. In particular, atomic clusters have been an interesting subject not only because they can form building blocks of a novel class of cluster assembled materials [1], but also an understanding of their stabilities has great scientific significance.

Nano-assemblies of light metal clusters have potential applications in hydrogen energy production technology, which is a safe, compact and inexpensive system able to store a large amount of hydrogen. Among them, aluminum clusters [2–5] are the most studied system. Because it is a common and cheap metal with lighter mass compared with precious hydrogen-absorbing metal, such as palladium [6] and platinum. The electronic structure of aluminum is free-electronlike just as the alkali metal. The electronic structure of alkali metal clusters has been successfully described by the jellium model [7,8]. So it is expected that aluminum clusters can also be studied by applying this simple model. The so-called jellium

model predicts that clusters with closed-shell electronic configurations are particularly stable. Thus, clusters with 2, 8, 20, 40... electrons can close $1s^2, 1p^6, 1d^{10}, 2s^2, 1f^{14}, 2p^6...$ shells, and should be very stable. In the case of aluminum clusters, Al_7^+ and Al_{13}^- clusters containing 20 and 40 electrons, respectively, are known to be stable [9]. Furthermore, Al_7 and Al_{13} are also tested to be particularly stable [10,11] because their valence electronic configurations approach closed-shell magic configurations, as characterized by the jellium model. However, several other experimental and theoretical studies [12,13] indicate that small aluminum clusters do not comply with this well-known jellium model. Compared with alkali metal clusters, the two important issues for aluminum clusters are that: the lack of s and p bands overlap and large perturbations due to +3 ionic cores. Al atom has $3s^2 3p^1$ configuration and the s and p orbitals are separated by an energy gap of 4.99 eV. So the s – p overlap [14,15] is very small in small Al clusters and aluminum may behave as a monovalent atom. According to these, it is believed it is only when the full s – p mixing is achieved that aluminum can be considered to be trivalent, and then it is expected the jellium model begins to work. The electronic structure of aluminum clusters is still unclear and controversial.

Hydrogenated and dehydrogenated aluminum clusters are interesting as candidates for hydrogen-absorbing nanomaterial [16,17]. It has been proposed that the adsorption of hydrogen on

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Table 1Experimental adiabatic detachment energies (ADE) of Al_n^{λ} and $\text{Al}_n\text{D}_2^{\lambda}$ ($n=2-9, 13$; $\lambda=0, -1$) compared to those calculated for the ground-state isomers.

N	ADE (eV)									
	Al_n^-				Al_nD_2^-					
	Exp. ^a	Exp. ^b	B3PW91	PW91	Exp. ^c	B3PW91	PW91	B3LYP	HF	MP2
2	1.46 ± 0.01		1.52	1.56		1.42	1.39	1.30	0.77	1.16
3	1.89 ± 0.04	1.53	1.59	1.75	1.90 ± 0.10	1.79	1.86	1.73	0.72	1.83
4	2.20 ± 0.05	1.74	2.14	2.12		1.95	1.95	1.81	1.50	1.63
5	2.25 ± 0.05	1.82	2.10	2.08		2.06	2.11	2.00	1.02	1.00
6	2.63 ± 0.06	2.09	2.50	2.49	1.66 ± 0.15	1.87	1.81	1.79	1.76	1.44
7	2.43 ± 0.06	1.96	2.09	2.12	2.95 ± 0.04	2.90	2.89	2.79	1.72	3.38
8	2.35 ± 0.08	2.22	2.25	2.17	2.27 ± 0.04	2.28	2.35	2.17	1.68	1.62
9	2.85 ± 0.08	2.47	2.59	2.63	2.91 ± 0.04	2.38	2.40	2.36	1.24	3.38
13	3.62 ± 0.06	2.86	3.39	3.36	3.64 ± 0.08	3.49	3.46	3.33	2.58	2.52

^a Ref. [41].^b Ref. [42].^c Ref. [33].

Al_{13} can provide an electron to complete its electronic configuration, therefore Al_{13}H may be suitable for the preparation of new cluster-assembled materials [18–21]. However, some early theoretical [22,23] and experimental [24] studies indicate that aluminum has a poor metal surface for dissociative adsorption of H_2 . In other words, it cannot adsorb molecular hydrogen under normal condition, and there is a large activation energy barrier (≥ 0.5 eV) [23] for dissociation of H_2 . Therefore, it is very interesting to study the interaction between H_2 and aluminum clusters, which are expected to have different properties from the bulk surface.

An early research to understand hydrogen interaction with aluminum clusters was made by Upton [25,26]. Their results suggested that Al_6 is the smallest cluster that will adsorb H_2 . Cox et al. [27] found that chemisorption of D_2 on neutral Al clusters is relatively slow and strongly size specific, with only Al_6 and Al_7 exhibiting significant reactivity. Very recently, Henry and co-workers have investigated the interaction of hydrogen with aluminum clusters, including the binding of H atoms to Al_{12} and doped Al_{12}X ($\text{X}=\text{Mg}, \text{Al}, \text{Si}$) clusters [28–31]. Reaction profiles for the formation of $(\text{Al}_{13})_2$ dimers from a range of cluster and H atom combinations were also determined by them [32]. Cui et al. [33] investigated Al_nD_2^- ($n=3, 6-15$) anions using photoelectron spectroscopy, which can reveal the nature of the interaction between D_2 and the Al_n^- clusters. Their results suggested that for the closed-shell Al_n^- ($n=9, 11, 13, \text{ and } 15$), D_2 is physisorbed on the clusters; whereas for the open-shell Al_n^- ($n=8, 12 \text{ and } 14$), D_2 is chemisorbed on the clusters; for Al_nD_2^- ($n=3, 6, 7, \text{ and } 10$), their PES spectra are totally different from those of the corresponding bare Al_n^- cluster, which suggested that D_2 is likely to be dissociatively adsorbed onto the clusters. In their experiment, D_2 is used instead of H_2 for better mass resolution. In theoretical calculations, the formation energies and electronic structure of D–Al and H–Al bonds are identical; however, the vibration states in the anharmonic D–Al potential are closer to each other than for H–Al. On the other hand, the zero-point energies, reduced masses, and IR intensities are unequal. Therefore, to gain insight into the electronic properties of aluminum clusters and offer more information for studying the interaction between molecular deuterium and aluminum clusters, we report a more extensive and systematic density functional theory investigation on the small sized neutral and anionic Al_n and $\text{Al}_n\text{D}_2^{\lambda}$ ($n=1-9, 13$; $\lambda=0, -1$) clusters. The main objective of this research is to investigate the nature of interaction between molecular deuterium and small neutral and anionic aluminum clusters, meanwhile, to compare our extensive computational results with previously experimental findings [33]. The various ground-state minimum structures for each sized clusters are also obtained.

2. Computational methods

Geometrical structure optimizations and frequency analysis of $\text{Al}_n\text{D}_2^{\lambda}$ ($n=1-9, 13$; $\lambda=0, -1$) clusters were performed by density functional theory (DFT) method using the GAUSSIAN 03 program [34]. Becke's hybrid three-parameter functional combined with Perdew–Wang's correlation functional (B3PW91) [35–38] were employed for studying the bare aluminum clusters and aluminum dideuteride clusters. Due to the aluminum atom has an unoccupied d orbital, it is necessary to describe aluminum systems which have high valence with using d functions in the basis set. As previously shown, an all-electron basis set with the addition of d functions is essential for a proper description of high-valence Al atoms [22]. We chose the triple- ξ basis set 6-311+G(2d, 2p) [39,40], which include a d -type polarization function on heavy atoms and a p -type polarization function on deuterium, for our systems. Moreover, the reliability of current computational method was tested by comparing calculated adiabatic detachment energies (ADEs) using several exchange-correlation DFT functionals, Hartree–Fock and MP2 method. The results comparing with experimental values [33,41,42] are presented in Table 1.

To search for the lowest energy structure of aluminum dideuteride clusters, the equilibrium geometries of bare aluminum clusters were first studied. The pure aluminum clusters in the range of 2–13 atoms have been well studied [8,15,43–46]. We searched the pure neutral and anionic aluminum clusters by considering all the possible structures reported in previous papers. Then the adsorption models of one D_2 molecule or two D atoms on the lowest energy Al_n and Al_n^- clusters were firstly built. According to earlier investigation [47], we considered not only the most stable structures of the pure clusters but also their other low-energy isomers during the adsorption addition, since the adsorption stabilities of the latter may be competitive with or even exceed that of the most stable conformations. Almost all the possible adsorption sites have been considered. Furthermore, the previous studies on the structure of Al–H and Al–O system are also employed as a guide [25,48,21,49–57].

All the initial structures are first optimized at B3PW91/6-311+G(2d, 2p) level. Afterwards, a selected set of the low-energy optimized structures was tested by PW91PW91 [34] and B3LYP [35,58] functional. Due to the spin polarization, every initial structure is optimized at various possible spin multiplicities. It is worth pointing out that all of the adsorption clusters are found to prefer the lowest spin state. In order to confirm that the optimized geometry corresponds to a local minimum in potential energy, each of them is followed by an analysis of harmonic vibrational frequencies. Three criteria are consulted in comparing the theoretical results with the experimental data to select most likely candidate structures: (1) the

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