

Photoelectron spectroscopy of $Al_nD_2^-$ ($n=3-15$): Observation of chemisorption and physisorption of dideuterium on aluminum cluster anions

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Photoelectron spectroscopy is used to investigate aluminum dideuteride cluster anions, $Al_nD_2^-$ ($n=3, 6-15$), produced by laser vaporization of a pure Al target with a D_2 -seeded helium carrier gas. Comparison between the well-resolved photoelectron spectra of $Al_nD_2^-$ and Al_n^- reveals the nature of interactions between D_2 and Al_n^- . Depending on the size of the Al_n^- clusters and their electronic structure, three types of $Al_nD_2^-$ species are observed, dideuteride (dissociative chemisorption), molecular chemisorption, and physisorption. Striking spectral similarities are observed between photoelectron spectra of $Al_nD_2^-$ and Al_n^- for $n=9, 11, 13$, and 15 , suggesting that D_2 is physisorbed on these closed-shell Al_n^- clusters. For $Al_nD_2^-$ with $n=3, 6, 7$, and 10 , completely different spectra are observed in comparison with the corresponding Al_n^- clusters, suggesting that the $Al_nD_2^-$ species may be characterized as dideuterides. For $Al_nD_2^-$ with $n=8, 12$, and 14 , in which the Al_n^- clusters are open shell, the D_2 is characterized as chemisorption on the basis of spectral shifts and similarities relative to those of the corresponding Al_n^- clusters. © 2006 American Institute of Physics. [DOI: 10.1063/1.2166633]

I. INTRODUCTION

Small atomic clusters exhibit unique size-dependent properties. In the cluster regime, the change of a single atom can dramatically alter the structural, electronic, chemical, and magnetic properties of a cluster. The size-dependent chemical reactivity of clusters with simple molecules is important to understand catalysis by small particles and has been a critical part of cluster science. H_2 is the simplest molecule with great technological and biological importance. Studies of the interaction of H_2 with metal clusters may lead to new catalysts and to nanomaterials with good hydrogen storage capacity. Thus, the chemical reactivities of transition-metal clusters with H_2 have been extensively studied.¹⁻⁸ Aluminum clusters are relatively simple electronic systems and have been intensively studied both theoretically⁹⁻¹⁶ and experimentally.¹⁵⁻²² Aluminum is a main group element with a $3s^23p^1$ electron configuration. In small aluminum clusters, the Al atom behaves as a monovalent atom because of the large energy separation between the $3s$ and $3p$ orbitals. With the increase of cluster size, the s and p bands start to overlap and the Al atom begins to behave as a trivalent atom.²² Although the electronic structure of Al clusters has been well understood, their chemical properties have been investigated relatively scarcely,²³⁻²⁶ in particular, the reactivity of Al clusters with H_2 .²³⁻²⁵

Aluminum metal surface is relatively inert toward hydrogen and has a large activation energy barrier (about 1 eV) for the dissociation of molecular hydrogen.²⁷ It is well

known that aluminum surface does not adsorb (extremely low sticking coefficient) molecular hydrogen under normal conditions.^{28,29} It would be interesting to study the interaction of H_2 with aluminum clusters, which are expected to have different properties from the bulk surface. Indeed, Cox *et al.* found that for neutral Al clusters only Al_6 and Al_7 seemed to exhibit significant reactivity with D_2 .²³ Using size-selected low-energy ion-beam techniques, Jarrold and Bower showed that Al_n^+ cationic clusters exhibit large activation barriers toward D_2 and the activation barriers increase with cluster size from a little over 1 eV for Al_{10}^+ to around 2 eV for Al_{27}^+ ,²⁴ quite analogous to the bulk surfaces. At high collision energies, they did observe chemical reactions. They observed $Al_{n-1}D^+$ for $n < 10$ and both Al_nD^+ and $Al_{n-1}D^+$ for larger clusters. More interestingly they also observed metastable $Al_nD_2^+$ adducts for larger n . Early theoretical calculations were carried out on the interactions between Al clusters and H_2 by Upton,⁹ who computed Al_nH_2 ($n=2-6$) and found that only Al_6H_2 is exothermic for the dissociation of H_2 , consistent with the high reactivity of Al_6 observed by Cox *et al.* Khanna and Jena showed computationally that H_2 is more reactive toward the open shell icosahedral Al_{13} cluster than the closed-shell icosahedral $Al_{12}C$ cluster.³⁰ More recently, extensive *ab initio* electronic structure calculations of hydrogenated aluminum clusters Al_nH_m ($n=1-8$; $m=1,2$) and $Al_{13}H$ have been performed by Kawamura *et al.*,³¹ who showed that the binding energies of the dihydride forms of Al_nH_2 are all higher than 5 eV, i.e., higher than the dissociation energy of H_2 , suggesting that H_2 should be dissociative on the smaller Al_n clusters.

It is important to understand the interactions of hydrogen

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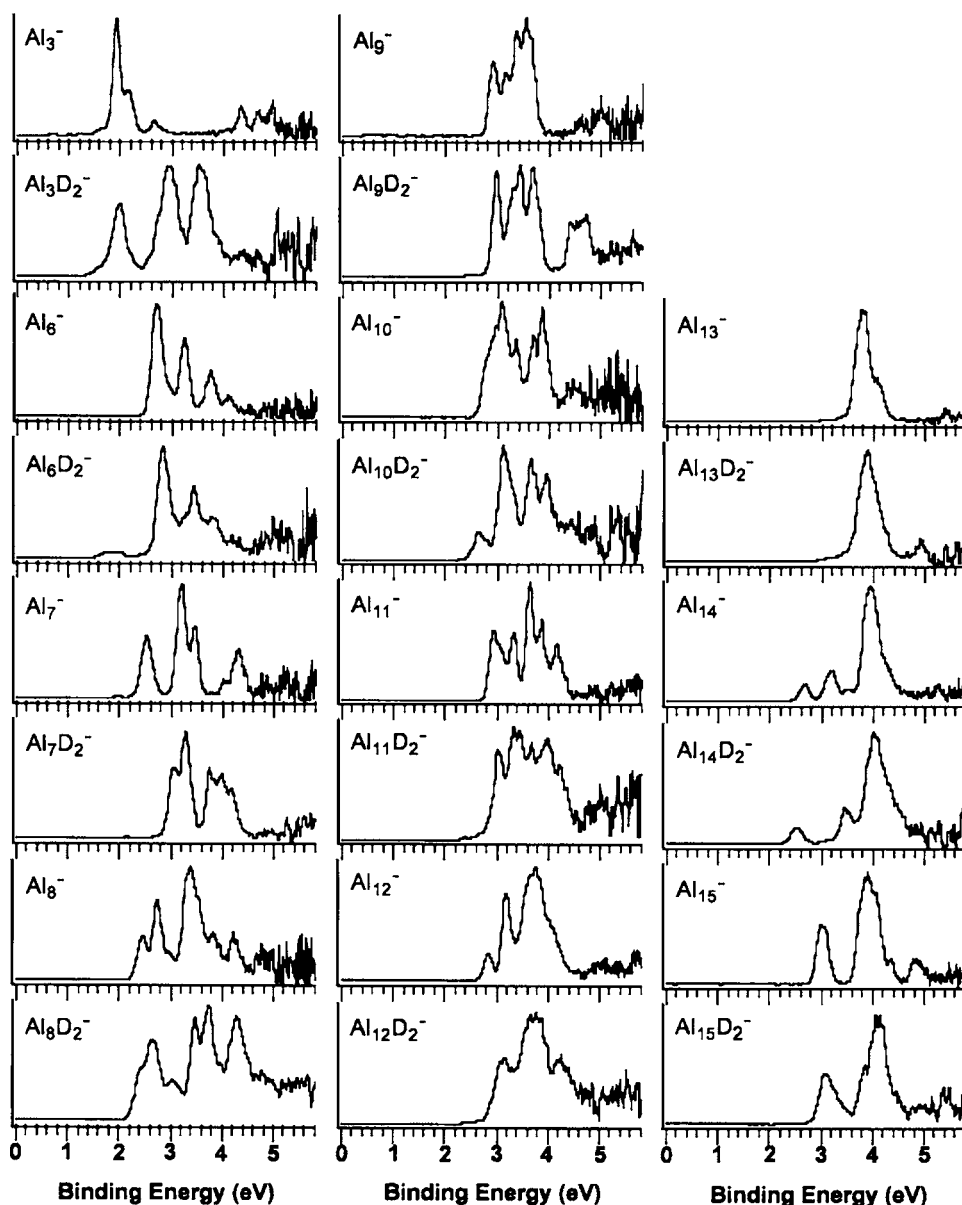


FIG. 1. Photoelectron spectra of Al_n^- and Al_nD_2^- taken at 193 nm (6.424 eV).

with nanostructured aluminum because aluminum plays an important role in many proposed hydrogen storage materials. Aluminum hydrides, alane (AlH_3) and dialane (Al_2H_6), similar to the boranes, are known stable molecules with high hydrogen content.^{32–36} Kawamura *et al.* performed theoretical calculations for higher alane clusters Al_nH_{3n} ($n=3–7$) and proposed these species prefer cyclic or linear polymeric structures.³⁷ Alkali alanates, MAlH_4 [$M=\text{Li}, \text{Na}, \text{and K}$], have also been studied as potential hydrogen storage materials.^{38–40} Yarovsky and Goldberg⁴¹ have theoretically suggested an $\text{Al}_{13}\text{H}_{12}$ species, where one H atom is adsorbed on each Al atom on the icosahedral Al_{13} surface. The $\text{Al}_{13}\text{H}_{12}$ cluster gives a hydrogen storage capacity of 3.3% by weight. A hypothetical $\text{Al}_{13}\text{H}_{42}$ cluster with much higher hydrogen storage capacity was also proposed by Yarovsky and Goldberg.

In this contribution, we report an experimental study of aluminum dideuteride cluster anions, Al_nD_2^- ($n=3, 6–15$), using photoelectron spectroscopy (PES). A similar PES work was reported by Burkart *et al.* for Al_nH_m^- ($n=12–14$;

$m=1, 2$) to confirm the high stability of Al_{13}H .⁴² The current work provides a more extensive and systematic study and focuses on the nature of interaction between molecular hydrogen and small Al_n^- cluster anions. D_2 is used instead of H_2 for better mass resolution. We expect that the present observations and conclusions should equally apply to H_2 . Our PES results suggest that D_2 can either dissociate, chemisorb, or physisorb onto Al_n^- clusters, depending on the size and electronic structure of the Al_n^- clusters. The current results provide new insight into the nature of the size-dependent interactions between hydrogen and aluminum clusters and should stimulate further theoretical studies.

II. EXPERIMENTAL METHODS

The experimental was carried out using a magnetic-bottle time-of-flight photoelectron spectrometer equipped with a laser vaporization cluster source, details of which have been described elsewhere.⁴³ Briefly, an aluminum disk target was vaporized at 532 nm (5–10 mJ/pulse) from a

TABLE I. Adiabatic detachment energies (ADEs) for Al_n^- and Al_nD_2^- .

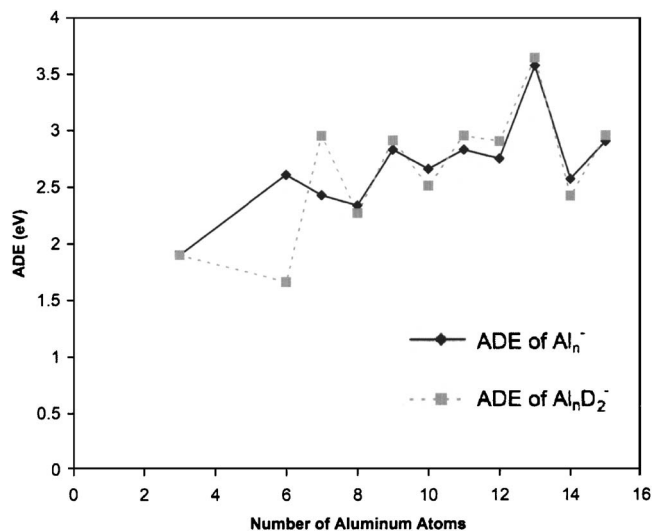
n	Al_n^- (eV)	Al_nD_2^- (eV)
3	1.90 ± 0.03^a	1.90 ± 0.10
6	2.61 ± 0.05^b	1.66 ± 0.15
7	2.43 ± 0.06^c	2.95 ± 0.04
8	2.34 ± 0.05^b	2.27 ± 0.04
9	2.83 ± 0.05^b	2.91 ± 0.04
10	2.66 ± 0.05^b	2.51 ± 0.04
11	2.83 ± 0.05^b	2.95 ± 0.04
12	2.75 ± 0.06^c	2.90 ± 0.10
13	3.57 ± 0.05^d	3.64 ± 0.08
14	2.57 ± 0.05^b	2.42 ± 0.10
15	2.90 ± 0.06^c	2.95 ± 0.10

^aFrom Ref. 45.^bMeasured more accurately in this work at 266 nm.^cFrom Ref. 22.^dFrom Ref. 44.

Nd:YAG (yttrium aluminum garnet) laser. The laser-produced plasma was mixed with a D_2 -seeded (5% D_2) helium carrier gas pulse at 10 atm backing pressure. A cold cluster beam was produced by a supersonic expansion of the cluster/carrier gas mixture through a 2-mm-diam nozzle and collimated by a 6-mm-diam skimmer. The anions were extracted from the cluster beam at 90° and mass analyzed by a time-of-flight mass spectrometer. The seeded D_2 reacted with the aluminum plasma and formed various aluminum deuteride clusters. Deuterium was used instead of hydrogen in order to better mass separate the different clusters. The Al_nD_2^- clusters of interest for the current study were each mass selected and decelerated before crossing with a detachment laser beam (355, 266, or 193 nm) in the interaction zone of the magnetic-bottle photoelectron analyzer. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5-m-long electron flight tube. The PES spectra were collected for 20 000–40 000 laser shots at 20 Hz repetition rate. The vaporization laser was off at alternating detachment laser shots for background subtraction. The presented binding-energy spectra were obtained by subtracting the kinetic energies of the photoelectrons from the photon energy of the detachment laser. The photoelectron spectra were calibrated using the known spectrum of Au^- . The apparatus has an electron energy resolution of about $\Delta E_k/E_k \sim 2.5\%$, i.e., 25 meV for photoelectrons of 1 eV kinetic energy.

III. RESULTS

Figure 1 displays the PES spectra of Al_nD_2^- ($n=3, 6-15$) taken at 193 nm compared with those of pure aluminum cluster anions Al_n^- , which were reported previously.²² The PES spectra for selected clusters were also obtained at 266 and 355 nm (not shown). Due to the very weak ion intensities of Al_nD_2^- ($n=1, 2, 4, \text{ and } 5$), we were not able to obtain their PES spectra. Well-resolved electronic transitions were obtained for all the observed Al_nD_2^- species. The adiabatic detachment energies (ADEs) or the electron affinities for the corresponding neutral clusters were measured from the lowest binding-energy peaks. Since no vibra-

FIG. 2. The adiabatic detachment energies of Al_n^- and Al_nD_2^- vs the number of aluminum atoms.

tional structures were resolved, the ADEs were estimated by drawing a straight line along the leading edge of the threshold peaks and then adding the instrumental resolution to the intersection with the binding-energy axis. The ADEs, given in Table I for both bare Al_n^- and the deuterated Al_nD_2^- clusters and also plotted in Fig. 2, were determined from the lower photon energy spectra, wherever available, due to the slightly better spectral resolution at the lower photon energies.

Comparison between the PES spectra of Al_nD_2^- and Al_n^- can reveal information about the electronic interaction of D_2 with Al_n^- . Three general behaviors were observed in comparing the spectra between the deuterated and bare clusters. First, for the smaller clusters with $n=3, 6, 7,$ and 10 , we observed that the spectra of Al_nD_2^- are totally different from those of the corresponding Al_n^- clusters, both in terms of the spectral features and the ADEs. Second, for $n=9, 11, 13,$ and 15 , the opposite was observed. The spectra of Al_nD_2^- for these four clusters are almost identical to those of the bare Al_n^- clusters both in terms of the spectral features and ADEs. This is particularly true for Al_9D_2^- , $\text{Al}_{13}\text{D}_2^-$, and $\text{Al}_{15}\text{D}_2^-$. The ADEs of the deuterated species for these species are only slightly increased relative to the bare clusters (Table I and Fig. 2). For $n=8, 12,$ and 14 , an intermediate behavior was observed; in that, certain spectral similarities seem to exist between those of Al_nD_2^- and Al_n^- . But there are also significant differences. In particular, the ADEs of Al_nD_2^- for these three species generally exhibit more significant changes than the corresponding Al_n^- clusters.

As noted in the Introduction, Burkart *et al.*⁴² reported the PES spectra for aluminum hydride clusters Al_nH_m^- with $n=12-14$ and $m=1, 2$, previously. The current spectra of $\text{Al}_{12}\text{D}_2^-$ and $\text{Al}_{14}\text{D}_2^-$ are better resolved and consistent with those on the hydrogenated species reported by Burkart *et al.* However, our $\text{Al}_{13}\text{D}_2^-$ spectrum is different from that of $\text{Al}_{13}\text{H}_2^-$ by Burkart *et al.* The $\text{Al}_{13}\text{H}_2^-$ spectrum by Burkart *et al.* exhibited an extra lower binding-energy band around 3.3 eV relative to the current spectrum of $\text{Al}_{13}\text{D}_2^-$. The $\text{Al}_{13}\text{H}_2^-$ spectrum reported by Burkart *et al.* had a rather low

count rate and poorer resolution. We suspect that the extra band in the spectrum of Burkart *et al.* could be due to either a structural isomer or contaminations.

IV. DISCUSSION

The geometrical and electronic structures of small aluminum clusters have been well studied. Small clusters are expected to be more reactive due to the presence of large number of surface atoms with low coordination numbers. The electron affinities (EAs) of the bare Al_n clusters display an even-odd effect for $n > 6$ (Fig. 2), where the odd-sized clusters possess higher EAs than their even-sized neighbors. This observation suggests that all odd-sized neutral Al_n clusters are open shell with an unpaired electron and their corresponding anions Al_n^- are all closed shell, giving rise to the enhanced electron binding energies in the anions. The even-sized neutral Al_n clusters are all closed shell with a highest occupied molecular-orbital–lowest unoccupied molecular-orbital (HOMO-LUMO) gap, thus giving rise to the reduced electron binding energies for their anions. The enhanced EA of Al_6 is because it has a triplet ground state with two unpaired electrons,¹³ instead of a closed-shell configuration. This electronic structure information is revealed clearly in the PES spectra of the bare Al_n^- clusters,²² as shown in Fig. 1.

If D_2 chemisorbs on Al_n^- , the PES spectra and ADEs of $Al_nD_2^-$ are expected to be different from those of the corresponding bare Al_n^- clusters. This is because the electronic energy levels of Al_n^- are expected to be perturbed by D_2 or in cases of dissociative chemisorption dideuterides are formed. If D_2 physisorbs on Al_n^- , one would expect that $Al_nD_2^-$ and Al_n^- should have similar PES spectra and similar ADE values since there is little electronic interaction between D_2 and Al_n^- . Based on our experimental data and the comparison between the spectra of $Al_nD_2^-$ and Al_n^- , we observed both dissociative and molecular chemisorptions, as well as physisorption of D_2 on Al_n^- clusters in $Al_nD_2^-$, depending on the size and the electronic properties of the Al_n^- cluster.

A. Dissociative chemisorption: $Al_nD_2^-$ ($n=3, 6, 7,$ and 10)

For these four species, their PES spectra are totally different from those of the corresponding bare Al_n^- clusters, i.e., their electronic structures are very different from those of the bare clusters. This observation suggests that D_2 is likely to be dissociatively chemisorbed on the Al_n^- clusters, forming two hydride bonds. There have been no theoretical calculations of hydrogen interacting with negatively charged Al_n^- clusters. But early calculations by Upton suggested that H_2 dissociates on neutral Al_6 .⁹ More recent calculations on neutral clusters by Kawamura *et al.*³¹ showed that the total binding energies of two H atoms in Al_nH_2 ($n \leq 8$) are always larger than the dissociation energy of H_2 , suggesting that H_2 prefers to dissociatively chemisorb onto the smaller Al clusters. Al_3H_2 is calculated to have a trigonal bipyramidal structure with each H atom coordinated to the three Al atoms. Al_6H_2 is shown to have a ground-state structure, in which the two H atoms coordinate to two nearby faces on an octahedral Al_6 , by both Upton and Kawamura *et al.* Al_7 has a ground-

state structure with an Al atom capping one face of the octahedral Al_6 . Kawamura *et al.* showed that in Al_7H_2 one H atom is bonded atop the capping Al atom and the second H atom bridges the capping Al atom and another Al atom on the octahedral Al_6 . In Al_3H_2 , Al_6H_2 , and Al_7H_2 , the two hydride atoms are all next to each other on the cluster surface. Thus a low activation barrier is expected when H_2 approaches the cluster during chemisorption. On the other hand, Kawamura *et al.* showed that the most stable structure of Al_8H_2 involves two H atoms on the opposite site of the Al_8 clusters, suggesting a high activation barrier for H_2 dissociation on the Al_8 cluster surface. This is consistent with the molecular chemisorption of D_2 in $Al_8D_2^-$ (*vide infra*). Although there have been no calculations on $Al_{10}H_2$, the very different PES spectrum observed for $Al_{10}D_2^-$ compared to Al_{10}^- suggests that D_2 is very likely to be dissociatively chemisorbed on Al_{10}^- , analogous to that in $Al_6D_2^-$ or $Al_7D_2^-$.

B. Physisorption: $Al_nD_2^-$ ($n=9, 11, 13,$ and 15)

The PES spectra of these four deuterated species are nearly identical to those of their corresponding bare Al_n^- clusters and their ADEs are also similar to those of the corresponding bare clusters, particularly for $n=9, 13,$ and 15 . These observations imply that D_2 has very little effect on the electronic structure of these Al_n^- clusters, suggesting van der Waals interactions between D_2 and Al_n^- or physisorption of D_2 on Al_n^- . These species can essentially be characterized as van der Waals complexes, $(Al_n^-)D_2$. This is not surprising because these odd-sized Al_n^- clusters are all closed-shell electronic systems and they are expected to exhibit high activation barriers toward reaction with D_2 . In particular, the electronic stability of Al_{13}^- is well known because it is a major shell closing in the jellium model. For example, it has the highest EA (3.57 eV) among the Al_n clusters,^{22,44} as shown in Fig. 2. Indeed, the electronic structure of the icosahedral Al_{13}^- is little perturbed in $Al_{13}D_2^-$, as evidenced in the nearly identical PES spectra of $Al_{13}D_2^-$ and Al_{13}^- (Fig. 1). Al_{15}^- is known to have a structure, in which two Al atoms capping an icosahedral Al_{13}^- on the opposite site.¹⁵ The nearly identical spectra of $Al_{15}D_2^-$ and Al_{15}^- suggest that D_2 is also very weakly bound to Al_{15}^- . Only the spectral features of $Al_{11}D_2^-$ show more variations from that of the bare Al_{11}^- cluster and a more significant ADE shift relative to Al_{11}^- as well, indicating a stronger interaction between D_2 and Al_{11}^- relative to the other three closed-shell clusters.

C. Chemisorption: $Al_nD_2^-$ ($n=8, 12,$ and 14)

For these three deuterated species, the PES spectra exhibit certain similarities, as well as visible differences from their corresponding bare clusters. The ADEs of these species also display more sizable shifts in general compared to their corresponding bare clusters. These observations indicate that D_2 has stronger interactions with the underlying Al cluster anions, and should probably be characterized as chemisorption. The bare Al_n^- clusters in these cases are even sized and they are all open-shell species with one unpaired electron. Thus, it is understandable that D_2 should have stronger inter-

actions with these open-shell clusters, compared to the closed-shell odd-sized clusters. Jarrold and Bower observed D_2 chemisorbed adducts onto Al_n^+ clusters in ion-beam experiments at a collision energy of 3 eV.²⁴ It is interesting to note that even though they observed strong $Al_nD_2^+$ adducts only for $n \geq 16$, in the smaller size range significant chemisorbed D_2 adducts were observed only for $Al_{12}D_2^+$ and $Al_{14}D_2^+$. This is very likely due to the fact Al_{12}^+ and Al_{14}^+ are open shell with one unpaired electron, thus exhibiting stronger interactions with D_2 , analogous to the open-shell anions, Al_8^- , Al_{12}^- , and Al_{14}^- . We further note that although Al_{13}^- is closed shell and chemically inert, theoretical calculations have suggested that the open-shell neutral Al_{13} is more reactive toward H_2 and can dissociatively chemisorb H_2 with a moderate activation barrier.^{30,41}

V. CONCLUSIONS

We report a photoelectron spectroscopic investigation of $Al_nD_2^-$ ($n=3, 6-15$), formed from laser vaporization of a pure aluminum target with a D_2 -seeded helium carrier gas. Well-resolved photoelectron spectra were obtained for the $Al_nD_2^-$ clusters. Comparison of the photoelectron spectra of $Al_nD_2^-$ with those of Al_n^- yielded information about the nature of D_2 in the $Al_nD_2^-$ clusters. Dissociative chemisorption, molecular chemisorption, and physisorption were inferred from the spectral comparison, depending on the cluster size and their underlying electronic structure. For $Al_nD_2^-$ ($n=9, 11, 13$, and 15), very similar PES spectra were observed with respect to the corresponding Al_n^- clusters, suggesting they are weakly bound van der Waals complexes (Al_n^-) D_2 . For $Al_nD_2^-$ ($n=3, 6, 7$, and 10), the spectra of the deuterated species are completely different from the corresponding Al_n^- clusters, suggesting dissociative chemisorption to form dideuterides. An intermediate behavior was observed for $Al_nD_2^-$ ($n=8, 12$, and 14), which were suggested to involve chemisorbed D_2 . The deuteride $Al_nD_2^-$ clusters for $n=3, 6, 7$, and 10 are consistent with the high reactivity expected for the very small clusters. The chemisorbed and physisorbed $Al_nD_2^-$ clusters are understood from the open-shell and closed-shell natures of the underlying Al_n^- clusters, respectively. The current PES data will be valuable to verify further theoretical calculations and contribute to elucidating the size-dependent chemical properties of Al clusters with H_2 .

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