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Citation: *J. Chem. Phys.* **138**, 124303 (2013); doi: 10.1063/1.4796200

View online: <http://dx.doi.org/10.1063/1.4796200>

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Photoelectron spectroscopy of the aluminum hydride anions: AlH_2^- , AlH_3^- , Al_2H_6^- , Al_3H_9^- , and $\text{Al}_4\text{H}_{12}^-$

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(Received 12 December 2012; accepted 7 March 2013; published online 25 March 2013)

We report measurements of the negative ion photoelectron spectra of the simple aluminum hydride anions: AlH_2^- , AlH_3^- , Al_2H_6^- , Al_3H_9^- , and $\text{Al}_4\text{H}_{12}^-$. From these spectra, we measured the vertical detachment energies of the anions, and we estimated the electron affinities of their neutral counterparts. Our results for AlH_2^- , AlH_3^- , and Al_2H_6^- were also compared with previous predictions by theory. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4796200>]

I. INTRODUCTION

While boron forms many hydrides, i.e., the boranes, aluminum was long thought to form only the hydrides, alane and dialane, i.e., AlH_3 and Al_2H_6 , along with the alkali alanates, e.g., LiAlH_4 .^{1,2} Over the past few years, however, many additional aluminum hydride cluster anions have been discovered in molecular beams. Most of these were prepared in a unique beam source, identified mass spectrometrically, and in several cases characterized by the combination of photoelectron spectroscopy and *ab initio* computations.^{3–11} The present work extends these studies by measuring the photoelectron spectra of the simple aluminum hydride anions, AlH_2^- , AlH_3^- , Al_2H_6^- , Al_3H_9^- , and $\text{Al}_4\text{H}_{12}^-$. Our results for AlH_2^- , AlH_3^- , and Al_2H_6^- were also compared with previous predictions by theory.

Complex hydrides of alane, $(\text{AlH}_3)_n$, were first synthesized as a white powder over 60 years ago, and they were presumed to be polymers.^{2,12} Reports of gaseous alane and dialane first appeared almost 50 years ago.¹³ More recently, interest in these species as possible hydrogen storage materials¹⁴ and/or as propellants¹⁵ led to several experimental and theoretical studies. Among these were matrix isolation infrared spectroscopic experiments on alane,¹⁶ computations that dealt with the structure and energetics of AlH_3 , Al_2H_6 , and their anions,¹⁷ matrix isolation infrared spectroscopic experiments that confirmed the di-bridged structure of Al_2H_6 ,¹⁸ calculations that focused on larger aluminum hydrides Al_nH_{3n} with cyclic or linear polymeric structures,¹⁹ collision-induced dissociation experiments that determined the binding energy of neutral dialane,²⁰ computations that explored the energetic, structure, and bonding of dialane and its anion,²¹ mass spectrometric and computational studies that characterized the polymeric structures of $\text{Al}_n\text{H}_{3n+1}^-$,⁷ and calculations that showed the structure of Al_6H_{18} to mimic the unit cell of $\gamma\text{-AlH}_3$.⁸

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II. EXPERIMENTAL

The present work utilized negative ion photoelectron spectroscopy as its primary probe. Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-energy photon beam and energy-analyzing the resulting photodetached electrons. This technique is governed by the energy-conservation relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$, EBE, and EKE are the photon energy, electron binding (transition) energy, and the electron kinetic energy, respectively. Our photoelectron spectrometer, which has been described in Ref. 22, consists of one of several ion sources, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser for photodetachment, and a magnetic bottle electron energy analyzer having a resolution of 35 meV at $\text{EKE} = 1$ eV. Photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu^- .²³ In the present experiments, aluminum hydride anions were generated in a pulsed arc cluster ionization source (PACIS), which has been described in detail in Ref. 3. In brief, ~ 30 μs duration, ~ 150 V electrical pulses were applied at 10 Hz across an anode and aluminum cathode vaporizing aluminum atoms and forming a plasma. Almost simultaneously, 250 psi of ultra-high purity hydrogen gas was injected into the discharge region, where it was dissociated into hydrogen atoms. The resulting mixture of atoms, ions, and electrons then reacted and cooled as it flowed along a 20 cm tube before exiting into high vacuum. The resulting anions were then extracted and mass-selected prior to photodetachment.

III. RESULTS

A mass spectrum showing most of the aluminum hydride anions investigated in this study is presented in Figure 1. Three homologous aluminum hydride cluster series are observed in this spectrum, i.e., those based on one, two, and three aluminum atoms per cluster. Unit mass resolution was

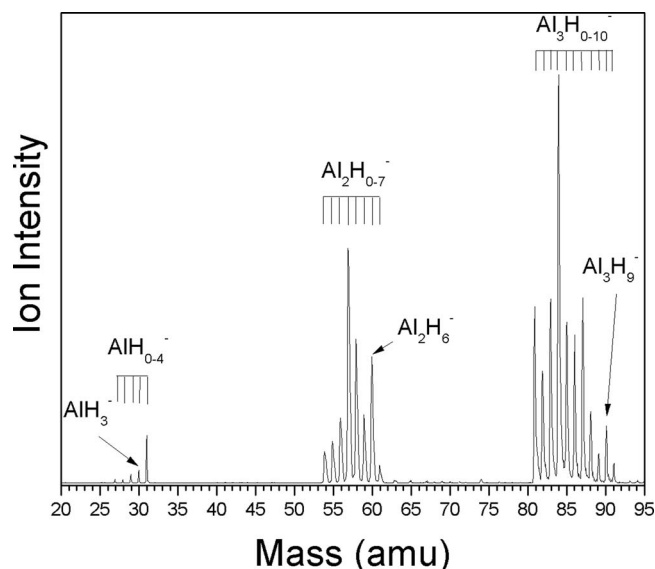


FIG. 1. The mass spectrum of Al_nH_m^- cluster anions ($n = 1-3$).

attained for all species studied. Anion photoelectron spectra are shown in Figures 2 and 3. The photoelectron spectra of $\text{Al}_n\text{H}_{3n}^-$, $n = 1-4$, are presented in Figures 2(a)–2(d). The photoelectron spectrum of AlH_3^- is shown in Figure 2(a). It was measured using 355 nm (3.49 eV) photons (third harmonic of the Nd:YAG laser). The EBE value corresponding to the intensity maximum in the observed band is its vertical detachment energy, VDE, the transition energy at which the Franck Condon overlap between the wavefunctions of the anion and its neutral counterpart is maximal. Thus, the VDE

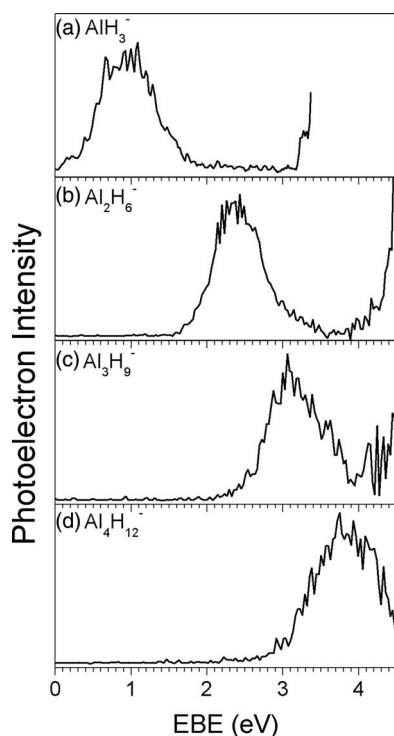


FIG. 2. Photoelectron spectra of (a) AlH_3^- , (b) Al_2H_6^- , (c) Al_3H_9^- , and (d) $\text{Al}_4\text{H}_{12}^-$.

value for AlH_3^- is 0.9 eV. The adiabatic electron affinity, EA, is the energy between the lowest energy state of the anion and the lowest energy state of its neutral counterpart. When significant Franck-Condon overlap exists between $v = 0$ of the anion and $v' = 0$ of its corresponding neutral (the origin transition) and when no vibrational hot bands (photoelectrons from vibrationally excited anions) are present, the EA value corresponds to the EBE of the intensity threshold. In most cases, the structural difference between the anion and its neutral is not so great as to preclude the presence of the origin transition within the observed spectrum, and based on previous calculations,¹⁷ this is the case in the photoelectron spectrum of AlH_3^- as well. However, the knee in the lowest EBE region in the observed AlH_3^- spectral band may indicate some degree of hot band intensity, and in fact hot bands often account for the first ~ 0.2 eV of observed intensity. For this reason, we estimate the value of $\text{EA}(\text{AlH}_3)$ to be ~ 0.3 eV, i.e., just beyond the knee. While this spectrum is truncated at $\text{EBE} = 3.49$ eV because of the photon energy utilized, it is clear that the photoelectron intensity is rising rapidly there, indicating the beginning of a higher energy transition. Thus, the energy spacing between the main band and the rising intensity feature is ~ 2.5 eV or more. This is a measure of the HOMO-LUMO gap (the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) in neutral AlH_3 , and it indicates that neutral AlH_3 is quite stable. Figure 2(b) presents the photoelectron spectrum of Al_2H_6^- . It was recorded using 266 nm (4.66 eV) photons (fourth harmonic of the Nd:YAG laser). The VDE value of Al_2H_6^- is seen to be 2.4 eV. By similar arguments to those given above and based on its spectrum alone, the EA value of Al_2H_6 could have been estimated to be ~ 1.8 eV. As we will see below, however, because of the unusually large structural difference between Al_2H_6 and Al_2H_6^- , this is not the case. Furthermore, there is also evidence of a higher energy transition in the Al_2H_6^- spectrum, implying a HOMO-LUMO gap for neutral Al_2H_6 of ~ 2 eV or more and thus its significant stability. Figure 2(c) presents the photoelectron spectrum of Al_3H_9^- , again recorded with 4.66 eV photons. Based on its spectrum, the corresponding VDE and EA values are 3.1 eV and ~ 2.5 eV, respectively. Figure 2(d) shows the photoelectron spectrum of $\text{Al}_4\text{H}_{12}^-$ recorded with 4.66 eV photons. The corresponding VDE and EA values extracted from this spectrum are 3.8 eV and ~ 3.0 eV, respectively. The principal spectral bands of all four of these anions have similar shapes and widths. Furthermore, while the energy shift between the spectra of AlH_3^- and Al_2H_6^- is greater than the subsequent shifts between Al_2H_6^- and Al_3H_9^- and between Al_3H_9^- and $\text{Al}_4\text{H}_{12}^-$, they all shift relatively smoothly to higher EBE values with size.

Figure 3 presents the photoelectron spectrum of AlH_2^- measured with 3.49 eV photons. The corresponding VDE and EA values extracted from this spectrum are 1.5 eV and ~ 0.9 eV, respectively. Again, there is evidence for the beginning of a second peak (a second transition) located ~ 2 eV higher in energy. Moreover, the shape and width of its main spectral band is comparable to that of the other species described above. The measured VDE and estimated EA values extracted from the five spectra are tabulated in

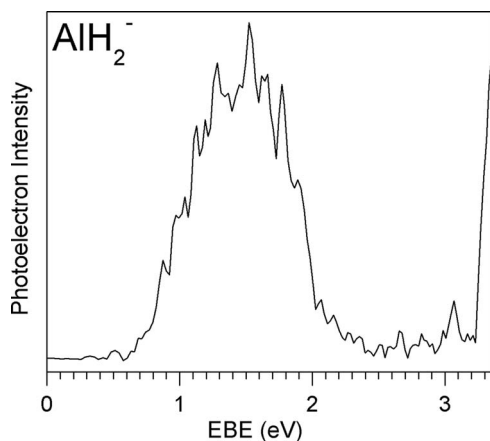
FIG. 3. Photoelectron spectrum of AlH_2^- .

Table I, where they are compared with the available values from theory.

IV. DISCUSSION

The theoretical study by Rao and co-workers¹⁷ calculated the geometric structures as well as the EA values of AlH_2 , AlH_3 , Al_2H_6 and the VDE value for Al_2H_6^- ; they also presented the photoelectron spectrum of Al_2H_6^- . With a low electron affinity, a high ionization potential, and a large binding energy, these investigators found AlH_3 to exhibit high stability. However, against the expectation that high stability molecules interact only weakly with one another, they also found that two AlH_3 molecules bind strongly, producing a dihydrogen-bridged Al_2H_6 structure that is similar to that of diborane. Thus, while one might imagine that AlH_3 units are the simple building blocks of larger Al_nH_{3n} species, the fact that Al_2H_6 exhibits two bridging hydrogen atoms in its structure shows that there are significant changes in bonding as n increases.

In most cases, the calculated energetic values of Rao and co-workers¹⁷ are consistent with our measured results. They calculated the EA values of AlH_2 and AlH_3 to be 0.9 eV and 0.28 eV, respectively, whereas we found them to be ~ 0.9 eV and ~ 0.3 eV, respectively. Their calculated VDE value of Al_2H_6^- was 2.4 eV, whereas we also found its value to be 2.4 eV.

There was disagreement, however, between their calculated EA value of 0.44 eV for Al_2H_6 and the EA value

of ~ 1.8 eV, estimated from the photoelectron spectrum of Al_2H_6^- . This discrepancy can be understood in terms of Rao *et al.*'s computational findings for the $\text{Al}_2\text{H}_6/\text{Al}_2\text{H}_6^-$ system, i.e., that there is an unusually large difference between the geometries of Al_2H_6^- and Al_2H_6 .¹⁷ With such poor Franck-Condon overlap between the $v = 0$ level of the Al_2H_6^- anion and the $v' = 0$ level of the Al_2H_6 neutral, the origin transition in the photoelectron spectrum of Al_2H_6^- might well not be observed. There is, in fact, very little photoelectron signal in the region of our Al_2H_6^- photoelectron spectrum where the origin transition is predicted to occur. That was also the case in their reported Al_2H_6^- photoelectron spectrum,¹⁷ which is identical to our Al_2H_6^- photoelectron spectrum in all significant aspects. Thus, both photoelectron spectra of Al_2H_6^- are consistent with this explanation.

Further support for this explanation comes from a consideration of dialane dissociation energies. Rao and co-workers calculated the dissociation energy of neutral Al_2H_6 breaking into two AlH_3 molecules to be 1.54 eV.¹⁷ Their predicted value is in good agreement with that measured a few years later through collision-induced dissociation experiments to be 1.43 eV.²⁰ Energetically,

$$\begin{aligned} \text{EA}(\text{Al}_2\text{H}_6) + \text{D}(\text{Al}_2\text{H}_6 \rightarrow 2\text{AlH}_3) \\ = \text{EA}(\text{AlH}_3) + \text{D}(\text{Al}_2\text{H}_6^- \rightarrow \text{AlH}_3^- + \text{AlH}_3), \quad (1) \end{aligned}$$

where $\text{EA}(\text{Al}_2\text{H}_6)$ is the electron affinity of Al_2H_6 , $\text{D}(\text{Al}_2\text{H}_6 \rightarrow 2\text{AlH}_3)$ is the dissociation energy of neutral Al_2H_6 splitting into two AlH_3 neutral molecules, $\text{EA}(\text{AlH}_3)$ is the electron affinity of AlH_3 , and $\text{D}(\text{Al}_2\text{H}_6^- \rightarrow \text{AlH}_3^- + \text{AlH}_3)$ is the dissociation energy of Al_2H_6^- splitting into an AlH_3^- anion and a neutral AlH_3 . Using the relatively solid values of $\text{EA}(\text{AlH}_3) = 0.3$ eV and $\text{D}(\text{Al}_2\text{H}_6 \rightarrow 2\text{AlH}_3) = 1.4$ eV in Eq. (1), along with trial values for $\text{EA}(\text{Al}_2\text{H}_6)$ of 1.8 eV versus 0.4 eV, implies $\text{D}(\text{Al}_2\text{H}_6^- \rightarrow \text{AlH}_3^- + \text{AlH}_3)$ values of ~ 2.9 eV versus ~ 1.5 eV, respectively. The latter value is comparable to the known $\text{D}(\text{Al}_2\text{H}_6 \rightarrow 2\text{AlH}_3)$ value of 1.43 eV. Several years after Rao *et al.*'s paper, Tian²¹ calculated values of $\text{D}(\text{Al}_2\text{H}_6^- \rightarrow \text{AlH}_3^- + \text{AlH}_3)$ for two Al_2H_6^- isomers, finding them to be 1.57 eV and 1.66 eV. Moreover, he also computed the EA values of neutral Al_2H_6 , referenced to the two Al_2H_6^- anion isomers, to be 0.22 eV and 0.32 eV,²¹ in substantial agreement with the EA value of Al_2H_6 originally predicted by Rao and co-workers.¹⁷ Taken together, this additional information decides the question in favor of the EA value for Al_2H_6 being much closer to 0.4 eV than to 1.8 eV. Rao *et al.*'s implied contention that a large structural difference between the structures of Al_2H_6 and Al_2H_6^- had obscured the origin transition in the photoelectron spectrum of Al_2H_6^- is supported by this work. For this reason, we have not included an experimentally determined value of $\text{EA}(\text{Al}_2\text{H}_6)$ in Table I.

V. CONCLUSION

Other than the alanate salts, alane (AlH_3) and dialane (Al_2H_6) are the best known of the aluminum hydrides. We have measured the photoelectron spectra of the mass-selected, aluminum hydride anions: AlH_2^- , AlH_3^- ,

TABLE I. Experimental and theoretical values of electron affinities (EA) and vertical detachment energies (VDE), all presented in units of eV. Experimental values are uncertain by ± 0.1 eV.

System	EA (Theo.) ^a	EA (Expt.)	VDE (Theo.) ^a	VDE (Expt.)
$\text{AlH}_3/\text{AlH}_3^-$	0.28	0.3	–	0.9
$\text{Al}_2\text{H}_6/\text{Al}_2\text{H}_6^-$	0.44	–	2.4	2.4
$\text{Al}_3\text{H}_9/\text{Al}_3\text{H}_9^-$	–	2.5	–	3.1
$\text{Al}_4\text{H}_{12}/\text{Al}_4\text{H}_{12}^-$	–	3.0	–	3.8
$\text{AlH}_2/\text{AlH}_2^-$	0.9	0.9	–	1.5

^aTheoretical values are all from Ref. 17. Experimental values are from this work.

Al_2H_6^- , Al_3H_9^- , and $\text{Al}_4\text{H}_{12}^-$. From their spectra, we determined VDE values for all five of them and EA values for all except Al_2H_6 . Comparisons with theory were possible in three cases. For the $\text{AlH}_2/\text{AlH}_2^-$ and $\text{AlH}_3/\text{AlH}_3^-$ systems, the agreement between experiment and theory was good. For the $\text{Al}_2\text{H}_6/\text{Al}_2\text{H}_6^-$ system, theory had predicted an unusually large difference between the structures of the anion and its neutral counterpart. This had the consequence that because of very poor Franck-Condon overlap, the origin transition (from which the EA value is estimated) was not observed in the photoelectron spectrum of Al_2H_6^- . Our work and associated arguments further supported the predictions made by theory about dialane and its anion.^{17,21}

ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research through Grant No. FA9550-11-1-0068 (K.H.B.). B.K. acknowledges the support by the funding by BoR-RCS grant.

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