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Aluminum hydride cluster cations: A mass spectrometric and computational study

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ABSTRACT

A combined study using mass spectrometry and density functional theory (DFT) was conducted to investigate aluminum hydride cluster cations, $Al_nH_m^+$ ($1 \le n \le 5$, $0 \le m \le 12$). The mass spectra revealed about 20 previously-unknown aluminum hydride cluster cations. Among these species, several showed high mass spectral intensities, suggesting that they had unusual stabilities. Density functional theory calculations were conducted to investigate the geometric structures of these clusters. Many of these clusters can be viewed as being composed of smaller, stable units, such as Al^+, AlH_3, $Al_2^{+/0}$, H^+ and H_2.

1. Introduction

Though boron forms many hydrides, i.e., the boranes, its sister element, aluminum was thought, until a few years ago, to form only a few. The known chemistry of aluminum hydrides had long been limited to AlH_3 and Al_2H_6 seen in cryogenic matrices and perhaps in the gas phase, to alane, $(AlH_3)_n$, a polymeric solid, and to AlH_4^- as a moiety in alkali metal salts, e.g., $LiAlH_4$. [1–4]. However, with the discovery of $Al_4H_6^-$ cluster anions in the gas phase [5], the known chemistry of aluminum hydrides expanded dramatically. Over subsequent years, hundreds of aluminum hydride cluster anions were discovered. [5–15] Most of these had been prepared in unique ion sources, identified by mass spectrometry, and in some cases studied by a combination of photoelectron spectroscopy and theoretical computations.

Despite the growing family of aluminum hydride cluster anions, research on their cations has been surprisingly scarce. The first report on aluminum hydride cations appeared a half century ago with the observation of AlH_3^+ and $Al_2H_6^+$, these having been prepared by slow evaporation of aluminum into hydrogen gas followed by ionization [16]. Subsequently, observation of $AlH_{1,2,4}^+$ and AlH_2^+ were reported [17,18]. Theoretical work found $Al_3H_6^+$ to form a non-planar structure [19].

Aluminum is electron deficient by nature, this being the principal reason why aluminum hydride clusters tend to capture electrons and form a large variety of anions. Its cation chemistry, however, is not well understood. With this near void of information available, we studied aluminum hydride cluster cations using a unique ion source to prepare them, mass spectrometry to identify them, and theoretical computations to elucidate their structures. We observed ~20 previously unseen $Al_nH_m^+$ clusters in our mass spectra. We carried out density functional theory (DFT) computations on the species with relatively high ion intensities, these including $Al_3H_4^+$, $Al_3H_6^+$, $Al_4H_3^+$, $Al_4H_6^+$, $Al_4H_9^+$, $Al_5H_6^+$, and $Al_5H_{12}^+$.

1.1. Experimental methods

In the present work, the aluminum hydride cations were generated using a pulsed arc cluster ionization source (PACIS), which has been described in detail elsewhere [20]. The PACIS source has been proven to be a powerful tool for generating metal and metal hydride cluster anions [20–31]. In this study, however, we used it to generate cations. Briefly, a ~30 μs long, 150 V, 1000 A electrical discharge, applied across an anode and the aluminum sample cathode, vaporized aluminum atoms. Almost simultaneously, 200 psi of ultra-high purity hydrogen gas was injected into the discharge region, where it

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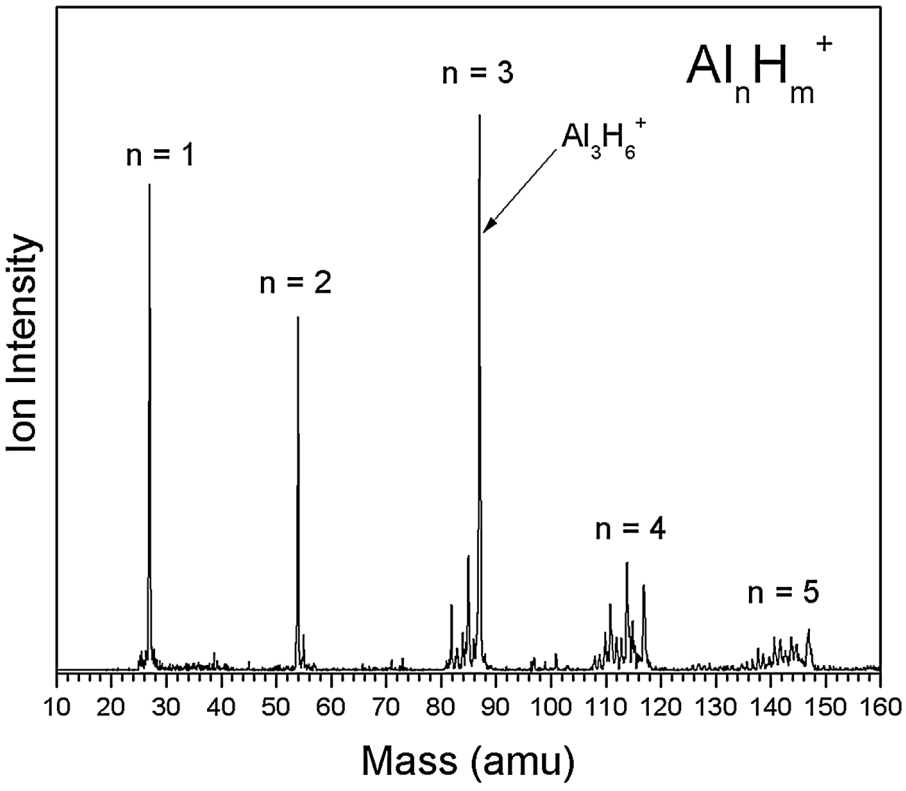

Fig. 1. The entire mass spectrum of $Al_nH_m^+$ cluster cations as measured in this study.

was dissociated into hydrogen atoms. The pressure of H_2 was optimized to obtain best ion signal. 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. Hence, the reactions were due to the recombination of aluminum and hydrogen atoms/ions to form stable cations upon cooling and not by reactions between aluminum clusters and H2 molecules. The resulting cations were then extracted and analyzed by mass spectrometer.

1.2. Computational methods

The lowest and the higher energy isomers of the cationic clusters, $Al_3H_4^+$, $Al_3H_6^+$, $Al_4H_3^+$, $Al_4H_6^+$, $Al_4H_9^+$, $Al_5H_6^+$ and $Al_5H_{12}^+$ were obtained using an unbiased systematic structure search based on the genetic algorithm (GA) [32]. In this method, initial structures were generated through a random population (parents) and subsequently allowed to cross-breed (children). Each successful "generation" becomes parents to breed the next set of children and so on. This process continued until no more mutations were possible. In our method, all levels of each structure were fully optimized without any constraints, using the BP functional and def2-SV(P) basis set [33], all employing TURBOMOLE [34]. The validity of this method had been tested against known aluminum hydride structures, and it correctly identified global minima for all of the previously studied $Al_nH_m^-$ clusters. [6] The most stable structures were further optimized using the B3LYP functional [35–37] with the 6–311 + G** basis set. [38,39] Furthermore, frequency calculations were carried out at the same level of theory to verify the nature of the stationary points. All structures reported here were found to be minima on potential energy surfaces. All these calculations were carried out using the Gaussian 09 program. [40]

2. Results and discussion

The full-range mass spectrum showing $Al_nH_m^+$ species observed in this study is presented in Fig. 1. Fig. 2(a)–(e) presents magnified, shorter-range versions of these mass spectra for n = 1-5. Distinct hydride formation trends were observed depending on the number of aluminum atoms present in the clusters. For n = 1, no hydride was formed; only the aluminum atomic cation was observed in the mass spectra, and it was intense. Aluminum hydride cations began to be seen at n = 2. However, the peak of Al_2H^+ was weak compared to the Al_2^+ peak [see Fig. 2(b)]. The tendency for aluminum hydride cluster cations to form changed dramatically at n = 3, and that trend continued for n = 4 and n = 5. For $Al_3H_m^+$ species, all m numbers from 1 to 7 were represented, although some $Al_3H_m^+$ clusters had relatively weak signals [Fig. 2(c)]. $Al_4H_m^+$ and $Al_5H_m^+$ clusters continued the pattern, with the number of hydrogen atoms going as high as m = 9 for $Al_4H_m^+$ and up to m = 12 for $Al_5H_m^+$ [Fig. 2(d, e)].

Let us first consider $Al_3H_4^+$ in the n = 3 series. The five most stable isomers of $Al_3H_4^+$, as identified by our unbiased-DFT-GA method, are shown as structures, (**1–5**), in Fig. 3. The most stable isomer of $Al_3H_4^+$ is (**1**). It has three bridging H atoms (H_b) between two Al atoms, with the remaining H and Al atoms occupying terminal positions (H_t) at both ends. All the isomers of $Al_3H_4^+$ (**1–5**), including (**1**), its global minimum (GM), can be viewed as two Al atoms, either separately (**2, 3**) or as a unit (**1, 4, 5**), interacting with their tetrahedral-AlH_4 moieties in various ways. For example, the second most stable isomer, (**2**), which is only 0.09 eV higher in energy than the GM, has two Al atoms each interacting with two of the four H atoms on AlH_4. The bonding in these structures and in all other AlH-cations discussed here can be understood as follows: Al-H_t and Al-H_b-Al form 2c-2e and 3c-2e bonds, respectively; moreover for a terminally-bonded aluminum atom, one electron can be donated, while the other two exist as a lone pair. With this