

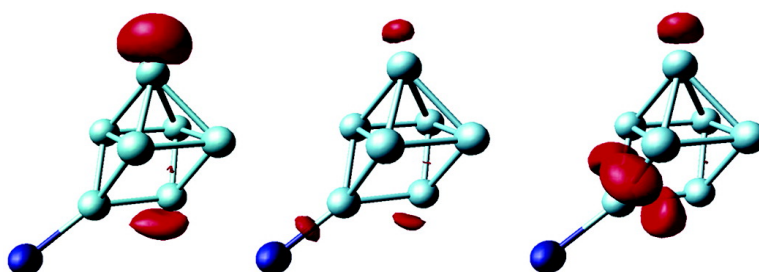
Article

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Reactions of Al_nI_x^- with Methyl Iodide: The Enhanced Stability of Al_7I and the Chemical Significance of Active Centers

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Abstract: Al_nI_x^- are reacted with methyl iodide, and the reaction mechanisms and products are discussed. The relevance of previous studies of the reactions between bare aluminum clusters and methyl iodide is addressed, and the chemical differences reported herein are explained. Particular attention is given to parallels with the known chemistry of alkyl halides on aluminum surfaces, where kinetically mediated etching reactions are prominent. The emergence of Al_7I^- as the dominant product in the present reactions is addressed via electronic structure calculations, which reveal that the cluster can be described in terms of an electron bound to a “jellium compound”. Other significant products of the etching reaction include I^- , I_3^- , and, importantly, the polyhalide-like $\text{Al}_{13}\text{I}_{2x}^-$ clusters. In the $\text{Al}_{13}\text{I}_x^-$ series, clusters with odd values for x are found to be reactive, and those with even x are far more stable. This observation is explained in terms of the presence or absence of active sites.

1. Introduction

A promising area of research on nanoscale materials is the identification of clusters that could serve as the building blocks of new materials. Since the properties of clusters can be tailored by changing their size and composition, their use is expected to enable the formation of materials with desirable collective traits. The challenge, however, is to find stable clusters and the corresponding electronic principles governing their stability that could help in the systematic search for such species. For alkali metal clusters (Na_n clusters), the mass spectra in beams, obtained over twenty years ago,¹ showed that clusters containing 2, 8, 18, 20... electrons are particularly stable. It was shown that a simplified model,^{1,2} often termed “jellium” where the almost free valence electrons of the metal are subjected to a uniform potential, can account for their stability. Extending these investigations to systems combining metal atoms with other elements and developing rules that can guide the systematic search for stable species is an important step in the development of cluster assemblies.^{3–5}

In this work, we report an unusually abundant cluster (Al_7I^-) composed of seven Al and one I atom. The cluster appears in the mass spectra of aluminum halide clusters generated by reacting aluminum clusters with iodine. Its true magic nature is, however, revealed in experiments when iodized aluminum clusters are reacted with increasing amounts of methyl iodide. The mass spectra reveal Al_7I^- as the dominant product of this reaction. We show that the relative inertness of the cluster is derived from the stability of the neutral Al_7I which can be looked upon as a “jellium compound” formed by the interaction between a Al_7 superatom and an I atom. The neutral Al_7I , which is very stable, carries a large electric dipole moment, leading to a situation where the cluster has a high electron affinity of 2.09 eV. Such a process enables both the neutral and anionic clusters to simultaneously exhibit enhanced stability.

2. Experiment

Reactions leading to the current findings were carried out in the fast-flow tube apparatus, which has been previously described in detail.^{6,7} To summarize, clusters are generated in a constant flow laser vaporization (LaVa) source. The high purity helium carrier gas is introduced at a flow rate of 8000 standard cubic centimeters per minute (sccm), and the flow tube is maintained at a pressure of ~ 0.3 Torr by a high volume Roots pump. Clusters exiting the source are thermalized via collisions with the carrier gas and can be exposed to various gases introduced through one of two reactant gas inlets (RGIs). In the present

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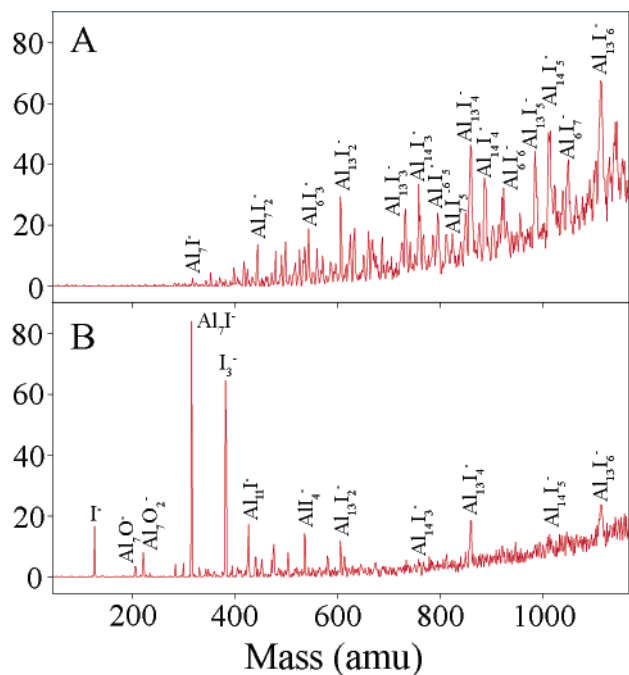


Figure 1. (A) $Al_nI_x^-$ clusters generated via reaction of Al_n^- with I_2 and (B) reacted with methyl iodide. Both spectra are shown on identical scales without normalization. Unlabeled peaks correspond to clusters with atomic oxygen or CH_3 present.

experiments, I_2 is generated via sublimation in the presence of a flow of He. The sublimation vessel is heated slightly to generate appropriate concentrations, and temperature and He flow are adjusted in order to achieve maximal signal intensity for the specific products of interest. Methyl iodide vapor is introduced similarly by passing a flow of helium over a room-temperature vessel containing the liquid. Reactants and products are sampled through a 1 mm orifice and analyzed via quadrupole mass spectrometry.

3. Experimental Results

Upon introduction of I_2 at the first RGI, the Al_n^- clusters react to generate a cluster distribution in which $Al_{13}I_x^-$ and $Al_{14}I_x^-$ constitute the major peaks (Figure 1A). When the products of this first reaction were exposed to methyl iodide, a drastic change in the mass spectrum was observed, as shown in Figure 1B.

We observed first that peaks corresponding to $Al_{13}I_x^-$ with odd x , as expected,⁵ disappear far more rapidly than those corresponding to $Al_{13}I_x^-$ with even x . In addition, we found that all $Al_{14}I_x^-$ were fairly reactive toward methyl iodide. Most notably, while in our recent investigations of iodized aluminum clusters we have consistently observed the formation of relatively high-mass clusters,^{4,5} in the present studies, the most intense peaks in the product spectrum were observed to appear in the lower mass region. Specifically, we found very intense peaks corresponding to I^- , I_3^- , and Al_7I^- . We reported previously that I^- is an important product in the reaction between Al_n^- and methyl iodide,⁶ and so its appearance here could be expected. Interestingly, the clusters of Al_n^- bound to I are not generated in such reactions. I_3^- appears as a product of the etching reaction described in detail in the next section.

The most abundant peak in the present distribution, Al_7I^- (which was previously observed to be a product of the oxygen etching of Al_nI^- clusters)⁴ will be treated in more detail below. The concentration of peaks in the lower mass region of the

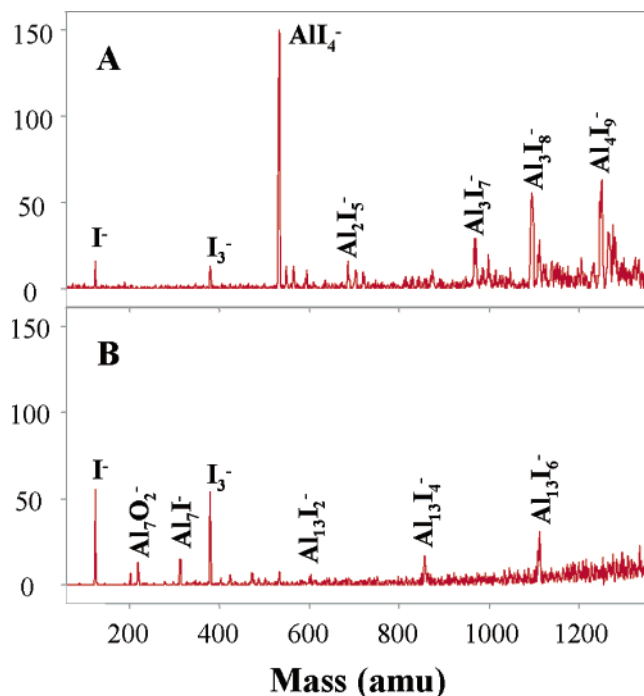


Figure 2. (A) Mass spectrum of I-rich $Al_nI_x^-$ clusters generated by increased heating of the I_2 vessel and then (B) reacted with methyl iodide. Both spectra are shown on identical scales without normalization.

spectra indicate an etching pathway, making it impossible to determine whether the $Al_{13}I_{2x}^-$ clusters are merely resistant to attack by methyl iodide, or whether they might be generated via etching of larger species. The peaks do not grow upon introduction of methyl iodide, and it cannot be determined whether the ion signal that persists originates solely from the initial $Al_{13}I_{2x}^-$ population, from $Al_{13}I_{2x+1}^-$ and $Al_{14}I_x^-$, or whether $Al_nI_x^-$ with larger n might play a role.

Attempts were made to increase the population of more I-rich species: the I_2 sublimation vessel was subjected to increased heating, and the He flow through this vessel was reduced. As a result, the mass distribution shown in Figure 2A was obtained. As was the case for the haloaluminate-like clusters generated via introduction of HI at the cluster source,² the species shown in Figure 2A were found not to be reactive toward oxygen. Note that we often observed the coexistence of $Al_{13}I_x^-$ clusters with I-rich $Al_nI_x^-$ species.

While a mass coincidence exists between Al_{10} and I_2O , we are confident in the assignment of the $Al_{13}I_x^-$ peaks; recall that I-rich clusters are familiar from the distributions obtained when trace HI is introduced at the cluster source and that the peaks corresponding to $Al_{13}I_x^-$ clusters are not endemic to that series.² A striking effect is observed when the I-rich clusters are subjected to reaction with methyl iodide, as is evident in Figure 2B. While most of the peaks in the distribution disappear, a sharp series corresponding to $Al_{13}I_{2x}^-$ emerges; this spectrum is actually nearly identical to the one seen in Figure 1B, except that the $Al_{13}I_{2x}^-$ clusters are now more prominent. The major products are again I^- , I_3^- , and Al_7I^- . Through experiments made when no $Al_{13}I_x^-$ peaks are present prior to reaction with methyl iodide, we see clearly that the $Al_{13}I_{2x}^-$ clusters are products of an etching reaction and not simply relatively resistant to attack by methyl iodide as could be inferred from the data in Figure 1. Due to the paucity of a broad distribution of $Al_nI_x^-$ with large

n in the mass window, the growth of the $\text{Al}_{13}\text{I}_{2x}^-$ peaks *must* be attributed to the etching by methyl iodide of I-rich Al_nI_x^- species with larger values of n . It is difficult to predict the exact structures and stoichiometries of our reactants, and we had difficulties in resolving and assigning peaks beyond about 1500 atomic mass units (amu), due at least partially to mass overlaps from various cluster sizes. Therefore, we cannot definitively identify the reactants that lead to the dramatic appearance of the I^- , I_3^- , Al_7I^- , and $\text{Al}_{13}\text{I}_{2x}^-$ products. What can be stated with certainty is that the formation of Al_7I^- and $\text{Al}_{13}\text{I}_{2x}^-$ clusters via etching with methyl iodide is quite favorable over a very wide range of starting reactants.

Our previous analyses^{4,5} and observations of active sites on $\text{Al}_{13}\text{I}_x^-$ and $\text{Al}_{14}\text{I}_x^-$ clusters lend themselves to a good understanding of the present results. Equipped with these principles and some knowledge of the surface chemistry of methyl iodide on aluminum (as described below), we can offer a detailed explanation of the chemical reactions observed here, the chemistry that leads to depletion of $\text{Al}_{13}\text{I}_{2x+1}^-$ and persistence of $\text{Al}_{13}\text{I}_{2x}^-$ is understood. While clusters with even numbers of I atoms are protected, the presence of active sites generated when the number of I atoms is odd leaves the clusters highly susceptible to chemical attack. The very intense peak at Al_7I^- , however, requires further scrutiny. To understand the enhanced stability of Al_7I^- , we carried out electronic structure studies on neutral and anionic Al_nI clusters using a first principles density functional approach.

4. Computational Methods

The calculations were carried out within a linear combination of atomic orbitals molecular orbital approach. Here, the molecular wave functions are expressed as a linear combination of atomic orbitals formed from a linear combination of Gaussian functions located at the atomic sites of the cluster. Further, gradient corrected density functionals were used for the exchange and correlation corrections.⁸ The actual studies employed the Naval Research Laboratory Molecular Orbital Library (NRLMOL) developed by Pederson and co-workers.^{9–11} In this approach, the Hamiltonian matrix elements are evaluated by numerical integration over a mesh of points. The basis set for Al had 6s, 5p, and 3d Gaussians; those for I had 8s, 7p, and 5d Gaussians. The basis sets were supplemented with a d-Gaussian. For details of the codes and the basis sets, the reader is referred to earlier papers.^{9–11}

5. Computational Results

To investigate the special nature of Al_7I^- , we first examined the change in stability of clusters in the vicinity of this size. To this end, we investigated the ground-state geometries and binding energies of neutral and anionic Al_nI clusters containing 5–8 Al atoms. To find the ground state, various possible initial arrangements were tried. In each case, starting from an initial configuration, the atoms were moved in the direction of forces until the forces dropped below a threshold value of 0.001 hartree/bohr. The search for the ground state included not only different geometries but also investigation of the possible spin multiplicities.

Figure 3A–C show the ground-state geometries of Al_nI^- clusters containing 6–8 Al atoms. In all cases, the I prefers to bind to a single Al atom and occupies an on-top site. Initial

configurations where the I atom was placed at a bridge site bonding to two Al atoms or to a hollow site where it bonded to three Al atoms were tried; however, in each case, the iodine moved to an on-top site during optimization. The Al–I bond length is around 2.6 Å and was found to be practically unchanged with increasing size. For an isolated AlI molecule, our calculations give a bond length of 2.59 Å. This shows that the molecular AlI bond length is maintained in the clusters. In all cases, the ground state had the lowest spin multiplicity. We also carried out studies on pure neutral and anionic Al_n clusters containing 6–8 Al atoms and found geometries similar to previously reported results.^{12,13} Comparing the iodized clusters to the pure clusters, the addition of I does change some of the Al–Al bond distances, but the geometrical shapes are largely unchanged. The main effect, however, appears in the electronic stability. To probe this we first calculated the following changes in energy:

$$\Delta_n^{\text{Al}} = E(\text{Al}_{n-1}\text{I}^-) + E(\text{Al}) - E(\text{Al}_n\text{I}^-) \quad (1)$$

$$\Delta_n^{\text{I}} = E(\text{I}) + E(\text{Al}_n^-) - E(\text{Al}_n\text{I}^-) \quad (2)$$

$$\Delta_n^{\text{AlI}} = E(\text{AlI}) + E(\text{Al}_{n-1}^-) - E(\text{Al}_n\text{I}^-) \quad (3)$$

$$\Delta_n^{\text{I}^-} = E(\text{I}^-) + E(\text{Al}_n) - E(\text{Al}_n\text{I}^-) \quad (4)$$

These energies correspond to the gain in energy in adding various units to the preceding cluster. Equivalently, these values can be considered as describing the energetics of various fragmentation pathways. In addition to the anions, we also studied the above fragmentations for neutral clusters. The results of these investigations are shown in Figure 3D and 3E for the anion and neutral case, respectively. A peak in the fragmentation channels is indicative of a very stable cluster. Considering only the lower energy fragmentation channels, irrespective of the fragment, neutral and anionic Al_7I are the most stable clusters.

In particular, if one considers the fragmentation leading to an Al atom, the neutral Al_7I exhibits an even more marked peak than the anion. The increased energy required for Al removal observed at Al_6I^- and Al_7I^- has particular relevance to these species previously observed as resistant to etching by O_2 ; assuming AlO_2 to be the most likely product in a sequential reaction, these results match perfectly with the experimental observations.^{4b} In the present calculations, the lowest fragmentation energy for the neutral Al_7I is higher than that of the anion, again underscoring the special stability of the neutral. We believe that the enhanced abundance of the Al_7I anion observed in the present experiments is related to the exceptional stability of the neutral. Can these enhanced stabilities be understood within a simple model?

6. Discussion

6.1. Stability of Al_7I . To make the arguments simpler, let us first focus on the neutral Al_7I . Within a simple jellium picture, clusters containing 2, 8, 18, 20, 34, 40 – electrons have closed electronic shells. Such clusters are particularly stable and relatively chemically inert. Since Al is trivalent, an Al_7 has 21 electrons, one more than the filled shell of 20 electrons. In the

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jellium picture, the cluster corresponds to an electronic configuration of $1s^2 1p^6 1d^{10} 2s^2 1f^1$. The I atom has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$. It is then interesting to probe the mechanism by which Al_7I acquires the added stability. To illustrate this we plot in Figure 4 the one-electron energy levels in I, Al_7 , Al_7I , Al_7^+ , and Al_7I^- . The arrows correspond to spin up and down states.

The continuous lines correspond to the filled levels while the dotted lines represent the unfilled levels. For Al_7 , we have only shown 19 states as the energy of the lowest two states is around -12.4 eV which is outside the scale. For I, Al_7 , and Al_7I , some of the levels are close in energy, and to facilitate the counting of the states, for each case, we have marked the degeneracy of states. A larger gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is generally a signature of the stability. Note that an I atom has an unfilled HOMO orbital while Al_7 has a small HOMO–LUMO gap of 0.79 eV. The formation of Al_7I proceeds by the interaction between the p-states of I and the HOMO (in a jellium picture) of Al_7 that has only one electron. This interaction leads to the formation of a bonding and antibonding pair. The bonding state lies in the occupied manifold of Al_7I (around -6.0 eV) while the antibonding state is raised in energy (around -2.0 eV). The bonding orbital is now filled with the single electron from the HOMO in Al_7 leading to a closed shell status for the Al_7I . This mechanism is easily seen by a comparison of the one electron levels in I, Al_7 , and Al_7I in Figure 4 where one can notice the displacement of the original 1f like jellium level in Al_7 in the formation of the complex that also results in an increase of the HOMO–LUMO gap to 1.74 eV. In fact, the transfer of an electron from the 1f state brings the HOMO–LUMO difference of Al_7I closer to that of Al_7^+ as seen from the Figure 4 which also shows the electron levels in Al_7^+ . We also show in Figure 3F and 3G the Mulliken population analysis of the total charge in Al_7I^- and Al_7I , respectively. Figure 3G then reveals that the I site carries a Mulliken charge of $-0.25 e^-$ while the Al site attached to the I site has a Mulliken charge of $+0.19 e^-$. In inorganic chemistry, it is common to find a central metal atom changing oxidation state to affect a specific shell filling depending upon the nature and number of the ligands with which it is compounded. The analogous situation, where a cluster (Al_7) can combine with another atom (I) to create a complex ($Al_7^+\delta I^-\delta$) is hereby called a jellium compound, and we believe that Al_7I is such an example. It is important to differentiate the concept of a jellium compound from the compound jellium model proposed by Leskiw *et al.*^{3c} to explain the stability of Al_7C^- . According to the compound jellium model, Al_7I would likely consist of Al_6 and AlI moieties bound by dipole interactions; the jellium compound that we describe here instead demonstrates a fundamental change in the properties of the “constituents” brought about by the chemical environment of the compound.

Our calculations show that the small charge transfer to I in Al_7I leads to an electric dipole moment of 1.10 au. As an extra electron is added leading to Al_7I^- , the HOMO–LUMO gap (see Figure 4) decreases as the extra electron occupies one of the f levels of the Al_7 cluster. To illustrate this, we show in Figure 3H the charge density of the HOMO in Al_7I^- which confirms that most of the charge is located around the Al_7 core. Indeed, the Mulliken population analysis in Figure 3F shows that only

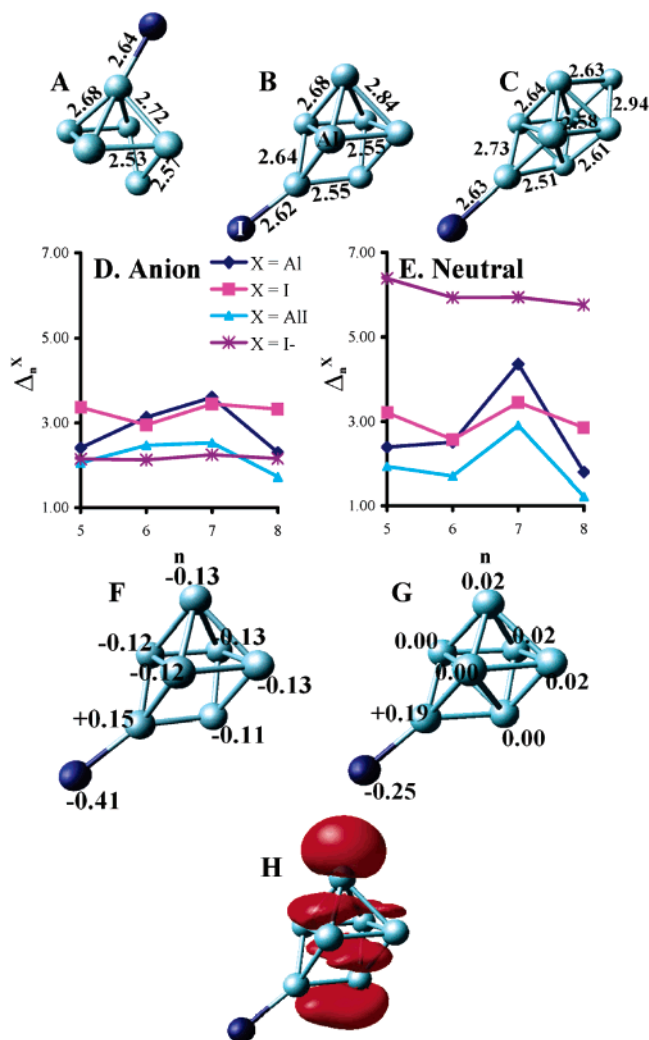


Figure 3. (A–C) Geometrical structure of Al_6I^- , Al_7I^- , and Al_8I^- clusters. The bond lengths are in Å. (D) The fragmentation energy Δ_n^X defined in eqs 1–4 to remove various fragments from Al_nI^- clusters. (E) The fragmentation energy Δ_n^X defined in eqs 1–4 to remove various fragments from neutral Al_nI clusters. The Mulliken population analysis for (F) Al_7I^- and (G) Al_7I . (H) The charge density of the HOMO in Al_7I^- .

$0.16 e^-$ charge of the added electron appears at the I site while $0.84 e^-$ charge is distributed to the Al_7 sites. The Mulliken charge shows that the cluster now resembles an $Al_7^{-0.6}$ bound to $I^{-0.4}$. The extra electron is thus bound to the dipole, and this provides added stability to the electronic charge. We believe that this is the reason that the Al_7I^- continues to be stable even though the addition of an electron to a closed shell cluster generally results in a reactive species. As a quantitative indication of the binding of the extra electron to the positive core, our calculations show that the cluster has an appreciable adiabatic electron affinity of 2.09 eV. We believe that it is this dipolar bonding that enables both the neutral and the anions to be simultaneously stable.

6.2. Chemistry of $Al_nI_x^-$ and Methyl Iodide. We now discuss the reactivity of the $Al_nI_x^-$ clusters with methyl iodide. In an earlier work, we had shown that the aluminum clusters are not susceptible to etching with methyl iodide.^{6,14} Significantly, the present work demonstrates that $Al_{13}I_n^-$ clusters undergo reactions with methyl iodide due to the presence of

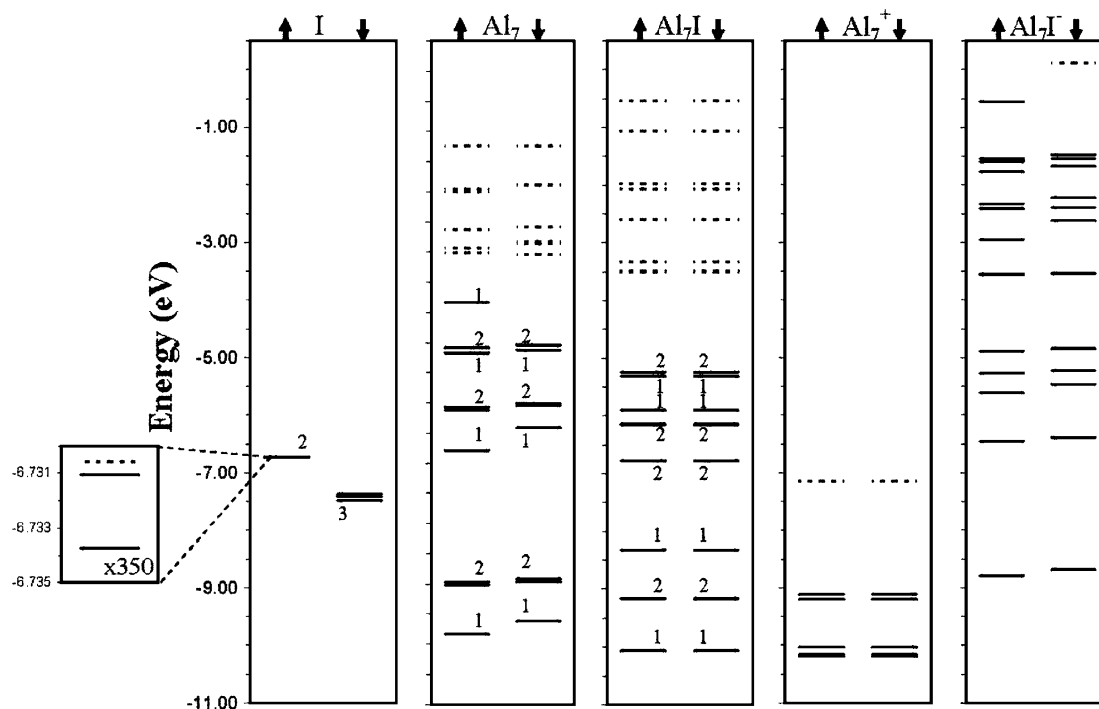
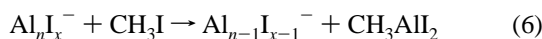


Figure 4. Electron energy levels for I, Al₇, Al₇I, Al₇⁺, and Al₇I⁻. Filled electron levels are indicated by a solid line, and a dotted line refers to unfilled levels. A number 1, 2, or 3 indicates the degeneracy type for filled electron levels.

active sites. The interaction of methyl iodide with bulk aluminum has been studied in some detail due to the synthetic importance of various Grignard-type reactions and due to relevant processes in chemical vapor deposition of components for microelectronic devices.^{15–18} The most prevalent reactions in bulk synthesis (industrially important to the production of aluminum sesquihalides) are of the type

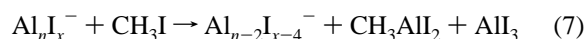


This type of reaction would not be expected to occur in cluster experiments with bare Al_{*n*}⁻ as it would require the adsorption of three methyl iodide molecules at one site on the cluster surface. This reaction is, however, very relevant to the cluster reactions described in the present work. In our current experiments, the presence of I on the surface of the Al_{*n*}I_{*x*}⁻ clusters serves to facilitate the formation of CH₃AlI₂ without the necessity of multiple reactive collisions with methyl iodide molecules according to

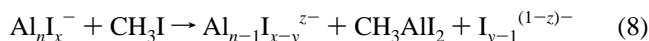


The introduction of a preexisting source of I atoms on the surface of the clusters effectively solves the problems of kinetics by eliminating the need for prolonged or coincident adsorption of methyl iodide and provides a clear example of chemical activation via I introduction in a vein similar to that described in ref 4. Further, in more I-rich clusters, the dissociative adsorption of methyl iodide could potentially lead to pathways

such as



or even



where $y = 2$ or 4 and $z = 0$ or 1 . Note that the etching reactions can account for the observation of I⁻ and I₃⁻ in the product spectra. We first examine reaction 6. The theoretical studies indicate that the energy gained in adding an AlI to CH₃I is 2.47 eV. Further, the energies required to remove an AlI molecule from Al₆I⁻, Al₇I⁻, and Al₈I⁻ are 2.47, 2.53, and 1.72 eV, respectively. From the energetics alone, it is clear that Al₇I⁻ would be stable against the removal of AlI. Considering this reaction pathway, it is obvious why Al₇I⁻ would be the terminal product; as larger species are sequentially etched, they encounter a bottleneck at the Al₇I⁻ size, so that even though the Al₆I⁻ is on the cusp of stability (with respect to reaction with methyl iodide), it is not populated by the etching of larger species which have stopped reacting upon being reduced to Al₇I⁻. The primary barrier to reaction in the etching pathways in eqs 7 and 8 is the removal of Al atoms from a cluster. As shown previously, the energy required to remove an Al from Al₇I⁻ is higher than those of the neighboring sizes so that these reactions may not be energetically accessible. The magic peak at Al₇I⁻ is thus explained in terms of electronic stability manifested in the form of chemical nobility.

7. Conclusions

We have studied the reaction of Al_{*n*}I_{*x*}⁻ clusters with methyl iodide, explaining how these reactions differ dramatically from the previously reported reactions with bare Al_{*n*}⁻ clusters. The I atoms of the Al_{*n*}I_{*x*}⁻ clusters enable reaction pathways closely

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resembling those known to occur on aluminum surfaces. The dependence of the reaction kinetics on methyl iodide adsorption was addressed in relation to known properties of the surface reactions. In the cluster regime, we have shown that these etching reactions preferentially produce (from a very broad range of reactants) several clusters, including $Al_{13}I_{2x}^-$ and Al_7I . Thus, a new scheme for the generation of the superpolyhalides is identified, and the mechanism for the stability of Al_7I^- is elucidated. It is possible that, under appropriate reaction conditions, a bulk synthesis of these clusters could be achieved from an appropriate haloaluminate and alkyl halide. We have also further established the idea that superatomic clusters can be activated by the addition of appropriate ligands. Whereas bare Al_{13}^- is unreactive toward methyl iodide, the activated $Al_{13}I_{2x+1}^-$ species are shown to be quite susceptible to attack

by the same reactant. Finally, we have demonstrated the emergence of a jellium compound cluster in the description of magic Al_7I^- , which is shown to form from two stable moieties to which an electron is added. We believe that the chemistry of aluminum clusters holds great potential for the development of future nanostructured materials, and we expect that the richness of this system will also provide many lessons of importance to the broader field of cluster science.

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