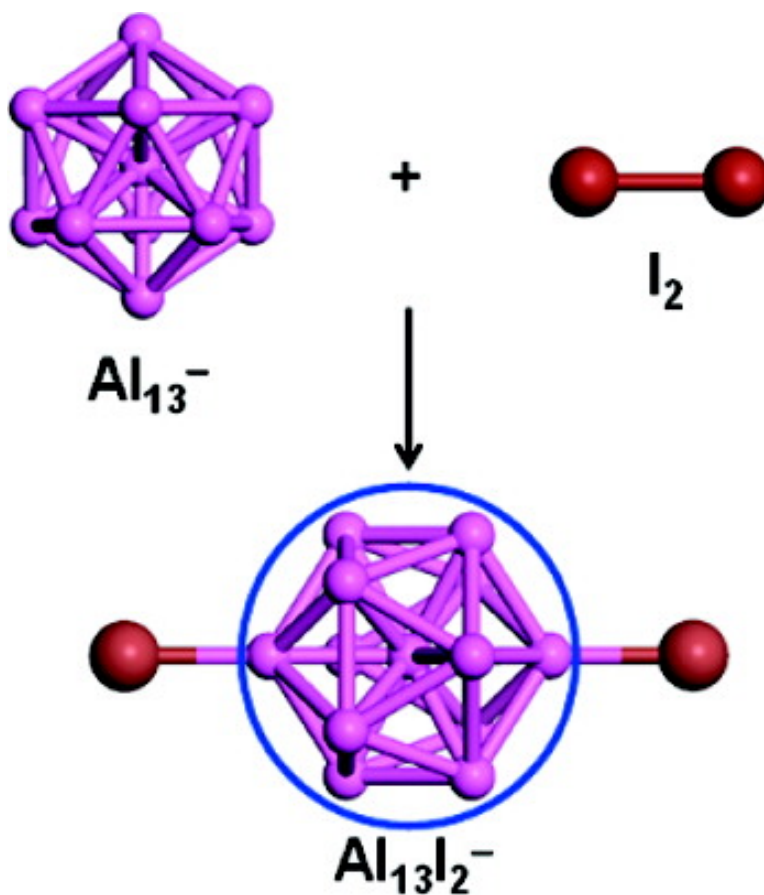


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## Does the “Superatom” Exist in Halogenated Aluminum Clusters?

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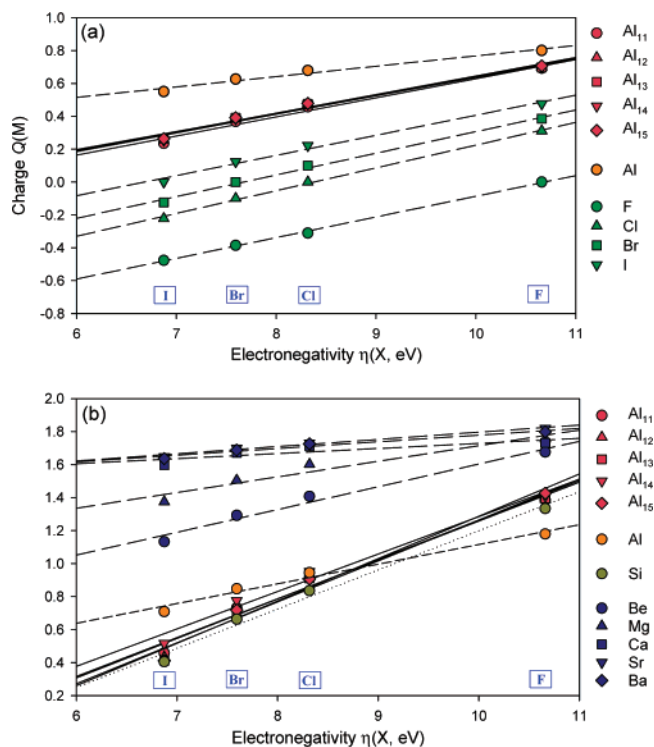
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Superatom chemistry is now one of the hot issues in cluster science. “Superatoms” are clusters of atoms that seem to exhibit some of the properties of element atoms. The superatom suggestion is that free electrons in the cluster occupy a new set of orbitals that are defined by the entire group of atoms rather than by each individual atom separately. Trivalent aluminum in bulk is a nearly free electron metal. Thus, the jellium model applies to the electronic structures of aluminum clusters.<sup>1</sup>

Bergeron et al.’s findings<sup>2</sup> are remarkable in that certain aluminum clusters appear to exhibit superatom properties in chemical reactions with iodine molecules. The authors reported that the  $\text{Al}_{13}\text{I}_2^-$  ( $\text{Al}_{13}^- \cdot 2\text{I}$ ) cluster behaves chemically like the triiodide ion. The  $\text{Al}_{13}$  cluster has a high electron affinity (EA) of 3.57 eV, and therefore, the aluminum cluster is called a superhalogen.<sup>2</sup> Similarly, it has been noted that  $\text{Al}_{14}$  clusters with 42 electrons appear to exhibit the properties of an alkaline earth metal, which typically adopts a +2 valence state. The  $\text{Al}_{14}\text{I}_3^-$  cluster has a total of 43 valence electrons, but the three iodine atoms each remove one of the electrons to leave 40 electrons in the jellium model ( $\text{Al}_{14}^{2+} \cdot 3\text{I}^-$ ). These observations revealed a new form of superatom chemistry, in which superatoms behave like atoms when they react with other molecules. Subsequently, many experimental and theoretical studies of superatom complexes have been performed,<sup>3</sup> but we note that it remains unclear whether superatom chemistry really exists, particularly for metal cluster systems with a few electronegative elements attached, such as  $\text{Al}_{13}\text{I}_2^-$  and  $\text{Al}_{14}\text{I}_3^-$ .<sup>4</sup> In this paper, we study halogenated  $\text{Al}_n$  ( $n = 11-15$ ) complexes to clearly examine the issue of whether  $\text{Al}_n$  clusters exhibit multiple atomic characteristics depending upon  $n$ . For the pure clusters, one can conclude that  $\text{Al}_{13}$  and  $\text{Al}_{14}$  have superhalogen and superalkaline earth characteristics, respectively (see Figure S1).

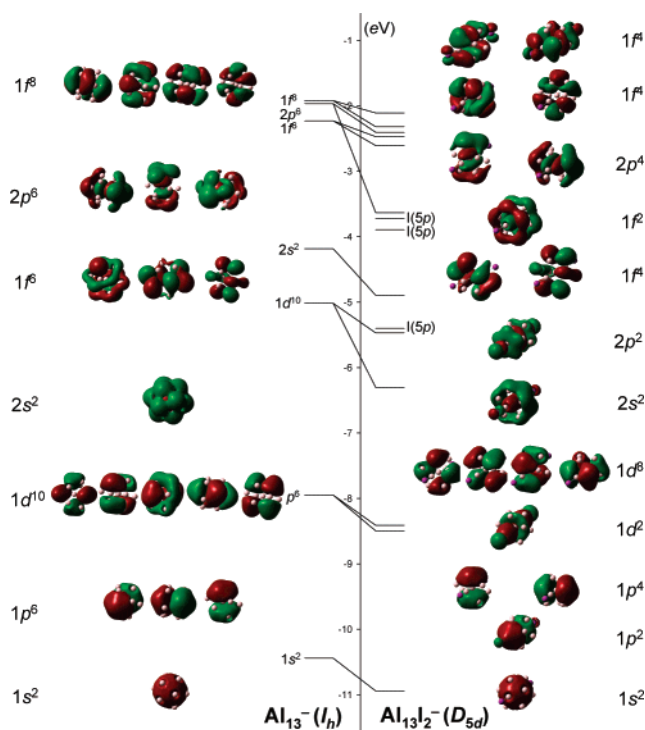
We seek to observe any superatom behavior of  $\text{Al}_{13}$  and  $\text{Al}_{14}$  in  $\text{MX}$  and  $\text{MX}_2$  systems ( $M = \text{Al}_{11}-\text{Al}_{15}$ ,  $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).<sup>5</sup> Figure 1 shows the charge distributions ( $Q$ ) versus the electronegativity ( $\eta$ ) of  $X$ .<sup>6</sup> There is a linear relationship between the charge separation and electronegativity of  $X$  in all cases.<sup>7</sup> A significant charge transfer occurs from  $\text{Al}_n$  to  $X$  in all of the  $\text{MX}$  and  $\text{MX}_2$  systems, which can be explained by  $\eta$  rather than EA. The  $\eta$  values for the  $\text{Al}_n$  clusters are 4.08–4.66 eV, much less than those of halogen atoms, 6.87–10.66 eV, although they are larger than the  $\eta$  value for Al of 3.14 eV. We plotted  $Q(M)$  of  $\text{MX}$  for  $M = \text{Al}, \text{Al}_n$ , and halogen atoms (Figure 1a) to explore any superhalogen behavior of  $\text{Al}_{13}$ . It is worth noting that the  $Q(\text{Al}_{13})$  values of  $\text{Al}_{13}\text{X}$  are nearly equal to those of neighboring clusters of  $\text{Al}_{13}\text{X}$ , with no prominent features. The variation of charge with respect to  $n$  is very small, less than 0.02 e. The  $Q(\text{Al}_n)$  values are between  $Q(\text{Al})$  and  $Q(X)$  and  $\text{Al}_{13}$  seems not to show any characteristics of halogen atoms, where the  $\text{Al}_n\text{X}$  clusters are  $\text{Al}_n^{\delta+}\text{X}^{\delta-}$  electronically for  $n = 11-15$ . We plotted  $Q(M)$  of  $\text{MX}_2$  for  $M = \text{Al}, \text{Al}_n, \text{Si}$ , and alkaline earth atoms (Figure 1b) to explore any superalkaline earth behavior of  $\text{Al}_{14}$ . The  $Q(\text{Al}_n)$  values show a maximum for  $n = 14$ , except for  $X = \text{F}$ , but the variation in charge with respect to  $n$  is also small, less than 0.11 e. The  $\text{Al}_n\text{X}_2$  ( $n = 11-15$ ) clusters have



**Figure 1.**  $Q(M)$  versus  $\eta(X = \text{F}, \text{Cl}, \text{Br}, \text{I})$  for (a)  $\text{MX}$  ( $M = \text{Al}_{11}-\text{Al}_{15}$ , Al, halogen atoms) and (b)  $\text{MX}_2$  ( $M = \text{Al}_{11}-\text{Al}_{15}$ , Al, Si, alkaline earth atoms). The data of  $\text{Al}_{11}$  through  $\text{Al}_{15}$  basically coincide without revealing any exceptions for  $\text{Al}_{13}$  or  $\text{Al}_{14}$ . The numerical values are summarized in Table S1.

the electronic structure  $\text{Al}_n^{\delta+}2\text{X}^{\delta-}$ . There is no evidence of an alkaline earth superatom in the  $\text{Al}_{14}$  clusters. Reveles et al.<sup>4f</sup> reported that  $\text{Al}_7^-$  is a multivalent superatom, showing atomic behavior analogous to Si. We found that the  $Q(\text{Si})$  values are in excellent agreement with the  $Q(\text{Al}_n)$  values, as shown in Figure 1b. In this respect, those  $\text{Al}_n$  clusters, as well as  $\text{Al}_7^-$ , seem to be analogous to Si. The  $\eta(\text{Si})$  value of 4.66 eV is similar to the  $\eta$  values of  $\text{Al}_n$ , supporting the view that electronegativity is a more relevant factor than EA in describing the charge distribution of such halogenated cluster systems.

We evaluated the charge distributions of  $\text{Al}_n\text{I}_2^-$  and  $\text{Al}_n\text{I}_3^-$  (Table S2)<sup>5</sup> because the  $\text{Al}_{13}\text{I}_2^-$  and  $\text{Al}_{14}\text{I}_3^-$  clusters were detected as magic clusters in the mass spectrometry experiment.<sup>2</sup> The  $Q(\text{Al}_n)$  variation in the  $\text{Al}_n\text{I}_2^-$  ( $-0.42$  to  $-0.32$ ) and  $\text{Al}_n\text{I}_3^-$  ( $-0.10$  to  $-0.01$ ) clusters is also small, less than 0.10 e. We conclude from our analysis that there are no theoretical grounds to regard  $\text{Al}_{13}\text{I}_2^-$  as  $\text{Al}_{13}^- \cdot 2\text{I}$ . No superatomic characteristics of  $\text{Al}_{13}$  and  $\text{Al}_{14}$  in comparison with those of their neighbors are shown. In  $\text{Al}_{13}\text{I}^-$ , the extra electron is strongly localized on the  $\text{Al}_{13}$  core, which was explained by the superhalogen nature of  $\text{Al}_{13}$ .<sup>4a</sup> However, such localization on the  $\text{Al}_n$  clusters is observed for all the  $\text{Al}_n$  iodide clusters. The additional electron is localized predominantly on the  $\text{Al}_n$  cores of  $\text{Al}_n\text{I}^-$  (0.88–0.93 e) and  $\text{Al}_n\text{I}_2^-$  (0.76–0.84 e). We believe that this localization



**Figure 2.** Molecular orbital (MO) diagram for  $\text{Al}_{13}^-$  and  $\text{Al}_{13}\text{I}_2^-$ .

**Table 1.** Cluster Molecular Orbital Energies (in eV)<sup>a</sup>

| shell | $\text{Al}_{13}^-$ | $\text{Al}_{13}\text{I}_2^-$ | $\text{Al}_{15}^-$ | $\text{Al}_{15}\text{I}_2^-$ |
|-------|--------------------|------------------------------|--------------------|------------------------------|
| 2p    | -1.97              | -2.81 (-0.84)                | -3.03              | -3.79 (-0.76)                |
| 1f    | -2.05              | -2.36 (-0.31)                | -2.56              | -3.16 (-0.60)                |
| 2s    | -4.18              | -4.90 (-0.72)                | -4.53              | -4.86 (-0.33)                |
| 1d    | -5.02              | -5.63 (-0.61)                | -5.64              | -6.14 (-0.50)                |
| 1p    | -7.95              | -8.44 (-0.49)                | -8.27              | -8.73 (-0.46)                |
| 1s    | -10.44             | -10.94 (-0.50)               | -10.55             | -10.96 (-0.41)               |

<sup>a</sup> Average values for the shells. The values in the parentheses refer to the energy changes by iodine atoms.

does not correlate with any superatomic behavior but has a simple electrostatic explanation.<sup>4c</sup> Now, we explain the abundance of  $\text{Al}_{13}\text{I}_2^-$  and  $\text{Al}_{14}\text{I}_3^-$  in the mass spectrometry experiment. It is known that the experimentally observed  $\text{Al}_{13}\text{I}_n^-$  (even  $n$ ) and  $\text{Al}_{14}\text{I}_n^-$  (odd  $n$ ) have enhanced chemical stabilities because of their large highest-occupied and lowest-unoccupied molecular orbital (HOMO–LUMO) gaps. The HOMO–LUMO gaps of  $\text{Al}_n\text{I}_2^-$  and  $\text{Al}_n\text{I}_3^-$  with  $n = 11–15$  also exhibit a prominent even–odd oscillation (see Figure S7). We ascribe such stability to the fact that even numbers of valence electrons can electronically stabilize the corresponding cluster with their pairing energy. The highly symmetric  $\text{Al}_{13}\text{I}_2^-$  ( $D_{5d}$ ) and  $\text{Al}_{14}\text{I}_3^-$  ( $C_{3v}$ ) clusters have conspicuously large HOMO–LUMO gaps of 1.69 and 1.37 eV, respectively, comparable to that of the magic cluster  $\text{C}_{60}$  (1.65 eV). Hence, the stability of halogenated aluminum clusters can be explained by the magic nature of the clusters, rather than by superatom chemistry.

We compare the molecular orbitals (MO) of  $\text{Al}_{13}^-$  and  $\text{Al}_{13}\text{I}_2^-$  in Figure 2 and summarize the MO energies in Table 1. If a minor perturbation of the metal clusters by the ligand leaves the electronic shell structures unchanged, the jellium model should remain fundamentally valid. However, our MO analysis shows that the presence of iodines, somewhat surprisingly, leads to loss of degeneracy of electronic states in the cluster orbital shells, particularly the 2p shell. It is worth noting that the MO energies are significantly decreased in the presence of two attached iodines, 0.31–0.84 eV, typical of strong binding with electronegative elements.<sup>8</sup> Our MO analysis implies the formation of a ligand-stabilized metal cluster

complex for  $\text{Al}_{13}\text{I}_2^-$ . For comparison, we obtained the MO of  $\text{Al}_{15}^-$  and  $\text{Al}_{15}\text{I}_2^-$ , which have a closed-shell high-symmetry structure (see Figure S9). We stress that the MO perturbation by two iodines for  $\text{Al}_{15}^-$  is found to be quite similar to that for  $\text{Al}_{13}^-$ , as shown in Table 1. The changes in MO energies of  $\text{Al}_{13}^-$  and  $\text{Al}_{15}^-$  are similar overall except for the 1f and 2s orbitals. The discrepancies in the 1f and 2s orbitals are ascribed to the more effective orbital overlap of  $1f_{z^2}$  with iodines than 2s in the ellipsoidal  $\text{Al}_{15}\text{I}_2^-$  form. One can easily predict that the jellium-like features would deteriorate with decreasing cluster symmetry or an increased number of attached electronegative elements. The geometrical symmetry of a cluster is a crucial factor in determining the validity of the electron-counting picture for that cluster. These MO analyses strongly support the notion that  $\text{Al}_n$  clusters do not have multiple characteristics depending upon  $n$ . The Al clusters are electropositive and form stable complexes with electronegative elements or ligands. It should be mentioned that Schnöckel et al.<sup>9</sup> have synthesized various types of  $\text{Al}_n\text{--L}_m$  complexes (named “metalloid” complexes), where L is usually an electronegative ligand. We conclude that these metalloid complexes are formally described by an  $\text{Al}_n^{\delta+}$  core with attached  $m\text{L}^{\delta-}$  ligands, irrespective of  $n$ .

The superatom concept would be useful only for describing systems with minimal electronic and geometric perturbation, such as  $\text{Al}_{13}^-\text{K}^+$ .<sup>3c</sup> We hope that this work will stimulate researchers to look for novel systems, in which a superatom does behave like an atom when it reacts with other molecules.

**Acknowledgment.** We thank Dr. Andreas Schnepf for helpful comments.

**Supporting Information Available:** Complete ref 9d and computational details. The optimized structures and relative energies of  $\text{Al}_n^q$  ( $n = 11–15$ ,  $q = -1, 0, 1, 2$ ),  $\text{Al}_n\text{X}$ ,  $\text{Al}_n\text{X}_2$  ( $n = 11–15$ ,  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ),  $\text{Al}_n\text{I}_2^-$ , and  $\text{Al}_n\text{I}_3^-$  ( $n = 11–15$ ). The MO diagram and energies of  $\text{Al}_{13}\text{K}^-$ ,  $\text{Al}_{15}^-$ , and  $\text{Al}_{15}\text{I}_2^-$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) Optimized geometries and relative energies are summarized in Figures S2–S6.
- (6) The  $\eta$  values were obtained as one-half of the sum of IP and EA.
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