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Structure and electronic properties of $Al_{13}X$ (X=F, Cl, Br, and I) clusters

Jaehoon Jung, Jong Chan Kim, and Young-Kyu Han*

Computational Chemistry Laboratory, Corporate R&D, LG Chem, Ltd. Research Park, Daejeon 305-380, Korea

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Theoretical electronic structure studies on the neutral $Al_{13}X$ (X=F, Cl, Br, and I) clusters have been carried out using a gradient-corrected density functional approach. A low-symmetry (ontop: C_s) isomer is found to be the most stable for the $Al_{13}X$ clusters. The shape of the Al_{13} moieties in the C_s isomers is significantly distorted from the highly symmetric icosahedral structure and is similar to the Al_{13} cationic structure. The binding energy between Al_{13} and the halogen atoms increases as X goes from I (2.96 eV) to F (5.79 eV). Population analysis shows that the bonding of Al_{13} to the halogen atoms is predominantly ionic. We found that there is a linear relationship between the binding energy of $Al_{13}-X$ and the electronegativity of X. From the calculated binding energies and highest occupied molecular orbital–lowest unoccupied molecular orbital gaps, we conclude that the $Al_{13}X$ clusters are kinetically and thermodynamically stable. The structure of $Al_{13}X^-$ clusters is highly symmetric (ontop: C_{5v}), implying that the cluster's extra electron is localized in the Al_{13} moiety.

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I. INTRODUCTION

Cluster physics has been a subject of intense research activity in recent years, because of such potential technological applications as fabrication of materials with desired properties.[1–5] Atomic metal clusters have dramatically different physical and chemical properties from the bulk, which is described by band theory, because of the high surface-area-to-volume ratio and the large energy gap near the highest occupied molecular orbital (HOMO). In particular, those clusters with a particular number of valence electrons show enhanced stability against dissociation. These clusters are termed "magic" clusters. The stability of such clusters is governed by two important factors: electronic and geometric shell closure. The spherical jellium model predicts that clusters with 2, 8, 20, 40,… valence electrons have higher stability because of the closure of electronic shells.[6–8] For example, Al_{13}^- has 40 electrons and can satisfy closure of the 2p shell. The precipitous drop in the mass-ion peak intensity after Al_{13}^- indicates that it is a very stable cluster.[9]

One of the important aspects of cluster science is the interaction of clusters with other atoms—*superatom-atom interaction*[10]—in determining their stability, as well as their catalytic properties. A pure Al_{13} cluster is a 39-electron system, short by just one electron of forming a closed-shell configuration. For this reason, many researchers have studied ways of doping Al_{13} in order to form highly stable closed-shell clusters such as $Al_{13}M$, where M is a monovalent atom such as an alkali[11–18] or coinage[19–21] metal.

On the other hand, Al_{13} is known to bind strongly with a hydrogen atom[5,22–27] or an iodine atom,[28] and the $Al_{13}H$ (Ref. 29) and $Al_{13}I$ (Refs. 31 and 32) clusters are highly stable and abundant, as observed experimentally. In contrast to $Al_{13}M$ (M=alkali metals), there is a transfer of charge from the Al_{13} cluster to the hydrogen atom[26,27] or the iodine atom.[28,31] The Al_{13} moiety of $Al_{13}M$ retains icosahedral (or decahedral) geometry, which is due to charge transfer from M to Al_{13}. Han and Jung[28] reported that a low-symmetry structure (ontop: C_s) is the most stable form for $Al_{13}I$ clusters, while its anion is highly symmetric. Density functional theory (DFT) calculations[28] show that the C_s-ontop $Al_{13}I$ isomer is more stable than the high-symmetry (bridge: C_{2v}) isomer by 0.2–0.4 eV. Bergeron *et al.*[31] reported, however, that the C_s-ontop isomer is very slightly unstable relative to the C_{2v}-bridge isomer, although the authors did not specify the relative energy. Recently, Bergeron *et al.*[10] presented experimental evidence for the formation of a class of polyhalide molecules by replacing an I atom in traditional polyiodides

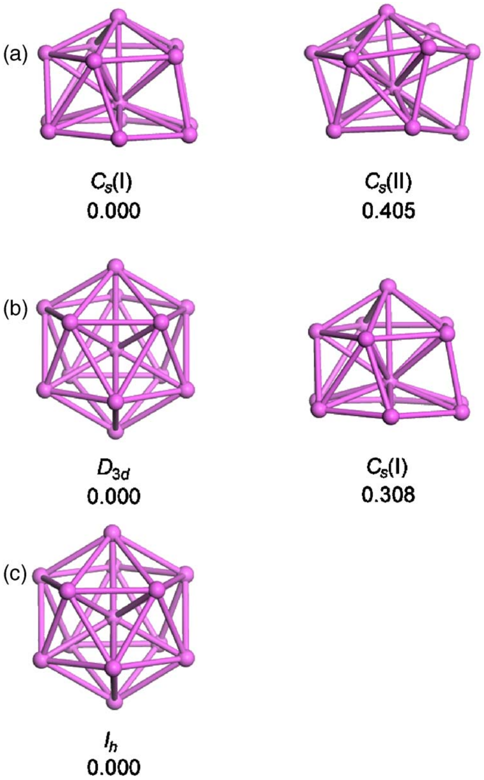

FIG. 1. (Color online) PBE optimized structures of (a) cationic, (b) neutral, and (c) anionic Al_{13} clusters. The relative energies are given in eV.

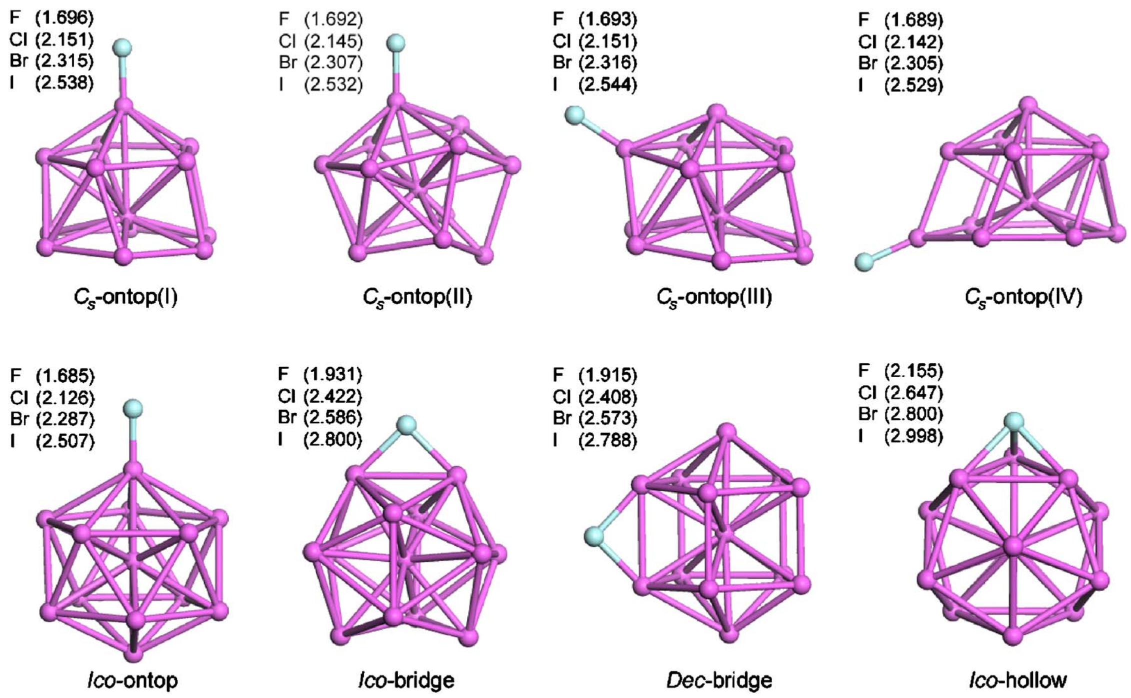

FIG. 2. (Color online) PBE optimized structures of $Al_{13}X$ (X=F, Cl, Br, and I). The bond distances between halogen atom and its neighboring Al atom are given in Å.

with an Al_{13} cluster. Hence, there is a growing interest in Al_{13} clusters with attached electronegative atoms.[10,30] To the best of our knowledge, there has been no attempt to study the binding of Al_{13} with all the halogen atoms in a systematic way.

In the present study, we have performed very extensive DFT calculations for the various low-lying $Al_{13}X$ (X=F, Cl, Br, and I) cluster isomers. Several questions are of interest: (1) Does the structure of Al_{13} undergo significant modification as the halogen atoms are attached?, (2) How does the binding energy change as one goes from Al_{13}-I to Al_{13}-F?, (3) Does the binding between Al_{13} and X originate because of charge transfer?, and (4) How does the structure change as an electron enters the $Al_{13}X$ clusters?

II. COMPUTATION DETAILS

Kohn-Sham DFT calculations were performed with the gradient-corrected exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE).[32] The correlation-consistent triple-ζ (cc-pVTZ) (Ref. 33) basis set was used. Scalar relativistic effects were treated with the energy-consistent small-core (25 valence electrons) pseudopotentials for the heavy halogen atoms, Br and I.[34] All of the vibrational frequencies have been calculated using the analytic second derivative evaluation of the energy to judge whether the structure is a local minimum or not. Natural population analysis (NPA) (Ref. 35) calculations were performed to estimate quantitatively the charge transfer from Al_{13} to X. All the calculations were carried out with the GAUSSIAN03 program.[36]

III. RESULTS AND DISCUSSION

We considered nine low-lying structures of Al_{13} with a halogen atom on a bridge, hollow, or ontop site as the initial structures in the geometry optimization. The Al_{13} structures were adopted from the low-lying structures of Al_{13}^+ and Al_{13}^-, as well as Al_{13}. Geometry optimizations were performed starting from a total of 150 initial structures—39 ontop, 68 bridge, and 43 hollow forms—at the PBE level of theory. One, two, and three Al atoms bind with the X atom for the ontop, bridge, and hollow structures, respectively. The PBE optimized structures of Al_{13}^+, Al_{13}, and Al_{13}^- considered here were determined along with the relative energies (Fig. 1). It is known that the ground-state structures of Al_{13}^+, Al_{13}, and Al_{13}^- are C_s(I),[27,37] D_{3d} (slightly Jahn-Teller distorted icosahedron),[22,26,27] and I_h,[26,27,38] respectively. It should be noted that the shapes of the two stable Al_{13}^+ clusters are significantly distorted from the highly symmetric icosahedral structure.

We display the structures and relative energies for eight low-lying isomers—five ontop, two bridge, and one hollow forms—of $Al_{13}X$ clusters in Fig. 2. The binding energy, relative energy, HOMO–LUMO gap (where LUMO denotes lowest unoccupied molecular orbital), number of imaginary frequencies, and natural populations of $X[Q(X)]$ are summarized in Table I. It is worth noting that only the C_s-ontop structures are local minima, whereas the bridge and hollow isomers are saddle points in the potential energy surface, and the C_s-ontop(I) isomer is the most stable for all the $Al_{13}X$ clusters. The relative energy between C_s-ontop(I) and *Ico*-bridge (C_{2v}) isomers increases as the charge transfer from Al_{13} to X increases, i.e., 0.17 and 0.57 eV for X=I and F, respectively. The Al_{13} moieties of C_s-ontop(I) and C_s-ontop(II) isomers are similar to the first C_s(I) and second C_s(II) stable isomers of the Al_{13}^+ clusters, respectively. We mention that the reported ground-state structures for $Al_{13}Cl$ and $Al_{13}I$ in Ref. 31 correspond to the C_s-ontop(II) and *Ico*-bridge isomers in this work, respectively.

TABLE I. Binding energy, relative energy, HOMO–LUMO (HL) gap, number of imaginary frequencies (NIMAG), and natural populations of X [$Q(X)$] for various possible isomers of $Al_{13}X$ (X=F, Cl, Br, and I). All energies are given in eV.

		C_s-ontop(I)	C_s-ontop(II)	C_s-ontop(III)	C_s-ontop(IV)	*Ico*-ontop	*Ico*-bridge	*Dec*-bridge	*Ico*-hollow
Binding Energy	$Al_{13}F$	5.785	5.581	5.519	5.465	5.256	5.211	5.181	4.803
	$Al_{13}Cl$	4.099	3.907	3.787	3.736	3.626	3.655	3.550	3.451
	$Al_{13}Br$	3.533	3.354	3.211	3.160	3.088	3.208	3.079	3.070
	$Al_{13}I$	2.956	2.804	2.615	2.562	2.560	2.786	2.626	2.711
Relative Energy	$Al_{13}F$	0.000	0.204	0.266	0.319	0.529	0.574	0.603	0.982
	$Al_{13}Cl$	0.000	0.192	0.312	0.363	0.472	0.444	0.549	0.648
	$Al_{13}Br$	0.000	0.179	0.322	0.373	0.444	0.325	0.454	0.463
	$Al_{13}I$	0.000	0.152	0.342	0.395	0.397	0.170	0.330	0.246
HL Gap	$Al_{13}F$	1.525	1.486	1.105	1.108	0.512	0.965	0.998	1.166
	$Al_{13}Cl$	1.524	1.493	1.097	1.108	0.580	1.151	1.173	1.276
	$Al_{13}Br$	1.521	1.432	1.090	1.106	0.584	1.148	1.191	1.271
	$Al_{13}I$	1.512	1.413	1.076	1.102	0.603	1.187	1.255	1.313
NIMAG	$Al_{13}F$	0	0	0	0	2	2	2	2
	$Al_{13}Cl$	0	0	0	0	2	1	2	2
	$Al_{13}Br$	0	0	0	0	2	1	2	2
	$Al_{13}I$	0	0	0	0	2	1	2	2
$Q(X)$	$Al_{13}F$	−0.698	−0.701	−0.706	−0.707	−0.688	−0.715	−0.720	−0.720
	$Al_{13}Cl$	−0.476	−0.466	−0.484	−0.482	−0.439	−0.427	−0.431	−0.445
	$Al_{13}Br$	−0.391	−0.370	−0.399	−0.396	−0.339	−0.310	−0.324	−0.328
	$Al_{13}I$	−0.263	−0.226	−0.272	−0.270	−0.190	−0.130	−0.148	−0.148

The bond strength between the Al_{13} cluster and halogen atoms significantly increases as X goes from I (2.96 eV) to F (5.79 eV), namely, the binding is stronger as the electronegativity of the attached atom is larger. It is worth noting that the bond strength of $Al_{13}-X$ is large, considering the PBE binding energies (2.39–2.78 eV) for the experimentally observed $Al_{13}Li$, $Al_{13}Na$, $Al_{13}K$, $Al_{13}Cs$,[18] $Al_{13}Cu$,[20] and $Al_{13}H$.[27] The large binding energies can be explained by strong Al-X bindings. Table II shows the binding energies, bond lengths, and NPA results for AlX (X=F, Cl, Br, and I) molecules. The calculated results are in good agreement with the experimental[39] values. The binding energy of $Al_{13}X$ has a trend very similar to AlX with systematically lower absolute values by about 1.0 eV. Such discrepancies can be ascribed to the different electronegativities of atom (Al) and superatom (Al_{13}). According to our calculations, the electronegativities of Al and Al_{13} are 3.14 and 4.67 eV, respectively, obtained as one-half of the sum of the ionization potential and the electron affinity.[40]

To understand the electronic structure of $Al_{13}X$ and its influence on the binding energy of X to Al_{13}, we studied the NPA charge of the X atom, $Q(X)$. The $Q(X)$ values are $-0.70e$, $-0.48e$, $-0.39e$, and $-0.26e$ for the clusters containing X=F, Cl, Br, and I, respectively. The bonding nature of $Al_{13}X$ could be characterized as ionic, i.e., $Al_{13}^{\delta+}-X^{\delta-}$. From this point of view, we can obviously understand that the most stable structure of $Al_{13}X$ is C_s-ontop(I), having a similar Al_{13} moiety to the most stable $C_s(I)Al_{13}^{+}$ structure. In Fig. 3, we show a plot of the binding energy versus electronegativity of X for both the AlX molecules and the $Al_{13}X$ clusters. There is a linear relationship between the binding energy and electronegativity of X for both cases, strongly supporting the ionic bonding character.

We also calculated the HOMO–LUMO gaps of the $Al_{13}X$ clusters (Table I), in order to estimate the kinetic stability. The energy difference between HOMO and the LUMO has been used as an index for kinetic stability.[41] A large HOMO–LUMO gap implies high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electrons to a high-lying LUMO or to extract electrons from a low-lying HOMO. It is worth noting that the C_s-ontop(I) isomer, with HOMO–LUMO gaps of about 1.52 eV, would be kinetically as well as thermodynamically more stable than the high-symmetry forms. The reported PBE HOMO–LUMO gaps are in the range of 1.53–1.83 eV for $Al_{13}M$ [M=H,[27] Li, Na, K,[15,17] and Cu (Ref. 20)]. By comparing the binding energy and HOMO–LUMO gap, we may conclude that the $Al_{13}X$ clusters have a kinetic and thermodynamic

TABLE II. Binding energy (BE), bond length (BL), and natural populations of X [$Q(X)$] for AlX (X=F, Cl, Br, and I). The experimental data are included in the parentheses (Reference 39, the D_0 values).

	BE (eV)	BL (Å)	$Q(X)$
AlF	7.009 (6.89)	1.696 (1.654)	−0.802
AlCl	5.211 (5.12)	2.173 (2.130)	−0.676
AlBr	4.632 (4.43)	2.339 (2.295)	−0.624
AlI	3.999 (3.77)	2.574 (2.537)	−0.542

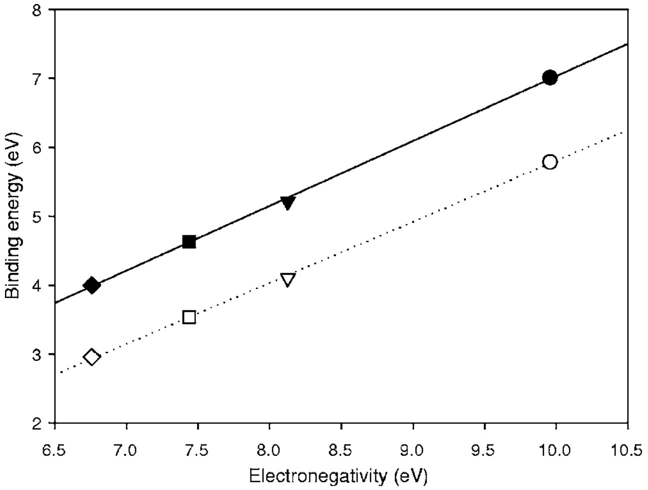

FIG. 3. Binding energy vs electronegativity of halogen atom for AlX (X=F, Cl, Br, I) and $Al_{13}X$: the solid symbols [F(●), Cl(▼), Br(■), and I(◆)] and the line are from data obtained for AlX, and the open symbols [F(○), Cl(▽), Br(□), and I(◇)] and the dotted line are from data obtained for $Al_{13}X$. The solid and dotted lines are determined via linear regression.

stability with respect to the experimentally known clusters. Although only the $Al_{13}I$ anion has so far been observed, our results suggest that the other $Al_{13}X$ clusters might be synthesizable.[30]

Let us now turn to the structure and electronic properties of $Al_{13}X^-$ clusters. Table III shows the binding energy, HOMO–LUMO gap, and natural charge $Q(X)$. The geometry optimization was performed using the initial geometries of the eight neutral $Al_{13}X$ clusters (Fig. 2). The highly symmetric *Ico*-ontop (C_{5v}) isomer is the most stable in the $Al_{13}X^-$ clusters. Such high symmetry originates from the fact that the extra electron is localized on the Al_{13} moiety for the $Al_{13}X^-$ clusters.[30] The C_s-ontop(III) and C_s-ontop(IV) isomers are also found to be local minima but to be less stable than the *Ico*-ontop isomer by more than 0.5 eV. The amount of extra electron entering the Al_{13} moiety is close to 1.0, regardless of the halogen atoms; $-0.99e$, $-0.96e$, $-0.95e$, $-0.94e$ for X=F, Cl, Br, and I, respectively. It is worth noting that the extra electron is entirely localized on the Al_{13} moiety for all the $Al_{13}X^-$ clusters, which leads to very similar adiabatic electron affinities of $Al_{13}X$; 2.74, 2.76, 2.78, and 2.80 eV for F, Cl, Br, and I, respectively. The halogen atoms are more weakly bound in the closed-shell Al_{13}^- than in the open-shell Al_{13} cluster, where the binding energies of $Al_{13}X^-$ are systematically lower than those of $Al_{13}X$ by about 0.5 eV.

TABLE III. Binding energy, HOMO–LUMO (HL) gap, and natural populations of X [$Q(X)$] for $Al_{13}X^-$ (X=F, Cl, Br, and I). All energies are given in eV.

	Binding energy	HL gap	$Q(X)$
$Al_{13}F^-$	5.193	1.677	−0.713
$Al_{13}Cl^-$	3.526	1.624	−0.512
$Al_{13}Br^-$	2.974	1.610	−0.438
$Al_{13}I^-$	2.426	1.580	−0.328

It is known that different functionals predict different ground states for $Al_{13}H$.[27] We repeated the DFT calculations using the B3LYP (Becke's three-parameter hybrid exchange[42] with the nonlocal correlation of Lee–Yang–Parr[43]) functional to verify the PBE results for neutral and anionic $Al_{13}X$ (X=F, Cl, Br, and I) clusters. Overall, the B3LYP method provides very similar results to the PBE values. We note that the B3LYP calculations greatly favor the C_s-ontop(I) isomers relative to the high-symmetry isomers for the $Al_{13}X$ clusters, while the *Ico*-ontop isomer is still the ground-state structure for the $Al_{13}X^-$ clusters. The relative energies of *Ico*-bridge with respect to C_s-ontop(I) at the B3LYP level are 0.92, 0.91, 0.82, and 0.70 eV for X=F, Cl, Br, and I, respectively. This is not surprising, because the C_s structure is the most stable isomer for neutral Al_{13} at the B3LYP level of theory.[27]

IV. CONCLUSIONS

To summarize, we have investigated the structure and electronic properties of $Al_{13}X$ (X=F, Cl, Br, and I) clusters. A low-symmetry C_s-ontop(I) isomer is found to be the most stable for the $Al_{13}X$ clusters, where the shape of the Al_{13} moiety in the $Al_{13}X$ cluster is significantly distorted from icosahedral and is similar to Al_{13} cationic structures. This result is due to charge transfer from Al_{13} to the electronegative halogen atoms. The bond strength between the Al_{13} cluster and halogen atoms significantly increases as X goes from I to F. We found a linear relationship between the bond strength and the electronegativity of X, which suggests that the bonding nature of $Al_{13}X$ is predominantly ionic, i.e., $Al_{13}^{\delta+}-X^{\delta-}$. The large binding energy and HOMO–LUMO gap of $Al_{13}X$ show that these clusters would be stable both kinetically and thermodynamically. $Al_{13}X^-$ (X=F, Cl, Br, and I) shows the highly symmetric *Ico*-ontop (C_{5v}) structure, where the cluster's extra electron is entirely localized on the Al_{13} moiety. A systematic experimental study of the electronic structure, binding energy, and electron affinity of $Al_{13}X$ (X=F, Cl, Br, and I) would be very useful.

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*Email address: ykhan@lgchem.com

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