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Experimental search and characterization of icosahedral clusters: $\mathrm{Al}_{12}X^-$ (X=C, Ge, Sn, Pb)

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Photoelectron spectra of $\mathrm{Al}_{12}X^-$ (X=C, Ge, Sn, Pb) were measured to probe the electronic structure of $\mathrm{Al}_{12}X$. These clusters, all possessing 40 valence electrons, were expected to be magic numbers with I_h-X@Al_{12} structures, closed electron shells, and large energy gaps. We showed that for X=Ge, Sn, and Pb that was indeed the case, although non-I_h isomers were also observed. The energy gaps of the three I_h-X@Al_{12} species range from 1.1 to 1.3 eV. The spectra of $\mathrm{Al}_{12}\mathrm{C}^-$ were distinctly different from the other species, confirming that it does not possess an icosahedral structure.

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One of the goals of cluster science is to discover "magic" clusters with special electronic and structural stabilities, so they might be used as building blocks for cluster-assembled materials. The discovery of fullerenes[1] and their subsequent bulk synthesis[2] have heightened research efforts in this area. Extensive theoretical calculations have been carried out to examine electronically stable metal clusters and to explore the potential to assemble crystals from them.[3–11] One critical guiding principle in this endeavor has been the electron-shell model,[12] which predicts that metal clusters with 2, 8, 20, 40,... valence electrons should exhibit an enhanced electronic stability. Al_{13} has been the subject of many previous theoretical efforts.[13–19] It has 39 valence electrons, indicating that Al_{13} would have a very high electron affinity (EA) and that $\mathrm{Al}_{13}{}^-$ would be an extremely stable cluster anion.[20–22] Indeed, this has been borne out experimentally, and Al_{13} has an EA of 3.6 eV,[22] which is similar to that of Cl (3.61 eV), the highest EA among the elements in the Periodic Table.[23] Furthermore, $\mathrm{Al}_{13}{}^-$ has a very high-symmetry icosahedral (I_h) structure, rendering it both electronic and structural stabilities.

The effort to examine neutral icosahedral clusters has focused on substituting an Al atom in Al_{13} with a tetravalent atom, such as C, Si, Ge, or Sn.[3–10] $\mathrm{Al}_{12}\mathrm{C}$ has been the most studied cluster in this regard,[3,4,7,8,24] and all previous calculations predicted it to have an icosahedral structure with a large energy gap between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO). $\mathrm{Al}_{12}\mathrm{Si}$ and $\mathrm{Al}_{12}\mathrm{Ge}$ were also predicted to have an icosahedral structure with a large HOMO-LUMO gap, whereas $\mathrm{Al}_{12}\mathrm{Sn}$ has been predicted to have a structure where the Sn atom substitutes a surface atom instead of the central atom in Al_{13}.[4,8–10] However, none of these theoretical predictions of the icosahedral $\mathrm{Al}_{12}X$ clusters has been verified. In this Brief Report, we describe an experimental characterization of all the $\mathrm{Al}_{12}X^-$ species, with X being one of the group-14 elements (C, Ge, Sn, Pb) using photoelectron spectroscopy (PES), which provides electronic structure information of the clusters and direct measures of their HOMO-LUMO gaps.

The experimental apparatus, involving a laser vaporization cluster source and a magnetic-bottle PES analyzer, was described previously.[25] Mixed targets between aluminum and the respective group-14 elements were used to produce the $\mathrm{Al}_{12}X^-$ clusters with a pure helium carrier gas. Alloy clusters produced from the source underwent a supersonic expansion, and were analyzed by a time-of-flight mass spectrometer. The mass of silicon is too close to that of aluminum, preventing us from separating $\mathrm{Al}_{12}\mathrm{Si}$ from $\mathrm{Al}_{13}{}^-$ because $\mathrm{Al}_{13}{}^-$ was a magic number that always had a dominating intensity. The Al/C and Al/Pb targets yielded fairly simple mass spectra, but the Al/Ge and Al/Sn targets gave very complicated mass patterns due to the numerous natural isotopes of Ge and Sn. The $\mathrm{Al}_{12}X^-$ clusters were mass selected and decelerated before photodetachment. In the current experiment, two photon energies were used, 193 and 266 nm. The resolution of the PES spectrometer was better than 30 meV for 1-eV electrons.

The PES spectra of $\mathrm{Al}_{12}X^-$ (X=C, Ge, Sn, Pb) at 193 and 266 nm are compared with that of $\mathrm{Al}_{13}{}^-$ in Fig. 1. The PES spectra of $\mathrm{Al}_{13}{}^-$ have been well understood, providing a basis for interpreting the spectra of the $\mathrm{Al}_{12}X^-$ species. According to the spherical shell model, $\mathrm{Al}_{13}{}^-$ should have a closed-shell configuration, $1s^21p^61d^{10}2s^21f^{14}2p^6$. Reduction of the spherical symmetry under the shell model results in a valence electron configuration for I_h-$\mathrm{Al}_{13}{}^-$, $1a_g^21t_{1u}^61h_g^{10}2a_g^21t_{2u}^61g_u^82t_{1u}^6$. Both molecular dynamic and *ab initio* calculations suggest that the PES features in Fig. 1(a) (A and B) for $\mathrm{Al}_{13}{}^-$ correspond to electron detachments from the $1t_{2u}$, $1g_u$, and $2t_{1u}$ orbitals, which are closely spaced in energy.[20,21] The 266-nm spectrum of $\mathrm{Al}_{13}{}^-$ [Fig. 1(f)] allows a more accurate EA to be determined (Table I), and also shows a strong photon-energy-dependent cross section for feature B.

The extra electron of the $\mathrm{Al}_{12}X^-$ species would occupy the $1h_u$ LUMO,[4] and a large energy gap should be observed in their PES spectra, if the $\mathrm{Al}_{12}X^-$ species possess the icosahedral structure. The spectrum of $\mathrm{Al}_{12}\mathrm{Pb}^-$ [Fig. 1(b)] indeed exhibits a large energy gap with a weak feature (X) at lower binding energies followed by broad features (A and B) at higher binding energies. Surprisingly, the A and B features of $\mathrm{Al}_{12}\mathrm{Pb}^-$ are identical to those of the $\mathrm{Al}_{13}{}^-$ spectrum [dotted curve in Fig. 1(a)] in both spectral shape and binding ener-

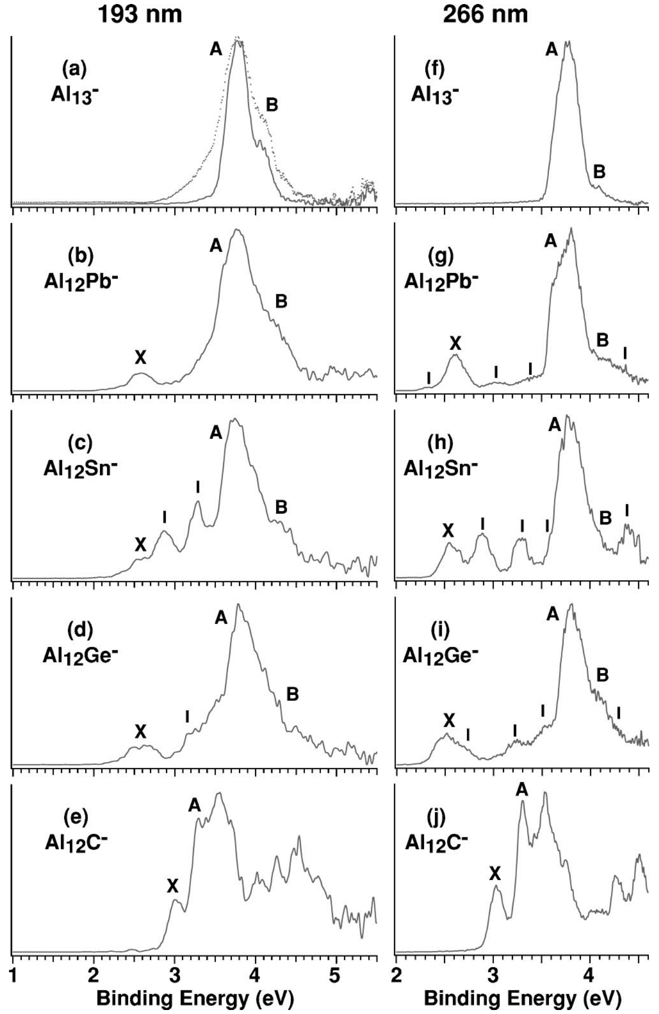

FIG. 1. Photoelectron spectra of Al_{13}^- and $Al_{12}X^-$ ($X=C$, Ge, Sn, Pb) at 193 and 266 nm. The dotted spectrum in (a) shows a Al_{13}^- spectrum with a vibrational temperature of ~570 K and the solid curve corresponds to a vibrational temperature of ~260 K (Ref. 21). '*I*' stands for features from non-icosahedral isomers.

gies. As we showed previously, the PES spectra of clusters are strongly influenced by cluster temperatures.[21,26] The dotted curve in Fig. 1(a) corresponds to an anion temperature of ~570 K, according to molecular-dynamics simulations,[21] whereas the solid spectrum corresponded to an Al_{13}^- anion temperature of 260 K. The close resemblance of the higher binding energy features (*A* and *B*) of $Al_{12}Pb^-$ and those of Al_{13}^- is remarkable, indicating a rigid filling of the electron shells in these systems. The 266-nm spectrum of $Al_{12}Pb^-$, taken at a colder condition and better resolution, revealed that the band shape of feature *A* changed slightly from that of the 193-nm spectrum. However, the adiabatic detachment energy (ADE) of feature *A* for $Al_{12}Pb^-$ (3.57 eV) is identical to that of feature *A* in the Al_{13}^- spectra within our experimental uncertainty. Feature *B* in the spectra of $Al_{12}Pb^-$ also showed a similar photon energy dependence to that of Al_{13}^-. In addition, the 266-nm spectrum of $Al_{12}Pb^-$ [Fig. 1(g)] clearly exhibited some weak features (labeled I), due to a minor isomer, which are more prominent in the spectra of $Al_{12}Sn^-$ and $Al_{12}Ge^-$. We measured an ADE and a vertical detachment energy (VDE) of 2.47 and 2.61 eV, respectively, and an energy gap of 1.10 eV for the I_h-$Al_{12}Pb^-$, as given in Table I.

TABLE I. Electron affinities (EA), vertical electron detachment energies (VDE), and HOMO-LUMO gaps (E_g) of $Al_{12}X$ ($X=C$, Ge, Sn, Pb), as well as the EA of Al_{13}. All energies are in eV.

	EA[a]	VDE[b]	E_g[c]
Al_{13}	3.57 ± 0.05		
$Al_{12}Pb$	2.47 ± 0.06	2.61 ± 0.04	1.10
$Al_{12}Sn$	2.44 ± 0.06	2.55 ± 0.05	~1.2
$Al_{12}Ge$	2.38 ± 0.08	2.52 ± 0.06	1.30
$Al_{12}C$	2.94 ± 0.05	3.03 ± 0.04	0.28

[a] Adiabatic detachment energies (ADEs) from the ground state of the anion to the ground state of the neutral.

[b] Vertical detachment energies from the ground state of the anion to the ground state of the neutral. No vertical electron detachment energy is given for Al_{13} because the ground-state transition is not resolved due to spectral congestion.

[c] The HOMO-LUMO gap is measured from the difference between the ADE's of the ground state (*X*) and that of the first excited state (*A*).

The main PES features of $Al_{12}Sn^-$ and $Al_{12}Ge^-$ (*A* and *B* in Fig. 1) are similar to those of $Al_{12}Pb^-$ and Al_{13}^-. A weak feature (*X*) is also present in the spectra of $Al_{12}Sn^-$ and $Al_{12}Pb^-$ at binding energies similar to those in the corresponding spectral feature for $Al_{12}Pb^-$. However, additional features (labeled *I* in Fig. 1) appeared prominently in the energy gap region in the spectra of $Al_{12}Sn^-$ and $Al_{12}Ge^-$. In Fig. 2, we show that the relative intensities of the additional spectral features in $Al_{12}Sn^-$ and $Al_{12}Ge^-$ strongly depend on the source conditions. The extra features became more dominating under hot conditions, suggesting they are due to a higher energy isomer. The main spectral features (*X*, *A*, *B*)

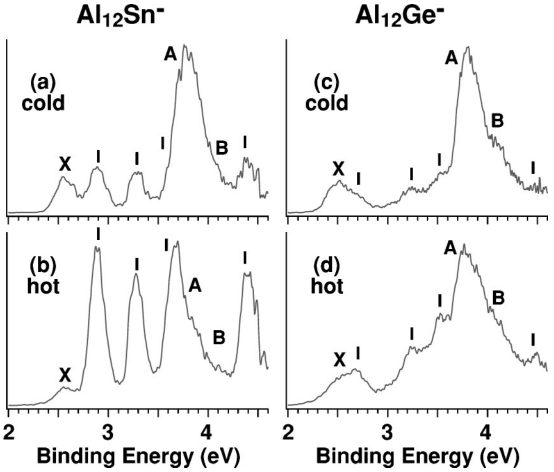

FIG. 2. Temperature-dependent photoelectron spectra of $Al_{12}Sn^-$ and $Al_{12}Ge^-$ at 266 nm, showing that the features due to isomers, labeled as '*I*,' are significantly enhanced under "hot" source conditions. The absolute temperatures of the clusters are not known.

for $Al_{12}Sn^-$ and $Al_{12}Ge^-$ should be derived from the icosahedral structure. The ADE, VDE, and HOMO-LUMO gap for $Al_{12}Sn^-$ and $Al_{12}Ge^-$ are given in Table I. We observed that the EA's decrease slightly for the I_h $X@Al_{12}{}^-$ species from $X = $Pb to Ge, while the HOMO-LUMO gaps increase slightly along the same direction.

To our knowledge there were no previous theoretical calculations for $Al_{12}Pb$. But our observation of the coexistence of two isomers for $Al_{12}Sn^-$ and $Al_{12}Ge^-$ was consistent with previous calculations,[4,9] which were made on neutral $Al_{12}Sn$ and $Al_{12}Ge$. $Al_{12}Ge$ was predicted to have an I_h ground-state structure, whereas the structure with Ge on the surface (C_{5v}) is 0.43 eV higher in energy. For $Al_{12}Sn$, Sn ''prefers'' to be on the outside (C_{5v}), because the I_h structure was predicted to be higher in energy by 0.42 eV.[9] In the anion, the I_h $Al_{12}Sn^-$ appeared to be more stable, but the C_{5v} isomer is likely to be nearly degenerate because its population was significant in all our experimental conditions and increased with temperatures. On the other hand, the C_{5v} isomer for $Al_{12}Ge^-$ was minor, indicating that the I_h structure is more stable in the anion, analogous to the neutral. For $Al_{12}Pb^-$, the I_h isomer is clearly much more stable than the C_{5v} isomer because the latter was only very weakly populated.

Surprisingly, the PES spectrum of $Al_{12}C^-$ was totally different from those of the other group-14 substituted $Al_{12}X^-$. It shows a much higher ADE and VDE and a much smaller HOMO-LUMO gap (Table I). The spectral features are also totally different. There did not appear to be any substantial isomers because the spectral features did not depend on the source conditions. The complexity of the PES features suggests that $Al_{12}C^-$ probably does not have an icosahedral structure and should have a lower symmetry. Neutral $Al_{12}C$ was extensively investigated theoretically,[3,4,7,8] and consistently predicted to have an I_h $C@Al_{12}$ structure. However, very recent theoretical calculations for the $Al_{12}C^-$ anion suggest that it has a lower symmetry C_{2v} structure, with an I_h structure only 0.18 eV higher in energy.[24] Our PES data showed no indication of the existence of an I_h isomer, which would presumably yield similar spectral features as the other group-14 I_h $Al_{12}X^-$ with a low-binding-energy feature and a large HOMO-LUMO gap.[4] In addition, the calculated ADE (1.73 eV) and VDE (2.56 eV) for the C_{2v} $Al_{12}C^-$ (Ref. 24) are inconsistent with the experimental measurements (Table I). The first PES band for $Al_{12}C^-$ [Fig. 1(j)] is relatively sharp, suggesting that there is very little geometry change between the anion and neutral $Al_{12}C$. The current experiment shows that the ground-state structures of $Al_{12}C^-$ and $Al_{12}C$ are still not well understood. We confirm that the $Al_{12}C^-$ anion is different from the other group-14 $Al_{12}X^-$ species, and it does not possess an I_h structure.

The most striking observation is that for all the $X@Al_{12}{}^-$ species ($X = $Ge, Sn, Pb) the shell filling seems to be rigid, that is; all species have similar electron binding energies and HOMO-LUMO gaps. In particular, the HOMO of $Pb@Al_{12}$ has an orbital energy identical to that of the HOMO of $Al_{13}{}^-$: 3.57 eV. The central atom seems to have very little effect on the valence orbitals, completely consistent with the jellium model. Our observed HOMO-LUMO gaps for the three $X@Al_{12}$ species range from 1.1 to 1.3 eV, significantly smaller than previous theoretical predictions.[4]

The structural evolution for the $Al_{12}X^-$ species from $X = $C to Pb is interesting. Two factors determine if the impurity X atom would ''prefer'' to be inside to form I_h $X@Al_{12}$. The first is the electronegativity of X, which determines if X is likely to lose its valence electrons to participate in metallic bonding. Despite the previous calculations, chemical intuition would suggest that C would be very unlikely to give up its four valence electrons because of its very high electronegativity. In fact, C would prefer to accept additional electrons like those in bulk Al_4C_3, where C can be formally viewed as C^{4-}.[27] Thus the strong C–Al bonding would likely be the dominating factor in determining the structure of $Al_{12}C$, rather than the electron shell closing, which requires C to give up its four valence electrons. As one moves down the Periodic Table, the element becomes increasingly more metallic and less electronegative, and the $X@Al_{12}$ structure is expected to be favored. However, the size of X increases as one goes down the Periodic Table, and too large an X would destabilize the Al_{12} cage. Thus Sn was predicted to be on the outside in $Al_{12}Sn$.[9] For the same reason, Pb is also expected to be on the outside. However, our experiment clearly indicates that Pb is the most favored to be on the inside to form $Pb@Al_{12}{}^-$ because there was a minute amount of isomer observed. We suspect that the strong metallic bonding character and the relativistic effects both favor the I_h-$Pb@Al_{12}$ structure. Thus this cluster would be expected to be the most promising I_h neutral cluster with both electronic and structural stabilities to be used as a ''super'' atom to assemble a cluster-based crystal.

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