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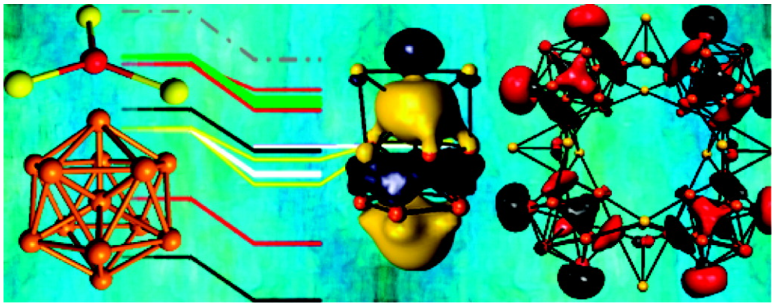

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Superatom Compounds, Clusters, and Assemblies: Ultra Alkali Motifs and Architectures

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Abstract: It has recently been demonstrated that chosen clusters of specific size and composition can exhibit behaviors reminiscent of atoms in the periodic table and hence can be regarded as superatoms forming a third dimension. An Al_{13} cluster has been shown to mimic the behavior of halogen atoms. Here, we demonstrate that superatom compounds formed by combining superhalogens (Al_{13}) with superalkalis (K_3O and Na_3O) can exhibit novel chemical and tunable electronic features. For example, $Al_{13}(K_3O)_3$ is shown to have low first and second ionization potentials of 2.49 and 4.64 eV, respectively, which are lower than alkali atoms and can be regarded as ultra alkali motifs. $Al_{13}K_3O$ is shown to be a strongly bound molecule that can be assembled into stable superatom assemblies $(Al_{13}K_3O)_n$ with Al_{13} and K_3O as the superatom building blocks. The studies illustrate the potential of creating new materials with an unprecedented control on physical and electronic properties.

Introduction

One of the most exciting developments in the field of clusters and cluster materials is the realization that chosen stable clusters can mimic the chemical behavior of atoms in the periodic table.[1−4] For cases where these clusters are fairly stable, they can form assemblies or compounds in combination with other atoms maintaining their identity, much in the same way as ordinary atoms, and these clusters can be classified as superatoms. Over the past few years, several such superatoms have been identified. For example, it has been shown that an Al_{13} cluster has an adiabatic electron affinity of 3.40 eV exhibiting behavior reminiscent to a halogen atom and hence can be regarded as a superhalogen.[1] An Al_{14} cluster, in combination with iodine atoms, exhibits electronic features like an alkaline earth atom (tendency to go toward a +2 valence state) and hence can be looked upon as a super alkaline earth atom.[2] Alkali oxides of the composition X_3O (X = Li, Na, K) display ionization potentials less than the alkali atoms and are regarded as superalkalis.[5−7] More recently, an Al_7^- has been shown to exhibit qualities reminiscent to atom with multiple valence states of +2 and +4 and has been classified as a multiple valence superatom.[8,9] While these are exciting developments, the next question is the nature of superatom chemistry. What kinds of compounds do the superatoms form and what features characterize superatom assemblies? Our interest in superatom assemblies is also motivated by another reason. The possibility of forming stable superatom assemblies by combining Al_{13} with alkali atoms (Li−Cs) has not been promising because the size of alkali atom is small as compared to the Al_{13} units.[10] The smaller cation units are unable to prevent direct contact between larger Al_{13} motifs. Using larger superatom cation motifs overcomes this problem.

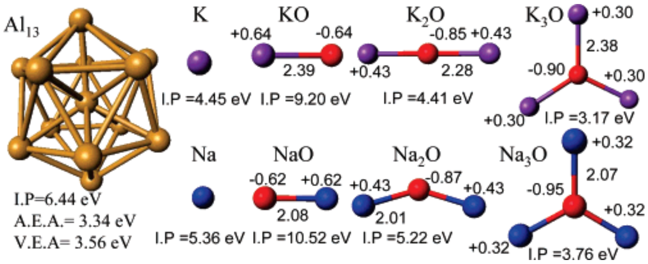

Figure 1. Structure, ionization potential, and Mulliken charges on Al_{13} and K_nO and Na_nO series. The bond lengths are in angstroms, and the Mulliken charges are labeled above the atoms. For Al_{13}, the adiabatic electron affinity (A.E.A.) and vertical electron affinity (V.E.A.) are also marked.

In this Article, we use first principles electronic structure studies to demonstrate that superatoms can be combined to form

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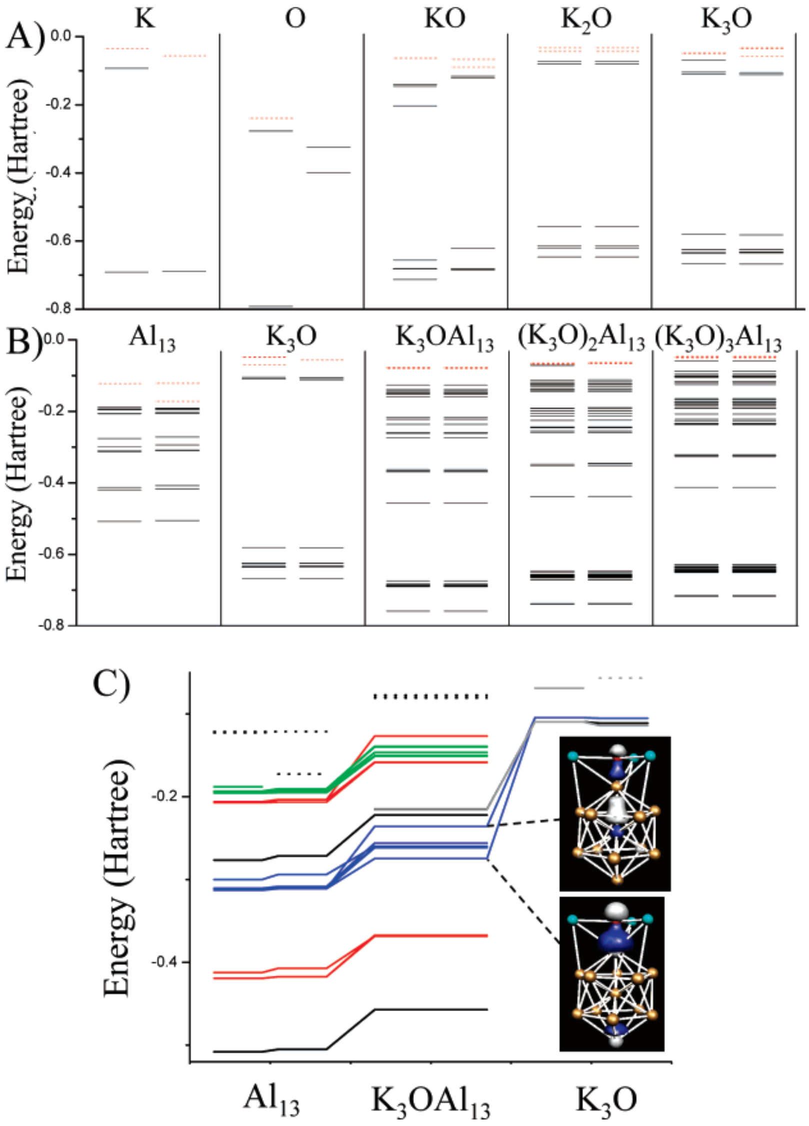

Figure 2. (A,B) One electron levels for Al_{13}, Al_{13} $(K_3O)_n$ ($n = 0-3$), and K_nO ($n = 1,3$) clusters. The continuous lines are the filled states, while the dashed red lines are the unoccupied states. (C) The one electron levels showing the formation of bonding orbitals between Al_{13} and K_3O. The insets show the electron density (gray and blue) regions indicating the bonding charge.

compounds, clusters, and extended assemblies with novel features that can be tuned. We first demonstrate that by combining superhalogen with superalkali, it is possible to form small superatom-based clusters with a desirable number of low ionization potentials. Our studies on clusters composed of superhalogen Al_{13} and superalkali K_3O show that the first ionization potential of $Al_{13}(K_3O)$ is 4.59 eV. Adding another superalkali to form $Al_{13}(K_3O)_2$ lowers the first ionization potential to 2.88 eV while the second ionization potential remains high at 6.47 eV. Adding a third superalkali to form $Al_{13}(K_3O)_3$ further lowers the first two ionization potentials to 2.27 and 4.51 eV while the third ionization potential remains high at 8.14 eV. The first two ionization potentials are so low that the unit can be thought of as an ultra alkali motif. An $Al_{13}(K_3O)$ is an ionic bound molecule much like a KCl, and it is natural to ask how such units will assemble to form extended structures. In this work, we present results on $(Al_{13}(K_3O))_n$ assemblies containing up to 6 units. Like $(NaCl)_n$ clusters, these units assemble to form rings.[11] Examination of the stability as a function of size shows that rings containing 4 units are most stable. The results support the contention that it should be possible to form extended assemblies based on $Al_{13}(K_3O)$ units.

Theoretical Approach

The ground-state geometries and the electronic properties were investigated using a first principles linear combination of atomic orbital molecular orbital approach within a gradient corrected density functional theory.[12] In brief, the molecular orbitals representing the electronic states in the clusters are expressed as a linear combination of atomic orbitals of various angular momentum centered at the atomic sites. The atomic orbitals are in turn expressed as a linear combination of Gaussian functions whose exponents are characterized by the choice of the basis set and whose coefficients are determined by the self-consistent solution of the Kohn−Sham equations. In this work, we have used the scheme developed by Pederson and co-workers to numerically solve the Kohn−Sham equations with the

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generalized gradient approximation for exchange and correlation.[13] Their numerical procedure is incorporated into the scheme called Naval Research Laboratory Molecular Orbital Library (NRLMOL) and was used for most of the calculations.[14−16] The further reiterate our findings, supplementary calculations on selected systems were performed using deMon code.[17−19] These calculations used the DZVP basis.[19] The basis set superposition errors for $Al_{13}K_3O$ were determined to be 0.20 eV, which are really small. Whenever possible, the theoretical results are supplemented with experimental findings.

Results and Discussion

As pointed out earlier, the electronic structure and stability of metal clusters can be broadly rationalized within a simple jellium model[20] where the ionic cores are replaced by a spherical positive background of uniform density. The valence electrons respond to this positive background, and the electronic spectrum of such a system is characterized by one electron levels 1s, 1p, 1d, 2s, 1f, 2p. A similar electronic spectrum is obtained for the electronic states in a square well and other forms of background potential,[21] indicating that the level structure is a generic property of the confined nearly free electron gas. Further evidence for this stems from the observed electronic and chemical behavior of clusters. For example, an Al_{13} with 39 valence electrons corresponds to the level structure of $1s^21p^6$-$1d^{10}2s^21f^{14}2p^5$ missing one electron in the highest occupied molecular orbital (HOMO), which presents a situation akin to halogen atoms. Indeed, theoretical[22,23] and experimental studies[24] reveal that it has a high adiabatic electron affinity of 3.40 eV (see Figure 1) as compared to 3.46 eV for Br and 3.61 eV for Cl making it like a halogen atom. Studies also reveal that Al_{13}^- with a closed shell of 40 electrons is a stable species that is chemically inert.[1,25] The exciting feature then is to examine what kind of chemistry governs the combination of superatoms. For example, what compounds[26] emerge when a superhalogen is combined with superatoms of alkali character. We therefore begin with a discussion of superalkali species.

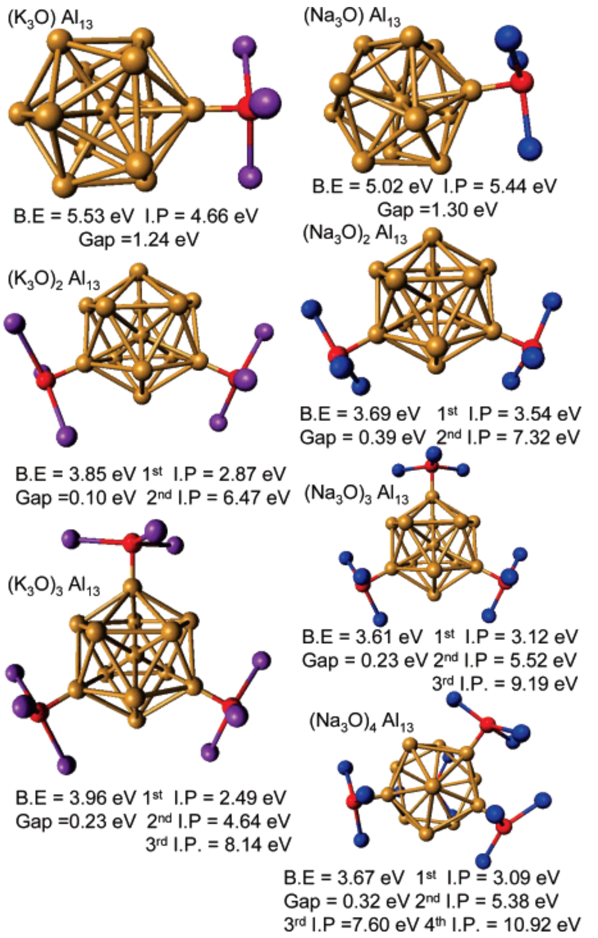

Figure 3. Structure binding energy (B.E.), HOMO−LUMO gap (Gap), and ionization potentials (I.P.) for $Al_{13}(K_3O)$ and $Al_{13}(Na_3O)$ series. All energies are in eV.

The alkali atoms Li, Na, K, Rb, and Cs have low ionization potential. However, even lower ionization potentials can be attained[6] by combining alkalis with other atoms in the formula ML_{k+1} where M is the main group atom with valence k and L are the alkali atoms (see ref 6 and additional references therein). Consider the case of O and its combination with alkali atoms to illustrate the electronic features relevant to this work. Figure 1 shows our calculated ground-state geometry of K_nO and Na_nO containing up to 3 alkali atoms. The bonding between alkali atoms and O is primarily ionic, and a Mulliken population analysis (Mulliken charges are marked over the atoms in Figure 1) shows that there is a significant charge transfer from alkali to O site. To analyze the electronic progression in more detail, Figure 2A shows the one electron levels in K, O, KO, K_2O, and K_3O clusters. The continuous lines represent the filled levels, while the dotted lines correspond to the unfilled states. An isolated O atom requires two electrons to fill the vacancies in the 2p level while the K levels are higher in energy. In KO, the K level mixes with O p-states to form the bonding state that is occupied by the electron from K while the antibonding state is higher in energy. In K_2O, both of the oxygen vacancies are filled, although the LUMO is shared by both K atoms resulting in a reasonably low I.P. The valence structure in K_3O has a filled shell followed by a high HOMO that leads to a low ionization potential and results in the superalkali behavior of the cluster. Similar progression is observed in Na_nO clusters. These considerations are borne out by experiments in our group.[5] For example, the calculated ionization potentials of 3.17 eV for K_3O and 3.76 eV for Na_3O are in reasonable agreement with the experimental values[5] of 3.65 ± 0.04 and 3.90 ± 0.1 eV, respectively. For K_2O and Na_2O, the calculations predict ionization potentials of 4.41 and 5.22 eV versus the experimental values[5] of 4.7 ± 0.4 and 5.06 ± 0.4 eV, respectively. The above studies bring out an interesting issue. The ionization potential of an isolated K atom is 4.45 eV while an O atom has a high electron affinity of 1.46 eV. Each K contributes one valence

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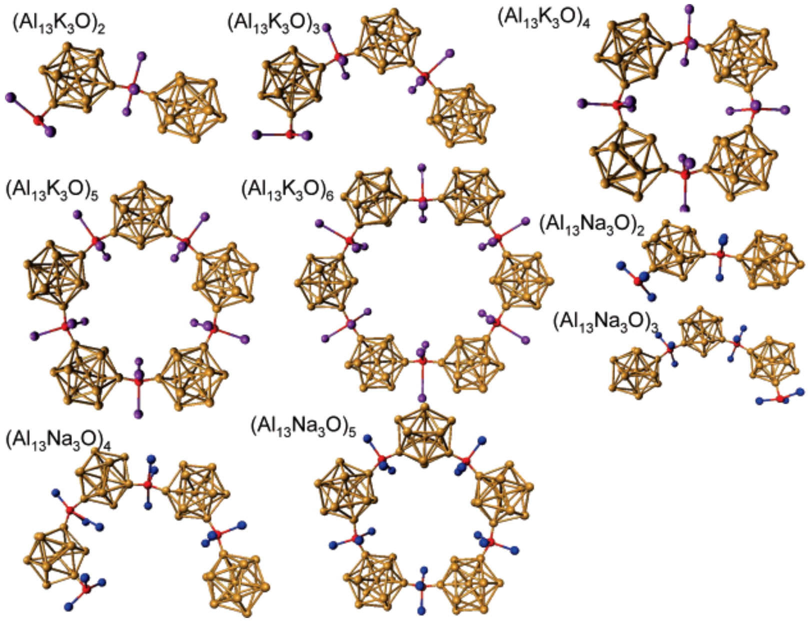

Figure 4. Assemblies of (A) $Al_{13}K_3O$ and (B) $Al_{13}Na_3O$ molecules.

electron while O atom requires two electrons to complete its valence shell. By adding three potassium atoms that can furnish one more electron than the number required to fill the O shell, the ionization potential is reduced from 4.34 eV in a K atom to 3.17 eV in K_3O.

One is next faced with two questions. (1) What kind of compounds and extended assemblies can be formed by combining superhalogens with superalkali's? (2) The chemistry of O and alkali atoms enables L_3O clusters to exhibit lower ionization potentials than the individual alkali atoms. Can a similar chemistry be performed with superatoms; that is, can one reduce the ionization potential from that in K_3O, by combining K_3O units with Al_{13}?

These exciting possibilities were explored through the progression of electronic properties as K_3O (Na_3O) units were successively added to Al_{13}. As an Al_{13} requires only one electron to fill its valence shell, we begin with K_3OAl_{13}. A K_3O was brought toward the Al_{13} cluster along an on-top, bridge, or hollow site above the Al_{13} icosahedron, and the geometry was fully optimized by moving atoms along the direction of forces without any symmetry constraints. Figure 3 shows the ground-state geometry of the K_3OAl_{13} unit. In the ground state, the O atom occupies an on-top site above an Al atom. The binding energy of the cluster motif was calculated through the equation:

$$\mathrm{B.E.} = E(\mathrm{K_3O}) + E(\mathrm{Al_{13}}) - E(\mathrm{K_3OAl_{13}})$$

where $E(\mathrm{K_3O})$, $E(\mathrm{Al_{13}})$, and $E(\mathrm{K_3OAl_{13}})$ are the total energies of the various species and the investigations included calculation of vertical ionization potential and the HOMO−LUMO gap. The studies reveal that the cluster has an ionization potential of 4.66 eV as compared to 3.17 eV for an isolated K_3O unit. The K_3O was found to bind to Al_{13} with a B.E. of 5.53 that is significantly larger than the ionic bond in $Al_{13}K$ where K is bound by only 2.51 eV. The origin of this stability is hidden in the ionic/covalent bonding. Figure 2C shows the one electron levels in Al_{13} and K_3O and K_3OAl_{13} units. The interaction between the valence level in K_3O and LUMO in Al_{13} leads to a bonding antibonding pair of states where the bonding state is filled leading to a closed shell unit with a large HOMO−LUMO gap of 1.24 eV. This gap is fairly large noting that the experimental HOMO−LUMO gap in C_{60} is around 1.9 eV.[27] A Mulliken population analysis of the total charge shows that there is a charge transfer of 0.37 e^- from K_3O to Al_{13} unit resulting in an ionically bonded stable motif much like the KCl. The ionic bonding is, however, supplemented by a covalent bond between oxygen 2p orbitals and Al_{13} orbitals. The charge density in these covalent bonds is shown in the inset in Figure 2. The large HOMO−LUMO gap shows that it is also electronically inert. The enhanced binding and the large HOMO−LUMO are an excellent combination to be an ideal system to assemble into cluster material. However, before we proceed along these lines, let us demonstrate the ultra alkali behavior in Al_{13}-based systems.

As pointed out earlier, for an oxygen atom with two unfilled states, addition of a third K atom to form K_3O resulted in a superalkali behavior. Because Al_{13} has only one unfilled state in the valence manifold, would a $(K_3O)_2Al_{13}$ have a lower ionization potential than K_3O? To examine this possibility, a second K_3O was added to K_3OAl_{13}. Structures where the initial K_3O fragmented into a K and K_2O, 2K and KO, or 3K and O atoms on the Al_{13} surface were also investigated. The structure shown in Figure 3 is the ground state of all such possibilities. Figure 3 also shows the B.E. of the additional K_3O units, the first and second ionization potentials, and the HOMO−LUMO gap in the parent and singly ionized species. It is remarkable that the first I.P. is only 2.87 eV as compared to 3.17 eV for the K_3O! The second ionization potential is, however, 6.46 eV. The lowering of the ionization potential can be understood from Figure 2C. Addition of K_3O results in a HOMO above the occupied band of energies in K_3OAl_{13}. Can the second I.P. be further lowered by adding a subsequent K_3O? To examine this we considered an $(K_3O)_3Al_{13}$ unit. The ground-state geometry, the first three ionization potentials, the HOMO−LUMO gap in the neutral, singly and doubly ionized cluster, and the B.E. of

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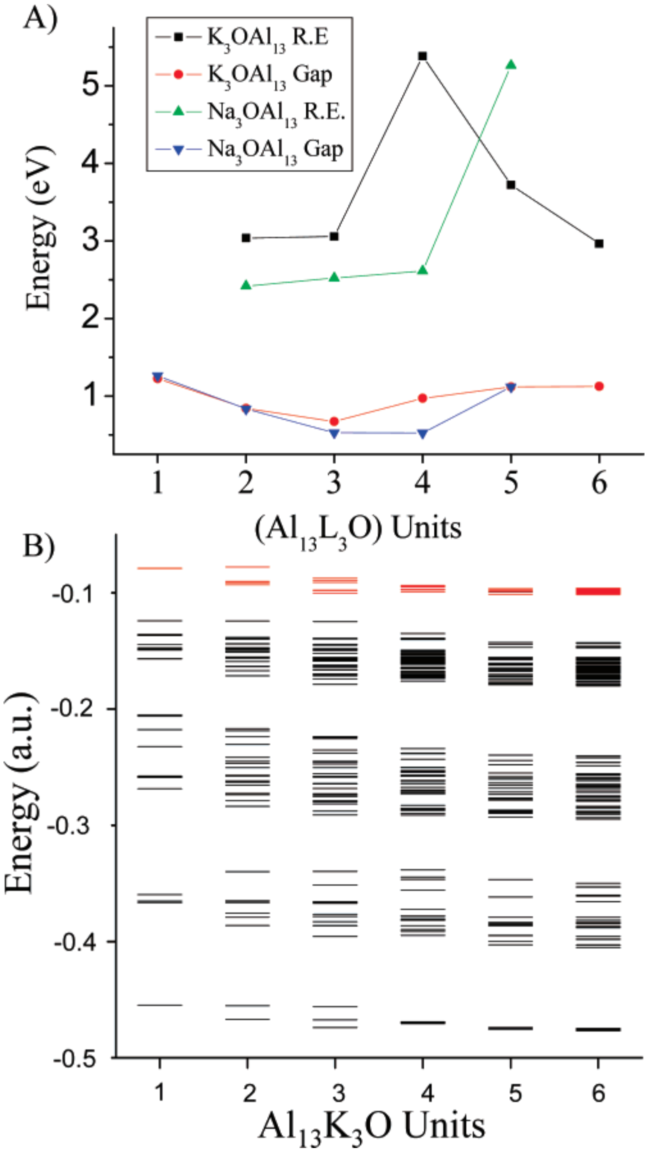

Figure 5. (A) Energy gain and HOMO−LUMO gap for superatom assemblies. R.E. is the removal energy indicating the energy required to remove a $Al_{13}K_3O$ unit in $(Al_{13}K_3O)_n$ assemblies. (B) One-electron levels for $(K_3O\ Al_{13})_n$ assemblies. The black lines are the occupied states, while the red lines are the unoccupied states.

the additional K_3O are given in Figure 3. It is truly remarkable that the motif has the first two ionization potentials of only 2.49 and 4.64 eV, respectively. Thus, the present study shows that by combining superhalogen and superalkali units, it is possible to design units that can be described as ultra alkali motifs! Because of the steric hindrance, it is not possible to put more than three K_3O units around an Al_{13} cluster. This limitation can be overcome by going to smaller Na_3O. Figure 3 shows that Na_3O additions also result in similar progressions. In this case, however, our studies indicate that the cluster $(Na_3O)_4Al_{13}$ is stable and has the first three ionization potentials of 3.09, 5.38, and 7.60 eV, respectively. Note that the removal of three electrons creates enormous coulomb repulsion and the cluster could fragment upon triple ionization.

As pointed out above, K_3OAl_{13} is bonded by a charge transfer from K_3O to Al_{13}. It is therefore an analogue of alkali halide, for example, CsCl molecules. Previous studies[28] on alkali halide clusters have revealed that $(CsCl)_n$ units form planar rings at small sizes. To look for similar architectures in K_3OAl_{13}, we investigated the ground-state geometries of the $(K_3OAl_{13})_n$ containing up to 6 units. Starting from the initial geometry consisting of Al_{13} and K_3O units, the geometries were fully optimized without any symmetry constraints as shown in Figure 4. The lowest energy dimer of $(K_3OAl_{13})_2$ is a bent structure with oxygen occupying on-top positions at the Al_{13} surface. (We would like to add that a structure composed of Al_{26} and K_6O_3 obtained by forcing Al_{13} units in K_3OAl_{13} to fuse together is 0.33 eV more stable that the dimer assembly shown in Figure 4. However, there was a barrier of more than 0.14 eV as the two $Al_{13}K_3O$ units were brought together. This shows that stable assemblies can be built by first forming the K_3OAl_{13} building blocks.) The bending continues and $(K_3OAl_{13})_4$ is the first cluster to exhibit a closed ring. Further addition of K_3O units results in larger rings. As pointed out earlier, this is similar to the case of CsCl clusters and shows that superatom assemblies follow the same progressions as the ordinary alkali-halide molecules. A single K_3OAl_{13} cluster has a large HOMO−LUMO gap of 1.24 eV. Are the electronic features of the single unit maintained as we go to larger sizes? This is critical to ascertain that the basic building blocks would maintain their identity. To this end, we examined the variation of the HOMO−LUMO gap as the clusters are assembled. Further, the progressions of the increase in binding energy as successive units are added were examined to identify any sizes that are particularly stable. Figure 5 shows the removal energy (R.E.) that represents the energy gain in forming the current size from the preceding cluster or the energy required to remove a single fragment from the current size. Note that R.E. peaks at $n = 4$, which corresponds to the smallest size at which a closed network is formed. Upon further growth, the R.E. decreases, indicating, probably, a tendency toward the formation of multiple cages as in case of ionic molecules. More important is the progression of electronic structure shown in Figure 5b. Note that while the assembly of clusters leads to additional levels, the electronic levels are bunched in individual bands maintaining a similar HOMO−LUMO gap that has a value of 1.13 eV for $(K_3OAl_{13})_6$. Because each K_3OAl_{13} is an ionically bonded system, the gain in binding is probably rooted in the ionic interaction. The HOMO−LUMO gap contracts in $(Al_{13}K_3O)_{2,3}$ because the HOMO remains the active site on the terminal Al_{13}, while LUMO is located on the Al_{13} cluster and is stabilized by multiple adjacent alkali metal atoms. Once the ring closes, both HOMO and LUMO are stabilized by an ionic interaction with the alkali metal atoms, such that the gap returns to close to that of the monomer. This shows that basic electronic features are maintained upon cluster assemblies, providing optimism that it should be possible to form them in actual experiments.

Conclusions

To summarize, we have presented what we believe is the first study of compound formation by superatom units. Unlike ordinary atoms, the interaction in superatoms involves interaction between multiple atoms. Yet, it is interesting that the same chemical principles, working for atomic clusters, can be extended to clusters with superatom motifs. For example, analogous to superalkalis, the ionization potentials can be

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successively lowered by adding K_3O units to superhalogen. In particular, $(K_3O)_3Al_{13}$ is shown to have first two ionization potentials lower than any other atom in the periodic chart and can be described as an ultra alkali motif. The superatom motifs can also be assembled to form extended structures, and here also the superatom architectures resemble assemblies of ionic molecules. However, the electronic states in super-assemblies evolve out of the molecular levels in clusters and not the atomic levels. It is also important to highlight that, while the atomic and superatomic assemblies have commonality, the superatom architectures do offer novel features. For example, our calculations of the vibrational spectrum of the $(K_3OAl_{13})_4$ cluster show that it exhibits three low-frequency vibrational modes at 37, 41, and 47 cm^{-1} that correspond to inter-cluster vibrations and are not exhibited by individual clusters. The world of superatoms does hold novelty along with the possibility of surprising behavior, and we hope this work will promote experimental investigations into these novel features.

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