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14. ABSTRACT The key objective of our work has been to study the interaction of aluminum and aluminum based clusters with organic templates, with oxygen and water, and develop protocols that would enable the synthesis of cluster assembled materials based on reactive and non-reactive motifs. Our studies on the reactivity of aluminum clusters with propene showed that the reactivity was related to the location of the unoccupied molecular orbital and that clusters like Al_{12}^- , Al_{15}^- , Al_{18}^- , and Al_{21}^- can readily bind to propene and hence may be suitable building blocks to generate such materials. For Al_{13} , a superhalogen superatom discovered by us, our studies showed that an ionic assembly composed of Al_{13} and super-alkali K_3O is stable and ideal to generate an ionic solid. Through synergistic efforts combining theoretical studies in my group and experiments in A. W. Castleman's (AWC) group at PSU, we identified $Al_4H_7^-$ as a very stable species that is resistant to oxygen and ideal building blocks for cluster materials. We also showed that the reactive aluminum clusters can be made less reactive by adding H atoms as it changes the spin state of the system. We also established general protocols for using the findings on free clusters to generate cluster assembled materials and in collaboration with experimental groups, synthesized a cluster solid of As_7K_3 species through a directed chemical synthesis. Recently, in a synergistic efforts combining experiments in AWC group at PSU, we have discovered an unusual size dependent reactivity of aluminum cluster anions with water, in that Al_{16}^- , Al_{17}^- , and Al_{18}^- are found to produce hydrogen through processes linked to their geometries. The studies provide a new Approach to synthesize hydrogen from water, on demand, and have just been published in SCIENCE. We believe that these developments are important towards cluster based materials for propulsion and nanoelectronic applications.					
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AFOSR PROGRESS REPORT

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Research Title:

Aluminum Cluster-Based Materials for Propulsion and other Applications

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Objective:

The key objective of the program is to carry out theoretical investigations of the geometries, stability, electronic structure and reactivity of aluminum based clusters and to explore the possibility of making materials using pure aluminum and compound aluminum based clusters as the building blocks. Previous studies have indicated Al_{13}^- as a very stable cluster with superhalogen attributes. Initial investigations will therefore focus on the possibility of materials using Al_{13}^- as a possible motif.

The proposed work is a synergistic effort combining the theoretical work at VCU and the experimental investigations in Prof. Castleman's group at Pennsylvania State University and in Prof. Bowen's group at Johns Hopkins University.

Status of the Effort:

This report covers the period beginning March 16, 2005 to August 31, 2005. During the first five months of the research project, we have embarked on three projects. (1) **Possibility of cluster materials using molecular templates.** Here, in a synergistic effort with Prof. A. W. Castleman, Jr., the interaction of aluminum clusters with propyne was undertaken to identify the factors governing the binding of clusters to organic templates. These investigations have just been accepted for publication in Chem. Phys. Letters. (2) **Possibility of composite units by combining Al_{13} with molecular units having low ionization potential.** Such combinations offer the possibility of forming ionic solids based on molecular units. We already have some preliminary promising results on a unit formed from Al_{13} and K_3O clusters. (3) **Identification of new aluminum based motifs that could serve as the building blocks.** The effort here is

directed towards developing principles that could guide the search of stable motifs called “superatoms”. A manuscript containing the results of these investigations is being prepared.

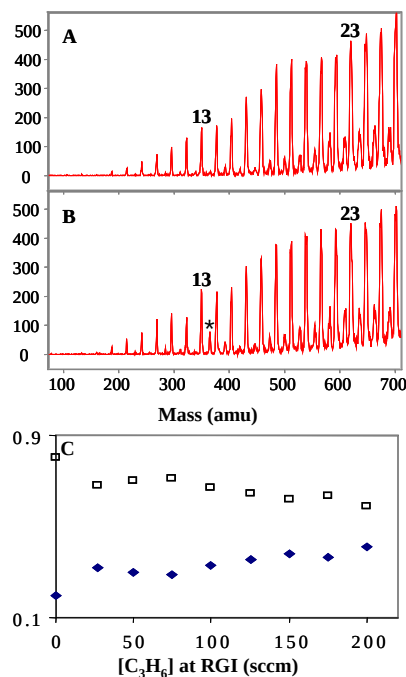
Accomplishments/New Findings:

(1) Interaction of Aluminum Clusters with Organic Templates:

One of the approaches envisioned to form cluster based materials is to deposit clusters of interest on organic and inorganic templates. An understanding of the factors governing the interaction between aluminum clusters and templates is vital to translating this possibility into practice. As a first step towards this understanding, the reaction between Al_n^- and propene, which we adopt as a model alkene system, were carried out. We believe that these investigations also extend our previous base of knowledge about the reactivity of aluminum clusters as pertaining to organic species.

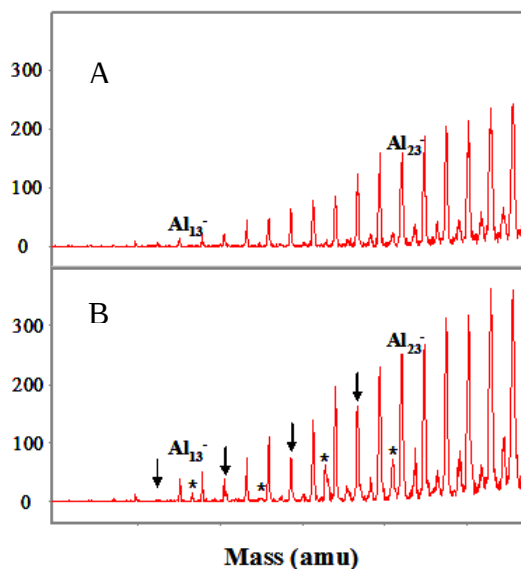
The experimental part of the program was carried out in the fast-flow tube apparatus in the laboratory of Prof. A. W. Castleman. In brief, clusters were generated via

Figure 1. Mass spectra of (A) Al_n^- clusters (B) reacted with 200 sccm of propene. The asterisk marks the $\text{Al}_{12}\text{C}_3\text{H}_6^-$ peak. The branching ratio (C) shows the contribution of Al_{12}^- (open squares) and $\text{Al}_{12}\text{C}_3\text{H}_6^-$ (closed diamonds) to the sum total of both species' ion signal as a function of increasing C_3H_6 concentration.



vaporization of an Al rod in the constant flow laser vaporization source and subsequently reacted with propene. Collisions with the carrier gas cooled the clusters prior to reaction with propene. Figure 1 shows the results of these investigations. It was found that at moderate concentrations of propene, only one Al_n^- cluster, Al_{12}^- , undergoes a reaction. Figure 1C confirms the formation of an association product, $\text{Al}_{12}\text{C}_3\text{H}_6^-$. In Figure 2B, we show that several other clusters belonging to the series Al_{12+3n}^- (where $n = 0, 1, 2, \text{ and } 3$) react with propene at higher concentrations, and in each case (with the possible exception of Al_{15}^-) it seems that an association product is formed.

Figure 2 Mass spectra of (A) Al_n^- clusters (B) subjected to a large dose of propene, the arrows point to the disappearing peaks that correspond to the Al_{12+3n}^- ($n = 0 - 3$); asterisks mark the $\text{Al}_{12+3n}\text{C}_3\text{H}_6^-$ adducts.

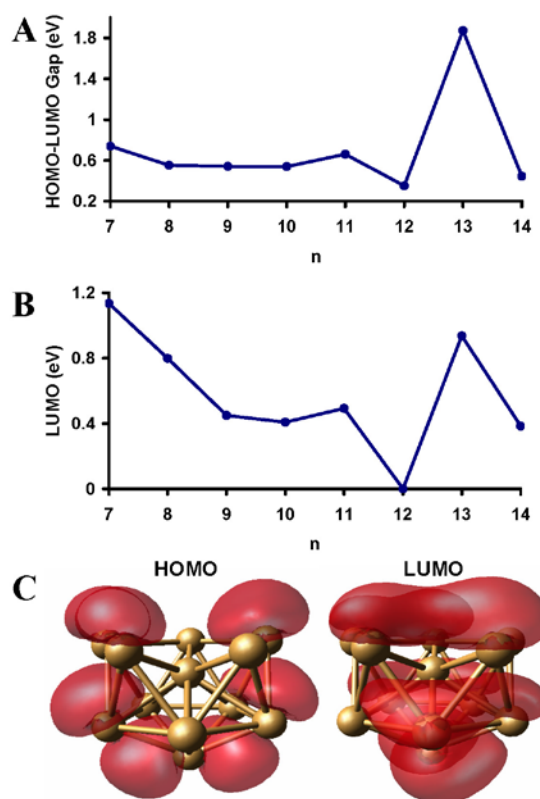


These experiments raised the question as to why Al_{12}^- is so reactive and what is the origin of the enhanced reactivity of Al_{12+3n}^- (where $n = 0, 1, 2, \text{ and } 3$) at higher concentrations.

To understand these results, ab-initio calculations of the structure of pure and reacted aluminum clusters were carried out. Previous investigations by Chrétien *et al.*¹ on reactions of propene to Ag_n and Au_n clusters had suggested that propene binds by donating charge from its HOMO to the metal cluster and that the binding is stronger

when the LUMO of the metal cluster is lower in energy as it facilitates the charge transfer. Further, propene binds preferentially to the site on the cluster where a lowest unoccupied molecular orbital (LUMO) protrudes most into vacuum. We find similar effects in aluminum clusters. In Figure 3, we show the HOMO-LUMO gap and the position of the LUMO relative to that in Al_{12}^- in clusters containing 7-14 atoms. Also shown are the charge densities of the HOMO and LUMO. Note that the Al_{12}^- has the lowest HOMO-LUMO gap and is expected to be reactive. However, one further notices that the actual energy of

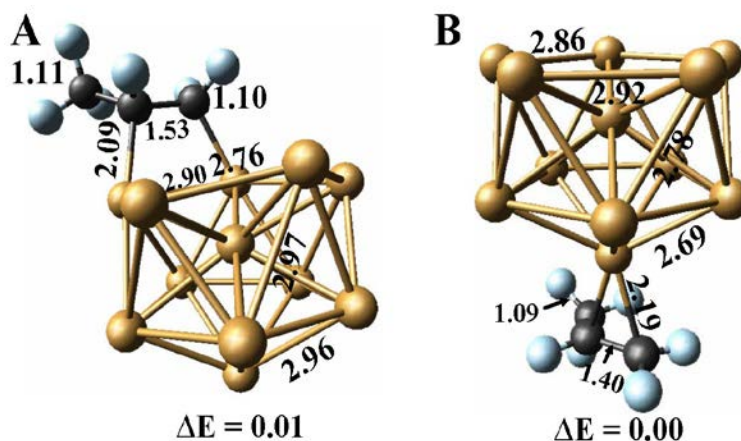
Figure 3 (A) Plot of the HOMO-LUMO gap as a function of cluster size in the series Al_n^- . (B) Plot of the energy of the LUMO as a function of cluster size in the series Al_n^- . The energy is set relative to the LUMO energy for Al_{12}^- , which is shown here as zero. (C) Lowest energy structure and maps of the charge density for the HOMO (left) and LUMO (right) of Al_{12}^- .



the LUMO is also anomalously low. The plot of the charge density of the LUMO of Al_{12}^- (Figure 3) shows a protruding lobe at the face-capping apical site mentioned above. Figure 4B shows that association of the C_3H_6 cluster to this site resulted in the ground state cluster. In addition, a large protruding lobe can be found above the uncapped

pentagonal Al ring. Propene association to this site of Al_{12}^- shown in Figure 4A is found to be an isomer of the cluster shown in Figure 4B. Either of these

Figure 4 (A) Geometry of a low lying isomer of C_3H_6 associated with Al_{12}^- and (B) the ground state structure.



lobes should provide the charge accepting behavior necessary for favorable adsorption of propene.

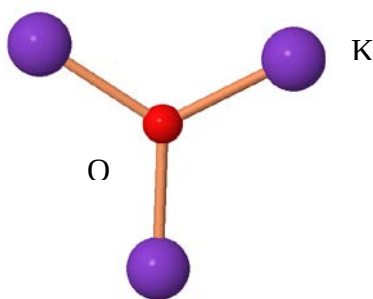
As mentioned above, at higher concentration of propene, Al_{15}^- , Al_{18}^- , and Al_{21}^- also react with propene. The Al_{13} cluster has a complete geometric shell around a central atom. The ground state of the anion is a perfect icosahedral structure that has a C_{3v} symmetry and can be described by two sets of two triangles each around the central site. The triangles closer to the central site have larger bond lengths while the triangles away from the site have smaller bond-lengths. One could grow the icosahedra by adding 3 atoms at a time leading to Al_{16}^- , Al_{19}^- and Al_{22}^- species corresponding to partially filled geometric sub-shells. One could therefore regard Al_{15}^- , Al_{18}^- , and Al_{21}^- as incomplete geometric shells like Al_{12}^- and hence more reactive. These investigations are currently being pursued. In the same vein, it will also be important to extend the present investigations to address the reactivity of activated Al_nI_x^- clusters towards propene. Present knowledge of Al_nI_x^- clusters allows the prediction that propene will bind selectively to species with active centers (those with odd x). Based on the reactivity

studies and the calculations that showed preferential attachment of additional I atoms to these sites, it is reasonable to assume that the lobes mapped for the HOMO levels in active Al_nI_x^- clusters will provide the electronic equivalent of the protruding LUMO's. If such reactions are shown to be possible with halogen-like superatom clusters²⁻⁴, an exciting step towards new synthetic chemistry would be realized.

(2) Ionically Bonded Al_{13}M Systems using Molecular (M) Cations:

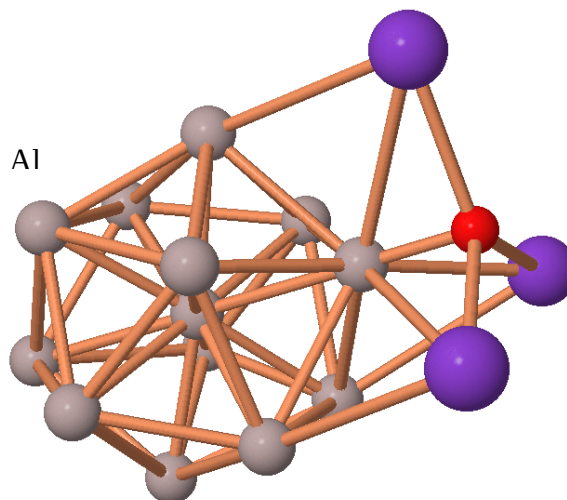
As Previous stated, an Al_{13}^- cluster has an electron affinity comparable to that of an halogen atom and hence it should be possible to form ionic compounds by combining Al_{13} with alkali atoms. Previous studies in our group on Al_{13}K indeed showed it to be an ionically bonded molecule composed of Al_{13}^- and K^+ units much like the ionic salt KCl. Since the size of K is much smaller than that of Al_{13} , attempts at forming materials by assembling Al_{13}K units resulted in strong interactions between the Al_{13} motifs resulting in the fusion of the clusters. One way to overcome this obstacle is to use larger molecular units with lower ionization potentials as cations. The first such unit that we are trying is K_3O . It has a planar structure shown below.

Fig. 5. Ground state geometry of K_3O .



Our studies indicate that it has an ionization potential of 3.25 eV which is much lower than that of even K. Using such a motif, initial calculations of the binding of K_3O to Al_{13} were performed. The following figure shows the final ground state geometry of

Fig. 6. Ground state geometry of $\text{Al}_{13}\text{K}_3\text{O}$.



the complex. Interestingly, the geometry of the Al_{13} cluster is very similar to that of Al_{13}^- indicative of some sort of ionic bond. The complex has a large binding energy of 5.65 eV (with respect to isolated Al_{13} and K_3O). The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 1.22 eV. The large binding and a substantial HOMO-LUMO gap are both indicative of the very stable nature. How do such units bond?

The next investigations focused on a dimer composed of $\text{Al}_{13}\text{K}_3\text{O}$ units. The two units were placed in several orientations and the energy minimized by moving atoms in the direction of forces till the forces became less than a critical value. The following figure shows the lowest energy structure.

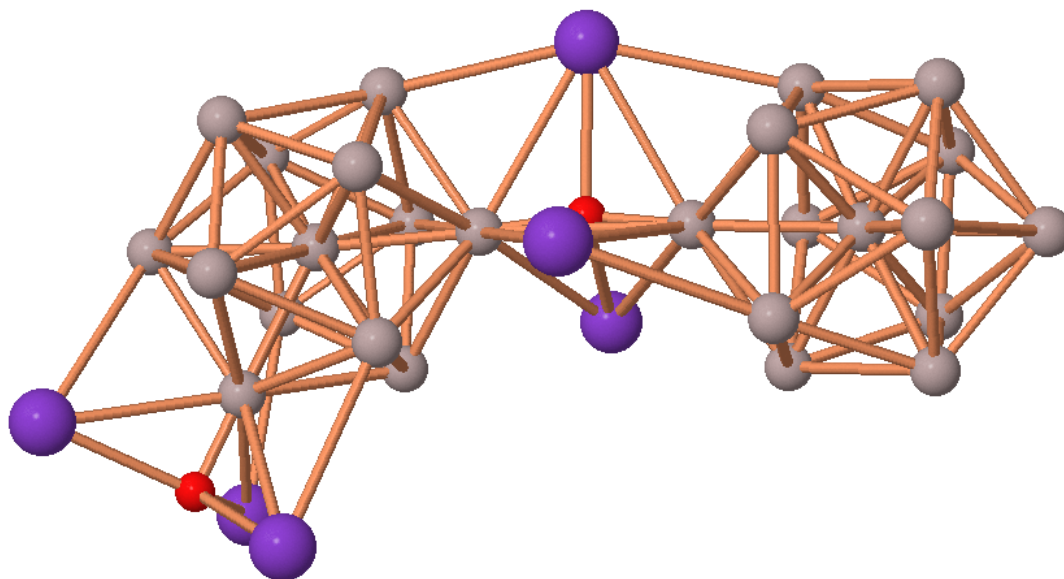


Fig. 7. The ground state geometry of $(\text{Al}_{13}\text{K}_3\text{O})_2$ cluster.

Note that the Al_{13} units maintain their identity providing optimism that one may be able to form cluster materials. We are in the process of exploring this possibility by extending these studies to bigger systems.

(3) Identification of New Superatoms:

In a synergistic effort combining experimental work in the group of Prof. Castleman and the theoretical investigations in our group, we had previously demonstrated that Al_{13}^- behaves like a halogen while Al_{14}^{++} behaves like an alkaline earth.

As the electronic, magnetic, optical or chemical properties in clusters are controlled by geometrical shape, size, and composition, the use of superatoms offers the possibility of forming materials with desirable collective traits using selected species. Our effort is now directed towards finding more members of the “superatom” family.

We have just demonstrated a new member of the superatom family, namely Al_7 . What is truly remarkable is that unlike previous members, this new member exhibits

multiple valence states in close analogy to non-unique valence states exhibited by several atoms. An important outcome of the multiple valence is the ability of the superatom to form stable compound clusters when combined with different atoms. In particular, one can not only understand the stability of Al_7C^- and Al_7N^- reported in previous mass spectra, but one can also predict stability of numerous other species namely Al_7O^- , Al_7O_2^- , Al_7Cl and Al_7Cl_3 . These are exciting developments and are currently being pursued.

References:

1. Chrétien, S.; Gordon, M.S.; Metiu, H. *J. Chem. Phys.* **2004**, 121, 3756 ; Chrétien, S.; Gordon, M.S.; Metiu, H. *J. Chem. Phys.* **2004**, 121, 9925.
2. Bergeron, D.E.; Castleman, A.W., Jr.; Morisato, T.; Khanna, S.N.; *Science* **2004**, 304, 84.
3. Bergeron, D.E.; Castleman, A.W., Jr.; Jones, N.O.; and Khanna, S.N. *J. Chem. Phys.* **2004**, 121, 10456.
4. Bergeron, D.E.; Roach, P.J.; Castleman, A.W., Jr.; Jones, N.O.; Khanna, S.N. *Science* **2005**, 307, 231

Personnel Supported:

S. N. Khanna (1 summer months), Principal Investigator

J. Ulises Reveles (Post Doctoral associate, will be supported starting November).

Publications:

1. Bergeron, D. E., Castleman, A. W., Jr., Jones, N. O., and Khanna, S. N., *Chem. Phys. Lett.* (in Press).

2. Ulises Reveles, J., Khanna, S. N., Castleman, Jr., :Multiple Valence Superatoms (Being Prepared).

Interactions/Transitions:

(a) *Participation/presentation at meetings, conferences, seminars, etc.*

1. US Army Research Laboratory at Aberdeen Proving Ground, Maryland, April, 2005.
2. Collegiate High School, May 2005.
3. AFOSR Contractors Meeting on Molecular Dynamics/Theoretical Chemistry May, 2005
4. XIV International Materials Research Congress”, Cancun, Mexico- Aug. 2005.
5. American Chemical Society Meeting, Washington, Aug. 2005.
6. International Chemical Congress of Pacific Basin Societies, Hawaii, 2005.

(b) *Consultative and Advisory Functions.*

(c) *Transitions.*

Discoveries/Inventions/Patent Disclosures.

Our finding that Al₁₃ has properties like halogen atoms and Al₁₄ has behaviors reminiscent of alkaline earth atoms has been covered by more than 50 news agencies around the world.



Honors/Awards: None