CENTENNIAL FEATURE ARTICLE

Clusters, Superatoms, and Building Blocks of New Materials[†]

A. W. Castleman, Jr.*

Departments of Chemistry and Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

S. N. Khanna

Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284

Received: July 31, 2008; Revised Manuscript Received: November 13, 2008

The physical and chemical properties of cluster systems at the subnano and nanoscale are often found to differ from those of the bulk and display a unique dependence on size, geometry, and composition. Indeed, most interesting are systems which have properties that vary discontinuously with the number of atoms and composition, rather than scale linearly with size. This realm of cluster science where "one atom makes a difference" is undergoing an explosive growth in activity, and as a result of extensive collaborative activities through theory at VCU and experiment at PSU, our groups are recognized as pioneers in this area in which we have been active for many years. Herein we provide an overview of the field with primary focus on our joint undertakings which have spawned the superatom concept, giving rise to a 3-D periodic table of cluster elements and the prospect of using these as building blocks of new nanoscale materials with tailored properties.

Introduction

The field of cluster science continues on a rapidly expanding trajectory due in large measure to two considerations. First and most significant is the connection to the field of nanoscale science where clusters offer the exciting prospect of serving as building blocks for new materials, whose desired properties may be tailored through selection of size and composition.[1,2] Indeed, unlike the approach being pursued by most other research groups involving the subdivision of bulk matter and building from the top down, we pursue the approach of forming new materials of nanoscale dimensions using clusters as building blocks: an approach "from the bottom up".[3–5] In this context, our efforts are directed toward systems whose properties dramatically vary with composition, one atom at a time. Most appealing among these are clusters that display interesting behaviors, whose composition can be selectively chosen, and whose individual characteristics might be retained when assembled into an extended material or one comprised of nanoscale composites.[3,6,7] As we have recently demonstrated, many of these stable clusters mimic the chemical behavior of elements in the periodic table and hence can be regarded as "superatoms", providing an unprecedented ability to design novel materials.[3,8–10] Quantum confinement effects[1] often govern the behavior of matter of this size regime, and studying the reactivity and properties of clusters provides fundamental insights into the interplay of structure,

geometry, and electronic properties and the chemical behavior that can be manipulated. Further reasons for interest in these clusters derive from the fact that they provide testing grounds for modeling reactions that are responsible for varying chemical and physical properties, allowing insights into behavior such as catalytic activity.[11–13] These various considerations represent the theme of the work presented in this feature article.

Individual Atom Effects: Controlling Chemical, Electronic, and Magnetic Behavior

Studying individual clusters of selected size provides the opportunity to investigate factors governing physical and chemical behavior and to explore fundamental mechanisms governing chemical reactivity. In particular, with well designed studies, clusters can serve as tractable models for unraveling mechanisms of catalytic reactions on the one hand and yield information of value in designing nanocatalysts with specific reactivity and/or selectivity on the other.

Our own work has brought out these aspects in investigations of numerous classes of reactions.[12,13] During the course of studies having particular focus on work related to cluster models of catalytic activity, findings were obtained which showed the dramatic effect that can arise due to minor compositional changes in a cluster. One example is seen from a consideration of the dehydration reaction of 1,3-butadiene initiated by vanadium oxide clusters of particular stoichiometries; see Figure 1. For example it was found that only $V_3O_7^+$ and $V_5O_{12}^+$ effected such a specific chemical transformation. An even more dramatic example is seen for the case of reactions of vanadium oxide clusters interacting with ethylene which can lead to oxygen-atom transfer and the formation of acetaldehyde;[11,14] see Figure 2. Among a wide range of clusters studied, only $V_2O_5^+$ and $V_4O_{10}^+$ functioned in this regard.

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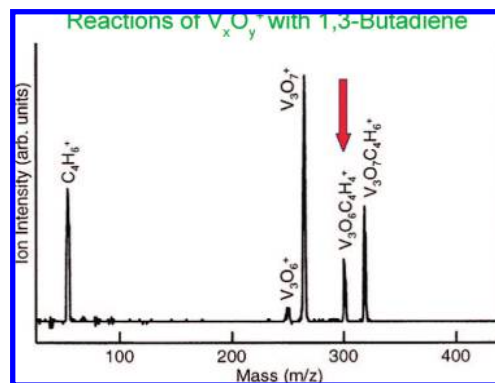
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A. W. Castleman, Jr. is Evan Pugh Professor of Chemistry and Physics and Eberly Distinguished Chair in Science at The Pennsylvania State University, having been professor of chemistry and member of CIRES at the University of Colorado (1975−1882) and previously on the staff at the Brookhaven National Laboratory. He served as a Senior Editor of the Journal of Physical Chemistry from 1988 to 1998. He is a member of the National Academy of Sciences, and a fellow of the American Academy of Arts and Sciences, as well as of the American Physical Society, the American Association for the Advancement of Science, the New York Academy of Sciences and the Royal Society of Chemistry. Included among his many awards and honors are the Doktors Honoris Causa from the University of Innsbruck, Austria, the American Chemical Society Award for Creative Advances in Environmental Science and Technology, the Wilhelm Jost Memorial Lectureship Award from the German Chemical Society, U. S. Senior Scientist von Humboldt Award, Fulbright Senior Scholar award, Senior Fellow of the Japanese Society for the Promotion of Science, Rensselaer distinguished Thomas W. Phelan Fellows alumni award, and Sherman Fairchild Distinguished Scholar at Cal Tech. He is engaged in studies to bridge the gas and condensed phase and to elucidate the fundamentals of solvation dynamics through investigation of cluster photophysics. He is particularly interested in exploring the properties of matter of finite dimension using ultrafast laser techniques, elucidating the physical basis for catalysis and surface phenomena at the molecular level, and developing with his theoretical collaborator S. N. Khanna of VCU the unique characteristics of superatom clusters as building blocks to cluster assembled nanoscale materials. Castleman has published over 600 papers dealing with these subjects.

Shiv N. Khanna is a Professor of Physics at Virginia Commonwealth University, having been a visiting associate professor at the Northeastern University (1983−84) and a scientific collaborator at the Swiss Federal Institute of Technology in Switzerland (1980−1983). He is a Fellow of the American Physical Society and has been twice the recipient of the Distinguished Scholar Award of the College of Humanities and Sciences at VCU. He is a member of the Advisory Board of the "Materials Science Forum" from Trans Tech Publications and "Journal of Mathematics and Sciences: Collaborative Explorations". He has co-authored more than 200 research publications in refereed journals, has edited six monographs, and has chaired/co-chaired several International Conferences. Dr. Khanna and his group are involved in theoretical studies of the electronic structure, magnetic properties, and catalytic properties of atomic clusters, cluster assemblies, and nanoscale materials. Along with A. W. Castleman, Jr. at PSU, they have proposed "superatoms" that extend the "Periodic Chart" to a third dimension and could lead to novel materials with tunable properties and potential for applications in numerous areas.

Figure 1. Reaction of $V_xO_y^+$ clusters with 1,3 butadiene. Only $V_3O_7^+$ and $V_5O_{12}^+$ display the dehydration channel during the reaction with 1,3-butadiene.[11a]

Yet, another example of the atomic control on the properties of clusters is highlighted by recent work on the reactivity of aluminum−hydrogen clusters with oxygen.[15−17] In these experiments, the clusters were produced through laser evaporation of an aluminum rod and then reacted with hydrogen. Figure 3 shows the mass spectrum of the hydrogenated clusters that contained 4 Al atoms, with varying numbers of hydrogen atoms, that were produced. When the clusters were reacted with oxygen, one's containing an even number of hydrogen atoms were completely etched away (see Figure 3) while clusters with odd numbers of hydrogen atoms showed variable reactivity. Pure Al_4^- is known to react strongly with oxygen, and yet adding a single H atom makes it resistant to oxidation as seen from the figure.

Another value of studying elementary cluster motifs is the ability to investigate quantum effects that can change significantly with size and composition. For example, early experiments on Na_n clusters[18] in beams had already established that the electronic properties like ionization potential, polarizability, and electron affinity can change discontinuously with the number of atoms. Later studies extended this nonscalability to other properties.

Recent experimental work[19,20] from our laboratory along with companion theoretical studies also highlights such possibilities as effecting a variation in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) attainable by making minor changes in the composition of certain metal cluster alloy systems. Systems comprised of Al, Bi, Ga, and Sn provide examples of what can be accomplished in this regard. We have shown, for example, that the HOMO−LUMO gap in Bi_3Ga_n clusters can change from 1.89 eV in $Bi_3Ga_2^-$ to 1.17 eV in $Bi_3Ga_4^-$. Knowledge of such variations finds use in efforts to synthesize materials with selected bands.

Other properties show equally interesting variations with alterations in composition. including magnetic ones.[21,22] An interesting case[23−25] is Mn where bulk Mn is known to exhibit complex magnetic order with a unit cell of 58 atoms. As opposed to bulk, Mn_2 molecule has antiferromagnetically coupled atomic spin moments while Mn_3 and Mn_4 clusters are found to have ferromagnetically coupled moments. The magnetic moments of small Ni_n clusters are also found to change with size, and Ni_5 was predicted to have a large spin moment.[26] This prediction was later confirmed by experiments[27] on Ni_n clusters which showed that the moments do change discontinuously with size and lie in the range of 0.85−1.81 μ_B. In fact, a Ni_5 cluster exhibits a moment of 1.81 μ_B, almost three times the bulk value, and the moment decreases by almost 25% in going from Ni_5 to Ni_6. Similarly, while bulk Rh is nonmagnetic, small Rh_n clusters display finite spin moments that vary strongly with size[28,29] the nonmagnetic behavior sets in for clusters containing around 100 atoms.

Unique Cluster Systems

Identifying the ability to tune properties through size and composition leads to the interesting possibility of synthesizing materials with desirable characteristics, providing that proper building blocks can be identified and methods to assemble them in large quantities developed.[30] The discovery of fullerenes[31] and the synthesis of fullerides[32] provided a feasibility demonstration of this important concept. If one follows the fullerene example, the process starts with the identification of the stable motifs in beams that are robust and likely to retain their special characteristics during the assembly. Developing physical principles that can provide guidance to the stability and the chemical features of the clusters is then the first step toward such an objective. The physical principles will vary according to the nature of bonding which was demonstrated for the case of Met-Cars discovered in the Castleman laboratory that revealed unique metal−carbon bonding.[33−36]

Cluster "Magic Numbers", Jellium, and Superatoms in Simple Metallic Systems

Cluster science emerged as a field of research in the 1960s, with pioneering undertakings by several groups including that
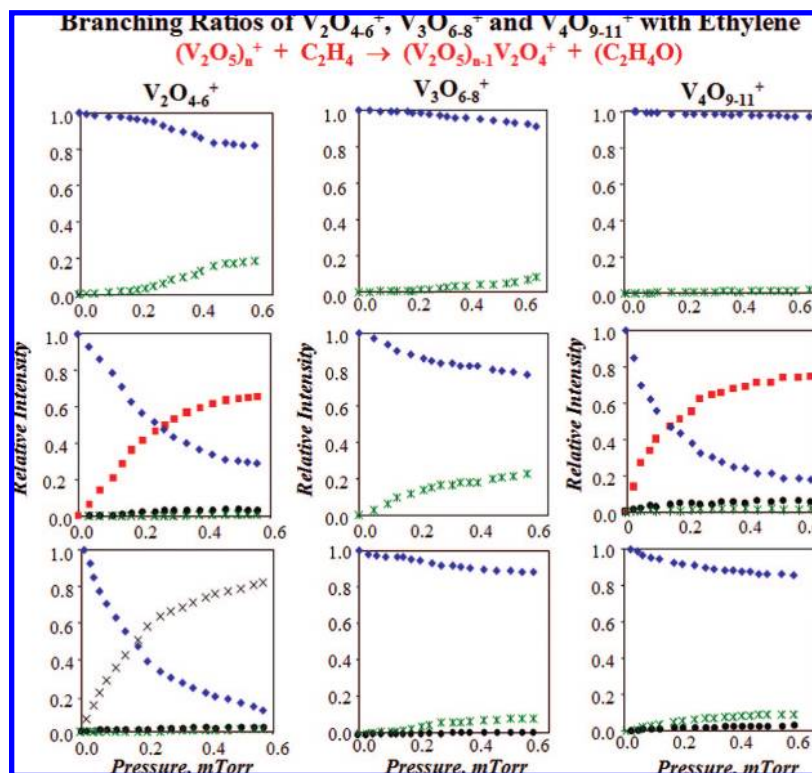
Figure 2. Branching ratios of $V_2O_{4-6}^+$ and $V_4O_{9-11}^+$ with ethylene.
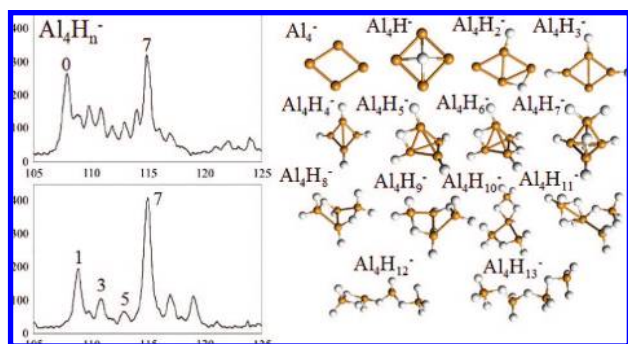

Figure 3. Mass spectra of $Al_4H_n^-$ clusters before and after etching with O_2 and the calculated structures of $Al_4H_n^-$ clusters.[15]

of one of the authors of this review.[37–40] One of the main focuses of early research in the field was accounting for magic numbers often observed in mass spectra of cluster distributions. These were either especially prominent species, or ones that displayed abrupt changes in intensity at specific cluster sizes. Great interest in the area of metal clusters arose due to observations made by Knight and co-workers on magic numbers in the mass spectra of free small sodium clusters.[41] The studies were made by vaporizing alkali metal from a gas aggregation source, ionizing the resulting clusters, and measuring the evolving cluster distribution using time-of flight mass spectrometry. The detected intensities showed large variations with size for clusters containing 2, 8, 18, 20, 34, 40.... atoms which were found to exhibit larger intensity compared to neighboring sizes. For such clusters, the jellium model[18] offers a simplified framework for explaining the observed behavior. Employing an extension of the independent nuclear shell model to a simple electron gas concept developed by Cohen and Chou,[41] Knight and co-workers accounted for the observations. In this model, one imagines that the positive charge of all of the ions in the cluster is distributed uniformly over a sphere of the size of the cluster. The energy

levels of electrons for such a charge distribution correspond to $1s^2\ 1p^6\ 1d^{10}\ 2s^2\ 1f^{14}\ 2p^6$,.... The magic sizes thus correspond to filled electronic shells, suggesting the role of these on the stability, a concept that was not at first accepted without controversy.

The major finding in the field of metal cluster science pertaining to the development of the superatom concept, originally termed a unified atom,[42] came from studies of aluminum cluster reactivities conducted in the Castleman group in 1989. Specifically, during the course of studying reactions of metal cluster anions comprised of aluminum, Leuchtner et al.[42] found a dramatic dependence of reactivity on size where cluster anions containing 13, 23, and 37 atoms were unreactive toward oxygen, while most other species were etched away. Since aluminum has three valence electrons, the number of free electrons in an anion cluster is $3n + 1$. Hence, the observations could be accounted for by shell closings at 40, 70, and 112 electrons predicted by the jellium shell model. The findings from these studies revealed that the electronic structure of the clusters not only accounted for overall mass abundances and hence stability of metal clusters as seen in mass spectra, but also had a direct impact on the overall chemical properties.[42]

Figure 4 displays an example of observed mass spectra of aluminum clusters reacted with oxygen in the vicinity of Al_{13}. In these experiments, metal cluster anions were produced by laser vaporization of an aluminum rod and then introduced into a helium stream in a flow-tube reactor, into which small concentrations of oxygen were added. The abundance of the "magic" clusters was observed to actually increase with extent of reaction, which has been traced to the successive etching of clusters of intermediate sizes until they reach a closed shell character. Soon thereafter we found experimentally other "magic numbers" of cations of aluminum and some of its alloys as well.[43a] With allowance for the number of electrons, the findings

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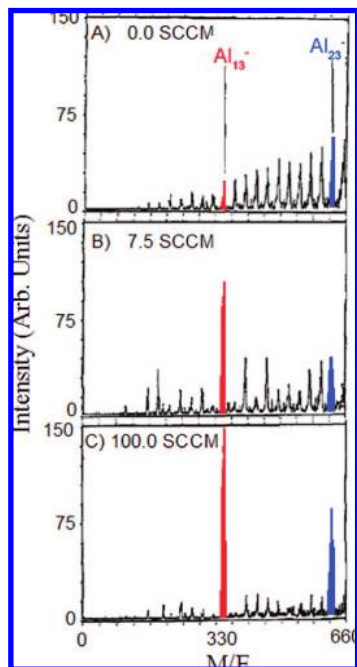
Figure 4. Oxygen etching of anionic aluminum clusters. Adapted from refs 31 and 42.

from these studies were also found to be in accord with the jellium shell model.

Further confirming evidence[44] of the importance of electronic shells came from work on anion alloys of aluminum which contained additions of Nb and V. Similar etching experiments also revealed that reactivities were influenced by shell closings. As an example, an especially prominent peak Al_4Nb^- was found for the 18-electron species. These significant findings further supported the conclusion that the closed electronic shells that were invoked to explain the magic numbers in the mass spectra of metals such as Na, also govern cluster reactivity. These and other observations including those on the Al−carbon system[45] showed that the jellium picture, though extremely simplistic and marked by indisputable limitations, is amazingly successful in describing many of the global observed electronic features.

Replacement of the term "superatom" for unified atom, and the initial conceptual framework behind the idea that clusters mimicking different elements of the periodic table could be designed by changing size, composition, and the charged state was introduced by Khanna and Jena in a series of pioneering papers starting in 1992.[6,7,46−56] Their initial work, which built on the unified atom model,[42] focused on designing stable clusters and was motivated by two findings, namely (1) that clusters with closed electronic shells exhibit enhanced stability and (2) that at large sizes the more stable species will likely correspond to sizes with closed geometric shells.[57] Khanna and Jena proposed that it should be possible to design highly stable clusters by combining electronic and geometric stability. Taking the example of Al_{13} that has 39 valence electrons, they proposed that replacing an Al in Al_{13} by C would lead to 40 electrons and hence the $Al_{12}C$ cluster would be energetically stable and chemically inert. The theoretical studies[6] indeed confirmed an increase in binding energy as an Al in Al_{13} was replaced by C, and a corresponding decrease in reactivity. The electronic structure of $Al_{12}C$ within the jellium concept corresponds to the shell structure $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$ and is consistent with the emerging "unified atom" picture presented (see Figure 5). The same electronic sequence occurs as for Al_{13}^-, and the

work by Castleman and co-workers confirmed that it is chemically inert.[42] The electronic structure also raised another possibility. Since the highest electronic shell is a p-shell, the electronic structure resembled that of halogen atoms. While the jellium model suggested the analogy, first principles studies were needed to determine the magnitude of the electron affinity. Noting this, Khanna and Jena calculated[46] the electron affinity of the Al_{13} cluster using the POLYATOM code and local density approximation. The calculated electron affinity was around 3.7 eV, close to that of Cl (the later calculations[8] using generalized gradients for the exchange and correlation corrections yielded a vertical electron affinity of 3.56 eV and an adiabatic electron affinity of 3.34 eV). This result suggested, for the first time, that an Al_{13} cluster displays characteristics analogous to a halogen atom (see Figure 6) and hence the name "superhalogen". Experimental evidence for this suggestion came from chemical reaction studies made in the Castleman group.[8,9] To gain further evidence that Al_{13} behaves like a halogen, calculations on the properties of $Al_{13}K$ were made[46] to explore if the Al_{13} would bind to alkali atoms in the same way as conventional halogens. The results showed that an $Al_{13}K$ was indeed an ionically bonded molecule much like KCl. Figure 7 shows the electronic charge density of the HOMO in an $Al_{13}K$ cluster, and it is centered around the Al_{13} motif confirming its halogen nature. This proposition started a flurry of activity in superatoms.[3,44−56,58,59] Measurements of the electron affinity of Al_{13} by Wang and co-workers[60] confirmed the theoretical finding that Al_{13} had an electron affinity close to that of an Cl atom. Evidence of the ionic character of $Al_{13}K$ was also later obtained in experimental work by Bowen and co-workers[61] based on the negative ion photodetachment spectra of $Al_{13}K$. The findings of the halogen nature of Al_{13} and the closed shell electronic structure of $Al_{12}C$ led to the introduction[6,7] of the term "super atom" to describe closed shell ($Al_{12}C$) and open shell (Al_{13}) clusters mimicking inert and halogen atoms of the periodic table.[8] In particular, they introduced the idea of an extension of the periodic table to a third dimension with $Al_{12}C$, and Al_{13} among the super elements.[6,7,44−56]

A modified and significantly extended conceptual basis providing fundamental insight behind the current definition of superatoms is due to the joint effort by the Castleman's group at PSU and Khanna's group at VCU. According to the modified newly devised picture, a superatom is not merely a cluster mimicking a selected property of an individual atom but a motif that is stable and demonstrates completely new chemical features beyond the analogue atoms. A superatom also has to satisfy a more stringent criterion in terms of energetic and chemical stability (maintaining of the chemical character). The current three-dimensional periodic table (see Figure 8), proposed by Khanna and Castleman contains only those units that satisfy this revised consideration. Note, for example, that $Al_{12}C$ is no longer included with the new and more fundamental based definition.

To highlight the basis behind this modern development, we begin with the experimental studies of the reactivity of aluminum clusters anions with HI, and subsequently I_2, undertaken by the Castleman group.[8,9,62] Especially crucial were results on the formation and reactivity of produced Al_nI^- clusters. The stability of two observed cluster series was determined by reacting them with oxygen. It was found that while other cluster species readily reacted away, $Al_{13}I^-$ and $Al_{13}I_2^-$, which bear direct resemblance to well-known di- and tri-halide ions, were quite resistant to etching. Theoretical studies[8] on $Al_{13}I^-$ showed that the cluster's stability resides in the ability of the Al_{13} moiety to retain its
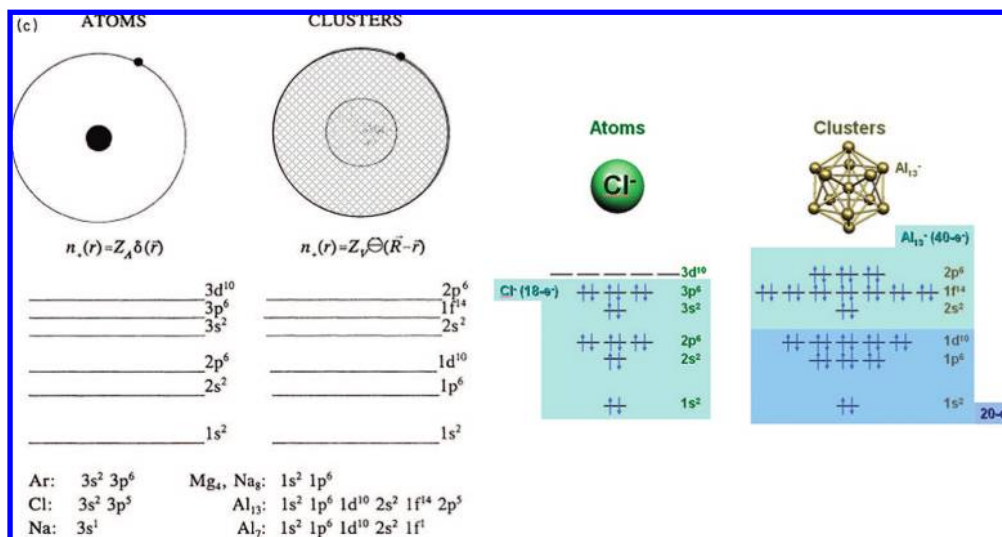
Figure 5. Energy levels in atoms and clusters. Also shown are the electronic levels in a Cl atom and that in an Al_{13} cluster.[7]
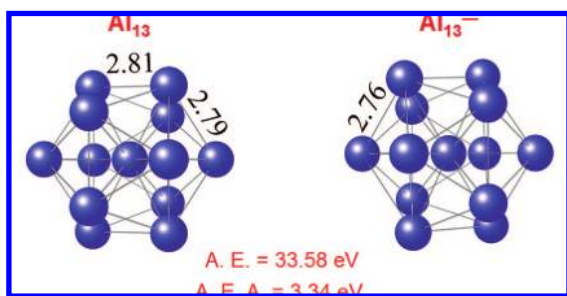

Figure 6. Geometries of Al_{13} and Al_{13}^- clusters. Bond lengths are marked in Å. A.E. is the atomization energy and A.E.A. is the adiabatic electron affinity which is large and consistent with superhalogen character.
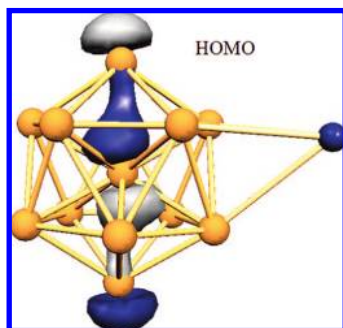

Figure 7. Electron charge density of the HOMO in an $Al_{13}K$ cluster. Most of the electron density is located around the Al_{13} cluster.

Figure 8. Three dimensional periodic table of cluster elements.
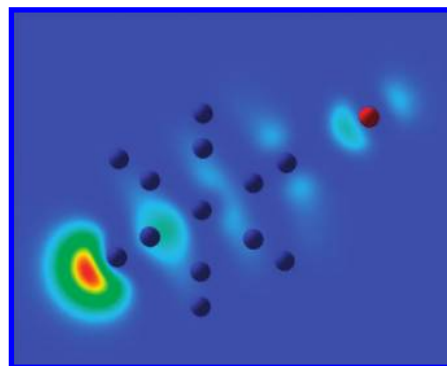
Figure 9. Charge density of the HOMO in $Al_{13}I^-$ showing that most of the charge is located around the Al_{13} moiety.

anionic characteristics, in terms of both geometry *and* charge state, even in the presence of an iodine atom. As shown in Figure 9, the aluminum cluster actually pulls charge away from the iodine atom. The discovery and characterization of $Al_{13}I^-$ and $Al_{13}I_2^-$ showed that Al_{13} can truly be described as a superhalogen (recall that stable X_2^- and X_3^- complexes, where X denotes a halogen, are well-characterized). It is worth noting that we also performed studies to determine how aluminum clusters interact with other halogens.[62] Interestingly, while most of the more stable Al_nX^- (X = Cl, Br, or I) clusters persisted irrespective of the identity of X, $Al_{13}X^-$ was only stable when X had an electron affinity less or approximately equal to that of Al_{13} (that is X = I or Br). This observation strongly points to the significance of Al_{13} being able to maintain its integrity as a stable anion complex.
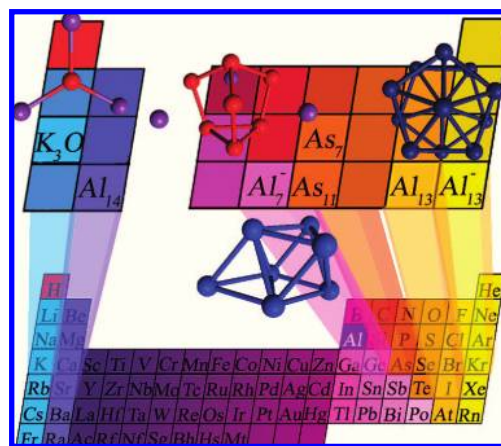
An especially important development that demonstrated that superatoms do offer novel chemical features that might have important implications in reactivity came during the course of studies of "polyhalides" formed upon reacting Al_{13} with I_2 at high concentrations.[9,62,63] The results of these experiments along with theoretical analysis, shown in Figure 10, revealed that $Al_{13}I_x^-$ with even x (but comprised of the equivalency of an odd number of "halogen atoms" where one is mimicked by Al_{13}^-) were stable toward etching by oxygen; indeed the odd halogen species reacted away. Clusters with x up to 8 were observed to be formed. Polyhalide aggregates that seem to

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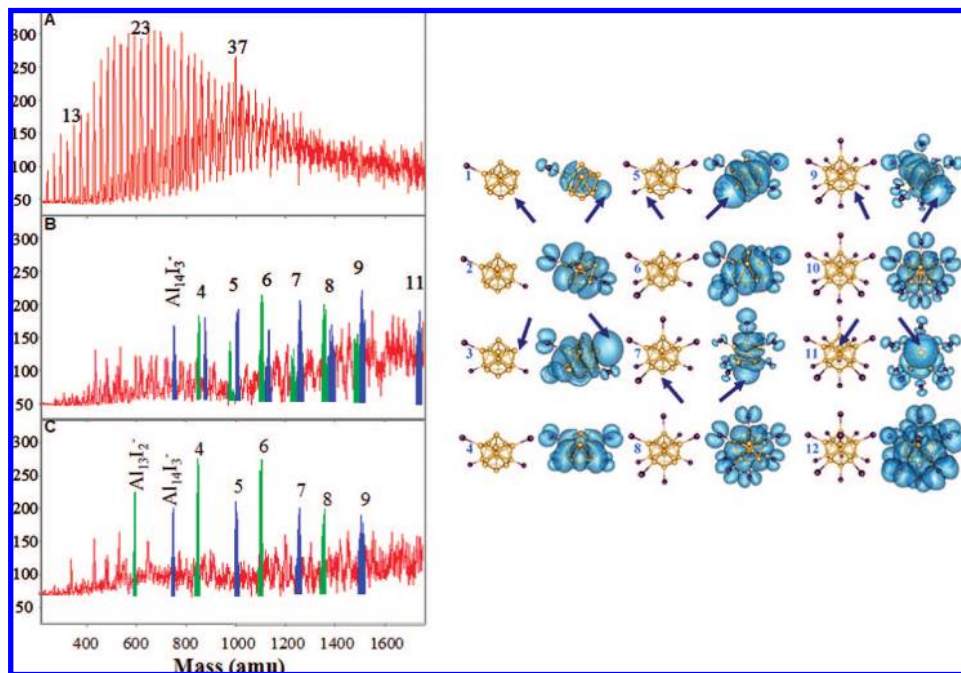
Figure 10. Left figure, top panel shows the mass spectra of pure Al_n^- clusters, the middle panel shows the clusters reacted with I_2, and the bottom panel shows the effect of etching with O_2. The right figure shows the ground-state structure and charge map of the HOMO in $Al_{13}I_n^-$ clusters.[9]

closely resemble the gas phase cluster series are well-known in the condensed phase. In these traditional polyhalides, the primary building blocks are X^-, X_2^-, X_3^-, X_5^-, etc. where the total number of halogen atoms must be odd in order to form a stable complex. As Al_{13}^- and $Al_{13}I_2^-$ were shown by us to be particularly stable, the superatom-containing analogs of halogens were, for the first time, demonstrated chemically[9] in the experimental discovery of $Al_nI_{2x}^-$. Theoretical studies, however, showed that the nature of polyhalides formed from Al_{13} with halogens was completely different as the aluminum centered species do not conform to the type of branching chain geometries common to polyiodides and interhalogen complexes of the heavier halogens.[9] Instead, due to the strength of the $Al-I$ bonds, I_2 units are broken up and individual I atoms attach to the central Al_{13}^- moiety (Figure 10).

Mapping the charge densities of these clusters provided insight as to the reactivity of those species with odd numbers of iodine atoms. As Figure 10 shows, when an I atom is left without a partner at an opposing Al vertex, an area of high charge density forms upon that vertex. This area of high charge density (believed to arise as a result of the Al_{13} cluster's tendency to horde charge away from the less electronegative I atoms) can act as a chemically active site, as we later demonstrated in reactivity studies with methyl iodide.[64]

Theoretical studies on $Al_{13}I_n^-$ clusters also brought out additional features. A Mulliken population analysis showed that each iodine had a charge of around -0.3 e$^-$. It has been suggested[65,66] that this might seem to imply that the Al_{13}^- core is somehow losing its identity. Detailed electronic structure analysis, however, provides a different picture. An Al_{13}^- is chemically inert as it has a high HOMO−LUMO gap. The key issue is whether this gap is maintained in all the $Al_{13}I_n^-$ clusters with even number of iodine atoms. Our recent theoretical investigations reveal that the HOMO−LUMO gap in $Al_{13}I_n^-$ clusters containing up to 9 iodine atoms retain large values for even number of I atoms (see Figure 11). Note that the unpaired I atoms in $Al_{13}I_n^-$ clusters create a lone pair leading to a charged region called the active site. The subsequent I atom binds
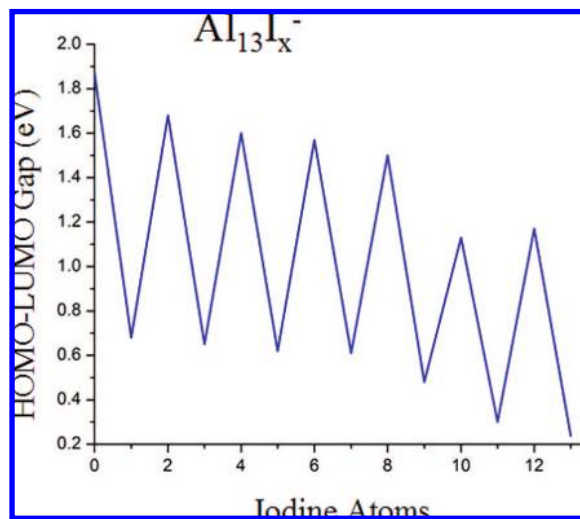
Figure 11. HOMO−LUMO gap in $Al_{13}I_n^-$ clusters.[9]

preferentially to this site to recreate a large HOMO−LUMO gap maintaining the chemical stability started in the Al_{13}^- motif.

The Periodic Table Goes 3-D

At this point it is fair to conclude that there had been some major advances in the field due to the joint experimental and theoretical activities of the PSU−VCU researchers in the groups of Castleman and Khanna. Indeed, the ideas behind the united atom model had been laid out and explored, with chemical evidence for a superhalogen comprised of Al_{13} and a rare gas-like superatom mimicked by its anion. And insights had been gained into the role of active centers in effecting cluster reactivity.

These various exciting findings prompted efforts to produce other element mimics. Another major finding soon emerged from the studies of the reactions of aluminum clusters with I_2. Specifically, a series of stable clusters corresponding to $Al_{14}I_{2x+1}^-$ ($x \geq 1$) were discovered, with x up to 4 (see Figures 10 and 12
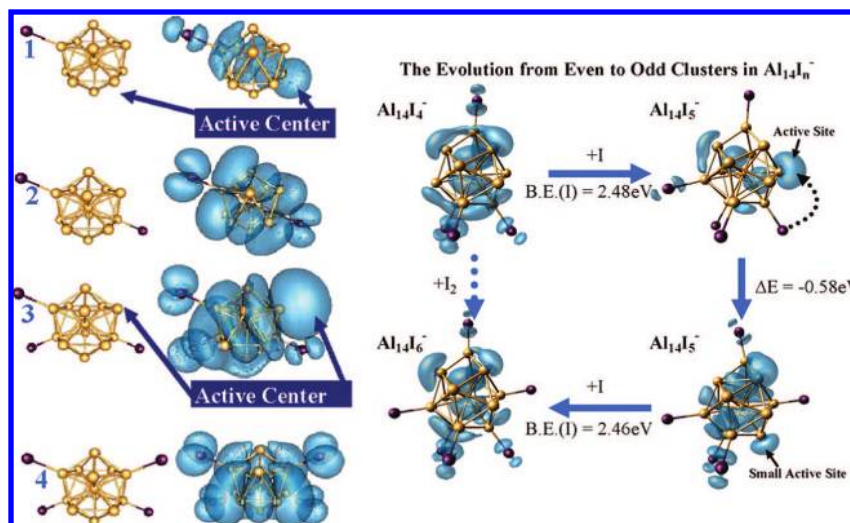
Figure 12. Active sites on iodized Al$_{13}$ and Al$_{14}$ clusters. The left panel shows the creation of active sites around an Al$_{13}$ cluster. The panel on the right shows similar behavior Al$_{14}$I$_n^-$ clusters.
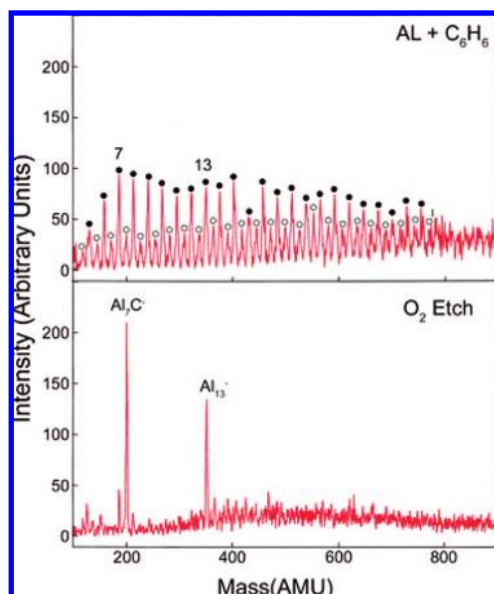
Figure 13. Mass spectra of the Al$_n^-$ clusters reacted with benzene to produce Al$_n$C$^-$ clusters. The lower panel shows the mass spectra after etching with O$_2$.[67]

for the location of I in Al$_{14}$I$_n^-$ clusters and a comparison of the active sites in Al$_{13}$ and Al$_{14}$ species). Studies by the authors of this review revealed that an Al$_{14}$ behaves like an alkaline earth atom,[9,63] thus furthering the prospect of selected clusters mimicking the chemical behavior of atoms in the periodic table and Al$_{14}$ acting as an alkaline earth superatom.[63]

Another milestone in this line of thinking came from the recent joint effort by authors of this article showing that, like many atoms, clusters can also exhibit multiple valences. In a paper published in *Proc. Natl. Acad. Sci.*,[67] we provided evidence that an Al$_7^-$ with 22 valence electrons can form stable compounds by combining with atoms that need 4 or 2 electrons to fill their shells. Specifically, as a result of a chemical combination, an Al$_7^-$ cluster was found to tend toward a shell closure of 18 or 20 electrons.

Figure 13 displays the experimental mass spectra of the Al$_n$C$_x^-$ species showing the prominent stability of Al$_7$C$^-$. Interestingly, such species readily arose from interactions of aluminum clusters with benzene and CH$_4$ [also see ref 45], and

upon oxidation, revealed the very stable species Al$_7$C$^-$. The calculated binding energy of all the atoms in the second, third, and fourth row of the periodic table to a Al$_7^-$ cluster is given in Figure 14. The tetravalent and divalent atoms are seen to bind more strongly than others. These and other observations showed that the jellium picture is amazingly successful in describing many of the global observed electronic features in a variety of systems, and that various metallic clusters can function as superatoms. This gave rise to the general concept of superatoms and the prospect of forming classes of these with analogues to various elements of the periodic table.[68,69] In order to assign a cluster to an appropriate group of the periodic table, its chemistry is characterized as is done by nuclear scientists in assigning new elements comprised of short-lived species.[70]

The validity of the superatom concept goes farther than aluminum and aluminum compound clusters outlined above. Jadzinsky et al. have recently reported[71] success in synthesizing a nanoscale material where Au$_{102}$ clusters serve as building blocks. The stability of the Au$_{102}$ motifs can be understood within a superatom concept where the outer 44 Au atoms are linked to thiols, while the core of 58 remaining Au atoms correspond to a closed electronic shell.

Spin and Reactivity: Jellium and Reactivity of Superatoms

One of the desirable characteristics for superatoms is that they should be chemically inert with respect to retaining their integrity upon interacting with other species. Finding new ways to control the reactivity is therefore an important undertaking. The PSU-VCU group recently examined this problem by considering the reactivity of aluminum clusters with oxygen and how the reactivity of aluminum clusters can be altered by changing their spin state.[15,16] Focusing on anion species, small aluminum cluster anions containing up to 12 aluminum atoms are known to be reactive toward oxygen. As mentioned previously (Figure 3) a new reactivity pattern emerges when H atoms are added. The surprising finding was that all the clusters containing even numbers of hydrogen atoms were etched away while those containing odd numbers of hydrogen atoms survived. For pure Al$_n^-$, most clusters except Al$_{13}^-$, Al$_{23}^-$, and Al$_{37}^-$ are reactive toward oxygen. Since pure aluminum anions containing up to 12 Al atoms and in particular, Al$_4^-$ is highly reactive to oxygen, the reduced reactivity of Al$_4$H$^-$ was quite

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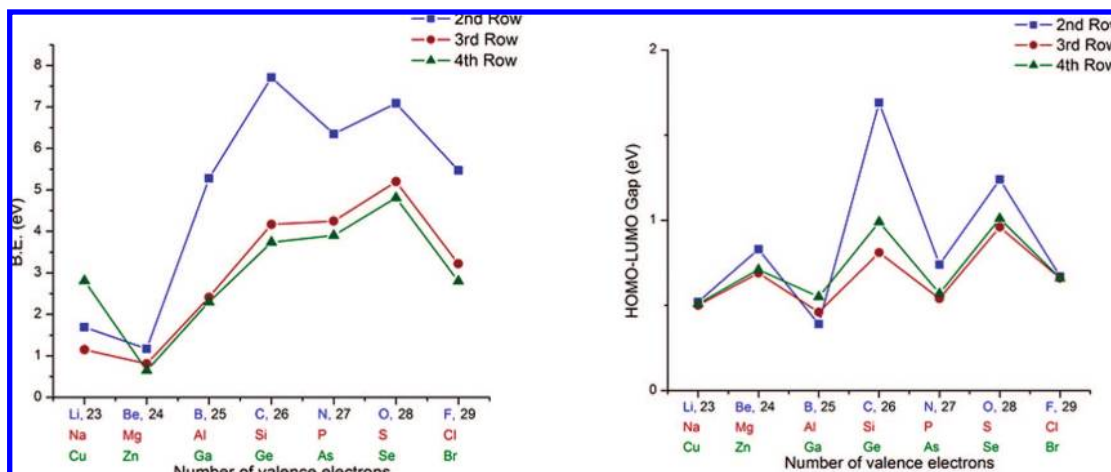
Figure 14. Binding energy of 2nd, 3rd, and 4th row atoms (M) with Al_7^- and the corresponding HOMO−LUMO gap in Al_7M^- clusters.[67]
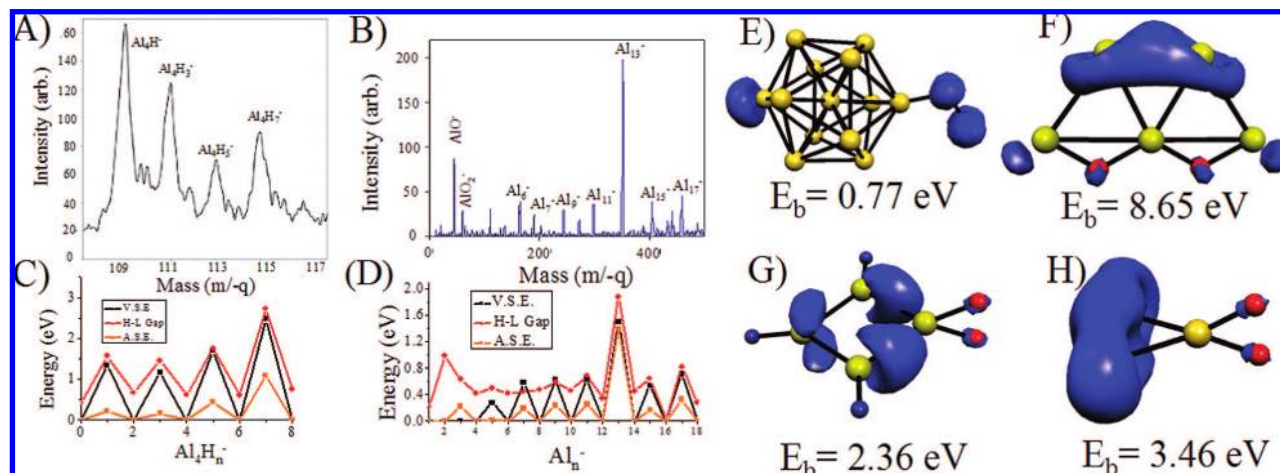
Figure 15. Etching spectra of (A) Al_n^- and (B) $Al_4H_n^-$. (C) Band gap and spin excitation energy $Al_4H_n^-$. (D) Band gap and spin excitation energy Al_n^-. Spin density and geometry of O_2 with (E) Al_{13}^-, (F) Al_5^-, (G) $Al_4H_3^-$, and (H) Al_3^-.

surprising. The theoretical investigations revealed that the reduction in reactivity was related to the conservation of the spin. Since molecular oxygen has a triplet spin multiplicity, the reactivity with clusters having an even number of valence electrons requires a spin excitation of the metal. For cases where the spin excitation energy of the metal counterpart is low, the O_2 binds more strongly, the O−O bond can break, and the clusters are reactive. On the other hand, when the spin excitation energy is high, the reactivity is reduced. This is shown in Figure 15 which displays the relation between vertical and adiabatic spin excitation energy and the reactivity.

These findings have important consequences. For example, clusters that are nonreactive, can be made reactive by either changing the spin configuration of the cluster (through e.g. addition of an hydrogen atom) or exciting oxygen to a spin singlet. On the other hand, even reactive aluminum clusters can be made nonreactive through controlling spin excitation energy. This is an exciting development and may be expected to play a major role in designing aluminum cluster based materials that are stable under exposure to oxygen and in general for controlling reactivity through spin.

Superatoms: Building Blocks

The discovery of the wide range of applicability of the revised superatom concept prompted studies to ascertain whether these "elemental" species could function as building blocks for new

nanoscale materials with tailored design of their properties. There are several reasons that the solids assembled from stable clusters would exhibit properties very different from materials composed of individual atoms. There is only one length scale and nature of bonding in atomic solids, whereas a cluster assembled solid will be marked by intracluster and intercluster length scales and directional bonding. The electronic properties of atomic solids are governed by the bands formed through the overlap of atomic orbitals, while in a cluster solid the energy bands will depend on the electronic states in individual clusters.[72] Figure 16 shows this via our recent theoretical results on the assembly of $Al_{13}K_3O$ motifs.[72]

The tuning of band gaps should be readily accomplished with such cluster-based materials. These factors can give rise to novel possibilities, as seen for example by the fact that the properties of fullerides are very different from those of graphite or diamond. As another example, the superconducting transition temperature of an alkali doped fulleride is an order of magnitude higher than that of intercalated graphite.[32] This difference is largely rooted in the vibrational characteristics of the cluster-like material.

The major difficulty in forming cluster materials is that clusters are generally metastable and in many cases have a tendency to coalesce. Potentially, there are various ways to overcome this. The clusters could be isolated by passivating them with organic ligands,[73] inserting them into cages (zeolite)[74]
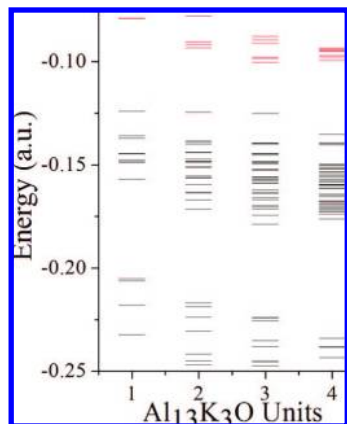
Figure 16. Progression of the electronic states in assemblies of $Al_{13}K_3O$ units. The black lines are the filled states, and the red lines represent unoccupied states.[72]

or depositing them on surfaces.[75,76] However, one has to consider the possible altered properties that might arise due to the interaction between the cluster and the support. An alternative approach is to identify clusters like C_{60} or Al_{13}^- that will maintain their identity when assembled. In this context, it will be ideal if findings from fundamental studies could establish the framework for systematically searching for superatoms with desirable properties. One of the main goals of the work in the VCU-PSU groups has been to realize this possibility by producing magic clusters that are both very stable and relatively unreactive. Identifying the factors that govern the stability of clusters is the first step toward this goal. However, these factors may vary according to the nature of bonding in various cluster systems.

Beyond these considerations,[30] concepts have also led to superatoms where it has been shown that As_7^{3-} and As_{11}^{3-} have characteristics analogous to phosphorus atoms and K_3O to alkali metals. It is important to recognize that, although the electronic shells were introduced via the jellium model, the existence of electronic shells in fermionic systems is known to occur for a far wider range of potentials.

Cluster Assembly: The Protocol

Interest in superatoms abounds for many reasons, one being the exciting prospects of using them as building blocks for tailoring the properties of new materials of nanoscale dimensions. The feasibility of this concept was recently highlighted in a publication involving the present authors and colleagues.[30] A protocol that provides a viable pathway from free clusters to cluster assemblies, more widely and with better control on primary units, was developed during the course of the work. The approach involves three synergistic steps: (1) Identification of the potential building blocks through experiments on size selected clusters in the gas phase. (2) Investigation of the energetic and chemical stability of the cluster motifs through compositional energy diagrams based on first principles theoretical investigations. This information along with experiments in step 1 enables identification of feasible units and pathways to their assembly. (3) Synthetic chemical approaches designed to assemble desired cluster blocks using the information derived in step 1 and 2, or cluster assembly via direct deposition.

In view of the interest and promise, we conducted some feasibility studies focused on the arsenic−metal system[30] as the model superatom composite. Following evidence we obtained from earlier studies on the Bi−Na system[77] that revealed

especially stable and prominent species (e.g., $Bi_7Na_3^+$), we undertook a detailed study of members of the same groups of the periodic table, namely arsenic in combination with potassium. Figure 17 displays the mass spectra of the $As_nK_m^+$ clusters generated in molecular beams, showing the existence of especially prominent peaks at $As_6K_3^+$ and $As_7K_3^+$. Theoretical electronic structure analysis indicated that the ionization potential of As_7K_3 was 5.07 eV, whereas that of As_6K_3 was only 3.96 eV. Since the 308 nm photon used to ionize and detect the various clusters has 4.03 eV of energy, ionization of As_7K_3 requires two photons, whereas As_6K_3 could be ionized with a single photon. This revealed that As_7K_3 was a prominent magic number, additional support for which came from theoretical investigations. Considering this species gave guidance for a search of composition from which to produce an actual representative cluster assembled material. Following the protocol procedure, compositional energy diagrams were employed to study fragmentation energy, HOMO−LUMO gap, energy required to remove a single K atom, and other quantities. Figure 18 shows a typical compositional diagram displaying the minimum energy required to break a cluster into two fragments. To facilitate the comparison, a Gaussian was placed at each calculated point so that the ensemble gives the perspective of a surface. Note that As_5K, As_7K_3, and $As_{11}K_3$ have the highest fragmentation energy. The planar structure of As_5 made it unsuitable for acquiring three-dimensional assemblies leaving As_7 and As_{11} as the potential motifs. Both of these do, in fact, form cluster materials. For As_7, the theoretical studies further indicated that the cluster could be regarded as an As_7^{3-} anion and that the role of the alkali atoms was to donate charge. Thus, it was predicted that it would be possible to generate different materials by changing the nature of the alkali atom as well as by replacing the alkali atoms by cryptated atoms that facilitate the electron transfer by reducing the ionization potential.

**Superatom Building Blocks and Nanoscale Assembly**

Guidance from the protocol opened the pathway to accomplishing the synthesis of numerous related cluster assemblies. Various materials have now been synthesized employing complexes comprised of As_7 and As_{11} in combination with different bare and cryptated alkali atoms.[78] These have been characterized using X-ray diffraction. Shown in Figure 19 are such assemblies consisting of As_7 units bound by K atoms, Cs atoms, and cryptated K atoms (not shown)) donating the remaining charge. A careful view shows that the As_7 motifs are bound by K atoms and form helical chains that are periodically joined together into hexagonal rings leading to a nanomattress arrangement. Theoretical electronic structure investigations reveal that the assemblies are marked by filled bands of levels separated by unoccupied bands leading to cluster based semiconductor character. What is important is that the band gap can be tuned by changing the alkali atom. To demonstrate this variability, we show in Figure 19, selected assemblies based on As_7 motifs and the resulting calculated band gaps using first principles electronic structure calculations where the exchange correlation effects were incorporated using the density functional approach. The calculations were carried out using the VASP software. It was intriguing that the band gap could be tuned between 2.58 and 1.30 eV, now established in preliminary experiments by Weiss and co-workers.[79] Sen et al.[78] have also synthesized similar assemblies based on As_{11} motifs and theoretical calculations predict large variations in the band gap depending on the cation and the crypt.

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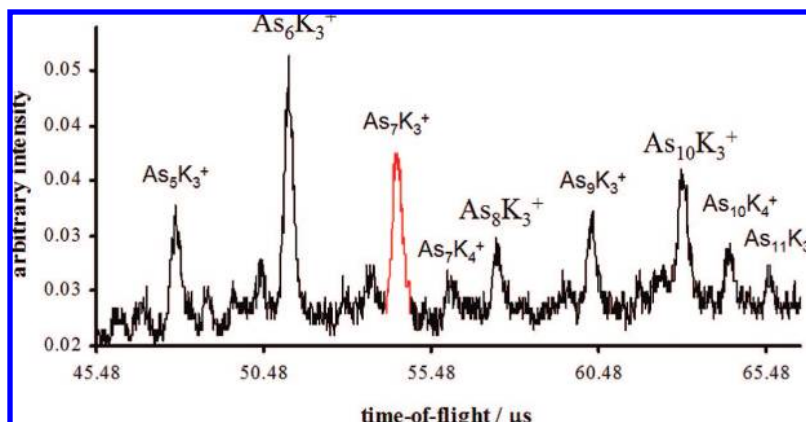
Figure 17. Mass spectra of As_nK_m clusters generated in a molecular beam by the laser vaporization of a mixture of arsenic and potassium and subsequently ionized.[30]
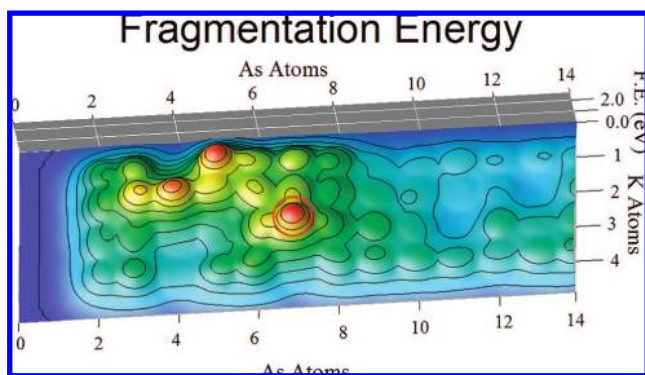
Figure 18. Fragmentation energy of $As_nK_m^+$ clusters. A Gaussian is placed at each value to generate a surface for better visualization.[30]
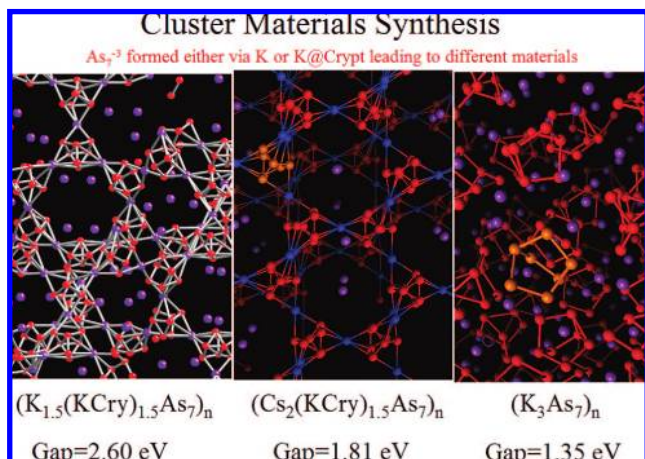
Figure 19. Geometrical structure of various cluster assembled materials made of As_7 combined with K, Cs. or cryptated K atoms. The calculated band gaps of the resulting solids are also marked.

Conclusions and Perspective: The Present and Prospects for the Future

The possibility of describing the electronic structure of clusters in terms of electronic shells raised the interesting possibility that clusters might be regarded as superatoms, a concept conceived and subsequently extended by the authors of the current review as the work beyond Al_{13}^- evolved through our extensive collaborative research undertakings. There are several reasons that such an analogy appeared to be plausible. The ionization potentials of simple metal clusters were found to exhibit peaks at sizes corresponding to filled electronic shells much in the same way as atoms. Importantly, more recent experiments, revealed that aluminum clusters can also take on properties associated with halogens, as well as ones similar to rare gases, and alkaline earth metals, giving promise to the possibility of forming a class of superatoms with analogies to virtually any element of the periodic table. Indeed, element mimics of diverse electronic nature including ones corresponding to alkali metals, phosphorus, and others even displaying multivalent character have also been devised by us in recent years.

It is important to emphasize that although we have introduced electronic shells through use of the jellium model, the existence of electronic shells in fermionic systems is known to occur for a far wider range of potentials.[18] For example, the energy levels in a three-dimensional harmonic oscillator, those in an intermediate and square well potential, and the energy levels in nuclei under a different class of potentials, all lead to shells that produce closings at 2, 8, 18, 20, 34, 40,... electrons. Note that our theoretical work on these cluster systems involves rigorous, first principles calculations, which use the jellium model only as a guide.

The promise of using superatoms as building blocks of new materials, whether ones composed of aluminum or of other "good" metals, is that new chemistry must be learned. The ideas we set forth take advantage of the strange quantum effects that emerge in systems of limited dimensions to reduce the chemistry of nanoparticles to those typically characteristic of atoms. This enables one to use the well-traveled roads of the chemistry of atoms as new pathways to nanostructured materials with novel electronic, optical, magnetic, and mechanical properties.

The unusual properties displayed by jellium based superatoms raises the prospect of manipulating the chemical behavior of materials or extending their chemical applications in terms of reactivity. Formation of superatom-containing molecules through selected chemical reactions opens many possibilities for the synthesis of novel nanostructured materials, and the tailoring of materials with unique reaction centers. As one rather obvious example, our findings that Al_{13} is a halogen-like superatom and the fact halogen chemistry is ubiquitous in organic synthesis opens up many new exciting aspects to explore. Moreover, pursuit of magic cluster peaks can offer potential insight in the identification of species promising for cluster assembly and the tailored design of nanoscale materials with selected properties. In this context, note that by taking advantage of the superatom character of various clusters, new possibilities may emerge in the integration of metal-based nanoelectronics with evolving new techniques in molecular electronics.

In concluding, we wish to take note of the fact that the interrelated fields of cluster science and nanoscience are merging and are providing many exciting new avenues of research to pursue. The prospects of significantly extending the cluster-element members of a 3-D periodic table to encompass all groups of the conventional atomic periodic table abound, and we see no limit to the possibilities that exist. Superatom mimics will certainly be an important component of the methods of nanoscale materials formation where they will function as the primary building blocks in order to tailor properties. As in the past, the future depends on a well coordinated synthesis of experiment and theory and we are very pleased to have had such a productive and rewarding collaboration between our groups enabling us to accomplish so much. We look forward to an exciting future for this field.

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