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Special and General Superatoms

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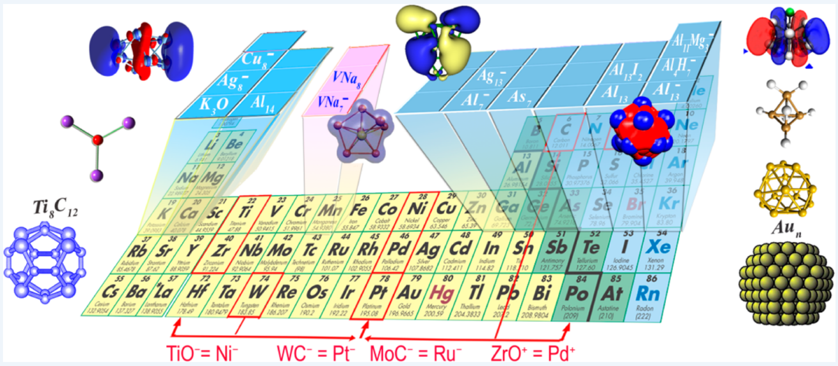

CONSPECTUS: Bridging the gap between atoms and macroscopic matter, clusters continue to be a subject of increasing research interest. Among the realm of cluster investigations, an exciting development is the realization that chosen stable clusters can mimic the chemical behavior of an atom or a group of the periodic table of elements. This major finding known as a superatom concept was originated experimentally from the study of aluminum cluster reactivity conducted in 1989 by noting a dramatic size dependence of the reactivity where cluster anions containing a certain number of Al atoms were unreactive toward oxygen while the other species were etched away. This observation was well interpreted by shell closings on the basis of the jellium model, and the related concept (originally termed "unified atom") spawned a wide range of pioneering studies in the 1990s pertaining to the understanding of factors governing the properties of clusters.

Under the inspiration of a superatom concept, advances in cluster science in finding stable species not only shed light on magic clusters (i.e., superatomic noble gas) but also enlightened the exploration of stable clusters to mimic the chemical behavior of atoms leading to the discovery of superhalogens, alkaline-earth metals, superalkalis, etc. Among them, certain clusters could enable isovalent isomorphism of precious metals, indicating application potential for inexpensive superatoms for industrial catalysis, while a few superalkalis were found to validate the interesting "harpoon mechanism" involved in the superatomic cluster reactivity; recently also found were the magnetic superatoms of which the cluster-assembled materials could be used in spin electronics. Up to now, extensive studies in cluster science have allowed the stability of superatomic clusters to be understood within a few models, including the jellium model, also aromaticity and Wade−Mingos rules depending on the geometry and metallicity of the cluster. However, the scope of application of the jellium model and modification of the theory to account for nonspherical symmetry and nonmetal-doped metal clusters are still illusive to be further developed. It is still worth mentioning that a superatom concept has also been introduced in ligand-stabilized metal clusters which could also follow the major shell-closing electron count for a spherical, square-well potential. By proposing a new concept named as special and general superatoms, herein we try to summarize all these investigations in series, expecting to provide an overview of this field with a primary focus on the joint undertakings which have given rise to the superatom concept. To be specific, for special superatoms, we limit to clusters under a strict jellium model and simply classify them into groups based on their valence electron counts. While for general superatoms we emphasize on nonmetal-doped metal clusters and ligand-stabilized metal clusters, as well as a few isovalent cluster systems. Hopefully this summary of special and general superatoms benefits the further development of cluster-related theory, and lights up the prospect of using them as building blocks of new materials with tailored properties, such as inexpensive isovalent systems for industrial catalysis, semiconductive superatoms for transistors, and magnetic superatoms for spin electronics.

1. INTRODUCTION

One of the major developments of the past century was the recognition of cluster science as a field that bears on so many others. Attributable to the reduced size and related aspects of quantum confinement, an exciting achievement in cluster science is the realization that chosen stable clusters can mimic the chemical property of an atom or a group of the periodic table of elements.[1,2] This major finding known as a superatom concept (which was originally termed a "unified atom"[3]) came from the

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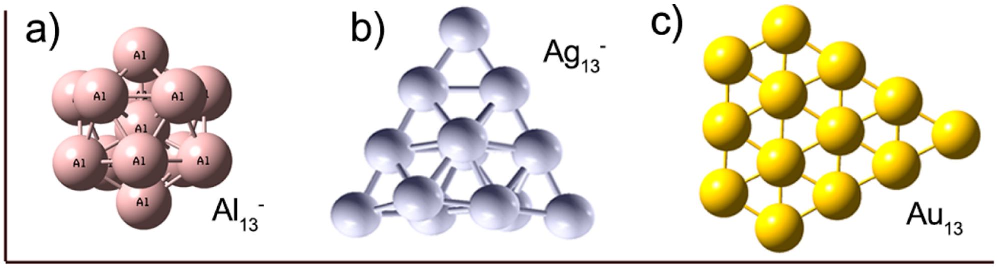

Figure 1. Structures of metal clusters with a magic number of 13 atoms: Al_{13}^- (a), Ag_{13}^- (b), Au_{13} (c).

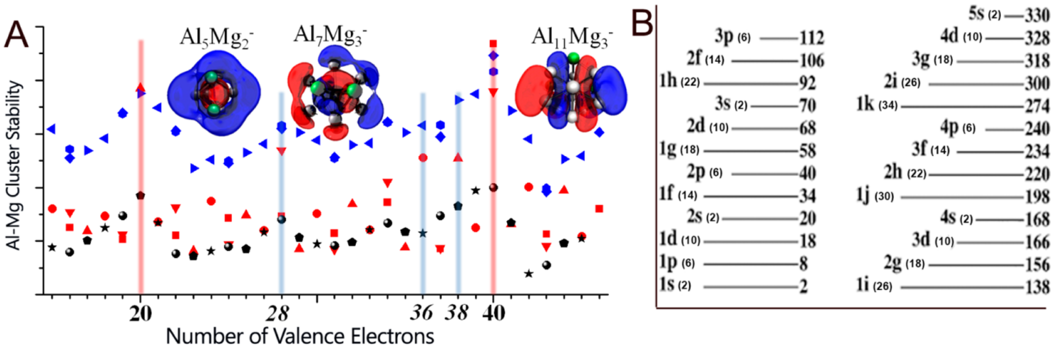

Figure 2. (A) The relationship of Al−Mg cluster stability with the number of valence electrons. (B) A sketch displaying the shell closing with orbitals associated with electron counts.

study of aluminum cluster reactivity conducted in the Castleman group in 1989,[4] where interesting size-dependent reactivity was noted in which Al cluster anions containing 13, 23, and 37 atoms were unreactive toward oxygen although the other species were etched away. This observation was accounted for by spin conservation and shell closings at 40, 70, and 112 electrons on the basis of a jellium model which refers to a variational spherical model for the small metallic clusters by assuming their electron shells follow a spherically symmetric efficitive, Woods−Saxon, potential function.[5,6]

With a replacement of the term superatom for "unified atom", Khanna and Jena performed a series of pioneering studies since the 1990s.[7] They proposed the initial conceptual framework behind the idea that clusters mimicking different elements of the periodic table could be designed by changing sizes, composition, and their charged states. While abundant stable clusters were assigned to superatomic noble gas (i.e., magic species), the recognition of superatoms with one less electron than a closed shell is ascertained as superhalogen, as known for neutral Al_{13} which bears an adiabatic electron affinity at 3.40 eV exhibiting behavior reminiscent to a halogen atom.[2] Another typical example is superalkali clusters having one more electron than a closed shell, such as Cu_8^-/Ag_8^- on which recent studies of their reactivity with chlorine display an increased reactive cross section,[8] due to the long-range transfer of valence electrons validating the harpoon mechanism known for the reaction "$K + Br_2$".

Recently there emerged interesting magnetic superatoms. Typically VNa_8 and VNa_7^- were found to mimic a Mn atom while the property of VNa_9/VNa_8^- resembles that of a Cr atom.[9] Among others, Castleman and co-workers[10] found that simple cluster ions such as ZrO^- could function as superatoms that are isovalent with foe example Pd^- in related reactivity and the counterpart species take up similar electronic properties. It is worth mentioning that the superatom concept was also introduced for gold nanoclusters since the discovery of a superatomic complex $Au_{102}(SR)_{44}$ in 2007,[11,12] where the major shell-closing electron count for a spherical, square-well potential follows as 2, 8, 18, 20, etc., significantly coincident with the gas-phase metal clusters under a jellium model.[13]

In the pursuit to find other superatoms, it is important to develop the nature of superatom chemistry and identify what kinds of compounds superatoms form. Regardless of the fact that the above-mentioned studies have been performed in different groups and even in different research fields, it is helpful to fully qualify the superatom concept in order to avoid possible confusion and to provide general insight for understanding their common nature. By proposing a new concept, named as special and general superatoms (i.e., stable metal clusters within a jellium model, vs nonmetal-doped and ligand-stabilized metal clusters), herein we are endeavoring to summarize all known common aspects of superatoms.

2. SPECIAL SUPERATOMS

While the behavior of metals is determined by the electronic levels near the Fermi energy, the entire valence electronic structure in simple metal clusters is made of discrete electronic shells which are multiple highly degenerate states and much like atoms. For such clusters a simplified framework to explain their behavior is the jellium model which was first proposed by Martins et al. in 1981[14] and verified experimentally by Knight et al. in 1984.[6] Sizes and electron counts of superatoms interpreted by the jellium model are quite stable compared with others of similar sizes; also their properties are dominated as expected to reach a certain valence state. Typical superatom species having a spherical-like structure are Al_{13} and Al_{13}^- which share an icosahedral structure of 13 aluminum atoms (Figure 1a). The stability of a cluster with 13 atoms is not limited to aluminum and allows for modifications of the theory to account for nonspherical symmetries. For example, some other metal clusters such as Ag_{13}^- (Figure 1b),[15] Au_{13} (Figure 1c),[16] Pt_{13}, and Pd_{13},[17] also exhibit enhanced stability although their lowest energy structures are not icosahedral. Among them, for instance, the stability of Ag_{13}^- is assigned to the large spin excitation energy and a big HOMO−LUMO gap is associated with its bilayer triangular cluster structure.

According to the metallic near-free electron gas (NFEG) theory, special superatoms can be simply classified into groups based on their valence electron counts, e.g., superatomic noble gas (with a closed shell), superhalogens (one less electron than a closed shell), superalkalis (one more electron than a closed shell), and superatomic alkaline-earth metals, also magnetic superatoms indicating importance in spin electronics.[9]

2.1. Superatomic Noble Gas

Numerous superatom species with closed electron shells have been theoretically predicted with enhanced stability over the past decades (we cannot list these studies here due to the limited space),[18] which continuously provide new topics and guidance for experimental studies to verify stable clusters.

As oxygen is a strong etchant, stable clusters such as magic species often can be experimentally determined by noting their survival against oxygen etching. Several magic species with closed electron shells have been thus identified, such as the aforementioned Al_{13}^-, Al_{23}^-, and Al_{37}^-, which are in good agreement with the established cluster theory based on the jellium model. Evidently these findings are not limited to Al clusters. Recently Z. Luo et al.[19] examined the stability of Al−Mg metal alloy cluster species (Figure 2), furthering the suggestion of jellium electronic shell closing.[6,13] Considering that Al and Mg possess three and two valence electrons respectively, $Al_nMg_m^-$ clusters containing up to 15 atoms involve all possible valence electron counts up to 46, hence allowing verification of the magic numbers within 46 predicted by the jellium model. As expected, $Al_5Mg_2^-$ and $Al_{11}Mg_3^-$ which correspond to magic numbers of 20 and 40 electrons were observed to exhibit inertness toward the oxygen etching reaction, in accordance with the predicted stability of Al−Mg clusters via theoretical calculations (on a basis of HOMO−LUMO gaps, orbitals, removal energies, etc.). While certain combinations of these clusters are of considerable interest for energetic materials, the magic species $Al_5Mg_2^-$ and $Al_{11}Mg_3^-$ indicate antioxidative application potentials in view of the extensive use of Al−Mg alloys in industry and aerospace manufacturing.

Among others, C. E. Jones et al.[20] reported a Bi-doped aluminum cluster, Al_5Bi, which has 20 valence electrons corresponding to a closed jellium shell and bears a symmetric and compact 3D geometry with a big HOMO−LUMO gap and a relatively large ionization potential compared with its counterpart clusters. Al_nAs and Al_nSb clusters were also studied using a synergistic approach combining negative ion photoelectron spectroscopy and DFT calculations, and it was found that Al_5As and Al_5Sb exhibit enhanced stability and also have a closed shell of 20 valence electrons ($1S^2|1P^6|1D^{10}|2S^2$).[21] Besides, Hiura et al.[22] reported the formation of a series of Si-cage clusters $M@Si_n^+$ (M = Hf, Ta, W, Re, Ir) and found that the clusters $M@Si_{12}$ are very stable, ascribed to electronic and geometrical shell closures within a jellium framework. These semiconductor-doped clusters attract research interest because of the likelihood that they could serve as a tunable building block for functional materials.

2.2. Superhalogens (VIIA Group)

As one of the most proverbial superatoms, Al_{13} behaves like a Cl atom and has been characterized to bear properties respected for a superhalogen.[2] Figure 3 displays the electronic levels for an Al_{13}^-/Al_{13} cluster compared with those for a Cl ion/atom. While a Cl atom displays in total 17 electrons, the cluster Al_{13} exhibits a configuration of 39 valence electrons corresponding to $1S^2|1P^6|1D^{10}|2S^2|1F^{14}|2P^5$. The similarity of the outermost layer electrons coincides with the anticipation for the mimic of halogen. The superhalogen character of Al_{13} has been further ascertained by both experimental and theoretical investigations in identifying stable cluster species of $Al_{13}I_x$,[1,23] as discussed in detail below.

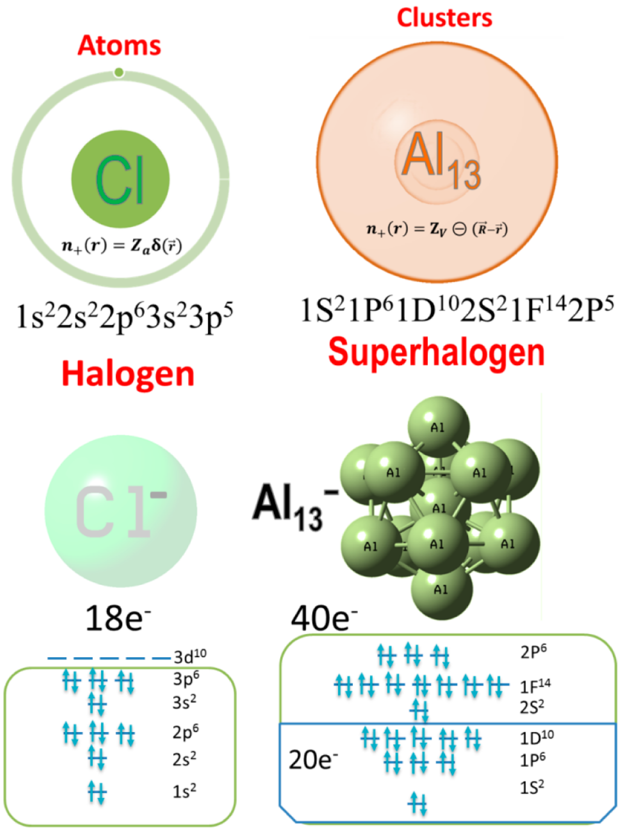

Figure 3. Electronic levels in a Cl atom and a Cl^- ion, compared with those in Al_{13} and Al_{13}^- clusters.

Figure 4 displays noteworthy results for aluminum clusters reacting with HI, where the observed products reveal the reaction mechanism involving etching and iodine addition for the Al clusters. While interesting findings shed light on several reactions in which Al_nI^- generation is energetically favorable,[2] trends in this reactivity suggested that halogen incorporation could leave the electronic properties unperturbed for some aluminum clusters. Among these Al_nI^- clusters, the lowest energy structure for $Al_{13}I^-$ was calculated to feature the icosahedral Al_{13} unit with the halogen atom located at an on-top site. Similar results were also found for Al_nBr^- and Al_nCl^-,[24] where the charge density of the highest occupied molecular orbital in these $Al_{13}X^-$ clusters is dependent on the identity of X. Investigations on the transition-state structures and reaction mechanisms for the dissociative chemisorption of HI, I_2, and CH_3I on the magic cluster Al_{13}^- have shown that the HI, I_2, and CH_3I molecules approach aluminum with an end-on orientation due to the more effective orbital overlap compared with a side-on orientation.[25] Through detailed calculations in different research groups, the structural, electronic, energy, and vibrational characteristics of $Al_{13}X^-$ (X = H, F, Cl, Br, OH, NH_2, CH_3, C_6H_5) have been unambiguously ascertained, with an Al-centered icosahedral cage Al_{13} linked with an outer-sphere ligand X.[1,2,23,26] The binding energy between Al_{13} and the halogen atom increases as X goes from I (2.96 eV) to F (5.79 eV).

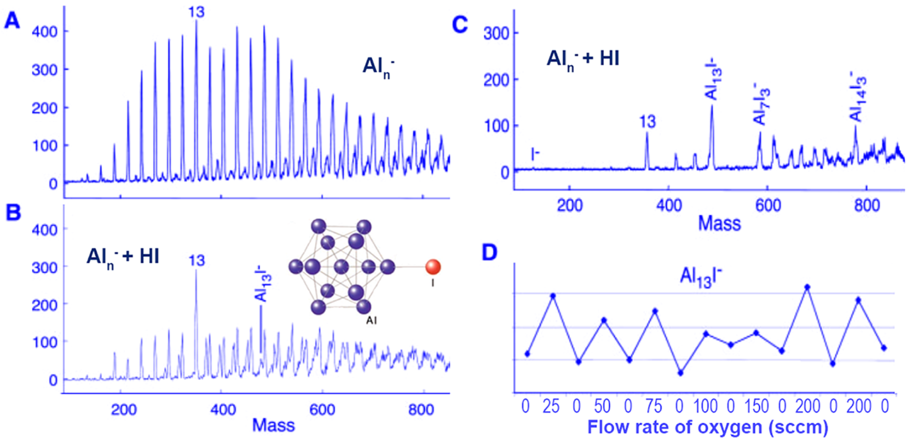

Figure 4. Mass spectra showing the reaction products of aluminum clusters with HI: 0 sccm (A), 25 sccm (B), and 200 sccm (C) of 10% HI seeded in He, where the inset shows the lowest energy structure of $Al_{13}I^-$. (D) Growth of $Al_{13}I^-$ peak in the presence of oxygen demonstrates the cluster's stability.

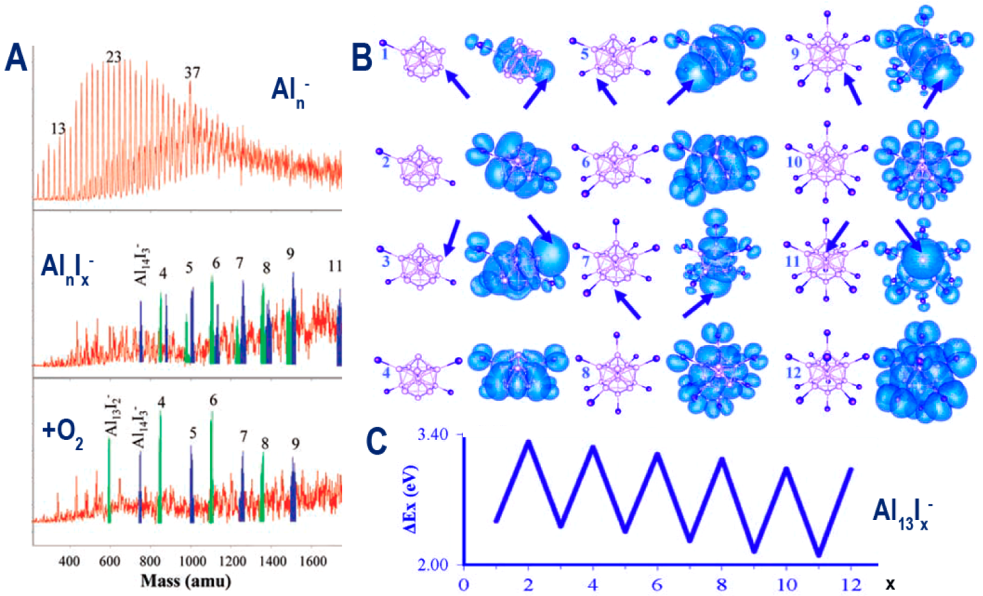

Figure 5. (A) Mass spectra of Al cluster anions upon reaction with I_2 vapor and then etched by O_2. Peaks shaded green fall into the $Al_{13}I_x^-$ family, whereas peaks shaded blue fall into the $Al_{14}I_x^-$ family. In all panels, the y axis is peak intensity (in arbitrary units). (B) Lowest energy structures and charge maps for $Al_{13}I_x^-$ (x values from 1 to 12). (C) ΔE_x, the energy to remove one I atom from $Al_{13}I_x^-$ for x values from 1 to 12.

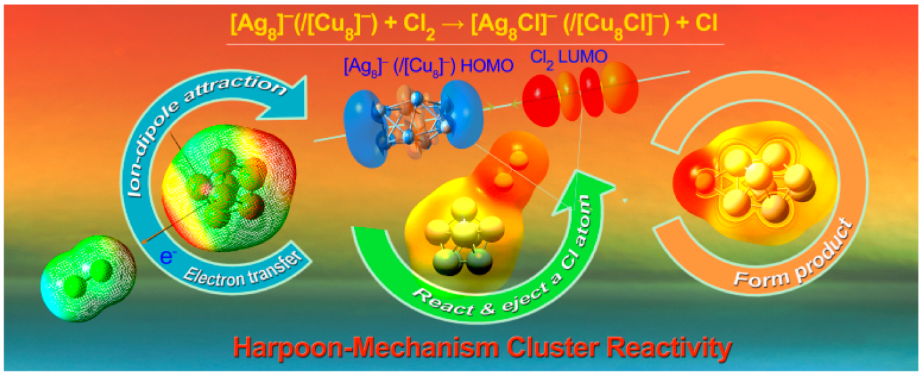

Figure 6. A cartoon depicting harpoon-mechanism cluster reactivity of "Ag_8^- ($/Cu_8^-$) + Cl_2 → Ag_8Cl^- ($/Cu_8Cl^-$) + Cl".

In addition to $Al_{13}I^-$, two series of $Al_nI_m^-$ clusters ($Al_{13}I_x^-$ and $Al_{14}I_y^-$) were also identified in the gas phase by studying their resistance to oxygen etching.[1] Figure 5 presents the mass spectra of Al cluster anions in a reaction with I_2 vapor first and then an etching by O_2. The experimental reactivity studies showed that $Al_{13}I_x^-$ clusters exhibit pronounced stability for even numbers of

I atoms, seen as $Al_{13}I_2^-$, $Al_{13}I_4^-$, $Al_{13}I_6^-$, and $Al_{13}I_8^-$, while, interestingly, the $Al_{14}I_x^-$ series exhibit stability for odd numbers of I atoms, such as $Al_{14}I_3^-$, $Al_{14}I_5^-$, $Al_{14}I_7^-$, and $Al_{14}I_9^-$, etc. In contrast with $Al_{13}I^-$, subsequent investigations demonstrated that the stabilization of $Al_nI_m^-$ ($m > 1$) clusters is size-dependent as the iodine ligands perturb the charge density of the metallic core and may induce Lewis acid−base sites for certain clusters to become reactive in a protic environment.[27] For the structures and stabilities of the clusters $Al_{13}I_x^-$, population analysis using the DFT level of theory showed that a significant charge transfer occurred from the Al cluster to the I atoms and hence could not maintain an electronically intact Al_{13}^- core.[28]

2.3. Superalkalis (IA Group)

Under the inspiration of superhalogens (one less electron than a closed shell), it is easy to understand that superatoms with one more electron than a fully filled valence shell may readily give up electrons and behave as alkali metal atoms in their intrinsic reactivity. For this, previous studies have found that alkali metal oxides M_3O (M = Li, Na, K) display ionization potentials less than the alkali atoms and can be regarded as superalkalis.[29,30] Recently Z. Luo et al.[8] reported an interesting study on the reactivity of coinage metal clusters and revealed that the reaction between Cu_8^-/Ag_8^- and chlorine gas is consistent with the well-known harpoon mechanism (Figure 6). The harpoon mechanism was demonstrated to explain reactions such as "$K + Br_2 \rightarrow KBr + Br$" where the K atom plucks a Br atom out of the Br_2 molecule. In view of the atomic electron configurations of Cu: $[Ar]3d^{10}4s^1$ and Ag:$[Kr]4d^{10}5s^1$, clusters Cu_8^- and Ag_8^- exhibit 9 valence electrons and their NFEG orbitals are best described as $|1S^2|1P^2|1P^4|2S^1|$, allowing their reactivity toward chlorine to follow the harpoon model with products of "$Cu_8Cl^- + Cl$" and "$Ag_8Cl^- + Cl$". Studies of the interaction energies between a Cu_8^-/Ag_8^- cluster and an approaching Cl_2 molecule enable the cross section to be determined from the point of view of both classical collision theory and quantum chemistry. Through the two methods, an extended collisional cross section was calculated respectively resulting in a steric factor "$P > 1$" for the reaction of the superatomic alkali-metal-like cluster Cu_8^-/Ag_8^-, which supports the idea that the harpoon mechanism involving the long-range transfer of valence electrons is operative in cluster reactions. Valuable insight into the reactivity of chlorine with the alkali-metal-like clusters is of significance for a better understanding of the reaction mechanisms of such superatomic species.

2.4. Superatomic Alkaline-Earth Metals (IIA Group)

An anionic cluster Al_7^- was shown to exhibit qualities reminiscent of an atom with multiple valence states of +2 and +4 and was classified as a multiple valence superatom.[31] Also an Al_{14} cluster exhibits electronic features like an alkaline earth atom (a tendency to go toward a +2 valence state) and hence is looked upon as a super alkaline earth atom.[1] It is notable that the geometry plays an important role in the stability of clusters, and when the electronic shell structures become modified in forming cluster compounds, it could be accompanied by rearrangement of their geometric structures.

2.5. Magnetic Superatoms (VIB and VIIB Group)

Recent investigations have stimulated reasonable interest in magnetic superatoms.[32] In a cooperative work between the Khanna and Bowen groups,[9] vanadium−sodium clusters were prepared utilizing a pulsed arc cluster ionization source and an in-depth study was performed via a combination of photoelectron spectroscopy and computational methods. It was found that clusters VNa_8 and VNa_7^- (Figure 7) function as magnetic superatoms with a similar valence electron configuration as that of Mn atoms, while VNa_9 and VNa_8^- mimic a Cr atom. Strong spin magnetic moments of these clusters (e.g., ∼5.0 μB for VNa_8) were noted and their low electron affinities are consistent with the filled subshells and enhanced stability, indicating potential applications in spintronic devices of which information is stored via electron spins rather than charges. Based on the jellium model, theoretical calculations have also predicted the existence of magnetic superatoms on some other systems, such as VCs_8,[32] $FeMg_8$,[33] $TiNa_9$,[34] $ScCs_{12}$,[35] etc.

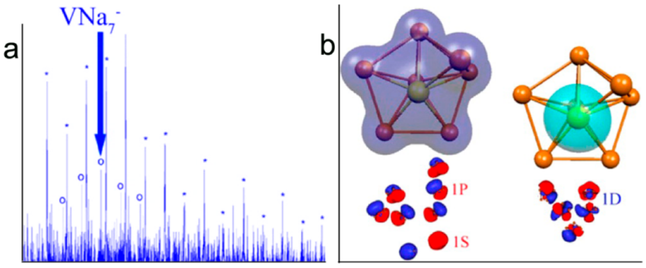

Figure 7. Time-of-flight mass spectrum of bimetallic VNa_n^- cluster anions (a), highlight with the magnetic superatom VNa_7^- (b). Adapted with permission from ref 9. Copyright 2013 American Chemical Society.

The emergence of the periodic table of elements in the 1800s allowed chemists to predict properties and structures of elements and molecules. Hopefully the interesting research on superatoms will enable the development of a 3D periodic table of elements hence leading to better predictability and design of related materials with tunable properties in nanoscale.

3. GENERALIZED SUPERATOMS

3.1. Nonmetal-Doped Metal Clusters

Several nonmetal-doped metal clusters have also been demonstrated as superatoms, such as a few magic species of Al_nC^-, Al_nN^-, and Al_nH^- clusters (typically $Al_4H_7^-$, Al_7H_7, Al_7H_3, etc.).[36,37] These clusters display enhanced stability due to large HOMO−LUMO gaps, low-electron affinities, and/or high ionization potentials; however, these superatoms do not strictly follow a jellium model on the basis of NFEG theory, and the electronic/geometric structure of the core metal cluster may alter when brought into contact with doped atoms or molecules.[38,39] A better interpretation of their stability could be ascertained by the use of molecular orbital analysis through which successful cases have been addressed for alkali metals coordinated with ammonia or ethylenediamine dopings.[40]

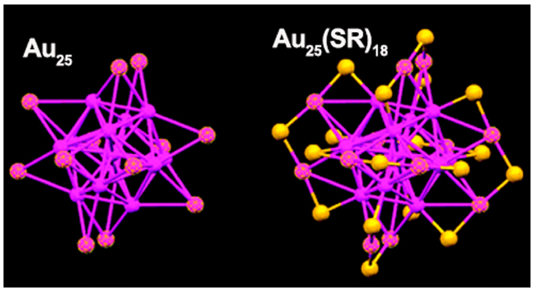

Figure 8. Structure determination of thiol-protected Au clusters, Au_{25} and $Au_{25}(SR)_{18}$. Adapted with permission from ref 57. Copyright 2008 American Chemical Society.

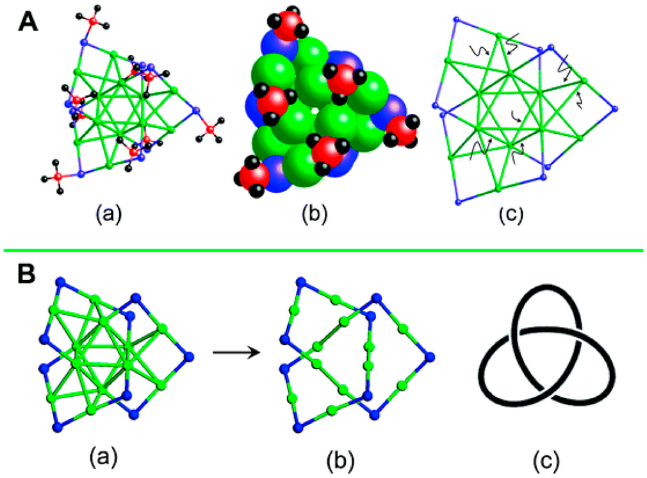

Figure 9. (A) DFT-optimized structure of $Au_{12}(SCH_3)_9^+$, viewed along the C_3 axis: (a) ball-and-stick model; (b) space-filling model; (c) $Au_{12}S_9$ framework with Au−Au distances labeled (in Å). Au, green; S, blue; C, red; H, black. (B) The $Au_{12}S_9$ framework (a) of $Au_{12}(SR)_9^+$ is related to the trefoil knot (c) by viewing the connections in the framework as in part (b). Adapted with permission from ref 58. Copyright 2009 American Chemical Society.

Further insight into the general superatom concept has made us recall investigations from several years ago when Metallo-Carbohedrenes ("Met-Cars" for short) were discovered in the Castleman group.[41,42] It was more or less serendipity when they used the laser to probe various titanium reactions and noticed a species showing a very strong peak at 528 mass units referring to Ti_8C_{12}. Subsequently, extensive studies were performed for the reaction with a number of other hydrocarbon gases (including those composed of deuterium and using ^{13}C in the hydrocarbon raw material) and also with a different transition metal to substitute titanium, until finally the stoichiometry M_8C_{12} (M = Ti, V, Zr, and Hf) and its pentagonal dodecahedral structure of T_h symmetry were ascertained.[41−44] In addition to the unique geometry and properties, Met-Cars exhibit low ionization potentials pointing to alkali-like character, and hence here we introduce them into the superatom family.[45]

Studies have also enabled the stability of several other superatomic clusters to be understood within a few different models, including the aromaticity[46] and Wade−Mingos rules[47] with a dependence on the geometry and metallicity of the cluster. For example, studies by L. S. Wang and coworkers[48] have rationalized the stability of several boron-related clusters utilizing the Wade−Mingos rules which were developed to understand structure and bonding in polyhedral boranes and related compounds. The Wade−Mingos rules have also been extended to many bare element clusters which bear structures similar to polyhedral boranes, providing a basis for extending the concept of aromaticity from 2D planar hydrocarbons to 3D polyhedral clusters.

3.2. Ligand-Stabilized Metal Clusters

Studies on superatom complexes have shed light on ligand-stabilized metal clusters.[49−51] Since the discovery of superatom complex $Au_{102}(SR)_{44}$ in 2007, considerable research interest has been attracted to this topic,[11,52] where both the structure determination and the superatom concept underlying its stability offer promising clues to unravel the nature of novel gold chemistry. Several successful examples reported in succession include $Au_{25}(SR)_{18}^-$,[53] $Au_{38}(SR)_{24}$,[54] $Au_{44}(SR)_{28}^{2-}$,[55] $Au_{144}(SR)_{60}$, etc.[56] Among them, the superatom $Au_{25}(SR)_{18}^-$ (Figure 8) bears a Au_{13} core with 12 additional Au atoms above 12 triangular faces. In comparison, $Au_{38}(SR)_{24}$ displays a face-sharing bi-icosahedral core complexed by three short and six long ligands, and it bears a significantly lower energy than the other Au:SR cluster systems.[54]

Moreover, an interesting result has also been reported on small metal-rich Au:SR clusters with less than 15 gold atoms, $Au_{12}(SCH_3)_9^+$,[58] as shown in Figure 9. It is notable that the stability of these gold superatom compounds (which could be crystallized) were also derived from the jellium model corresponding to the major shell-closing electron count for a

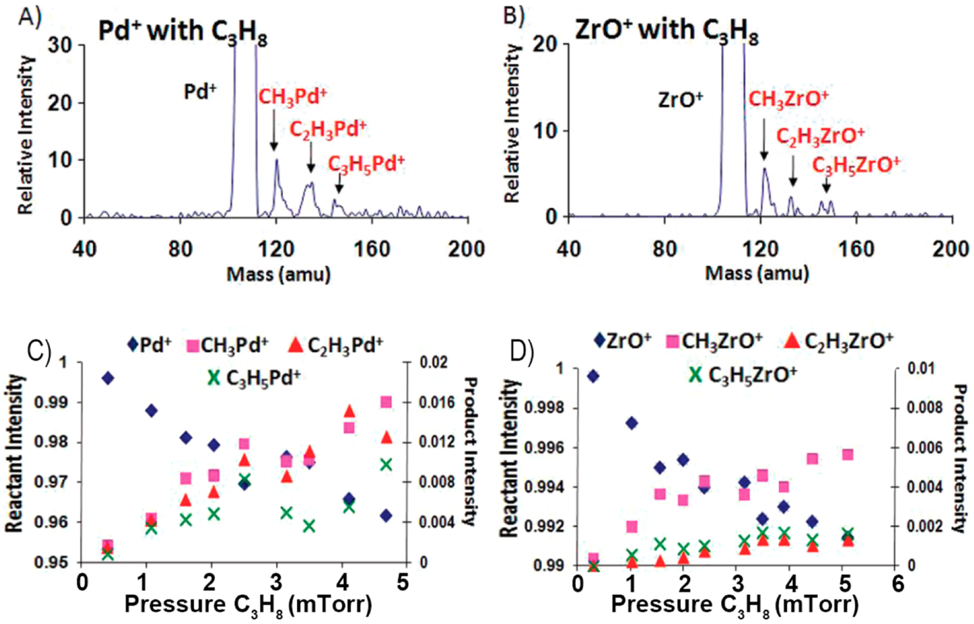

Figure 10. Mass spectra for the interaction of (A) Pd^+ with 3.50 mTorr of C_3H_8 and (B) ZrO^+ with 3.90 mTorr of C_3H_8 both occurring at 20 eV in the lab frame. (C) Pd^+ and (D) ZrO^+ reacted with 0−5 mTorr of C_3H_8 at 20 eV in the lab frame.

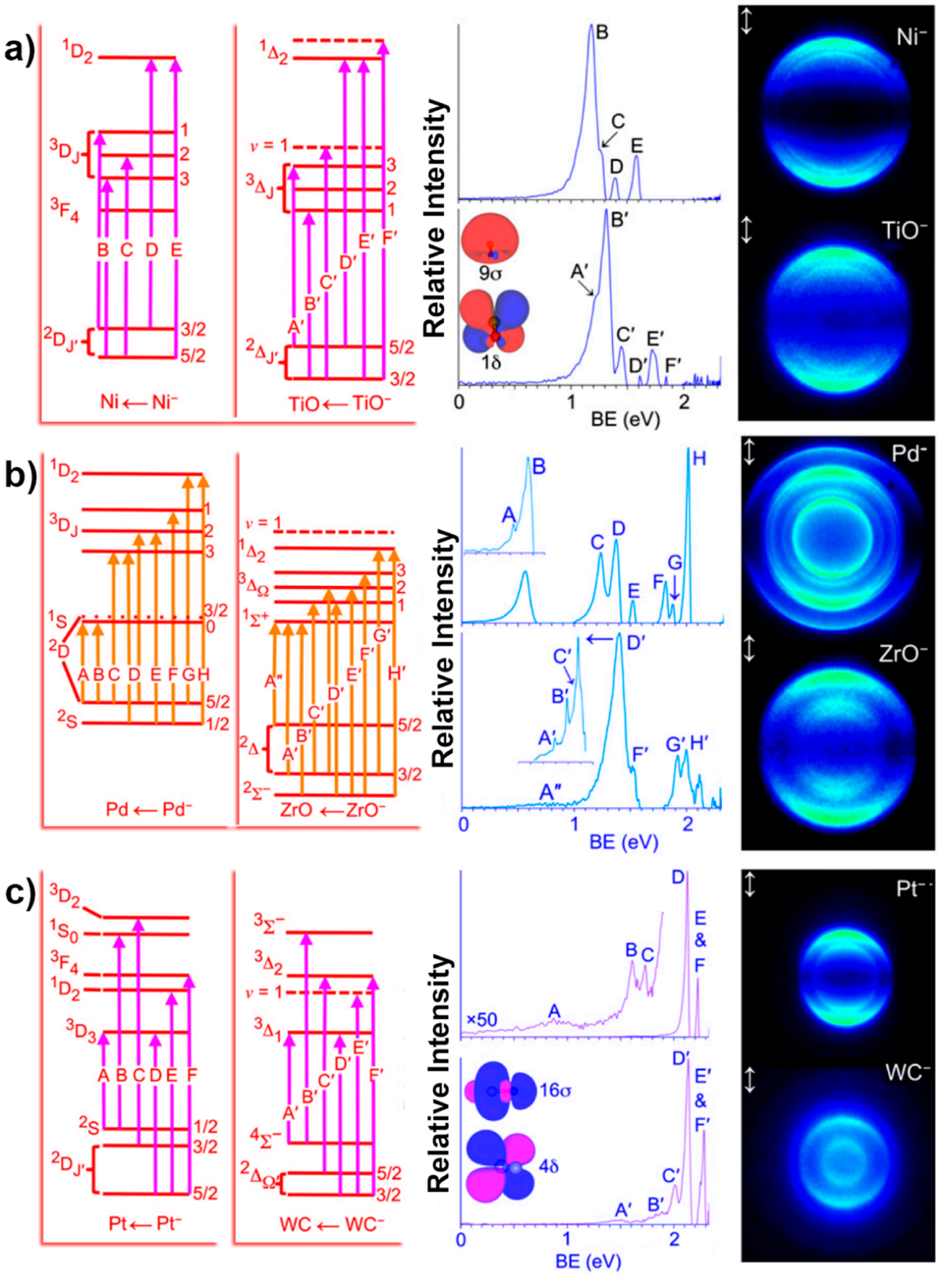

Figure 11. Energy level diagrams (left), binding energy spectra (middle), and raw photoelectron images (right) at a photon energy of 2.33 eV (532 nm) for TiO^-/Ni^- (a), ZrO^-/Pd^- (b), and WC^-/Pt^-(c). The insets on the binding energy spectra display the highest occupied molecular orbitals.

spherical, square-well potential that follows as 2, 8, 18, 20, 34, 40, 58, 92, etc., where both the valence electrons from gold and the electrons withdrawn by the electronegative linkers were taken into account.[58] It is anticipated that general cluster approaches and the superatom concept will further the frontier studies in gold chemistry, as well as superatom compounds of other metal systems.[59]

3.3. Isovalent Cluster Systems

Early investigations in seeking stable clusters demonstrated that Al_7C^- and Al_7O^- clusters could mimic SiC and CO molecules, respectively.[31,60] Further, Peppernick et al.[10] found that the cluster ions of ZrO function as superatoms and are isovalent with Pd, where the two species take up similar electronic properties determined by photoelectron spectroscopy. Utilizing a guided-ion-beam mass spectrometer, they noted that the reaction of cationic Pd^+/ZrO^+ with propane (C_3H_8) closely resembles the reactivity of Pd^+ with C_3H_8, as shown in Figure 10.[61] Similar reactions of Pd^+ and ZrO^+ with C_2H_6 were also observed, where the branching ratios display a comparable decrease in reactant intensity and a concomitant rise in product intensity. These studies upon comparable reactivity of Pd^+/ZrO^+ with hydrocarbons clearly verified the chemical mimic for ZrO in place of the precious metal Pd.

In addition to the cationic ZrO^+ and Pd^+, the analogous reactivity of anionic ZrO^- and Pd^- has also been ascertained.[10] From the binding energy spectra and raw photoelectron images shown in Figure 11, one can easily see how ZrO^-, WC^-, and TiO^- were viewed as the superatomic form of Pd^-, Pt^-, and Ni^-. Electronic-state correlations between the elements and their isoelectronic molecular counterparts have also been examined for MoC^-/Ru^-.[62] All these couples reveal comparable electronic transitions and orbital symmetry enabling the development of valuable superatom-based materials used for catalytic reactions (e.g., expensive Pt catalysts used in combustion engines or other applications).[63]

3.4. Superatom Assemblies

From the point of view of material science, researchers in the Khanna group[64] proposed cluster complexes and assemblies on the basis of the phosphorus-like superatoms. For example, the cluster As_7^{3-} was used as a stable building block and linked together with multiple lithium, potassium, rubidium, or cesium atoms, in which they demonstrated the assemblies of a new class of semiconductor cluster materials for potential electronics.[64] Further, interesting cluster assemblies were postulated with a focus on the superatom units of both Al_{13} and K_3O.[29] Among the various $(Al_{13}K_3O)_n$ superatom compounds that they studied, $(Al_{13}K_3O)_3$ has its first two ionization potentials lower than any other atom in the periodic table and was described as an ultra-alkali motif (3.17 eV for K_3O). Calculation results on assembly structures of three typical species, $(Al_{13}K_3O)_{4,5,6}$, are displayed in Figure 12.

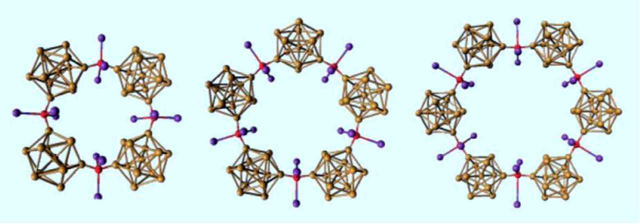

Figure 12. Examples of cyclical cluster-assembled materials consisting of Al_{13} superatoms and K_3O ligands, with a class of repeating or multidecker sandwich structures.

4. SUMMARY AND OUTLOOK

In this account, we have summarized the related investigations of superatoms in series by proposing a novel concept of special and general superatoms. It is expected that the new conceptual category of special and general superatoms will not only help to clarify the superatom concept in interdiscipline research fields but also aid in attaining a better understanding of the cluster building blocks and elementary reaction mechanisms of such superatoms, including those of isovalent cluster systems and gold complexes. Having clarified such conceptual issues and basic theory, one of the prime objectives of current research is to lay the foundation for forming new nanoscale materials via techniques of cluster assembly. Knowledge acquired from cluster reactions and properties which serve to identify promising species is also expected for further advancement in superatom investigations, leading to a 3D periodic table of cluster elements in the future.

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Notes

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A. W. Castleman, Jr. is a full professor in the departments of both Chemistry and Physics, The Pennsylvania State University (PSU). He was given the distinction of the Evan Pugh Professor title in 1986, and in 1999 he was appointed Eberly Distinguished Chair in Science. Prof. Castleman was elected a Member of the National Academy of Sciences (USA) in 1998, a Fellow of the American Academy for Arts and Sciences. Castleman has been devoted to research in cluster science throughout his career.

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