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14. ABSTRACT The program which ended December 31, 2006 was directed towards: 1) developing approaches for the design of new nanoscale materials that can be tailored to have desired properties; 2) investigating electronic and reactive properties that will find applications of interest to the Air Force in energetic, electromagnetic, optical and structural materials; and 3) finding synthetic methods to produce materials as condensed phase deposits for further characterization. This section summarizes progress and accomplishments made during the first two years of this 3-year program.					
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AFOSR FINAL REPORT

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Brief Overview of Current Activities and Recent Accomplishments

It would be difficult to overstate the prospects of new technological developments likely to arise from innovative achievements in the area of nanoscale science. Currently, we are engaged in a basic research program in this field entitled “Cluster Dynamics: Foundations for Developing Nanoscale Materials”, supported through the AFOSR. As indicated by the title of the grant, this fundamental research activity has the goal of providing underpinning knowledge pertinent to the formation of new materials of nanoscale dimensions using clusters as building blocks – an approach “from the bottom up”.

The program which ended December 31, 2006 was directed towards: 1) developing approaches for the design of new nanoscale materials that can be tailored to have desired properties; 2) investigating electronic and reactive properties that will find applications of interest to the Air Force in energetic, electromagnetic, optical and structural materials; and 3) finding synthetic methods to produce materials as

condensed phase deposits for further characterization. This section summarizes progress and accomplishments made during the first two years of this 3-year program.

A major thrust of the current work was devoted to the study of energetic materials comprised of aluminum and aluminum compounds.^{GP552,GP574,GP575,GP577,GP578,GP582,GP589} Certain aluminum species have been identified as being stable in particular cluster sizes and electronic states, offering the prospect of being passivated through cluster assembly but becoming very reactive upon electron detachment as would proceed in a combustion reaction. Another phase of the program was devoted to unraveling the behavior and dynamics of the unique Met-Car clusters discovered in our laboratory,¹ species that offer interesting prospects for new electronic, optical, catalytic materials,² and even hydrogen storage. An overview of some of our most significant recent findings follows; details are given in the publications listed at the end of the proposal, which have resulted from our AFOSR sponsored program.

a) Aluminum Clusters and Approaches to Tailoring the Properties of Superatoms

During the last two years, through close collaboration with the theoretical group of Khanna at VCU, we made several exciting discoveries pertaining to metal clusters.^{GP541,GP558,GP569,GP575} In particular, we have identified several stable cluster species that give future promise as building blocks for new materials with tailorable properties. Indeed, we have found a number of species that display characteristics analogous to elements of the periodic table. This has led us to describe certain metal clusters as superatoms. Within the jellium model framework, clusters of free electron metals are predicted to exhibit enhanced stability when the total number of valence electrons corresponds to a filled electronic shell for a uniform spherical potential.^{3,4} Our laboratory showed some years ago^{5,6} that the chemical behaviour of Al_{13}^- could serve as a good example of a jellium cluster with a noble gas electron configuration. In oxygen etching reactions, Al_{13}^- , as well as Al_{23}^- and Al_{37}^- , all of which correspond to jellium shell closures, exhibit remarkable inertness. Theoretical treatments later showed Al_{13}^- to hold great promise as a building block for cluster-assembled nanostructured materials owing both to its electronic structure and its nearly spherical icosahedral geometry,⁷ a suggestion that we have actively pursued.

We recently established that Al_{13} behaves chemically like a halogen in complexes with iodine, having a higher electron affinity than iodine.^{GP569,GP574,GP575,GP582} It was found that the Al_{13}I^- cluster readily forms and is resistant to oxygen etching (Figure 1)

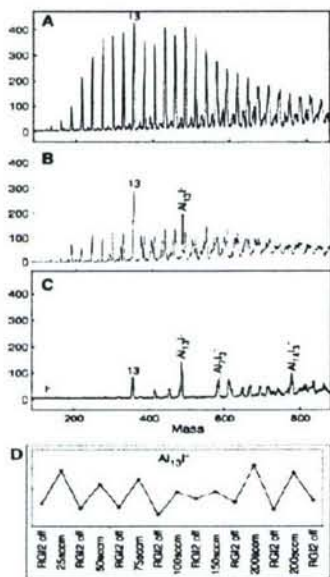


Figure 1. (A to C) Mass spectra showing the reaction of aluminum clusters with HI: 0 sccm (A), 25 sccm (B) and 200 sccm (C) of 10% HI seeded in He. (D) Growth of Al_{13}I^- peak in the presence of oxygen demonstrates the cluster's stability. Experiments from the Castleman Group^{GP574,GP569}

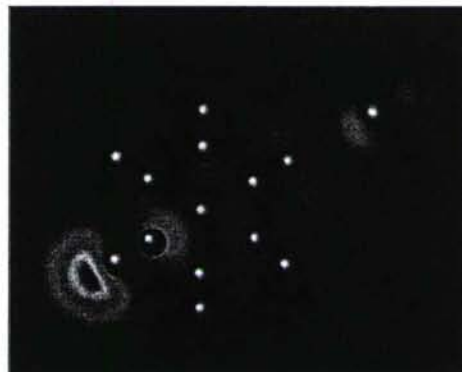


Figure 2. Charge density map of the highest occupied molecular orbital for Al_{13}I^- . Theoretical calculations from the Khanna group at VCU.

Furthermore, theoretical studies revealed that the cluster's stability arises from the ability of the Al_{13}^- moiety to retain its anionic characteristics in terms of both geometry and charge state, even when bonded to an iodine atom. This has been verified from experimental etching experiments with iodine and other halogens.^{GP574} As seen from the electron density in Figure 2, the aluminium cluster actually pulls electron density away from the iodine atom. Molecules with electronegativities exceeding those of halogens are often termed "superhalogens". The discovery and characterization of Al_{13}I^- showed that not only could Al_{13} be described as a halogen-like superatom, but as a superhalogen as well.

To further demonstrate the chemical capability of Al_{13} to behave as a halogen atom, we subsequently investigated the possibility of forming "polyhalides" by reacting Al_{13} with I_2 .^{GP575} The results of these experiments again supported the description of Al_{13} as a halogen-like superatom. Only $\text{Al}_{13}\text{I}_x^-$ with even x (resulting in an odd number of "halogen atoms") were especially stable towards etching by oxygen, see Figure 3.

Also discovered in reactions with I_2 was a series of stable clusters corresponding to $Al_{14}I_{2x+1}$ ($x \geq 1$), see Figure 3. Our investigations showed that these species consist of a core that resembles Al_{14}^{2+} . Thus, the first stable anion requires three atoms for formation of the central dication. Within the framework of the jellium model, Al_{14} has two electrons in excess of a closed electronic shell, giving it an electron configuration chemically equivalent to that of an alkaline-earth metal. Thus, we have provided a demonstration of Al_{14} acting as an alkaline earth-like superatom.^{GP575,GP582} At present, we can find no logical impediment to the realization of a vast periodic table of superatoms, with clusters of appropriate electronic and chemical properties filling every column. In fact, preliminary findings within recent weeks suggest that other aluminium cluster “superatoms,” such as Al_7X^- , can display multi-valent characteristics in analogy to certain elements of the periodic table.^{GP589}

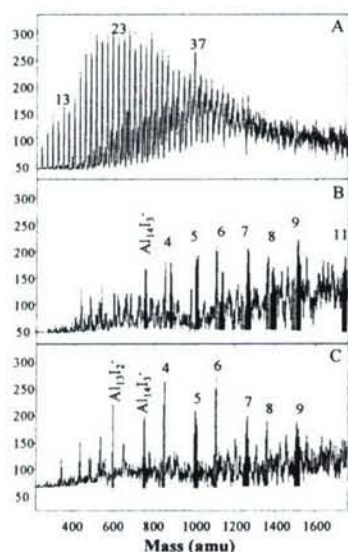


Figure 3. (A) Aluminum clusters (B) reacted with I_2 . (C) Products from (B) reacted with oxygen.^{GP575}

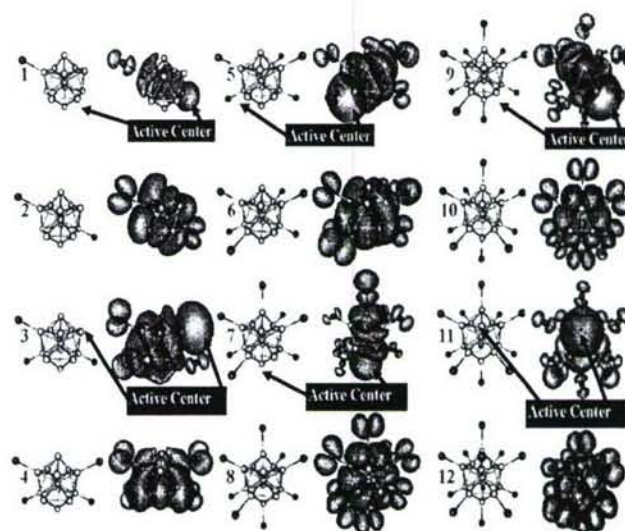


Figure 4. Ground state structures and charge map of the highest occupied molecular orbital for $Al_{13}I_x^-$.^{GP575}

In traditional condensed phase polyhalides, the primary building blocks are X^- , X_2 , and X_3^- , so the total number of halogen atoms must be odd in order to form stable complexes.⁸ As Al_{13}^- and $Al_{13}I_2^-$ were shown by our group to be particularly stable, the superatom-containing analogs were demonstrated chemically. Interestingly, these species do not conform to the type of branched-chain geometries common to polyiodides and interhalogen complexes of the heavier halogens. 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 4). Mapping the charge densities of these clusters provides insight as to the reactivity of those with odd numbers of iodine atoms. As Figure 4 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 because of the Al_{13} cluster's tendency to horde charge away from the less electronegative iodine atoms, was found in our laboratory to act as a chemically active site.^{GP577,GP582}

The active site characteristics of the aluminum clusters offer a new synthetic route in the chemistry of cluster assembly. To test the active site hypothesis, experiments were undertaken in which $Al_{13}I_x^-$ were reacted with methyl iodide.^{GP577} In our previous studies, we found Al_{13}^- to be unreactive towards methyl iodide,^{GP552} so any reaction of the $Al_{13}I_x^-$ species must be attributed to chemical activation via iodine introduction. When we react Al_n^- clusters with I_2 , we find a cluster distribution in which $Al_{13}I_x^-$ and $Al_{14}I_x^-$, also seen in Figure 3c, constitute the major peaks. Upon exposing the products of this first reaction to methyl iodide, a drastic change in the mass spectrum is observed. First, the peaks corresponding to $Al_{13}I_x^-$ with odd x, as expected, disappeared far more rapidly than did peaks corresponding to $Al_{13}I_x^-$ with even x. Additionally, very intense mass peaks corresponding to I^- , I_3^- and Al_7I^- were found to arise. The emergence of Al_7I^- as a favored product and magic number has been recently published.^{GP577} This small cluster provides yet another example of a very stable entity with potential for utilization as a building block in materials.

As we have focused more attention on the halogen-like jellium superatoms, we have realized a steadily increasing ability to chemically manipulate species of high-energy content. Notably, we have succeeded in binding aluminum clusters to model organic molecules.^{GP578} The stabilization of species with polyhalide-like properties and organo-cluster compounds represents two of our recent hallmark achievements, and in the past year, we have made substantial headway in this expanding program. The above findings have given us a greater understanding and control of the chemistry of aluminum clusters, allowing us to propose synthetic pathways for forming large quantities of assembled aluminum clusters. For example, in the reaction of aluminium clusters with iodine, it is possible to shift the product distribution towards more I-rich clusters by dramatically increasing the amount of I_2 introduced. As described above, $Al_nI_x^-$ clusters with

stoichiometries near those of bulk aluminium iodide actually react with methyl iodide to yield $\text{Al}_{13}\text{I}_{2x}^-$ clusters. This observation seems to suggest that the etching of nanocrystalline AlI_3 with methyl iodide could yield the superpolyhalides described above, which could then be available in the solution phase for further chemical manipulation. The impact on materials synthesis of such a reaction pathway could be staggering. The question, then, is how might these principles be applied in a medium more technologically relevant than the gas phase? The findings related to active sites could provide the answer, and we intend to explore this prospect in depth during the coming grant period using the newly developed deposition instrument.⁹

In summary, the stabilization of aluminum clusters for introduction into fuel matrices is a chief goal of our studies on the chemistry of superatoms. It is truly remarkable to note the degree of complexity added to reaction pathways by the addition of I atoms to the surface of an Al_n^+ cluster. Even more remarkable, however, is the fact that these complex pathways lead to startlingly few products, the most striking of which are the familiar $\text{Al}_{13}\text{I}_{2x}^-$ super-polyhalide clusters, which may lead to high-yield synthetic pathways for aluminum superatoms. These various and unexpected reactions agree with the theoretical predictions made by the Khanna group.^{GP575,GP577} By identifying and understanding the formation mechanisms of these very stable clusters, we expect to facilitate their implementation as the building blocks of novel nanostructured materials of high energy density.

b) Studies of Metal-Carbon Interactions

During the report period, we continued studies of the electronic, structural and dynamical properties of Met-Cars.^{GP583} The studies are providing further insights into factors governing some of their unique properties and yielding information on ways to enhance their formation and to alter the growth of metal-carbon complexes from cubic to the Met-Car, M_8C_{12} , structure. Particularly noteworthy are recent findings we have made employing photoelectron spectroscopy, which show that in some cases, niobium replaces carbon, yielding electronic characteristics that depend on the total number of atoms and not whether they are carbon or niobium.^{GP587} Another significant finding is the very strong evidence obtained indicating that excited metal dicarbide clusters are the source of the delayed atomic ion emission,^{GP585} a long-standing puzzle. Some planned negative ion experiments should finally settle this issue.

i) Photoelectron Spectroscopy of Met-Cars and Related Building Blocks

The magnetic bottle photoelectron spectrometer enabled by an earlier DURINT grant was used to monitor the evolving electronic properties, and hence by comparison with calculations, geometries as a function of cluster size for various metal-carbon Met-Car building blocks.^{GP587,GP591} Niobium is an especially important metal with which to investigate Met-Car formation as it has been found to readily switch between the formation of cubic metal-carbide and Met-Car structures upon small changes in laser vaporization conditions by alterations in the MC to MC₂ ratios.¹⁰ Our recent focus was on a study of carbon rich dinobium carbon clusters containing four to nine carbon atoms that were formed in a laser vaporization plasma reactor.

In these recent studies, we have found evidence for the co-existence of at least two classes of structural isomers, monocyclic rings and linear chains.^{GP587} This is the first transition metal system to display such behavior. Importantly, the linear and cyclic isomers were determined to exhibit an even-odd alternation in electron affinity, commonly seen in pure carbon clusters. The data suggest that for sizes between Nb₂C₄ and Nb₂C₆, the cyclic isomer is a preferred structure, but a transition to a linear structure occurs in going to Nb₂C₇. Further, the data indicate there is a transition back to a cyclic structure at Nb₂C₉.

These results support the proposal that a niobium atom may serve as a substitute for a carbon atom in some all carbon networks.^{GP587,22,23} While experiments have stemmed belief in the substitutional properties of niobium, the underlying principle is not yet fully understood. The behavior likely results from the valence electronic configuration of niobium being 4d⁴5s¹. This leaves niobium with four valence electrons in d-orbitals that may form directional bonds by overlap with hybridized carbon orbitals. From this point, a pedagogical approach to understanding this phenomenon would include a study of other transition metals with a similar ns¹ valence electronic configuration. Suitable metals include chromium (3d⁵4s¹), molybdenum (4d⁵5s¹) and tungsten (5d⁵6s¹), which we plan to investigate in this context.

In other related studies, we have employed a range of cluster source conditions that have enabled us to investigate the electronic structure of several classes of vanadium-carbon clusters.^{GP591} This is a valuable system for the comparison of results obtained for niobium, which is in the same group of the periodic table.

This system is comprised of clusters that are likely to have geometries including planar cyclic rings and larger three-dimensional clusters. We have found that the methane content of the cluster source, which provides the carbon atoms of the clusters, significantly influences these geometries. Our results indicate that high carbon mono-vanadium clusters prefer cyclic ring geometry.^{GP591} When going to the di-vanadium distribution, evidence exists for the transition to planar structures when the carbon content is high. Photodetachment experiments conducted on vanadium carbide clusters replaced clusters that are more likely to take on a three-dimensional structure when the methane content is low. Further, the results show that VC_2 , V_2C_3 and V_4C_6 clusters exhibit the lowest electron affinities of the distribution.^{GP591} A low electron affinity has also been reported previously for M_8C_{12} clusters. This is taken as providing some evidence for the importance of VC_2 , V_2C_3 and V_4C_6 in the formation of larger three-dimensional clusters including the Met-Car species. Though vanadium is in the same group of the periodic table, its different electronic character from niobium evidently impedes hybridization with carbon, and hence leads to quite different stabilities in the complexes formed with carbon. Details are given in two papers in the final stage of preparation.^{GP587,GP591}

Another recent experimental accomplishment has been the electron photodetachment from anions with femtosecond laser pulses, yielding PES data with adequate resolution to extract a combination of energetic and dynamical information. This opens a number of opportunities for research in the future. For example, the experiments discussed above employed nanosecond lasers. As a result, the data were comprised of both direct and indirect processes, which are known to occur for many transition metal clusters. Photodetachment experiments conducted with femtosecond lasers will circumvent this and enable the measurement of direct, coherent processes. By employing femtosecond photodetachment along with the multi-component fitting method, one will be able to analyze competitive mechanisms in complex metal clusters. Further, the coupling between electronic states and the resultant electron transfer between them can be determined. The fundamental mechanisms that influence electron transfer and electron dynamics are of paramount importance to the outcome of chemical processes. Exposure to the instrumentation and techniques developed in the last several years are providing students the opportunity to become well poised to approach and contribute to a better understanding of these dynamical aspects of nanoscale science.

ii) Delayed Ionization and Delayed Atomic Ion Emission

The mechanism of delayed ionization, which plays a major role in the ionization of Met-Cars, continues to be investigated in the dynamics phase of our work on matter of nanoscale dimensions. Delayed ionization is a fascinating phenomenon that has been observed in a few metal, fullerene and metal carbide systems. Generally, good candidates to display delayed ionization characteristics are clusters containing a significant number of vibrational modes that have large bonding energies and low ionization potentials. The magnitude of the cluster's ionization potential, therefore, must be in competition with its binding energy. These properties allow the cluster to store energy from the initial excitation in vibrational modes without undergoing fragmentation. The mechanism most commonly used to explain the delayed emission of electrons is termed thermionic emission. This mechanism is modeled after a modified form of the Richardson-Dushman equation for macroscopic thermionic emission that takes into account the finite size of the clusters under investigation.

One aspect that has continued to baffle the scientific community is the mechanism we discovered,^{GP415} which involves delayed atomic ion emission from clusters. It has only been observed in the case of Met-Car containing mass distributions, but the identification of the precursor has eluded direct observation. At one time, it was believed that Met-Cars might be directly involved, but findings acquired during the recent progress report period, strongly indicate the parent of the atomic ion to be the MC_2 species, which is the building block of the Met-Car and hence usually present along with it.^{GP585}

Since its discovery, a great deal of effort has been spent in an attempt to explain this delayed atomic ion due to the obvious fact that atoms do not contain any vibrational modes in which to store energy in excess of the ionization potential. Recently, new experiments have been conducted to delve further into the origin of the delayed atomic ion by studying the delayed ionization of zirconium and titanium carbides simultaneously using a mixed metal alloy rod in a standard laser vaporization source coupled to a reflectron time-of-flight mass spectrometer. This has provided the ability to observe for the first time both the zirconium and titanium delayed atomic ions concomitantly, but more importantly has enabled study of the

delayed emission characteristics of the titanium atom without the presence of the titanium Met-Car. Through these experiments, it was found that the origin of the delayed atomic ion is an energetic titanium dicarbide complex.^{GP585}

Moreover, laser fluence experiments also have been conducted on the Nb_xC_y and Zr_xC_y cluster systems in order to ascertain a more thorough description of multiphoton absorption processes occurring in these metal carbide clusters.^{GP522,GP531,GP542,GP543,GP562} In performing these experiments, the intensity (fluence) of the ionization laser is systematically varied and plotted against the intensity of the resulting time-of-flight signal. By implementing this time-resolved fluence study, one can determine the photon order, or the number of photons absorbed by a particular cluster after being irradiated by an ultraviolet (308 nm) XeCl Excimer laser. Hence, information concerning the degree to which these clusters store energy is obtained, providing further insight into what roles the vibrational and electronic degrees of freedom play in such phenomena as delayed ionization. A paper reporting these new findings is in press that shows the origin of the atomic ion emission to involve an ion-pair state of the MC_2 species.^{GP585}

c) Production of Nanoscale Materials from Clusters: Materials Synthesis, Cluster Deposition and Particle Formation

Recently, using our newly implemented method for the production of metal-carbon species in liquid environments, we have continued work on Met-Car production through laser ablation of a metal rod immersed in carbon-rich solvents. Over the past year, we have created and investigated a myriad of nanoparticles by the ablation of a metal within a liquid environment. Nanoparticles created in this manner form a colloidal suspension within the liquid in which they are created and have shown great stability over a period of months. The nature of the solvent has the largest impact on the nanoparticle characteristics. Over the course of the last year, we have focused on titanium, analyzing the effects that fluence and liquid environment have on the dynamics of particle formation. We have used transmission electron microscopy (TEM), selected-area electron diffraction patterns (SADP), energy dispersive x-ray spectroscopy (EDS), electrospray ionization, and Raman spectroscopy to characterize the resulting nanoparticles.

Ablation of titanium in 2-propanol has produced a large variety of nanoparticles. Nanoparticle sizes ranged from 5 nm to 80 nm, with the majority of particles ranging between 20 and 40 nm. Lower fluences were found to lead to smaller overall size distributions, with the particles being very spherical, which is believed to be due to the high pressures exerted on nanoparticles during formation. EDS has given us a great deal of insight into the nature of the particles. Based on literature values from the Hanawalt Powder Diffraction Files, it was concluded that the particles were likely to be titanium carbide. To further verify this, the particles were analyzed by Raman spectroscopy, and many of the particles did indeed show Raman signals matching that of a titanium carbide standard.

Reactions were conducted in water for comparison with the studies in organic solvents. As expected, the composition of the nanoparticles, based on EDS analysis, was found to reveal a range from pure titanium particles to titanium oxide (TiO; not TiO₂). A publication reporting the findings of the titanium laser ablation experiments is in preparation and soon to be submitted.^{GP590}

Recent investigations of the Met-Car have yielded further understanding of mechanisms involved in bulk phase particle synthesis; fundamental knowledge of electron affinities and geometric structures of the Met-Car building blocks that make it unique; and definitive explanation of the delayed ion effect observed in Met-Car precursors.

Castleman Group Publication (GP) Arising from Studies Sponsored by AFOSR

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