

## **AFOSR FINAL REPORT**

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### **Research Title:**

Cluster Dynamics: Laying the Foundations for  
Tailoring the Design of Cluster Assembled Nanoscale Materials

### **Grant No:**

FA9550-07-1-0151

### **Period of Performance:**

December 1, 2006 – November 30, 2009

## REPORT DOCUMENTATION PAGE

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Service Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

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<b>1. REPORT DATE (DD-MM-YYYY)</b> 02/16/2010		<b>2. REPORT TYPE</b> Final Report		<b>3. DATES COVERED (From - To)</b> 12/1/2006-11/30/2009	
<b>4. TITLE AND SUBTITLE</b> Cluster Dynamics: Laying the Foundations for Tailoring the Design of Cluster Assembled Nanoscale Materials				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b> FA9550-07-1-0151	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> A. W. Castleman, Jr.				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> Penn State University 104 Chemistry Building University Park, PA 16802				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> DISTRIBUTION A					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The overall goal of our AFOSR sponsored research program is to gain sufficient knowledge of cluster dynamics to enable the design and synthesis of cluster-assembled materials with tailored properties. The properties of a cluster, such as band gap and reactivity, can change dramatically with the addition or subtraction of even a single atom. It has been theorized that materials assembled from clusters will also possess unique and tunable attributes dependent upon the individual cluster building blocks. Materials with a tunable band gap and chemical affinity would facilitate the design of devices that could behave ideally in an individual application. We are interested in determining the fundamental properties that govern the behavior of clusters so that the groundwork for a new chemistry using clusters as the building blocks of new materials can be established.					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
a. REPORT	b. ABSTRACT	c. THIS PAGE			<b>19b. TELEPHONE NUMBER (Include area code)</b>

## **I. Introduction**

The overall goal of our AFOSR sponsored research program is to gain sufficient knowledge of cluster dynamics to enable the design and synthesis of cluster-assembled materials with tailored properties. The properties of a cluster, such as band gap and reactivity, can change dramatically with the addition or subtraction of even a single atom. It has been theorized that materials assembled from clusters will also possess unique and tunable attributes dependent upon the individual cluster building blocks. Materials with a tunable band gap and chemical affinity would facilitate the design of devices that could behave ideally in an individual application. We are interested in determining the fundamental properties that govern the behavior of clusters so that the groundwork for a new chemistry using clusters as the building blocks of new materials can be established.

Our contributions toward this objective include the experimental investigation of chemical, structural, and electronic characteristics of individual clusters, including aluminum-based clusters and other prospective high energy density materials. Using unique technologies developed in our laboratory, we can directly observe the chemical behavior of clusters in controlled environments. By characterizing the different ways in which a cluster will respond to a specific perturbation, we are building knowledge of fundamental dynamic processes, and in doing so are learning how to tailor the properties of materials on an atomic scale. Special attention is paid to systems with potential use in nano-structured materials, novel optical materials, catalysts for the enhancement of combustion reactions, and especially high energy density materials. We believe that the continued pursuit of these goals will provide the stepping stone necessary for the development of new classes of materials.

## II. Brief Overview of Accomplishments

During the prior two-year grant period we have published and/or submitted for publication 27 papers that have been supported by AFOSR funding (see Section IV B). Selections of our current and previous accomplishments are summarized here to provide an introduction to the concepts we have developed in the past and upon which future planned studies are based.

### A. The Unified Atom Approximation

In 1989, our group first applied the “unified atom approximation” to a cluster of atoms for the purpose of understanding chemical reactivity.<sup>1-2</sup> This approximation simplifies the complex identity of a cluster to provide a description of chemical bonding through the application of concepts from valence bond theory to clusters. Discrete shell closings exist in the electronic structure of clusters of free-electron metals, which result from the confinement of itinerant valence electrons and such clusters are now termed “superatoms”.<sup>3-4, GP632</sup> An example is depicted in Figure 1. Clusters having electron counts that correspond to filled shells exhibit local maxima in ionization potentials and show resistance to certain chemical interactions. We have recently concluded that aluminum clusters with incomplete valences also fit the superatom analogy, which allows reactivity to be predicted based on their deviation from a closed electronic shell.<sup>5-6</sup> Our studies show that the addition of I atoms to Al<sub>13</sub> leads to a new class of polyhalide-like compounds with no I-I bonds, where the aluminum cluster unit maintains its integrity. Furthermore, we have shown that Al<sub>7</sub> is capable of accessing multiple inert valence states with either 18 or 20 electrons, suggesting the possibility of redox-like superatom chemistry.<sup>GP589</sup> Walter *et al.* recently synthesized a thiol monolayer-protected gold nanoparticle, wherein the stability of the gold nanoparticle could be approximated as a unified atom.<sup>7</sup> These and other observations legitimize the unified atom approximation for the description of chemical systems that will have relevance in cluster-assembled materials.

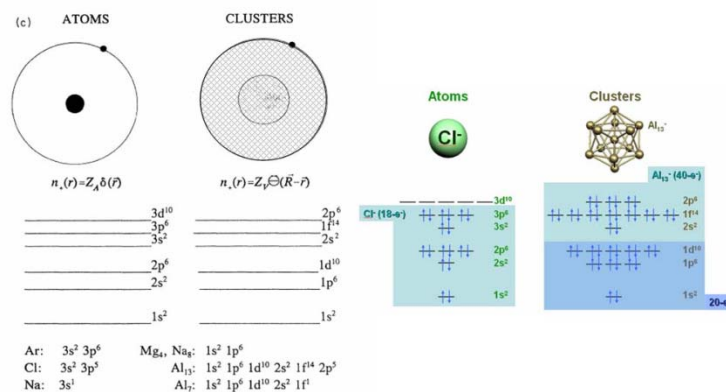


Figure 1. Energy levels in atoms and clusters, outlining the unified atom concept. Also shown are the electronic levels in a Cl atom and that in an Al<sub>13</sub><sup>-</sup> cluster. Adapted from GP632.

## B. Spin-Accommodation in Oxygen Etching Reactions

The aluminum-hydrogen system has allowed the investigation of cluster systems that differ incrementally by one proton and one electron.<sup>GP614,GP616</sup> The experimental investigation of the aluminum hydride system began with the formation of the cluster series Al<sub>4</sub>H<sub>n</sub><sup>-</sup> through the addition of hydrogen atoms to the cluster Al<sub>4</sub><sup>-</sup>. Spectra representing this distribution are shown in Figure 2. An artifact that we have referred to as an “ice cube tray” filling effect is observable in the spectra, where hydrogen addition is arrested at the size Al<sub>4</sub>H<sub>7</sub><sup>-</sup>. At low hydrogen concentrations (Figure 2B), Al<sub>4</sub>H<sub>n</sub><sup>-</sup> clusters are formed up to n = 7. However, even at extremely high concentrations (Figure 2D), there is no significant “overflow” to Al<sub>4</sub>H<sub>n</sub><sup>-</sup> (n > 7). We attributed this behavior to the presence of stabilization factors in the calculated energetic quantities of interest and a major structural rearrangement of the four atom core necessary to permit the formation of Al<sub>4</sub>H<sub>8</sub><sup>-</sup> in its lowest energy structure (Figure 3). First-principles molecular orbital studies made in collaboration with the Khanna group show that as more hydrogen atoms are added, Al-Al bonds are broken in favor of lower energy Al-H bonds to stabilize the molecular structure by forming aluminum hydride chains that resemble α-alane.<sup>8</sup> The species Al<sub>4</sub>H<sub>7</sub><sup>-</sup> shows resistance to this trend and as such represents a possible building block for cluster-assembled materials.

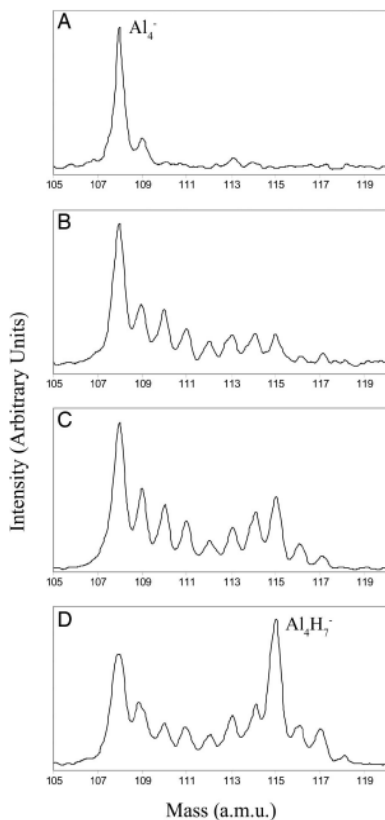


Figure 2. Mass spectra of aluminum hydride formation with carrier gas hydrogen concentration increasing from A to D. Adapted from GP614.

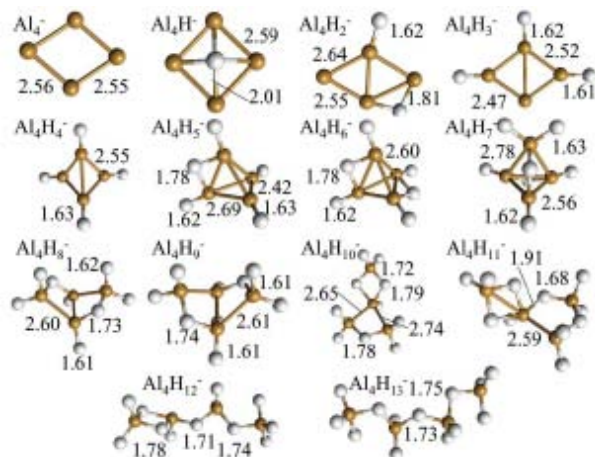


Figure 3. The optimized structures of the  $Al_4H_n^-$  clusters where  $n = 0-13$ . Al atoms are bronze, H atoms are white. The bond lengths are marked in angstroms. Adapted from GP614.

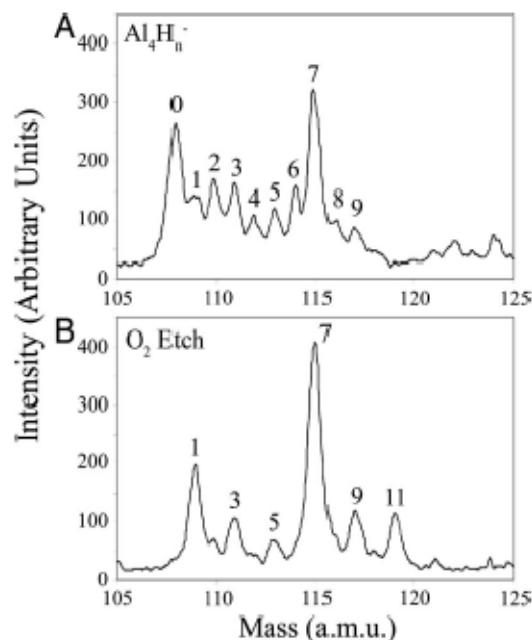


Figure 4. Oxygen etching of  $Al_4H_n^-$ . (A) Mass spectrum after aluminum plasma is exposed to  $H_2$  gas. (B) The clusters are subsequently exposed to molecular oxygen. Adapted from GP 614 and GP616.

The aluminum hydride series was then exposed to oxygen as is shown in Figure 4. Species containing an odd number of electrons reacted rapidly with molecular oxygen, whereas even electron species did not. This observation led to the realization that spin-accommodation plays a role in determining the reactivity of aluminum-based anion clusters with oxygen.

According to the rules set forth by Wigner and Witmer, spin is a conserved quantity in a chemical reaction, and without conservation of spin from reactants to products, a spin excitation is required, which costs the system energy.<sup>9-10</sup> Aluminum clusters with an even number of electrons have a singlet spin multiplicity in their ground state. Molecular oxygen has a triplet ground state, with its two lowest unoccupied molecular orbitals being a pair of minority orbitals that are antibonding in nature. Because the etching reaction's products all have singlet spin multiplicity, the reaction requires a spin excitation. Theoretical investigations show that without sufficient energy to permit a spin excitation, the species does not react. This explanation is consistent with behavior observed in the oxygen etching of aluminum iodides, aluminum hydrides, and aluminum carbides.<sup>GP616</sup> Additionally, the proposed mechanism provides a physical explanation for the success of the HOMO-LUMO gap for predicting oxygen etching behavior.

### C. The Role of Geometry in Aluminum-Water Reactions

During the report period we examined the selective reactivity of specific aluminum cluster anions with water. Our experimental observations exposed selective reactivity that is not supported by jellium concepts.<sup>GP633</sup> Specifically, we established that complementary active sites on the aluminum clusters are responsible for the dissociative chemisorption of water. These active sites consist of two aluminum atoms, one behaving like a Lewis acid and the other like a Lewis base. While similar behavior is known in metal oxides,<sup>11-12</sup> this is the first time such behavior has been observed in homoatomic clusters. In addition to the proposal of the primary mechanism through which aluminum and water interact, we observed that specific clusters,  $\text{Al}_{16}^-$ ,  $\text{Al}_{17}^-$ , and  $\text{Al}_{18}^-$ , were absorbing two water molecules and releasing hydrogen gas. Density functional theory in collaboration with Khanna group was used to examine the geometric and electronic factors that result in this unique selective reactivity.

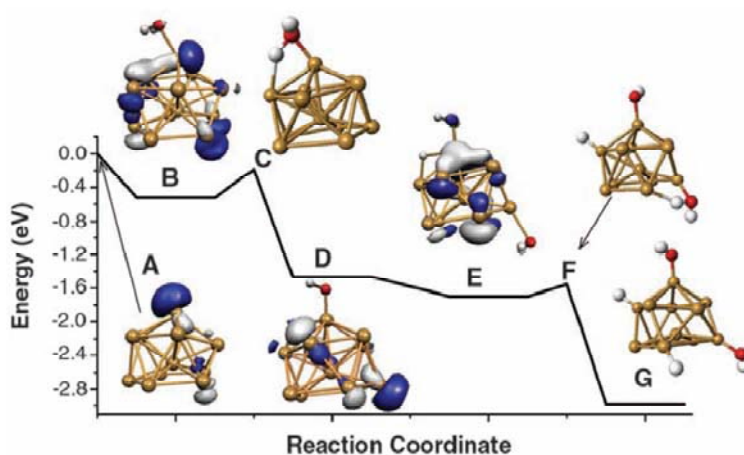


Figure 5. Reaction coordinates for  $\text{Al}_{12}^- + 2\text{H}_2\text{O}$ . (A) The calculated LUMO+1 for  $\text{Al}_{12}^-$ . (B) The HOMO for the chemisorbed  $[\text{Al}_{12}\text{-H}_2\text{O}]^-$  complex. (C) A proposed transition state. (D) The dissociatively chemisorbed product and LUMO+1. (E) The HOMO after a second water is bound to the active site. (F) The transition state for the second water. (G) The final product. Al atoms, bronze; O atoms, red; H atoms, white. Adapted from GP633.

$\text{Al}_{12}^-$ , being the smallest observed cluster to react with water, was analyzed using a first-principles approach within a gradient-corrected density functional formalism. A reaction coordinate was specified where water first adsorbs onto a cluster surface and then undergoes dissociative chemisorption. In the chemisorption event a hydrogen atom is separated from water, creating a surface bound Al-H bond and an Al-OH bond. A mechanism explaining this chemical



behavior was proposed (Figure 5), involving the lone-pair electrons on the oxygen nucleophilically attacking the cluster at a point where the lowest unoccupied molecular orbital protrudes out from the cluster. An area of high charge density existing adjacent to the location of the original nucleophilic attack promotes the formation of an Al-H bond, which allows the splitting of the water molecule. This is the rate-limiting step, and thus when the geometry of the aluminum cluster sufficiently reduces the energy of the transition state, a reaction is observed. The findings reveal the importance of geometrical arrangements in governing cluster reactivity and provide insight into our overall goal of tailoring the design of nanoscale materials through cluster assembly. A similar reaction mechanism was found for the reactions of CH<sub>3</sub>OH with aluminum clusters.

#### **D. Superatoms: Elemental Mimicry via the Superposition of Molecular Electronic States**

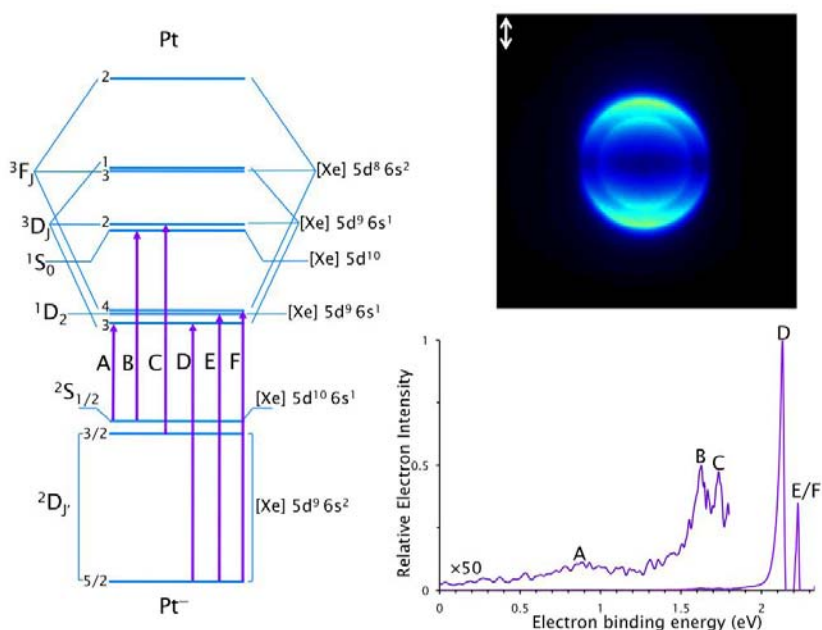
During the report period, employing velocity map imaging to investigate a variety of clusters and elements, we discovered spectroscopically that the electronic features produced independently from an atom or molecules, with the same number of valence electrons, are equivalent. In particular, the isoelectronic systems Ni<sup>-</sup> and TiO<sup>-</sup> were studied utilizing photoelectron imaging. Remarkably, nearly identical photoelectron angular distributions (PAD) are observed. This finding suggests that the molecular counterpart is adopting, in a highly predisposed fashion, the electronic level structure and orbital angular momentum of the bound state of an isolated atomic analogue. It is deduced that the electronic configuration of TiO represents a superposition of two elements (Ti and O) which imitates another element, namely Ni. This fundamental observation of the correspondence linking isoelectronicity and electronic spectra has hitherto been unreported. This correlation is found to exist between other molecular combinations and atoms, provided the valence electron count in both systems remains a conserved quantity.

The fascinating results linking the correspondence of complementary PADs and isoelectronicity between molecular and atomic systems are not isolated to the case presented between the isoelectronic species, TiO<sup>-</sup> and Ni<sup>-</sup>. Indeed, we have also observed this phenomenon in the photoelectron signatures of ZrO<sup>-</sup>, HfO<sup>-</sup> coincident with the isoelectronic atoms Pd<sup>-</sup> and Pt<sup>-</sup>. Moreover, preliminary results on MoC<sup>-</sup> exhibit a similar PAD to Pd<sup>-</sup>, suggesting this mimicry extends across rows as well as columns of the periodic table. These

topics will be the subject of future publications. Nevertheless, similar patterns emerge, signifying an elementary mechanism interwoven within these concepts which may provide a more detailed description of matter, opening the prospective doorway to a multi-dimensional periodic table. The findings for the first time quantify the concept of superatoms that we are exploring to use as building blocks for new nanoscale materials.

The Photoelectron Binding energy spectrum and summed photoelectron images were obtained by a time-of-flight (TOF) mass spectrometer coupled to a photoelectron imaging apparatus. The anions were created using laser vaporization (LAVA) source which consists of a translating and rotating metal rod (e.g. Pt/WC) and a pulsed valve to introduce a backing gas (He). The anions are extracted using the TOF grid setup and the arrival times of the Pt<sup>-</sup> and WC<sup>-</sup> are noted. The photodetachment laser (Nd<sup>3+</sup>:YAG 532nm) pulse is intersected with the anion beam and the photodetached electrons are repelled towards the electron detection assembly consisting of the microchannel plate (MCP) detectors and a phosphor screen. The images are recorded by a charge coupled device camera, summed and background subtracted to eliminate noise. The images contain electron kinetic energy and angular distribution information. The electrons with higher kinetic energy are on the outer edges of the obtained image and the angular distribution provides insight pertaining to the nature of the orbital from which the electron was photodetached. See Figures 6 and 7.

Figure 6. Energy level schematic, raw photoelectron image and reconstructed binding energy spectrum for excitation from the ground (<sup>2</sup>D<sub>5/2</sub>) and excited (<sup>2</sup>D<sub>3/2</sub>, <sup>2</sup>S<sub>1/2</sub>) states of Pt<sup>-</sup> acquired at a photon energy of 2.33 eV (532 nm). The laser polarization axis is vertical in the plane of the image (indicated by the double headed arrow). The separation between the neutral excited states, <sup>1</sup>D<sub>2</sub> and <sup>3</sup>F<sub>4</sub>, is not resolved. Hence, peak E/F is assigned to contributions from both <sup>1</sup>D<sub>2</sub> ← <sup>2</sup>D<sub>5/2</sub> and <sup>3</sup>F<sub>4</sub> ← <sup>2</sup>D<sub>5/2</sub> transitions.



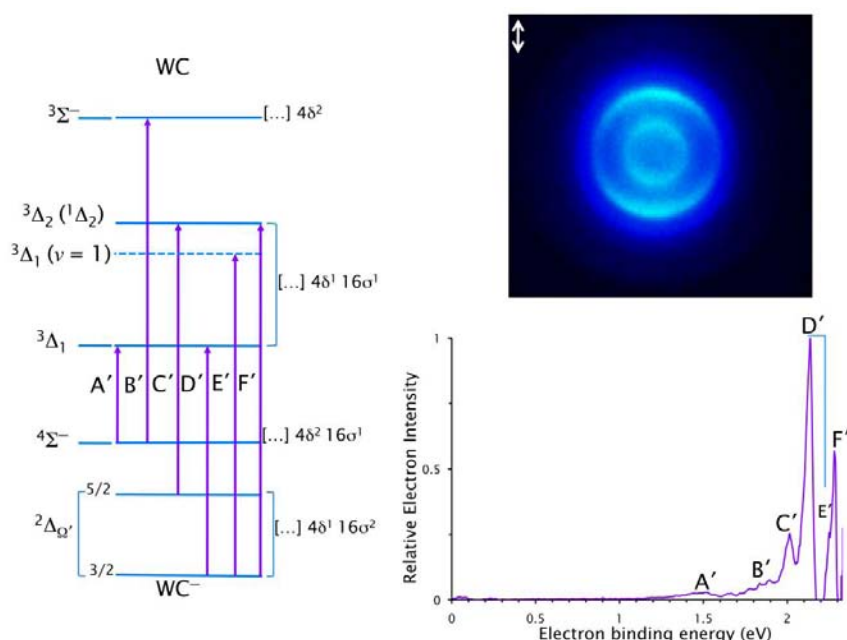


Figure 7. Energy level schematic, raw photoelectron image and reconstructed binding energy spectrum for excitation from the ground ( ${}^2\Delta_{3/2}$ ) and excited ( ${}^2\Delta_{5/2}$ ,  ${}^4\Sigma^-$ ) states of  $WC^-$  acquired at a photon energy of 2.33 eV (532 nm). The laser polarization axis is vertical in the plane of the image (indicated by the double headed arrow). The peak labeled E' is a transition into the first vibrational level of the ground  ${}^3\Delta_1$  electronic state.

### E. Electronic Structure Evolution of $Pb_n^-$

Toward the goal of learning more about the potential use of VMI in ascertaining the orbital occupation of cluster systems, experiments were conducted on several metals and metalloids including lead. The evolution of lead clusters' electronic properties as a function of size was investigated using velocity map imaging photoelectron spectroscopy, which simultaneously measures the kinetic energies and the angular distributions of detached electrons, thus providing information about both the partial wave functions and the orbitals from which the photodetachment process occurs.<sup>GP634</sup> A 2.3 eV laser was used to photodetach electrons from small  $Pb_n^-$  clusters ( $n = 2-4$ ), and the recorded images (Figure 8) show distinct variations in the angular distribution of the electronic bands arising from the change in cluster size. Anisotropy parameters of the  $Pb_n^-$  clusters were determined and found to be dependent on both the orbital symmetry and electron kinetic energy. Even though in some cases this technique has limitations for large cluster systems, the fundamental information gained is important, thereby enhancing our comprehensive knowledge of the evolution of electronic structure with cluster size.

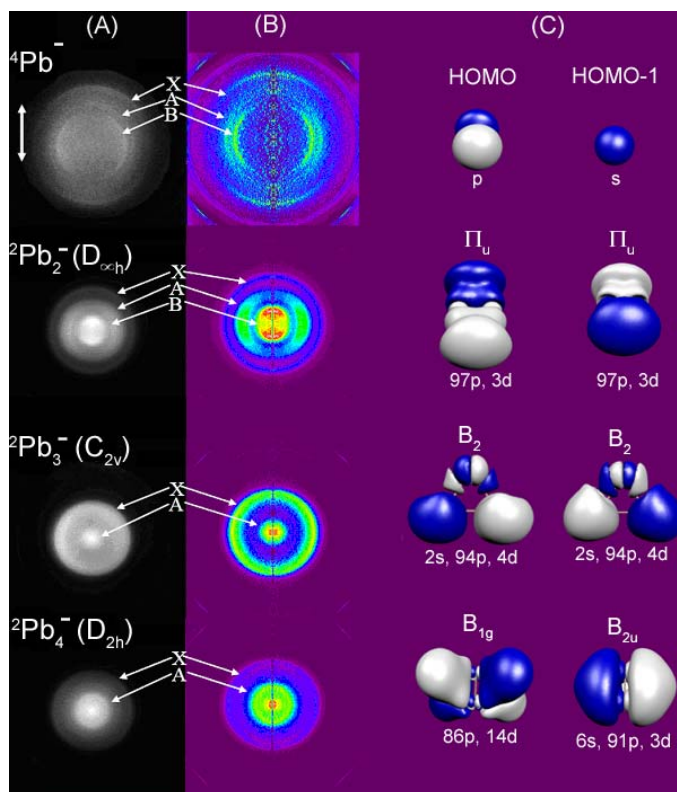


Figure 8. The raw and reconstructed photoelectron images of  $\text{Pb}_n^-$  clusters ( $n = 1-4$ ) recorded using a 527 nm laser are depicted in columns A and B, respectively. The symbols X, A, and B denote the electronic transitions from the anionic ground state to the first and higher excited states of the neutral species. Column C depicts the charge density of the HOMO and HOMO-1, and their symmetry character and percentage of atomic orbital composition. Adapted from GP634.

## F. Soft Landing Neat Clusters

Development of our deposition facility has continued during the grant period. With this instrumentation we are extending our investigation of the interactions of clusters to deposited species, both on surfaces and in rare gas matrices. We are investigating these clusters as they interact with surfaces, each other, and various reactants, using imaging techniques as well as electronic absorption spectroscopy. We have implemented a liquid helium cryostat to control the temperature of deposition experiments, allowing us to control the rate of diffusion on a surface or within a rare gas matrix. We have begun the characterization of soft landing using tunneling electron microscopy (TEM) and scanning electron microscopy (SEM) to examine cluster deposits. More recently we have developed *in situ* cavity ringdown absorption spectroscopic capabilities for the characterization of cluster deposits. Additionally, we have constructed a load-

lock transfer chamber to allow environmental control over the cluster deposits during transfer between instrumentation. Future development will focus on the investigation of clusters and cluster interactions in the condensed phase, a necessary step in the advancement of a methodology for the design, formation, and implementation of cluster-assembled materials.

### **G. Growth Mechanisms of $\text{Nb}_3\text{C}_n^-$ Clusters**

Met-Cars,  $\text{M}_8\text{C}_{12}$ , were discovered in our laboratory<sup>13</sup> and implementing them into cluster-assembled materials requires detailed knowledge of their electronic properties and structure. To this end, during the grant period we investigated the potential building blocks and growth mechanisms of Met-Cars. Our more recent studies focused on anion photoelectron spectroscopy experiments to examine the electronic structures and geometries of the tri-niobium carbide species  $\text{Nb}_3\text{C}_n^-$  ( $n = 5-10$ ).<sup>GP629</sup> In many cases we determined the presence of multiple isomers, a consequence of our laser vaporization source. However, our data suggests that the  $\text{Nb}_3\text{C}_n^-$  clusters favor structures with three niobium atoms positioned in a triangular arrangement, with a “capping” carbon atom bound to a face. As carbon atoms are added,  $\text{C}_2$  bridging units emerge between metal atoms. This distinct evolution can be seen in Figure 9, which displays the photoelectron spectra and lowest energy isomers for  $\text{Nb}_3\text{C}_5^-$ ,  $\text{Nb}_3\text{C}_6^-$ , and  $\text{Nb}_3\text{C}_7^-$ . These findings provide geometries that are reminiscent of proposed structures for the Met-Car, in which two carbon atoms bridge between metal atoms. A paper detailing these findings has been published that provides further insight to the growth mechanisms of the Met-Car.<sup>GP629</sup>

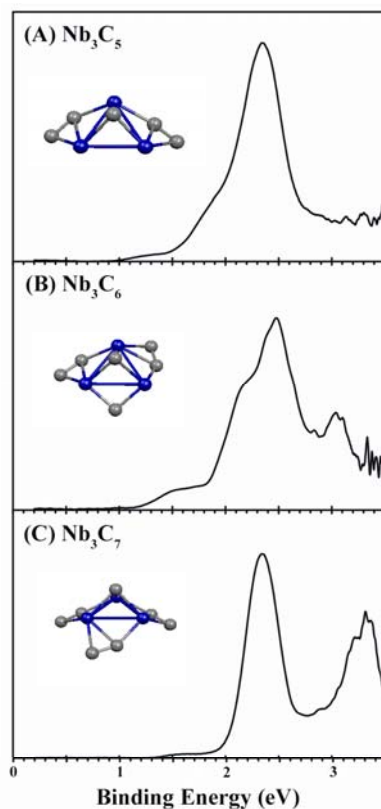


Figure 9. Photoelectron spectra of  $\text{Nb}_3\text{C}_n^-$  ( $n = 5-7$ ) clusters taken with a 308 nm laser. Adapted from GP629.

## H. Controlling the Morphology of Transition Metal Carbide Nanoparticles

We have continued our studies of transition metal carbide nanoparticles using an arc discharge method.<sup>GP590,GP612</sup> Our main focus has been on ZrC, TiC, and NbC nanoparticles. In these studies, different proportions of methane and helium can be used to control the morphology of the metal-carbon nanoparticles. As shown in Figure 10A, titanium carbide produced from 12% methane mixed with helium yields nanoparticles that are cubic shaped, where each facet being expressed reveals the (100) plane. Interestingly, when the methane is increased to 100%, the nanoparticle's morphology changes to cuboctahedron shaped as shown in Figure 10B. The facets expressed are comprised of four (111) planes and two (100) planes. This work on the synthesis of nanoparticles in solution is proving valuable as we expand our pursuit of cluster-assembled materials on the macro scale.

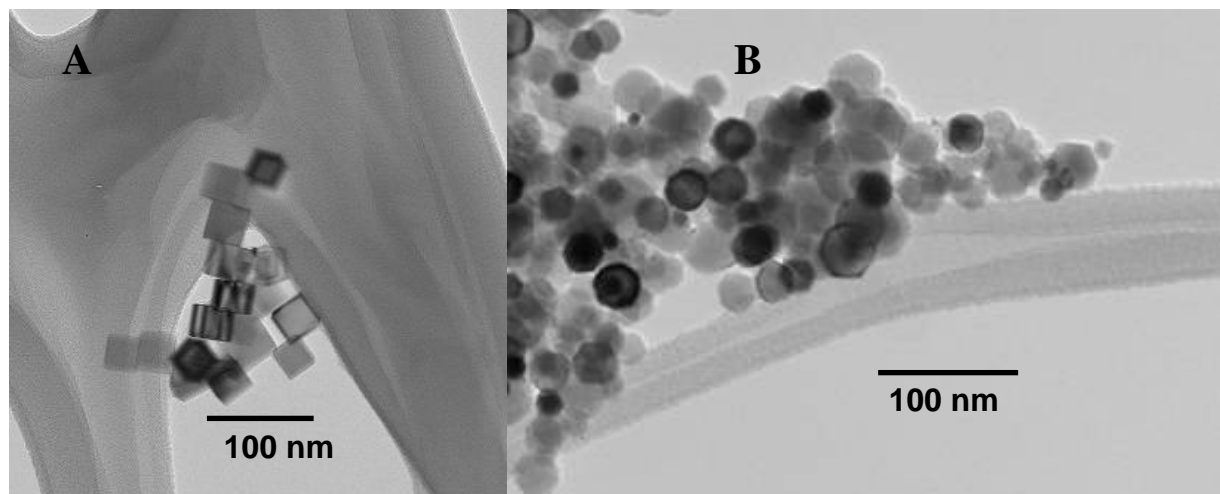


Figure 10. A) TEM of TiC synthesized with a mixture of 12% methane in helium. B) TEM of TiC synthesized with 100% methane. See GP642.

### Cluster Science Reviews

In addition to these new studies, we have also been involved in the production of two major review articles outlining the history and importance of cluster science and cluster-assembled materials. The first is an invited feature article<sup>GP632</sup> in the *Journal of Physical Chemistry* in honor of the centennial year of the division. It provides a board overview of cluster science, beginning with the jellium model and focuses on our research which led to the superatom concept. The paper highlights the three-dimensional periodic table concept and was written in order to deliver a comprehensive explanation of cluster science to a broad scientific community. The second review is an invited review article<sup>GP636</sup> in the new journal *ACS Nano*, and it outlines some important developments in the field of cluster-assembled material, which we have pioneered. It provides a clear explanation as to why nanoscale materials with tunable properties will advance global technology, and should create an increased amount of interest in cluster science. Beginning with the discovery of C<sub>60</sub>, the article outlines the development of organic nanostructures, and then continues with our work on aluminum, which led to our proposing a three-dimensional periodic table consisting of superatoms. It also covers the cluster-assembled materials work performed by two of our collaborators, Weiss and Sen, on arsenic-based building blocks. Finally, the review outlines recent developments in nanocrystal supelattice formation, a field that initially used lead and iron-based molecules but has now expanded across the period table.

## **Summary**

To close, in the past several years we have made substantial progress towards the goal of cluster-assembled materials with tunable properties. Our research involving the interactions between aluminum cluster anions and water will undoubtedly generate new interest surrounding the stability of aluminum clusters and their reactivity with various nucleophiles. Additionally, our studies using photoelectron spectroscopy have continued to provide valuable insights into the chemical properties of clusters; information that is important to understanding how these species will behave once incorporated into a materials. Finally our research involving the quantification of the concept of superatoms via isoelectronic systems and their element mimics has opened up new endeavor in the field of nanoscale material. This research and the two review papers bring us even closer to achieving our overall goal and we hope will spark interest in our research as we continue our pursuit of cluster-assembled materials.



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### Group Publications (GP) During Current Grant Period:

- GP582. "Structural, Electronic, and Chemical Properties of Multiply Iodized Aluminum Clusters" N. O. Jones, J. U. Reveles, S. N. Khanna, D. E. Bergeron, P. J. Roach, and A. W. Castleman, Jr., *Journal of Chemical Physics*, **124**, 154311 (2006).
- GP585. "Metal-carbon clusters: the origin of the delayed atomic ion", K. M. Davis, S. J. Peppernick, and A. W. Castleman, Jr., *Journal of Chemical Physics*, **124**, 164304 (2006).
- GP586. "Clusters – A Bridge Across Disciplines", A. W. Castleman, Jr. and P. Jena, *PNAS* – (Invited perspective on the cluster field)- *PNAS*, **103**, 28, 2006.
- GP587. "Anion Photoelectron Spectroscopy and Density Functional Investigation of Diniobium-Carbon Clusters", K. L. Knappenberger, Jr., P. A. Clayborne, M. A. Sobhy, C. E. Jones, Jr., U. U. Gupta, S. N. Khanna, I. Jordanov, J. Sofo, and A. W. Castleman, Jr., *ACS Nano*, **1**, 4, 319-326 (2007).
- GP589. "Multiple Valence Superatoms", J. Ulises Reveles, S. N. Khanna, P. J. Roach, and A. W. Castleman, Jr. *PNAS*, **103**, 49, 18405-18410 (2006).
- GP590. "Analysis of Titanium Nanoparticles Created by Laser Irradiation Under Liquid Environments", J. S. Golightly and A. W. Castleman, Jr., *Journal of Physical Chemistry B* **110**, 19979-19984 (2006).
- GP591. "Silicon Oxide Nanoparticles Reveal the Origin of Silicate Grains in Circumstellar Environments", A. C. Reber, P. A. Clayborne, J. U. Reveles, S. N. Khanna, A. W. Castleman, Jr., A. Ali, *Nano Letters*, **6**, 1190-1195 (2006).
- GP592. "Clusters – A Bridge Across Disciplines: Physics and Chemistry", Puru Jena and A. W. Castleman, Jr., *PNAS*, **103**, 28, 2006.
- GP593. "Clusters – A Bridge Across Disciplines: Environment, Materials Science, and Biology", A. W. Castleman, Jr. and Puru Jena, *PNAS*, **103**, 28, 2006
- GP596. "From Designer Clusters to Synthetic Crystalline Nano-Assemblies", A. W. Castleman, Jr., S. N. Khanna, A. Sen, A. C. Reber, K. M. Davis, S. J. Peppernick, A. Ugrinov, and M. D. Merritt, *Nano Letters*, **7**, 9, 2734-2741 (2007).
- GP598. "Versatile Cluster Based Photoelectron Spectrometer" K.L. Knappenberger, Jr., C.E. Jones, Jr., M.A. Sobhy, A.W. Castleman, Jr. *Review of Scientific Instruments*, **77**, 123901 (2006).

- GP601. “Recent Advances in Cluster Science”, A. Welford Castleman, Jr., (Proceedings for the Advances in Mass Spectrometry for the 17<sup>th</sup> IMSC), **13**, 7-11 (2007).
- GP602. “Superatoms: Building Blocks of New Materials”, A. W. Castleman, Jr. and S. N. Khanna, *The Chemical Physics of Solid Surfaces; Volume 12 Atomic Clusters: From Gas Phase to Deposited*, Publishers; Elsevier, Editor: Phil Woodruff, Vol. **12**, pp. 409-425 (2007) ISBN 978 0 444 52756 1.
- GP604. “Electron dynamics of metal-carbon clusters “, K. L. Knappenberger, Jr., C. E. Jones, Jr., M. A. Sobhy, and A. W. Castleman, Jr., *Femtochemistry VII: Fundamental Ultrafast Processes in Chemistry, Physics, and Biology*, Editors: A. W. Castleman, Jr. and Michele L. Kimble, pp. 33-38, Elsevier: ISBN 0 444 52821 0.
- GP605. “A density-functional study of the structural, electronic, and vibrational properties of Ti<sub>8</sub>C<sub>12</sub> metallocarbohedrynes with relevance to ultrafast time-resolved spectroscopy”, M. A. Sobhy, J. O. Sofo, and A. W. Castleman, Jr., *Femtochemistry VII: Fundamental Ultrafast Processes in Chemistry, Physics, and Biology*, Editors: A. W. Castleman, Jr. and Michele L. Kimble, pp. 80-86, Elsevier: ISBN 0 444 52821 0.
- GP608. “On the Magic Character of Al<sub>6</sub>Au” M. L. Kimble, A. W. Castleman, Jr., J. U. Reveles, and S. N. Khanna, *Collection of Czechoslovak Chemical Communications*; In honor and memory of Prof. Dr. Jaroslav Koutecky, **72**, 2, pp. 185-196 (2007).
- GP609. “Photoelectron Imaging of Copper and Silver Mono and Di-Amine Anions”, M. A. Sobhy and A. W. Castleman, Jr., *J. Chem. Phys.*, **126**, 154314 (2007).
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- GP612. “Synthesis of Zirconium Nanoparticles by Ultrafast Laser Ablation”, Justin Golightly and A. W. Castleman, Jr., Special issue of *Zeitschrift für Physikalische Chemie* dedicated to Konrad Weil 80<sup>th</sup> Birthday, **221**, 1455-1468 (2007).
- GP614. “Al<sub>4</sub>H<sub>7</sub><sup>-</sup>: A Resilient Building Block for Aluminum Hydrogen Cluster Materials”, P. J. Roach, A. C. Reber, W. H. Woodward, S. N. Khanna and A. W. Castleman, Jr., *PNAS*, **104**, 37, 14565-14569 (2007).
- GP616. “Spin Accommodation and Reactivity of Aluminum Based Clusters with O<sub>2</sub>”, A. C. Reber, S. N. Khanna, P. J. Roach, W. H. Woodward, and A. W. Castleman, Jr., *JACS*, **129**, 16098-1601 (2007).

- GP618. "On Becoming Aromatic: A Combined Experimental and Theoretical Study of  $\text{Al}_3\text{Bi}$ ", C. E. Jones, Jr., P. A. Clayborne, J. U. Reveles, J. J. Melko, U. Gupta, S. N. Khanna, and A. W. Castleman, Jr., *The Journal of Physical Chemistry*, **112**, 13316-13325 (2008).
- GP620. "From  $\text{SiO}$  molecules to Silicates in Circumstellar Space: Atomic Structures, Growth Patterns, and Optical Signatures of  $\text{Si}_n\text{O}_m$  Nanoparticles", A. C. Reber, S. Paranthaman, P. A. Clayborne, S. N. Khanna, and A. W. Castleman, Jr., *ACS Nano*, **2**, 1729-1737 (2008).
- GP629. "Structural Evolution in Triniobium Carbide Clusters Studied by Anion Photoelectron Spectroscopy and Density Functional Theory", C. E. Jones, Jr., P. A. Clayborne, U. Gupta, J. J. Melko, S. N. Khanna, and A. W. Castleman, Jr., *J Phys Chem A*, **114**, 1290-1297 (2010)
- GP632. "Clusters, Superatoms and Building Blocks of New Materials", A. W. Castleman, Jr. and S. N. Khanna, Invited Featured Article for the Invited Featured Article for the *Journal of Physical Chemistry*, **113**, 2664-2675 (2009).
- GP633. "Complementary Active Sites Are Responsible for the Size-Selected Reactivity of Aluminum Cluster Anion with Water", P. J. Roach, W. H. Woodward, A. W. Castleman, Jr., A. C. Reber and S. N. Khanna, *Science*, **323**, 492-495 (2009).
- GP634. "Photoelectron Imaging and Theoretical Investigation of Bimetallic  $\text{Bi}_{1-2}\text{Ga}_{0-2}^-$  and Lead  $\text{Pb}_{1-4}^-$  Cluster Anions", M. A. Sobhy, J. Ulises Reveles, U. Gupta, S. N. Khanna and A. W. Castleman, Jr., *The Journal of Chemical Physics* **130**, 054304 (2009).
- GP636. "Cluster-Assembled Materials", S. A. Claridge, A. W. Castleman, Jr., S. N. Khanna, C. B. Murray, A. Sen and P. S. Weiss, *ACS Nano*, **3**, 2 244-255 (2009).
- GP640. "Superatom Spectroscopy and Evidence of the Electronic State Correlation Between Elements and Isoelectronic Molecular Counterparts", S. J. Peppernick, K. D. Gunaratne and A. W. Castleman, Jr., *PNAS*, **107**, 3 975-980 (2010).
- GP642. "Effect of Carbon Concentration on Changing the Morphology of Titanium Carbide Nanoparticles from Cubic to Cuboctahedron", D. Grove, U. Gupta and A. W. Castleman, Jr., *ACS Nano*, **4**, 1, 49-54 (2010).
- GP644. "Crystal Field Effects on the Reactivity of Aluminum-Copper Cluster Anions", P. J. Roach, W. H. Woodward, A. C. Reber, S. N. Khanna and A. W. Castleman, Jr., *PRA* (submitted Sept. 2009).

- GP648. “Generation of Radical Centers in Binary Neutral Metal Oxide Clusters for Catalytic Oxidation Reactions”, M. Nöbller, R. Mitrić, V. Bonačić-Koutecký, G. E. Johnson, E. Tyo, A. W. Castleman, Jr., *Angewandte Chemie Int. Ed.*, **49**, 407 (2010).
- GP 649. “Reactivity of Aluminum Cluster Anions with Water: Origins of Reactivity and Mechanisms for H<sub>2</sub> Release”, A. C. Reber, S. N. Khanna, P. J. Roach, W. H. Woodward and A. W. Castleman, Jr., *Journal of Physical Chemistry A* (submitted Dec. 2009).
- GP652. “Towards Comprehending the Superatomic State of Matter”, S. J. Peppernick, K. D. D. Gunaratne and A. W. Castleman, Jr., *Chemical Physics Letters*, *Frontiers in Science* article (in press Jan. 2010).

### **Interactions/Transitions:**

*(a) Participation/presentations at meetings, conferences, seminars, etc. during report period:*

“From Designer Clusters to Synthetic Cluster Assemblies”, (S. N. Khanna presented joint work from the Castleman/Khanna group – Talk), 2007 Contractors' Meeting in Molecular Dynamics and Theoretical Chemistry, AFOSR, Irvine, CA, May 20-22, 2007.

“From Superatoms to Materials”, (A. W. Castleman, Jr. – Poster), 2007 Contractors' Meeting in Molecular Dynamics and Theoretical Chemistry, AFOSR, Irvine, CA, May 20-22, 2007.

“New Assemblies Combining Super-halogens and Super-alkalis”, APS March Meeting, 2007, Colorado Convention Center, Denver, CO March 5-9, 2007

“Nano-Assemblies Using Designer Clusters”, APS March Meeting, 2007, Colorado Convention Center, Denver, CO March 5-9, 2007

“Influence of Charge State on the Reaction of FeO<sub>3</sub><sup>+/-</sup> with Carbon Monoxide”, APS March Meeting, 2007, Colorado Convention Center, Denver, CO March 5-9, 2007

“From Designer Clusters to Synthetic Cluster Assemblies”, S3C meeting, Brand Austria, March 12-16, 2007

“Superatoms: Building Blocks of New Materials”, (A. W. Castleman, Jr., - Talk), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“From Designer Clusters to Synthetic Cluster Assemblies”, (A. C. Reber – Talk), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Investigations of Mass Selected Transition Metal Oxides Clusters via Tandem TOF-MS”, (D. E. Blumling and S. G. Sayres – Posters), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“The Production of Nanoparticles in Different Environments Through the Use of Laser Ablation and Arc Discharge”, (D. E. Grove – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Bimetallic Cluster Studies Using Negative Ion Photoelectron Spectroscopy and Imaging”, (U. Gupta – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Understanding the Unique Nature of Niobium Carbide Clusters”, (C. E. Jones – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Reaction of Aluminum Iodide Cluster Anions with CH<sub>3</sub>OH”, (N. O. Jones – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Investigations into the Electronic and Magnetic Behavior of Semiconductor Transition Metal Clusters via Velocity Map Imaging”, (S. J. Peppernick – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“The Superatomic Identity of Aluminum Clusters: Designing Building Blocks for Cluster-Assembled Materials”, (P. J. Roach – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Formation of Silicate Grains in Circumstellar Environments: Experiment, Theory and Observations”, (P. Clayborne - Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“Experimental and Theoretical Studies of the Oxidation of CO by Fe<sub>1-2</sub>O<sub>≤6</sub><sup>-</sup> and Fe<sub>1-2</sub>O<sub>1-5</sub><sup>+</sup> Clusters”, (J. Ulises Reveles – Poster), 5<sup>th</sup> International Symposium on Theory of Atomic and Molecular Clusters, Richmond, VA, May 13-17, 2007.

“From Designer Clusters to Synthetic Cluster Assemblies”, (S. N. Khanna presented joint work from the Castleman/Khanna group – Talk), 2007 Contractors' Meeting in Molecular Dynamics and Theoretical Chemistry, AFOSR, Irvine, CA, May 20-22, 2007.

“From Superatoms to Materials”, (A. W. Castleman, Jr. – Poster), 2007 Contractors' Meeting in Molecular Dynamics and Theoretical Chemistry, AFOSR, Irvine, CA, May 20-22, 2007.

“Cluster Research – Exploring the Giant World of Tiny Matter”, (A. W. Castleman, Jr. – Talk), Einladung, Humboldt-Universitaet, Berlin, June 19, 2007.

“Superatoms and Metal-Semiconductor Motifs for Cluster Materials”, (A. W. Castleman, Jr. – Talk), Fundamental Synthesis Research Challenges for 21<sup>st</sup> Century Materials: Mechanism and Methods, DOE Contractors Meeting – 2007, Baltimore, MD, July 8-11, 2007.

“Bi<sub>x</sub>Ga<sub>y</sub><sup>-</sup> Cluster Studies using Photoelectron Spectroscopy/Imaging” (U. Gupta – Poster), Gordon Conference Meeting, Mount Holyoke College, South Hadley, MA, July 29 – August 3, 2007.

“Al<sub>4</sub>H<sub>7</sub><sup>-</sup>: A resilient building block for aluminum hydrogen cluster assembled materials”, (P. Roach and W. Woodward – Poster), Gordon Conference Meeting, Mount Holyoke College, South Hadley, MA, July 29 – August 3, 2007.

“Experimental and Theoretical Study of the Structure and Reactivity of FeO<sub>3</sub>+/- with CO”, (G. Johnson – Poster), Gordon Conference Meeting, Mount Holyoke College, South Hadley, MA, July 29 – August 3, 2007.

“Investigating the Mechanisms of Oxidation Reactions Occurring on Heterogeneous Catalysts”, (A. W. Castleman, Jr.), U.S. Department of Energy 2007 Meeting on Condensed Phase and Interfacial Molecular Sciences, Airlie Conference Center, October 21 – 24, 2007.

“Superatoms: Prospect of New Energetic Materials via Cluster Assembly”, (A. W. Castleman, Jr.), 4<sup>th</sup> Advanced Energetics Technical Exchange, Fort Belvoir, VA, January 22-25, 2008.

“From Superatoms to Cluster Assembled Materials”, (A. W. Castleman, Jr.), 2008 March APS Meeting, New Orleans, Louisiana, March 10-14, 2008.

“Investigating the Molecular Level Details of Catalytic Oxidation Reactions”, (Invited Talk delivered by G. Johnson), 2008 March APS Meeting, New Orleans, Louisiana, March 10-14, 2008.

“Structure, Growth and Optical Properties of Si<sub>n</sub>O<sub>m</sub> Nanoparticles: From SiO molecules to Silicates in Circumstellar Space”, (Poster: S. Paranthaman), 2008 March APS Meeting, New Orleans, Louisiana, March 10-14, 2008.

“From Designer Clusters to Synthetic Crystalline Nano-Assemblies”, (Poster: M. Qian), 2008 March APS Meeting, New Orleans, Louisiana, March 10-14, 2008.

“Anion Photoelectron Spectroscopy and Density Functional Investigation of Diniobium-Carbon Clusters”, (Poster: P. A. Clayborne), 2008 March APS Meeting, New Orleans, Louisiana, March 10-14, 2008.

“From Superatoms to Cluster Assembled Materials”, (Keynote Speaker A. W. Castleman, Jr.), 5<sup>th</sup> Annual Conference on Self-Assembled Architectures and Devices (FNANO08), Snowbird, Utah, April 22 – 24, 2008.

“Cluster Dynamics: Laying the Foundations of Developing Nanoscale Materials”, (A. W. Castleman), AFRL Nanotechnology Initiative Program Review, Dayton, OH, May 5-7, 2008.

“Aluminum Cluster-Based Materials for Propulsion and Other Applications”, (Invited Talk covering our joint work: delivered by S. N. Khanna), AFRL Nanotechnology Initiative Program Review, Dayton, OH, May 5-7, 2008.

“Structure and Dynamics of Energetic and Catalytic Materials”, (Poster: A. W. Castleman, Jr.), Molecular Dynamics Contractors’ Meeting, Vienna, VA, May 19-21, 2008.

“Novel Nanomaterials Using Superatom Cluster-Assemblies”, (Poster: S. N. Khanna), Molecular Dynamics Contractors’ Meeting, Vienna, VA, May 19-21, 2008.

“Coulomb Explosion of Transition Metal Oxides”, (Poster: S. Sayres), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“Velocity Map Imaging of Semiconductor-Metal Cluster Systems”, (Poster: S. J. Peppernick), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“Aluminum Anions and Water: Nucleophilic Reactivity and Free-Electron Metal Clusters”, (Poster: P. Roach), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“Photoelectron Spectroscopy of Mixed-Metal Clusters”, (Poster: C. E. Jones, Jr.), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“Study of III-V Semiconductor Clusters Using Anion Photoelectron Spectroscopy”, (Poster: U. Gupta), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“The Solvation and Photochemistry of  $\text{HI}(\text{H}_2\text{O})_n$  Clusters: Evidence of Excited State Biradical Formation and Implications to the Solvated Electron”, (Poster: N. Bianco), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“Influence of Structure and Charge State on the Mechanism of CO Oxidation on Gold Clusters”, (Poster: G. Johnson), DAMOP – 2008, Penn State University, University Park, PA, May 27-31, 2008.

“Efficiently Transporting Ions From Viscous Flow to Ultra-High Vacuum with Minimal Loss”, (Poster: P. Roach and W. Woodward), 56<sup>th</sup> ASMS Conference, Denver, CO, June 1 – 5, 2008.

“An Ultrafast Glimpse of Ionization Processes in Clusters”, (A. W. Castleman, Jr.) Gordon Research Conference, Aussois, France, September 7-12, 2008.

“Reactivity and Cooperative Catalysis by Superatoms: Spin, Electronic and Geometric Effects”, (Invited Talk covering our joint work: delivered by S. N. Khanna), Cancun, Mexico.



“Overview of MURI project objectives and accomplishments during the first 2 years”, (A. W. Castleman, Jr.), ARO Review, The Pennsylvania State University, October 6-7, 2008.

“Elucidating the Molecular – Level Details of Heterogeneous Catalytic Oxidation Reactions”, (A. W. Castleman, Jr.), 2008 Condensed Phase and Interfacial Molecular Science Research Meeting, Office of Basic Energy Science, Warrenton, VA, October 19-22, 2008.

“Superatoms and Prospects of Cluster Assembled Materials: The Next Frontier in Nanoscale Research”, (A. W. Castleman, Jr.), Colloquium at Argonne National Lab, Argonne, IL, October 28, 2008.

“Superatom Assemblies: Towards Novel Nano-Materials with Precise Control over Properties”, (invited talk: S. N. Khanna) International Symposium on Clusters, Cluster Assemblies and Nanoscale Materials, Allahabad, India, February 9-11, 2009. (Invited talk given by collaborator, S. N. Khanna due to conflict with dates).

“The Prospect of Designer Materials via Cluster Assembly: The Next Frontier in Nanoscale Science”, (Plenary Lecture A. W. Castleman, Jr.), GRI Symposium II On Cluster Science – Reactivity of Clusters, Genesis Institute, Nagoya, Japan, February 24-26, 2009.

“Modeling Catalytic Reactions via Ion Clusters”, (invited talk: A. W. Castleman, Jr.), Gordon Research Conference, Galveston, TX, March 1-6, 2009.

“Cluster Dynamics: Laying the Foundation for Tailoring the Design of Cluster Assembled Nanoscale Materials”, (talk – A. W. Castleman, Jr.), AFOSR Contractor’s Meeting, Sand Diego, CA, May 17-19, 2009.

Discussion Leader for Spectroscopy II, (A. W. Castleman, Jr.), Gordon Research Conference, South Hadley, MA, July 19-24, 2009.

“Superatoms and Prospects of Cluster Assembled Materials: The Next Frontier in Nanoscale Science”, (invited talk – A. W. Castleman, Jr.), Sagamore XVI, Santa Fe, NM, August 2-7, 2009.

“Structure, Stability and Reactive Centers in Binary-Metallic Clusters and Their Compounds”, (invited talk – A. W. Castleman, Jr.), 238<sup>th</sup> ACS Meeting, Washington, DC, August 16-20, 2009.

“Fundamental Studies in Nanocatalysts in Propulsion – The Approach: Study of Isolated Clusters”, (talk – A. W. Castleman, Jr.), MURI Review, Arlington, VA, December 3, 2009.

*(b) Consultative and advisory functions during report period:*

Member of the U.S. National Committee for IUPAC; TAMC VI 2009 International Conference Committee; Elected Liaison from the Chemistry Section of the National Academy of Sciences to the NRC; Chair of the Division of Chemical Physics; APS Program Chair March 2008 Planned 8 Focus Sessions for the APS March 2008 in New Orleans: Frontiers in Electronic Structure Theory (DCP/DCOMP), Surfaces and Interfaces II (DCMP), Quantum Control (DCP), Cluster Assembled Nanoscale Materials (DCP), Fundamental Issues in Catalysis (DCP), Advances in Atmospheric Aerosol Science (DCP), Photophysics of Cold Molecules (DCP), Advances in Spectroscopy (DCP)

**New Discoveries, Inventions, or Patent Disclosures:**

Additional superatoms; established feasibility of cluster assembly to produce new nanoscale materials.

Patent Application – PSU Invention Disclosure No. 2008-3458; “Collisional-Focusing of Disperse Ions with a Non-Parallel Multi-Polar Ion Guide”, P. Roach and A. W. Castleman, Jr.

Patent Application – PSU Invention Disclosure No. 2008-3428; “Hydrogen on Demand via Aluminum Clusters”, A. W. Castleman, Jr., P. Roach, S. N. Khanna (VCU) and A. C. Reber (VCU)

**Honors/Awards:**

- 2010 Irving Langmuir Award in Chemical Physics – American Chemical Society
- 2008 Awarded Fellow of the Royal Society of Chemistry
- 2007 Thomas W. Phelan Fellows Award (Rensselaer Polytechnic Institute Alumni award)
- 2007 Chair, Gordon Conference on Clusters, Nanocrystals, and Nanostructures (Elected Co-Vice Chair 2003)
- 2006 Vice Chair (Chair-elect) Chemical Physics Division of the American Physical Society
- 2006 Program chair for the Division of Chemical Physics of the APS for the March 2008 meeting New Orleans, Louisiana
- 2006 U.S. Senior Scientist Award (4<sup>th</sup>) Stay – von Humboldt Award (3<sup>rd</sup> Award) /Humboldt University of Berlin (Collaboration with Theoretical Group of Professor Vlasta Bonačić-Koutecký).
- 2006 Chair position of the Division of Chemical Physics of the APS

**Prior to current grant period:**

- 2005 Chair Elect, Femtochemistry VII
- 2004 Co-Chair, Board of Chemical Sciences and Technology, National Research Council/National Academy of Science
- 2001 Jost Memorial Award, German Chemical Society

- 1999 Appointed Eberly Distinguished Chair in Science
- 1998 Elected Member of the National Academy of Sciences
- 1998 Elected Fellow of the American Academy of Arts and Sciences
- 1998 Elected Fellow of the New York Academy of Sciences
- 1990 Conference Organizer and Chairman of Gordon Conference on Molecular and Ionic Clusters, first Gordon Conference held in Europe, Volterre, Italy, September 2-7, 1990.
- 1989 Fulbright Senior Scholar Award
- 1988 Recipient of the ACS Award for Creative Advances in Environmental Science and Technology
- 1987 Doktors Honoris Causa, University of Innsbruck, Austria
- 1986 Named Evan Pugh Professor of Chemistry
- 1986 U.S. Senior Scientist von Humboldt Award (2<sup>nd</sup> 1998; 3<sup>rd</sup> 2006)
- 1985 Elected Fellow of the American Association for the Advancement of Science
- 1985 Elected Fellow of the American Physical Society
- 1983 Awardee Senior Scientist Fellow Japanese Society for the Promotion of Science (2<sup>nd</sup> in 1997)
- 1977 Sherman Fairchild Distinguished Scholar, California Institute of Technology (for senior faculty/researchers)