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13. ABSTRACT (Maximum 200 words)

Metal-compound microclusters are produced in the gas phase with laser vaporization in a pulsed nozzle cluster source. The clusters which grow are measured with mass spectrometry and their energetics are measured with photoionization and laser photodissociation. The abundant species found and/or the inert species found are evaluated as prospects for the synthesis of macroscopic cluster assembled materials.

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- Final Technical Report -

Synthesis and Characterization of Novel Metal-Compound Clusters

For the Period July 1, 1994 to June 30, 1997

AFOSR Contract No. F49620-94-1-0267

August 1997

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OBJECTIVES

This project has the goal of investigating the structure and bonding in stable metal compound clusters, which are produced and studied in the gas phase, but may be used as precursors for cluster assembled materials of various kinds. We use laser vaporization in a pulsed nozzle cluster source to generate these species and laser photoionization and photodissociation in conjunction with mass spectrometry measurements to characterize their properties.

STATUS OF EFFORT

Experiments on compound clusters were conducted using two molecular beam machines. One machine focuses on neutral photoionization, and the second machine focuses on ion cluster mass spectrometry and mass-selected photodissociation experiments. Smaller vacuum systems were constructed and used for the preparation of samples for laser vaporization composed of layered films of metals and/or other materials, as described below. The development of these new techniques for thin film deposition has made it possible to prepare a variety of mixed metal and/or metal-non metal *composite samples* for laser vaporization experiments, which in turn have made it possible to produce and study a variety of novel cluster systems.

ACCOMPLISHMENTS/NEW FINDINGS

Metal Oxide Clusters

We have searched for interesting new metal compound systems which may produce stable clusters useful as precursors for ceramic (also microelectronic, optical, magnetic, etc.) materials preparation. The belief is that gas phase experiments, which have highly refined diagnostics on the clusters produced, are the best way to conduct survey measurements to identify interesting cluster systems. Species produced with extreme abundance and/or which exhibit special inertness toward reaction are the best candidates for attempts at isolation in macroscopic quantities. This is the same line of reasoning which led to the discovery of C_{60} and the fullerenes. We are investigating metal oxides and metal carbides, etc.

As a main result of the granting period, we have identified for the first time interesting new "magic number" mass spectra for metal oxide clusters of antimony and bismuth. These species were observed in both the positive and negative ion modes of our mass spectrometer. The species $M_3O_4^+$, $M_4O_5^+$, $M_5O_7^+$, $M_6O_8^+$, $M_7O_{10}^+$, $M_9O_{14}^+$ and $M_{11}O_{17}^+$ are produced with especially enhanced abundance for both antimony and bismuth. At each cluster size, there is a unique oxide stoichiometry produced. In negative ions, the oxide clusters have only been observed at smaller sizes so far, but there is also a unique oxide stoichiometry which is the same for antimony and bismuth, but which is different from the corresponding cation with the same number of metal atoms (e.g. $M_3O_5^-$). These observations imply that there is a strong electronic structure effect working to produce stable clusters, rather than a geometric effect. Otherwise, there would not be such a dramatic change in the cluster stoichiometry for different charge states. In an interaction with one of our inorganic chemistry colleagues, we have been able to propose geometries and bonding schemes for essentially all of these clusters which have fully satisfied valence for both metal and oxygen. The bonding scheme is thus one of single covalent bonds connecting the framework of the cluster through M-O-M-O- connectivity, i.e., there are no metal-metal bonds. We have also contacted colleagues at other universities (Prof. Puru Jena, Virginia Commonwealth Univ.) who are actively working on ab initio calculations to understand the structure and bonding in these species. Both our work and theory agree that these clusters are close-shelled electronically, and that they have symmetric geometries, making them likely candidates for isolation in macroscopic quantities. New experiments in our lab are constructing a flow reactor system for cluster synthesis in macroscopic quantities, and these systems will be one of the first which will be examined.

Metal Carbide Clusters

We have also made progress in the production and study of new metal carbide clusters. In previous work we had documented interesting mass spectral patterns and photodissociation behavior of metal carbide clusters of the early transition metals (Ti, V, Zr, etc.). These species were produced by vaporizing solid metal with gaseous hydrocarbons added to the plasma. As shown first by Castleman and coworkers, the reactivity of the early transition metals is great enough so that insertion chemistry takes place with elimination of hydrogen, producing pure metal-carbides. While carbides of the late transition metals may also be intrinsically stable, they cannot be formed by this plasma chemistry presumably because the metals are less reactive. Plasma chemistry reactions for these metals lead to addition to hydrocarbon species in the gas phase without elimination of hydrogen, or to no metal carbide clusters at all. We have therefore built a vapor deposition apparatus, and have used it to prepare metal films deposited on graphite rods, to produce metal-carbide samples without the presence of hydrogen. Vaporization of these composite samples produces the metal carbide clusters in many cases where plasma chemistry does not, and this method also works for those metal systems which *are* produced also from hydrocarbon plasma environments. For example, carbides of antimony or bismuth cannot be produced by the hydrocarbon plasma chemistry method, but they are produced readily from composite sample (metal film on carbon rod) vaporization. Another technique we have used with some success is *electrochemical* film deposition. Standard electrochemical preparations make it possible to deposit thin films of many transition metals on carbon rods. We have used this approach to produce composite samples of carbon coated with silver, copper, cobalt and nickel. In each case, vaporization experiments of metal film coated carbon rods samples produces metal carbide clusters in the gas phase.

We have discovered that mixed clusters can be formed by the electrochemical preparation of composite samples, but these clusters are generally more rich in carbon than in metal. The electrochemical technique allows the study of transition metals, but it makes films which are too thin. To make thicker films, we have secured from surplus a large vacuum sublimation apparatus which allows high temperature metal sublimation, and have refurbished it. This machine, which is now in full operation, allows thin films of gold, silver, cobalt, iron, titanium, etc., to be deposited by direct thermal vaporization. We anticipate that composite samples produced by this method will produce more interesting clusters which have more balanced metal:carbon compositions.

Exohedral Metal-Fullerene Clusters

In a new application of our ability to make thin films, we have prepared samples consisting of a solid rod of metal coated around the circumference with a thin film of C_{60}. Laser vaporization of these samples produces *metal-C_{60} clusters* in the gas phase, which we have now studied with photoionization of neutrals, direct sampling of cations, and mass-selected photodissociation of cations. Masses are observed corresponding to multiple metal atoms attached to a single C_{60}, or to two or more C_{60} units, for metals such as silver, iron, nickel, cobalt, titanium, aluminum, indium and copper. The central question about these species is their structure and bonding. Do the M_x/C_{60} masses represent a metal cluster bound to a C_{60} cluster via a single connecting bond, or do they represent multiple metal atoms bound individually to the surface of C_{60} as an adsorbed layer? Photodissociation experiments indicate that both scenarios are found depending on the nature of the metal and the preparation process. Silver, for example, appears not to "wet" the C_{60} surface. Clusters such as $[Ag_3/C_{60}]^+$ are formed, but photodissociation eliminates an intact Ag_3^+ unit, presumably suggesting that this mass represents a "cluster+cluster" species. Iron/C_{60} clusters eliminate mostly metal atoms, with some diatomic metal, indicating that the metal exists as a layer on the C_{60} surface.

Such metal-coated C_{60} species are particularly interesting as precursors for cluster materials. While several endohedral metallo-fullerenes ($M@C_{60}$) have now been produced, their synthesis and isolation is still problematic. However, no exohedral metallo-fullerenes (M_x/C_{60}) have been isolated (with the exception of those containing ligated metal). We are now investigating ways to optimize the production of these species for a variety of metals and to characterize their structure and bonding via photodissociation experiments. In association with a new project just begun, we are constructing an apparatus for the preparation of macroscopic cluster materials, and we also plan to try large-scale synthesis of these exohedral metallo-fullerene species.

PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH PROJECT

Faculty:

Professor Michael A. Duncan, PI

Professor R.B. King, University of Georgia: Collaborator on the metal oxide cluster studies.

Graduate Students:

Student	Degree Program	Social Security Number
Kenneth R. Berry	Ph.D.	[redacted]
Steve Pullins	Ph.D.	[redacted]
John Reddic	Ph.D.	[redacted]
John Buchanan	M.S.	[redacted]

Undergraduate Student:

Jason Robinson B.S. [redacted]

PUBLICATIONS IN THIS FUNDING PERIOD

1. J.S. Pilgrim and M.A. Duncan, "Metal-Carbon Clusters: The Construction of Cages and Crystals," *Advances in Metal and Semiconductor Clusters,* Volume III, M.A. Duncan, ed., JAI Press, Greenwich, CT, 1995.

2. J.S. Pilgrim, L.R. Brock and M.A. Duncan, "Photodissociation of Niobium-Carbon Nanocrystal Clusters," *J. Phys. Chem.* **99**, 544 (1995).

3. L.R. Brock and M.A. Duncan, "Near-Threshold Photoionization to Probe Neutral "Met-Cars" Clusters," *J. Phys. Chem.* **100**, 5654 (1996).

4. J.E. Reddic and M.A. Duncan, "Composite Samples and the Generation of New Metal Carbide Clusters," *Chem. Phys. Lett.* **264**, 157-162 (1997).

5. M.A. Duncan, "Synthesis and Characterization of Metal-Carbide Clusters in the Gas Phase," *J. Cluster Sci.* **8**, 239-266 (1997) (invited review).

6. S.H. Pullins, M.R. France, J.L. Tucker, J. Buchanan and M.A. Duncan, "Antimony and Bismuth Oxide Clusters: A New Family of Magic Number Clusters," *J. Phys. Chem.*, in press.

7. J.E. Reddic, J.C. Robinson and M.A. Duncan, "Electronic Structure Effects in Calcium-Coated C_{60}," *J. Phys. Chem.*, submitted.

INTERACTIONS/TRANSITIONS

a) PRESENTATIONS

Invited Lectures Presented on this Research

1. "Photodissociation and Photoionization Spectroscopy of Metal Clusters," *Physical Chemistry Seminar*, University of North Carolina-Chapel Hill, September 1994.

2. "Photoionization and Photodissociation Spectroscopy of Metal Clusters and Metal Complexes," *Physical Chemistry Seminar*, Arizona State University, October 1994.

3. "Photodissociation Spectroscopy of Small Metal Clusters," *Chemical Physics Seminar*, California Institute of Technology, November 1994.

4. "The Chemistry of Microclusters," *EΦΔ Science Club Colloquium*, Oakwood College, Huntsville, AL, January 1995.

5. "Photoionization and Photodissociation of Metal Clusters," *McGill Chemical Society Lecture*, McGill University, Montreal, Canada, January 1995.

6. "Photodissociation of Metal Clusters: From Solvated Ions to Nanocrystals," *Chemistry Department Colloquium*, University of Puerto Rico, March 1995.

7. "Photodissociation Studies of Metal Clusters and Metal Ion Complexes," *Analytical/Physical Chemistry Seminar*, Texas A&M University, April 1995.

8. "Photodissociation Studies of Metal Clusters and Metal Ion Complexes," *Analytical/Physical Chemistry Seminar*, University of Texas-Austin, April 1995.

9. "Synthesis and Spectroscopy of Gas Phase Metal Clusters," *Departmental Colloquium*, Western Carolina University, November 1995.

10. "Gas Phase Clusters: From Nanocrystals to Solvated Metal Ions," *Physical Chemistry Seminar*, Yale University, December 1995.

11. "Gas Phase Metal Clusters: From Nanocrystals to Solvated Metal Ions," *Departmental Colloquium*, University of South Carolina, December 1995.

12. "Tandem Mass Spectrometry with Lasers and Time-of-Flight Spectrometers," *Athens-Atlanta Mass Spectrometry Group*, Athens, GA, March 1996.

13. "Photoionization and Photodissociation Studies of Metal Carbide Clusters," *70th Colloid and Surface Science Symposium*, Clarkson University, Potsdam, NY, June 1996.

14. "Photodissociation of Gas Phase Metal Clusters: From Nanocrystals to Solvated Cations," *Departmental Colloquium*, Baylor University, October 1996.

15. "Photodissociation of Gas Phase Metal Clusters: From Nanocrystals to Solvated Cations," *Departmental Colloquium*, Virginia Commonwealth University, October 1996.

16. "Photoionization and Photodissociation of Metal Carbide and Metal Oxide Clusters," *Symposium on Metal Clusters*, National Meeting of the American Physical

Society, Kansas City, March 1997.

17. "Spectroscopy of Gas Phase Clusters," *Departmental Colloquium*, Erskine College, April 1997.

18. "Photodissociation Spectroscopy of Gas Phase Clusters: From Solvated Metal Atoms to Nanocrystals," *Departmental Colloquium*, Johns Hopkins University, May 1997.

Poster and Contributed Presentations of this Research

1. "Photodissociation Studies of Metal-Carbon Clusters and Nanocrystals," *AFOSR Conference on Chemical Dynamics and New Materials*, Washington, DC, October 1994.

2. L.R. Brock and M.A. Duncan, "Near-Threshold Photoionization of Metal-Carbide Clusters, *Gordon Conference on Metal and Semiconductor Clusters*, New London, NH, August 1995.

3. M.A. Duncan, "Photodissociation and Photoionization of Metal Compound Clusters," *AFOSR Molecular Dynamics Program Contractor's Meeting*, Boulder, CO, June 1996.

4. M.A. Duncan, "Production and Characterization of Exohedral Metallo-Fullerenes in the Gas Phase," Gordon Research Conference on Clusters, Nanoparticles and Nanostructures, Plymouth, NH, July 1997.

b) CONSULTATIVE AND ADVISORY FUNCTIONS

c) TRANSITIONS

Transitions have been made to the general scientific community, including the academic, industrial, and military, through the development of a new software package for Mass Spectrometry Isotope Distribution Modeling. While programs of these general types have been previously available, the former versions were usually written for mainframe computers and were difficult, if not impossible, to implement on modern PC computers. The new program we have written are in the Visual Basic language, which makes its implementation and use extremely convenient in the standard PC/Windows 95 environment. Input is in the form of pull-down menus, making these programs extremely user-friendly. The isotope program is a significant improvement over former such programs because it allows calculations of mass spectrometer isotope peaks for a chemical formula containing many elements, each with multiple isotopes. This feature is essential for mass spectrometry studies of such species as semiconductor nanoparticles or high molecular weight biopolymers. This program is presently available for distribution from our research group, and will be added to a web site (presently under construction) for down-loading.

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

None

HONORS/AWARDS

None