**Title and Subtitle:**
Cluster Models of Metal-Seeded Energetic Materials

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AFOSR/ML
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**Abstract:**
Metal containing cluster molecules are produced in the gas phase and studied with mass spectrometry and laser spectroscopy. These systems are evaluated to explore the fundamental interactions between metal atoms and small molecules. These studies probe metal van der Waals bonding, metal-metal bonding and related interactions likely to be encountered when metals are condensed in cryogenic matrices in the form of metal seeded fuels. Additional studies probe new gas phase metal carbide and metal oxide clusters important as potential ceramic materials precursors.

**Subject Terms:**
metal atom clusters; metal dimers; electronic spectroscopy; photodissociation

**Security Classification of Report:**
unclassified

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**Form Approved OMB NO. 0704-0188**
- Final Report -

For the Period December 1, 1993 to November 30, 1996

CLUSTER MODELS OF METAL SEEDED ENERGETIC MATERIALS

AFOSR Contract No. F49620-94-1-0063

January 1997

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Athens, GA 30602
OBJECTIVES

The goal of this project is to prepare and characterize novel molecules containing metals which are relevant for the understanding of prospective high energy propellant systems. Two classes of molecules are studied: 1) weakly bound van der Waals complexes containing light metal atoms (Li, Al, Mg) and 2) mixed metal diatomics of these same light elements (LiB, LiAl, AlB, AlMg, etc.). Both of these classes of molecules are prepared and studied in supersonic molecular beams, and they are characterized with laser spectroscopy and time-of-flight mass spectroscopy. In a related area, we are also investigating metal compound clusters (transition metal carbides and oxides) which exhibit novel patterns of cluster growth, and which may have applications as microparticle ceramic materials.

STATUS OF EFFORT

A variety of weakly bound complexes have been prepared and characterized containing aluminum atoms bound by van der Waals forces to rare gas atoms or small molecules. Threshold photoionization has been applied to Al-(CO$_2$)$_x$ and Al-(N$_2$)$_x$. Attempts to extend these studies to Al-(H$_2$)$_x$ complexes or Li-R$_2$ complexes have been thusfar unsuccessful. High resolution photoelectron spectroscopy has been applied to the Al-Ar and Al-Kr complexes, and these are the only metal complexes to be studied with this technique in any laboratory, but attempts to extend these studies to other complexes have also been unsuccessful. Our efforts to make new metal dimers and new metal compound clusters have been far more productive. Both of these experiments are made possible by the development of new techniques for mixed metal and metal
composite sample preparation. Using this new methodology, we have been able to generate mixed clusters of lithium and magnesium, and we have measured the first spectroscopy for the diatomic LiMg. Samples have now been prepared to enable spectroscopic searches for AlMg, MgC, AlB, etc. The same kind of composite sample preparation has allowed the production and characterization of several new metal carbide cluster systems. We have measured the first ionization potentials for \( M_8C_{12} \) “met-car” clusters and compared these results to recent theoretical calculations. We have also produced bismuth and antimony oxides (both negative and positive ions), which exhibit striking magic number patterns.

ACCOMPLISHMENTS/NEW FINDINGS

Metal Dimers

The production and spectroscopy of metal dimers such as LiB, LiMg and AlB is difficult because these elements do not exist as compounds or alloys in readily available solid form. We have therefore designed and constructed a vapor deposition apparatus, using a metal oven source, to produce films of one metal component on the surface of a solid rod sample of the other component. This deposition apparatus has made it possible to produce rod samples of lithium on aluminum, lithium on magnesium, lithium on BN ceramic, etc. Laser vaporization of these samples penetrates through the thin surface film to the underlying metal, producing both components in the gas phase where mixed molecules can form.

The initial success of this methodology has resulted in the first spectroscopy of LiMg. To make this molecule, we vaporized a composite sample which had a thin film of lithium deposited
on a solid rod of magnesium. We have measured spectra for two electronic band systems, obtaining vibrational frequencies and extrapolated dissociation energies for the excited states. Isotope shifts in the vibronic levels make it possible to assign the electronic origins for these states. These states are easily correlated to the Li(3p)(2P) + Mg(1S) atomic asymptote, making it possible to determine the ground state dissociation energy for the molecule, which is 3400 cm\(^{-1}\). This value is in good agreement with theory. The low dissociation energy is understandable because the bonding results from the Li 2s\(^1\) + Mg 3s\(^2\) configuration, which produces a \(\sigma^2\sigma^*\) (\(^2\Sigma\)) ground state and a bond order of 1/2. The spectroscopic constants determined for LiMg are shown in the table below. LiMg (\(D_0=3434\) cm\(^{-1}\); 0.43 eV) is less strongly bound in its ground electronic state than Li\(_2\) (\(D_0=1.04\) eV), but much more strongly bound than Mg\(_2\) (\(D_0=0.05\) eV). It is difficult to form, but a reproducible spectrum can be obtained.

Table 1. Spectroscopic constants for LiMg. All units are cm\(^{-1}\).

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<th>(v_{00})</th>
<th>(\omega_e)</th>
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<tr>
<td>(X^2\Sigma)</td>
<td>-</td>
<td>191.8</td>
<td>3434</td>
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<tr>
<td>C</td>
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<tr>
<td>D</td>
<td>31,161</td>
<td>255.9</td>
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Metal Oxide Clusters

We are searching for interesting new metal compound systems which may produce stable clusters useful as precursors for ceramic materials preparation. This investigation includes metal oxides and metal carbides, etc. We have recently obtained interesting new "magic number" mass spectra for metal oxide clusters of antimony and bismuth in both the positive and negative ion modes of our mass spectrometer. The species \( \text{M}_3\text{O}_4^+ \), \( \text{M}_4\text{O}_5^+ \), \( \text{M}_5\text{O}_7^+ \), \( \text{M}_6\text{O}_8^+ \), \( \text{M}_7\text{O}_{10}^+ \), \( \text{M}_9\text{O}_{14}^+ \) and \( \text{M}_{11}\text{O}_{17}^+ \) are produced with especially enhanced abundance for both antimony and bismuth. Figure 1 shows the mass distributions of Bi/O cluster cations produced. 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. \( \text{M}_2\text{O}_5^- \)). 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. For many of these systems, we are able to build model cage structures which have fully satisfied valence for metal and oxygen. Some of these proposed structures are shown in Figure 2. We have contacted theoretical research groups to secure some additional justification for these proposed structures.

We have also studied these same metal oxide clusters with multiphoton ionization at 193 nm (ArF excimer laser), and the abundant cations produced by this process are the same as those produced when cations grow directly. We have mass selected these cations and photodissociated them at 355 nm, and the fragments produced are smaller cations which were themselves magic number species in the growth distribution. As an example, Figure 3 shows the photodissociation of
$\text{Bi}_7\text{O}_{10}^+$ at 355 nm. The fragment ions produced are $\text{Bi}_3\text{O}_7^+$ and $\text{Bi}_3\text{O}_4^+$, which are also evident in Figure 1 as magic number cations.

Metal Carbide Clusters

We have also made progress in the study of metal carbide clusters and in the production 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, 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 interesting, and they may be intrinsically stable, they cannot be formed by this plasma chemistry 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 employed our vapor deposition method, using metal films deposited on graphite rods, to produce metal-carbide samples without the presence of hydrogen. Vaporization of these samples produces the desired metal carbide clusters in many cases. 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 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 produce metal carbide clusters in the gas phase. We have found that each system requires a different metal film thickness for best cluster production. Depending on this variable, the metal carbide clusters produced may be rich in carbon, like the nickel system shown in the figure, or they may be rich in metal. We have not found any metal which does not produce carbide clusters. However, we have not yet found the dramatic magic number patterns for later transition or main group metal carbides like those observed for the early transition metals. Additional experiments to optimize cluster production by variation of the film thicknesses, and to explore photodissociation of these new systems are underway. We have used similar methods to produce metal silicide clusters from films deposited on a silicon rod.

In a final area of progress, we have continued the characterization of magic number metal carbides of the early transition metals, where the 8/12 M/C stoichiometry is produced with extraordinary abundance. We have used tunable ultraviolet lasers to obtain threshold photoionization of these species in the limit of extremely low laser power (to eliminate multiphoton effects). We find that Ti$_8$C$_{12}$ has an ionization potential of 4.9 eV, which seems to be an extremely low value for a closed shell system. V$_8$C$_{12}$, Zr$_8$C$_{12}$ and Nb$_8$C$_{12}$ all have ionization potentials greater than our highest tunable laser energy (5.7 eV). The low IP of Ti$_8$C$_{12}$ is consistent with the predictions of some theoretical studies, but the trend for the other metal carbides (all having a greater IP's than Ti$_8$C$_{12}$) is not consistent with the predictions of any theoretical study. This is the first direct measurement of a physical property of met-cars clusters which has been calculated by theory, and the discrepancy illustrates the difficulties of theory on such systems.
Figure 1.
PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH PROJECT

Faculty:
Professor Michael A. Duncan (one month summer salary)

Graduate Students:

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<tr>
<th>Student</th>
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<tr>
<td>Lori R. Brock</td>
<td>Ph.D. (rec'd 6/96)</td>
<td></td>
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<td>Kenneth R. Berry</td>
<td>Ph.D.</td>
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<td>Steve Pullins</td>
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<td>Michele France</td>
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<td>John Reddic</td>
<td>Ph.D.</td>
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<tr>
<td>Areatha Knight</td>
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Undergraduate Student:

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<tr>
<td>Jeff Tucker</td>
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<td>Jason Robinson</td>
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Postdoctoral Fellows:

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<tr>
<td>Dr. Chris Scurlock</td>
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<td>Dr. Andreas Stangassinger</td>
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PUBLICATIONS IN THIS FUNDING PERIOD


INTERACTIONS/TRANSITIONS

a) PRESENTATIONS

Invited Lectures Presented on this Research


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


**Poster and Contributed Presentations of this Research**


b) CONSULTATIVE AND ADVISORY FUNCTIONS

None

c) TRANSITIONS

Our measurements of the spectroscopy and dissociation energies of magnesium cation ion-molecule complexes have been used by researchers at the Air Force Philips Laboratory, Hanscom AFB, in their analysis of atmospheric chemistry of Mg$^+$. In particular, our demonstration that Mg$^+$-N$_2$ is a relatively stable molecule provides a possible explanation for anomalous low concentrations of Mg$^+$ in the ionosphere (W.J. McNeil, S.T. Lai and E. Murad, J. Geophys. Res. 101, 5251 (1996)).

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

None

HONORS/AWARDS

Appointment as University Research Professor, University of Georgia, May 1995.