A variety of weakly bound and/or metastable molecules have been investigated in the environment of a pulsed supersonic molecular beam. Experiments were attempted with little success for the production of metastable oxygen ring systems. Other experiments focused on metal ion and metal neutral complexes with small molecules or rare gas atoms. Spectroscopic studies were successful for magnesium ion complexes with the rare gases and with carbon dioxide, water, and nitrogen. Aluminum atom van der Waals complexes were studied with high resolution photoelectron spectroscopy. These studies obtained a variety of new data on metal condensation energetics and the structure of the initial phases of condensation.
PHOTOGENERATION AND CHARACTERIZATION
OF ENERGETIC MOLECULES
IN SUPersonic MOLECULAR BEAMS

AFOSR-91-0001

June 1994

Michael A. Duncan
Department of Chemistry
University of Georgia
Athens, GA 30602
INTRODUCTION

The goal of this project was to prepare and characterize weakly bound or metastable molecular complexes relevant for the understanding of prospective high energy propellant systems. Two classes of molecules were studied: 1) metastable oxygen ring system, and 2) weakly bound van der Waals or ion-molecule complexes containing light metals (Li, Al, Mg). Both of these classes of molecules are prepared and studied in supersonic molecular beam machines, and they are characterized with laser spectroscopy and time-of-flight mass spectroscopy.

OXYGEN RINGS

Oxygen ring systems were proposed by Schaefer and coworkers to exist as O₄, O₈, and O₁₂ metastable ring system analogous to similar sulfur ring systems. High level theoretical calculations indicated that these systems exist as local minima on their respective global energy surfaces, with substantial activation barriers toward decomposition to molecular oxygen. It was therefore the goal of our work to make these systems by condensation of "hot" oxygen plasmas so that these systems might be formed and then to measure their electronic spectra to prove that they exist in the desired metastable ring structures.

Figure 1 shows the mass spectrum obtained when oxygen is pulsed through a supersonic nozzle source and a plasma is ignited by focused laser excitation at 532 nm. As shown, charged Oₓ species are observed to be formed in this environment. However, from
the mass spectrum alone, it is impossible to distinguish between weakly bound ion-molecule complexes of the form \((\text{O}_2)^+\) and the desired covalent species such as \(\text{O}_4^+\) and \(\text{O}_8^+\). We had planned to pursue electronic spectroscopy on these species under the guidance of the Schaefer group. With our high resolution laser systems, searches for new electronic spectra are prohibitive in time unless the approximate wavelength region for the spectrum can be established in advance. However, the Schaefer group was not able to complete the calculations of excited electronic states for these systems. Therefore, we were not able to complete the spectroscopic characterization of the oxygen ring systems.

**LIGHT METAL COMPLEXES**

Weakly bound metal complexes are interesting as model systems with which to investigate the possibility of condensation of metal atoms in solid fuel systems. Calculations of the specific impulse of solid hydrogen/solid oxygen systems, for example, are found to be significantly increased upon the addition of metal atoms or metal dimers at roughly the 5% level. These metal-seeded fuel systems appear promising on energetic grounds, but questions remain about the possibility of producing these systems in usable quantities under reasonable conditions. The studies of metal complexes, in our lab and others, makes it possible to measure the interactions (binding energies, etc.) in a finite-sized system, and to evaluate the prospects for scaling up promising systems to larger scales. In the past funding period, we have focused on magnesium ion complexes and on neutral van der Waals complexes of aluminum.

During the past funding period, we have synthesized and studied several magnesium
ion complexes of the form $\text{Mg}^+\cdot\text{L}_x$, where $\text{L}$ is a small molecule ($\text{CO}_2$, $\text{H}_2\text{O}$, $\text{N}_2$, $\text{CH}_3\text{OH}$, etc.) or a rare gas atom ($\text{Ar}$, $\text{Kr}$, $\text{Xe}$). These complexes were produced in a specially designed laser vaporization cluster source which produced ionized metal atoms, rather than metal clusters (dimers, trimers, etc.), for condensation with added gases. This general class of systems had not been studied previously in any other labs, but theoretical calculations on these systems were beginning to appear when we first began our work. Various sizes of these metal ion complexes were studied by mass selected photodissociation spectroscopy in a specially designed reflectron time-of-flight mass spectrometer. Photodissociation studies as a function of energy provided information on the energetics of condensation and wavelength dependent photodissociation excitation spectra provided the absorption spectra of the complexes. Electronic transition energies and vibrationally resolved spectra were measured for the complexes $\text{Mg}^+\cdot\text{Ar}$, $\text{Mg}^+\cdot\text{Kr}$, $\text{Mg}^+\cdot\text{Xe}$, $\text{Mg}^+\cdot\text{CO}_2$, $\text{Mg}^+\cdot\text{H}_2\text{O}$ (and $\text{Mg}^+\cdot\text{D}_2\text{O}$), and $\text{Mg}^+\cdot\text{N}_2$. As an example, Figure 2 shows the photodissociation electronic spectrum of $\text{Mg}^+\cdot\text{Ar}$. The $\text{Mg}^+\cdot\text{H}_2\text{O}$ spectrum was measured with partial rotational resolution. The $\text{Mg}^+\cdot\text{CO}_2$ complex was determined to be linear, and the $\text{Mg}^+\cdot\text{H}_2\text{O}$ complex was determined to have $\text{C}_{2v}$ symmetry. These are the first, and still the only, polyatomic metal ion complexes for which structures have been determined. The spin-orbit interaction in the $^2\Pi_{1/2,3/2}$ excited state was investigated for the linear complexes formed with the rare gases and $\text{CO}_2$. Table 1 contains a summary of the spectroscopic constants and dissociation energies measured for these various magnesium ion complexes.

In a new development, we have applied a new form of high resolution photoelectron spectroscopy to the study of aluminum-rare gas neutral van der Waals complexes. For these studies, we employed the new techniques of *Mass-Analyzed Threshold Ionization* (MATT)
spectroscopy. The experiments in our lab on Al-Ar were the first ever to use MATI to study a metal cluster molecule. Figure 3 shows the MATI spectrum of Al-Ar, which yields the vibrational structure in the ground electronic state of the Al-Ar\(^+\) ion and also provides the vibrational fundamental for the ground electronic state of the neutral Al-Ar. We are developing MATI for applications to lithium complexes and for the study of metal dimers such as LiAl, LiMg, AlB, etc. These latter systems are also potential candidates for metal seeded fuel systems. The spectroscopic constants for Al-Ar are also given in Table 1.
<table>
<thead>
<tr>
<th>Complex</th>
<th>( \text{Mg}^+ - \text{L} ) Stretch (cm(^{-1}))</th>
<th>( D_{\text{e}}^* ) (kcal/mol)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}^+ - \text{Ar} )</td>
<td>272</td>
<td>3.37</td>
<td>Diatomic</td>
</tr>
<tr>
<td>( \text{Mg}^+ - \text{Kr} )</td>
<td>258</td>
<td>5.2</td>
<td>Diatomic</td>
</tr>
<tr>
<td>( \text{Mg}^+ - \text{Xe} )</td>
<td>258</td>
<td>11.7</td>
<td>Diatomic</td>
</tr>
<tr>
<td>( \text{Mg}^+ - \text{CO}_2 )</td>
<td>382</td>
<td>14.7</td>
<td>Linear</td>
</tr>
<tr>
<td>( \text{Mg}^+ - \text{H}_2\text{O} )</td>
<td>517</td>
<td>32.2</td>
<td>Linear</td>
</tr>
<tr>
<td>( \text{Mg}^+ - \text{N}_2 )</td>
<td>1137</td>
<td>3.03</td>
<td>Diatomic</td>
</tr>
<tr>
<td>( \text{Al}^+ - \text{Ar} )</td>
<td>67 (ground state)</td>
<td>2.81</td>
<td>Diatomic</td>
</tr>
</tbody>
</table>

Table 1. A comparison of the metal-ligand vibrational frequencies (excited state) and dissociation energies of magnesium and aluminum ion complexes.
Figure Captions

Figure 1. The mass distribution of oxygen cluster ions generated from a laser plasma.

Figure 2. The photodissociation excitation spectrum of Mg$^+$-Ar. The spectrum consists of a vibrational progression with each member doubled by the excited state spin-orbit splitting.

Figure 3. The MATI photoelectron spectrum of Al-Ar.
Oxygen Clusters

Figure 1.
Figure 2.
\[ \text{Al}^+ - \text{Ar}^{(1\Sigma^+)} \leftrightarrow \text{Al} - \text{Ar}^{(2\Pi_{1/2})} \]
Publications Resulting from this Research


Invited Lectures Presented on this Research


Poster and Contributed Presentations of this Research


