Spectroscopy at Metal Cluster Surfaces

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Research Scope and Objectives

The focus of our research program is the study of gas phase metal clusters to evaluate their potential to model fundamental interactions present on metal surfaces. To do this, we characterize the chemical bonding present between the component atoms in metal clusters as well as the bonding exhibited by "physisorption" on cluster surfaces. Electronic spectra, vibrational frequencies and bond dissociation energies are measured for both neutral and ionized clusters with a variety of laser/mass spectrometry techniques. We are particularly interested in bimetallic cluster systems, and how their properties compare to those of corresponding pure metal clusters.

Description of Research Effort

Our research program is composed of two main parts. In the first, metal-metal bonding interactions are probed through the study of bare metal clusters. Pure component metal clusters (Ag$_2$, Ag$_3$, etc.) or metal mixtures (e.g., Bi/Cr, Bi/Fe, Ag/Al, Ag/Li) are produced in molecular beam environments with a pulsed nozzle laser vaporization source. Resonant two-photon ionization spectroscopy (R2PI) is employed to obtain electronic spectroscopy of neutral clusters, while mass-selected photodissociation spectroscopy provides similar information for cluster ions. In the ion experiments, the energies at which dissociation occurs and the resulting mass spectrum of dissociation products provides metal-metal bond dissociation energies. Both experiments yield cluster electronic states, and in favorable cases, vibrational and rotational constants. These data elucidate the nature of metal-metal bonding in these systems.

The second focus of our research is on the weak bonding interactions exhibited by physisorption on metal cluster surfaces. Molecular beam techniques are used to synthesize weakly bound complexes containing a metal cluster with an adsorbed small molecule or rare gas atom. In neutral complexes, van der Waals, dipole-induced dipole, dipole-dipole, etc. interactions are studied, while ionized systems introduce the added dimension of charge-
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induced dipole, etc. forces. Again, electronic spectra with vibrational and sometimes rotational resolution are obtained, yielding vibrational frequencies and dissociation energies. These data are used to investigate metal-adsorbate bonding in finite-sized cluster systems.

Progress in the Present Funding Period

Resonant two-photon ionization electronic spectroscopy has been applied to several new bimetallic diatomic systems. New spectra were reported last year for Ag-K and Ag-Al. We have now obtained similar spectra for Ag-Li\(^1\) and Ag-Na. The silver-alkali systems provide the first examples of spectroscopy for any transition metal-alkali metal mixed dimers. The these dimers are particularly interesting because they have partial ionic character in the ground electronic state resulting from the large electronegativity difference between Ag and the alkalis. The electronic transitions observed are intense with a significant change in the bond distance between the ground and excited states, suggesting that these resonances may have charge transfer character. Extensive vibrational progressions are observed, making it possible to obtain the excited state dissociation energies. We believe that the study of these diatomics will be valuable for comparison to the bulk surfaces composed of alkali metal films on silver, which also have ionic bonding character.\(^2\) Ongoing experiments are using our new high resolution laser to measure rotationally resolved spectra (previous spectra had vibrational resolution only) for this mixed metal diatomics to obtain their bond distances.

In a new area, studies of bimetallic cluster photodissociation carried out over the last few years have been extended to include novel metal-carbon clusters. Castleman and coworkers have recently discovered a new class of clusters composed of early transition metals (e.g., Ti, V, Zr) and carbon.\(^3\) Cluster mass spectra produced from these metal-carbon mixtures exhibit intense "magic number" cluster peaks, reminiscent of those first seen for C\(_{60}\). These peaks occur at the precise stoichiometry of M\(_8\)C\(_{12}\) (e.g., Ti\(_8\)C\(_{12}\)). Castleman has designated these species as "metallo-carbohedrenes", or "met-cars", clusters. We have found that met-cars clusters are also formed for the middle transition metals (Fe, Cr, and Mo).\(^4\) We have also performed photodissociation experiments on all the M\(_8\)C\(_{12}\) cations containing both early and middle transition metals. These studies determine the pattern of bonding energies in these clusters. In other work, we have shown that a family of met-cars clusters larger than the 8/12 stoichiometry are also formed.\(^5\) The prominent mass peaks correspond to the M\(_{14}\)C\(_{13}\) cation species. This 14/13 cluster, and other larger species, turn out to have stoichiometries characteristic of face-centered cubic crystal structures. Surprisingly, these crystal fragments (e.g., the Ti\(_{14}\)C\(_{13}\)\(^+\) species, which has a 3x3x3 lattice structure) dissociate to form the magic number 8/12 cluster. It is interesting that these larger clusters containing early transition metals and carbon tend to form crystalline structures rather than metallo-fullerene caged species. In the current year, we have extended these studies to investigate the fragmentation of larger crystalline clusters\(^5\) and metal-carbon cages/crystals composed of niobium.\(^6\) The larger nanocrystal clusters dissociate by cleaving crystal planes - a kind of photochemistry not observed previously. Niobium is significantly different from other metal-carbon species in that it forms small crystallites (e.g., the cubic Nb\(_4\)C\(_4\)) in competition with the met-cars cages. We have also
carried out threshold photoionization studies of various met-cars clusters to measure their ionization potentials. To investigate the surface chemistry on met-cars clusters and on metal-carbon nanocrystals, we have completed construction of a new molecular beam machine. This machine includes a modified cluster source which makes it possible to grow clusters and then run them through a reaction chamber to adsorb various small molecule species on their surface. After preparation, photodissociation will be used to probe the nature of adsorbed species and their desorption energetics.

A final recent area is the spectroscopy of metal atom van der Waals complexes with rare gas atoms and small molecules. vibrationally resolved electronic spectra have been measured and analyzed for the new species In-N₂, Ag-Ar, Ag-Kr, Ag-Xe and Cu-Ar. New spectra have been measured but not yet analyzed for Cu-Kr, Cu-Xe and Cu-Ar₂. In each of these systems, the complex electronic states observed correlate to the metal atom 2P-2S resonance line. Extensive vibrational band progressions are measured, making it possible to fit the excited state potential and in turn to carry out an energetic cycle to derive the ground state dissociation energy. This information is especially interesting for the silver atom rare gas complexes, because we have previously determined dissociation energies for the rare gases bound to silver dimer. This is therefore the best characterized system to compare atom and cluster binding energies to the binding on bulk metal surfaces. The dissociation energies for these systems are shown in the table below, where it is evident that there is a significant increase in binding between the atom and the dimer, and that the dimer is already somewhat close to the binding on the Ag(111) surface. This data lends some credence to the idea that local binding interactions are important on surfaces and that cluster models of surfaces are useful constructs.

Table 1. The binding energies (cm⁻¹) for Ag-Rg and Ag₂-RG clusters and the comparison of these values to binding energies on Ag(111) surfaces.

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<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Ag₂</th>
<th>Ag(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>59</td>
<td>275</td>
<td>532</td>
</tr>
<tr>
<td>Kr</td>
<td>107</td>
<td>394</td>
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<td>Xe</td>
<td>235</td>
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References Cited


Papers Published on this Research in the Present Report Period


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Invited Lectures Presented on this Research


