**PHOTODISSOCIATION AND SPECTROSCOPY
OF
GAS PHASE BIMETALLIC CLUSTERS**

ANNUAL PROGRESS REPORT

**Dr. Michael A. Duncan
University of Georgia
Research Foundation
Athens, Georgia**

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Progress Report

PHOTODISSOCIATION AND SPECTROSCOPY OF GAS PHASE BIMETALLIC CLUSTERS

Michael A. Duncan

Department of Chemistry
University of Georgia
Athens, Georgia 30602

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 clusters as well as the bonding exhibited by adsorption 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 composed of main group-transition metal mixtures.

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. Main group-transition metal mixtures (e.g., Bi/Cr, Bi/Fe, Ag/Fe, Al/Cr) 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 energy levels.

The second focus of our research is on the weak bonding interactions exhibited by adsorption on metal cluster surfaces. Molecular beam techniques like those above are used to synthesize weakly bound complexes containing a metal cluster and a 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-induced dipole, etc. forces.

In both areas, the goal is to characterize the fundamental interactions present in single component metal clusters and then to measure the modified or new features introduced with a corresponding bimetallic.

Progress to Date

Small bimetallic cluster cations containing the metals Bi/Cr and Bi/Fe have been synthesized and subjected to mass-selected photodissociation at various ultraviolet wavelengths in a reflectron time-of-flight mass spectrometer system.¹ Photodissociation channels indicate that the heteronuclear bonding in these systems is comparable in strength to the respective homonuclear bonding interactions. Lower limits on the dissociation energies (D_0'') are obtained for the bimetallic dimers Bi-Fe (≥ 1.85 eV), $\text{Bi}^+ \text{-Fe}$ (≥ 1.85 eV), Bi-Cr (≥ 2.58 eV) and Bi-Cr^+ (≥ 2.06 eV). These are the first data available for main group-transition metal heteronuclear dimers. The bulk mixtures of these metals do not exist as stable solids, but the microscopic cluster particles can be synthesized and (as these studies show) they have significant covalent bonding.

Similar photodissociation studies have been performed on bimetallic cluster cations containing Sn/Bi and Pb/Sb mixtures.² Product channels in these systems are compared to those in the corresponding pure component clusters. Highly non-statistical stoichiometries are observed in the product branching ratios of the bimetallic systems. The branching ratios can be rationalized, and also *predicted* (qualitatively) when a simple electron counting rule is employed to determine which bimetallic systems are closed shelled molecules. The electron counting rule assumes that the bonding in these systems involves inert *s* orbitals, and occurs through both localized and delocalized *p* bonding.

These photodissociation experiments utilize a new reflectron time-of-flight mass spectrometer system. The design of this instrument and its application for photodissociation experiments have been developed in our laboratory. To fully characterize its performance, we have conducted various calibration tests and ion trajectory calculations. The details of these experiments and guidelines for operating this kind of instrument have been presented in a recent publication.³

Silver dimer van der Waals complexes have been produced with a series of rare gas atoms ($\text{Ag}_2\text{-Ar}$, $\text{Ag}_2\text{-Kr}$, $\text{Ag}_2\text{-Xe}$). R2PI electronic spectroscopy has been applied to these systems, yielding their vibrational frequencies and dissociation energies.^{4,5} Electronic spectra are observed to be red-shifted with respect to the $\text{Ag}_2 \text{B} \leftarrow \text{X}$ electronic transition. As shown in Table 1, the complete set of three vibrational frequencies in the excited state are obtained for each of these complexes. Extended progressions in the metal-rare gas stretching vibrational mode make it possible to model the excited state potential surfaces and to obtain the dissociation energies. Combination with the spectral red shift and the known origin of the Ag_2 electronic state provides the *ground state* dissociation energies for each complex. The dissociation energies obtained are within a factor of two of the desorption energies for these rare gases from the Ag(111) surface.

Table 1. Spectroscopic constants for $\text{Ag}_2\text{-Ar}$, $\text{Ag}_2\text{-Kr}$ and $\text{Ag}_2\text{-Xe}$ complexes. All entries are in cm^{-1} units. ω_1 is the Ag-Ag stretch, ω_2 is the RG bend and ω_3 is the RG stretch.

	$\text{Ag}_2\text{-Ar}$	$\text{Ag}_2\text{-Kr}$	$\text{Ag}_2\text{-Xe}$	$^{107,109}\text{Ag}_2$
ω_1'	156.3	157.7	165.3	151.3
ω_2'	28.3	27.9	25.7	-
ω_3'	73.9	72.6	79.9	-
D_0'	755	1205	2761	-
D_0''	275	394	1243	-

We have been working on an improved molecular beam source for the generation of both bimetallic and pure component metal clusters. This new source uses a pulsed hollow cathode discharge in a pulsed supersonic expansion. While other research groups have described electrical discharge cluster sources, our hollow cathode design provides improved metal sputtering yields, more stable shot-to-shot signals, and better cooling of the metal cluster species formed. The advantage of this kind of source in general is that it is far less expensive than a laser source while providing similar performance.

Future Research

Ongoing work and work planned for the upcoming year includes the photodissociation of silver clusters in mixtures with the transition metals chromium, iron and molybdenum. We also plan to study R2PI spectroscopy of silver dimer complexes with small molecules such as CO_2 , N_2 and H_2O . Bimetallic effects will be probed in similar studies of AgCu complexes. In heteronuclear dimers, the van der Waals forces we have already investigated will be modified because of the dipole moment.

Publications Resulting From This Work

1. T.G. Taylor, K.F. Willey, M.B. Bishop and M.A. Duncan, "Photodissociation of Mass-Selected Bi/Cr and Bi/Fe Bimetallic Clusters," *J. Phys. Chem.* **1990**, *94*, 8016.
2. T.G. Taylor, K.F. Willey and M.A. Duncan, "Photodissociation of Pb/Sb Bimetallic Clusters," in preparation.
3. D.S. Cornett, M. Peschke, K. LaiHing, P.Y. Cheng, K.F. Willey, and M.A. Duncan, "A Reflectron Time-of-Flight Mass Spectrometer for Laser Photodissociation," *Rev. Sci. Instrum.* **1992**, *63*, 2177.
4. K.F. Willey, P.Y. Cheng, C.S. Yeh, D.L. Robbins and M.A. Duncan, "Electronic Spectroscopy of Silver Dimer Rare Gas Complexes," *J. Chem. Phys.* **1991**, *95*, 6249.
5. D.L. Robbins, K.F. Willey, C.S. Yeh and M.A. Duncan, "Electronic Spectroscopy of Ag₂-Xe," *J. Phys. Chem.*, in press.
6. J.S. Pilgrim and M.A. Duncan, "Pulsed Hollow Cathode Electric Discharge Metal Cluster Source," in preparation.

Invited Lectures Presented on This Research

1. "Spectroscopy and Photochemistry of Mass-Selected Cluster Complexes," Physical Chemistry Seminar, University of Florida, April 4, 1991.
2. "Electronic Spectroscopy of Metal Dimer Rare Gas Complexes," *Symposium on Metal-Rare Gas Interactions*, National Meeting of the American Physical Society, Washington, DC, April 1991.
3. "Spectroscopy and Photochemistry in Clusters and Cluster Complexes", Physical Chemistry Seminar, University of Edinburgh, Scotland, September 1991.
4. "Spectroscopy at Metal Cluster Surfaces," *Symposium on Cluster Spectroscopy*, Southeast Regional Meeting of the American Chemical Society, Richmond, VA, November 1991.

Other Lectures and Contributed Papers on This Research

1. M.A. Duncan, "Spectroscopy of Rare Gas Adsorption on Metal Cluster Surfaces," *1992 DOE Surface Chemistry and Catalysis Contractor's Meeting*, Santa Monica, CA, March 1992.
2. D.L. Robbins, K.F. Willey, C.S. Yeh, J.S. Pilgrim, J.E. Salcido and M.A. Duncan, "Spectroscopy and Photochemistry of Metal Dimer Rare Gas Complexes," *XXth Informal Conference on Photochemistry*, Atlanta, GA, April 1992.
3. J.E. Pilgrim and M.A. Duncan, "A Pulsed Electrical Discharge Metal Cluster Source," *XXth Informal Conference on Photochemistry*, Atlanta, GA, April 1992.

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