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

**Progress Report For
1990-1991**

**University of Georgia Research Foundation, Inc.
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Progress ReportPhotodissociation and Spectroscopy
of Gas Phase Bimetallic Clusters .

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This project originated on September 15, 1990. Equipment acquisition and set-up occupied the initial month or so of activity, with experiments and analysis of results following soon thereafter.

The general goals of this research project are 1) to synthesize novel bimetallic clusters in the gas phase; 2) to characterize their geometry, electronic structure, and chemical bonding; and 3) to compare these heterogeneous systems to corresponding pure component clusters. Clusters are synthesized by pulsed laser vaporization of solid metal rods coincident with laser photolysis of volatile metal complexes (e.g., metal carbonyls). Two techniques are used to characterize cluster properties: resonant two-photon ionization spectroscopy (R2PI) of neutral clusters and laser photodissociation spectroscopy of cluster ions. The project focusses on the selected mixtures of iron, chromium, and molybdenum with bismuth, aluminum and silver to probe a variety of heterogeneous effects in transition metal-main group metal mixtures.

Two initial aspects of this work have been pursued in the first few months of the project. The first area focusses on weakly

bound metal cluster-rare gas complexes. Previous studies in our research group had observed vibrationally resolved R2PI spectra for the complex $\text{Ag}_2\text{-Ar}$. This is the first example of spectroscopy on a cluster "surface," where the fundamental interactions in "adsorption" can be characterized. To establish this system as a benchmark for comparison to corresponding bimetallic systems, we have pursued more expanded and detailed studies of its spectroscopy and energetics. This work includes modelling the potential surfaces for the ground and excited states of the argon complex, and performing new measurements on the related $\text{Ag}_2\text{-Kr}$ complex.

Vibrational frequencies for $\text{Ag}_2\text{-Kr}$ ($\omega_1=157.7$, $\omega_2=27.9$, $\omega_3=72.6$ cm^{-1}) are quite similar to those for $\text{Ag}_2\text{-Ar}$ ($\omega_1=156.3$, $\omega_2=28.3$, $\omega_3=73.9$ cm^{-1}), where ω_1 is the Ag-Ag stretch, ω_2 is the rare gas bend, and ω_3 is the rare gas stretch. The similarity of the rare gas mode frequencies arises from stronger binding (hence greater force constants) in the Kr complex, offset by the heavier mass of krypton. The excited state potentials in both systems are well described by a modified Lennard-Jones potential of the form:

$$U(R) = Ae^{-BR} - C_6/R^6$$

Binding energies in the both the excited state (980 and 1648 cm^{-1}) and ground state (500 and 837 cm^{-1}) are greater for the krypton complex. The trend in binding energies is predicted by the "Drude" model of van der Waals interactions, suggesting that there are no covalent interactions involved. The model of "physisorption" on a cluster surface is therefore a good one for these systems. The

greater binding energies for both complexes in their excited state is attributed to an order of magnitude increase in the Ag_2 polarizability in this state. Potential surface-fitting gives metal-rare gas bond distances of 4.18 and 4.09 Å for argon and krypton complexes in their excited states. Franck-Condon analysis yields ground state bond distances of 4.51 and 4.40 Å and rare gas stretching frequencies of 24 and 20 cm^{-1} for argon and krypton complexes.

In a second area of work, mass selected dissociation experiments are in progress on Bi/Cr and Bi/Fe bimetallic cluster cations. Preliminary work has established the dissociation energies of the bimetallic dimers to be: $D_0''(\text{BiFe}) \geq 1.85 \text{ eV}$; $D_0''(\text{Bi}^+-\text{Fe}) \geq 1.85 \text{ eV}$; $D_0''(\text{BiCr}) \geq 2.58 \text{ eV}$; and $D_0''(\text{Bi}-\text{Cr}^+) \geq 2.06 \text{ eV}$. During the course of this work, we also synthesized unusual metal ion-molecular complexes (e.g., $\text{Bi}^+[\text{Cr}(\text{CO})_6]$). Photodissociation of these species is also ongoing to probe unusual formation mechanisms for bimetallic systems.

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. 94, 8016 (1990).
2. 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., submitted.

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