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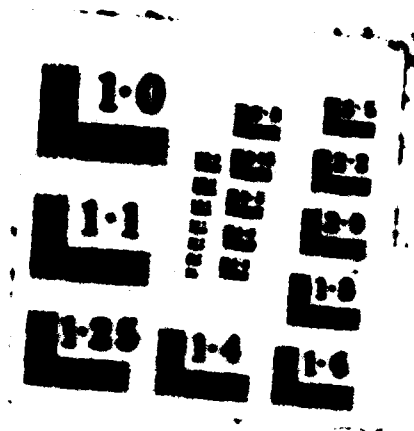
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Reactions of transition metal cluster ions are examined using guided ion beam techniques. These techniques allow ionic clusters of variable size and composition to be isolated. Measurement of reaction cross sections and branching ratios characterize the interactions of the clusters with a variety of neutral gases. By examining the variation of these quantities with the kinetic energy of the cluster ions, extensive thermochemical data for both ionic and neutral cluster species can be determined. Prototypical data for M_n^+ and Co_2^+ have been obtained. In addition, a new source of cold metal cluster ions (both bare and ligated) has been developed and demonstrated.

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Transition Metal Cluster Chemistry

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Statement of Problem Studied

The proposed research was to study the gas phase chemistry and thermodynamics of transition metal clusters using ion beam methods. Mass spectrometric techniques allow ionic clusters of variable size and composition to be isolated. Measurement of reaction cross sections and branching ratios characterize the interactions of the clusters with a variety of neutral gases. By examining the variation of these quantities with the kinetic energy of the cluster ions, extensive thermochemical data for both ionic and neutral cluster species can be determined. These data include metal-metal binding energies and binding energies of inorganic and organic fragments to clusters.

The proposed research was to be broken down into three phases. First, existing equipment and technology would be used to examine cluster chemistry. Second, a new cluster source and apparatus would be developed. This instrument would be capable of generating larger clusters of more metals and examining their chemistry. Finally, this apparatus would be used to greatly extend the scope of the proposed chemical studies.

Summary of Results

In the first phase of the proposed research, we have conducted comprehensive studies of the reactions of Mn_2^+ with O_2 , CO , CO_2 and C_2H_6 . In addition, reactions of atomic Mn^+ have also been performed for comparison. These are presently being prepared for publication. Also, we have generated Co_2^+ [from $Co_2(CO)_8$] and studied its chemistry in several systems. So far, preliminary studies of the reactions with Ar (collision induced dissociation), O_2 , D_2 , and C_2H_6 have been performed. Our studies show that the cobalt dimer ion is much more strongly bound than Mn_2^+ . This difference

clearly evidences itself in the resultant chemistry. Thus, this should be a nice diagnostic system for our new cluster source and apparatus. Results of our work on Mn_2^+ and Co_2^+ were reported in invited lectures at the 86 O-E LASE meeting of the Society of Photo-Optical Instrumentation Engineers (SPIE) and at a NATO Advanced Study Institute. The proceedings of these meetings have been published and are listed below (publications 1 and 3, respectively).

In the second phase of the proposed research, progress in development of a near continuous cluster ion source has been very good. Initially, quite a bit of effort was expended in characterizing and optimizing the performance of the mass spectrometer and ion optics which will mass separate the cluster ion beam and will eventually deliver it to the interaction region. We performed an initial test of the particle beam sputtering/supersonic expansion source as originally designed. These studies convinced us that substantially more pumping was needed in order to achieve sufficiently high stagnation pressures to induce cluster condensation. We therefore included a roots blower to enhance the pumping in the source region. A second potential source, a DC arc discharge, has also been evaluated and found to be rather unstable and prone to clog.

Meanwhile, our efforts concentrated on using a high repetition rate (6-8 kHz) Cu vapor laser (CVL) to vaporize the metal sample in the expansion. These efforts have been rewarded with success. Details of our initial work were reported in Chemical Physics Letters (publication 2 below). We have now demonstrated that by using the CVL to vaporize metal in a continuous flow of He, a near continuous source of metal cluster ions with sufficient intensities for chemical studies can be produced. Ion distributions up to 1000 amu have been examined for iron and aluminum and for

iron/oxygen mixtures. Most significantly, no separate ionization step is required. Sufficient ions are produced in the vaporization step that the ions cluster and undergo adiabatic expansion. Thus, the internal energy of the ions should be quite low, a necessity for many studies of interest. We feel this is really a very significant development for future studies of metal clusters.

Our main efforts near the end of the grant centered on improving the instrument designed for chemical studies of metal cluster ions. These improvements include the reconstruction of the ion source region to provide more substantial differential pumping. In our preliminary setup, this pumping was the limiting factor in determining the source pressure conditions in the supersonic nozzle. We have tested the present arrangement and find that it will enable us to exceed the previous maximum working pressure by over an order of magnitude. We have obtained a new copper vapor laser (Cooper LaserSonics Model 3051) having higher power than the model we used previously. These changes are designed to enable us to generate more ions and to enhance the cluster size available to us experimentally. We have recently demonstrated that these expectations are indeed realized.

The other improvement was the addition of a newly designed interaction region incorporating an octopole ion beam guide. This will enable us to control the reaction conditions much better and will provide substantially higher sensitivity. We have also added a new quadrupole mass filter from Extranuclear (purchased with funds from my NSF Presidential Young Investigator grant) which has a substantially higher mass range than previously available. Initial tests of these devices are now complete and their performance meets all our expectations.

We are now in a position to begin the third phase of the proposed research. This research will be conducted under U. S. Army Research Office Grant No. DAAL03-87-K-0122.

List of Publications

1. Transition Metal Cluster Ion Chemistry

P. B. Armentrout, "Laser Applications in Chemistry and Biophysics",
M. El-Sayed, Editor, Proc. SPIE 620, 38-45 (1986).

2. A Continuous Source for Production of Cold, Mass-Selected Transition
Metal Cluster Ions

S. K. Loh, David A. Hales, and P. B. Armentrout, Chem. Phys. Lett.
129, 527-532 (1986).

3. Kinetic Energy Dependence of Ion-Molecule Reactions: From Triatomics
to Transition Metals

P. B. Armentrout, "Structure/Reactivity and Thermochemistry of Ions",
P. Ausloos and S. G. Lias, Editors (D. Reidel, Dordrecht, 1987), 97-
164.

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