OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Contract No. N00014-86-K-0501

Synthesis and Characterization of Mixed Semiconductor-Transition Metal Clusters

Mark A. Johnson

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Johnson, Mark A.

PART I

A. Papers Submitted to Refereed Journals (and not yet published).


B. Papers Published in Refereed Journals


C. Sections Published


E. Technical Reports


H. Invited Talks


I. Contributed Presentations at Topical or Scientific Conferences


J. Honors, Awards, and Prizes

Presidential Young Investigator Award, 1987-1992
National Science Foundation (Feb. 1987)

Junior Faculty Fellowship
Yale University (1988-1989)

K. Number of Graduate Students Receiving ONR Support
None.

L. Number of Post docs Receiving ONR Support

One: 100%
Dr. Chau-Chung Han
Ph.D. Stanford University 1987
PART II

Principal Investigator: Mark A. Johnson, Assistant Professor
(203 432-5226)

ONR Scientific Officer: Dr. David L. Nelson (202-696-4409)

Project Description: Our primary objectives are to study the electronic and geometrical structures of mass selected cluster ions, with emphasis on clusters containing semiconductors, metals and mixed compositions. Our early efforts focussed on the use of ultraviolet photoelectron spectroscopy (UPS) of a mass selected negative ion beam to provide a low resolution diagnostic of the electronic band structure. In order to determine cluster geometries, we are expanding our techniques to include high resolution laser photofragmentation spectroscopy.

Significant Results in the Past Year:

Technique development:
In the past year, we have completed construction of a single-longitudinal mode pulsed dye laser and demonstrated its performance on the mass-selected ion beam using \( \text{NNO}^+ \) as a target ion. This system is state-of-the-art in terms of power and linewidth capabilities, which will be invaluable in unravelling the spectral congestion expected in the cluster systems. We have also been working on photoelectron spectroscopy on a technical level where we have developed a way to control the photon-energy resolution problem inherent in the pulsed PES technique which we developed at Yale.

Cluster Photophysics:
We have undertaken a series of experiments to understand why many cluster systems (e.g., \( \text{Ag}_n^- \), \( \text{C}_n^- \)) efficiently photodissociate when excited near their electron detachment thresholds. We have looked at the water and oxygen negative ions, where water physically stabilizes the electron in an otherwise closed shell system while oxygen has an open shell structure similar to metal systems. The water experiment is particularly enlightening since we were able to show that the photodissociation propensity is simply related to the excess kinetic energy of the electron after excitation, which was determined using photoelectron spectroscopy. Thus, intra-cluster electron-phonon scattering appears to mediate the ability of clusters to capture the excited electron before it leaves the cluster.

Internal energy control:
In yet another "first," we have succeeded in controlling the internal energy content of \( (\text{H}_2\text{O})_n^- \) clusters by varying conditions of the expansion. So far we have seen cooling in the ensemble on the order of one monomer bond energy.
Summary of Plans for next year: Since our contract expires on July 1, 1989, we summarize likely future directions for this research. It is now clear that optical excitation of negatively charged clusters is quite complex and not understood even in very simple systems. A particularly fruitful direction therefore appears to be a high resolution study of the near threshold region of clusters in which the charge is initially localized. An outstanding candidate for this study is the I⁻(O₂)n clusters. Here, we envision two complementary experiments to probe the electron scattering after excitation where the photofragmentation cross section and the photoelectron spectra are obtained as a function of excitation energy near the I⁻ photodetachment threshold. A particularly exciting prospect is the opportunity to directly observe scattering into the autodetaching levels of O₂⁻ solvent molecules. This type of photon energy-dependent probe can then be extended to the case of metals which are characterized by a delocalized electron.

G. STUDENTS AND POSTDOCS

Students:
Lynmarie A. Posey
Michael J. DeLuca
Paul J. Campagnola
Yu-Fong Yen
Donna Cyr

Post-doc:
Dr. Chau-Chung Han

PART III.

SEE ATTACHED SHEETS
PROBING THE "CONDUCTION BAND" OF CLUSTERS WITH OPTICAL SPECTROSCOPY

1. THE NEED FOR NEW DIAGNOSTICS

2. DETERMINE THE ELECTRON BINDING ENERGIES USING PHOTOEMISSION-
   SIZE SELECTION USING NEGATIVE ION PHOTOELECTRON SPECTROSCOPY

3. PHOTOEXCITE THE CLUSTER NEAR THE ELECTRON BINDING ENERGY

4. MONITOR THE BRANCHING BETWEEN PHOTODETACHMENT AND PHOTOFRAGMENTATION

5. LOOK FOR SIMPLE MODELS TO RECOVER BEHAVIOR OF BRANCHING RATIO USING ELECTRON-PHONON SCATTERING
CONCLUSIONS

1. PHOTOEXCITATION OF EXCESS ELECTRON IS CHANNELED INTO ELECTRON KINETIC ENERGY

2. CAPTURE OF THE ELECTRON IS MEDIATED BY INELASTIC SCATTERING SIMILAR TO THAT SEEN IN ELECTRON SCATTERING FROM SOLIDS

3. OTHER SYSTEMS STUDIED SO FAR WHICH INDICATE PHOTOEXCITATION OF THE ELECTRON OR HOLE INTO "CONDUCTING" STATES OF THE BULK:

\[ \text{Ar}^+_{n}, \text{Xe}^+_{n}, \text{(O}_2\text{)}^{-}, \text{I}^{-}(\text{O}_2\text{)}_{n}, \text{C}^{-}_{n} \]

4. RELEVANCE TO HETEROGENEOUS SYSTEMS:

   EXPLORE CHARGE LOCALIZATION IN MIXED SYSTEMS SUCH AS \([\text{O}_2\text{Ag}_n]^\text{−}\)
PART IIID.

In the design of materials at the atomic and molecular level, we are lead to explore the properties of a collection containing anywhere from a few to a few hundred atoms, as these clusters may provide the building blocks for materials with tailored properties. A major challenge facing experimentalists studying these microscopic systems is that, while ordered solids can be characterized by many highly developed techniques (LEED, Auger, photoemission, conductivity, optical spectroscopy, etc.) the cluster systems require either entirely new or highly adapted methodologies to define their behavior.

We have therefore undertaken the task of developing cluster diagnostics and have succeeded in demonstrating a gas phase analogue of photoemission, negative ion photoelectron spectroscopy, on cluster systems. The novelty of this technique is that clusters with precisely determined compositions can be systematically studied as a function of size and stoichiometry. We are now working on methods for probing the nature of the conducting states in the clusters by photoexciting an excess electron and monitoring the propensity of the cluster to capture the outgoing electron before it escapes the clusters. This method couples photoelectron spectroscopy with photofragmentation spectroscopy to get the best overall view of the excited state dynamics.

In the figure shown in part IIIC., we show the photoelectron spectrum (dashed line) and photofragmentation quantum yield (points) of the excess electron attached to water clusters, \((H_2O)_{25}^-\). The dashed line gives a map of the distribution of electron binding energies (taken by Kit Bowen at Johns Hopkins University), while the photofragmentation quantum yield provides a measure of the propensity of the photoexcited electron to escape. The solid line through the points is derived from a simple theory for the electron capture process where electrons photoexcited with less than 0.1 eV kinetic energy are captured with unity efficiency. Interestingly, this value of 0.1 eV is also the characteristic of the inelastic scattering of electrons off of solid water surfaces.

Future directions for this study include mixed metal/insulator systems such as oxygen adsorbed onto silver with an excess electron, \([O_2 Ag_m]^-\). Here we investigate the propensity of the system to localize the charge on the \(O_2\) moiety and again look for excitation into the conduction band of the material, this time presumably into the states associated with the silver component of the clusters. Since the negative ion channel seems to mediate vibrationally inelastic scattering of CO from surfaces, this study can also provide a direct probe of the nature of the adsorbate in the presence of the negative charge.

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In preparation for Publication

in

Review of Scientific Instruments

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Characterization of Mixed Clusters

Cluster ion photoelectron spectroscopy, electron optics, PES of mass-selected clusters.

Since its introduction in 1986, pulsed photoelectron spectroscopy of mass selected ion beams is rapidly becoming a central tool in the study of cluster ions, molecular ions with high electron affinities (≥3.5 eV) and even in the spectroscopy of the transition states of neutral chemical reactions. A traditional shortcoming of time-of-flight photoelectron spectroscopy when applied to negative ion beams is that the resolution, ΔE, is highly dependent on the electron energy as:

$$\Delta E \propto E^{3/2} \times \Delta t$$

where Δt is the pulse width of the laser. We present a simple electrostatic lensing scheme which manipulates the electron kinetic energies in order to access the highest resolution possible to the spectral region of interest. An unanticipated benefit of this approach is that very low energy electrons can also be collected, allowing PES to probe the region very close to the electron binding energy.
**Title**: Characterization of Mixed Clusters

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**MONITORING ORGANIZATION**: Chemistry Program

**Address**: 800 N. Quincy Street, Arlington, VA 22217

**TECHNICAL REPORT**: Technical Report #7

**No of Pages**: 88/7/25

**REPORT DATE**: 1988

**ABSTRACT**: We describe the performance of a pulsed spectrometer which ionizes ions using an ionized free jet, mass selects a particular m/e ion for interaction with a single-mode pulsed dye laser, and then analyzes the photofragments with a second mass spectrometer. Of particular interest is the result that the rotational cooling of the N$_2$O$^+$ ion achieved in the source can be maintained even after extraction through the unskimmed jet. Details of the amplification scheme used in the frequency locked, single mode, pulsed dye laser are also presented.

**Abstract Security Classification**: Unclassified

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**Procurement Instrument Identification Number**: N00014-86-K-0501
Wavelength Dependent Photofragmentation of Hydrated Electron Clusters, (H_2O)_n^−: A "Half-Collision" View of the Zero Energy Electron Capture Resonance

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Prepared for Publication
in
Journal of Chemical Physics

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**Characterization of Mixed Clusters**

**Abstract**

Photoexcitation of size-selected hydrated electron clusters, \((\text{H}_2\text{O})_n^-\), in the near IR results in a competition between photofragmentation and photodetachment. To investigate the origin of this competition, the decay probability into ionic fragments for the \(n=25\) cluster was measured as a function of photon energy from 0.91 to 3.49 eV. The photofragmentation probability increases rapidly with decreasing excitation energy in the general vicinity of the vertical electron binding energy of this clusters (1.3 eV) determined via photoelectron spectroscopy. This result suggests that fragmentation accompanies photoexcitation of the excess electron with near zero kinetic energy. Thus, photofragmentation appears to proceed through an optically prepared intermediate similar to that reached in electron scattering from neutral clusters which displays an enhanced dissociative attachment pathway with near zero kinetic energy electrons.
| FORM 1473, 63 APR | EDITION OF 1 JAN 73 IS OBSOLETE. | 19 |

**Title:** Characterization of Mixed Clusters

**Author:** Mark A. Johnson

**Technical Report Number:** Final Report

**Funding Organization:** Yale University

**Address:** 800 N. Quincy Street, Arlington, VA 22217

**Performing Organization:** Yale University

**Address:** Department of Chemistry, 225 Prospect Street, New Haven, CT 06511

**Monitoring Organization:** Chemistry Program

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**Purpose:** This document has been approved for public release and sale, distribution of this document is unlimited.

**Report Date:** 89/6/20

**Abstract:** See attached sheet.
OFFICE OF NAVAL RESEARCH
CONTRACT #N00014-86-K-0501
TECHNICAL REPORT #7

A Pulsed High Resolution Spectrometer for Mass Selected Ions

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In preparation for Publication

in

Review of Scientific Instruments

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In the design of materials, we are often faced with the problem that a desirable set of electrical or mechanical properties may be associated with a disordered or unstable stoichiometry of the system. The long standing problem of introducing Ohmic contacts onto GaAs is such an example where we seek a method of tailoring the junction with a partially diffused metal layer. We immediately ask the questions:

1. How do we determine the electronic properties of unstable, probably disordered systems?
2. How do these properties vary as the compositions are systematically varied?
3. How do we fabricate devices based upon these molecular-level building blocks?

In order to pursue the answers to these questions, we have initiated an avenue of research to explore the properties of atomic and molecular aggregates which are size selected using mass spectrometry and then analyzed using optical and photoelectron spectroscopies [technical report #1]. Thus, arbitrary compositions can be synthesized in a free jet expansion and interrogated directly in the gas phase. This methodology is sufficiently new that an entirely new class of species has only recently become amenable for study, creating a fertile ground for investigating the physical chemistry of heterogeneous systems at the atomic level [see technical reports #2 and #3].

The specific questions at the focus of our attention are the electronic structures and physical properties of cluster ions. In order to study the fundamental aspects of electrical conduction in these microscopic systems, we have chosen as a test case a system where only one electron is isolated in a sea of species which are polarizable but which have no available states
in which to propagate the electronic wavefunction. Such a system represents a kind of hydrogen atom for cluster research. The rare gas ions such as \((\text{Xe})_n^-\) would appear ideal for such a study; however, they are exceedingly difficult to prepare. We, therefore, presently content ourselves with the \((\text{H}_2\text{O})_n^-\) system as a prototype. We study this system using angle- and energy-resolved photoelectron spectroscopy, photofragmentation spectroscopy, and reaction chemistry [technical report #8]. We have, in fact, pioneered the development of a new technique, pulsed photoelectron spectroscopy of mass selected negative ions [technical report #1] to carry out this project.

Thus far in the water system we have determined the nature of the ground state electron configuration, the scattering events which occur upon photexcitation and the competition between evaporation of the electron (detachment) and a water monomer (fragmentation). We have extended these ideas to the carbon dioxide anion system, the rare gas cation systems \((\text{Xe}_n^+, \text{Ar}_n^+)\) with one extra hole instead of an electron, and finally, we begin to extend this work to systems to species with a high ground state degeneracy which characterizes metals and semiconductors where we have worked on oxygen [technical report #5] as well as on carbon \(C_n^-\) [technical report #4].
Technical reports


5. "Photofragmentation of (O2)n−, n=3,4: Direct determination of the O2−(v) vibrational distribution using pulsed photoelectron spectroscopy," C.-C. Han, Y.-F. Yen and M. A. Johnson.


Papers


Students participating in research:

Lynmarie A. Posey
Michael J. DeLuca
P. J. Campagnola
Yu-Fong Yen
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Donna Cyr

Postdocs:

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