Fourier transform ion cyclotron resonance (FTICR) mass spectrometry was used to obtain information about the reactivity and physical properties of gaseous cluster ions, and to develop various mass spectrometric surface and bulk analysis techniques. New values for electron affinities and ionization potentials of many different semiconductor clusters were determined. Ultra-high resolution glow discharge FTICR mass spectrometry was developed to better characterize solid materials.
Mass Spectrometric Studies of Clusters and Surfaces

by

Prof. John R. Eyler
Principal Investigator

Department of Chemistry
University of Florida
P.O. Box 117200
Gainesville, FL 32611-7200

August 29, 1994
Objective

The objective of the research carried out under this contract was to obtain information about the physical properties and reactivity of gaseous cluster ions, and to develop various mass spectrometric surface and bulk analysis techniques (such as laser desorption - LD - and glow discharge - GD). Better understanding of cluster ion properties and reactivity makes possible further development of this important form of matter for catalysis and synthesis of new materials. Improved mass spectrometric analysis of surface and bulk materials can enhance the design and synthesis of solid state materials with new superconducting properties and lead to much higher capabilities of solid state devices.

Approach

The work carried out under this grant utilized the unique capabilities of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry to trap ions and study their structures and reactivities, as well as to determine their masses.

Conclusions

The superior ability of FTICR to follow ion/molecule reactivity was used to determine rate coefficients and product distributions of metal and non-metal cluster ion reactions. Charge transfer reactions were used to determine the adiabatic ionization potentials (IP's) and electron affinities (EA's) of gas-phase clusters. New sources of metal cluster ions were explored, such as metal oxides and metal-containing solid materials. A two-laser infrared multiphoton dissociation technique was used to obtain infrared spectra of gaseous ions. Electrospray ion generation/injection was used to transfer multiply-charged metal clusters surrounded by a ligand shell from solution into the FTICR cell for determination of their reactivities and other properties. Glow discharge sources were coupled in two different ways to FTICR mass spectrometers to permit ultra-high mass resolution studies which allowed contaminants or isobaric interferences to be identified by separating their peaks in the mass spectrum from those of the sample of interest. The highest mass resolution ever attained in GD mass spectrometry was reported.
Publications/Patents/Presentations/Reports Under this Grant

Published Papers in Refereed Journals


Chapters Published


Most Significant Publications (marked with an * above)

The first of these, "Magic Number" Carbon Clusters: Ionization Potentials and Selective Reactivity," represented the first accurate determination of the ionization potential of C₆₀. Our work, done on laser-generated ions in the gas phase, was later verified by photoelectron spectroscopy on bulk quantities of C₆₀ after the facile synthesis of this important compound was reported by Huffman and Kratchmer.

The second publication, "High Mass Resolution Glow Discharge Mass Spectrometry using an External Ion Source FT-ICR Mass Spectrometer," was our demonstration of the highest mass resolution ever attained with a glow discharge source,
better by a factor of 20-50 than the existing commercial instruments.

The third publication, "Ion/Molecule Reactions of Metal and Semiconductor Clusters: Ionization Potentials and Electron Affinities," a chapter in the book *Advances in Metal and Semiconductor Clusters, Vol II: Cluster Reactions* (JAI Press Inc., Greenwich CT, 1994) summarizes almost all the significant results we have obtained on cluster species with ONR support.

**Patents**

None

**Invited Presentations**


"Ultrahigh Resolution Elemental Mass Spectrometry," invited seminar presented to the Chemistry Department, West Virginia University, Morgantown, WV, March 1994.


Submitted Presentations


Most Significant Presentation (marked with an * above)

The presentation at the Workshop on Gas Phase Ion Chemistry and Physics of Carbon Clusters in Berlin in March, 1994 allowed workers from around the world to gain familiarity with our results on carbon cluster IP's and EA's. In addition, some of our earlier studies were quoted in a number of other presentations. Many requests for reprints/preprints resulted from this presentation.

Technical Reports Published


Personnel Funded Under this Grant

Postdoctoral Associates

Dr. George Alameddin (part-time)
Dr. Christopher Barshick (part-time)
Dr. Mitchell Cheeseman (part-time)

Graduate Students

Mr. James Bruce
Mr. Kevin Goodner (summer)
Mr. Tom Hayes (summer)
Mr. Eric Milgram (summer)
Ms. Dil Peiris
Mr. Ragulan Ramanathan
Ms. Yar-Jing Yang

Undergraduates

None
Transitions Resulting from Research under this Grant

Fourier transform ion cyclotron resonance (FTICR) mass spectrometry has demonstrated the highest mass resolving power of any type of mass spectrometry. This is because mass measurement in this technique is directly related to frequency measurement, and frequency is a physical quantity which can be measured with extreme accuracy and precision. Very high mass resolving power is essential in many studies of ions generated by glow discharge (GD) and inductively coupled plasma (ICP) sources. Reliable determination of low levels of contaminants or dopants in a number of materials is often hampered by the presence of "interferants" - species (atomic or polyatomic) of the same nominal mass as that of the species of interest. As part of this ONR-funded research, we carried out collaborative experiments with Dr. Christopher M. Barshick of Oak Ridge National Laboratory and Dr. Clifford H. Watson of Bruker Instruments, Inc., in Billerica, Mass. These experiments demonstrated a mass resolving power of over 650,000 for glow discharge - generated ions, a value 25-50 times higher than that possible with currently available commercial instruments. For example, we demonstrated that $^{198}\text{Hg}^+$, and $^{198}\text{Pt}^+$, both nominally of mass 198, produced in a glow discharge source from a pressed pin of 10% PtO, 10% HgO and 80% Ag, can easily be resolved from each other. Potential applications of this approach in the analysis of semiconductor, alloy, and meteorite samples are numerous. The mass resolution demonstrated with this approach is more than sufficient for GD-FTICR analysis of the radioactive $^{238}\text{Pu}$ in the presence of much higher levels of $^{238}\text{U}$, of potential importance in hazardous waste remediation efforts.

Because of a significant potential for future sales, the glow discharge source developed by us and used in the collaborative research described above is now being offered commercially by Bruker Analytical Systems, Inc. as an optional ion source for their Fourier transform ion cyclotron resonance mass spectrometers.
FINANCIAL STATUS REPORT
(Short Form)

1. Federal Agency and Organizational Element
   United States Navy

2. Federal Grant or Other Identifying Number
   Assigned by Federal Agency
   N00014-87-J-1248

3. Recipient Organization (Name and Complete address, including ZIP code)
   University of Florida
   Contracts & Grants Fiscal Services
   P.O. Box 115650
   Gainesville, FL 32611-5650

4. Employer Identification Number
   1596001874C7

5. Recipient Account Number
   1606422-12

6. Final Report
   X Yes No
   X Cash Accrual

7. Basis
   III Cumulative

8. Funding / Grant Period (See Instructions)
   From: (Month, Day, Year) 07/01/87
   To: (Month, Day, Year) 05/31/94

9. Period Covered by this Report
   From: (Month, Day, Year) 10/01/90
   To: (Month, Day, Year) 05/31/94

10. Transactions:
    a. Total outlays 367,124.22
    b. Recipient share of outlays 0.00
    c. Federal share of outlays 367,124.22
    d. Total unliquidated obligations
    e. Recipient share of unliquidated obligations
    f. Federal share of unliquidated obligations
    g. Total Federal share
    h. Total funds authorized this funding period
    i. Unobligated balance of Federal funds

11. Indirect Expense
    a. Type of Rate
       Provisional X Predetermined Final Fixed
    b. Rate
       43%
       46%
       45%
    c. Base 8205,036.35
    d. Total Amount 990,620.05

12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.
    See Attached

13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purpose set forth in the award documents.

   Typed or Printed Name and Title
   Headley B. Taylor
   Accounting Coordinator

   Signature of Authorized Certifying Official

   Telephone (Area code, number and extension)
   (904) 392-1235

   Date Report Submitted
   August 15, 1994

   Address
   265-201

   Standard Form 269A (REV 4-88)
August 15, 1994

Summary of Overhead:

Agency: Navy N00014-87-J-1248  
UF#: 1606422-12

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DIRECT: $275,886.78  
IDC: $366,506.83
### FINANCIAL STATUS REPORT

#### 1. Federal Agency and Organizational Element
United States Navy

#### 2. Federal Grant or Other Identifying Number
Awarded by Federal Agency

#### 3. Recipient Organization (Name and Complete address, including ZIP code)
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Contracts & Grants Fiscal Services
P.O. Box 115650
Gainesville, FL 32611-5650

#### 4. Employer Identification Number
1596001874C7

#### 5. Recipient Account Number
1606422-12

#### 6. Final Report
X Yes No

#### 7. Basis
X Cash Accrual

#### 8. Funding / Grant Period (See Instructions)
From: (Month, Day, Year) 07/01/87
To: (Month, Day, Year) 10/01/90

#### 9. Period Covered by this Report
From: (Month, Day, Year) 05/31/94
To: (Month, Day, Year) 05/31/94

#### 10. Transactions:

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Typed or Printed Name and Title

Nedley B. Taylor
Accounting Coordinator

Signature of Authorized Certifying Official

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August 15, 1994

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Standard Form 269A (REV 4-85)
August 15, 1994

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Agency: Navy N00014-87-J-1248
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