OFFICE OF NAVAL RESEARCH

150-6660A

FINAL REPORT

FOR

N00014-88-K-0483

R&T CODE 412m008

6/1/88-12/31/90

Photoionized Cluster Beams
1) Inter- and Intramolecular Reactivity
2) Generation of Superconducting Thin Films

James F. Garvey

Department of Chemistry
Acheson Hall
State University of New York at Buffalo
Buffalo, NY
14214

May 1991

Accomplishments under ONR Contract

New Chemical Reactions within Clusters: For $(C_2H_2F_2)_n^+$, $(C_2H_4)_n^+$ and $[(CH_3)_2O]_n^+$ clusters, we have observed new ion-molecule reactions which do not occur in the gas phase. Both of these reaction mechanisms are rationalized in that the typically unstable intermediate, can exist in the stabilizing environment of the cluster on a long enough time scale for the reaction to proceed! *J.P.C.* **94**, *1619 (1990); J.A.C.S.* **112**, *3693 (1990); C.P. Lett.* **168**, *337 (1990); C & E News 4/30/90; Accts. of Chem Res.* **24**, *48 (1991).*

Cationic Polymerization within Clusters of Unsaturated Molecules: For clusters of $(C_2H_4)_n^+$, $(C_2H_2F_2)_n^+$ & $(C_3H_6)_n^+$ a series of sequential ion-molecule condensation reactions are observed within these clusters similar to the type of ionic polymerization one observes in condensed media. These reaction sequences terminate within the cluster to give stable cyclic molecular ions, identifiable by the observation of unique magic numbers in the mass spectrum. *C.P. Lett.* **168**, *337 (1990); J. Phys. Chem. invited paper, submitted (1991).*

Novel Photochemistry within Clusters of Metal Hexacarbonyls: A <u>new class</u> of chemical reactions were discovered which occur only within the confines of van der Waals clusters of metal hexacarbonyls, generating oxo and dioxo metal ions. The fact that this chemistry occurs with Mo and W, but not Cr is explained on the basis of orbital size and overlap. *JPC* **93**, *5906, (1989); J.Int.M.S.* **102**, *1 (1989).*

Ar Mediated Electron Impact Ionization within $Ar_n(CH_3OH)_m^+$ Clusters: Through measurements of appearance potentials, we observe that all Ar-methanol heterocluster ions have the same appearance potential of 11.5 eV. This suggests that the ionization process is not occurring a direct ionization of the methanol specie, but rather electronic excitation of the Ar atom to the metastable 4s state. Indirect ionization can then occurs via a Penning ionization mechanism. *J. Chem. Phys.* **94**, *1850 (1991).*

Multiply Charged Ammonia Clusters: These cluster ions consist of separate and distinct, singly charged ammonia cations, which react independently within the bulk ammonia cluster. That is, for the case of doubly charged ammonia clusters we see three stable forms, which correspond to one, both or neither of the two singly charged ammonia ions reacting with the bulk neutrals. *JPC* **93**, *4700 (1989); C.P. Lett.* **156**, *19 (1989); C.P. Lett.* **164**, *441 (1989).*

Anomalous Critical Size for 1,1-Difluoroethylene: Critical size for multiply charged clusters is defined as the smallest size for which the doubly charged cluster is observable. For the 30-some systems observed this size ranges from 99 for N_2 all the way down to 21 for SO_2. We have discovered that 1,1-difluoroethylene clusters exhibit a critical size of 9. Not only is this a new world record (two cations held together by 7 neutral molecules!) it suggests that this doubly charged cluster has a non-spherical structure (planes, chains or rings). *JCP* **91**, *1940 (1989).*

'Magic Numbers' for Ammonia Clusters: Observation of n=7 being especially prominent for $(NH_3)_nNH_2^+$ leads to the conclusion that NH_2^+ cation reacts with a neutral NH_3 to form a protonated hydrazine molecule. The magic number is explained 5 NH_3 molecules forming a full solvent shell around the $N_2H_5^+$ cation. Under cold expansion conditions these magic numbers disappear suggesting a phase transition within the cluster. *JCP* **91**, *6684 (1989); JCP,* **93**, *3725 (1990).*

LAMBE Source Generates Thin Films of Superconductors: Our 'Smalley-type source' is shown to be capable of generating high quality Cu thin films (as characterized by SEM, EDEX and ESCA work). By changing carrier gas in the source, we observe that the heavier the gas (He vs. H_2 vs. Ar vs. N_2) the slower the growth rate of the film presumably through reduction of the temperature of the plasma. By using O_2 as a carrier gas we generate 100% CuO, demonstrating that this source can be used to generate *in situ* high temperature molecules. That is, in the short duration of the laser pulse, the oxygen gas is completely dissociated and reacts with the evaporated Cu atoms forming a new molecule. By using the superconducting $Y_1Ba_2Cu_3O_7$ (123) compound as the target rod, under the appropriate expansion conditions we can generate films of the correct composition and morphology. *U.S. patent # 4,966,887 (1990); Mat. Res. Soc. Proc.,* **206**, *(1991).*

List of Current Group Workers

Dr. William R. Peifer	Post-Doctorate	B.S. & Ph.D, U. C. Davis
M. Todd Coolbaugh	Grad Student (Ph.D)	B.A., Alfred University
Gopal Vaidyanathan	Grad Student (Ph.D)	B.Sc., (tech), Ramnarain Ruia, College Univ. Dept. of Chemical Technology, Bombay India
William J. Herron	Grad Student (Ph.D)	B.S., Indiana Univ. of Pa.
Mike Lykety	Grad Student (Ph.D)	B.S., Utica College
Rob Wilson	Grad Student (Ph.D)	B.S., SUNY/Oswego
Stephine Gumina	Grad Student (M.S.)	B.A., State University College, Geneseo, NY

Past Group Graduates

Gopal Vaidyanathan	M.S., 1989	Thesis Title: Chemistry in Clusters

Outside Collaborators

Dr. Robert deLeon	Senior Scientist	Calspan, Buffalo, NY
Dr. Robb Grover	Senior Scientist	Brookhaven National Labs, Uptown, NY