- Final Report -

Structure and Dynamics in Metal-Containing Clusters

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13. ABSTRACT ***(Maximum 200 Words)***

Gas phase clusters were produced composed of a metal ion bound to one or more molecular "ligands" (e.g., water, nitrogen, acetylene, methanol, etc.). These gas phase complexes were studied with mass-selected laser photodissociation spectroscopy and laser photoelectron spectroscopy (ZEKE). These studies determine the structures and energetics of these clusters and they probe the dynamics of nascent solvation processes. Other metal clusters and metal-organic complexes were produced in the gas phase and evaluated for their potential for isolation in macroscopic quantities. Mass spectrometry and laser photodissociation measurements were employed for metal carbides, metal-C_{60} complexes and complexes of metal with polyaromatic hydrocarbons. These studies provide detailed experimental data which can be compared to theory to improve the overall understanding of metal-molecular interactions.

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OBJECTIVES

This project had two main goals: 1) the investigation of fundamental interactions present in weakly bound clusters containing metals and how these interactions influence the dynamics of "solvation"; and 2) the investigation of the structure and bonding in extremely stable metal-containing clusters, which may be useful as precursors for "cluster-assembled materials." In both lines of work, metal clusters are prepared in the gas phase via pulsed laser vaporization of solid targets. We used laser photoionization and laser photodissociation in conjunction with mass spectrometry measurements to characterize these clusters. The fundamental properties of these clusters were measured in the molecular beam environment, and the prospects were evaluated for macroscopic synthesis of cluster materials.

STATUS OF EFFORT

Gas phase experiments on various weakly bound and strongly bound clusters were conducted using three molecular beam machines and one newly constructed flow-tube reactor machine. One molecular beam machine focused on neutral cluster photoionization and was used to study metal van der Waals complexes. The other machines focused on ion cluster mass spectrometry and mass-selected photodissociation experiments. Additional gas phase experiments were conducted on a similar molecular beam machine constructed at the "FELIX" free electron laser together with the group of Gerard Meijer (University of Nijmegen) at the F.O.M. Institute for Plasma Physics in Nieuwegein, The Netherlands. A new flow-tube reactor instrument was constructed at Georgia and it is now employed for the stabilization and isolation of macroscopic amounts of cluster-based materials. Graduate, undergraduate students and postdoctoral researchers were trained in various aspects of physical and inorganic chemistry as they apply to the gas phase synthesis and characterization of unusual cluster molecules.

ACCOMPLISHMENTS/NEW FINDINGS

Metal Ion Complexes

Experiments on metal ion complexes measure the details of electrostatic interactions between metal ions and small molecules. There are two areas in which such interactions are important. Meteor ablation in the thermosphere produces neutral and ionized metal atoms of sodium, magnesium, aluminum, calcium, etc., and these species condense with and/or react with atmospheric gases. Fundamental information about the energetics of electrostatic interactions and the reactivity of these metals are used in Air Force models of atmospheric chemistry. In a second area, we explore the fundamental dynamics of metal solvation. In the gas phase, small metal complexes with solvent molecules necessarily contain singly charged metal. Although the normal charge states of many metals in solution is +2 or +3, such multiply charged species spontaneously undergo charge transfer in contact with limited numbers of neutral solvent molecules in the gas phase. Larger clusters, however, are eventually able to stabilize (i.e., “solvate”) multiply charged metal ions. However, the critical size required for solvation and the details of the energetics involved are not well understood. Our studies in the past three years have focused on single molecule complexes with metal ions, where more detailed pictures of the structures and energetics could be obtained.

Over the last several years, new spectroscopy has been measured for species such as Ca^+-N_2, Mg^+-methanol, Mg^+-C_2H_2, etc. Improvements in our laser vaporization cluster source have made it possible to produce some of the most weakly bound metal ion complexes ever detected. We have measured vibrationally and rotationally resolved spectroscopy for Mg^+-Ne and Ca^+-Ne. Table 1 shows some of the spectroscopic constants measured for these species. Both are bound by charge-induced dipole interactions, but there are dramatic differences in the bonding in different electronic states due to the interactions between the "ligand" (Ne) and the metal orbitals. In both complexes the ground state is $^2\Sigma$, while an excited state of $^2\Pi$ is probed near the excited ^2P state of the isolated metal ions. The bonding in the excited $^2\Pi$ states is much stronger than it is in the ground $^2\Sigma$ states because the p-π orbital orientation minimizes repulsive interactions. In the case of Ca, another excited state is detected near the excited metal ^2D state. A $^2\Sigma$ excited state is measured which has a metal *d* orbital oriented along the molecular axis. This configuration maximizes repulsion, and an extremely shallow potential bound by only 62 cm^{-1} results. In this $^2\Sigma$-$^2\Sigma$ band system, all the bound levels in the excited state are measured, providing a chance to test appropriate functional forms (Morse, electrostatic) with which to describe the potential.

Our experiments have also obtained the first spectra for isolated metal π-complexes which are able to confirm their structures. Vibrationally resolved spectra are obtained for Mg^+-C_2H_2 near the region predicted by theory and with the same vibrational frequency predicted by theory. However, the spectra obtained are broadened by predissociation. Spectra with more structure and more extensive vibrational activity are obtained for Ca^+-

C_2H_2 and Ca^+-C_2D_2. These spectra also contain enough partially resolved rotational structure to confirm that the hydrogen atoms are equivalent, which confirms the π-complex structure. Vibrational frequencies in the excited state are measured for the metal-acetylene stretch, the C-C stretch, the symmetric C-H stretch, and the cis-bend (D-C-C-D only). Binding energies are estimated to be about 18 kcal/mol. The spectroscopic constants for these ions are also listed in Table 1.

In a new experimental effort, we have completed construction and testing of a new configuration of our instrument for ZEKE photoelectron spectroscopy. ZEKE experiments provide a nice complement to our photodissociation experiments because they probe the previously uncharted *ground electronic states* of metal ion complexes. We have obtained new spectra with this equipment for the Al-(H_2O) and Al-(D_2O) complexes. These measurements begin with the neutral complexes, which are photoionized with one photon near 245 nm. The ionization potential (IP) for the neutral complex is determined, and a progression in the metal-ligand stretching mode is measured for the cation ground state. A thermochemical cycle using the IP, the known bond energy of Al^+-(H_2O) and the Al atomic IP produces a neutral bond energy of 1440 cm^{-1}. This is higher than expected for a van der Waals complex, but is consistent with the coordinate-covalent bonded complex predicted by theory. Rotationally resolved structure confirms that the cation complexes have C_{2v} symmetry, while the neutrals are non-planar. These structures are predicted by theory for the charge-dipole complex and coordinate-covalent bonded complex, respectively. The constants for the Al^+-water ground state are also given in Table 1.

Table 1. Spectroscopic constants for recently studied metal ion complexes. All units are cm^{-1}.

Complex	Electronic State	ω_e	D_0	Structure
Mg^+-Ne	$^2\Pi$	219	1696	diatomic
Ca^+-Ne	$^2\Pi$	135	900	diatomic
	$(2)^2\Sigma$	22	62	diatomic
Mg^+-C_2H_2	$^2B_1$	331	13,100	C_{2v}
Ca^+-C_2H_2	$^2B_1$	258	13,400	C_{2v}
Al^+-(H_2O)	X^1A_1	328	-	C_{2v}
Al^+-(D_2O)	X^1A_1	316	-	C_{2v}

Metal Carbide Clusters

Our research group performed extensive studies of transition metal carbide clusters (so-called "met-cars" and "nanocrystal" species) in the mid 1990's. In new work in this area, this PI went to Holland in May-June 1999 as a Visiting Research Professor at the University of Nijmegen. In a collaboration with Professor Gerard Meijer and his group, we built a new molecular beam/metal cluster experiment at the "FELIX" free electron laser facility at the F.O.M. Institute for Plasma Physics in Nieuwegein. The FELIX laser is the only free electron laser worldwide which is conveniently tunable. Free electron lasers provide infrared light in the 100-2000 cm^{-1} region where the low frequency vibrations of metal clusters are expected. Initial experiments produced spectacular results. Using the technique of infrared resonance-enhance multi-photon ionization (IR-REMPI), we were able to measure vibrational spectra for the met-cars species Ti_8C_{12} and V_8C_{12} and their ^{13}C substituted isotopomers. IR-REMPI is possible in these clusters because they are so strongly bound. Multiple photon absorption therefore leads eventually to ionization (known as "thermionic emission") rather than fragmentation. These represent the first spectroscopic data for the met-cars species other than low-resolution photoelectron spectra. Additionally, these experiments represent the first infrared spectra ever recorded for gas phase metal clusters.

Other spectra were also measured for the $Ti_{14}C_{13}$ and $V_{14}C_{13}$ "nanocrystal" clusters and for a collection of many larger but less prominent nanocrystal masses, including clusters of over 100 atoms in size. These spectra provide the first experimental insight into the structures of these clusters. The IR spectra of the met-cars species have a giant resonance near 1400 cm^{-1}, which is assigned to a C-C stretching mode. Theory has predicted the presence of C_2 moieties along the edges of these clusters, and this result confirms that C_2 groups are present. In the nanocrystal clusters, no high frequency vibrations are detected. Instead, resonances at 500 and 650 cm^{-1} are measured. Significantly, these occur at exactly the positions of the known surface phonon bands in bulk TiC and VC (measured previously with EELS). This observation confirms that these clusters have the crystal-fragment structures suggested previously. Surprisingly, the vibrational resonances in these metal-carbide nanocrystal clusters do not change significantly with cluster size. Clusters from the 3x3x3 crystallite (27 atoms) up to the 5x5x5 crystallite (125 atoms) all have the same prominent band at 500 cm^{-1}. However, the 650 cm^{-1} feature becomes much weaker in all clusters larger than the 3x3x3 crystallite. No other bands are seen in these species in the region of 400 to 1700 cm^{-1}. Theory on the 3x3x3 crystallite (Dance and coworkers) is in almost perfect agreement with this measured vibrational pattern. We interpret the absence of a size effect to mean that the vibration responsible is largely a surface mode which is mostly localized on individual M-C moieties.

Thus, as the crystallite size increases, the number of oscillators increases but the basic nature of the vibration remains constant.

A surprising development followed from this new spectroscopic study of titanium-carbide nanocrystals. A group of astronomers visited the FELIX lab and learned about the unusual IR spectra of these nanocrystals and their strong resonance at the wavelength of 500 cm^{-1} (=20.0 microns). They pointed out to us the strong similarity of this wavelength with an unassigned IR emission feature known for many years in the spectra of so-called "post-AGB" stars as the "21 micron line." The line was initially miscalibrated, and is now known to occur at 20.1 microns. We checked a composite spectrum of our nanocrystals against the astrophysical spectra, and found an exact match! This establishes that titanium-carbide nanocrystals are seeds present in the early phases of the formation of stardust. Titanium-carbide crystallites are actually expected to be present in these environments because TiC micron-sized crystallites are found in meteorites which come from these stars (e.g., the Murcheson meteorite). However, there was no previous laboratory measurement of the spectroscopy to establish that the IR emission was also from these metal-carbides. This work was published in *Science* in April, 2000, and news stories on it appeared in *Chemical and Engineering News* (April 17 issue) and in *Physics Today* (June 2000 issue).

Novel Metallo-Organic Clusters

In work begun in the last two years, we have developed methods to produce novel organometallic cluster complexes consisting of multiple metal atoms aggregated on the surface of large organic molecules. The species produced include metal-C_{60} and metal-polyaromatic hydrocarbon clusters. Photodissociation experiments on the mass-selected cations of these complexes probe their stability and structural patterns. For example, it is of interest to know if metal binds to the organic in the form of metal clusters or islands attached to the organic or whether metal atoms interact individually with the organic surface. Photodissociation shows that some metals (e.g., silver) are always eliminated as molecular units, suggesting a cluster-plus-cluster growth pattern. Other metals (e.g., iron on coronene) are always eliminated as atoms, suggesting that the interaction is atom-by-atom. In the case of most transition metals (chromium, vanadium, nickel on C_{60} or on coronene) there is a distribution of fragments including both atomic and molecular units of metal. In several cases, the fragmentation of species such as M_4-coronene$^+$ produces a substantial yield of M_4^+, suggesting that all the metal was bound on the same side of the organic. Many multi-metal/multi-organic clusters are also formed. In some cases these fragment exclusively to masses associated with sandwiches (M-(coronene)$_2$), multi-decker sandwiches (M_2-coronene$_3$) or multi-metal sandwiches (M_3-coronene$_2$). In some species (e.g., iron with C_{60} or niobium with coronene), the metal inserts into the organic ring system.

Unfortunately, these studies remain qualitative in nature. In work done in collaboration with Kaya and coworkers in Japan, we have obtained photoelectron spectroscopy for V_x-coronene clusters, which provide the first spectroscopy on these species. Experiments are planned to attempt the isolation of some of these complexes with our new flow reactor system. Other experiments planned will use an ion trap to study vibrational spectroscopy of these species with the free electron laser.

PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH THIS PROJECT

Faculty:

Professor Michael A. Duncan (one month summer salary)

Graduate Students:

Student	Degree Program	Social Security Number
Steve Pullins	Ph.D.	[redacted]
Michele France	M.S.	[redacted]
John Reddic	Ph.D.	[redacted]
John Buchanan	M.S.	[redacted]
Greg Grieves	Ph.D.	[redacted]
Jose Velasquez	Ph.D.	[redacted]

Undergraduate Student:

Matt Nee

Postdoctoral Fellows:

Dr. James Fye (Ph.D. 1998, Northwestern University)

Dr. Juergen Agreiter (Ph.D. 1998, Technical University of Munich, Germany)

PUBLICATIONS IN THIS FUNDING PERIOD

1. J.E. Reddic and M.A. Duncan, "Composite samples and the generation of new metal carbide clusters," *Chem. Phys. Lett.* **264**, 157 (1997).

2. M.A. Duncan, "Spectroscopy of metal ion complexes: Gas phase models for solvation," *Ann. Rev. Phys. Chem.* **48**, 63 (1997) (invited review).

3. M.A. Duncan, "Synthesis and characterization of metal-carbide clusters in the gas phase," *J. Cluster Sci.* **8**, 239-266 (1997) (invited review).

4. M.R. France, J.W. Buchanan, J.C. Robinson, S.H. Pullins, J.L. Tucker, R.B. King and M.A. Duncan, "Antimony and bismuth oxide clusters: A new family of magic number clusters," *J. Phys. Chem. A* **101**, 6214 (1997).

5. K.R. Berry and M.A. Duncan, "Photoionization spectroscopy of LiMg," *Chem. Phys. Lett.* **279**, 44 (1997).

6. S.H. Pullins, J.E. Reddic, M.R. France and M.A. Duncan, "Photodissociation spectroscopy of Ca^+-N_2," *J. Chem. Phys.* **108**, 2725 (1998).

7. M.R. France, S.H. Pullins and M.A. Duncan, "Spectroscopy of the Ca^+-acetylene π-complex," *J. Chem. Phys.* **108**, 7049 (1998).

8. J.W. Buchanan, J.E. Reddic, G.A. Grieves and M.A. Duncan, "Metal and Multi-Metal Complexes with Polyaromatic Hydrocarbons: Formation and Photodissociation of Fe_x-(Coronene)$_y$ Cations," *J. Phys. Chem. A* **102**, 6390 (1998).

9. K.N. Kirschner, B. Ma, J.P. Bowen and M.A. Duncan, "Theoretical Investigation of the Ca^+-N_2 and Ca^{2+}-N_2 Complexes," *Chem. Phys. Lett.* **295**, 204 (1998).

10. M.R. France, S.H. Pullins and M.A. Duncan, "Photodissociation Spectroscopy of Ca^+-C_2H_2 and Ca^+-C_2D_2 π-Complexes," *J. Chem. Phys.* **109**, 8842 (1998).

11. M.R. France, S.H. Pullins and M.A. Duncan, "Photodissociation of Mg^+-$(CH_3OH)_N$ Complexes: Evidence for the Onset of Solvation," *Chem. Phys.* **239**, 447 (1998).

12. J.W. Buchanan, G.A. Grieves, J.E. Reddic and M.A. Duncan, "Novel Mixed-Ligand Sandwich Complexes: Competitive Binding of Iron with Benzene, Coronene and C_{60}," *Intl. J. Mass Spectrom.* **182**, 323 (1999).

13. J.E. Reddic and M.A. Duncan, "Photodissociation Spectroscopy of the Mg^+-Ne Complex," *J. Chem. Phys.* **110**, 9948 (1999).

14. J.E. Reddic and M.A. Duncan, "Photodissociation spectroscopy of Mg^+-C_2H_2," *Chem. Phys. Lett.* **312**, 96 (1999).

15. J.K. Agreiter, A.M. Knight and M.A. Duncan, "ZEKE-PFI Spectroscopy of the Al-H_2O and Al-D_2O Complexes," *Chem. Phys. Lett.* **313**, 162 (1999).

16. D. van Heijnsbergen, G. von Helden, M.A. Duncan, A.J.A. van Roij and G. Meijer, "Vibrational Spectroscopy of Gas Phase Metal Carbide Clusters and Nanocrystals," *Phys. Rev. Lett.* **83**, 4983 (1999).

17. J.E. Reddic and M.A. Duncan, "Photodissociation Spectroscopy of Ca^+-Ne," *J. Chem. Phys.* **112**, 4974 (2000).

18. G. von Helden, A.G.G.M. Tielens, D. van Heijnsbergen, M.A. Duncan, S. Hony, L.B.F.M. Waters and G. Meijer, "Titanium Carbide Nanocrystals in Circumstellar Environments," *Science* **288**, 313 (2000).

INTERACTIONS/TRANSITIONS

a) PRESENTATIONS

Invited Lectures Presented by the PI on this Research

1. "Spectroscopy of Metal Ion Complexes," *Lake Arrowhead Ion Chemistry Conference*, Lake Arrowhead, CA, January 1997.

2. "Photoionization and Photodissociation of Metal Carbide and Metal Oxide Clusters," *Symposium on Metal Clusters*, National Meeting of the American Physical Society, Kansas City, March 1997.

3. "Spectroscopy of Gas Phase Clusters," *Departmental Colloquium*, Erskine College, April 1997.

4. "Photodissociation Spectroscopy of Gas Phase Clusters: From Solvated Metal Atoms to Nanocrystals," *Departmental Colloquium*, Johns Hopkins University, May 1997.

5. "Spectroscopy of Cation and van der Waals Complexes Containing Metal Atoms," *Symposium on Recent Advances in the Spectroscopy of Ions, Radicals and van der Waals Molecules*, Canadian Society of Chemistry Meeting, Windsor, Ontario, Canada, June 1997.

6. "Photodissociation Spectroscopy of Mass-Selected Metal Ion Complexes," University of Sussex, England, August 1997.

7. "Weak Bonding Interactions Probed Through the Spectroscopy of Metal Ion Complexes," *Physics Department Colloquium*, University of Georgia, November

1997.

8. "Photodissociation of Size Selected Metal Clusters in the Gas Phase," *Physical Chemistry Seminar*, University of California-Santa Barbara, January 1998.

9. "Spectroscopy and Dynamics In Novel Metal Containing Clusters," *Physical Chemistry Seminar*, University of Pennsylvania, February 1998.

10. "Spectroscopy and Dynamics In Novel Metal Containing Clusters," Air Force Geophysics Laboratory, Hanscom Air Force Base, March 1998.

11. "Spectroscopy and Dynamics In Novel Metal Containing Clusters," *Physical Chemistry Seminar*, Massachusetts Institute of Technology, March 1998.

12. "Structure and Bonding Patterns in Gas Phase Clusters Containing Metals," National Sun Yat-Sen University, Kaohsiung, Taiwan, R.O.C., April 1998.

13. "Structure and Bonding Patterns in Gas Phase Clusters Containing Metals," National Cheng Kung University, Tainan, Taiwan, R.O.C., April 1998.

14. "Spectroscopy and Dynamics in Novel Gas Phase Clusters Containing Metals," Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, R.O.C., April 1998.

15. "Spectroscopy and Dynamics in Novel Gas Phase Clusters Containing Metals," National Tsing Hua University, Hsinchu, Taiwan, R.O.C., April 1998.

16. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," University of Tokyo, Tokyo, Japan, October 1998.

17. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," Keio University, Hiyoshi, Yokohama, Japan, October 1998.

18. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," Institute for Molecular Science, Okazaki, Japan, October 1998.

19. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," Tohoku University, Sendai, Japan, October 1998.

20. "Spectroscopy and Dynamics In Novel Metal Containing Clusters," *Chemistry Department Colloquium*, University of Kentucky, December 1998.

21. "Photodissociation Spectroscopy of Novel Metal Ion Complexes," *Centennial National Meeting of the American Physical Society*, Atlanta, GA, March 1999.

22. "Photodissociation Spectroscopy and Dynamics in Novel Metal Containing Cluster

Complexes," Department of Atomic, Molecular and Laser Physics, University of Nijmegen, The Netherlands, May 1999.

23. "Photodissociation Spectroscopy of Novel Metal Ion Complexes," *XVIII International Symposium on Molecular Beams,* Ameland, The Netherlands, June 1999.

24. "IR-REMPI Spectroscopy of Gas Phase Metal Carbide Clusters and Nanocrystals," Symposium on *Metal Clusters: From Molecules to Nanocrystals*, Southeast Regional Meeting of the American Chemical Society, Knoxville, TN, October 1999.

25. "IR-REMPI Spectroscopy of Gas Phase Metal Carbide Clusters and Nanocrystals," *International Symposium on Cluster and Nanoparticle Interfaces*, Richmond, VA, October 1999.

26. "Photodissociation and Photoionization Spectroscopy of Gas Phase Metal Clusters," *Physical Chemistry Seminar,* University of Tennessee, Knoxville, November 1999.

27. "Synthesis and Characterization of Gas Phase Metal Clusters," *Chemistry/Physics Colloquium*, Berea College, Kentucky, November 1999.

28. "Spectroscopic Probes of Metal Cation Complexes," *International Symposium on the Interplay of Theory and Experiment in the Structural Analysis of Molecular Clusters*, Institute for Molecular Science, Okazaki, Japan, December 1999.

Poster and Contributed Presentations of this Research

1. J.E. Reddic, S.H. Pullins and M.A. Duncan, "Photodissociation Spectroscopy of Ca^+-N_2 Complexes," *International Symposium on Molecular Spectroscopy*, Columbus, OH, June 1997.

2. S.H. Pullins, J.E. Reddic, and M.A. Duncan, "Rotationally Resolved Photodissociation Spectroscopy of Ca^+-N_2 Complexes," *International Symposium on Molecular Spectroscopy*, Columbus, OH, June 1997.

3. M.A. Duncan, "Production and Characterization of Exohedral Metallo-Fullerenes in the Gas Phase," Gordon Research Conference on Clusters, Nanoparticles and Nanostructures, Plymouth, NH, July 1997.

4. M.A. Duncan, "Photodissociation Spectroscopy of Mass-Selected Metal Ion Complexes: Ca^+-N_2 and Ca^+-C_2H_2," *Gordon Research Conference on Molecular Electronic Spectroscopy*, Oxford, England, September 1997.

5. J.E. Reddic, J.C. Robinson, S.H. Pullins, G.A. Grieves and M.A. Duncan, "Production and Photodissociation of Exohedral Metal-C_{60} Complexes in the Gas Phase," *Gordon Research Conference on Molecular and Ionic Clusters*, Ventura,

CA, January 1998.

6. M.R. France, S.H. Pullins and M.A. Duncan, "Photodissociation Spectroscopy of the Ca^+-C_2H_2 π-Complex," *Gordon Research Conference on Molecular and Ionic Clusters*, Ventura, CA, January 1998.

7. M.R. France, S.H. Pullins and M.A. Duncan, "Photodissociation Spectroscopy of the Ca^+-C_2H_2 π-Complex," *International Symposium on Molecular Spectroscopy*, Columbus, OH, June 1998.

8. D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of C_{60} and Metal Carbide Clusters," *XVIII International Symposium on Molecular Beams,* Ameland Island, The Netherlands, June 1999.

9. J.E. Reddic and M.A. Duncan, "Photodissociation Spectroscopy of the Mg^+-Ne and Ca^+-Ne Complexes," *International Symposium on Molecular Spectroscopy*, Columbus, OH, June 1999.

10. D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of Ti_8C_{12}, Ti_8C_{11} and $Ti_{14}C_{13}$: Vibrational Spectroscopy of Size-Selected Metal Carbide Clusters," *Gordon Conference on Photoions, Photoionization and Photodetachment*, Plymouth State College, New Hampshire, July 1999.

11. J.K. Agreiter, A.M. Knight and M.A. Duncan "ZEKE-PFI Spectroscopy of the Al-H_2O Complex," *Gordon Conference on Photoions, Photoionization and Photodetachment*, Plymouth State College, New Hampshire, July 1999.

12. J.W. Buchanan, N.D. Flynn, G.A. Grieves, M. Nee and M.A. Duncan, "Photodissociation of Chromium-Coronene Cluster Cations," *Undergrad Research Symposium*, Southeast Regional Meeting of the American Chemical Society, Knoxville, TN, October 1999.

13. G.A. Grieves, J.W. Buchanan, N.D. Flynn, N. McKee and M.A. Duncan, "Production and Photodissociation of Exohedral Metal-C_{60} Complexes in the Gas Phase," *Symposium on Nanostructured Materials*, Georgia Institute of Technology, Atlanta, November 1999.

14. J.W. Buchanan, N. McKee, G.A. Grieves, M. Nee and M.A. Duncan, "Photodissociation of Chromium-Coronene Cluster Cations," *Symposium on Nanostructured Materials*, Georgia Institute of Technology, Atlanta, November 1999.

b) CONSULTATIVE AND ADVISORY FUNCTIONS

Professor Duncan visited the Air Force Geophysics Lab at Hanscom AFB in March of 1998 to consult with Air Force Scientists there (Murad, Dressler, Viggiano, etc.) and discuss topics of mutual interest.

c) TRANSITIONS

Transitions have been made to the general scientific community, including the academic, industrial, and military, through the development of two new software packages. These are: 1) Mass Spectrometry Isotope Distribution Modeler; and 2) Electronic Spectroscopy Franck-Condon Analysis. While programs of these general types have been previously available, the former versions were usually written for mainframe computers and were difficult, if not impossible, to implement on modern PC computers. The new programs we have written are in the Visual Basic language, which makes their implementation and use extremely convenient in the standard PC/Windows 95 environment. Input is in the form of pull-down menus, making these programs extremely user-friendly. The isotope program is a significant improvement over former such programs because it allows calculations of mass spectrometer isotope peaks for a chemical formula containing many elements, each with multiple isotopes. This feature is essential for mass spectrometry studies of such species as semiconductor nanoparticles or high molecular weight biopolymers. Both of these programs are presently available for distribution from our research group. Thermochemical data we obtained for the Ca^+-N_2 complex will be included in the atmospheric chemistry models used by Dr. Edmond Murad at the Air Force Geophysics Lab, Hanscom AFB.

News stories on our TiC nanocrystals in space article appeared in *Chemical and Engineering News* (April 17 issue) and in *Physics Today* (June 2000 issue).

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

The discovery of titanium carbide nanocrystals in post-AGB stars was a surprising new discovery which continues to excite the astrophysics community as this work becomes disseminated.

PI HONORS/AWARDS

Appointment as Senior Editor, Journal of Physical Chemistry, March 1998

Visiting Professor, National Science Council, Taiwan, R.O.C., April 1998

Yamada Foundation Visiting Professor, Keio University, Hiyoshi, Yokohama, Japan, October 1998

Visiting Professor, University of Nijmegen, The Netherlands, May-June 1999