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- Final Report -

Metal Solvation and Novel Metal-Ligand Interactions in Gas Phase Clusters

For the Period January 1, 2000 to December 31, 2002

AFOSR Contract No. F49620-00-1-0118

July 2003

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OBJECTIVES

This research program has two main goals: 1) the study of weakly bound clusters containing metals and how their bonding interactions influence the dynamics of "solvation"; and 2) the investigation of the structure and bonding in stable metal-containing clusters which may be useful as precursors for "cluster-assembled materials." In both of these related lines of work, metal-containing clusters are prepared in the gas phase via laser vaporization of solid targets. We use laser spectroscopy and mass spectrometry to measure the properties of these clusters, and comparisons are made to the predictions of theory to enhance the understanding of metal bonding interactions. Additionally, prospects are evaluated for macroscopic synthesis of cluster materials and synthesis experiments are attempted for promising candidates using a new laser vaporization flowtube apparatus.

STATUS OF EFFORT

Gas phase experiments on various weakly bound and strongly bound clusters are conducted using three pulsed molecular beam machines equipped with time-of-flight mass spectrometers located in our labs at the University of Georgia. Additional gas phase experiments are conducted on a similar molecular beam machine located 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. Graduate students, undergraduate students and postdoctoral researchers are trained in various aspects of physical and inorganic chemistry as they apply to the gas phase synthesis and characterization of unusual cluster molecules. During the past two years, we hosted one faculty member (Professor John Reddic, Coastal Carolina University) and one foreign graduate student (Deniz van Heijnsbergen, University of Nijmegen, The Netherlands) for collaborative research visits.

ACCOMPLISHMENTS/NEW FINDINGS

Metal Ion Complexes

Experiments on metal ion complexes investigate the details of electrostatic interactions between metal ions and small molecules. These weak interactions are important in metal ion atmospheric chemistry and in metal ion solvation. 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 the area of metal solvation, small metal ion complexes with solvent molecules are prepared in the gas phase and studied with mass spectrometry and laser spectroscopy. Although the normal charge states of many metals in solution is +2 or +3, such multiply charged species often spontaneously undergo charge transfer when they are in contact with limited numbers of neutral solvent molecules in the gas phase. Larger clusters, however, may be able eventually 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 work in the past employed *electronic* photodissociation spectroscopy of size-selected

complexes of Mg⁺ and Ca⁺ to investigate both atmospheric and solvation problems. Electronic spectroscopy is convenient for these ions because they have convenient atomic resonance lines $(^{2}P \leftarrow ^{2}S)$ and these same chromophores are active in weakly bound complexes. In new work begun three years ago, we have extended these studies to infrared photodissociation spectroscopy. The IR experiments have the advantage that they probe the ground electronic state and are therefore less susceptible to spectroscopic complications such as predissociation or photoinduced reactions. The ground state data are more easily compared to theory, which has serious difficulties in treating excited states. On the other hand, photodissociation processes with low energy IR photons were expected to suffer from problems due to the lower cross sections for IR absorption (compared to UV-VIS) and the lower photodissociation yields. The latter issue arises because the IR photons that excite ligand vibrational modes often have less energy than the metal ion-ligand binding. Onephoton IR dissociation is therefore not energetically possible in many clusters. However, our work over the last two years has shown that this problem does not preclude the measurement of IR photodissociation spectroscopy. We have found that IR absorption is rather highly efficient given the pulsed OPO/OPA laser source that we employ (Laser Vision OPO/OPA; tuning range: 2000 to 4500 cm⁻¹; pulse energy: up to 15 mJ/pulse near 3000 cm⁻¹), and multiphoton processes are reasonably efficient. We are therefore able to see resonance-enhanced multiphoton dissociation processes (i.e., IR-REMPD). We are also able to measure photodissociation with improved yields by producing mixed complexes with a rare gas atom such as argon attached to the cluster of interest. For example, to measure the spectrum of $Mg^+(CO_2)$, we make the complex $Mg^+(CO_2)Ar$. The argon atom is more weakly bound and when the cluster is excited into the asymmetric stretch vibration of CO₂ (near 2380 cm⁻¹ in the complex), intramolecular vibrational relaxation (IVR)

occurs, the cluster is heated internally, and the argon atom is ejected. This mass change provides the "action" needed to detect the spectrum via the fragment ion yield. We and other groups using this method call it "argon tagging," or, more generally, "rare-gas tagging." In many cases we are able to measure the spectrum of a specific complex both with and without tagging to verify that the presence of the argon does not perturb or shift the vibrational resonances. We find that the argon enhances the dissociation yield and that it also leads to the observation of sharper lines in the spectra. We have compared the spectra that we measure to those predicted by theory. We find that the IR-REMPD spectra have the same resonances and the same relative intensities as those predicted for the infrared absorption spectrum, thus validating this method.

During this project, we applied these infrared photodissociation spectroscopy measurements to obtain the first IR spectroscopy for $Mg^+(CO_2)_n$ and $AI^+(CO_2)_n$ complexes for n=1-14. Clusters such as these are possibly formed in the atmosphere after meteor ablation. In the small cluster sizes (n=1-3), these spectra were predicted by density functional theory done by Brinkman and Schaefer in our same department. While $Fe^+(CO_2)_n$ complexes were observed previously to form in symmetric structures with ligands surrounding a central metal (i.e., linear for n=2, trigonal planar for n=3, tetrahedral for n=4), the Mg^+ and AI^+ complexes were found by both experiment and theory to be asymmetric. Bent structures were found for the n=2 complexes, the n=3 complexes were pyramidal and after n=4, the CO₂ molecules were found to attach to other CO₂ and not to the metal. In other words, the metal ions in these clusters occupy an asymmetric surface site within a molecular cluster. This occurs for these metals because they have 3s valence electrons with high polarizabilities. When ligands attach to the metal, the valence electron density is initially polarized to the opposite side of the metal, and then this region of charge repels further addition of electronrich ligands (e.g., the negative end of CO_2). These studies, together with our other work on $Fe^+(CO_2)_n$ complexes, are the first that provide vibrational spectroscopy for multiple-ligand complexes. As such, they are also the first to probe the dynamics of cluster growth in such systems.

We have also continued our collaboration with the Dutch group of Gerard Meijer and coworkers in the area of infrared spectroscopy on clusters using a free electron laser. In the past, this laser was employed for studies of infrared resonance enhanced multiphoton ionization (IR-REMPI) spectroscopy of metal carbide and oxide clusters (see below). As a new area in the present period, we have explored the use of this laser for IR-REMPD experiments on mass-selected ionmolecule clusters. The free electron laser provides infrared light at lower frequencies than the OPO system in the 400-1700 cm⁻¹ region, so that lower frequency ligand vibrations can be studied. Although there is then even less energy per photon to accomplish photodissociation, the intensity of the free electron laser (up to 50 mJ/macro-pulse) is high enough so that multiphoton processes are much more efficient. Using this system and an ion-trap for mass selection, we were able for the first time to make transition metal ion-benzene complexes, e.g., V^+ -(benzene) and V^+ (benzene)₂ and to obtain their infrared spectra. We examined ring distortion vibrations and hydrogen bending vibrations that occur in this frequency region, and were able for the first time to compare the spectra of isolated cation sandwich complexes to those known for the neutral condensed phased metal dibenzene complexes. In the future, this IR-REMPD method will make it possible to compare the vibrational spectra and bonding in a variety of transition metal-benzene complexes and in transition metal complexes with other novel ligands (polycyclic aromatic hydrocarbons, fullerenes) that are of interest for potential new cluster-assembled materials.

Metal Carbide and Oxide Clusters

Our research group performed extensive studies of transition metal carbide clusters (socalled "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 (located just outside of Utrecht). The FELIX laser is the only free electron laser worldwide which is conveniently tunable in the far-infrared region of the spectrum. It provides 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} . 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 IR-REMPI 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 over 100 atoms in size. These spectra provide the first insight into the structures of these clusters.

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In a continuation of this work in the present funding period, we have applied the IR-REMPI method to study a number of metal oxide cluster systems including zirconium oxide, magnesium

oxide, titanium oxide and aluminum oxide. Vibrational spectra were obtained in these systems for clusters containing up to 300 atoms. In the zirconium system, we find evidence for ring structures that do not match up in their vibrational spectra to any of the known bulk phases of zirconium oxide. On the other hand, magnesium, aluminum and titanium oxide systems all have vibrations near those of the corresponding bulk surfaces analogous to known surface phonons. In the magnesium system there is a gradual size dependence in the spectra, but titanium and aluminum have resonances that essentially match those of the solids. In the aluminum, the spectra in the small cluster size match those for the α -alumina phase, while larger clusters seem to have amorphous structures.

In a final area of metal carbide work, we have studied the Ti_8C_{12} cations with IR resonanceenhanced multiphoton photodissociation (IR-REMPD) spectroscopy. We were then able to compare the vibrations of this cation to its corresponding neutral whose spectrum was measured with IR-REMPI. We found that both clusters have a strong resonance near 1400 cm⁻¹ that we assign to a C-C stretch. The cation had a slightly higher frequency than the neutral, consistent with bonding in a more rigid framework. This was expected based on molecular orbital pictures of the bonding in these two clusters. If the structure is the expected tetrahedral one, the neutral has at least two electrons in anti-bonding orbitals, and the cation therefore has less antibonding character.

Synthesis of Macroscopic Cluster Materials

As a new strategy toward cluster materials, we have constructed a laser vaporization flowtube reactor to produce macroscopic quantities of ligand-coated nanoparticles. This device employs the same kind of laser vaporization cluster source that we have used over the years in our

molecular beam research, and therefore it retains the capability for producing clusters out of highly refractory materials that is missing in most other methods used for cluster materials. These clusters are produced with a high power-high repetition rate excimer laser at 248 nm. This laser allows us to defocus the radiation incident on the metal target so that vaporization from a larger surface area spot is possible and the rep-rate (50-100 Hz) increases the duty cycle of cluster production. The clusters are produced in a 2 inch I.D. flowtube with a continuous flow of argon or helium as a thermalization medium. At the end of the flowtube, located 20-40 cm from the source, ligand and/or solvent species are injected into the gas flow via a simple vapor inlet or via a liquid nebulizer spray. Either method provides reactions that coat and stabilize the clusters, preventing their reactions with air or the solvent and providing solubility so that they can be collected and manipulated in solution. A trap consisting of a 500 mL round-bottom flask filled with ¼ inch diameter glass beads immersed in liquid nitrogen is located after the ligand/solvent injection, and this is where we collect clusters in solution. Runs of 30-60 minutes have been enough to collect 5-10 mL of cluster-containing solution.

The ultimate goal of these experiments is to isolate species such as the titanium carbide met-car or nanocrystal clusters. We therefore began experiments using titanium as the metal sample and ligands such as ethylenediamine (en) or tetrahydrofuran (THF). These experiments isolated various $Ti_x(en)_y$ and $Ti_xO_y(THF)_z$ clusters that had not been synthesized previously. The oxide species were demonstrated to result from a reaction of titanium with THF rather than by oxygen present in the background. We also found clusters of the form $(TiO_2)_n(THF)_m$, where n=10-15 and m=2-8. These experiments are quite promising and are the subject of continuing work in the new AFOSR grant that started in January 2003.

PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH THIS PROJECT

Faculty:

Professor Michael A. Duncan (one month summer salary each year)

Graduate Students:

Greg Grieves Angela Carroll Todd Jaeger Richard Walters Deniz van Heijnsbergen	Ph.D., 2000 Ph.D., 2003 M.S. program Ph.D. program Ph.D. program Ph.D., 2003 (visiting graduate student from the University of Nijmegen, The Netherlands)
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Postdoctoral Fellows:

Dr. Quan Li Dr. Nicholas Walker

PUBLICATIONS IN THIS FUNDING PERIOD

- J.E. Reddic and M.A. Duncan, "Photodissociation Spectroscopy of Ca⁺-Ne," J. Chem. Phys. 112, 4974 (2000).
- 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).
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- N.R. Foster, G.A. Grieves, J.W. Buchanan, N.D. Flynn and M.A. Duncan, "Growth and Photodissociation Cr_x-(Coronene)_y Complexes," J. Phys. Chem. A 104, 11055 (2000).
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- 8. N.R. Foster, J.W. Buchanan, N.D. Flynn and M.A. Duncan, "Ring Destruction and Carbide Formation in Niobium-PAH Complexes," *Chem. Phys. Lett.* **341**, 476 (2001).
- 9. J. Velasquez, K.N. Kirschner, J.E. Reddic and M.A. Duncan, "Ca⁺-Ar₂ Complexes: Linear or Bent?," *Chem. Phys. Lett.* **343**, 613 (2001).
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- G. Gregoire, N. Brinkman, H.F. Schaefer and M.A. Duncan, "Infrared Photodissociation Spectroscopy of Mg⁺-(CO₂)_n and Mg⁺-(CO₂)_nAr_m Complexes," J. Phys. Chem. A 107, 218 (2003).

INTERACTIONS/TRANSITIONS

a) **PRESENTATIONS**

Invited Lectures Presented by the PI on this Research

- 1. "Stable Metal Carbide Nanoclusters: Photochemistry, Spectroscopy and Astrochemistry," Departmental Colloquium, West Georgia College, Carrollton, GA, February 2000.
- 2. "Photodissociation Spectroscopy of Novel Metal Ion Complexes," Universite Paris-Sud, Orsay, France, April 2000.
- 3. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *Gordon Conference on Molecular and Ionic Clusters*, Toulouse, France, April 2000.
- 4. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *Gordon Conference on Multiphoton Processes*, New Hampshire, June 2000.
- 5. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," School of Physics, Georgia Institute of Technology, Atlanta, August 2000.

- 6. "Infrared Spectroscopy of Gas Phase Metal Clusters," *Physical Chemistry Seminar*, University of Utah, September 2000.
- 7. "Infrared Spectroscopy of Gas Phase Metal Clusters," Pacific Northwest National Lab, Environmental Molecular Sciences Center, September 2000.
- 8. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *Resonance Ionization Spectroscopy-2000*, Knoxville, TN, October 2000.
- 9. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *International Symposium on Small Particles and Inorganic Clusters* (ISSPIC-10), Atlanta, GA, October 2000.
- 10. "Stable Metal Carbide Nanoclusters: Photochemistry, Spectroscopy and Astrochemistry," *Physics Departmental Colloquium*, University of Georgia, November 2000.
- 11. "Metal Carbide Nanoclusters and Nanocrystals: From Georgia to Holland to the Stars," *Northeast Georgia Section of the American Chemical Society*, annual banquet speaker, Athens, GA, January 2001.
- 12. "Stable Metal Carbide Nanoclusters: Photochemistry, Spectroscopy and Astrochemistry," *Physical Chemistry Seminar*, University of North Carolina-Chapel Hill, February 2001.
- 13. "Spectroscopy of Metal Cation Complexes," Southeast Regional Meeting of the American Chemical Society (SERMACS), Savannah, GA, September 2001.
- "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide and Oxide Clusters," Southeast Regional Meeting of the American Chemical Society (SERMACS), Savannah, GA, September 2001.
- 15. "Infrared Photodissociation Spectroscopy of Transition Metal Cation Complexes," *East Tennessee Mass Spectrometry Discussion Group*, Oak Ridge, TN, October 2001.
- "Infrared Spectroscopy of Metal Containing Clusters: New Molecules and New Ways to Study Them," *Chemistry and Physics Colloquium*, Berea College, Berea, KY, October 2001.
- 17. "Infrared Spectroscopy of Metal Clusters and Metal Complexes," *Chemistry Department Colloquium*, University of Tennessee, February 2002.
- "Infrared Spectroscopy of Metal Carbide and Oxide Nanoclusters in the Gas Phase," James Franck Institute Colloquium, University of Chicago, February 2002.

- "Infrared Spectroscopy of Metal Nanoclusters in the Gas Phase," Georgia College and State University, February 2002.
- 20. "Infrared Spectroscopy at Metal Cluster Surfaces," *National Meeting of the American Physical Society*, Indianapolis, IN, March 2002.
- 21. "Infrared Spectroscopy of Metal Cation Complexes," *National Meeting of the American Chemical Society*, Orlando, FL, April 2002.
- 22. "Infrared Spectroscopy of Metal Carbide and Oxide Nanoclusters in the Gas Phase," *Physics Department Colloquium*, Georgia Institute of Technology, April 2002.
- 23. "Infrared Spectroscopy of Metal Clusters and Complexes," *Physical Chemistry Seminar*, Texas A&M University, May 2002.
- 24. "Infrared Photodissociation Spectroscopy of Metal Cation Complexes," *DAMOP 2002 Meeting of the American Physical Society*, Williamsburg, VA, May 2002.
- 25. "Infrared Photodissociation Spectroscopy of Metal Cation Complexes," *Laser Science XVIII Meeting of the American Physical Society*, Orlando, FL, October 2002.
- 26. "Infrared Spectroscopy of Metal Clusters and Complexes," *High Resolution Spectroscopy Meeting of the Royal Society of Chemistry*, University of Sussex, Brighton, UK, December 2002.

Poster and Contributed Presentations of this Research

- M.I. Nee, N.R. McKee and M.A. Duncan, "Production and characterization of novel silicon-metal clusters in the gas phase," 219th ACS National Meeting, San Francisco, CA, March 2000.
- D. van Heijnshergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of Ti₈C₁₂, Ti₈C₁₁ and Ti₁₄C₁₃: Vibrational Spectroscopy of Size-Selected Metal Carbide Clusters," *Gordon Conference on Molecular* and Ionic Clusters (MIC2000), Toulouse, France, April 2000.
- D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of Ti₈C₁₂, Ti₈C₁₁ and Ti₁₄C₁₃: Vibrational Spectroscopy of Size-Selected Metal Carbide Clusters," Air Force Office of Scientific Research, Contractor's Meeting, Boston, May 2000.
- 4. D. Van Heijnsbergen, G. Von Helden, A. Van Roij, G. Meijer and M.A. Duncan, "On the Structure of Metal Carbide Clusters and Nanocrystals," *International Symposium on Small Particles and Inorganic Clusters (ISSPIC X)*, Atlanta, GA, October 2000.

- G. Gregoire, J. Velasquez and M.A. Duncan, "Infrared Photodissociation Spectroscopy of Fe⁺-L_x Complexes", Gordon Research Conference on Gaseous Ions: Structures, Energetics and Reactions, Ventura, CA, February 2001.
- 6. G. Gregoire, J. Velasquez and M.A. Duncan, "Infrared Photodissociation Spectroscopy of Fe⁺-L_x Complexes", *Air Force Office of Scientific Research Contractor's Meeting*, Newport Beach, CA, May 2001.
- D. Van Heijnsbergen, G. Von Helden, A. Van Roij, G. Meijer and M.A. Duncan, "On the Structure of Metal Carbide Clusters and Nanocrystals," *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2001.
- 8. G. Gregoire, J. Velasquez and M.A. Duncan, "Infrared Photodissociation Spectroscopy of Transition Metal Cation Complexes," *Gordon Research Conference on Molecular and Ionic Clusters*, Ventura, CA, January 2002.
- D. Van Heijnsbergen, G. Von Helden, G. Meijer and M.A. Duncan, "IR-REMPI Spectroscopy of Metal Carbide and Oxide Nanoclusters," Gordon Research Conference on Molecular and Ionic Clusters, Ventura, CA, January 2002.
- G. von Helden, D. van Heijnsbergen, M.A. Duncan and G. Meijer, "IR-REMPI Spectroscopy of Metal Carbide and Oxide Nanoclusters," *National Meeting of the American Physical Society*, Indianapolis, IN, March 2002.
- M.A. Duncan, "Infrared Photodissociation Spectroscopy of Metal Ion Complexes," Molecular Dynamics Program Review, Air Force Office of Scientific Research, Waltham, MA, May 2002.
- M.A. Duncan, D. van Heijnsbergen, G. von Helden and G. Meijer, "Infrared Photodissociation Spectroscopy of Metal Ion-Benzene Complexes," *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2002.
- R.S. Walters, T. Jaeger, N. Brinkman, H.F. Schaefer and M.A. Duncan, "Infrared Resonance Enhanced Photodissociation Spectroscopy of Al⁺-(CO₂)_n and Al⁺-(CO₂)_nAr Clusters," *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2002.
- 14. G. Grieves, G. Gregoire and M.A. Duncan, "Infrared Photodissociation Spectroscopy of Metal-Water Complexes," *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2002.

b) CONSULTATIVE AND ADVISORY FUNCTIONS

none

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c) TRANSITIONS

none

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

none

PI HONORS/AWARDS

Elected Fellow of the American Physical Society, 2001