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Architecture and Surface Chemistry of Compound Nanoclusters

Michael A. Duncan
University of Georgia Research
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Fundamental studies are conducted on metal atom and oxide nanoparticles to develop new synthetic strategies, to elucidate electronic structure and bonding principles, and to evaluate these materials for applications relevant to the Air Force. Transition metal and main group metal oxide clusters are produced in the gas phase with laser vaporization of solid targets. Molecular beam and mass spectrometry studies on size-selected ions include laser photodissociation measurements to reveal stability patterns and infrared spectroscopy to determine structures and reveal ligand/adsorbate interactions. CO and CO2 ligands are the focus of this latter work. In other related work, clusters produced initially in the gas phase are ligand-coated and isolated in solution. This new synthetic process allows ultra-small metal particles to be produced for the first time. Vanadium oxide, chromium oxide and cobalt oxide systems in the 5-25 atom size range coated with THF or acetonitrile ligands have been isolated and characterized.

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Michael A. Duncan

Department of Chemistry, University of Georgia, Athens, GA 30602-2556

maduncan@uga.edu
www.arches.uga.edu/~maduncan

Abstract

Fundamental studies are conducted on metal atom and oxide nanoparticles to develop new synthetic strategies, to elucidate electronic structure and bonding principles, and to evaluate these materials for applications relevant to the Air Force. Transition metal and main group metal oxide clusters are produced in the gas phase with laser vaporization of solid targets. Molecular beam and mass spectrometry studies on size-selected ions include laser photodissociation measurements to reveal stability patterns and infrared spectroscopy to determine structures and reveal ligand/adsorbate interactions. CO and CO_2 ligands are the focus of this latter work. In other related work, clusters produced initially in the gas phase are ligand-coated and isolated in solution. This new synthetic process allows ultra-small metal particles to be produced for the first time. Vanadium oxide, chromium oxide and cobalt oxide systems in the 5-25 atom size range coated with THF or acetonitrile ligands have been isolated and characterized.

Objectives

The goal of this research program is to investigate the structure and bonding in stable metal-containing clusters which may be useful as precursors for "cluster-assembled materials," and to investigate the mechanisms of small molecule adsorption on metal clusters to elucidate the mechanism of "nanocatalysis." Nanoparticles containing metals may provide new catalysts with enhanced selectivity or synthetic routes to improved ceramic materials. The enabling technology for potential new applications is the controlled synthesis of desired nanoparticles with favorable composition and stability. Our research project explores new ways to make nanoparticles with new compositions and new experiments with which to characterize their properties. In this work, metal-containing clusters in the size range of up to 50-100 atoms are prepared in the gas phase via laser vaporization of solid targets. We focus on metal oxide species, which have many known applications in catalysis. 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. Prospects are evaluated for macroscopic synthesis of cluster materials, and new synthetic experiments employing ligand-coating strategies have been initiated using a “laser ablation flowtube reactor.”

Status of Effort

Gas phase experiments using laser photodissociation and laser spectroscopy were conducted on various metal-containing clusters using pulsed molecular beam machines coupled with time-of-flight mass spectrometers. These experiments explored the new kinds of nanocluster materials that can be produced and investigated their structures and stabilities. Synthesis experiments that isolate ligand-coated nanoclusters in solution were conducted using a new laser ablation flowtube reactor. Graduate, undergraduate, and postdoctoral students were trained in various aspects of physical and inorganic chemistry as they apply to the gas phase synthesis and characterization of unusual nanocluster molecules.

Accomplishments/New Findings

Research in this project over the last three years has focused on three main areas: 1) production and photodissociation studies of metal oxide clusters; 2) infrared spectroscopy of metal carbonyl complexes and 3) the development of new technology (laser vaporization flowtube reactor) for the production and isolation of ligand-coated nanoclusters. Significant progress has been made in each of these areas.

Metal Oxide Clusters

Over the last several years, we have investigated many examples of transition metal oxide clusters produced in molecular beams and studied with mass spectrometry and laser photodissociation measurements. Clusters of the form $M_nO_m^+$ for transition metals (V, Nb, Ta, Fe, Cr, Y, La) were studied the bonding patterns in these systems with mass spectrometry, mass-selected laser photodissociation and density functional theory calculations.

Mass-selected laser photodissociation experiments reveal the patterns in cluster growth. These patterns are almost identical for the V, Nb and Ta oxide clusters. Clusters with excess oxygen fragment by elimination of oxygen only (sometimes atoms, sometimes O_2). Smaller clusters with the same number of metal atoms but fewer oxygen atoms exhibit a stable core that does not eliminate more oxygen. Instead, these clusters are difficult to dissociate at all, and when they do fragment, they eliminate metal-containing oxide species, in a process analogous to fission. The same clusters identified as core species in oxygen stripping experiments are also produced as fragments when larger clusters dissociate. For example, oxygen stripping identifies MO_2^+, $M_2O_4^+$, $M_3O_7^+$, $M_4O_9^+$, $M_5O_{12}^+$ and $M_7O_{17}^+$ species as the core oxides at each of these metal sizes; dissociation of $M_7O_{17}^+$ produces $M_4O_9^+$, $M_3O_7^+$, etc. as fragments. The stable core oxides at each metal increment are the same for V, Nb and Ta. Significantly, these core oxide are not the most abundant species in the initial mass spectrum, and they were not identified by earlier experiments on the photoionization of the neutral clusters. The stoichiometries that occur throughout these clusters indicate that the average metal oxidation state is greater than it is in the common solid oxide compounds.

Chromium oxide clusters exhibit patterns similar to clusters in the vanadium group. However, there is a strong indication for a magic number at the $Cr_4O_{10}^+$ cluster. This cluster is more abundant in the initial mass spectrum produced by the cluster source, and it is also prominent as a fragment from several larger clusters. On the other hand, iron oxides have stoichiometries and fragmentation patterns that are quite different. These clusters grow with excess oxygen beyond the 1:1 stoichiometry, except at small sizes where the $Fe_2O_2^+$ and $Fe_3O_3^+$ species are prominent. The $Fe_3O_3^+$ cluster has been suggested by Khanna to have a six-membered ring structure. However, fragmentation strongly prefers the formation of species with 1:1 M:O ratios, thus indicating a preference for the +2 oxidation state rather than the more common +3 state found for solid iron oxides. In the yttrium and lanthanum oxide systems, we investigated metals that have an especially strong tendency to form the +3 oxidation state. In these two oxide cluster systems, stoichiometries in the gas phase systems also indicated that the +3 oxidation state is preferred.

In work done over the most recent funding period, we extended these measurements to the oxide clusters of indium, nickel and cobalt. The stable indium oxide clusters identified were the In_2O^+ and In_3O^+ cations and the In_2O_2 neutral. In the cobalt and nickel systems, there was no strong preference for any particularly stable clusters, but the species formed for cobalt usually had the 1:1 stoichiometry. For nickel, the stoichiometry revealed in the fragmentation patterns was $Ni_xO_{x-1}^+$, i.e., the ratio of metal-to-oxygen was close to 1:1, but was slightly metal rich. Theory on these late transition metal oxide species was extremely challenging. We used density functional theory (DFT/B3LYP or DFT/BP86) to examine the Co_4O_4 cluster, since this species has been identified as a possible ingredient in water-splitting catalysis. Depending on the level of theory employed and the basis set, we found either cyclic or cubic structures to be more stable. Because of issues with spin states and the variation with methods, we initiated a collaboration with the group of Don Truhlar at Minnesota. He used his M06-L version of density functional theory and found (in agreement with our DFT/BP86 result) that Co_4O_4 is more stable in a ring structure than it is in the more commonly viewed cubic structure. Much work remains to understand these late transition metal oxides.

Infrared Spectroscopy of Metal Carbonyl Complexes

Infrared spectroscopy is a well-established method with which to probe the structure of molecular species in a variety of chemical situations, especially on the surfaces of metal or metal oxide catalysts. To investigate metal-adsorbate interactions on small model systems relevant for the study of nanocatalysis, we have focused on metal carbonyl complexes in the gas phase. We study cation species, which we can mass-select and probe with tunable laser photodissociation spectroscopy. These experiments are only possible because of our efficient sources for making gas phase clusters, and the newly available infrared optical parametric oscillator laser systems that now provide IR light across the 700-4500 cm^{-1} range. We have measured infrared spectroscopy for these systems in the carbonyl stretching region near 2200 cm^{-1}. Photodissociation channels, and the shifts of C-O stretching vibrations, compared to the predictions of DFT theory, make it possible to determine the coordination number for these systems (CN), their electronic spin states, and their structures.

In the past, we studied open-shell transition metal systems for Cr, V, Nb, Ta and Mn and the noble metals Ag, Au and Pt. The C–O stretches for these cation species are generally shifted to the red like those found for the corresponding neutrals, although the cation shifts are smaller. Gold and platinum exhibit unusual blue-shifted C–O stretches. We find CN values of 6 for Mn^+ , 5 for Co^+, 2 for Au^+, and 4 for Ag^+ and Pt^+. The CN values for Co^+ and Mn^+ are expected based on the 18 electron rule. In new work, we have examined the cation-carbonyls of V^+, Nb^+ and Ta^+, where the 18-electron rule predicts CN=7. However, we find that V^+ produces only a six-carbonyl complex under our conditions. Nb^+ produces both a six-coordinate and a seven-coordinate complex, while Ta^+ produces only the seven-coordinate species. Apparently the unusual seven-coordinate species is only possible for the larger metal ions.

In other new carbonyl species, we have studied copper cation carbonyls, which form a four-coordinate complex isoelectronic and iso-structural with the known neutral $Ni(CO)_4$. However, unlike the nickel complex, the copper systems have blue-shifted CO stretches, like the behavior seen previously for gold. Silicon cation produces a very unusual two-coordinate carbonyl, with a bent structure. Even though there are no *d* electrons in this system, the occupied *p* orbital undergoes some back-donation and the carbonyl stretch is slightly red-shifted.

Synthesis of Ligand-Coated Oxide Clusters

Macroscopic amounts of cluster-based materials have been isolated in the past for species such as the fullerenes, metal-encapsulated fullerenes, semiconductor quantum dots, noble metal clusters and a few examples of metal oxide nanoparticles. Except for the fullerenes, these species are stabilized for isolation because they have ligand or surfactant coatings. However, there is no general method for the production of transition metal clusters or those containing transition metal oxides in isolated form. Our research program has studied many of these latter cluster systems in the gas phase, and we have set out to obtain them in macroscopic quantities. To do this, we have developed a laser ablation flowtube reactor (LAFR) that produces gas phase clusters via the same laser vaporization method that we use in the gas phase. The laser repetition rate is higher to allow greater duty cycle for the method. Clusters are produced in a flowing gas mixture where they are cooled as they grow and then stabilized against reactions and further growth by coating them with ligands. Using the LAFR device, we have found conditions needed to isolate a number of interesting cluster species. For example, we have focused on the same vanadium oxide clusters that were shown to have high stability in our molecular beam experiments. The mass spectrum of the *solution* produced when vanadium oxide clusters are produced in the gas phase and coated with THF ligands and trapped in excess THF solvent shows that we have isolated the same abundant stoichiometries $V_3O_7^+$, $V_4O_9^+$, etc. To our knowledge, this is the first time that magic number clusters from gas phase experiments have been isolated as ligand-coated species. Slightly different clusters are captured with tetrahydrofuran or acetonitrile ligands, showing that acetonitrile binds to existing oxide clusters, while THF reacts with them to displace surface terminal oxygen atoms. Characterization of both kinds of ligand-coated oxides included laser desorption mass spectrometry, infrared and UV-visible spectroscopy and fluorescence lifetimes.

Surprisingly, similar isolation experiments on cobalt oxide clusters produced nearly pure isolation of $Co_4O_4(CH_3CN)_6$. The selective capture of this single cluster size was quite surprising, because the gas phase study of cobalt oxides gave no strong preference for any particular stoichiometry. Apparently, a strong ligand effect leads to the selective capture of this cluster size. Surface enhanced Raman spectroscopy on silver nanorods substrates were undertaken to determine the structure of the $Co_4O_4(CH_3CN)_6$ species. As noted above, the isolated Co_4O_4 species was found to be more stable in a ring form, but theory (in collaboration with Truhlar and coworkers) indicated that the cubic form is more stable with ligands present. However, the measured SERS spectrum seems to indicated that both cyclic and cubic structures may be present. Ongoing experiments are applying these cluster isolation methods to chromium oxides and to small clusters of pure aluminum.

Personnel Supported by and/or Associated with this Project

Faculty:

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

Postdoctoral Fellow:

Dr. Shaun Ard (Ph. D., University of Tennessee; now employed at Air Force Research Lab, Albuquerque, NM, in Group of Dr. Al Viggiano)

Graduate Students:

Zach Reed	Ph.D. 2009 (presently NRC Postdoc at NIST, Washington, DC)
Allen Ricks	Ph.D. 2010 (presently employed at Ultrafast Systems, Sarasota, FL)
Antonio Brathwaite	Ph. D. program
Collin Dibble	Ph. D. program
Scot Akin	Ph. D. program

Publications Resulting from this Project

1. A. M. Ricks, J. M. Bakker, G. E. Douberly and M. A. Duncan, "IR spectroscopy of $Co^+(CO)_n$ complexes in the gas phase," *J. Phys. Chem. A* **113**, 4701-4708 (2009). **DOI:** 10.1021/jp900239u

2. A. M. Ricks, G. E. Douberly and M. A. Duncan, "IR Photodissociation Spectroscopy of O_4^+, O_6^+ and O_8^+ Cluster Ions," *Int. J. Mass Spectrom.* **283**, 69-76 (2009). **DOI:** 10.1016/j.ijms.2009.01.009

3. A. M. Ricks, Z. D. Reed and M. A. Duncan, "Seven-coordinate homoleptic metal carbonyls in the gas phase," *J. Am. Chem. Soc.* **131**, 9176-9177 (2009). **DOI:** 10.1021/ja903983u

4. O. Kostko, S. R. Leone, M. A. Duncan, M. Ahmed, "Determination of ionization energies of small silicon clusters: Vacuum ultraviolet (VUV) photoionization experiments and ab initio calculations," *J. Phys. Chem. A* **114**, 3176-3181 (2010). **DOI:** 10.1021/jp9091688

5. Z. D. Reed and M. A. Duncan, "Infrared spectroscopy and structures of manganese carbonyl cations, $Mn(CO)_n^+$ (n=1-9)," *J. Am. Soc. Mass Spectrom.* **21**, 739-749 (2010). **DOI:** 10.1016/j.jasms.2010.01.022

6. S. Ard, C. Dibble, S. T. Akin and M. A. Duncan, "Ligand-coated vanadium oxide nanoclusters: Capturing gas phase magic numbers in solution," *J. Phys. Chem. C* **115**, 6438-6447 (2011). **DOI:** 10.1021/jp200691k

7. M. A. Duncan, "IR spectroscopy of gas phase metal carbonyl cations," *J. Mol. Spec.* **266**, 63-74 (2011) (invited feature article; cover art). **DOI:**10.1016/j.jms.2011.03.006

8. A. M. Ketch, C. L. Anfuso, K. S. Molek and M. A. Duncan, "Photodissociation of small indium oxide cluster cations," *Int. J. Mass Spectrom.* **304**, 29-35 (2011). **DOI:**10.1016/j.ijms.2011.03.005

9. A. D. Brathwaite, Z. D. Reed and M. A. Duncan, "Infrared spectroscopy of copper carbonyl cations," *J. Phys. Chem. A* **115**, 10461-10469 (2011). **DOI:** 10/1021/jp206102z.

10. A. D. Brathwaite and M. A. Duncan, "Infrared spectroscopy of $Si(CO)_n^+$ complexes: Evidence for asymmetric coordination," *J. Phys. Chem. A* **116**, 1375-1382 (2012). **DOI:** 10.1021/jp211578t.

11. M. A. Duncan, "Laser Vaporization Cluster Sources," *Rev. Sci. Instrum.* **83**, 041101/1-19 (2012)(invited review). Selected for April 23, 2012 issue of *Virtual Journal of Nanoscale Science & Technology*, published by AIP.

12. C. J. Dibble, S. T. Akin, S. Ard, C. P. Fowler and M. A. Duncan, "Photodissociation of cobalt and nickel oxide cluster cations," *J. Phys. Chem. A* **116**, 5398-5404 (2012).

Interactions/Transitions

a) Presentations

Invited Lectures Presented by the PI on this Research

1. "Infrared Spectroscopy of Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Physical Chemistry Seminar,* Rice University, March 2009.

2. "The role of golf on infrared spectroscopy and cluster ions," 70th Birthday Symposium for Michael T. Bowers, University of California, Santa Barbara, June 2009.

3. "Infrared spectroscopy of mass-selected cluster ions," *International Symposium on Mass Spectrometry* (keynote speaker), Bremen, Germany, September 2009.

4. "Infrared spectroscopy of mass-selected cluster ions: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, Georgia Institute of Technology, September 2009.

5. "Infrared spectroscopy of mass-selected cluster ions," *Chemistry Department Colloquium*, University of the Pacific, October 2009.

6. "Infrared spectroscopy of mass-selected cluster ions," *Asilomar Symposium on Ion Spectroscopy*, Monterey, CA, October 2009.

7. "Infrared Spectroscopy of Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Albert Moscowitz Lecture*, University of Minnesota, January 2010.

8. "Metal oxide and carbide nanoclusters in the gas phase and in solution," *Jekyll Island Symposium on Clusters*, Jekyll Island, GA, February 2010.

9. "Metal oxide and carbide nanoclusters and interstellar dust," Workshop on *Dust and Ice: Their Role in Astrophysical Environments,* Southeastern Laboratory Astrophysics Community, University of Georgia Physics Department, March 2010.

10. "Photodissociation and infrared spectroscopy of metal clusters in the gas phase," *Molecular and Optical Physics Seminar*, Technical University of Berlin, Germany, June 2010.

11. "Infrared spectroscopy of metal carbonyls and carbocations: Inorganic and organic chemistry in the gas phase," *Molecular Dynamics Seminar*, Fritz Haber Institute, Berlin, Germany, June 2010.

12. "Infrared spectroscopy of metal carbonyl cations," *Journal of Molecular Spectroscopy Review Lecture*, *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, OH, June 2010.

13. "Infrared spectroscopy of metal carbonyls and metal-CO_2 complexes in the gas phase," *Conference on Molecular & Ionic Clusters*, Niigata, Japan, September 2010.

14. "Metal carbide and oxide nanoclusters: Discovering stardust in the lab," *Departmental Colloquium*, Tennessee Tech University, October 2010.

15. "Infrared spectroscopy of metal carbonyls and carbocations: Inorganic and organic chemistry in the gas phase," *Departmental Colloquium*, University of North Texas, November 2010.

16. "Novel metal carbonyls and metal-CO_2 complexes studied with selected-ion infrared spectroscopy," *Workshop on Metal Clusters*, Oxford University, U.K., February 2011, (plenary lecture).

17. "Infrared spectroscopy of metal ion-molecule clusters of CO and CO_2," *Gordon Research Conference on Gaseous Ions*, Galveston, TX, February 2011.

18. "Synthesis and Isolation of Ligand-Coated transition Metal Oxide Nanoclusters," *Molecular Dynamics Contractor's Meeting*, Air Force office of Scientific Research, Pasadena, CA, May 2011.

19. "Metal oxide nanoclusters: From the gas phase to solution," *International Symposium on Clusters and Nanostructures*, Richmond, VA, November 2011.

20. "Metal carbide and oxide nanoclusters: Discovering stardust in the lab," *Departmental Colloquium*, Kennesaw State University, November 2011.

Contributed Presentations by the PI and Students

1. Z. D. Reed, A. M. Ricks and M. A. Duncan, Infrared spectroscopy and structures of metal carbonyl cations, $M(CO)_n^+$ (M= Nb, Ta, Mn), (n=1-11), *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2009.

2. A. M. Ricks and M. A. Duncan, "Spectroscopy and structure of metal carbonyl systems, $M(CO)_n^+$ M = V, CO (n=1-10), *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2009.

3. A. M. Ricks and M. A. Duncan, "Infrared spectroscopy of metal-ligand and metal oxide-ligand complexes," *International Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2010.

4. A. D. Brathwaite, A. M. Ricks, Z. D. Reed, and M. A. Duncan, "Infrared photodissociation spectroscopy of first-row transition metal carbonyl cations," *66th international Symposium on Molecular Spectroscopy*, Ohio State University, Columbus, OH, June 2011.

5. C. Dibble, S. Ard, S. D. Akin, M. A. Duncan, "Metal oxide nanoclusters: From the gas phase to solution," *International Symposium on Clusters and Nanostructures*, Richmond, VA, November 2011.

b) consultative and advisory functions

none

c) Transitions

none

New Discoveries, Inventions or Patent Disclosures

none

Pi Honors/Awards

Alexander von Humboldt Fellowship (Fritz Haber Institute, Berlin), 2007-present
American Chemical Society, Physical Chemistry Division, Award for Experimental Physical Chemistry, 2011
University of Georgia, Lamar Dodd Award, 2011