



Structure, Bonding and Surface Chemistry of Metal Oxide Nanoclusters

Michael Duncan
UNIVERSITY OF GEORGIA RESEARCH FOUNDATION INC.

06/23/2015
Final Report

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REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188								
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1. REPORT DATE (DD-MM-YYYY) 06-10-2015		2. REPORT TYPE Final		3. DATES COVERED (From - To) 01-01-2012 to 03-14-2015								
4. TITLE AND SUBTITLE Structure, Bonding and Surface Chemistry of Metal Oxide Nanoclusters				5a. CONTRACT NUMBER								
				5b. GRANT NUMBER FA9550-12-1-0116								
				5c. PROGRAM ELEMENT NUMBER								
6. AUTHOR(S) Duncan, Michael A.				5d. PROJECT NUMBER								
				5e. TASK NUMBER								
				5f. WORK UNIT NUMBER								
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Georgia Research Foundation, Inc. Boyd Graduate Studies Research Center 200 D.W. Brooks Dr. Athens, Georgia 30602-7415				8. PERFORMING ORGANIZATION REPORT NUMBER								
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research (Program Director: Dr. Michael R. Berman) AFOSR/RTE 875 N. Randolph St. Suite 325, Rm 3112 Phone: (703) 696-7781 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S)								
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)								
12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION A: Distribution approved for public release.												
13. SUPPLEMENTARY NOTES												
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15. SUBJECT TERMS metal oxide nanoclusters, laser spectroscopy, mass spectrometry												
16. SECURITY CLASSIFICATION OF: <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; padding: 2px;">a. REPORT</td> <td style="width: 33%; padding: 2px;">b. ABSTRACT</td> <td style="width: 33%; padding: 2px;">c. THIS PAGE</td> </tr> <tr> <td style="text-align: center; padding: 2px;">unclassified</td> <td style="text-align: center; padding: 2px;">unclassified</td> <td style="text-align: center; padding: 2px;">unclassified</td> </tr> </table>			a. REPORT	b. ABSTRACT	c. THIS PAGE	unclassified	unclassified	unclassified	17. LIMITATION OF ABSTRACT unlimited		18. NUMBER OF PAGES 9	
a. REPORT	b. ABSTRACT	c. THIS PAGE										
unclassified	unclassified	unclassified										
			19a. NAME OF RESPONSIBLE PERSON Michael A. Duncan									
			19b. TELEPHONE NUMBER (Include area code) 706-542-1998									

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5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5d. PROJECT NUMBER. Enter all project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.

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Final Report

Project title: Structure, Bonding and Surface Chemistry of Metal Oxide Nanoclusters

For the Period December 1, 2011 to March 14, 2015

AFOSR Contract No. FA9550-12-1-0116

AFOSR Program Director: Dr. Michael Berman

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Abstract

Ultra-small metal oxide nanoclusters are produced and characterized in the gas phase using laser ablation of solid metal targets and then subsequently captured in solution. Fundamental measurements in the gas phase use mass spectrometry and infrared laser spectroscopy, complemented by computational quantum chemistry. Recent experiments have investigated the carbonyl complexes of Ti, Zr, Hf, Sc, Y and Rh, as well as those of vanadium oxides. In synthetic experiments, metal oxide clusters are captured from the gas phase into solution, stabilized with ligand coatings, using a new fast-flow reactor. We are interested in the structure of these clusters and its influence on their reactivity, which is most relevant for their applications in catalysis. New experiments have isolated ligand-coated oxides of Co, Cr and Al, as well as pure aluminum clusters. Additional work has examined vanadium carbide clusters as well as metal-silicon clusters of several transition metals. These ultra-small clusters are studied with laser desorption and electrospray ionization mass spectrometry, optical spectroscopy methods (IR, surface-enhanced Raman, UV-visible absorption and fluorescence) and computational chemistry. The fundamental and applied studies complement each other, providing unanticipated discoveries and improved understanding of oxide nanocluster systems.

Objectives

The goal of this research program is to investigate the structure and bonding in stable metal-containing clusters which may be useful for "cluster-assembled materials." A secondary goal is to investigate the mechanisms of small molecule adsorption on the surface of metal clusters. Molecular adsorbates are required for ligand-coating stabilization of metal clusters, allowing them to be isolated in solution. Nanoparticles containing metals may provide new catalysts with enhanced selectivity, optical or electronic materials for plasmonics or solar energy conversion, or synthetic routes for improved ceramics. The enabling technology for all of these potential applications is the controlled synthesis of desired nanoparticles with desirable composition and stability. Our research project explores new ways to make nanoparticles with specific 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 mass spectrometry and infrared laser spectroscopy to measure the properties of these clusters in the gas phase to evaluate their likely stability, and comparisons are made to the predictions of theory to enhance the understanding of metal bonding interactions. Promising candidate species are transitioned from the gas phase experiments to higher throughput synthesis experiments in a specially designed laser vaporization flow reactor. In this approach, ultra-small oxide or other metal-compound clusters are produced at higher concentrations, coated and solubilized with specific ligands, and captured as materials in solution. Optical spectroscopy, mass spectrometry, and microscopy are applied to characterize these new cluster materials.

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 1) the infrared spectroscopy of metal carbonyl complexes and 2) the synthesis of new ligand-coated metal oxide clusters with our laser vaporization flowtube reactor. Significant progress has been made in each of these areas.

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 nanocatalysis, we have focused on metal carbonyl complexes in the gas phase. We study cation species, which can be mass-selected and probed with tunable laser photodissociation spectroscopy. These experiments are only possible because of our efficient sources for making gas phase clusters, and the new infrared optical parametric oscillator laser systems that now provide IR light across the 600-4500 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 the carbonyls of Co, V, Nb, Ta, Mn, 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 found CN values of 6 for Mn^+ , 5 for Co^+ , 2 for Au^+ , and 4 for Pt^+ . The CN values for Co^+ and Mn^+ are expected based on the 18 electron rule. The cation-carbonyls of V^+ , Nb^+ and Ta^+ were studied because the 18-electron rule predicts an unusual CN of 7. However, we found 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. According to electron counting and the predictions of density functional theory computations, the earlier transition metals should have even higher CN values, e.g., 7 or 8 for the Ti, Zr, Hf, which are odd-electron species as singly charged cations, or 8 for Sc and Y, which could conceivably form an 18-electron species. However, in new experiments, we found experimentally that there were CN values of 6 for all the titanium-group metals. Scandium had a coordination number of 7, and only Y had the expected 8-coordinate structure, the first time such a high-coordinate structure has been seen for a transition metal carbonyl. The lower CN values seen for several metals that did not form 18-

electron complexes were interpreted to arise from a kinetic bottle-neck in cluster growth, resulting from an electron spin change required to add the last CO ligand. This caused heavier metals, which have stronger spin-orbit coupling, to have a better chance of forming the higher CN complexes.

In other new carbonyl species, we studied copper cation carbonyls, which form a four-coordinate complex isoelectronic and iso-structural with the known neutral $\text{Ni}(\text{CO})_4$. However, unlike the nickel complex, the copper systems have blue-shifted CO stretches, like the behavior seen previously for gold. Rhodium carbonyl complexes were found to form both the 4-coordinate (16-electron) and 5-coordinate (18-electron) complexes, with square planar and square pyramid structures, respectively.

In a final area, we examined oxide-carbonyls of vanadium, i.e., the $\text{VO}^+(\text{CO})_n$, $\text{VO}_2^+(\text{CO})_n$ and $\text{VO}_3^+(\text{CO})_n$ systems. In each of these ions, the coordination number involved a combination of oxygen atoms and CO ligands, but a total CN of six was found for each complex, consistent with the CN value of $\text{V}^+(\text{CO})_n$. The CO stretches for these systems were blue-shifted, like CO stretches when this ligand is adsorbed on oxide surfaces. The extended range of our new infrared lasers also allowed us to measure the V–O stretches (near 1000 cm^{-1}) of these complexes for the first time, providing additional information about structures and spin states.

Synthesis of Ligand-Coated Oxide Clusters

In the last several years, we have developed a laser ablation flowtube reactor (LAFR) that produces gas phase clusters via laser vaporization, but with a higher repetition rate to allow greater duty cycle. Clusters are produced in a flowing gas mixture where they are cooled as they grow, and then stabilized against reactions and further growth by ligand-coating. We have found conditions needed to isolate a number of interesting cluster species using this new method. In the vanadium oxide system, specific cluster stoichiometries (V_3O_7 , V_4O_9 , V_5O_{12}) that were shown to have high stability in our molecular beam experiments were isolated in solution with ligand coatings of THF or acetonitrile. To our knowledge, this is the first time that magic number clusters from gas phase experiments have been isolated as ligand-coated species. Moreover, the clusters produced in this way are *ultra-small*, much smaller than those produced by other synthesis methods, and therefore likely to have very different properties. Characterization of these ligand-coated oxides included laser desorption mass spectrometry, infrared, Raman and UV-visible spectroscopy, fluorescence spectrometry and lifetimes, as well as TEM microscopy.

Newer work extended these studies to cobalt and chromium oxides and to both oxides and pure metal clusters of aluminum, using acetonitrile as the ligand. The chromium solutions produced were brown, and mass spectra indicated the formation of coated Cr_4O_{10} and Cr_6O_{14} under different conditions. Both of these masses were also seen in molecular beam experiments. The cobalt oxide sample produced a blue solution, and mass spectra had a single main peak at 551 amu. Mass assignment indicates the formation of a $\text{Co}_3\text{O}_8(\text{CH}_3\text{CN})_6$ complex. Theory and higher mass measurements are planned for this system. The aluminum experiment produced ligand-coated Al_2O_3 even though oxygen was not added, presumably it comes from surface oxide. Surprisingly, however, the main cluster isolated was ligand-coated Al_3 . This small cluster has been studied previously in the gas phase, and its liquid sample fluoresces in the same region as the gas phase spectrum. Surface enhanced Raman spectroscopy (SERS) was employed on each of these samples, providing vibrational spectra that could be compared to theory. The concentrations of the chromium and aluminum samples were great enough for analysis with HPLC. Full characterization of these samples is ongoing as of this writing.

To continue to develop our capability for the synthesis of these new cluster materials, we have focused on improved instrumentation for their synthesis and characterization. The most important addition to the program was a new excimer laser (Coherent LPXPro 240F), allowing higher efficiency laser ablation for the synthesis process. This laser operates at higher laser pulse energy (300 mJ/pulse) and higher repetition rate (400 Hz), proving more ablation energy per pulse and more pulses per second. A second development was the addition of an electrospray ionization time-of-flight (ESI-TOF) mass spectrometer to the lab (PerSeptive Biosystems Mariner), which provides a different ionization mechanism for our sample and higher mass resolution than possible in the laser desorption process.

Personnel Supported by and/or Associated with this Project

Faculty:

Professor Michael A. Duncan (one month summer salary)

Prof. Heather Abbott-Lyons, summer visiting faculty and collaborator from Kennesaw State University (no support).

Postdoctoral Fellows:

none

Graduate Students:

Antonio Brathwaite	Ph. D. degree received December 2013
Collin Dibble	Ph. D. degree received May 2013
Scott Akin	Ph. D. program
Xianji Liu	Ph.D. program

Publications Resulting from this Project

1. A. D. Brathwaite, M. A. Duncan, "Infrared spectroscopy of $\text{Si}(\text{CO})_n^+$ complexes: Evidence for asymmetric coordination," *J. Phys. Chem. A* **116**, 1375-1382 (2012). DOI: 10.1021/jp211578t.
2. M. A. Duncan, "Laser vaporization cluster sources," *Rev. Sci. Instrum.* **83**, 041101/1-19 (2012)(invited review). DOI: 10.1063/1.3697599. Selected for April 23, 2012 issue of *Virtual Journal of Nanoscale Science & Technology*, published by AIP.
3. C. J. Dibble, S. T. Akin, S. Ard, C. P. Fowler, M. A. Duncan, "Photodissociation of cobalt and nickel oxide cluster cations," *J. Phys. Chem. A* **116**, 5398-5404 (2012). DOI: 10.1021/jp302560p.
4. A. M. Ricks, A. D. Brathwaite, M. A. Duncan, "Coordination and spin states of $\text{V}^+(\text{CO})_n$ clusters revealed by IR spectroscopy," *J. Phys. Chem. A* **117**, 1001–1010 (2013). (Peter Armentrout Festschrift) DOI: 10.1021/jp301679m.
5. A. D. Brathwaite, M. A. Duncan, "Infrared photodissociation spectroscopy of saturated group IV (Ti, Zr, Hf) metal carbonyl cations," *J. Phys. Chem. A* **117**, 11695-11703 (2013). (Curt Wittig Festschrift) DOI: 10.1021/jp400793h.
6. T. C. Cheng, S. T. Akin, C. J. Dibble, S. Ard, M. A. Duncan, "Tunable infrared laser desorption and ionization of fullerene films," *Int. J. Mass. Spectrom.* **354–355**, 159–164 (2013). (Detlef Schröder Memorial Issue) DOI: 10.1016/j.ijms.2013.05.031.
7. A. M. Ricks, A. D. Brathwaite, M. A. Duncan, "IR Spectroscopy of $\text{V}^+(\text{CO}_2)_n$ Clusters: Solvation-Induced Electron Transfer and Activation of CO_2 ," *J. Phys. Chem. A* **117**, 11490–11498 (2013). DOI: 10.1021/jp4089035.
8. A. D. Brathwaite, A. M. Ricks, M. A. Duncan, "Infrared Spectroscopy of Vanadium Oxide Carbonyl Cations," *J. Phys. Chem. A* **117**, 13435–13442 (2013). (Terry Miller festschrift) DOI: 10.1021/jp4068697.
9. T. M. Ayers, S. T. Akin, C. J. Dibble, M. A. Duncan, "Laser Desorption Time-of-Flight Mass Spectrometry of Inorganic Nanoclusters: An Experiment for Physical Chemistry or

- Advanced Instrumentation Laboratories," *J. Chem. Educ.* **91**, 291–296 (2014). DOI: 10.1021/ed4003942.
10. A. D. Brathwaite, J. A. Maner, M. A. Duncan, "Testing the Limits of the 18-Electron Rule: The Gas Phase Carbonyls of Sc^+ and Y^+ ," *Inorg. Chem.* **53**, 1166–1169 (2014). DOI: 10.1021/ic402729g.
 11. S. Luo, C. J. Dibble, M. A. Duncan, D. G. Truhlar, "Ligand-Mediated Ring $\rightarrow$ Cube Transformation in a Catalytic Subnanocluster: $\text{Co}_4\text{O}_4(\text{CH}_3\text{CN})_n$ with $n = 1\text{--}6$," *J. Phys. Chem. Lett.* **5**, 2528–2532 (2014). DOI: 10.1021/jz501167s.

Interactions/Transitions

a) Presentations

Invited Lectures Presented by the PI on this Research

1. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Departmental Colloquium*, University of Tennessee, February 9, 2012.
2. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, University of Pennsylvania, February 16, 2012.
3. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Departmental Colloquium*, Virginia Tech University, October 5, 2012.
4. "Production, isolation and characterization of metal compound nanoparticles," *Workshop on Controlling the Electronic Structure of Semiconductor Nanoparticles by Doping and Hybrid Formation*, Technical University of Berlin, Germany, October 19, 2012.
5. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, Wayne State University, November 7, 2012.
6. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, Purdue University, February 6, 2013.
7. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, Indiana University, February 7, 2013.
8. "Spectroscopy of mass-selected metal ions and clusters," *International Symposium on Size-Selected Clusters*, Davos, Switzerland, March 6, 2013.
9. "Metal oxide nanoclusters: From the gas phase to solution," *International Symposium on Clusters and Nanostructures*, Jekyll Island, GA, April 24, 2013.
10. "Infrared spectroscopy of cold ions and clusters: Inorganic chemistry in the gas phase," *Florida Annual Meeting and Expo (FAME)*, Tampa, FL, May 10, 2013.

11. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Chemistry Department Seminar*, Baylor University, September 30, 2013.
12. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, Texas A&M University, October 1, 2013.
13. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, University of Florida, October 8, 2013.
14. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Chemistry Department Seminar*, University of Alabama, November 14, 2013.
15. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Physical Chemistry Seminar*, University of Wisconsin-Madison, February 4, 2014.
16. "Synthesis and isolation of transition metal oxide nanoclusters," *Department Colloquium*, University of West Georgia, March 7, 2014.
17. "Metal-ligand and metal-solvent interactions studied with selected ion infrared spectroscopy," *Gordon Research Conference on Molecular & Ionic Clusters*, Il Ciocco, Italy, April 30, 2014.
18. "Gas Phase Synthesis of Ligand-Coated Metal Nanoclusters and their Capture in Solution," *Molecular Dynamics Contractor's Meeting*, Air Force Office of Scientific Research, Arlington, VA May 21, 2014.
19. "Infrared spectroscopy of cold ions and clusters," *Physics Department Colloquium*, University of Tennessee, September 29, 2014.
20. "Infrared spectroscopy of cold ions and clusters: Inorganic and organic chemistry in the gas phase," *Departmental Colloquium*, Johns Hopkins University, November 4, 2014.

Contributed Presentations by the PI, Postdoc, Collaborator and Students

1. A. D. Brathwaite, M. A. Duncan, "Infrared spectroscopy of mass-selected metal carbonyl cations," Gordon Research Conference on *Molecular and Ionic Clusters*, Ventura, CA, January 2012.
2. A. D. Brathwaite, M. A. Duncan, "Infrared photodissociation spectroscopy of silicon-carbonyl cations: Evidence for asymmetric coordination," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, OH, June 2012.
3. A. D. Brathwaite, A. M. Ricks, M. A. Duncan, "Infrared photodissociation spectroscopy of vanadium-carbon dioxide cations: Evidence for an intracluster reaction," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, OH, June 2012.

4. H. L. Abbott, A. D. Brathwaite and M. A. Duncan, "Infrared spectroscopy and structures of mass-selected rhodium carbonyl and rhodium dinitrogen cations," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, OH, June 2013.
5. J. A. Maner, M. D. McDowell and M. A. Duncan, "Intracuster reactions in Ni-CO₂ clusters," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, OH, June 2013.
6. A. D. Brathwaite and M. A. Duncan, "Infrared photodissociation spectroscopy of metal oxide carbonyl cations," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, OH, June 2013.
7. S. T. Akin, C. J. Dibble, S. Ard and M. A. Duncan, "Production and Isolation of Ligand Coated Nanoclusters using a Laser Vaporization Flowtube Reactor," Gordon Research Conference on *Clusters, Nanocrystals & Nanostructures*, Mount Holyoke College, South Hadley, MA, August 4–9, 2013.

b) consultative and advisory functions

Dr. Shaun Ard, a previous postdoc on this project, moved to the Air Force Research Lab at Kirtland AFB, where he is presently working as a postdoc with Dr. Al Viggiano. Our group is collaborating with the Viggiano group on the design and implementation of a laser vaporization source for the production of gaseous metal ions and clusters.

Dr. Justin Young, a former postdoc from our group, moved to the Air Force Research Lab at Kirtland AFB, where he is presently working as a postdoc with Dr. Jaime Stearns.

c) Technology Assists, Transitions and Transfers

none

New Discoveries, Inventions or Patent Disclosures

none

Pi Honors/Awards

none

1.

1. Report Type

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Primary Contact E-mail**Contact email if there is a problem with the report.**

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Primary Contact Phone Number**Contact phone number if there is a problem with the report**

706-542-1998

Organization / Institution name

University of Georgia

Grant/Contract Title**The full title of the funded effort.**

Structure, Bonding and Surface Chemistry of Metal Oxide Nanoclusters

Grant/Contract Number**AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".**

FA9550-12-1-0116

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

Michael A. Duncan

Program Manager**The AFOSR Program Manager currently assigned to the award**

Michael R. Berman

Reporting Period Start Date

01/01/2012

Reporting Period End Date

03/14/2015

Abstract

Ultra-small metal oxide nanoclusters were produced and characterized in the gas phase using laser ablation of solid metal targets and then subsequently captured in solution. Fundamental measurements in the gas phase use mass spectrometry and infrared laser spectroscopy, complemented by computational quantum chemistry. Recent experiments have investigated the carbonyl complexes of Ti, Zr, Hf, Sc, Y and Rh, as well as those of vanadium oxides. In synthetic experiments, metal oxide clusters are captured from the gas phase into solution, stabilized with ligand coatings, using a new fast-flow reactor. New experiments have isolated ligand-coated oxides of Co, Cr and Al, as well as pure aluminum clusters. Additional work has examined vanadium carbide clusters as well as metal-silicon clusters of several transition metals. These ultra-small clusters are studied with laser desorption and electrospray ionization mass spectrometry, optical spectroscopy methods (IR, surface-enhanced Raman, UV-visible absorption and fluorescence) and computational chemistry. The fundamental and applied studies complement each other, providing unanticipated discoveries and improved understanding of oxide nanocluster systems.

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1. A. D. Brathwaite, 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.
2. M. A. Duncan, "Laser vaporization cluster sources," Rev. Sci. Instrum. 83, 041101/1-19 (2012)(invited review). DOI: 10.1063/1.3697599. Selected for April 23, 2012 issue of Virtual Journal of Nanoscale Science & Technology, published by AIP.
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Changes in research objectives (if any):

none

Change in AFOSR Program Manager, if any:

none

Extensions granted or milestones slipped, if any:

none

AFOSR LRIR Number**LRIR Title**

Reporting Period**Laboratory Task Manager****Program Officer****Research Objectives****Technical Summary****Funding Summary by Cost Category (by FY, \$K)**

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document**Report Document - Text Analysis****Report Document - Text Analysis****Appendix Documents****2. Thank You****E-mail user**

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