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Concepts and Materials for Sub-Nano Chemistry

Michael Duncan
UNIVERSITY OF GEORGIA RESEARCH FOUNDATION INC.

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Final Report

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14. ABSTRACT

Ultra-small metal and metal compound 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, laser photodissociation and infrared laser spectroscopy, complemented by computational quantum chemistry. In spectroscopy experiments, we have investigated metal ion-acetylene complexes of vanadium and zinc which are important as models for catalytic combustion processes. In synthesis experiments, metal-containing clusters produced initially in the gas phase are coated with ligands and captured in solution, stabilized with ligand coatings, using a new fast-flow reactor. Recent work has completed the characterization of chromium oxide clusters coated with acetonitrile, including extensive measurements of spectroscopy and computational studies of structures and spectra. Additional work has discovered and characterized a new molybdenum oxide material, which forms unanticipated nanorod structures. These various ultra-small clusters and new materials are studied with laser desorption and electrospray ionization mass spectrometry, optical spectroscopy methods (IR, surface-enhanced Raman, UV-visible absorption and fluorescence), transmission electron microscopy (TEM), and computational chemistry. The fundamental and applied studies complement each other, providing unanticipated discoveries and improved understanding of metal nanocluster systems.

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Final Report

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Principle investigator:	Prof. Michael A. Duncan Department of Chemistry, University of Georgia, Athens, GA 30602 Phone: 706-542-1998 Email: maduncan@uga.edu Web site: http://research.franklin.uga.edu/maduncan

Abstract

Ultra-small metal and metal compound 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, laser photodissociation and infrared laser spectroscopy, complemented by computational quantum chemistry. In spectroscopy experiments, we have investigated metal ion-acetylene complexes of vanadium and zinc which are important as models for catalytic combustion processes. In synthesis experiments, metal-containing clusters produced initially in the gas phase are coated with ligands and captured in solution, stabilized with ligand coatings, using a new fast-flow reactor. Recent work has completed the characterization of chromium oxide clusters coated with acetonitrile, including extensive measurements of spectroscopy and computational studies of structures and spectra. Additional work has discovered and characterized a new molybdenum oxide material, which forms unanticipated nanorod structures. These various ultra-small clusters and new materials are studied with laser desorption and electrospray ionization mass spectrometry, optical spectroscopy methods (IR, surface-enhanced Raman, UV-visible absorption and fluorescence), transmission electron microscopy (TEM), and computational chemistry. The fundamental and applied studies complement each other, providing unanticipated discoveries and improved understanding of metal 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." An additional goal is to investigate the mechanism of small hydrocarbon molecule adsorption on the surface of metal atoms or clusters to elucidate their catalytic activity, with specific focus on analogs of "single atom catalysts." 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 synthesis of desired particles with controlled composition and stability. Our research project explores new ways to make ultra-small particles 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 10−100 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 have been 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 energetics. Synthesis experiments that isolate ligand-coated nanoclusters in solution were conducted using our laser ablation flowtube reactor. Graduate and undergraduate students were trained in various aspects of physical and inorganic chemistry, as well as computational chemistry, as they apply to the gas phase synthesis and characterization of unusual nanocluster molecules.

Accomplishments/New Findings

Mass Spectrometry and Theory of Gas Phase Metal Oxide Clusters

To survey for stable metal oxide clusters that may later be isolated as materials, we have produced new oxide clusters and studied them with mass-selected photodissociation experiments. The experiments have included cerium, manganese, tungsten, and molybdenum oxides. Computational studies using density functional theory were conducted to determine the most stable structures and electronic states for these systems, including their spin configurations. Clusters with the $(MnO)_n^+$ stoichiometry were found to be most stable for the manganese-oxide system. Cubic structures were identified for the larger clusters, whereas open ring structures were favored for the smaller systems. Figure 1 shows an example of a dissociation pattern for the $Mn_6O_6^+$ ion with structures that were computed for the stable fragments. Similar photodissociation experiments and theory have been completed for cerium oxide clusters; mass spectrometry has been completed on molybdenum and tungsten oxide clusters, but the computational work for those systems is still in progress.

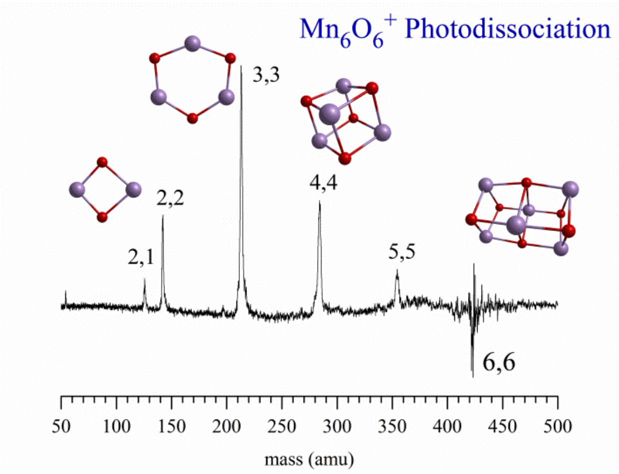


Figure 1. Multiphoton dissociation of the mass-selected $Mn_6O_6^+$ cation, showing the production of stable $(MnO)_n^+$ fragments. According to DFT theory the larger clusters favor cubic structures, whereas the smaller ones form rings.

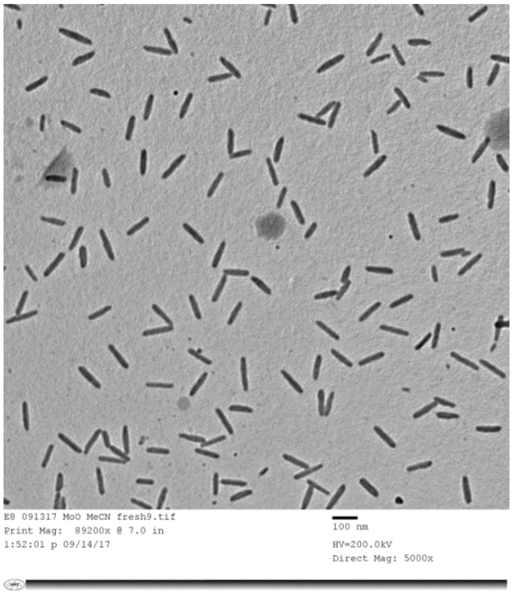
Synthesis of Ligand-Coated Clusters

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. A typical system is that of chromium oxide clusters coated with acetonitrile ligands. Mass spectrometry experiments indicated that these solutions contained a mixture consisting primarily of ligand-coated Cr_4O_{10}, Cr_5O_{14}, and Cr_6O_{14} clusters. We isolated enough material for UV-vis, infrared and Raman spectroscopy for these systems. To interpret the spectroscopy, we did extensive computational work using density functional theory. For each cluster size we explored multiple isomeric structures, multiple spin/electronic states for each isomer, and structures with different numbers of ligands for each of these. Even with this extensive computational work, we were unable to get a definitive answer about cluster structures because the spectra were measured for solutions containing a mixture of cluster sizes. Purification of each cluster size followed by size-specific spectroscopy will be necessary to make further progress with this system.

An example of a pure metal cluster system is that of silver nanoclusters in the 20−50 nm size range with acetonitrile as the surface coating rather than the standard surfactants used by others. The clusters produced were stable for long periods of time, soluble in acetonitrile or water, and had optical spectra in the plasmon region characteristic of similar sized clusters with surfactant coatings. However, we extended the optical spectroscopy into the far UV region where the acetonitrile ligand has a well-known molecular spectrum. This spectrum was enhanced in intensity by a factor of more than 10^5 by the adsorption on the metal nanoparticle. This kind of electronic enhancement of ligand spectra has not been documented previously.

Molybdenum oxide formed small clusters efficiently in molecular beam experiments, but did not produce any small ligand-coated clusters in solution. Instead, larger nanorod particles were produced (Figure 2). A purple solution was obtained, which has been seen previously for other molybdenum oxide nanomaterials produced by other methods. These moly-oxide rods contain relatively pure MoO_3 and can be reproduced reliably. UV-visible experiments find an absorption onset consistent with the bandgap of the MoO_3 semiconductor (about 3.5 eV, depending on morphology and production method). The Raman spectrum is particularly compelling. If the cluster solution is dried on a slide, the Raman spectrum in the upper trace of Figure 3 has broad features matching only somewhat close to those of commercial MoO_3 powder. However, if the sample is annealed in air at 400°C, it turns white and the Raman spectrum sharpens to match the spectrum of commercial MoO_3 powder almost exactly. This implies that the "as-produced" sample is amorphous and off-stoichiometry at the rod surfaces, and that annealing completes the oxidation process. After annealing, the sample is no longer soluble, apparently because the acetonitrile ligands that provided solubility were burned off. Molybdenum oxide nanoparticles have been produced by many methods and demonstrated to have interesting optical properties as well as catalytic and microbial activity. However, none of the previous work has produced anything like these small, uniformly sized nano-rods.

The reactivity of these molybdenum oxide nanorods was studied with respect to photocatalytic decomposition of methylene blue. We compared the reactivity to commercial MoO_3 particles, determining that our particles were much more reactive. The decomposition lifetime for our nanorods was half that of the commercial particles, and our rods also reacted even without photo-irradiation. The reactivity was also correlated with the amorphous surface structure and oxygen-deficient stoichiometry of the as-produced rods. After annealing, which changed the Raman spectrum dramatically, the nanorods lost their enhanced reactivity.



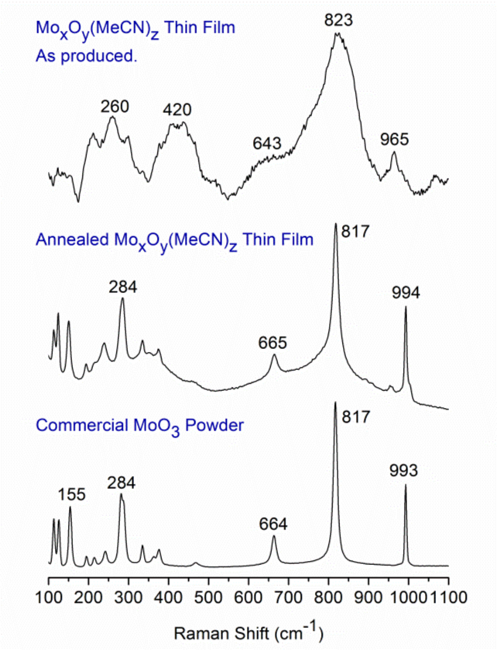


Figure 2 (left). TEM image of molybdenum oxide nanorods coated with acetonitrile. Figure 3 (right). The Raman spectrum of the "as-produced" moly-oxide nanorods and that after annealing, compared to that for a standard MoO_3 powder sample.

Magnetism in Ligand-Coated Clusters

We initiated work in a new area focusing on the magnetism of ligand coated metal clusters. This was done in a collaboration with the group of Bernd von Issendorff and Tobias Lau at the BESSY synchrotron facility at the Helmholtz-Zentrum Berlin, Germany. The Berlin group provided the instrumentation, materials and travel support (two trips to date) for a graduate student (Scott Akin), whose salary was supported by AFOSR. Beam time was awarded via competitive proposals submitted to the facility. The PI, M. A. Duncan made one trip (Feb. 2015) using his Alexander von Humboldt funding.

Initial experiments focused on cobalt clusters coated with benzene as a ligand. Pure cobalt clusters have strong magnetic moments, as demonstrated in previous experiments. However, if these systems are to be used in practical devices, they need to be stabilized via ligand coatings or immobilized on inert surfaces. We chose to investigate the representative metal cluster cobalt trimer, which has a strong magnetic moment and is easily produced, together with benzene as a ligand. Theory had suggested that benzene might enhance magnetism, and benzene is also a model for graphene surfaces.

The experiments produced Co_3^+ and $Co_3^+(\text{benzene})_{1\text{-}3}$ clusters with a magnetron source, cooled these to 10 K in a cryogenic ion trap, and then measured core electron transitions of cobalt at the $L_{2,3}$ edge with the output of the BESSY synchrotron. X-ray absorption spectra (XAS) and X-ray magnetic circular dichroism (XMCD) were recorded for each cluster size. The spin and orbital components of the magnetism were derived from the difference in the absorption for right- and left-circularly polarized light. These data showed that Co_3^+ has a strong magnetism in isolated form ($6\mu_B$), which was slightly reduced with one or two benzene ligands, and then the magnetism was completely quenched ($0\mu_B$) with three benzene ligands. This is caused by the coupling of electron spins and consequent change in spin state that occurs to minimize the metal electron-ligand electron repulsion. This surprising result represents the first high quality experimental data on such ligand effects on magnetism of metal clusters. These experimental measurements were complemented by theory from Truhlar and coworkers, that accurately predicts these effects.

Infrared Spectroscopy of Metal-Adsorbate Complexes

To study the details of catalytic reactions involving hydrocarbons at single-atom catalytic sites important in zeolite or metal-organic framework (MOF) catalysts, we investigated model $M^+(\text{acetylene})_n$ complexes in the gas phase. Previously, we studied copper and gold complexes. New work has focused on vanadium, zinc, cobalt, silver and platinum systems. In several of the complexes studied, cation-π interactions were found to dominate, with red-shifted C–H stretches compared to the vibrations of isolated acetylene. The acetylene ligand in these systems was only slightly distorted from its free-molecule structure, making the symmetric C–H stretch weakly IR active. In the vanadium system, stronger metal-carbon bonds formed, producing metallacycle structures. A single metal ion with one acetylene produced a three-membered ring, and V^+ with two acetylenes produced a double three-membered ring (bow-tie) structure. The spectra of larger complexes exhibited an interesting dependence on the acetylene concentration; at the highest concentrations, we could confirm that V^+(benzene) was formed! The metallacycles are intermediates along this cyclo-trimerization reaction path. The cyclo-trimerization reaction has been seen previously, but this is the first time that intermediates along the way have been detected with any form of spectroscopy. Careful computational studies have now characterized the energetics along this reaction path, which is shown schematically in Figure 4.

Interesting chemistry was also seen for the zinc-acetylene system. Again, covalent metal-carbon bonds formed, but with the metal attached to a single carbon in a bent M-C-C configuration. Three such metal-acetylene species formed in the first coordination sphere. When a fourth acetylene was added, the IR spectrum provided evidence that ligand activation had occurred, producing a metal-vinyl radical moiety in the cluster. The vinyl radical had a bent structure, with a strongly red-shifted C–H stretch. When a fifth acetylene is added, poly-vinyl formation was initiated at the terminal radical site.

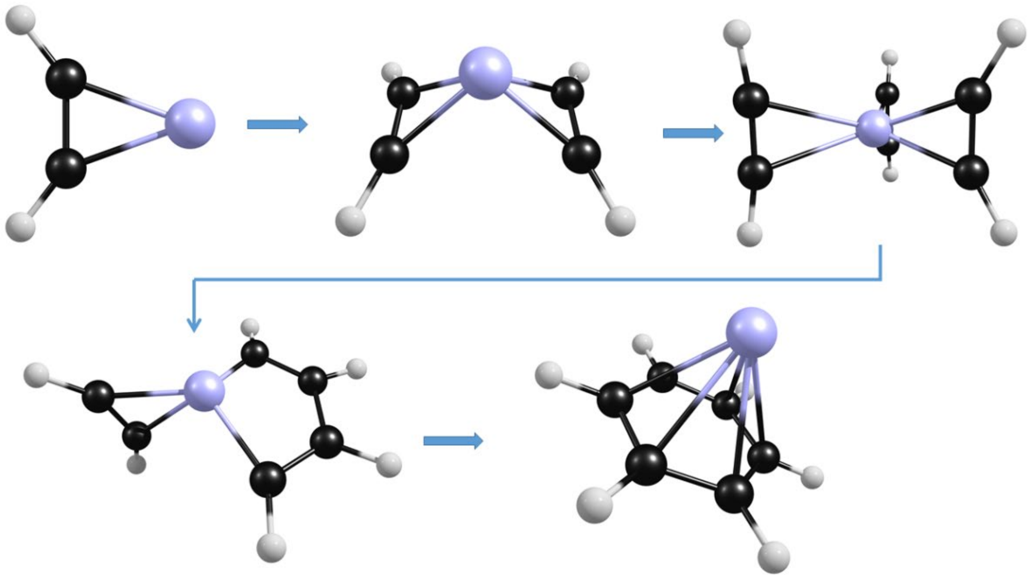


Figure 4. The reaction sequence coupling acetylene to form benzene at an atomic vanadium ion center.

We initiated a new collaboration with the research group of Prof. Gereon Niedner-Schatteburg at the University of Kaiserslautern in Germany. This was possible because of international travel money allocated to us by AFOSR. One graduate student (David McDonald) made the trip in the summer of 2017 and another (Brandon Rittgers) made a similar visit in the summer of 2018. In this work, we studied the adsorption of nitrogen or hydrogen on Ru_8^+ clusters. These clusters, which have a cubic structure, provide interesting models for the Haber-Bosch reaction that is used to synthesize ammonia. Infrared spectroscopy and theory showed that hydrogen dissociates on these clusters, forming hydrides at opposite distal sites on cube corners. When nitrogen is adsorbed first, it does not dissociate, but blocks the mobility of hydrogen so that a different set of hydride vibrations corresponding to adjacent binding sites are produced. This interesting chemistry, which may have significant implications for catalysis, is under continued investigation.

Synthesis and Theory of Metal-PAH Complexes

Highly dispersed transition metal atoms on graphite (HOPG), graphene, or carbon nanotubes are under active investigations for a number of catalytic systems. Transition metal complexes with polycyclic aromatic hydrocarbons (PAHs) provide a convenient model system for such single atom catalysts. We have employed our laser ablation flow reactor to attempt to make complexes between chromium and coronene, and have successfully isolated both the single-ligand and sandwich complexes of these materials. These systems have so far been characterized only by mass spectrometry. We have also employed extensive density functional theory computations to explore the preferred kinds of binding sites that would be adopted by chromium atoms on the surface of coronene. Figure 5 shows the results of these computations, which indicate that binding is preferred in sites just above the double bond of an interior ring. This site is much more stable than the site over the center of an exterior ring, and very much more stable than a site above the center ring. Interestingly, the lowest energy configuration has the chromium in a high spin (septet) electronic state. This is in contrast to the well-known di-benzene chromium sandwich complex, which has a singlet ground state. This implies that binding to the more extended surface favors high spin states, which would cause such complexes to have high magnetic moments. However, because of the known issues with transition metal spin state predicted by DFT, further studies are underway with several different functionals.

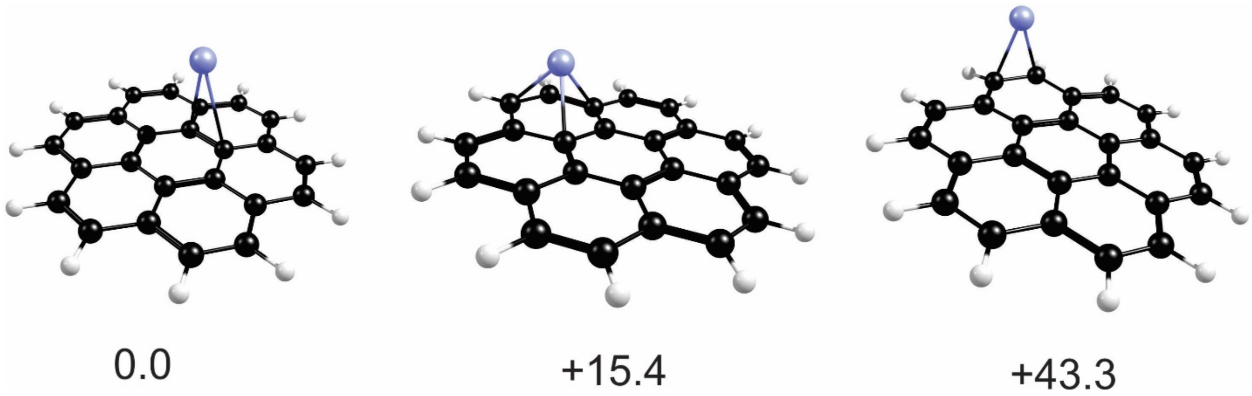


Figure 5. Relative energies of the most stable configurations for neutral chromium atoms binding on the surface of coronene (kcal/mol) from computations done at the DFT/B3LYP.def2-TZVP level of theory.

Personnel Supported by and/or Associated with this Project

Faculty

Professor Michael A. Duncan (one partial month summer salary)
Dr. Antonio Brathwaite (Instructor of Chemistry, Emory University; visiting summer research)

Postdoctoral Fellows

none

Graduate Students

Scott Akin	Ph.D. degree received 2016
Natalie Johnson	M.S. degree received 2017
David McDonald	Ph.D. degree received 2018
Melissa Woodard	Ph.D. degree received 2019
Xiangji Liu	Ph.D. degree received 2020
Ian Webster	Ph.D. program
Joshua Marks	Ph.D. program
Brandon Rittgers	Ph.D. program

Undergraduate Students

Jean Devera (University of the Virgin Islands), summer 2015.
Dylan Orr (University of Georgia), spring 2016; graduate school at University of Georgia.
Sojourna Ferguson (University of the Virgin Islands), summer 2016.
Deidre Lee (University of the Virgin Islands), summer 2017.
Tione Grant (University of the Virgin Islands), summer 2017.
Jacob Beckham (University of Georgia), fall 2017–2019; graduate school at Rice University.
Alyssa McDonald (University of Georgia), spring–fall 2018.
Anna Batchelor (University of Georgia), fall 2018–present.
David Durden (University of Georgia), fall 2018–fall 2019.

Erick Martinez (Emory University), summer 2019.
Conner Blais (University of Georgia), fall 2019–present.

Publications Resulting from this Project

1. S. T. Akin, X. Liu and M. A. Duncan, "Laser synthesis and spectroscopy of acetonitrile/silver nanoparticles," *Chem. Phys. Lett.* **640**, 161−164 (2015). DOI:10.1016/j.cplett.2015.10.022.

2. S. T. Akin, S. G. Ard, B. E. Dye, H. F. Schaefer, M. A. Duncan, "Photodissociation of cerium oxide nanocluster cations," *J. Phys. Chem. A* **120**, 2313–2319 (2016). DOI: 10.1021/acs.jpca.6b02052.

3. S. T. Akin, V. Zamudio-Bayer, K. Duanmu, G. Leistner, K. Hirsch, C. Bülow, A. Ławicki, A. Terasaki, B. von Issendorff, D. G. Truhlar, J. T. Lau, M. A. Duncan, "Size-dependent ligand quenching of ferromagnetism in $Co_3(benzene)_n^+$ clusters studied with XMCD spectroscopy," *J. Phys. Chem. Lett.* **7**, 4568–4575 (2016). DOI: 10.1021/acs.jpclett.6b01839.

4. T. B. Ward, A. D. Brathwaite, M. A. Duncan, "Infrared spectroscopy of $Au(Acetylene)_n^+$ complexes in the gas phase," *Topics in Catalysis* **61**,49–61 (2018). DOI: 10.1007/s11244-017-0859-0.

5. S. Dillinger, M. P. Klein, A. Steiner, D. C. McDonald II, M. A. Duncan, M. M. Kappes, G. Niedner-Schatteburg, "Cryo IR spectroscopy of N_2 and H_2 on Ru_8^+: The effect of N_2 on the H-migration," *J. Phys. Chem. Lett.* **9**, 914–918 (2018). DOI: 10.1021/acs.jpclett.8b00093.

6. M. P. Woodard, S. T. Akin, C. J. Dibble, M. A. Duncan, "Synthesis and spectroscopy of ligand-coated chromium oxide nanoclusters," *J. Phys. Chem. A* **122**, 3606–3620 (2018). DOI: 10.1021/acs.jpca.8b01219.

7. J. H. Marks, T. B. Ward, M. A. Duncan, "Photodissociation of manganese oxide cluster cations," *J. Phys. Chem. A* **122**, 3383−3390 (2018). DOI: 10.1021/acs.jpca.8b01441.

8. S. C. Meier, A. Holz, J. Kulenkampff, A. Schmidt, D. Kratzert, D. Himmel, D. Schmitz, E.-W. Scheidt, W. Scherer, C. Bülow, M. Timm, R. Lindblad, S. T. Akin, V. Zamudio-Bayer, B. von Issendorff, M. A. Duncan, T. Lau, I. Krossing, "Cationic sandwich complexes of cobalt(I): The parent bis-benzene cobalt(I) complex and access to its weakly bound homologues - Synthons for a "naked" cobalt(I) source…?, *Angew. Chem., Int. Ed.* **57**, 9310–9314 (2018). (communication) DOI: 10.1002/anie.201803108.

9. J. H. Marks, T. B. Ward, M. A. Duncan, "Infrared spectroscopy of the coordination and solvation in $Cu^+(ethylene)_n$ ($n = 1–9$) complexes," *Int. J. Mass Spectrom.* **435**, 107–113 (2019). (Helmut Schwarz issue). DOI: 10.1016/j.ijms.2018.10.008.

10. M. P. Woodard, M. A. Duncan, "Laser synthesis and spectroscopy of molybdenum oxide nanorods," *J. Phys. Chem. C* **123**, 9560–9566 (2019). DOI: 10.1021/acs.jpcc.9b00627.

11. M. A. Duncan, "Metal cation coordination and solvation studied with infrared spectroscopy in the gas phase," in *Physical Chemistry of Cold Gas Phase Functional Molecules and Clusters*, T. Ebata and M. Fujii, eds., Springer, Berlin, 2019, p. 157. DOI: 10.1007/978-981-13-9371-6_6

12. J. H. Marks, T. B. Ward, A. D. Brathwaite, S. Ferguson, M. A. Duncan, "Cyclotrimerization of acetylene in gas phase $V^+(C_2H_2)_n$ complexes: Detection of intermediates and products with infrared spectroscopy," *J. Phys. Chem. A* **123**, 6733−6743 (2019). DOI: 10.1021/acs.jpca.9b04962.

13. J. H. Marks, T. B. Ward, A. D. Brathwaite, M. A. Duncan, "Infrared spectroscopy of $Zn(Acetylene)_n^+$ complexes: Ligand activation and nascent polymerization," *J. Phys. Chem. A* **124**, 4764−4776 (2020). DOI: 10.1021/acs.jpca.0c03358.

Interactions/Transitions

a) Presentations

Invited Lectures Presented by the PI on this Research

1. "Metal-Ligand and Metal-Solvent Interactions in the Gas Phase," *Wilhelm Ostwald Institute of Physical Chemistry*, University of Leipzig, Germany, April 27, 2015.

2. "Infrared Spectroscopy of Cold Ions and Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Oscar K. Rice Lecture*, University of North Carolina, October 22, 2015.

3. "Metal Ion-Molecular Complexes Studied with Photodissociation Spectroscopy," *Symposium on New Molecules and Clusters*," Fudan University, Shanghai, China, May 28, 2016.

4. "Infrared Spectroscopy and Photofragment Imaging of Cation-Molecular Complexes," *Physical Chemistry Seminar*, Technical University of Kaiserslautern, Kaiserslautern, Germany, September 6, 2016.

5. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Frontiers in Chemistry Lecture*, Wayne State University, Detroit, MI, September 19, 2016.

6. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Departmental Colloquium*, Auburn University, Auburn, AL, February 23, 2017.

7. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Departmental Seminar*, UNC-Charlotte, March 23, 2017.

8. "Concepts and Materials for Sub-Nano Chemistry, *AFOSR Molecular Dynamics Program Review*, Kirtland AFB, Albuquerque, NM, May 25, 2017.

9. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," *Smalley/Curl Institute Lecture*, Rice University, November 7, 2018.

10. "Infrared Spectroscopy of Transition Metal Cation-π Complexes," Symposium on Frontiers in Vibrational Spectroscopy: Experiment & Theory, *National Meeting of the American Chemical Society*, Orlando, FL, April 3, 2019.

11. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," University of Karlsruhe, Germany, May 14, 2019.

12. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase," German Chemical Society Lecture, Tübingen, Germany, May 16, 2019.

13. "Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic Chemistry in the Gas Phase," University of Kaiserslautern, Germany, May 17, 2019.

14. "Infrared Spectroscopy of Transition Metal Cation-π Complexes," *Wintergreen Conference on Physical Chemistry*, Wintergreen, VA, June 11, 2019.

15. "Infrared Spectroscopy of Transition Metal Cation-π Complexes," University of Manchester, U.K., June 21, 2019.

16. "Laser Synthesis of Ligand-Coated Metal Nanoclusters," Symposium on Surface Chemistry and Structure in Ligand Protected Metal Nanoparticles, *National Meeting of the American Chemical Society*, San Diego, CA August 25-29, 2019.

17. "Infrared Spectroscopy of Transition Metal Cation-π Complexes," *Symposium on Metals in Biology and Chemistry*, Duquesne University, Pittsburgh, PA, September 13, 2019.

18. "Laser Synthesis of Ligand-Coated Metal Nanoclusters," *International Symposium on Clusters and Nanomaterials*, Richmond, VA, November 5, 2019.

Contributed Presentations by the PI, Postdoc, Collaborators and Students

(undergraduate authors in italics)

1. <u>*Jean L. Devera*</u>, Antonio D. Brathwaite, Michael. A. Duncan, "Vibrational Scaling Factors for Transition Metal Carbonyls," *17th Annual Fall Undergraduate Student Research Symposium*, St. Thomas, U.S. Virgin Islands, September 27, 2015.

2. <u>*Jean L. Devera*</u>, Antonio D. Brathwaite, Michael. A. Duncan, "Vibrational Scaling Factors for Transition Metal Carbonyls," *2015 Annual Biomedical Research Conference for Minority Students*, Seattle, WA, November 11-14, 2015.

3. <u>A. D. Brathwaite</u>, T. B. Ward, M. A. Duncan, "Infrared photodissociation spectroscopy of early and late transition metal-acetylene complexes," 71st Southwest Regional/67th

Southeast Regional Meeting of the American Chemical Society, Memphis, TN, November 5, 2015.

4. S. T. Akin, V. Zamudio-Bayer, T. Lau, M. A. Duncan, "X-ray spectroscopy as a probe of the magnetism in cobalt-benzene cluster cations," 71st Southwest Regional/67th Southeast Regional Meeting of the American Chemical Society, Memphis, TN, November 5, 2015.

5. *Jean L. Devera*, Antonio D. Brathwaite, Michael. A. Duncan, "Vibrational Scaling Factors for Transition Metal Carbonyls," *2016 Emerging Researchers National Conference in STEM*, Washington DC, February 25-27, 2016.

6. *Sojourna Ferguson*, Antonio D. Brathwaite, Michael. A. Duncan, "Single-Atom Catalysis in the Gas Phase," *18th Annual Fall Undergraduate Student Research Symposium*, St. Thomas, U.S. Virgin Islands, September 25, 2016.

7. *S. Ferguson*, A. B. Brathwaite, M. A. Duncan, "Single Atom Catalysis in the Gas Phase," *Annual Biomedical Research Conference for Minority Students*, Tampa, FL, November 9-12, 2016.

8. *Deidre Lee*, Antonio D. Brathwaite, Timothy Ward, Michael. A. Duncan, "Structural Trends of Gas-Phase Metal Cation-Acetylene Complexes Investigated via Infrared Spectroscopy," *2017 Annual Biomedical Research Conference for Minority Students*, Phoenix, AZ, November 1-4, 2017.

9. M. P. Klein, S. Dillinger, A. Steiner, D. C. McDonald II, M. A. Duncan, M. M. Kappes, G. Niedner-Schatteburg, "Cryo IR Spectroscopy of N_2 and H_2 on Ru_8^+," *Gordon Research Conference on Molecular and Ionic Clusters*, Il Ciocco, Italy, February 25–March 2, 2018.

10. J. H. Marks, T. B. Ward, M. A. Duncan, "Infrared Spectroscopy of Zn(acetylene)$_{1-5}^+$: Evidence for Acetylene Activation by a Metal Radical," *International Symposium on Molecular Spectroscopy*, Champaign-Urbana, Illinois, June 22, 2018.

11. J. H. Marks, T. B. Ward, M. A. Duncan, "Single Atom Catalytic Cyclotrimerization of V(acetylene)$_3^+$ Studied with Infrared Spectroscopy," *International Symposium on Molecular Spectroscopy*, Champaign-Urbana, Illinois, June 22, 2018.

12. M. Woodard, M.A. Duncan, "Laser synthesis of molybdenum oxide nanorods," *Southeastern Regional Meeting of the American Chemical Society*, Augusta, Georgia, November 1, 2018.

13. J. H. Marks, T. B. Ward, M. A. Duncan, "Coordination and Intracluster Reactions of Vanadium and Zinc Cation Complexes with Acetylene Complexes Studied with Infrared Spectroscopy," *Gordon Research Conference on Gaseous Ions*, Ventura, CA, February 17–22, 2019.

14. J. H. Marks, T. B. Ward, M. A. Duncan, "Coordination and Structure of Late Transition Metal Cation (Co, Rh, Pt) Acetylene Complexes Studied with Infrared Photodissociation

Spectroscopy," *International Symposium on Molecular Spectroscopy*, Champaign-Urbana, Illinois, June 20, 2019.

15. J. H. Marks, D. S. Orr, T. B. Ward, A. D. Brathwaite, M. A. Duncan, "Coordination and Intracluster Reactions of Vanadium and Zinc Cation Complexes with Acetylene Complexes Studied with Infrared Spectroscopy," *Gordon Research Conference on Molecular and Ionic Clusters*, Ventura, CA, January 26–30, 2020.

b) consultative and advisory functions

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

Mr. David McDonald from our group spent the summer of 2016 working as a visiting summer graduate student in the lab of Al Viggiano and Shaun Ard at the Air Force Research Lab at Kirtland AFB. The following publications resulted from his work during this period:

1. B. C. Sweeny, S. G. Ard, D. C. McDonald II, O. Martinez, A. A. Viggiano, N. S. Shuman. Discrepancy Between Experimental and Theoretical Predictions of the Adiabaticity of $Ti^+ + CH_3OH$. *Chem. Eur. J.* **23**, 11780 (2017).

2. D. C. McDonald II, B. C. Sweeny, S. G. Ard, J. Melko, J. Ruliffson, M. White, A. A. Viggiano, N. S. Shuman. Temperature and Isotope Dependent Kinetics of Nickel-Catalyzed Oxidation of Methane by Ozone. *J. Phys. Chem. A* **122**, 6655–6662 (2018).

McDonald applied for and received an offer for an NRC Postdoctoral Fellowship to continue work in the Albuquerque lab. He began work there in August of 2018 and is presently continuing in this role.

c) Technology Assists, Transitions and Transfers

Our design for a laser vaporization cluster source has been integrated into the flowing afterglow apparatus in the Ard/Viggiano lab at Kirtland AFB. This addition has made it possible to study the reactions of metal-containing ions of atmospheric interest. The technology "assist" has happened via shared source drawings and on-site consultation with our graduate student David McDonald during his visit to Kirtland in summer 2016 and has continued during his NRC postdoctoral work there since then.

New Discoveries, Inventions or Patent Disclosures

none

PI Honors/Awards

M. A. Duncan has served as Vice Chair Elect (2016), Vice Chair (2017), Chair Elect (2018), Chair (2019) and Past Chair (2020) of the Physical Division of the American Chemical Society.