# PRODUCTION AND ISOLATION OF LIGAND

### COATED NANOCLUSTERS

### By

# COLLIN JOSEPH DIBBLE

(Under the Direction of Michael A. Duncan)

### ABSTRACT

Ultra-small metal and metal oxide clusters in the 10-30 atom size range are produced in the gas phase with laser vaporization, coated with organic ligands, and captured in solution using a laser vaporization flow reactor. These clusters are analyzed by laser desorption time-of-flight mass spectrometry as well as UV-visible, IR, and Raman spectroscopies. Density functional theory is used to predict the geometries of the captured clusters and predict their spectra. Both size and structure of these clusters are affected by ligand interactions. Vanadium and chromium oxides complexed with acetonitrile form "magic number" cluster sizes which have been observed previously in the gas phase. However, tetrahydrofuran is shown to react with similar vanadium oxide clusters. Cobalt oxide is shown to prefer no particular cluster size by gas phase photodissociation experiments, although one stable size,  $Co_4O_4(MeCN)_6$ , is captured in solution. Acetonitrile coated aluminum clusters form a trimer in solution which exhibits interesting fluorescence.

INDEX WORDS: Laser Vaporization, Metal Oxide Clusters, Metal Clusters, Ligand Interactions, Nanoparticles, Physical Chemistry

# PRODUCTION AND ISOLATION OF LIGAND

# COATED NANOCLUSTERS

By

# COLLIN JOSEPH DIBBLE

B.S., University of Georgia, 2008

A Dissertation Submitted to the Graduate Faculty of the University of Georgia

in Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

©2013

Collin Joseph Dibble

All Rights Reserved

# PRODUCTION AND ISOLATION OF LIGAND

# COATED NANOCLUSTERS

By

# COLLIN JOSEPH DIBBLE

Major Professor: Michael A. Duncan

Committee:

John Stickney Gregory Robinson

Electronic Version Approved:

Maureen Grasso Dean of the Graduate School The University of Georgia August 2013

### DEDICATION

I dedicate this dissertation to my loving friends and family.

To my parents: Thank you for having the strength to say, "No," and wisdom to sometimes let me

fail. I am only very recently learning how hard this is. To my wife: Thank you for being everything I am not. Your hard work and attentiveness to every detail has facilitated my clumsy and rambling successes. To Nolan and Elsie: You are the light of my world. Thank you for teaching me what love truly is.

"All that is gold does not glitter, not all those who wander are lost; the old that is strong does not wither, deep roots are not reached by the frost. From the ashes a fire shall be woken, a light from the shadows shall spring; renewed shall be blade that was broken, the crownless again shall be

king."

- J.R.R. Tolkien, The Fellowship of the Ring

### ACKNOWLEDGEMENTS

My time under Mike Duncan has taught me many things. Firstly, that I should probably know what the ionization potential of helium is, as knowledge of this number is the key to passing a defense. Also, that a successful project is successful because the people who work on it are willing to pour their hearts and souls into it. Being clever doesn't hurt either. Mike, you have taught me so much over the years, both scientifically and personally. One of the most fortunate days of my life is the day I walked into your office, and you showed me how easy it is to sell a project to an idiot. You are an inspiration and I will always carry what I have learned in your lab in my head and in my heart.

I must also give thanks to my co-workers, especially those whose contributions have been instrumental to this dissertation. Without you this work would have not been possible. I could not have asked for better collaborators than Shaun Ard and Scott Akin. Learning from, and with them, has been a large part of my growth as a scientist. Most importantly though the entire Duncan group has kept my day to day entertaining. Wether I was laughing with you or at you, at least I was always laughing. My experience in the lab has been incredibly enjoyable, and it is something I will never forget.

A special thanks to all my other friends and family. Your support over the years has made me what I am today, and I could not be more grateful.

Last but not least, Robert Newton, you will ever be my boon companion. You have seen me through my darkest hour and never left my side.

# TABLE OF CONTENTS

Page

ACKNOWLEDGMENTSv		
CHAPTER		
	Ι	INTRODUCTION AND LITERATURE REVIEW
	II	EXPERIMENTAL SETUP
	III	SYNTHESIS AND ISOLATION OF VANADIUM OXIDE NANOCLUSTERS
		COMPLEXED TO ACETONITRILE OR TETRAHYDROFURAN <sup></sup>
	IV	SELECTIVE PRODUCTION OF LIGAND COATED Co <sub>4</sub> O <sub>4</sub> VIA
		A LASER VAPORIZATION FLOWTUBE REACTOR
	V	CAPTURING LIGAND COATED ANALOGUES
		OF STABLE GAS PHASE CHROMIUM OXIDE CLUSTERS
		IN SOLUTION
	VI	PRODUCTION AND ISOLATION OF LIGAND COATED
		ALUMINUM CLUSTERS USING A LASER
		VAPORIZATION FLOWTUBE REACTOR
	VII	CONCLUSIONS

### CHAPTER I

### INTRODUCTION AND LITERATURE REVIEW

Metal and metal oxide nanoparticles are an intense area of research due to their interesting size dependent properties. Indeed, the electronic, magnetic, and structural characteristics of these materials have been well studied. These properties allow them to play significant roles in catalysis, chemical sensors, fuel cells, magnetic materials and many other applications.<sup>1-15</sup> This dissertation focuses on the production and analysis of ligand coated metal and metal oxide sub-nano particles which occupy a size regime inaccessible by traditional techniques and which exhibit new and interesting properties.

Typical production techniques for nanoparticles include precipitation, micro-emulsions, micelle/reverse micelle, and sol-gel techniques.<sup>16-24</sup> These techniques have been successful in producing an incredible assortment of particles with limited size control. Gas phase synthesis techniques which utilize thermal plasmas, laser ablation and spark ablation coupled with condensation also exist.<sup>26-28</sup> Although solution and gas phase techniques can incorporate various materials they have only thus far been successful in producing particles in the size range of 1 - 10 nm. Significant challenges remain then, specifically, in the realm of very small clusters or sub-nanometer sized particles. Size dependent properties vary from bulk to particle, and so it is reasonable to suggest that particles on this small size scale (10 - 30 atoms) might have electronic structures, geometries and reactivities that change rapidly with size and are far different from the bulk. In gas phase molecular beams, clusters of this size have been produced by laser vaporization with great success. Gas phase experiments coupled with theoretical

calculation have given insight into some of their structures and reactivities.<sup>29-44</sup> Although much has beenlearned, to date most clusters made by molecular beams have remained in the gas phase and outside the realm of solution phase chemistry and its plethora of analytical tools. Furthermore, some cluster species have properties which cannot be determined through gas phase techniques alone. These include the structures of large metal oxides, which form particularly strong bonds. There then is a need not only to produce stable sub-nanometer sized clusters for their own sake, but also to gain further insight into clusters which are difficult to study in the gas phase.

By merging gas phase cluster growth with solution phase capture we have developed the laser vaporization flowtube reactor (LVFR) which can produce ultra-small coated nanoclusters. With this technique we are able to produce new materials which are analogous to clusters seen in the gas phase. The ligand coating of these clusters renders them soluble and stable at room temperature for several weeks. These clusters can be studied using standard techniques such as Fourier transform infrared spectroscopy (FT-IR) or surface enhanced Raman spectroscopy (SERS). These analytical techniques can elucidate the properties of these materials which were notoriously difficult to determine in gas phase experiments. In addition, other properties such as photoluminescence or catalytic activity can be measured. This project occupies the unexplored region between gas phase molecular beam experiments and solution phase nanoparticle synthesis techniques.

This work concentrates on the production of vanadium, cobalt and chromium oxides as well as pure metal aluminum sub-nanometer clusters. Gas phase studies on these systems have already been undertaken by our group and others.<sup>29-41</sup> We use the information gathered there to guide our initial interpretation which we then test with analytical methods. These methods

generally include: neat laser desorption ionization time-of-flight mass spectrometry (LDI ToF-MS), Fourier-transform infrared spectroscopy (FT-IR) and surfaced enhanced Raman spectroscopy (SERS). We also utilize density functional theory (DFT) computations to interpret our spectra and determine reasonable structures. These new materials also exhibit interesting luminescent properties which we investigate. More work is needed particularly in increasing the purity and concentration of these samples. Nevertheless, the LVFR has proven to be a powerful technique for the production of novel ultra-small materials.

# References

- 1. Schmid, G. Nanoparticles, Wiley-VCH, Weinhiem, 2004.
- 2. Johnson, R. L. Atomic and Molecular Clusters, Taylor & Francis, London, 2002.
- 3. Feldhiem, D. L.; Foss, C. A., Jr, Metal Nanoparticles, Marcel Dekker, New York, 2002.
- 4. Heiz, U.; Landman, U. Nanocatalysis, Springer, Berlin, 2007.
- 5. Aiken, J. D.; Finke, R. G. "A review of modern transition-metal nanoclusters: their synthesis, characterization, and applications in catalysis," *J. Mol. Catal. A: Chem.* **1999**, *145*, 1-44.
- 6. Kodama, R. H. "Magnetic nanoparticles," J. Magn. & Magn. Mater. 1999, 200, 359-372.
- a) Hill, C. L. "Introduction: Polyoxometalates Multicomponent molecular vehicles to probe fundamental issues and practical problems," *Chem. Rev.* 1998, 98, 1-2. b) Hill, C. L. "Special issue: Polyoxometalates in catalysis - Foreword," *J. Mol. Catal. A: Chem.* 2007, 262, 1-1.
- 8. Pope, M. T.; Müller, A. *Polyoxometalate Chemistry from Topology via Self -Assembly to Applications*, Kluwer, Boston, 2001.
- Schlögl, R.; Abd Hamid, S. B. "Nanocatalysis: Mature science revisited or something really new?" *Angew. Chem. Int. Ed.* 2004, 43, 1628-1637.
- Luo, X. L.; Morrin, A.; Killard, A. J.; Smyth, M. R. "Reagentless glucose biosensor based on the direct electrochemistry of glucose oxidase on carbon nanotube-modified electrodes," *Electroanalysis* 2006, 18, 1131-1134.
- Franke, M. E.; Koplin, T. J.; Simon, U. "Metal and metal oxide nanoparticles in chemiresistors: Does the nanoscale matter?" *Small* 2006, *2*, 36-50.
- Dorcioman, G.; Ebrasu, D.; Enculescu, I.; Serban, N.; Axente, E.; Sima, F.; Ristoscu, C.; Mihailescu, I. N. "Metal oxide nanoparticles synthesized by pulsed laser ablation for proton exchange membrane fuel cells," *J. Power Sources* 2010, *195*, 7776-7780.

- 13. Maeda, K.; Domen, K. "Photocatalytic water splitting: Recent progress and future challenges," *J. Phys. Chem. Lett.* **2010**, *1*, 2655-2661.
- 14. Joshi, U.; Palasyuk, A.; Arney, D.; Maggard, P. A. "Semiconducting oxides to facilitate the conversion of solar energy to chemical fuels," *J. Phys. Chem. Lett.* **2010**, *1*, 2719-2726.
- Patzke, G. R.; Zhou, Y.; Kontic, R.; Conrad, F. "Oxide nanomaterials: Synthetic developments, mechanistic studies, and technological innovations," *Angew. Chem. Int. Ed.* 2011, *50*, 826-859.
- 16. a) Rockenberger, J.; Scher, E. C.; Alivisatos, A. P." A new nonhydrolytic single-precursor approach to surfactant-capped nanocrystals of transition metal oxides," J. Am. Chem. Soc. 1999, 121, 11595-11596. b) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. "Formation of hollow nanocrystals through the nanoscale Kirkendall Effect," Science 2004, 304, 711-714. d) Casula, M. F.; Jun, Y. W.; Zaziski, D. J.; Chan, E. M.; Corrias, A.; Alivisatos, A. P. "Faceting of nanocrystals during chemical transformation: From solid silver spheres to hollow gold octahedra," J. Am. Chem. Soc. 2006, 128, 12671-12673. f) Cabot, A.; Puntes, V. F.; Shevchenko, E. V.; Yin, Y.; Balcells, L.; Marcus, M. A.; Hughes, S. M.; Alivisatos, A. P. "Vacancy coalescence during oxidation of iron nanoparticles," J. Am. Chem. Soc. 2007, 129, 10358-10360. g) Liu, H. T.; Owen, J. S.; Alivisatos, A. P. "Mechanistic study of precursor evolution in colloidal group II-VI semiconductor nanocrystal synthesis," J. Am. Chem. Soc. 2007, 129, 305-312. h) Shevchenko, E. V.; Bodnarchuk, M. I.; Kovalenko, M. V.; Talapin, D. V.; Smith, R. K.; Aloni, S.; Heiss, W.; Alivisatos, A. P. "Photodeposition of Pt on colloidal CdS and CdSe/CdS semiconductor nanostructures," Adv. Mater. 2008, 20, 4306-4311. i) Cabot, A.; Alivisatos, A. P.; Puntes, V. F.; Balcells, L.; Iglesias, O.; Labarta, A. "Magnetic domains and

surface effects in hollow maghemite nanoparticles," *Phys. Rev. B* **2009**, *79*, 094419/1-7. j) Ma, W.; Swisher, S. L.; Ewers, T.; Engel, J.; Ferry, V. E.; Atwater, H. A.; Alivisatos, A. P. "Photovoltaic performance of ultrasmall PbSe quantum dots," *ACS Nano* **2011**, *5*, 8140-8147. k) Iablokov, V.; Beaumont, S. K.; Alayoglu, S.; Pushkarev, V. V.; Specht, C.; Gao, J.; Alivisatos, A. P.; Kruse, N.; Somorjai, G. A. "Size-controlled model Co nanoparticle catalysts for CO<sub>2</sub> hydrogenation: synthesis, characterization, and catalytic reactions," *Nano Lett.* **2012**, *12*, 3091-3096.

- 17. Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. "Recent advances in the liquid-phase syntheses of inorganic nanoparticles," *Chem. Rev.* **2004**, *104*, 3893-3946.
- 18. a) Tang, J.; Redl, F.; Zhu, Y.; Siegrist, T.; Brus, L. E.; Steigerwald, M. L. "An organometallic synthesis of TiO<sub>2</sub> nanoparticles," *Nano Lett.* 2005, *5*, 543-548. b) Blagojevic, V. A.; Carlo, J. P.; Brus, L. E.; Steigerwald, M. L.; Uemura, Y. J.; Billinge, S. J. L.; Zhou, W.; Stephens, P. W.; Aczel, A. A.; Luke, G. M. "Magnetic phase transition in V<sub>2</sub>O<sub>3</sub> nanocrystals," *Phys. Rev. B* 2010, *82*, 094453/1-6.
- 19. a) Lim, J.-K.; Tilton, R. D.; Eggeman, A.; Majetich, S. A. "Design and synthesis of plasmonic magnetic nanoparticles," *J. Magn. & Magn. Mater.* 2007, *311*, 78-83. b) Lim, J.-K.; Majetich, S. A.; Tilton, R. D. "Stabilization of superparamagnetic iron oxide core-gold shell nanoparticles in high ionic strength media," *Langmuir* 2009, *25*, 13384-13393. c) Majetich, S. A.; Wen, T.; Booth, R. A. "Functional magnetic nanoparticle assemblies: formation, collective behavior, and future directions," *ACS Nano* 2011, *5*, 6081-6084.
- Chaudret, B.; Philippot, K. "Organometallic nanoparticles of metals or metal oxides," *Oil Gas Sci. Technol.* 2007, 62, 799-817.
- 21. Rao, C. N. R.; Vivekchand, S. R. C.; Biswasa, K.; Govindaraja, A. "Synthesis of inorganic

nanomaterials," Dalton Trans. 2007, 34, 3728-3749.

- Kwon, S. G.; Hyeon, T. "Colloidal chemical synthesis and formation kinetics of uniformly sized nanocrystals of metals, oxides, and chalcogenides," *Acc. Chem. Res.* 2008, *41*, 1696-1709.
- 23. Gvishi, R. "Fast sol-gel technology: from fabrication to applications," J. Sol-Gel Sci. Technol. 2009, 50, 241-253.
- 24. Wang, D. S.; Xie, T.; Li, Y. D. "Nanocrystals: Solution-based synthesis and applications as nanocatalysts," *Nano Res.* **2009**, *2*, 30-46.
- 25. a) Bowles, R. S.; Kolstad, J. J.; Calo, J. M.; Andres, R. P. "Generation of molecular clusters of controlled size," *Surf. Sci.* 1981, *106*, 117-124. b) Chao, L. C.; Andres, R. P. "Synthesis of a supported metal catalyst using nanometer-size clusters," *J. Colloid Interface Sci.* 1994, *165*, 290-295. c) Mahoney, W.; Andres, R.P. "Aerosol synthesis of nanoscale clusters using atmospheric arc evaporation," *Mater. Sci. Eng. A* 1995, *204*, 160-164.
- 26. a) El-Shall, M. S.; Slack, W.; Vann, W.; Kane, D.; Hanley, D. "Synthesis of nanoscale metal-oxide particles using laser vaporization condensation in a diffusion cloud chamber," *J. Phys. Chem.* 1994, 98, 3067-3070. b) El-Shall, M. S.; Graiver, D.; Pernisz, U.; Baraton, M. I.
  "Synthesis and characterization of nanoscale zinc oxide particles. 1. Laser vaporization condensation technique," *Nanostruct. Mater.* 1995, *6*, 297-300.
- 27. Flagan, R. C.; Lunden, M. M. "Particle structure control in nanoparticle synthesis from the vapor phase," *Mat. Sci. Eng. A-Struct.* **1995**, *204*, 113-124.
- Malekzadeh, M.; Halali, M. "Production of silver nanoparticles by electromagnetic levitation gas condensation," *Chem. Eng. J.* 2011, *168*, 441-445.
- 29. Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. "Laser production of supersonic

metal cluster beams," J. Chem. Phys. 1981, 74, 6511-6512.

30. a) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W. "Thermal metal cluster anion reactions behavior of aluminum clusters with oxygen," J. Chem. Phys. 1989, 91, 2753-2754. b) Bell, R. C.; Zemski, K. A.; Kerns, K. P.; Deng, H. T.; Castleman, A. W., Jr. "Reactivities and collision-induced dissociation of vanadium oxide cluster cations," J. Phys. Chem. A 1998, 102, 1733-1742. c) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. "From molecules to materials: Current trends and future directions," Adv. Mater. 1998, 10, 1297-1336. d) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W. "Aluminum cluster reactions," J. Chem. Phys. 1991, 94, 1093-1101. e) Kooi, S. E.; Castleman, A. W., Jr. "Photofragmentation of vanadium oxide cations," J. Phys. Chem. A **1999**, 103, 5671-5674. f) Bell, R. C.; Zemski, K. A.; Castleman, A. W., Jr. "Size-specific reactivities of vanadium oxide cluster cations," J. Cluster Sci. 1999, 10, 509-524. g) Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. "Reactions of group V transition metal oxide cluster ions with ethane and ethylene," J. Phys. Chem. A 2001, 105, 10237-10245. h) Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. "Studies of metal oxide clusters: Elucidating reactive sites responsible for the activity of transition metal oxide catalysts," J. *Phys. Chem. B* **2002**, *106*, 6136-6148. i) Justes, D. R.; Moore, N. A.; Castleman, A. W., Jr. "Reactions of vanadium and niobium oxides with methanol," J. Phys. Chem. B 2004, 108, 3855-3862. j) Bergeron, D. E.; Castleman, A. W.; Morisato, T.; Khanna, S. N. "Formation of A<sub>13</sub>31<sup>-</sup>: Evidence for the superhalogen character of Al<sub>13</sub>," Science **2004**, 304, 84-87. k) Moore, N. A.; Mitric, R.; Justes, D. R.; Bonačić-Koutecký, V.; Castleman, A. W., Jr. "Kinetic analysis of the reaction between  $(V_2O_5)_{n=1,2}^+$  and ethylene," J. Phys. Chem. B 2006,

*110*, 3015-3022. 1) Castleman, A. W., Jr.; Khanna, S. N. "Clusters, superatoms, and building blocks of new materials," *J. Phys. Chem. C.* 2009, *113*, 2664-2675. m) Roach, P. J.;
Woodward, W. H.; Castleman, A. W., Jr.; Reber, A. C.; Khanna, S. N. "Complementary active sites cause size-selective reactivity of aluminum cluster anions with water," *Science* 2009, *323*, 492-495. n) Castleman, A. W., Jr. "Cluster structure and reactions: gaining insights into catalytic processes," *Catal. Lett.* 2011, *141*, 1243-1253. o)
Ross, M. W.; Castleman, A. W., Jr. "Ionization and Coulomb explosion of small group 10 transition metal oxide clusters in strong light fields," *J. Chem. Phys.* 2012, *137*, 084307/1-7.

31. a) Foltin, M.; Stueber, G. J.; Bernstein, E. R. "On the growth dynamics of neutral vanadium oxide and titanium oxide clusters," J. Chem. Phys. 1999, 111, 9577-9586. b) Foltin, M.; Stueber, G. J.; Bernstein, E. R. "Investigation of the structure, stability, and ionization dynamics of zirconium oxide clusters," J. Chem. Phys. 2001, 114, 8971-8989. c) Matsuda, Y.; Bernstein, E. R. "On the titanium oxide neutral cluster distribution in the gas phase: Detection through 118 nm single-photon and 193 nm multiphoton ionization," J. Phys. Chem. A 2005, 109, 314-319. d) Dong, F.; Heinbuch, S.; He, S. G.; Xie, Y.; Rocca, J. J.; Bernstein, E. R. "Formation and distribution of neutral vanadium, niobium, and tantalum oxide clusters: Single photon ionization at 26.5 eV," J. Chem. Phys. 2006, 125, 164318/1-8. e) Jakubikova, E.; Rappe, A. K.; Bernstein, E. R. "Density functional theory study of small vanadium oxide clusters," J. Phys. Chem. A 2007, 111, 12938-12943. f) Dong, F.; Heinbuch, S.; Xie, Y.; Rocca, J. J.; Bernstein, E. R. "Reactions of neutral vanadium oxide clusters with methanol," J. Phys. Chem. A 2009, 113, 3029-3040. f) Heinbuch, S.; Dong, F.; Rocca, J. J.; Bernstein, E. R. "Experimental and theoretical studies of reactions of neutral vanadium and tantalum oxide clusters with NO and NH<sub>3</sub>," J. Chem. Phys. 2010, 133, 174314/1-11. g) Xie,

Y.; Dong, F.; Heinbuch, S.; Rocca, J. J.; Bernstein, E. R. "Oxidation reactions on neutral cobalt oxide clusters: experimental and theoretical studies," *Phys. Chem. Chem. Phys.* 2010, *12*, 947-959. h) Yin, S.; Bernstein, E. R. "Gas phase chemistry of neutral metal clusters: Distribution, reactivity and catalysis," *Int. J. Mass. Spectrom.* 2012, *321*, 49-65.

- 32. a) Engeser, M.; Weiske, T.; Schröder, D.; Schwarz, H. "Gas-phase solvation behavior of Ni(II) in water/N,N-dimethylformamide mixtures," *J. Phys. Chem. A* 2003, *107*, 9575-9581.
  b) Feyel, S.; Schröder, D.; Rozanska, X.; Sauer, J.; Schwarz, H. "Gas-phase oxidation of propane and 1-butene with V<sub>3</sub>O<sub>7</sub><sup>+</sup>: Experiment and theory in concert," *Angew. Chem. Int. Ed.* 2006, *45*, 4677-4681. c) Feyel, S.; Schröder, D.; Schwarz, H. "Gas-phase chemistry of vanadium oxide cluster cations V<sub>m</sub>O<sub>n</sub><sup>+</sup> (m=1-4; n=1-10) with water and molecular oxygen," *Eur. J. Inorg. Chem.* 2008, *31*, 4961-4967. d) Feyel, S.; Schröder, D.; Schwarz, H. "Pronounced cluster-size effects: gas-phase reactivity of bare vanadium cluster cations V<sub>n</sub><sup>+</sup> (n=1-7) toward methanol," *J. Phys. Chem. A* 2009, *113*, 5625-5632. e) Dietl, N.; Engeser, M.; Schwarz, H. "Competitive hydrogen-atom abstraction versus oxygen-atom and electron transfers in gas-phase reactions of X<sub>4</sub>O<sub>10</sub><sup>+</sup> (x = P, V) with C<sub>2</sub>H<sub>4</sub>," *Chem.-Eur J.* 2010, *16*, 4452-4456.
- 33. a) Willey, K. F.; Robbins, D. L.; Yeh, C. S.; Duncan, M. A. "Laser photodissociation spectroscopy of mass-selected metal-clusters," *Faraday Discuss.* 1991, *92*, 269-277. b) Van Heijnsbergen, D.; von Helden, G.; Meijer, G.; Duncan, M. A., "Infrared resonance-enhanced multiphoton ionization spectroscopy of magnesium oxide clusters," *J. Chem. Phys.* 2002, *116*, 2400-2406. c) Van Heijnsbergen, D.; Demyk, K.; Duncan, M. A.; Meijer, G.; von Helden, G., "Structure determination of gas phase aluminum oxide clusters," *Phys. Chem. Chem. Phys.* 2003, *5*, 2515-2519. d) Molek, K. S.; Jaeger, T. D.; Duncan, M. A.

"Photodissociation of vanadium, niobium, and tantalum oxide cluster cations," *J. Chem. Phys.* 2005, *123*, 144313/1-10. e) Molek, K. S.; Reed, Z. D.; Ricks, A. M.; Duncan, M. A.
"Photodissociation of chromium oxide cluster cations," *J. Phys. Chem. A* 2007, *111*, 8080-8089. f) Reed, Z. D.; Duncan, M. A. "Photodissociation of yttrium and lanthanum oxide cluster cations," *J. Phys. Chem. A* 2008, *112*, 5354-5362. g) Molek, K. S.; Anfuso-Cleary, C.; Duncan, M. A. "Photodissociation of iron oxide cluster cations," *J. Phys. Chem. A* 2008, *112*, 9238-9247. h) Knight, A. M.; Bandyopadhyay, B.; Anfuso, C. L.; Molek, K. S.; Duncan, M. A., "Photodissociation of indium oxide cluster cations," *Int. J. Mass Spectrom.* 2011, *304*, 29-35. i) Dibble, C. J.; Akin, S. T.; Ard, S.; Fowler, C. P.; Duncan, M. A., "Photodissociation of cobalt and nickel oxide cluster cations," *J. Phys. Chem.* A 2012, *116*, 5398-5404.

- 34. Fielicke, A.; Rademann, K. "Stability and reactivity patterns of medium-sized vanadium oxide cluster cations  $V_x O_y^+$  ( $4 \ge x \ge 14$ )," *Phys. Chem. Chem. Phys.* **2002**, *4*, 2621-2628.
- 35. a) Xu, J.; Rodgers, M. T.; Griffin, J. B.; Armentrout, P. B. "Guided ion beam studies of the reactions of V<sub>n</sub><sup>+</sup> (n=2-17) with O<sub>2</sub>: Bond energies and dissociation pathways," *J Chem. Phys* 1998, *108*, 9339-9350. b) Armentrout, P. B. "Guided ion beam studies of transition metal-ligand thermochemistry," *Int. J. Mass Spectrom.* 2003, *227*, 289-302. c) Liu, F. Y.; Li, F. X.; Vardhan, D.; Liyanage, R.; Armentrout, P. B. "Guided ion beam studies of the reactions of Ni<sub>n</sub><sup>+</sup> (n=2-18) with O<sub>2</sub>: Nickel cluster oxide and dioxide bond energies," *J. Chem. Phys.* 2003, *119*, 4166-4178. d) Armentrout, P. B. "Guided ion-beam studies of the reactions of Co<sub>n</sub><sup>+</sup> (n=2-20) with O<sub>2</sub>: Cobalt cluster-oxide and -dioxide bond energies. *J. Chem. Phys.* 2005, *123*, 064304/1-15. e) Hinton, C. S.; Li, F.; Armentrout, P. B. "Reactions of Hf<sup>+</sup>, Ta<sup>+</sup>, and W<sup>+</sup> with O<sub>2</sub> and CO: Metal carbide and metal oxide cation bond

energies," *Int. J. Mass Spectrom.* **2009**, *280*, 226-234. f) Li, M.; Liu, S.-R.; Armentrout, P. B. "Collision-induced dissociation studies of  $\text{Fe}_{m}O_{n}^{+}$ : Bond energies in small iron oxide cluster cations,  $\text{Fe}_{m}O_{n}^{+}$ , (m=1-3, n=1-6)," *J. Chem. Phys.* **2009**, *131*, 144310/1-16.

- 36. a) Wang, L.-S.; Wu, H.; Desai, S. R.; Lou, L. "Electronic structure of small copper oxide clusters: From Cu<sub>2</sub>O to Cu<sub>2</sub>O<sub>4</sub>," Phys. Rev. B 1996, 53, 8028-8031. b) Gutsev, G. L.; Rao, B. K.; Jena, P.; Li, X.; Wang, L.-S. "Experimental and theoretical study of the photoelectron spectra of M<sub>n</sub>O<sub>x</sub><sup>-</sup>(x=1-3) clusters," J. Chem. Phys. 2000, 113, 1473-1483. c) Zhai, H. J.; Wang, L.-S. "Electronic structure and chemical bonding of divanadium-oxide clusters (V<sub>2</sub>O<sub>x</sub>, x=3-7) from anion photoelectron spectroscopy," J. Chem. Phys. 2002, 117, 7882-7888. d) Gutsev, G. L.; Bauschlicher, C. W., Jr.; Zhai, H. J.; Wang, L.-S. "Structural and electronic properties of iron monoxide clusters  $Fe_nO$  and  $Fe_nO^-$  (n=2-6): A combined photoelectron spectroscopy and density functional theory study," J. Chem. Phys. 2003, 119, 11135-11145. e) Zhai, H. J.; Huang, X.; Cui, L. F.; Li, X.; Li, J.; Wang, L.-S. "Electronic and structural evolution and chemical bonding in ditungsten oxide clusters:  $W_2O_n^-$  and  $W_2O_n^-$  (n=1-6)," J. Phys. Chem. A 2005, 109, 6019-6030. f) Zhai, H.-J.; Wang, L.-S. "Probing the electronic structure of early transition metal oxide clusters: Molecular models towards mechanistic insights into oxide surfaces and catalysis," Chem. Phys. Lett. 2010, 500, 185-195. g) Li, S.; Zhai, H.-J.; Wang, L.-S.; Dixon, D. A. "Structural and electronic properties of reduced transition metal oxide clusters,  $M_4O_{10}$  and  $M_4O_{10}$  (M = Cr, W), from photoelectron spectroscopy and quantum chemical calculations," J. Phys. Chem. A 2012, 116, 5256-5271.
- 37. Green, S. M. E.; Alex, S.; Fleischer, N. L.; Millam, E. L.; Marcy, T. P.; Leopold, D. G.
  "Negative ion photoelectron spectroscopy of the group 5 metal trimer monoxides V<sub>3</sub>O,
  Nb<sub>3</sub>O, and Ta<sub>3</sub>O," *J. Chem. Phys.* 2001, *114*, 2653-2668.

- 38. a) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Photoelectron spectroscopy of yttrium oxide cluster anions: Effects of oxygen and metal atom addition," *J. Phys. Chem. A.* 2001, *105*, 7534-7540. b) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Photoelectron spectroscopy of cobalt oxide cluster anions," *J. Phys. Chem. A* 2002, *106*, 4891-4896. c) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Anion photoelectron spectroscopy of V<sub>n</sub>O<sub>m</sub><sup>-</sup> (n=4-15; m=0-2)," *J. Chem. Phys.* 2002, *116*, 6521-6528.
- 39. a) Shiroishi, H.; Oda, T.; Hamada, I.; Fujima, N.; "Structure and magnetism on iron oxide clusters Fe<sub>n</sub>O<sub>m</sub> (n=1-5): Calculation from first principles," *Eur. Phys. J. D* 2003, *24*, 85-88.
  b) H Shiroishi, H.; Oda, T.; Hamada, I.; Fujima, N.; "Structure and magnetism on anion iron oxide clusters Fe<sub>n</sub>O<sub>m</sub><sup>-</sup> (n=1-2)," *Molec. Sim.* 2004, *30*, 911-915. c) Shiroishi, H.; Oda, T.; Hamada, I.; Fujima, N.; "Structure and magnetism of anion iron oxide clusters, Fe<sub>n</sub>O<sub>m</sub><sup>-</sup> (n = 3,4)," *Polyhedron* 2005, *24*, 2472-2476.
- 40. a) Fielicke, A.; Meijer, G.; von Helden, G. "Infrared spectroscopy of niobium oxide cluster cations in a molecular beam: Identifying the cluster structures," *J. Am. Chem. Soc.* 2003, *125*, 3659-3667. b) Fielicke, A.; Meijer, G.; von Helden, G. "Infrared multiple photon dissociation spectroscopy of transition metal oxide cluster cations Comparison of group Vb (V, Nb, Ta) metal oxide clusters," *Eur. Phys. J. D* 2003, *24*, 69-72. c) Von Helden, G.; van Heijnsbergen, D.; Meijer, G. "Resonant ionization using IR light: A new tool to study the spectroscopy and dynamics of gas-phase molecules and clusters." *J. Phys. Chem. A* 2003, *107*, 1671-1688.
- 41. a) Asmis, K. R.; Meijer, G.; Brümmer, M.; Kaposta, C.; Santambrogio, G.; Wöste, L.; Sauer, J. "Gas phase infrared spectroscopy of mono- and divanadium oxide cluster cations," *J. Chem. Phys.* 2004, *120*, 6461-6470. b) Asmis, K. R.; Sauer, J. "Mass-selective vibrational

spectroscopy of vanadium oxide cluster ions," *Mass Spectrom. Rev.* 2007, 26, 542-562. c)
Feyel, S.; Schwarz, H.; Schröder, D.; Daniel, C.; Hartl, H.; Dobler, J.; Sauer, J.;
Santambrogio, G.; Wöste, L.; Asmis, K. R. "Gas-phase infrared photodissociation
spectroscopy of tetravanadiumoxo and oxo-methoxo cluster anions," *ChemPhysChem* 2007, 8, 1640-1647. d) Santambrogio, G.; Brümmer, M.; Wöste, L.;
Dobler, J.; Sierka, M.; Sauer, J.; Meijer, G.; Asmis, K. R. "Gas phase vibrational
spectroscopy of mass-selected vanadium oxide anions," *Phys. Chem. Chem. Phys.* 2008, 10,
3992-4005. e) Asmis, K. R.; Sauer, J. "Mass-selective vibrational spectroscopy of vanadium
oxide cluster ions (vol 26, pg 542, 2007)," *Mass Spectrom. Rev.* 2008, 27, 205-205. f) Asmis,
K. R. "Structure characterization of metal oxide clusters by vibrational spectroscopy:
possibilities and prospects," *Phys. Chem. Chem. Phys.* 2012, 14, 9270-9281. g) Asmis, K. R.;
Wende, T.; Bruemmer, M.; Gause, O.; Santambrogio, G.; Stanca-Kaposta, E. C.; Doebler, J.;
Niedziela, A.; Sauer, J. "Structural variability in transition metal oxide clusters: gas phase
vibrational spectroscopy of V<sub>3</sub>O<sub>6-8</sub><sup>+</sup>," *Phys. Chem. Chem. Phys.* 2012, 14, 9377-9388.

- 42. Yoder, B. L.; Maze, J. T.; Raghavachari, K.; Jarrold, C. C. "Structures of Mo<sub>2</sub>O<sub>y</sub><sup>-</sup> and Mo<sub>2</sub>O<sub>y</sub> (y=2, 3, and 4) studied by anion photoelectron spectroscopy and density functional theory calculations," *J. Chem. Phys.* 2005, *122*, 094313/1-9.
- 43. a) Veliah, S.; Xiang, K. H.; Pandey, R.; Recio, J. M.; Newsam, J. M. "Density functional study of chromium oxide clusters: Structures, bonding, vibrations, and stability," *J. Phys. Chem. B* 1998, *102*, 1126-1135. b) Xiang, K. H.; Pandey, R.; Recio, J. M.; Francisco, E.; Newsam, J. M. "A theoretical study of the cluster vibrations in Cr<sub>2</sub>O<sub>2</sub>,Cr<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>4</sub>," *J. Phys. Chem. A* 2000, *104*, 990-994.

- 44. a) Reddy, B. V.; Khanna, S. N. "Chemically induced oscillatory exchange coupling in chromium oxide clusters," *Phys. Rev. Lett.* 1999, *83*, 3170-3173. b) Jones, N. O.; Reddy, B. V.; Rasouli, F.; Khanna, S. N. "Structural growth in iron oxide clusters: Rings, towers, and hollow drums," *Phys. Rev. B* 2005, *72*, 165411. c) Jones, N. O.; Reddy, B. V.; Rasouli, F.; Khanna, S. N. "Errata: Structural growth in iron oxide clusters: Rings, towers, and hollow drums," *Phys. Rev. B* 2006, *73*, 119901.
- 45. a) Calatayud, M.; Andres, J.; Beltran, A. "A systematic density functional. theory study of V<sub>x</sub>O<sub>y</sub><sup>+</sup> and V<sub>x</sub>O<sub>y</sub> (X=2-4, Y=2-10) systems," *J. Phys. Chem. A* 2001, *105*, 9760-9775. b) Calatayud, M.; Berski, S.; Beltran, A.; Andres, J. "An atom-in-molecules and electron-localization-function study of the interaction between O<sub>2</sub> and V<sub>x</sub>O<sub>y</sub><sup>+</sup>/V<sub>x</sub>O<sub>y</sub> (x=1, 2, y=1-5) clusters," *Theor. Chem. Acc.* 2002, *108*, 12-20.

# CHAPTER II

### EXPERIMENTAL SETUP

Ligand coated clusters are produced in a home-made apparatus called the Laser Vaporization Flowtube Reactor (LVFR). This device is based on the design of Andres and coworkers,<sup>1</sup> and has been described in detail previously.<sup>2</sup> Whereas Andres used an oven source for gold, we employ laser vaporization which is more general for all metals. This allows the LVFR to produce a wide variety of coated clusters, which are easily reproduced and have some degree of size selectivity.

Figure 2.1 and Figure 2.2 show the schematic of the LVFR in the straight or bent configurations, respectively. Clusters material can be grown in either, thought we find that the straight configuration produces higher yields. The apparatus consists of three parts: the laser vaporization source, the ligand interaction region and a liquid nitrogen cooled trap. In the source region a rotating metal rod is ablated by a laser to create a plasma which is entrained in a flow of carrier and reactant gases. This creates small metal containing particles similar to those produced in traditional gas phase molecular beam studies. Our source employs a Lambda Physik Compex 110 KrF excimer laser (248 nm). Powerful laser pulses (60 - 250 mJ/pulse, spot size of 1 x 12 mm) at high repetition rates (50 - 100 Hz) are used to ablate a metal rod. Altering the carrier and reactant gas mixture can produce different materials. Metal oxides require a mixture of 5 - 10% oxygen in helium. We have also made vanadium carbide which can be made from 5% methane in helium. Pure metal clusters can be made in helium. Our reactant gas mixture is



Figure 2.1. Schematic of the laser vaporization flowtube reactor in the straight configuration.



Figure 2.2. Schematic diagram of the laser vaporization flowtube reactor in a bent configuration.

held at 30 psi and passed through a 750  $\mu$ m hole positioned 8 mm away from metal rod, resulting in a pressure of 2 – 5 torr in the flowtube. Clusters move down the flowtube into the second part of the apparatus, the ligand addition region, through a 13 mm aperture (aperture 1 in Figure 2.1). This aperture promotes collisional cooling of the clusters, and without this aperture little material is captured. The addition of ligands is important because they promote stability and solubility of our materials. Control experiments without ligands produce largely aggregate metal oxide soot. The most successful ligands we have employed are

MeCN and THF, although we have found THF sometimes reacts with the clusters. Propionitrile, pyridine and ethylenediamine have also been employed as ligands, but the materials produced using these surfactants tends to be viscous and non-homogenous which has made them impossible for us to characterize. We believe this to be due to back flow of the ligand into the source region where reactions can take place between the hot plasma and these larger ligand materials. After ligand coating, the clusters flow through a 7 mm aperture (aperture 2 in Figure 2.1) and into the final part of the apparatus, the liquid nitrogen trap, where they are captured. The system is evacuated by an Edwards E2M30 rotary vane mechanical pump to an ultimate pressure of  $1 \times 10^{-3}$  torr. Two additional liquid nitrogen traps are placed in between this pump and our collection trap in order to prevent back-streaming of oil into our sample and to protect the pump from organic solvents. The collection trap consists of a two-necked round bottom flask and what we call "the stem," which is a glass tube down the center of the flask to about 2 mm clearance at the bottom. The round bottom flask is filled to an approximate depth of 50 mm with 5 mm diameter glass beads. These beads and the stem increase the trapping efficiency by forcing the flow to encounter many cold surfaces. After run times of 3 - 6 hours, the collected material is largely ligand ice with some brown, yellow, black or gray (depending on the metal

being ablated) spots. The cold flask is removed from the instrument while still frozen and excess solvent (usually the same as the ligand) is poured over the beads so that they are completely submerged. After the collection flask warms to room temperature the beads are drained and the excess solvent is removed using a Buchi Rotovapor-R rotovap. We have also found that allowing the collection flask to soak overnight produces these same samples but with increased yields. The end product of this process is about 0.5 - 2 mL of colored solution. When completely dried the samples appear to be either film or powder on the microgram scale. These samples are usually stable over several weeks, not air sensitive, and soluble in solvents in which the ligand employed is miscible.

The first step in the characterization of these materials is neat laser desorption ionization time-of-flight mass spectrometry (LDI ToF-MS). A schematic of the home-made ToF-MS instrument used in this experiment can be seen in Figure 2.3. Mass analysis using any ToF instruments requires two things: ionization of the sample and separation of ions by their flight times. Desorption and Ionization of our samples is accomplished using a the second (532 nm) or third (355 nm) harmonic of a Nd:YAG laser (New Wave Research, Polaris II). The acceleration region of the mass spectrometer consists of a repeller plate typically held at a 15 kV bias (Glassman EL30) and a draw-out grid (DOG) at 8 – 10 kV (Bertan 205B-20R). An Einzel lens at 5 – 10 kV (Glassman EL20) is also employed to focus the accelerated ions, while a set of deflection plates at around 500 – 1000 V (Bertan 205A-03R) help to steer the ions toward the detector. The flight tube, which is approximately two meters long, is evacuated to 1 x 10<sup>-7</sup> torr by two Varian M4 diffusion pumps each back by an Edwards E2M28 mechanical pump. Ions are detected using an electron multiplier tube (EMT) (Hamamatsu R595) and the signal is amplified (Stanford Research Systems SR445A) before being collected using an oscilloscope



Figure 2.3 Schematic for the home-made LDI ToF-MS.

(LeCroy Waverunner LT342). Data is collected on a PC connected to the oscilloscope using an IEEE-488 digital card.

Sample preparation begins by drying the sample on a stainless steel probe tip. The probe tip is injected into the acceleration region of the mass spectrometer and rests in a hole in the repeller plate. A laser is then used to desorb/ionize the sample. The process by which a sample can absorb laser radiation, be desorbed/ablated from the surface of the probe and then ionized has been discussed in great detail, but is still not completely understood.<sup>3-6</sup> The likely explanation is that thermionic electrons are emitted from the sample/probe as it is heated by the laser. These electrons are then accelerated toward the positive repeller plate and impact the sample. The power of the laser must be finely adjusted so that the laser does not create clusters or fragments of the sample in the mass spectrometer and this is done by controlling the high voltage on the flash lamps of the laser as well as adjusting the focus (1 - 5 mm diameter). Also, careful control experiments must be done which involve comparing mass spectra of bulk materials on which our sample is based to the mass spectrum of the flowtube sample. For example, a sample of vanadium oxide clusters complexed with acetonitrile should be compared to a mass spectrum of bulk vanadium oxide suspended in acetonitrile. This is to ensure that the mass spectrum produced is a result of the LVFR and not a product of our laser desorption/ionization method.

Mass analysis takes place by using an electric field to accelerate the sample ions down a field-free flight tube. The velocity of these ions depends on their kinetic energy and there mass described by the following equation:

K.E. = 
$$\frac{1}{2}mv^2$$
 (Eq. 1)

All of the ions have equivalent kinetic energies (K.E.) since they all experience the same electric field. Thus more massive ions will move more slowly down the flight tube while lighter ions

will move more quickly. Theoretically determination of an ion's mass should be related to its arrival time. Unfortunately, this is not possible since the length of the flight tube is not known with sufficient accuracy. Also the K.E. of every ion is not known because we do not know where in the field ions are produced. Because of these uncertainties, we then relate the arrival times to mass by using two ions whose masses and arrival times are already known as calibrants. This is typically done with sodium (23 amu) and potassium (39 amu) ions which are always present in our mass spectra. To describe an unknown peak in the mass spectrum the following relationships can be used:

$$m_u v_u^2 = m_r v_r^2$$
 (Eq. 4)

$$m_u = m_r (t_u/t_r)^2 \qquad \qquad (Eq. 5)$$

where  $m_r$  is the known mass,  $m_u$  is the unknown mass and  $t_r$  and  $t_u$  are their flight times, respectively. A typical mass spectrum taken by this instrument can be seen in Figure 2.4.

After the samples have been analyzed by mass, and the composition of our captured particles is hypothesized, we test this hypothesis first using vibrational spectroscopy. This is done using either Fourier transform infrared (FT-IR) or surface enhanced Raman (SERS) spectroscopies. For FT-IR a commercial instrument is used (Digilab FTS 7000). The sample is dried and about 1 mg is pressed into a pellet of KBr. This pellet is placed into a nitrogen purged chamber and the signal is collected using a liquid nitrogen cooled detector. Although FT-IR measurements are simple to make, we find that for most samples SERS performs much better than FT-IR. For SERS spectra, we place a drop of the sample onto a film of Ag nanorods. These films are produced by the Dluhy group and the method for their production has been described previously.<sup>7</sup> The enhance the Raman signal of our samples greatly, and we are able to use small amounts (< 1  $\mu$ g) to collect these spectra. Once the film has dried we place



Figure 2.4. Typical mass spectrum of vanadium oxide coated with acetonitrile.

it in a commercial instrument (Renishaw InVia Raman Microscope) to take the spectrum. A 785 nm diode laser is used to excite the sample in these experiments. Use of a low energy per photon laser is required in order to prevent fluorescence of the sample from interfering with the Raman signal. Our spectroscopic data is then compared to theoretical spectra we compute using DFT via the Gaussian 09 program.<sup>8</sup> The functional we prefer is BP86, as we find that this non-hybridized functional performs well with large clusters with several ligands. The more common hybridized functional B3LYP has been employed on small clusters and gives roughly the same results as BP86, but computations using B3LYP struggle to converge with larger clusters. The TZVP basis set we use was developed by Ahlrichs et al. and is commonly employed for metal oxides.<sup>9</sup>

Further characterization is done with solution phase UV-visible absorption spectroscopy. To measure these spectra, we dissolve 0.1 - 1 mg of sample in to one or more solvents (usually the solvent is the same as the ligand) and place it in a 1 cm cuvette. These spectra are collected using a Shimadzu UV-2401 PC spectrometer. We also measure the fluorescence emission spectra of these samples using a SPEX Fluorolog 1692T. The fluorescence lifetimes are measured using a simple home-made apparatus (see Figure 2.5) which uses the second (355 nm) or third (532 nm) harmonic of a Nd:YAG laser (New Wave Research, Polaris II) to excite the sample and detects emission with a photomultiplier tube (PMT). This signal is collected as a function of time by an oscilloscope (LeCroy Waverunner LT262).

In addition to mass and spectroscopic analysis, purification methods are also being explored. In order to separate different size clusters in solution, we have employed high purity

liquid chromatography (HPLC) (Thermo Scientific SpectraSYSTEM). Some success has been achieved using a C18 column, and further investigations are underway using liquid chromatography-mass spectrometry.



Figure 2.5. Apparatus for fluorescence life time measurements. Second (355 nm) or thrid (532 nm) harmonic of a Nd:YAG laser used to excite the sample. Emission measured by a photomultiplier tube (PMT) and collected as a function of time by an oscilloscope

# References

- a) Bowles, R. S.; Kolstad, J. J.; Calo, J. M.; Andres, R. P. "Generation of molecular clusters of controlled size," *Surf. Sci.* 1981, *106*, 117-124. b) Chao, L. C.; Andres, R. P. "Synthesis of a supported metal catalyst using nanometer-size clusters," *J. Colloid Interface Sci.* 1994, *165*, 290-295. c) Mahoney, W.; Andres, R.P. "Aerosol synthesis of nanoscale clusters using atmospheric arc evaporation," *Mater. Sci. Eng. A* 1995, *204*, 160-164.
- a) Ayers, T. M.; Fye, J. L.; Li, Q.; Duncan, M. A., "Synthesis and isolation of titanium metal cluster complexes and ligand-coated nanoparticles with a laser vaporization flowtube reactor," *J. Clust. Sci.* 2003, *14*, 97-113. b) Ard, S.; Dibble, C. J.; Akin, S. T.; Duncan, M. A. "Ligand-coated vanadium oxide clusters: capturing gas-phase magic numbers in solution," *J. Phys. Chem. C* 2011, *115*, 6438-6447.
- Honig, R. E.; Woolston, R.J. "Laser induced emission of electrons, ions, and neutral atoms from solid surfaces," *Appl. Phys. Lett.* 1963, 2, 138-141.
- Fenner, N. C.; Daly, N. R. "Laser used for mass analysis," *Rev. Sci. Instrum.* 1966, 37, 1068-1072.
- Hillenkamp, F.; Kaufmann, R.; Nitche, R.; Unsöld, E. "Laser microprobe mass analysis of organic materials," *Nature* 1975, 57, 2935-2939.
- Hillenkamp, F.; Peter-Katalinic, J. MALDI MS: A Practical Guide to Instrumentation Methods and Applications, Wiley-VCH, Weinheim, 2007.
- 7. a) Chaney, S. B.; Shanmukh, S.; Dluhy, R. A.; Zhao, Y. P. "Aligned silver nanorod arrays produce high sensitivity surface-enhanced Raman spectroscopy substrates," *Appl. Phys. Lett.* 2005, *87*, 031908/1-3. b) Leverette, C. L.; Jacobs, S. A.; Shanmukh, S.; Chaney, S. B.; Dluhy, R. A.; Zhao, Y. P. "Aligned silver nanorod arrays as substrates for surface-enhanced

infrared absorption spectroscopy," *Appl. Spectrosc.* **2006**, *60*, 906-913. c) Negri, P.; Marotta, N. E.; Bottomley, L. A.; Dluhy, R. A. "Removal of Surface Contamination and Self-Assembled Monolayers (SAMs) from Silver (Ag) Nanorod Substrates by Plasma Cleaning with Argon," *Appl. Spectrosc.* **2011**, *65*, 66-74.

- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2009.
- 9. Schafer, A.; Huber, C.; Ahlrichs, R. "Fully optimized contracted Gaussian-basis sets of triple zeta valence quality for atoms Li to Kr," *J. Chem. Phys.* **1994**, *100*, 5829-5835.
#### CHAPTER III

# SYNTHESIS AND ISOLATION OF VANADIUM OXIDE NANOCLUSTERS COMPLEXED TO ACETONITRILE OR TETRAHYDROFURAN

## Introduction

The properties of transition metal oxide nanoparticles allow them to play significant roles in catalysis, chemical sensors, fuel cells, magnetic materials and many other applications.<sup>1-15</sup> Typical particles (> 1 nm diameter) are commonly synthesized using solution phase methods including precipitation, micro-emulsions, micelle/reverse micelle, and sol-gel techniques.<sup>16-24</sup> These methods yield oxide nanoparticles from a variety of metals, including notably, the family of vanadium polyoxometalates (POMs).<sup>8,9</sup> Gas phase production of small particles has also been successful.<sup>25</sup> Laser vaporization<sup>26</sup> can produce gas phase metal oxides clusters in the subnanometer range, whose properties have been studied extensively with experimet<sup>27-39</sup> and theory.<sup>40-42</sup> However, these small clusters have been produced and studied only in the gas phase. To bring gas phase clusters into the condensed phase where they can be manipulated more easily, we have developed the Laser Vaporization Flow Reactor (LVFR).<sup>43</sup> Here, we investigate the chemistry by which sub-nanometer vanadium oxide clusters can be captured from the gas phase into solution, and the compositions and structures that result.

Vanadium oxide nanoparticles have been studied extensively on surfaces, in solution and in the gas phase. They are ubiquitous in POMs<sup>8,9,44-47</sup> and are often used as supported catalysts in industrial processes.<sup>48,49</sup> The mass spectra of positive and negative cluster ions, <sup>27,31,32</sup> as well

as photoionized neutrals,<sup>29</sup> suggest that, in the gas phase, certain stoichiometries of vanadium oxide are formed with striking preference. Photodissociation experiments have confirmed that the stable cluster cations are  $V_2O_4$ ,<sup>+</sup>  $V_3O_{6-7}^+$ ,  $V_4O_9^+$ ,  $V_5O_{12}^+$  and  $V_7O_{17}^+$ .<sup>27,32</sup> Theory, in combination with photoelectron spectroscopy<sup>34-37</sup> or infrared spectroscopy experiments,<sup>38,39</sup> has provided insight into the structures of these "magic number" clusters, and has shown that their stabilities and structures are largely independent of charge state. Gas phase reactions of these clusters with small molecules also show remarkable size variations.<sup>28,30,31,33</sup> In a recent study by Zhang and Schwarz, small vanadium oxide clusters in the same size range as the gas phase species were produced by a solution nucleation reaction and studied in the gas phase with electrospray ionization and collision induced dissociation (CID).<sup>50</sup> Hydrides and hydroxides were produced in addition to pure oxides. CID experiments provided evidence for some of the same magic number cations seen previously (e.g.,  $V_3O_7^+$ ,  $V_5O_{12}^+$ ,  $V_7O_{17}^+$ ) and also evidence for the preferential elimination of neutral  $V_4O_{10}$  from these clusters.

In our initial experiment using the LVFR, titanium and titanium oxide nanoclusters were produced in the gas phase, and then captured in solution using ligand coating with tetrahydrofuran (THF) or ethylenediamine.<sup>43</sup> Previous gas phase studies on small titanium oxide clusters had found no strong preference for any stoichiometries other than that of the most common bulk titania,  $TiO_2$ .<sup>29</sup> However, in the LVFR, small clusters were found to react strongly with THF, producing unanticipated new Ti-O-Ti-O chain structures coated with THF ligands, as well as larger  $(TiO_2)_n(THF)_m$  particles having the same stoichiometry as the bulk oxide. Reactions with ethylenediamine produced chain-like structure of pure titanium with ligand coatings. The vanadium oxide clusters represent a quite different situation, where prominent stoichiometries are produced in the gas phase which are quite different from the most common  $V_2O_5$  bulk phase.<sup>27-33,38,39</sup> It is therefore interesting to investigate ligand-coating-capture in this system to see if the gas phase "magic numbers" might survive the ligand-coating process.

We find successful ligand-coating and capture in solution for two different ligands, THF and acetonitrile (MeCN). However, the chemistry of the capture process is quite different for these two ligands, resulting in vanadium oxide clusters in solution with different stoichiometries. Preliminary characterization of clusters having different cores and ligand environments find that their optical properties are quite insensitive to these differences.

#### **Experimental and Theoretical Methods**

The Laser Vaporization Flow Reactor (LVFR) has been described previously,<sup>43</sup> but its design has gone through several iterations. It is based on earlier design concepts by Andres and coworkers.<sup>51</sup> Although the most recent design of the LVFR features a straight flowtube (see Chapter II, Figure 2.1) which we find increases the collection efficiency of the apparatus, the earlier work reported here uses a design with a 90 degree bend (Chapter II, Figure 2.2). However, the general principle is still the same, in short, a laser vaporization source produces metal-containing clusters in the gas phase in a flowtube reactor, where ligands are added to react with and coat clusters to arrest further growth and achieve solubility. Vanadium oxide clusters are produced efficiently at a laser fluence of 100 mJ/pulse and a repetition rate of 50 Hz. The laser output is focused to a 3 x 12 mm rectangular spot on a  $\frac{1}{2}$ " diameter rotating vanadium rod. Using higher powers and the larger irradiation area, this configuration produces more metal ablation per shot and more shots per second than laser sources used in typical molecular beam experiments.<sup>27-39</sup> A mixture of 95% helium (UHP) and 5% oxygen (UHP) at 30 psi is expanded continuously through a 750 µm hole positioned 8 mm away from and alongside of the metal rod,

resulting in an ambient pressure of 2-5 torr in the flowtube. The flowing gas undergoes reactions with the metal plasma to produce oxide clusters, and also provides collisional cooling and entrainment of these clusters in the flow. The cluster growth tube is connected to a region for ligand addition by a  $\frac{1}{2}$ " diameter aperture (A1 in Figure 2.3), which slows the flow to promote collisional cooling of the initially grown clusters. The ambient vapor over liquid THF at room temperature is mixed with 40 psi argon, while MeCN is heated to 38°C and its vapor is mixed with 5 psi argon. The resulting gas mixtures of ligand and argon are injected into the region after A1 using a needle valve to obtain a partial pressure of 50 mtorr. Metal oxide clusters interact with ligands in the  $1\frac{1}{2}$ " inch diameter coating zone which ends in a  $\frac{1}{4}$ " aperture (A2 in the figure), also designed to slow the flow and increase the reaction time. The contents of the reactor are then collected in a liquid nitrogen trap consisting of a round bottom flask filled with 0.2" diameter glass beads submerged in liquid nitrogen. The beads increase collection efficiency by forcing the gas phase cluster/ligand mixture to encounter many cold surfaces before it exits to the downstream vacuum pump. Samples are kept under argon until they are characterized.

The first stage of sample analysis employs a laser desorption time-of-flight mass spectrometer (TOF-MS).<sup>52</sup> Several drops of the collected solution are placed on a stainless steel probe tip, which is then inserted directly into the acceleration region of the TOF. Samples are desorbed with a Nd:YAG laser (New Wave Research, Polaris II) at either 355 nm or 532 nm with pulse energies of ~400  $\mu$ J/pulse. Similar mass spectra are observed at both wavelengths. Similar mass spectra are also obtained from solutions that have been exposed to open air and/or aged for several weeks, suggesting that these clusters are not particularly air sensitive and exhibit

reasonable long-term stability. Mass calibration, which is critical for these experiments, employs coronene (300 amu) or  $C_{60}$  (720 amu) added to the samples.

Further characterization is done with a standard Fourier transform infrared spectrometer (FT-IR; Digilab FTS-7000). The solution is dried to form a powder and then mixed with KBr (1 -2% sample) and compressed into a pellet, from which transmission spectra are obtained. Solution phase UV-visible spectra are obtained using a Shimadzu UV-2401PC. Emission spectra are taken of the samples in solution using a SPEX Fluorolog FL3-12. Both emission and absorption measurements were made in various solvents (THF, MeCN, water, methanol, hexane). Emission lifetimes are obtained by exciting the samples with the second harmonic of a Nd:YAG laser (New Wave Research, Polaris II) in a homemade sample holder. The emission detected with a photomultiplier tube is collected with a digital oscilloscope (LeCroy) connect to a PC.

Density functional theory (DFT) calculations are performed with the BP86 functional using the Gaussian 03 program suite.<sup>53</sup> Selected systems were also investigated using the B3LYP functional. The TVZP basis set developed by Ahlrichs and co-workers is employed.<sup>54</sup> Computations were not counterpoise corrected due to the difficulty of computations on these large clusters. Multiple isomeric structures, as reported in the literature for the bare clusters, were investigated with attached ligands.

#### **Results and Discussion**

Dark solid material is observed in the collection flask after as little as sixty minutes of LVFR operation. This material consists of both the ligand-coated clusters and frozen excess ligand molecules. Upon warming to room temperature, the solid material and excess ligands

liquefy together to form a solution, with no agitation or stirring. Control experiments in the absence of any ligand also produce dark material in the collection flask, but this product does not dissolve. Typically the results of five one-hour collection runs combined produce a few milligrams of dried sample. The properties of the samples are somewhat different depending on which ligand is employed. After evaporative concentration, solutions appear as a bright or dark yellow for the THF and MeCN samples, respectively. In the case of MeCN, drying a sample results in a yellow film, which can be scraped to form a powder, whereas drying a THF sample results in a viscous yellow oil. Both the oil and film promptly re-dissolve in their respective solvents and are reproduced upon subsequent drying. These materials are also soluble in methanol and water. Analysis of these samples with mass spectrometry, etc., were the same upon initial capture, after drying, or after re-dissolving the samples.

The first stage of analysis for these samples produced by the LVFR is laser desorption mass spectrometry. Mass spectra for selected samples are presented in Figures 3.1 - 3.4. It is important to understand how these mass spectra are interpreted. Careful control experiments with bulk oxide and ligand on the probe of the mass spectrometer do not produce any mass spectra remotely resembling those presented here. Therefore, desorption laser induced reactions on the mass spectrometer probe tip can be ruled out as a major contributor to these spectra. Likewise, ligand-only or cluster-only runs in the flow reactor do not produce these spectra. These spectra are only seen when the clusters are first grown in the flow reactor and then exposed to ligands. Remarkably, we do not see evidence for significant fragmentation of the ligands in these spectra. This suggests that ligands add to clusters as intact units, and that the laser desorption process is gentle enough to avoid large-scale decomposition. If fragmentation occurs, it is by loss of vanadium or oxygen atoms, or intact ligands. The lack of ligand



Figure 3.1. Mass spectrum of MeCN-coated vanadium oxide clusters.



Figure 3.2. Mass spectrum of THF-coated vanadium oxide clusters at threshold desorption powers (300-500  $\mu$ J/pulse).



Figure 3.3. Mass spectrum of THF-coated vanadium oxide clusters at high desorption powers (1mJ/pulse).



Figure 3.4. Mass spectrum of THF-coated vanadium oxide clusters at higher laser power and higher mass range.

fragmentation also indicates that ligands likely add to the external surface of pre-grown oxide clusters, consistent with the desired sequence of events in the flowtube. Based on the computed (and expected) thermochemistry for these systems (see below), the metal-oxygen bonds are much stronger than the ligand-cluster bonds. Therefore, if fragmentation happens in the laser desorption process, it likely involves the loss of ligands. However, we do not see a strong dependence on the laser power, and so believe that fragmentation is minimized to the extent possible, especially at low desorption laser powers. Finally, we recognize that detection of these clusters in the mass spectrometer requires both desorption into the gas phase and ionization, both of which are likely to have efficiencies that vary for different complexes. Therefore, species detected here with intense mass peaks must be present with good abundances, but we cannot rule out that other clusters not detected are not present. Considering all of this, it is remarkable that relatively simple mass spectra are obtained.

A representative positive ion mass spectrum for a sample containing clusters coated with MeCN is shown in Figure 3.1. Rather than a random distribution of vanadium oxide/acetonitrile masses, a few specific mass peaks dominate the spectrum, specifically, those at 331, 430 and 570 amu. These same peaks consistently stand out for all samples produced from different runs, and they are rather insensitive to film thickness, desorption laser wavelength and power, or mass spectrometer focusing. Higher desorption laser powers result in some apparent fragmentation, primarily evident as increases in the intensity of mass peaks assigned to vanadium (51 amu) and vanadium oxide (67 amu), but no larger masses emerge under these conditions. The three prominent peaks are assigned to  $V_3O_6(MeCN)_2^+$ ,  $V_4O_9(MeCN)_2^+$  and  $V_5O_{12}(MeCN)_3^+$ , which are indicated as 3,6,2, 4,9,2 and 5,12,3 in the Figure. There are no significant mass peaks found that

can be assigned to a pure metal or oxide cluster without ligands. This trend remains constant for all systems investigated here and indicates that only ligand-coated clusters are captured.

As discussed earlier, gas phase experiments on vanadium oxide have shown that  $V_2O_4^+$ ,  $V_3O_6^+$ ,  $V_3O_7^+$ ,  $V_4O_9^+$ ,  $V_5O_{12}^+$  and  $V_7O_{17}^+$  are particularly stable cluster cations, as shown by their repeated formation in cluster growth and in the fragmentation of larger clusters.<sup>27,28,30</sup> Theory has shown that these same clusters are also stable as neutrals, i.e., that the relative stabilities do not depend strongly on the charge state. The prominent clusters detected here have the same stoichiometries as several of these stable bare oxides, but with the addition of one or more MeCN ligands. The smallest  $V_2O_4$  and largest  $V_7O_{17}$  clusters, which were also prominent in the gas phase, are not detected here as ligand-coated species. The  $V_3O_7$  cluster is also detected here with two ligands attached (i.e., 3,7,2), but it is not as prominent as the  $V_3O_6$  species. Ligand-coating apparently captures some, but not all of, the exact magic number clusters.

Mass spectra for samples containing clusters coated with THF are shown in Figures 3.2 - 3.4. Near the threshold desorption power at which signals are first detected (~300 - 500  $\mu$ J/pulse) (Figure 3.2), we observed an intense signal at 433 amu, although several smaller features are also present. The dominant peak here is assigned to  $V_3O_4(THF)_3^+$  and the lower intensity peak at 217 amu is  $V_3O_4^+$ . A sequence of peaks on the higher mass side of the main  $V_3O_4(THF)_3^+$  feature corresponds to  $V_4O_n(THF)_2^+$  masses. There is no clear evidence in this spectrum for  $V_3O_{6,7}^+$ ,  $V_4O_9^+$ ,  $V_5O_{12}^+$  or  $V_7O_{17}^+$  clusters complexed with THF. Therefore, in the case of THF, we also find ligand-coated clusters, but unlike the MeCN results, the clusters here are not simple adducts of known magic number oxides with added ligands.

At higher desorption powers (>1 mJ/pulse), additional larger clusters are produced from the THF samples, as well as evidence for fragmentation. As shown in Figure 3.3, in addition to the 3,4,3 cluster, there are now intense peaks at lower masses assigned to 3,3,3 and 3,3,2 species, which apparently result from fragmentation of the 3,4,3 ion. Figure 4 also shows the higher mass range, where a number of larger clusters are indicated. All clusters in this region have rather weak intensities, indicating either that the concentrations of these larger species are quite low, or that they are difficult to desorb and/or ionize. Because of the higher laser power employed, some fragmentation of the clusters can be expected. However, virtually all the mass peaks here can still be assigned to multiples of vanadium, oxygen and THF. If fragmentation is occurring, it involves loss of metal, oxygen or intact THF molecules. In the 500 - 1000 amu range, the clusters observed have 4 - 7 vanadiums, while above 1000 amu there is a series of doublets. These doublets differ by an oxygen increment, and the series of peaks are assigned to progressions built off the 7,14,7 and 8,11,8 starting points with added increments of the 2,3,0 mass. Figure 3.4 shows a further expansion of this mass spectrum into the much higher mass range. As indicated, the doublets extend out to a point where the mass resolution does not distinguish the two peaks anymore, but the progression continues to roughly 5000 amu, corresponding to clusters having 40 or more vanadium atoms. Because of the repeated addition of the  $V_2O_3$  unit, clusters in the size range of 1000 - 5000 amu have essentially the  $V_2O_3$ stoichiometry. This is a well-known compound of vanadium seen previously in bulk and nanoparticle samples, with fascinating electronic properties (i.e., a low temperature metalinsulator transition).<sup>1,18</sup>

The comparison between the species coated with MeCN and THF is quite interesting. For comparable sized species, both systems produce vanadium oxide clusters with roughly the same numbers of attached ligands, but the oxides involved are not exactly the same. MeCN seems to coat certain vanadium oxide clusters that correspond exactly to magic number species

seen previously in the gas phase.<sup>27-33,38,39</sup> However, not all of the previous magic number species are collected efficiently this way. Instead, three main clusters  $(V_3O_6, V_4O_9 \text{ and } V_5O_{12})$  are captured. On the other hand, THF experiments capture primarily just one ligand-coated cluster. Unlike the MeCN clusters, the  $V_3O_4$  species obtained with THF was not prominent in any previous gas phase studies. Likewise, the larger THF-coated clusters seen at much lower concentrations under higher laser power conditions also do not correspond to previously known vanadium oxide species. Instead, virtually all the THF-coated clusters contain fewer oxygens than the familiar stoichiometries. Apparently, ligand coating also leads to some elimination of oxygen from these clusters. The only apparent exceptions to this trend are the 4,10,2 species, which has both one extra oxygen and two ligands more than the stable  $V_4O_9$  stoichiometry, and the 3,7,5, which has five ligands added to the stable  $V_3O_7$  cluster. The 4,10 species was in fact seen as a prominent leaving group in the CID experiments of Zhang and Schwarz,<sup>50</sup> so the observation of this cluster here is not too surprising. But while the 4,10 cluster is seen weakly in both our THF and MeCN data, it is not nearly as prominent as the 4,9 species coated with MeCN.

To investigate the structures of these various clusters, we have performed computational studies on both the bare vanadium oxide species and their ligand-coated products. The resulting structures are shown in Figures 3.5 - 3.7. For the un-coated clusters, we have performed a systematic study of both the neutrals and their corresponding cations, and we have extended this to include clusters larger than those investigated previously. The structures derived for the neutrals are shown in Figure 3.5. In cases where comparisons are possible (V<sub>3</sub>O<sub>6</sub>; V<sub>3</sub>O<sub>7</sub>; V<sub>4</sub>O<sub>9</sub>), we obtain structures for bare vanadium oxide clusters that are consistent with those reported in the previous literature (see Supporting Information for details of calculations).<sup>27,29,39,42</sup> Although



 $V_3O_6$ 







V<sub>5</sub>O<sub>12</sub>



Figure 3.5. Calculated structures for stable vanadium oxide neutral clusters corresponding to species detected as magic numbers in previous gas phase experiments.



Figure 3.6. Calculated structures of MeCN-coated vanadium oxide clusters.



Figure 3.7. Calculated structures of  $V_3O_4(THF)_3$  and  $V_4O_7(THF)_2$  THF-coated vanadium oxide clusters, as well as schematic structures for the  $V_5O_8(THF)_5$  and  $V_7O_{11}(THF)_6$  species. These latter clusters were too large for computations, but were derived from computed core structures and assumed ligand positions.

some anion clusters having approximately these same stoichiometries have been investigated previously, our computed structures for the  $V_5O_{12}$  and  $V_7O_{17}$  neutrals are the first to our knowledge on these species. All of these structures have two distinguishing features relating to the positions of the oxygen atoms. There are "framework" oxygens binding to two or three vanadium atoms in the skeleton of the cluster core, as well as "terminal" oxygens bound to only a single vanadium that protrude outwards from the core. All vanadium atoms are in the skeleton. The number of framework versus terminal oxygens varies with each cluster size, but the qualitative structure obtained is almost always the same for corresponding neutrals and cations. The exception to this is the  $V_3O_6$  species, which has a double-ring or chain-like structure for the cation versus a more compact half-cage for the neutral, also consistent with previous computational work.<sup>39,42</sup> The chain-like structure for this cation, and structures of several other small  $V_x O_y$  cations (e.g., the  $V_2 O_4^+$  magic number), were confirmed with infrared spectroscopy by Asmis and coworkers.<sup>39</sup> Unfortunately, there are no measurements that provide experimental evidence for structures of the neutral species. Clusters containing three or fewer vanadium atoms are computed to have ring, double-ring or half-cage structures, while those with four or more vanadium atoms have cage structures with an enclosed volume.

The clusters ligand-coated with MeCN have some of the same metal oxide stoichiometries as known magic-number clusters from the gas phase, and it is therefore natural to suspect that the coated clusters might have structures similar to those of bare oxides. This indeed turns out to be the case, as shown in Figure 3.6. In each case, the bare oxide structure is preserved in its coated analog, with only minor changes in bond distances or angles. The MeCN ligands bind at vanadium atom sites, in the same positions where terminal oxygens are attached, and thus expand the coordination at these metal sites. The main geometry changes involve the

binding angles of terminal oxygens, which have shifted to accommodate the MeCN ligands that bind at the same metal. However, according to the stoichiometries detected by mass spectrometry, not all metal atom sites have attached ligands. It is not clear whether these partially coated clusters are indeed the most stable species formed. It is conceivable that fully coated clusters with a ligand at each metal site are formed and are present in solution, but that some ligands are lost in the desorption/ionization process in the mass spectrometer. However, no masses corresponding to clusters with additional ligands are detected down to the lowest desorption laser powers employed. In any event, the combined mass spectrometry and theory provide a consistent picture, indicating that certain gas phase magic number clusters have indeed been coated with ligands and captured in solution.

The computed structures for the THF-coated cluster reveal their relationship to the bare clusters. We first consider the  $V_3O_4(THF)_3$  species seen with highest abundance in Figure 3.2. Based on the stoichiometry alone, it is evident that this 3,4,3 species has fewer oxygens than the nearest magic number cluster known from the gas phase work, i.e., the  $V_3O_6$  or  $V_3O_7$  species. Examination of the computed structure shows that the core of the  $V_3O_4$  cluster is nearly identical to that of the magic number  $V_3O_6$  or  $V_3O_7$  clusters, but that it has lost two or three of the terminal oxygens. It is therefore apparent that the abundant  $V_3O_4(THF)_3$  cluster formed from ligand-coating of the  $V_3O_6$  or  $V_3O_7$  clusters, but with the ligand displacing the terminal oxygens. The number of ligands present in this species is in fact exactly the same as the "missing" three terminal oxygens for the  $V_3O_7$  cluster.

If THF ligation does occur by substitution of terminal oxygens, other clusters in the distribution might be expected to exhibit this same pattern, and indeed, there is evidence for this. As noted above, nearly all the clusters seen in Figure 3.3 have fewer oxygens than the stable

stoichiometries seen in the gas phase. The next larger magic number species  $V_4O_9$  has three external oxygens (see computed structure in Figure 3.5), and so we can look for evidence of a  $V_4O_6$  core with attached ligands. We do not see the fully substituted 4,6,3 complex, but we do see the bare 4,6 ion in the low mass range of Figure 3.3, and there is also a 4,7,2 complex. The computed structure for this latter species (Figure 3.7) has two terminal oxygens substituted by ligands, with retention of one, i.e., it is partially coated. Likewise, the bare  $V_5O_{12}$  cluster has terminal oxygens on four of the five metal sites. In the ligand coated species, we detect both the 5,8,4 and 5,8,5 ions. Our attempts at theory on such large multi-ligand clusters have been unsuccessful so far. However, the stoichiometries here are completely consistent with the 5,8,4 having four ligands substituting for the terminal oxygens and the 5,8,5 having an additional ligand binding to the metal where there was no terminal oxygen before. The appealing (schematic - not computed) structure of 5,8,5 is shown in Figure 3.8, generated from the computed core of 5,12 with ligand substitution on its surface. The next larger stable cluster from the gas phase work is  $V_7O_{17}$ , whose bare structure, computed for the first time as a neutral, is shown in Figure 3.6. It has six terminal oxygens and one metal site without an external oxygen. Again, some of the masses found in Figure 3.3 correspond to ligand coating and oxygen substitution of this cluster. 7,11,6 is observed as a very weak feature, and we also detect a series of related weak bands corresponding to 7,n,6 (n=12-14) and 7,n,7 (n=13,14) stoichiometries. All of these can be rationalized in relation to the  $V_7O_{17}$  bare cluster. Like the  $V_5O_{12}$  complexes noted above, the  $V_7O_{11}$  (THF)<sub>6</sub> complex is too large for computational studies on a reasonable timescale. We therefore present a proposed schematic structure for this complex in Figure 3.8, using the computed core cluster from the  $V_7O_{17}$  computations and adding the ligands in place of terminal oxygens. The 7,14,7 species appears to be the starting point in the mass spectrum of

Figure 3.4 for the lower member of the nested doublet series of mass peaks that add the  $V_2O_3$  mass increment. The higher starting mass for the nested series seems to begin on the 8,10,8 and 8,11,8 doublet. Although the  $V_8O_{19}$  cluster was not detected as stable in photodissociation experiments (larger clusters would be required to see this as a photofragment), its mass was prominent in the mass spectra reported by several groups. It is reasonable then that this cluster also has high stability, and that it is also apparently captured by ligand substitution of terminal oxygens. Therefore, the ligand-substitution chemistry with THF ligands is well established for the smaller clusters, and there is reasonable evidence that this same theme applies throughout the clusters studied here.

It is apparent from the mass spectra recorded here, and supported by theory, that MeCN addition in these systems occurs by ligand binding at the same metal sites as the terminal oxygens, effectively expanding the coordination at this site, whereas THF ligands prefer to displace the terminal oxygens. The reasons for this very different ligation chemistry are not completely clear. It is conceivable that this is an artifact of the experimental conditions. If one ligand is added with much greater concentration than the other, then the vapor from that ligand might diffuse backwards against the gas flow into the cluster growth region of the flowtube, where nascent clusters still retain significant internal condensation energy from their growth. Higher energy reactions in this part of the flowtube might lead to more decomposition products in the ligand addition process. However, we have studied the cluster growth process over a wide variety of ligand concentrations, and the reactive trends reported here do not seem to depend strongly on this variable. Ligand mobility in the gas flow could also be a factor, but THF is a larger molecule and should be *less* likely to backflow than MeCN. Because THF is larger, steric effects could limit its bonding at the same vanadium as a terminal oxygen, whereas the smaller

Total Energy (hartrees)	Ligand Binding Energy (kcal/mol)
-3366.2763470	25.2
-3592.2887223	28.7
-3266.5526695	26.8
-3492.5588105	26.4
	Total Energy (hartrees) -3366.2763470 -3592.2887223 -3266.5526695 -3492.5588105

Table 3.1: Calculated energies of coated vanadium oxide particles and the binding energy of one ligand (THF or acetonitrile) to the particle.

MeCN is better able to be accommodated here. If this is so, it could perhaps be detected in the ligand binding energies. To explore this possibility, we employed DFT calculations to probe the binding energies of MeCN and THF to different vanadium oxide cores, and the results for V<sub>3</sub>O<sub>4</sub> and  $V_{3}O_{7}$  are shown in Table 3.1. Admittedly, DFT calculations are problematic in determining thermochemistry, especially for systems as large as these coated metal oxide clusters. However, the size of these systems make them difficult to study at higher levels of theory, and so we carry out the calculations with due skepticism about the results. Unfortunately, the computed ligand binding energies provide virtually no insight to the preferential ligand chemistry. All binding energies are found to be virtually the same, varying between 25 - 29 kcal/mol when MeCN or THF is added either alongside a terminal oxygen or in its place. A final possibility is some bias in the desorption/ionization process, which might favor clusters with lower ionization energies. We have studied the desorption/ionization process at different wavelengths and laser powers, and the differences reported here are also not affected strongly by these variables. Therefore, we conclude that the ligand-coating chemistry is indeed different for THF versus MeCN ligands, but that the source of the difference is not clear with the information presently available.

If the ligand-coating chemistry is indeed different for these two systems, this difference might be detected by analysis methods other than mass spectrometry. Complete characterization of these samples is limited because the solutions contain a mixture of clusters and the concentrations in solutions are quite low. However, we have been able to perform some optical spectroscopy on these samples by collecting and combining the results of several LVFR runs taken over a period of several days, and then concentrating these solutions by solvent evaporation. Figure 3.8 shows the FT-IR spectra of THF versus MeCN samples, recorded in each case by drying the samples as much as possible and then combining them with KBr salt to



Figure 3.8. FT-IR spectra of vanadium oxide clusters coated with MeCN (black) or THF (red). The broad absorption at higher energy is from residual water in the sample.

make a pressed pellet. While the spectra for the two samples are relatively similar, having features associated with the respective ligand vibrations, a significant difference is apparent in the form of an intense band at 1110 cm<sup>-1</sup>, which is seen for the MeCN samples but not for the THF samples. Previous gas phase infrared studies, as well as our DFT calculations, show that a band in this position is consistent with the stretching vibration of terminal V=O groups. According to our mass spectrometry, such terminal oxygens should be present for the MeCN-coated clusters, which do not displace terminal oxygens, and they should be missing or less prominent for THF-coated clusters, which usually displace the terminal oxygens. Therefore, the infrared spectroscopy is completely consistent with the results from the mass spectrometry about the different ligand attachment chemistry for THF and MeCN.

UV-visible spectra of both samples are shown in Figure 3.9. These spectra were obtained in methanol, though spectra taken in various solvents show essentially the same features. Both MeCN and THF samples show strong absorption in the UV with an extensive low energy tail. A shoulder around 280 nm is observed for the MeCN coated particles but is not evident for those with THF. Since our samples contain mostly 1 - 3 cluster sizes, we can use approximate molecular weights to derive concentrations of these samples, and then we can derive approximate extinction coefficients for the strength of these absorptions. This analysis results in rough estimates of 6000 l/mol-cm for the absorption strengths of both samples. Intense bands in this region are common for numerous vanadium oxide systems seen in the past, and are typically assigned to charge transfer bands ( $\pi \rightarrow d$ ) between oxygen and vanadium.<sup>55,56</sup>

Samples coated by both ligands are found to exhibit an intense and broad photoluminescence from 350 - 600 nm, as shown in Figure 3.10. This type of nearly white light emission has been observed for a variety of vanadium oxide species such as thin films supported



Figure 3.9. Solution phase UV-visible spectra of vanadium oxide clusters coated with MeCN (black) and THF (red) dissolved in methanol.



Figure 3.10. Photoluminescence spectra of vanadium oxide clusters coated by, and in solutions of, MeCN (black) and THF(red). Emission spectra are obtained at excitation wavelengths of a) 320 nm b) 340 nm c) 360 nm and d) 400 nm.

on Al<sub>2</sub>O<sub>3</sub>, MgO or SiO,<sup>57-60</sup> vanadate oxides (complexed with Ca, K, Rb, Cs, Mg and Zn),<sup>61-63</sup> and for vanadium oxide nanoparticles.<sup>64</sup> Various systems based on units of  $VO_3$ ,<sup>61</sup>  $VO_4$ ,<sup>58,60</sup>  $V_2O_5$ , <sup>57,59,61</sup>  $V_2O_7$ , <sup>63,64</sup> and  $V_2O_8$ <sup>61</sup> display similar luminescence. Observation of a vibrational progression corresponding to v(V=O) in the emission of vanadium oxide dispersed in silica led many to believe that this emission arises from a triplet charge transfer state associated with the terminal V=O bond.<sup>59</sup> However, in these previous cases, the emission was clearly phosphorescence because of the long lifetimes (~10 ms) observed. For A<sub>2</sub>CaV<sub>2</sub>O<sub>7</sub> (A=Rb, Cs) a shorter lifetime of approximately 46 µs was observed.<sup>56</sup> In the present work, the emission lifetimes are much shorter, i.e.,  $\sim 10 - 20$  ns for both samples, with excitation at either 532 or 355 nm. As these samples contain clusters coated with different ligands, both with and without the terminal V=O bonds, it seems that the emission must be coming from the oxide core, rather than from cluster-ligand charge transfer or from the terminal oxygen moieties. Figure 3.11 shows excitation curves associated with different features of the measured emission for the THF samples. As indicated, the excitation wavelengths giving rise to different emission features are distinct, likely indicating the presence of multiple components in the sample having spectra that are similar, but not exactly the same. This suggests that the different cluster sizes present have slightly different spectra, i.e., that the spectra depend on the size of the cluster. Like other measurements reported here, these optical spectroscopy experiments could certainly benefit from separation and purification of the different cluster sizes present as mixtures in these solutions, which we plan to do in the future when larger amounts of sample can be made. Nevertheless, the data already show that the optical properties of these sub-nano clusters are in some ways similar to, but in other ways significantly different from, those of the corresponding nanoparticles or bulk materials.



Figure 11. Excitation spectra (a) of vanadium oxide particles coated with THF for emission at I) 416 nm II) 403 nm III) 385 nm and IV) 465 nm. Emission spectra (b) of the same sample excited at 355 nm.

The emerging picture from these initial results is that the LVFR method is indeed able to capture some of the same magic number clusters seen previously in the gas phase. With the MeCN ligand, clusters are captured intact via simple ligand addition, with the exact same metal oxide stoichiometry seen in the gas phase. However, not all of the oxides seen previously are captured with equal efficiency; the 4,9 and 5,12 species are collected with much greater concentrations than others. With the THF ligand, capture is even more specific, producing almost exclusively the  $V_3O_4(THF)_3$  species. This cluster is derived from either the 3,6 or 3,7 species seen in the gas phase, but with substitution of ligands for terminal oxygens. It is not at all clear why certain sized clusters are captured more effectively than others. The ligand coating chemistry is quite different from that seen previously for titanium oxide clusters, in the only other study of LVFR cluster growth. In that work, titanium strongly reacted with THF and formed oxides even in the absence of oxygen gas. Smaller clusters produced from this reaction had novel structures of titanium and THF unrelated to any gas phase clusters, while larger clusters resembled bulk TiO<sub>2</sub> coated by ligands. The direct relationship here between gas phase vanadium oxides and the solution phase species captured is apparently caused by the exceptional stability of the gas phase vanadium oxide clusters. Once formed, they can survive to be captured, and then after capture they can also survive in solution for extended periods. Although the different ligand chemistry for MeCN versus THF is clearly evident, the reasons for the difference are not yet clear. Apparently, in addition to the role of cluster stability, complex ligand-surface interactions determine which clusters are captured efficiently and how the ligands bind. This may explain why the clusters captured most efficiently are different for the two ligands.

A second finding from this work is that the sub-nanometer clusters captured here have optical properties quite different from their larger particles or bulk materials. The optical spectroscopy work is admittedly on solutions containing a mixture of cluster sizes. However, the inhomogeneities in the emission curve are almost certainly caused by different sized clusters with different spectra. The lifetimes of all of these clusters are definitely much shorter than those of the nanoparticles or bulk materials. Further details in this area will require the separation and purification of samples corresponding to specific cluster sizes. Vanadium oxides have known catalytic activity, and it will also be interesting to investigate the size dependence of reactivity for these systems.

#### Conclusions

Acetonitrile and tetrahydrofuran have been employed to coat and capture sub-nanometer sized vanadium oxide clusters in solution. The clusters obtained contain 10 - 30 atoms of oxide core, making them some of the smallest metal oxide clusters/particles yet isolated. Clusters coated by acetonitrile have vanadium oxide stoichiometries exactly matching those found to be particularly stable in the gas phase. Clusters coated with tetrahydrofuran have the same oxide cores as gas phase analogs, but with the terminal oxygens replaced by THF. The core structures of both kinds of ligand-coated oxides have essentially the same structures as the corresponding gas phase species. Mass spectrometry, infrared spectroscopy and computational studies agree on the structures of the clusters and the nature of the ligand coating chemistry. Both samples absorb strongly in the UV and fluorescence at visible wavelengths. The emission spectra are similar to those for other vanadium oxide systems, and are minimally affected by the ligand employed. These data illustrate the fascinating chemistry of ligand-coated clusters in the sub-nanometer size

regime. Future work will optimize the production processes involved, increasing production yields, which will hopefully lead to size-separation and purification of these samples. More detailed comparisons of the properties of ultra-small clusters with those of larger nano-systems are expected as this work proceeds and is applied to a variety of other oxide materials

### References

- 1. Cox, P. A. Transition Metal Oxides, Clarendon: Oxford, 1992.
- 2. Hayashi, C.; Uyeda, R.; Tasaki, A. Ultra-Fine Particles, Noyes, Westwood, 1997.
- 3. Rao C. N.; Raveau, B.; Transition Metal Oxides, Wiley, New York, 1998.
- 4. Campbell, C. T. "Ultrathin metal films and particles on oxide surfaces: Structural, electronic and chemisorptive properties," *Surf. Sci. Rep.* **1997**, *27*, 1.
- 5. Aiken, J. D.; Finke, R. G. "A review of modern transition-metal nanoclusters: their synthesis, characterization and applications in catalysis," *J. Mol. Catal. A: Chem.* **1999**, *145*, 1.
- 6. Kodama, R. H. "Magnetic nanoparticles," J. Magn. & Magn. Mater. 1999, 200, 359.
- a) Hill, C. L. "Introduction: Polyoxometalates Multicomponent molecular vehicles to probe fundamental issues and practical problems," *Chem. Rev.* 1998, 98, 1. b) Hill, C. L. "Progress and challenges in polyoxometalate-based catalysis and catalytic materials chemistry," *J. Mol. Catal. A: Chem.* 2007, 262, 2.
- 8. M. T. Pope and A. Müller, *Polyoxometalate Chemistry From Topology via Self -Assembly to Applications*, Kluwer, Boston, 2001.
- Schlögl, R.; Abd Hamid, S. B. "Nanocatalysis: Mature science revisited or something really new?" *Angew. Chem. Int. Ed.* 2004, *43*, 1628.
- Luo, X. L.; Morrin, A.; Killard, A. J.; Smyth, M. R. "Application of nanoparticles in electrochemical sensors and biosensors," *Electroanalysis* 2006, 18, 319.
- 11. Franke, M. E.; Koplin, T. J.; Simon, U. "Metal and metal oxide nanoparticles in chemiresistors: Does the nanoscale matter?" *Small* **2006**, *2*, 36.
- Dorcioman, G.; Ebrasu, D.; Enculescu, I.; Serban, N.; Axente, E.; Sima, F.; Ristoscu, C.;
  Mihailescu, I. N. "Metal oxide nanoparticles synthesized by pulsed laser ablation for proton

exchange membrane fuel cells," J. Power Sources 2010, 195, 7776.

- Maeda, K.; Domen, K. "Photocatalytic water splitting: Recent progress and future challenges," J. Phys. Chem. Lett. 2010, 1, 2655.
- 14. Joshi, U.; Palasyuk, A.; Arney, D.; Maggard, P. A. "Semiconducting oxides to facilitate the conversion of solar energy to chemical fuels," *J. Phys. Chem. Lett.* **2010**, *1*, 2719.
- Patzke, G. R.; Zhou, Y.; Kontic, R.; Conrad, F. "Oxide nanomaterials: Synthetic developments, mechanistic studies, and technological developments," *Angew. Chem. Int. Ed.* 2011, *50*, 826.
- 16. a) Rockenberger, J.; Scher, E. C.; Alivisatos, A. P. "A new nonhydrolytic single-precursor approach to surfactant-capped nanocrystals of transition metal oxides," J. Am. Chem. Soc. **1999**, 121, 11595. b) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. "Formation of hollow nanocrystals through the nanoscale kirkendall effect," Science 2004, 304, 711. d) Casula, M. F.; Jun, Y. W.; Zaziski, D. J.; Chan, E. M.; Corrias, A.; Alivisatos, A. P. "The concept of delayed nucleation in nanocrystal growth demonstrated for the case of iron oxide nanodisks," J. Am. Chem. Soc. 2006, 128, 1675. f) Cabot, A.; Puntes, V. F.; Shevchenko, E. V.; Yin, Y.; Balcells, L.; Marcus, M. A.; Hughes, S. M.; Alivisatos, A. P. "Vacancy coalescence during oxidation of iron nanoparticles," J. Am. Chem. Soc. 2007, 129, 10358. g) Liu, H. T.; Owen, J. S.; Alivisatos, A. P. "Mechanistic study of precursor evolution in colloidal group II-VI semiconductor nanocrystal synthesis," J. Am. Chem. Soc. 2007, 129, 305. h) Shevchenko, E. V.; Bodnarchuk, M. I.; Kovalenko, M. V.; Talapin, D. V.; Smith, R. K.; Aloni, S.; Heiss, W.; Alivisatos, A. P. "Gold/iron oxide core/hollow-shell nanoparticles," Adv. Mater. 2008, 20, 4323. i) Cabot, A.; Alivisatos, A. P.; Puntes, V. F.; Balcells, L.; Iglesias, O.; Labarta, A. "Magnetic domains and surface effects in

hollow maghemite nanoparticles," Phys. Rev. B 2009, 79, 094419.

- Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. "Recent advances in the liquid-phase syntheses of inorganic nanoparticles," *Chem. Rev.* 2004, *104*, 3893.
- 18. a) Tang, J.; Redl, F.; Zhu, Y.; Siegrist, T.; Brus, L. E.; Steigerwald, M. L. "An organometallic synthesis of TiO<sub>2</sub> nanoparticles," *Nano Lett.* 2005, *5*, 543. b) Blagojevic, V. A.; Carlo, J. P.; Brus, L. E.; Steigerwald, M. L.; Uemura, Y. J.; Billinge, S. J. L.; Zhou, W.; Stephens, P. W.; Aczel, A. A.; Luke, G. M. "Magnetic phase transition in V<sub>2</sub>O<sub>3</sub> nanocrystals," *Phys. Rev. B* 2010, *82*, 094453.
- 19. a) Lim, J.-K.; Tilton, R. D.; Eggeman, A.; Majetich, S. A. "Design and synthesis of plasmonic magnetic nanoparticles," *J. Magn. & Magn. Mater.* 2007, *311*, 78. b) Lim, J.-K.; Eggeman, A.; Lanni, F.; Tilton, R. D.; Majetich, S. A. "Synthesis and single-particle optical detection of low-polydispersity plasmonic-superparamagnetic nanoparticles," *Adv. Mater.* 2008, *20*, 1721. c) Lim, J.-K.; Majetich, S. A.; Tilton, R. D. "Stabilization of superparamagnetic iron oxide core-gold shell nanoparticles in high ionic strength media," *Langmuir* 2009, *25*, 13384.
- Chaudret, B.; Philippot, K. "Organometallic nanoparticles of metals or metal oxides," *Oil Gas Sci. Technol.* 2007, 62, 799.
- Rao, C. N. R.; Vivekchand, S. R. C.; Biswasa, K.; Govindaraja, A. "Synthesis of inorganic nanomaterials," *Dalton Trans.* 2007, 34, 3728.
- 22. Kwon, S. G.; Hyeon, T. "Colloidal chemical synthesis and formation kinetics of uniformly sized nanocrystals of metals, oxides, and chalcogenides," *Acc. Chem. Res.* **2008**, *41*, 1696.
- 23. Gvishi, R. "Fast sol-gel technology: from fabrication to applications," *J. Sol-Gel Sci. Technol.* 2009, *50*, 241.

- Wang, D. S.; Xie, T.; Li, Y. D. "Nanocrystals: Solution-Based Synthesis and Applications as Nanocatalysts," *Nano Res.* 2009, 2, 30.
- 25. a) El-Shall, M. S.; Slack, W.; Vann, W.; Kane, D.; Hanley, D. "Synthesis of nanoscale metal-oxide particles using laser vaporization condensation in a diffusion cloud chamber," *J. Phys. Chem.* 1994, 98, 3067. b) El-Shall, M. S.; Graiver, D.; Pernisz, U.; Baraton, M. I. "Synthesis and characterization of nanoscale zinc oxide particles. 1. Laser vaporization condensation technique," *Nanostruct. Mater.* 1995, *6*, 297.
- 26. Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. "Laser production of supersonic metal cluster beams," J. Chem. Phys. 1981, 74, 6511.
- 27. a) Deng, H. T.; Kerns, K. P.; Castleman, A. W., Jr. "Formation, structures, and reactivities of niobium oxide cluster ions," *J. Phys. Chem.* 1996, *100*, 13386. b) Bell, R. C.; Zemski, K. A.; Kerns, K. P.; Deng, H. T.; Castleman, A. W., Jr. "Reactivities and collision-induced dissociation of vanadium oxide cluster cations," *J. Phys. Chem. A* 1998, *102*, 1733. c) Kooi, S. E.; Castleman, A. W., Jr. "Photofragmentation of V<sub>x</sub>O<sub>y</sub><sup>+</sup> clusters," J. Phys. Chem. A 1999, *103*, 5671. d) Bell, R. C.; Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. "Formation, structure and bond dissociation thresholds of gas-phase vanadium oxide cluster ions," *J. Chem. Phys.* 2001, *114*, 798. e) Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. "Studies of metal oxide clusters: Elucidating reactive sites responsible for the activity of transition metal oxide catalysts," *J. Phys. Chem. B* 2002, *106*, 6136. f) Bergeron, D. E.; Castleman, A. W., Jr.; Jones, N. A.; Khanna, S. N. "Stable cluster motifs for nanoscale chromium oxide materials," *Nano. Lett.* 2004, *4*, 261.
- 28. a) Bell, R. C.; Zemski, K. A.; Castleman, A. W., Jr. "Size-specific reactivities of vanadium oxide cluster cations," *J. Cluster Sci.* 1999, *10*, 509. b) Zemski, K. A.; Justes, D. R.;
Castleman, A. W., Jr. "Reactions of group v transition metal oxide cluster ions with ethane and ethylene," *J. Phys. Chem. A* **2001**, *105*, 10237. c) Justes, D. R.; Mitrić, R.; Moore, N. A.; Bonačić-Koutecký, V.; Castleman, A. W., Jr. "Theoretical and experimental consideration of the reactions between  $V_xO_y^+$  and ethylene," *J. Am. Chem. Soc.* **2003**, *125*, 6289. d) Justes, D. R.; Moore, N. A.; Castleman, A. W., Jr. "Reactions of vanadium and niobium oxides with methanol," *J. Phys. Chem. B* **2004**, *108*, 3855. e) Moore, N. A.; Mitric, R.; Justes, D. R.; Bonačić-Koutecký, V.; Castleman, A. W., Jr. "Kinetic analysis of the reaction between  $(V_2O_5)_{n=1,2}^+$  and ethylene," *J. Phys. Chem. B* **2006**, *110*, 3015.

- 29. a) Foltin, M.; Stueber, G. J.; Bernstein, E. R. "On the growth dynamics of neutral vanadium oxide and titanium oxide clusters," *J. Chem. Phys.* 1999, *111*, 9577. b) Foltin, M.; Stueber, G. J.; Bernstein, E. R. "Investigation of the structure, stability, and ionization dynamics of zirconium oxide clusters," *J. Chem. Phys.* 2001, *114*, 8971. c) Matsuda, Y.; Bernstein, E. R. "On the titanium oxide neutral cluster distribution in the gas phase: Detection through 118 nm single-photon and 193 nm multiphoton ionization," *J. Phys. Chem. A* 2005, *109*, 314. d) Dong, F.; Heinbuch, S.; He, S. G.; Xie, Y.; Rocca, J. J.; Bernstein, E. R. "Formation and distribution of neutral vanadium, niobium, and tantalum oxide clusters: Single photon ionization at 26.5 eV," *J. Chem. Phys.* 2006, *125*, 8. e) Jakubikova, E.; Rappe, A. K.; Bernstein, E. R. "Density functional theory study of small vanadium oxide clusters," *J. Phys. Chem. A* 2007, *111*, 12938.
- 30. Dong, F.; Heinbuch, S.; Xie, Y.; Rocca, J. J.; Bernstein, E. R. "Reactions of neutral vanadium oxide clusters with methanol," *J. Phys. Chem. A* **2009**, *113*, 3029.
- 31. a) Engeser, M.; Weiske, T.; Schröder, D.; Schwarz, H. "Oxidative degradation of small cationic vanadium clusters by molecular oxygen: On the way from V<sub>n</sub><sup>+</sup> (n=2-5) to VO<sub>m</sub><sup>+</sup>

(m=1,2)," *J. Phys. Chem. A* **2003**, *107*, 2855. b) Feyel, S.; Schröder, D.; Rozanska, X.; Sauer, J.; Schwarz, H. "Gas-phase oxidation of propane and 1-butene with  $V_3O_7^+$ : Experiment and theory in concert," *Angew. Chem. Int. Ed.* **2006**, *45*, 4677. c) Feyel, S.; Schröder, D.; Schwarz, H. "Gas-phase chemistry of vanadium oxide cluster cations  $V_mO_n$ + (m=1-4; n=1-10) with water and molecular oxygen," *Eur. J. Inorg. Chem.* **2008**, *31*, 4961. d) Feyel, S.; Schröder, D.; Schwarz, H. "Pronounced cluster-size effects: gas-phase reactivity of bare vanadium cluster cations  $V_n^+$  (n=1-7) toward methanol," *J. Phys. Chem. A* **2009**, *113*, 5625.

- 32. a) Molek, K. S.; Jaeger, T. D.; Duncan, M. A. "Photodissociation of vanadium, niobium, and tantalum oxide cluster cations," *J. Chem. Phys.* 2005, *123*, 10. b) Molek, K. S.; Reed, Z. D.; Ricks, A. M.; Duncan, M. A. "Photodissociation of chromium oxide cluster cations," *J. Phys. Chem. A* 2007, *111*, 8080. c) Reed, Z. D.; Duncan, M. A. "Photodissociation of yttrium and lanthanum oxide cluster cations," *J. Phys. Chem. A* 2008, *112*, 5354. d) Molek, K. S.; Anfuso-Cleary, C.; Duncan, M. A. "Photodissociation of iron oxide cluster cations," *J. Phys. Chem. A* 2008, *112*, 9238.
- 33. Fielicke, A.; Rademann, K. "Stability and reactivity patterns of medium-sized vanadium oxide cluster cations  $V_x O_v^+$  ( $4 \le x \le 14$ )," *Phys. Chem. Chem. Phys.* **2002**, *4*, 2621.
- 34. a) Wang, L.-S.; Wu, H.; Desai, S. R.; Lou, L. "Electronic structure of small copper oxide clusters: From Cu<sub>2</sub>O to Cu<sub>2</sub>O<sub>4</sub>," *Phys. Rev. B* 1996, *53*, 8028. b) Gutsev, G. L.; Rao, B. K.; Jena, P.; Li, X.; Wang, L.-S. "Experimental and theoretical study of the photoelectron spectra of M<sub>n</sub>O<sub>x</sub><sup>-</sup> (x=1-3) clusters," *J. Chem. Phys.* 2000, *113*, 1473. c) Zhai, H. J.; Wang, L.-S. "Electronic structure and chemical bonding of divanadium-oxide clusters (V<sub>2</sub>O<sub>x</sub>, x=3-7) from anion photoelectron spectroscopy," *J. Chem. Phys.* 2002, *117*, 7882. d) Gutsev, G. L.;

Bauschlicher, C. W., Jr.; Zhai, H. J.; Wang, L.-S. "Structural and electronic properties of iron monoxide clusters Fe<sub>n</sub>O and Fe<sub>n</sub>O<sup>-</sup>: A combined photoelectron spectroscopy and density functional theory study," *J. Chem. Phys.* **2003**, *119*, 11135. e) Zhai, H. J.; Huang, X.; Cui, L. F.; Li, X.; Li, J.; Wang, L.-S. "Electronic and structural evolution and chemical bonding in ditungsten oxide clusters: W<sub>2</sub>O<sub>n</sub><sup>-</sup> and W<sub>2</sub>O<sub>n</sub> (n=1-6)," *J. Phys. Chem. A* **2005**, *109*, 6019. f) Zhai, H.-J.; Wang, L.-S. "Probing the electronic structure of early transition metal oxide clusters: Molecular models towards mechanistic insights into oxide surfaces and catalysis," *Chem. Phys. Lett.* **2010**, 500, 185.

- 35. Green, S. M. E.; Alex, S.; Fleischer, N. L.; Millam, E. L.; Marcy, T. P.; Leopold, D. G.
  "Negative ion photoelectron spectroscopy of the group 5 metal trimer monoxides V<sub>3</sub>O, Nb<sub>3</sub>O, and Ta<sub>3</sub>O," *J. Chem. Phys.* 2001, *114*, 2653.
- 36. a) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Photoelectron spectroscopy of yttrium oxide cluster anions: Effects of oxygen and metal atom addition," *J. Phys. Chem. A.* **2001**, *105*, 7534. b) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Photoelectron spectroscopy of cobalt oxide cluster anions," *J. Phys. Chem. A* **2002**, *106*, 4891. c) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Anion photoelectron spectroscopy of V<sub>n</sub>O<sub>m</sub><sup>-</sup> (n=4-15; m=0-2)," *J. Chem. Phys.* **2002**, *116*, 6521.
- 37. Yoder, B. L.; Maze, J. T.; Raghavachari, K.; Jarrold, C. C. "Structures of Mo<sub>2</sub>O<sub>y</sub> and Mo<sub>2</sub>O<sub>y</sub> (y=2,3,4) studied by anion photoelectron spectroscopy and density functional theory calculations," *J. Chem. Phys.* 2005, *122*, 094313.
- 38. a) Fielicke, A.; Meijer, G.; von Helden, G. "Infrared spectroscopy of niobium oxide cluster cations in a molecular beam: Identifying the cluster structures," *J. Am. Chem. Soc.* 2003, *125*, 3659. b) Fielicke, A.; Meijer, G.; von Helden, G. "Infrared multiple photon dissociation

spectroscopy of transition metal oxide cluster cations - Comparison of group Vb (V, Nb, Ta) metal oxide clusters," *Eur. Phys. J. D* 2003, *24*, 69. c) Von Helden, G.; van Heijnsbergen, D.; Meijer, G. "Resonant ionization using IR light: A new tool to study the spectroscopy and dynamics of gas-phase molecules and clusters," *J. Phys. Chem. A* 2003, *107*, 1671.

- 39. a) Asmis, K. R.; Meijer, G.; Brümmer, M.; Kaposta, C.; Santambrogio, G.; Wöste, L.; Sauer, J. "Gas phase infrared spectroscopy of mono- and divanadium oxide cluster cations," *J. Chem. Phys.* 2004, *120*, 6461. b) Asmis, K. R.; Sauer, J. "Mass-selective vibrational spectroscopy of vanadium oxide cluster ions," *Mass Spectrom. Rev.* 2007, *26*, 542. c) Feyel, S.; Schwarz, H.; Schröder, D.; Daniel, C.; Hartl, H.; Dobler, J.; Sauer, J.; Santambrogio, G.; Wöste, L.; Asmis, K. R. "Gas-phase infrared photodissociation spectroscopy of tetravanadiumoxo and oxo-methoxo cluster anions," *ChemPhysChem* 2007, *8*, 1640. d) Santambrogio, G.; Brümmer, M.; Wöste, L.; Dobler, J.; Sierka, M.; Sauer, J.; Meijer, G.; Asmis, K. R. "Gas phase vibrational spectroscopy of mass-selected vanadium oxide anions," *Phys. Chem. Chem. Phys.* 2008, *10*, 3992.
- 40. a) Veliah, S.; Xiang, K. H.; Pandey, R.; Recio, J. M.; Newsam, J. M. "Density functional study of chromium oxide clusters: Structures, bonding, vibrations, and stability," *J. Phys. Chem. B* 1998, *102*, 1126. b) Xiang, K. H.; Pandey, R.; Recio, J. M.; Francisco, E.; Newsam, J. M. "A theoretical study of the cluster vibrations in Cr<sub>2</sub>O<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>4</sub>," *J. Phys. Chem. A* 2000, *104*, 990.
- 41. a) Reddy, B. V.; Khanna, S. N. "Chemically induced oscillatory exchange coupling in chromium oxide clusters," *Phys. Rev. Lett.* 1999, *83*, 3170. b) Jones, N. O.; Reddy, B. V.; Rasouli, F.; Khanna, S. N. "Structural growth in iron oxide clusters: Rings, towers, and hollow drums," *Phys. Rev. B* 2005, *72*, 165411. c) Jones, N. O.; Reddy, B. V.; Rasouli, F.;

Khanna, S. N. "Errata: Structural growth in iron oxide clusters: Rings, towers, and hollow drums," *Phys. Rev. B* **2006**, *73*, 119901.

- 42. Calatayud, M.; Andres, J.; Beltran, A. "A systematic density functional theory study of  $V_x O_y^+$  and  $V_x O_Y$  (X=2-4, Y=2-10) systems," *J. Phys. Chem. A* **2001**, *105*, 9760.
- 43. Ayers, T. M.; Fye, J. L.; Li, Q.; Duncan, M. A. "Synthesis and isolation of titanium metal cluster complexes and ligand-coated nanoparticles with a laser vaporization flowtube reactor," *J. Cluster Sci.* **2003**, *14*, 97.
- 44. Muller, A.; Sessoli, R.; Krickemeyer, E.; Bogge, H.; Meyer, J.; Gatteschi, D.; Pardi, L.; Westphal, J.; Hovemeier, K.; Rohlfing, R.; Doring, J.; Hellweg, F.; Beugholt, C.; Schmidtmann, M. "Polyoxovanadates: High-nuclearity spin clusters with interesting host-guest systems and different electron populations. Synthesis, spin organization, magnetochemistry and spectroscopic studies," *Inorg. Chem.* 1997, *36*, 5239.
- 45. Livage, J. "Synthesis of polyoxovanadate s via 'chimie douce'," *Coord. Chem. Rev.* **1998**, *178*, 999.
- 46. Long, D. L.; Orr, D.; Seeber, G.; Kogerler, P.; Farrugia, L. J.; Cronin, L. "The missing link in low nuclearity pure polyoxovanadate clusters: Preliminary synthesis and structural analysis of a new V<sub>16</sub> cluster and related products," *J. Cluster Sci.* **2003**, *14*, 313.
- 47. Wang, L.; Sun, X. P.; Liu, M. L.; Gao, Y. Q.; Gu, W.; Liu, X. "Syntheses, structures and properties of three heteronuclear complexes containing V<sub>10</sub>O<sub>28</sub><sup>6–</sup> units," *J. Cluster Sci.* 2008, *19*, 531.
- 48. Surnev, S.; Ramsey, M. G.; Netzer, F. P. "Vanadium oxide surface studies," *Prog. Surf. Sci.*2003, 73, 117.
- 49. Bond, G. C.; Tahir, S. F. "Vanadium-oxide monolayer catalysts preparation,

characterization and catalytic activity," Appl. Catal. 1991, 71, 1.

- 50. Zhang, X.; Schwarz, H. "Generation of gas-phase nanosized vanadium oxide clusters from a mononuclear precursor by solution nucleation and electrospray ionization," *Chem. Eur. J.* **2010**, *16*, 1163.
- 51. a) Bowles, R. S.; Kolstad, J. J.; Calo, J. M.; Andres, R. P. "Generation of molecular clusters of controlled size," *Surf. Sci.* 1981, *106*, 117. b) ) Chao, L. C.; Andres, R. P. "Synthesis of a supported metal catalyst using nanometer-size clusters," *J. Colloid Interface Sci.* 1994, *165*, 290. c) Mahoney, W.; Andres, R.P. *Mater. Sci. Eng. A* 1995, *A204*, 160.
- 52. Cornett, D. S.; Amster, I. J.; Duncan, M. A.; Rao, A. M.; Eklund, P. C. "Laser desorption mass spectrometry of photopolymerized C<sub>60</sub> films," *J. Phys. Chem.* **1994**, *97*, 5036.
- 53. Frisch, M. J. et al.; Gaussian, Inc., Wallingford CT, 2004.
- 54. Schafer, A.; Huber, C.; Ahlrichs, R. "Fully optimized contracted Gaussian-basis sets of triple zeta valence quality for atoms Li to Kr," *J. Chem. Phys.* **1994**, *100*, 5829.
- Selbin, J.; Morpurgo, L. "Spectral studies of low symmetry oxo-vanadium (IV) complexes," *J. Inorg. Nucl. Chem.* 1965, 27, 673.
- 56. Gharbi, N.; Sanchez, C.; Livage, J.; Lemerle, J.; Néjem, L.; Lefebvre, J. "Mixed-valence polyvanadic acid gels," *Inorg. Chem.* 1982, 21, 2758
- 57. Iwamoto, M.; Furukawa, H.; Matsukami, K.; Takenaka, T.; Kagawa, S. "Diffuse reflectance infrared and photo-luminescence spectra of surface vanadyl groups – direct evidence for change of bond strength and electronic-structure of metal oxygen bond upon supporting oxide," J. Am. Chem. Soc. 1983, 105, 3719.

- 58. Garcia, H.; Nieto, J. M. L.; Palomares, E.; Solsona, B. "Photoluminescence of supported vanadia catalysts: linear correlation between the vanadyl emission wavelength and the isoelectric point of the oxide support," *Catal. Lett.* **2000**, *69*, 217.
- Kawashima, M.; Oda, N.; Uchida, Y.; Matsui, K. "Phosphorescence of vanadium oxide dispersed in silica," *J. Lumin.* 2000, 87, 685.
- 60. Teramura, K.; Hosokawa, T.; Ohuchi, T.; Shishido, T.; Tanaka, T. "Photoactivation mechanism of orthovanadate-like (V = O)O<sub>3</sub> species," *Chem. Phys. Lett.* **2008**, *460*, 478.
- 61. Nakajima, T.; Isobe, M.; Tsuchiya, T.; Ueda, Y.; Kumagai, T. "A revisit of photoluminescence property for vanadate oxides AVO<sub>3</sub> (A:K, Rb and Cs) and M<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (M:Mg and Zn)," *J. Lumin.* 2009, *129*, 1598.
- 62. Zubkov, V. G.; Tyutyunnik, A. P.; Tarakina, N. V.; Berger, I. F.; Surat, L. L.; Slobodin, B. V.; Svensson, G.; Forslund, B.; Shulgin, B. V.; Pustovarov, V. A.; Ishchenko, A. V.; Cherepanov, A. N. "Synthesis, crystal structure and luminescent properties of pyrovanadates A<sub>2</sub>CaV<sub>2</sub>O<sub>7</sub> (A = Rb, Cs)," *Solid State Sci.* 2009, *11*, 726.
- 63. Slobodin, B. V.; Surat, L. L.; Samigullina, R. F.; Ishchenko, A. V.; Shulgin, B. V.;
  Cherepanov, A. N. "Thermochemical and luminescent properties of the K<sub>2</sub>MgV<sub>2</sub>O<sub>7</sub> and M<sub>2</sub>CaV<sub>2</sub>O<sub>7</sub> (M = K, Rb, Cs) vanadates," *Inorg. Mater.* 2010, *46*, 522.
- 64. Pol, V. G.; Pol, S. V.; Calderon-Moreno, J. M.; Gedanken, A. "Core-shell vanadium oxide-carbon nanoparticles: Synthesis, characterization and luminescence properties," *J. Phys. Chem. C* 2009, *113*, 10500

# CHAPTER IV

# SELECTIVE PRODUCTION OF LIGAND COATED Co<sub>4</sub>O<sub>4</sub> VIA

#### A LASER VAPORIZATION FLOWTUBE REACTOR

# Introduction

The interesting properties of transition metal oxide nanoparticles make them useful in catalysts, chemical sensors, fuel cells, magnetic materials and in many other diverse applications.<sup>1-12</sup> Cobalt forms a particularly interesting oxide which has been noted for its interesting magnetic<sup>13-14</sup> and catalytic properties.<sup>15-21</sup> For example, ultra-small (sub-nanometer) cobalt oxide structures have been suggested as photocatalysts for solar energy conversion and water splitting.<sup>22-28</sup> The Co<sub>4</sub>O<sub>4</sub> cubane species has drawn intense interest is this regard, as it is analogous to the manganese oxide cube at the heart of photosystem II.<sup>29</sup> Although the production and analysis of a pure cubic Co<sub>4</sub>O<sub>4</sub> species is a challenge, it has been accomplished by inorganic synthesis using cobalt salts and acetate, acetyl, pyridine and/or bipyridine ligands.<sup>22,23,25-27</sup>

Cobalt oxide clusters have also been studied in gas phase molecular beams<sup>30-40</sup> and in solid rare gas matrices.<sup>41</sup> These experiments have investigated the bonding,<sup>30,31,33-35,38,40,41</sup> reactivity,<sup>32,34,36,37,39,41</sup> and electronic structure<sup>33,35</sup> of small clusters. Cationic and/or anionic cobalt oxide clusters have been shown, using collision induced dissociation (CID) or photodissociation, to prefer 1:1 cobalt to oxygen ratios with larger clusters fragmenting

by loss of O<sub>2</sub>.<sup>37,40</sup> Reaction rates of neutral cobalt oxide with small molecules revealed a similar trend where clusters with 1:1 ratios had lower reaction rates. For small cluster in the gas phase the consensus has been that equal numbers of cobalt and oxygen form clusters which are both thermodynamically favorable and chemically inert. The most common bulk phase of cobalt oxide is cobalt (II, III) oxide (Co<sub>3</sub>O<sub>4</sub>), although cobalt (II) and cobalt (III) oxide have been observed. Interestingly, gas phase materials seem to form stoichiometries which are different from those of the bulk. Computations on cobalt oxide represent a serious challenge and it is among the least theoretically studied of the first row (3d) transition metal oxides.<sup>42,43</sup> This difficulty is due to the occurrence of many low-lying excited states which often differ only by their electronic spin configuration. In spite of this, some computational studies of small cobalt oxides have been accomplished using density functional theory (DFT).<sup>34,35,41-43</sup> The interesting electronic structure and catalytic activity of cobalt oxide, as well as its propensity to form different structures in the gas phase than in the bulk, make it an ideal candidate for experiments with the laser vaporization flowtube reactor (LVFR).

Although molecular beam studies have shown that many different cobalt oxide cluster sizes are stable, we find that under some conditions the LVFR is able to produce a relatively pure sample of one cluster size coated with MeCN:  $Co_4O_4(MeCN)_6$ . The combination of vibrational spectroscopy and careful theoretical investigations suggest that this material grows as a ring, but with the addition of ligands, transitions to a more stable cube-like structure.

#### **Experimental and Theoretical Methods**

The LVFR has been described in previous publications<sup>44</sup> as well as in earlier chapters. Coated cobalt oxide clusters can be produced using either the linear (see Chapter II, Figure 2.1)

or bent (see Chapter III, Figure 2.1) configuration of the apparatus, although we find a linear configuration to produce better yields. Cobalt oxide clusters are produced using a Lambda Physik Compex 110 KrF excimer laser which ablates a 1/4 inch cobalt rod in the presence of an oxygen/helium gas mixture. The fluence of this laser is important for the successful production of coated clusters. We focus this laser to 3 x 13 mm rectangle and use 60 mJ pulses at a repetition rate of 100 Hz. A mixture of 10% oxygen in helium is used as the reactant gas, although successful production of coated cobalt oxide clusters has been achieved with as low as 5% O<sub>2</sub>. The oxygen-helium mixture is injected into the flowtube through a small ( $\sim$ 750 µm) hole positioned 8 mm away from the metal rod. This gas flow interacts with the laser induced plasma to create small metal oxide clusters. In these experiments acetonitrile is heated to  $60 \,^{\circ}\text{C}$ and backed by 5 psi of argon gas. The mixture of acetonitrile vapor and argon gas is injected into the flowtube downstream from the laser vaporization region. Coated clusters are condensed and collected in a liquid nitrogen trap. We find MeCN complexes efficiently with ultra-small clusters created in the LVFR and that the resulting samples are stable, soluble and well behaved. After three to six hour collection times, dark grey material surrounded by frozen acetonitrile is visible in the trap. After the sample has been extracted and excess solvent has been removed using a Buchii Rotovapor-R, ~0.1 mL of bright blue solution is obtained (Figure 1). It is important to note that the conditions for making this blue sample, which we have found is largely homogeneous (discussed below), must be very exact compared to those in our previous work with vanadium and titanium oxides.<sup>44</sup> Changes in the focus of the laser, the laser power, the position of the laser plasma relative to the oxygen/helium gas flow and ultimate pressure inside the flowtube can produce drastically different results. If the laser is slightly defocused, or if pulses lower than 60 mJ are used, we collect only ligand ice. If a slightly higher fluence is used

a yellow sample is collected. If significantly higher powers are used (80-100 mJ/pulse) insoluble gray powder is produced. Higher temperatures of the ligand reservoir (> 60 °C) or increased flow rates of the ligand/argon mixture can create a buildup of frozen ligand on the walls of the flowtube which can block the flow. This can result in higher overall pressures in the tube leading to the production of the same insoluble powder which we observe from high fluence. Under the correct conditions, coated cobalt oxide clusters produced by this method are stable over several weeks and not air sensitive.

Characterization tools for theses coated clusters includes laser desorption time-of-flight mass spectrometry (LDI ToF-MS), surface enhanced Raman spectroscopy (SERS), UV-visible spectroscopy and fluorescence emission. Mass spectra are obtained using green laser pulses (532 nm) from a Nd:YAG laser (New Wave Research, Polaris II) and a home-made time-of-flight instrument, which has been described in detail (Chapter II). Mass calibration, which is critical for these experiments, employs coronene (300 amu) or  $C_{60}$  (720 amu) added to the samples. For SERS spectra, we place a drop of the sample onto a film of Ag nanorods. These films are produced by the Dluhy group and the method for their production has been described previously.<sup>45</sup> A 785 nm diode laser is used to excite the sample in these experiments and the spectrum is recorded using a commercial Renishaw InVia Raman Microscope. Use of a low energy per photon laser is required in order to prevent fluorescence of the sample from interfering with the Raman signal. UV-visible absorption spectra are collected using a Shimadzu UV-2401 PC spectrometer and fluorescence emission spectra are obtained using a SPEX Fluorolog 1692T.

Computational studies on clusters containing multiple cobalt atoms are difficult due to the complex electronic structure of cobalt, which leads to multiple low lying electronic states.

Therefore, we have begun collaboration with Truhlar and co-workers in order to predict reasonable structures for cobalt complexes. Density functional theory is used to compute these structures, and their vibrational patterns are compared with the spectra obtained from SERS. The M06 and M06-L functionals developed by Truhlar<sup>46</sup> have been used to investigate coated and uncoated cobalt clusters. The computational cost of optimizing structures of cobalt clusters coated with acetonitrile is high and so the hybridized M06 functional could not be used. The non-hybridized functional M06-L performed much better. Both functionals give roughly equivalent structures for the bare clusters. Computations by both our group and Truhlar's were carried out using the Gaussian 09 program suite.<sup>47</sup> We have also computed the structure of these clusters in house using the non-hybridized BP86 functional. We obtain qualitatively similar results to those of Truhlar and coworkers. The TVZP basis set developed by Ahlrichs and coworkers<sup>48</sup> has been employed for computations using the M06 and M06-L functionals while the smaller 6-31g basis set is used with BP86.

### **Results and Discussion**

A frozen mixture of ligand-coated clusters and excess ligand molecules is observed in the collection flask after as little as 30 minutes of LVFR operation. As this mixture warms to room temperature, the solid material and frozen ligand liquefy together to form a solution, with no agitation or stirring. The collection flask can be soaked overnight in excess acetonitrile to increase the collection efficiency. Control experiments in the absence of any ligand also produce dark material in the collection flask, but this product does not dissolve. Successful operation for three to six consecutive hours produces approximately a milliliter of colored solution. As we have noted above, precise control of the LVFR parameters can produce a strikingly blue solution

(Figure 4.1), while laser powers that are too low produce nothing, and higher fluences create a yellow solution or insoluble material.

Analysis of these materials begins with LDI ToF-MS. First, careful control experiments were conducted by taking mass spectra of bulk cobalt oxide suspended in acetonitrile. This was done to avoid presenting mass spectra of ions which are created by the LDI process and are not representative of material produced in the LVFR. These control experiments produced nothing remotely resembling the mass spectra of our sample. Mass spectra of our coated cobalt clusters are presented in Figures 4.2 and 4.3. For our previous study on vanadium oxide clusters we captured clusters which were roughly analogous to stable clusters produced in molecular beams.<sup>44</sup> Gas phase studies on cobalt clusters have suggested that no particularly stable cluster sizes exist, but that they do prefer to form with 1:1 cobalt to oxygen ratios.<sup>30-40</sup> It was incredibly surprising then when we first observed the mass spectrum of the bright blue sample (Figure 4.2). Here we find one main mass: 546 amu, which we assign to Co<sub>4</sub>O<sub>4</sub>(MeCN)<sub>6</sub>, and some smaller fragments of this dominant cluster. Higher laser powers increase the intensity of these fragments but do not produce higher mass ion signals. Figure 4.3 shows a mass spectrum of the yellow solution produced when slightly more powerful laser pulses are used to ablate the cobalt rod. This mass spectrum indicates that  $Co_4O_4(MeCN)_6$  is still present in the yellow solution but it is accompanied by masses corresponding to clusters with three cobalt atoms. These lower mass peaks at 307, 291 and 250 amu are assigned to Co<sub>3</sub>O<sub>3</sub>(MeCN)<sub>2</sub>, Co<sub>3</sub>O<sub>2</sub>(MeCN)<sub>2</sub> and Co<sub>3</sub>O<sub>3</sub>(MeCN)<sub>1</sub> respectively. These intense lower masses are only observed when higher ablation laser powers are used in the LVFR. This suggests that source conditions which are "hot" or too energetic favor the production of smaller cluster sizes, or that larger clusters cannot survive the harsher environment. The analysis here, focuses on the pure blue sample, as



Figure 4.1. Photograph of cobalt oxide sample produced with 60mJ laser pulses.



Figure 4.2. Mass spectrum of the blue sample solution of cobalt oxide nanoclusters coated with acetonitrile.



Figure 4.3. Mass spectrum of the yellow solution of cobalt oxide nanoclusters coated with acetonitrile.

characterization of the yellow sample is still underway. The production of almost solely  $Co_4O_4(MeCN)_6$  is interesting not only because of its striking contrast with the previous gas phase studies, but also because ligand coated  $Co_4O_4$  has been created by inorganic methods<sup>22,23,25-27</sup> and has been postulated as an active catalysis for water splitting. <sup>22-28</sup>

Reports in the literature have shown that cores of Co<sub>4</sub>O<sub>4</sub> can be synthesized in solution using cobalt salts.<sup>22,23,25-27</sup> Characterization of these materials using <sup>1</sup>H NMR, spectroscopy, and X-ray crystallography show that the core has a cubic structure.<sup>22,23</sup> This cluster has also been studied in the gas phase and shown to be stable and relatively inert. The structure of this gas phase cluster has not been determined experimentally because absorption spectroscopy is impossible in mass selected molecular beams due to low density of ions, and strong oxide bonds make dissociation spectroscopy difficult. The structure of bare cobalt clusters has been investigated with theory, though even this is challenging. As noted above, this arises from the complex electronic structure of clusters containing multiple cobalt atoms. Some previous theoretical work has suggested that gas phase cobalt oxide clusters form rings which stack to form towers or hollow drums.<sup>38</sup> These ring-like structures were shown to be lower in energy than their cubic isomers. Other mid-row transition metal oxides have also been shown to form rings or towers.<sup>49</sup> It is unclear whether clusters grown using the LVFR will have the same structure as those grown in solution or those predicted for the gas phase. Since  $Co_4O_4(MeCN)_6$ is produced in a gas phase reactor, but is captured in solution, we must investigate both ring and cubic structures.

First we investigated the structure of coated cobalt oxide clusters computationally. With the complexity of cobalt oxide computations in mind, we began collaboration with Truhlar and co-workers from the University of Minnesota, who are experts in the field of DFT. Several

functionals were used to compute ferromagnetic (FM), antiferromagnetic (AFM) and closed shell (CS) spin states of both uncoated ring and cube. The relative energies of these clusters are shown in Table 4.1. We find that a ring FM structure is the most stable at all levels of theory. Cubic structures also converge, although they are higher in energy. The lowest spin state of cubic Co<sub>4</sub>O<sub>4</sub> is AFM when using M06 and FM when using M06-L or BP86. Structures for the bare cube and ring computed at M06, M06-L and BP86 levels can be seen in Figure 4.4. The ring structure remains mostly the same when using the different functionals, but the cube distorts when using non-hybridized functionals (M06-L, BP86). The M06 level of theory proved too computationally expensive for coated cobalt clusters and so M06-L was used. Relative energies for ring and cube structures of  $Co_4O_4(MeCN)_6$  are presented in Table 4.2. A FM cubic structure is more stable than the ring by 12.4 kcal/mol and the AFM structures are even higher in energy. As shown in Figure 4.5, the "ring" structure appears to distort into a structure with Co-O bond distances and Co-O-Co bond angles which closely resemble the cubic structure. This suggests that the addition of ligands to the cobalt oxide core has a profound effect on its structure. To investigate this idea, we compared the ligand binding energy of acetonitrile to the cobalt oxide ring and cube. Figure 4.6 shows the total ligand binding energy, computed at the M06-L level, as an increasing number ligands is added to the oxide cores. As shown, the ring binds the first two ligands strongly, but the interaction of the third acetonitrile and the ring is very weak (only 0.4 kcal/mol). In fact, the coated cube becomes more stable than the ring when >2 acetonitriles are attached to the core. This theoretical investigation supports the idea the cobalt oxide can exist as a ring in the gas phase, but ligand interaction causes the oxide core to transition to a cube.

Cluster (Spin state)	M06/def2-TZVP	M06-L/def2TZVP	BP86/6-31g
Co <sub>4</sub> O <sub>4</sub> cube (S=6, FM)	+17.6	+29.6	+26.5
Co <sub>4</sub> O <sub>4</sub> cube (S=0, AFM)	+15.6	+31.9	+76.3
Co <sub>4</sub> O <sub>4</sub> cube (S=0, CS)	+136.3	+113.5	+76.5
Co <sub>4</sub> O <sub>4</sub> ring (S=6, FM)	0	0	0
Co <sub>4</sub> O <sub>4</sub> ring (S=0, AFM)	+21.1	+8.2	+10.3
Co <sub>4</sub> O <sub>4</sub> ring (S=0, CS)	+405.5	+108.5	71.6

Table 4.1. Relative energy in kcal/mol of ferromagnetic (FM), antiferromagnetic (AFM) and closed shell singlet (CS) cobalt oxide nanoclusters using various functionals.



Figure 4.4. Computed structures for bare cobalt oxide clusters. Rings (a-c) and cubes (d-f) are computed at M06/def2-TZVP (a,d), M06-L/def2-TZVP (b,e) and BP86/6-31g (c,f) levels of theory.

Cluster (Spin state)	M06-L/def2TZVP	
Co <sub>4</sub> O <sub>4</sub> (MeCN) <sub>6</sub> cube (S=6, FM)	0	
Co <sub>4</sub> O <sub>4</sub> (MeCN) <sub>6</sub> cube (S=0, AFM)	+18.1	
Co <sub>4</sub> O <sub>4</sub> (MeCN) <sub>6</sub> ring (S=6, FM)	+12.4	
Co <sub>4</sub> O <sub>4</sub> (MeCN) <sub>6</sub> ring (S=0, AFM)	+14.7	

Table 4.2. Relative energy in kcal/mol of ferromagnetic (FM) and antiferromagnetic (AFM) coated cobalt oxide nanoclusters using the M06-L functional.



Figure 4.5. Computed structures for acetonitrile coated cobalt oxide clusters. Coated cube (left) and distorted ring (right).



Figure 4.6. Total ligand binding energies for ring (red) and cubic (black)  $Co_4O_4$  as up to six acetonitrile ligands are added to the cluster. Energies here are relative to total energy of the  $Co_4O_4$  ring. Computed at the M06-L/def2-TZVP level of theory.

Many attempts were made to crystallize this sample as x-ray crystallographic data would definitively determine its structure. These attempts were not successful, which we believe is due to an insufficient quantity of material. We are investigating ways by which we can improve the yield of the LVFR, but until then we use SERS to experimentally probe the structure of our product. This is because the enhancement effect of the SERS technique facilitates characterization of samples with extremely low concentration. Our cobalt sample adheres to, and creates an ideal film on the silver nanorod arrays which were provided by the Dluhy group. We observed intense Raman spectra that were consistent over the entire surface and between samples. In Figure 4.7 we compare this spectrum to the theoretical predictions for both isomers of  $Co_4O_4(MeCN)_6$ . The bands predicted at 985 cm<sup>-1</sup> for the cube and 978 cm<sup>-1</sup> for the distorted ring are MeCN stretches. Vibrations at 1019 and 1022 cm<sup>-1</sup> are CH<sub>3</sub> wags for the cube and ring, respectively. Since these modes are attributed to the ligand, the scaling factor for them was developed by comparing literature values for acetonitrile to the vibrational frequencies computed for a lone acetonitrile. These values as well as our observed and predicted frequencies for acetonitrile either free or attached cobalt oxide cores can be seen in Table 4.3. The scaling factor is determined to be 1.006 and computational frequencies have been scaled accordingly. The bands lower than 800 cm<sup>-1</sup> are due to metal-oxygen stretches or a combination of acetonitrile and metal-oxygen vibrations. The scaling factor for these frequencies was developed by comparing our computational results to matrix isolation studies for  $Co_2O_2$ .<sup>41</sup> The observed vibrations of  $Co_2O_2$  in Ne and Ar matrices as well as our predicted frequencies are shown in Table 4.4. The scaling factor for metal-oxygen stretches computed at M06-L level of theory is determined to be 1.095. The SERS spectrum of coated cobalt oxide is not completely explained by either the predicted cube or distorted ring spectra. Both the distorted ring and cube have similar vibrational

Mode	Lit Gas	Lit Liq.	Exp. SERS	M06-L MeCN	M06-L 4,4,6 cube	M06-L 4,4,6 ring
C-C Stretch	920.2	918	1010-1029	960	967-987	967-986
CH <sub>3</sub> Wag	1040.8		1055	1030	1009-1019	1005-1018
CH <sub>3</sub> Wag		1376	11387	1376	1370-1378	1371-1378
CH <sub>3</sub> Asym Bend	1447.9	1440		1428	1414-1428	1415-1428
C-N Stretch	2266.5	2249	2246	2346	2277-2324	2213-2264
C-H Sym Stretch	2954.1	2942	2941-2953	3058	3025-3026	3018-3031
C-H Asym Stretch	3009.2	2999	3006-3036	3180	3138-3155	3130-3149

Table 4.3. Vibrational frequencies of acetonitrile. Literature gas and liquid phase values, calculated values and observed SERS values for coated cobalt oxide sample.

Observed in Ne	Observed in Ar	M06-L	Assignment
708 (0.00)*		695.9 (0.00)	Ag
684.5 (1.00)	685.2 (1.00)	654.2 (1.00)	B3u
467.2 (0.67)	469.5 (0.57)	429.2 (0.98)	B2u
460 (0.00)*		403.4 (0.00)	B1g
293.4 (0.24)	304.1 (0.17)	255.0 (0.52)	Blu
183 (0.00)*		261.8 (0.00)	Ag

Table 4.4. Vibrational frequencies for  $\text{Co}_2\text{O}_2$  in Ne and Ar matrices (Relative intensities in parentheses) reported by L. Manceron et. al.<sup>1</sup> Compared to calculated frequencies for this species.

\*Estimated from combination bands

<sup>1</sup>Danset, D.; Manceron, L. "Reactivity of cobalt dimer and molecular oxygen in rare gas matrices. IR spectrum, photophysics and structure of Co<sub>2</sub>O<sub>2</sub>." *Phys. Chem. Chem. Phys.* **2005**, *7*, 583-591.



Figure 4.7. Experimental SERS spectrum (top) of coated cobalt oxide clusters. Predicted spectra for the coated cube (middle) and distorted ring (bottom).

frequencies in the ligand and metal-oxygen regions of the spectrum. Some combination of the two predicted spectra is the best explanation for the observed SERS pattern. Therefore, we conclude that both cube and distorted ring structures are present in our sample. Since we have suggested that these clusters grow as rings first then transition to cubes with the addition of ligands, it seems reasonable that some clusters do not complete the transformation, and are trapped as distorted rings.

The UV-visible spectrum of this coated cobalt oxide species dissolved in MeCN is shown in Figure 4.8. An intense band at 220 nm has an absorption strength of approximately 6000 l/molcm. Similar bands have been seen for cobalt-oxo cubanes coated with pyridine, where it was attributed to transitions of the ligand.<sup>23</sup> This band is likely due to the  $\pi$  -  $\pi$ \* absorption of attached acetonitrile. The visible transitions at 586 (~150 l/mol-cm) and 672 (~ 160 l/mol-cm) nm have also been observed for cubic cobalt oxide clusters in the past.<sup>23</sup> These bands are characteristic of d-d transitions which give metal oxide complexes their brilliant color. The sample is found to exhibit intense photoluminescence from 350 - 600 nm (see Figure 4.9). This emission can be observed when the sample is irradiated with a wide range of wavelengths but is most intense when 355 nm light is used. We have reported this type of behavior for vanadium oxide clusters of similar size coated with MeCN and tetrahydrofuran (THF).<sup>44</sup> As we discussed in that work, this type of white light emission is similar for many metal oxide systems including thin films and nanoparticles. Indeed, photoluminescence has been attributed to cobalt oxide supported on thin films,<sup>50</sup> doped into nanocrystrals or films,<sup>51,52,53,54</sup> and in sol-gel matriels.<sup>55</sup> The coated cobalt oxide clusters produced with the LVFR are unique among the materials synthesized so far. We have produced a material which is composed of largely one cluster size, and which shares similarities to species produced in solution and in the gas phase.



Figure 4.8. Solution phase UV-visible spectrum of cobalt oxide clusters coated and dissolved in MeCN.



Figure 9. Photoluminescence emission spectra of cobalt oxide clusters coated with MeCN. Spectra are obtained at excitation wavelengths of 266, 355, 400, 450, 532 and 550 nm.

But some challenges remain. Low yields have rendered any attempt at accessing this material's catalytic or magnetic properties fruitless. The same issue has prevented the formation of crystals. Theoretical studies have likewise proved challenging, and although we have had some success the predicted spectra for a cubic or distorted ring-like  $Co_4O_4(MeCN)_6$  do not completely agree with the measured spectrum. We intend to increase our production yield and thereby enable a more complete characterization of this material in the future.

### Conclusions

Ultra-small cobalt oxide clusters have been produced in the gas phase, coated with acetonitrile and captured in solution using a Laser Vaporization Flowtube Reactor (LVFR). Previously this apparatus has been used to create coated titanium and vanadium oxide clusters, and in those studies, samples were composed of many cluster sizes and closely resembled stable gas phase clusters.<sup>44</sup> Cobalt oxide appears to be unique then, as our mass spectral analysis reveals mainly one cluster size:  $Co_4O_4(MeCN)_6$ . Previous gas phase studies did not find a  $Co_4O_4$ cluster size particularly stable, although cobalt-oxo cubanes with a  $Co_4O_4$  core have been synthesized using solution chemistry. Spectroscopic and theoretical investigation show the addition of ligands might change structure of Co<sub>4</sub>O<sub>4</sub> from a ring to cube. Perhaps this strong ligand interaction is responsible for the collection of a single cluster size. The UV-visible spectrum for this material is consistent with those observed for other  $Co_4O_4$  ligand coated species. Its broad visible fluorescence is similar to what we observed for coated vanadium oxide clusters and to what has been reported for many metal oxide materials containing cobalt. Characterization of this sample, while illuminating, has been difficult due to low production yields. We plan to scale up the production rate of the LVFR by procuring a faster and more powerful laser which will enable a more complete characterization of future materials.

# References

- 1. Cox, P. A. Transition Metal Oxides, Clarendon: Oxford, 1992.
- 2. Hayashi, C.; Uyeda, R.; Tasaki, A. Ultra-Fine Particles, Noyes, Westwood, 1997.
- 3. Rao C. N.; Raveau, B.; Transition Metal Oxides, Wiley, New York, 1998.
- 4. Aiken, J. D.; Finke, R. G. "A review of modern transition-metal nanoclusters: their synthesis, characterization and applications in catalysis," *J. Mol. Catal. A: Chem.* **1999**, *145*, 1-44.
- 5. Kodama, R. H. "Magnetic nanoparticles," J. Magn. & Magn. Mater. 1999, 200, 359-372.
- 6. a) Hill, C. L. "Introduction: Polyoxometalates Multicomponent molecular vehicles to probe fundamental issues and practical problems," *Chem. Rev.* 1998, *98*, 1-2. b) Hill, C. L. "Progress and challenges in polyoxometalate-based catalysis and catalytic materials chemistry," *J. Mol. Catal. A: Chem.* 2007, *262*, 2-6.
- Schlögl, R.; Abd Hamid, S. B. "Nanocatalysis: Mature science revisited or something really new?" *Angew. Chem. Int. Ed.* 2004, *43*, 1628-1637.
- Luo, X. L.; Morrin, A.; Killard, A. J.; Smyth, M. R. "Application of nanoparticles in electrochemical sensors and biosensors," *Electroanalysis* 2006, *18*, 319-326.
- 9. Franke, M. E.; Koplin, T. J.; Simon, U. "Metal and metal oxide nanoparticles in chemiresistors: Does the nanoscale matter?" *Small* **2006**, *2*, 36-50.
- 10. Maeda, K.; Domen, K. "Photocatalytic water splitting: Recent progress and future challenges," *J. Phys. Chem. Lett.* **2010**, *1*, 2655-2661.
- 11. Joshi, U.; Palasyuk, A.; Arney, D.; Maggard, P. A. "Semiconducting oxides to facilitate the conversion of solar energy to chemical fuels," *J. Phys. Chem. Lett.* **2010**, *1*, 2719-2726.
- 12. Patzke, G. R.; Zhou, Y.; Kontic, R.; Conrad, F. "Oxide nanomaterials: Synthetic developments, mechanistic studies, and technological developments," *Angew. Chem. Int. Ed.*

2011, 50, 826-859.

- Cheng, G. J.; Dennis, C. L.; Shull, R. D.; Walker, A. R. H., "Probing the growth and aging of colloidal cobalt nanocrystals: A combined study by transmission electron microscopy and magnetic measurements," *Cryst. Growth Des.* 2009, *9*, 3714-3720.
- Apatiga, L. M.; Castano, V. M. "Magnetic behavior of cobalt oxide films prepared by pulsed liquid injection chemical vapor deposition from a metal-organic precursor," *Thin Solid Films* 2006, 496, 576-579.
- 15. Belew, J. S.; Garza, C.; Mathieso, J. W. "Catalysis autoxidation in presence of active cobalt oxide," *J. Chem. Soc. D-Chem. Comm.* **1970**, 11, 634-635.
- 16. Jacobs, G.; Das, T. K.; Zhang, Y. Q.; Li, J. L.; Racoillet, G.; Davis, B. H. "Fischer-Tropsch synthesis: Support, loading, and promoter effects on the reducibility of cobalt catalysts," *App. Catal. A-Gen.* 2002, 233, 263-281.
- Cohen, C. T.; Chu, T.; Coates, G. W. "Cobalt catalysts for the alternating copolymerization of propylene oxide and carbon dioxide: Combining high activity and selectivity," *J. Am. Chem. Soc.* 2005, *127*, 10869-10878.
- Jana, S. K.; Kubota, Y.; Tatsumi, T. "Cobalt-substituted polyoxometalate pillared hydrotalcite: synthesis and catalysis in liquid-phase oxidation of cyclohexanol with molecular oxygen," *J. Catal.* 2008, 255, 40-47.
- Zacharaki, I.; Kontoyannis, C. G.; Boghosian, S.; Lycourghiotis, A.; Kordulis, C. "Cobalt oxide supported on alumina catalysts prepared by various methods for use in catalytic afterburner of PEM fuel cell," *Catal. Today* 2009, *143*, 38-44.

- 20. Jia, C.-J.; Schwickardi, M.; Weidenthaler, C.; Schmidt, W.; Korhonen, S.; Wecichuysen, B.
  M.; Schueth, F. "Co<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> Nanocomposite: A very active catalyst for co oxidation with unusual catalytic behavior," *J. Am. Chem.Soc.* 2011, *133*, 11279-11288.
- 21. Guyon, C.; Barkallah, A.; Rousseau, F.; Giffard, K.; Morvan, D.; Tatoulian, M. "Deposition of cobalt oxide thin films by plasma-enhanced chemical vapour deposition (PECVD) for catalytic applications," *Surf. Coat. Tech.* **2011**, *206*, 1673-1679.
- 22. Dimitrou, K.; Folting, K.; Streib, W. E.; Christou, G. "Dimerization of the Co(III)<sub>2</sub>(OH)<sub>2</sub> core to the 1st example of a Co(III)<sub>4</sub>O<sub>4</sub> cubane potential insights into photosynthetic water oxidation," *J. Am. Chem. Soc.* **1993**, *115*, 6432-6433.
- 23. a) Chakrabarty, R.; Bora, S. J.; Das, B. K. "Synthesis, structure, spectral and electrochemical properties, and catalytic use of cobalt(III)-oxo cubane clusters," *Inorg. Chem.* 2007, *46*, 9450-9462. b)Das, B. K.; Chakrabarty, R. "Cobalt(III)-Oxo Cubane Clusters as Catalysts for Oxidation of Organic Substrates," *J. Chem. Sci.* 2011, *123*, 163-173.
- 24. a) Kanan, M. W.; Nocera, D. G. "In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co<sup>2+</sup>," *Science* 2008, *321*, 1072-1075. b) Lutterman, D. A.; Surendranath, Y.; Nocera, D. G. "A self-healing oxygen-evolving catalyst," *J. Am. Chem. Soc.* 2009, *131*, 3838-3839. c) McAlpin, J. G.; Stich, T. A.; Ohlin, C. A.; Surendranath, Y.; Nocera, D. G.; Casey, W. H.; Britt, R. D. "Electronic structure description of a Co(III)<sub>3</sub>Co(IV)O<sub>4</sub> cluster: A model for the paramagnetic intermediate in cobalt-catalyzed water oxidation," *J. Am. Chem. Soc.* 2011, *133* (39), 15444-15452.
- 25. Katsenis, A. D.; Inglis, R.; Slawin, A. M. Z.; Kessler, V. G.; Brechin, E. K.; Papaefstathiou, G. S. "Transforming the cube: A tetranuclear cobalt(II) cubane cluster and its transformation to a dimer of dimers," *Crystengcomm* 2009, *11*, 2117-2120.

- 26. Risch, M.; Khare, V.; Zaharieva, I.; Gerencser, L.; Chernev, P.; Dau, H. "Cobalt-oxo core of a water-oxidizing catalyst film," *J Am. Chem. Soc.* 2009, *131*, 6936-6937.
- 27. McCool, N. S.; Robinson, D. M.; Sheats, J. E.; Dismukes, G. C. "A Co<sub>4</sub>O<sub>4</sub> "cubane" water oxidation catalyst inspired by photosynthesis," *J. Am. Chem. Soc.* **2011**, 133, 11446-11449.
- 28. Wang, L.-P.; Van Voorhis, T. "Direct-coupling O<sub>2</sub> bond forming a pathway in cobalt oxide water oxidation catalysts," *J. Phys. Chem. Lett.* **2011**, *2*, 2200-2204.
- 29. a) Brimblecombe, R.; Bond, A. M.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L.
  "Electrochemical investigation of Mn<sub>4</sub>O<sub>4</sub> cubane water-oxidizing clusters," *Phys. Chem. Chem. Phys.* 2009, 11, 6441-6449. b) Brimblecombe, R.; Kolling, D. R. J.; Bond, A. M.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. "Sustained water oxidation by Mn<sub>4</sub>O<sub>4</sub><sup>7+</sup> core complexes inspired by oxygenic photosynthesis," *Inorg. Chem.* 2009, *48*, 7269-7279. c)
  Dismukes, G. C.; Brimblecombe, R.; Felton, G. A. N.; Pryadun, R. S.; Sheats, J. E.; Spiccia, L.; Swiegers, G. F. "Development of bioinspired Mn<sub>4</sub>O<sub>4</sub> cubane water oxidation catalysts: Lessons from photosynthesis," *Acc. Chem. Res.* 2009, *42*, 1935-1943.
- 30. Jacobson, D. B.; Freiser, B. S. "Transition-metal cluster ions in the gas-phase oxide chemistry of dimeric and trimeric clusters containing iron and cobalt," *J. Am. Chem. Soc.* 1986, *108*, 27-30.
- Nieman, G. C.; Parks, E. K.; Richtsmeier, S. C.; Liu, K.; Pobo, L. G.; Riley S. J.
   "Multiphoton ionization and fragmentation of transition metal cluster oxides: High temperature metal oxide compositions," *High. Temp. Sci.* **1986**, *22*, 115-138.
- 32. Klaassen, J. J.; Jacobson, D. B. "Facile oxygen-exchange by cobalt cluster oxides ions with water-O<sup>18</sup> in the gas-phase," *Inorg. Chem.* **1989**, *28*, 2024-2026.

- 33. Sun, Q.; Sakurai, M.; Wang, Q.; Yu, J. Z.; Wang, G. H.; Sumiyama, K.; Kawazoe, Y.
  "Geometry and electronic structures of magic transition metal oxide clusters M<sub>9</sub>O<sub>6</sub> (M = Fe, Co, and Ni)," *Phys. Rev. B* 2000, 62, 8500-8507.
- 34. a) Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. "Studies of metal oxide clusters: Elucidating reactive sites responsible for the activity of transition metal oxide catalysts," *J. Phys. Chem. B* 2002, *106*, 6136-6148. b) Johnson, G. E.; Reveles, J. U.; Reilly, N. M.; Tyo,
  E. C.; Khanna, S. N.; Castleman, A. W., Jr. "Influence of stoichiometry and charge state on the structure and reactivity of cobalt oxide clusters with CO," *J. Phys. Chem. A* 2008, *112*, 11330-11340. c) Castleman, A. W., Jr. "Cluster structure and reactions: Gaining insights into catalytic processes," *Catal. Lett.* 2011, *141*, 1243-1253.
- 35. Pramann, A.; Koyasu, K.; Nakajima, A.; Kaya, K. "Photoelectron spectroscopy of cobalt oxide cluster anions," *J. Phys. Chem. A* **2002**, *106*, 4891-4896.
- 36. Yi, M. N.; Fisher, K. J.; Dance, I. G. "The generation of gaseous Co<sub>x</sub>O<sub>y</sub><sup>-</sup> clusters and their reactions with alcohols: Formation of homoleptic cobalt alkoxides Co<sup>-4</sup>(OR)<sub>8</sub>," *Int. J. Mass. Spectrom.* 2002, 216, 155-168.
- 37. a) Liu, F. Y.; Li, F. X.; Armentrout, P. B. "Guided ion beam studies of the reactions of Co<sub>n</sub><sup>+</sup> (n=2-20) with O<sub>2</sub>: Cobalt cluster-oxide and -dioxide bond energies," *J. Chem. Phys.* 2005, *123*, 64304-64319. b) Liu, F.; Li, M.; Tan, L.; Armentrout, P. B. "Guided ion beam studies of the reactions of Co<sub>n</sub><sup>+</sup> (n=1-18) with N<sub>2</sub>: Cobalt cluster mononitride and dinitride bond energies," *J. Chem. Phys.* 2008, *128*, 194313/1-12. c) Citir, M.; Liu, F.; Armentrout, P. B. "Methane activation by cobalt cluster cations, Co<sub>n</sub><sup>+</sup> (n=2-16): Reaction mechanisms and thermochemistry of cluster-CH<sub>x</sub> (x=0-3) complexes," *J. Chem. Phys.* 2009, *130*, 054309/1-16.
- 38. Yin, S.; Xue, W.; Ding, X. L.; Wang, W. G.; He, S. G.; Ge, M. F. "Formation, distribution and structures of oxygen-rich iron and cobalt oxide clusters," *Int. J. Mass. Spectrom.* 2009, 281, 72-78.
- 39. a) Xie, Y.; Dong, F.; Heinbuch, S.; Rocca, J. J.; Bernstein, E. R. "Oxidation reactions on neutral cobalt oxide clusters: Experimental and theoretical studies," *Phys. Chem. Chem. Phys.* 2010, *12*, 947-959. b) Wang, Z.-C.; Yin, S.; Bernstein, E. R. "Gas-phase neutral binary oxide clusters: Distribution, structure, and reactivity toward CO," *J. Phys. Chem. Lett.* 2012, *3*, 2415-2419.
- 40. Dibble, C. J.; Akin, S. T.; Ard, S.; Fowler, C. P.; Duncan, M. A. "Photodissociation of cobalt and nickel oxide cluster cations," *J. Chem. Phys. A* **2012**, *116*, 5398-5404.
- 41. a) Danset, D.; Manceron, L. "Reactivity of cobalt dimer and molecular oxygen in rare gas matrices. IR spectrum, photophysics and structure of Co<sub>2</sub>O<sub>2</sub>," *Phys. Chem. Chem. Phys.* 2005, *7*, 583-591. b) Souvi, S. O.; Danset, D.; Alikhani, M. E.; Manceron, L. "Formation and structure of Co<sub>2</sub>O<sub>4</sub>: a combined IR matrix isolation and theoretical study," *J. Phys. Chem.A* 2010, *114*, 11399-11407
- 42. a) Uzunova, E. L.; St Nikolov, G.; Mikosch, H. "Electronic structure and vibrational modes of cobalt oxide clusters CoO<sub>n</sub> (n=1-4) and their monoanions," *J. Phys. Chem. A* 2002, *106*, 4104-4114. b) Uzunova, E. L.; St. Nikolov, G.; Mikosch, H. "Manganese, iron, cobalt and nickel oxo-, peroxo-, and superoxoclusters: A density functional theory study," *ChemPhysChem* 2004, *5*, 192-201. c) Uzunova, E. L. "Density functional study of the stable oxidation states and the binding of oxygen in MO<sub>4</sub> clusters of the 3d elements," *J. Phys. Chem. A* 2011, *115*, 10665-10678.
- 43. Schroeder, D.; de Jong, K. P.; Roithova, J. "Gas phase model studies relevant to the

decomposition of transition-metal nitrates M(NO<sub>3</sub>)<sub>2</sub> (M =Co, Ni) into metal-oxo species," *Eur. J. Inorg. Chem.* **2009**, *14*, 2121-2128.

- 44. a) Ayers, T. M.; Fye, J. L.; Li, Q.; Duncan, M. A. "Synthesis and isolation of titanium metal cluster complexes and ligand-coated nanoparticles with a laser vaporization flowtube reactor," *J. Clust. Sci.* 2003, *14*, 97-113. b) Ard, S.; Dibble, C. J.; Akin, S. T.; Duncan, M. A. "Ligand-coated vanadium oxide clusters: capturing gas-phase magic numbers in solution," *J. Phys. Chem. C* 2011, *115*, 6438-6447.
- 45. Chaney, S. B.; Shanmukh, S.; Dluhy, R. A.; Zhao, Y. P. "Aligned silver nanorod arrays produce high sensitivity surface-enhanced Raman spectroscopy substrates," *Appl. Phys. Lett.* 2005, 87, 031908/1-3.
- 46. a) Zhao, Y.; Truhlar, D. G. "A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions," *J. Chem. Phys.* 2006, *125*, 194101/1-18. b) Zhao, Y.; Truhlar, D. G. "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals," *Theor. Chem. Acc.* 2008, *120*, 215-241.
- 47. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.;

Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.;
Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.;
Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.;
Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.;
Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.;
Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

- 48. Schafer, A.; Huber, C.; Ahlrichs, R. "Fully optimized contracted Gaussian-basis sets of triple zeta valence quality for atoms Li to Kr," *J. Chem. Phys.* **1994**, *100*, 5829-5835.
- Jones, N. O.; Reddy, B. V.; Rasouli, F.; Khanna, S. N. "Structural growth in iron oxide clusters: Rings, towers, and hollow drums," *Phys. Rev. B* 2005, 72, 165411-165415.
- 50. Shirai, M.; Asakura, K.; Iwasawa, Y. "Anisotropic structure-analysis for cobalt oxides on alpha-Al<sub>2</sub>O<sub>3</sub> (0001) by polarized total-reflection fluorescence extended x-ray absorption finestructure," *Catal. Lett.* **1992**, *15*, 247-254.
- 51. Lim, M. H.; Kuang, C.; Lippard, S. J. "Nitric oxide-induced fluorescence enhancement by displacement of dansylated ligands from cobalt," *Chembiochem* **2006**, *7*, 1571-1576.
- 52. Bohle, D. S.; Spina, C. J. "Cationic and anionic surface binding sites on nanocrystalline zinc oxide: surface influence on photoluminescence and photocatalysis," *J. Am. Chem. Soc.* 2009, *131*, 4397-4404.
- 53. Vempati, S.; Shetty, A.; Dawson, P.; Nanda, K. K.; Krupanidhi, S. B. "Solution-based synthesis of cobalt-doped ZnO thin films," *Thin Solid Films* **2012**, *524*, 137-143.
- Yamamoto, S. "Photoluminescence quenching in cobalt doped ZnO nanocrystals," *J. Appl. Phys.* 2012, *111*, 094310/1-6.

55. Kirit, S.; Dimple, S. "Characterization of nanocrystalline cobalt doped TiO<sub>2</sub> sol-gel material," J. Cryst. Growth 2012, 352, 224-228.

#### CHAPTER V

# CAPTURING LIGAND COATED ANALOGUES OF STABLE GAS PHASE CHROMIUM OXIDE CLUSTERS IN SOLUTION

## Introduction

Transition metal oxides can be found at the heart of a diverse number of technical applications.<sup>1</sup> Chromium oxide in particular has many uses as both a catalyst<sup>2</sup> and as a magnetic material.<sup>3</sup> Thin films of chromium oxide or supported chromium oxide have been shown to assist in polymerization of hydrocarbons<sup>4</sup> as well as in the oxidation or reduction of small molecules with industrial relavence.<sup>5-7</sup> For many years, chromium oxides have been used as the basis of magnetic recording systems.<sup>8-10</sup> The interesting properties of chromium oxide materials is due to chromium's high spin <sup>7</sup>S<sub>3</sub> (3d<sup>5</sup>4s<sup>1</sup>) electronic ground state and charge transfer between Cr and O. Here we use the laser vaporization flowtube reactor (LVFR) to produce very small clusters of this material coated with small organic ligands.

Metal oxides have been studied extensively in the gas phase.<sup>11-18</sup> Small clusters have been shown to sometimes form preferential stoichiometries which are different than those of the bulk. These stable or "magic number" clusters have been the subject of much interest due to their exotic nature. Castleman and co-workers have investigated the reactivity of these small clusters with small hydrocarbons.<sup>11</sup> Neutral cluster formation has been investigated by Bernstein and co-workers.<sup>12</sup> These reports show that these "magic number" cluster sizes are formed by laser vaporization with greater relative intensity and that they are unreactive. These observations were used to suggest the enhanced stability of these clusters, although mass-selected photofragmentation performed by our group has been shown to be a clearer indication of cluster stability.<sup>14</sup> It should be noted though that all of these methods often suggest stability of the same stoichiometries. Structures of several metal oxide systems have been investigated using infrared spectroscopy by our group<sup>19</sup> and others.<sup>20,21</sup> Since the metal-oxygen vibrations are typically observed at or below 1000 cm<sup>-1</sup>, free electron lasers which produce high energies pulses at these frequencies were used to perform either IR-resonance enhanced multiphoton ionization (IR-REMPI) or IR-resonance enhanced multiphoton dissociation to acquire the spectral data. Recently, ion traps have been used to tag these clusters with weakly bound "messenger" atoms, making photodissociation spectroscopy using bench top lasers possible.

The chromium oxide system in particular has shown strong preference for "magic number" clusters. The  $Cr_4O_{10}$  species has displayed remarkable prevalence. It forms with abundance in gas phase cluster distributions and is also observed as a common neutral leaving group or as a charged photofragment in photodissociation experiments.  $Cr_3O_{6-7}$ ,  $Cr_5O_{11-13}$ ,  $Cr_6O_{14-15}$ , and  $Cr_7O_{16-17}$  have also been shown as particularly stable cluster sizes. In previous reports we have shown that stable gas phase clusters can be captured using the LFVR.<sup>22</sup> In that work we showed that acetonitrile (MeCN) ligands could be used to capture vanadium oxide cluster stoichiometries similar to those seen in gas phase, while tetrahydrofuran (THF) could be used to capture analogous clusters with terminal oxygen atoms replaced with ligands. We have also shown, in the previous chapter, that some oxides, cobalt in that case, behave differently in the LFVR than they do in traditional gas phase molecular beams. It is with this in mind that we turn our attention to chromium oxide. Since this oxide has been shown to have strong preference for specific stoichiometries in the gas phase, we expect to be able to capture these same clusters in solution. Indeed, with careful operation of the LVFR we are able not only to produce many of the same "magic number" cluster sizes coated with MeCN, but also produce them in much larger quantities than we have been able to achieve with other systems. The size of these ligand coated chromium oxide clusters can also be adjusted with careful control of the LVFR parameters.

#### **Experimental and Theoretical Methods**

The LVFR has been described in earlier chapters of this work as well as in previous publications.<sup>22</sup> Coated chromium oxide clusters are produced using the bent (see Chapter III, Figure 3.1) configuration of the apparatus. Oxide clusters are produced using a Lambda Physik Compex 110 KrF excimer laser which ablates a 1/4 inch chromium rod in the presence of an oxygen/helium gas mixture. We focus this laser to 3 x 13 mm rectangle and use 100-200 mJ pulses at a repetition rate of 100 Hz. 10% oxygen in helium is used as the reactant gas and is injected into the flowtube through a small (~750 µm) hole positioned 8 mm away from the metal rod, resulting in an ambient pressure of 5 torr. The laser induced plasma reacts with this gas to create small metal oxide clusters. In this work as well as in previous studies we find MeCN to complex efficiently to ultra-small clusters created in the LVFR. Although we have investigated the use of other ligands (tetrahydrofuran, propionitrile, pyridine), we find that the oxide cores complex efficiently with MeCN and that the resulting samples are more easily characterized. Acetonitrile is heated to 60 °C and backed by 5 psi of argon gas. This mixture of acetonitrile vapor and argon gas is injected into the flowtube downstream from the laser vaporization region, and contributes 100 mtorr to the partial pressure of the flowtube. Coated clusters are collected further downstream in a liquid nitrogen trap. Typical run times of six hours produce

approximately one milligram of brown powder which dissolves in excess MeCN. The resulting solution can be seen in Figure 5.1. Coated chromium oxide clusters produced by this method are stable over several weeks and not air sensitive.

Characterization tools for coated clusters include laser desorption time-of-flight mass spectrometry (LDI ToF-MS), surface enhanced Raman spectroscopy (SERS), UV-visible spectroscopy, fluorescence emission, high purity liquid chromatography (HPLC) and liquid chromatography/mass spectrometry (LC-MS). For an initial characterization, mass spectra are obtained using UV (355 nm) or green laser pulses (532 nm) from a Nd:YAG laser (New Wave Research, Polaris II) and a home-made time-of-flight instrument, which has been described in detail (Chapter II). Mass calibration, which is critical for these experiments, employs coronene (300 amu) or  $C_{60}$  (720 amu) added to the samples. For SERS spectra, we place a drop of the sample onto a film of Ag nanorods provided by the Dluhy group.<sup>23</sup> A 785 nm diode laser is used to excite the sample in these experiments and the spectrum is recorded using a commercial Renishaw InVia Raman Microscope. A low energy per photon laser is required in order to prevent fluorescence of the sample from interfering with the Raman signal. UV-visible absorption spectra are collected using a SPEX Fluorolog 1692T.

In addition to mass and spectroscopic analysis, purification methods are also being explored. HPLC (Thermo Scientific SpectraSYSTEM) featuring a C18 column is used to separate components of the sample. We have begun a very preliminary study using LC-MS to determine if the separated components of the sample correspond to different sized clusters.

Density functional theory (DFT) calculations reported are performed using the BP86 functional and the Gaussian 09 program suite.<sup>24</sup> The TVZP basis set developed by Ahlrichs and



Figure 5.1. Photograph of chromium oxide sample solution.

co-workers is employed.<sup>25</sup> Multiple isomeric structures, as reported in the literature for the bare clusters, were investigated with attached ligands.

#### **Results and Discussion**

Brown frozen material is observed in the collection flask in as little as thirty minutes of LVFR operation. Upon warming to room temperature, this material forms a brown solution. Excess solvent can be removed and the resulting sample is a brown powder. Six hours of collection time can produce 1-2 mg of this powder. Control experiments where the LVFR was operated with no MeCN resulted in dark grey material which was not soluble in MeCN. The production yield observed for coated chromium oxide clusters is much higher than the yield for the vanadium or cobalt clusters previously produced with the LVFR. Characterization of coated chromium oxide clusters shows similar results when analyzed immediately after capture, after drying/re-solvating, or after several weeks.

Promptly after collection, analysis of these clusters begins with LDI ToF-MS. A few drops of sample solution are placed on a stainless tip and allowed to dry forming a thin film. Mass spectra are collected by neat desorption of this sample inside the acceleration region of the mass spectrometer. Control experiments are performed by measuring mass spectra of bulk chromium oxide suspended in MeCN and these spectra do not resemble those of our samples. Sample mass spectra of coated chromium oxide clusters can be seen in Figures 5.2 - 5.4. These spectra are taken at threshold desorption powers, as higher powers only increase the intensity of low mass peaks (< 100 amu) indicating that they are fragment ions. In our previous studies on vanadium and cobalt oxides we found that specific vaporization laser powers used in the LVFR were required for the successful production of coated clusters, but for chromium oxide we find



Figure 5.2. Mass spectrum of acetonitrile coated chromium oxide clusters produced with approximately 100 mJ laser pulses.



Figure 5.3. Mass spectrum of acetonitrile coated chromium oxide clusters produced with approximately 120-140 mJ laser pulses.



Figure 5.4. Mass spectrum of acetonitrile coated chromium oxide clusters produced with approximately 160-180 mJ laser pulses.

that interesting samples can be produced at a variety of laser powers. The window at which successful creation of these clusters is possible is 100-200 mJ/pulse. Lower energy pulses produce nothing, while higher energies create only insoluble material. A mass spectrum of clusters synthesized by 100 mJ pulses can be seen in Figure 5.2. Peaks in this spectrum are assigned primarily to chromium oxide clusters containing four chromium atoms and 9-11 oxygen atoms complexed with to up to three ligands. The largest peaks, 409 and 434 amu, are assigned to  $Cr_4O_{10}(MeCN)$  and  $Cr_4O_9(MeCN)_2$  respectively. Gas phase molecular beam studies have shown that  $Cr_4O_{10}$  and  $Cr_4O_9$  clusters are particularly stable species. These results suggest that we are indeed able to capture "magic number" cluster sizes of chromium oxide clusters. Similar behavior was observed in our previous study on vanadium oxide clusters, although in that work several stable clusters sizes were produced at once. Here, the chromium oxide sample produced with 100 mJ pulses exhibits a smaller distribution of cluster sizes. Figure 5.3 is a representative mass spectrum for samples created with higher vaporization powers (120 - 140 mJ/pulse). In this spectrum  $Cr_4O_{10}$  (MeCN) and  $Cr_4O_9$  (MeCN)<sub>2</sub> are still observed, although ions with higher mass are also seen. These higher mass signals are assigned to clusters with 5 or 6 chromium atoms. The largest peak is observed at 566 amu and is assigned as  $Cr_5O_{14}$  (MeCN)<sub>2</sub>. Clusters containing either one less or one more oxygen atom are also seen. The stable "magic number" cluster for chromium oxide with 5 chromium atoms has been reported to be Cr<sub>5</sub>O<sub>12-13</sub>, and while  $Cr_5O_{13}$  complexed to two ligands is observed it is only with low intensity. A low intensity peak can be seen at 700 amu, this peak is assigned to  $Cr_6O_{14}(MeCN)_4$ .  $Cr_6O_{14}$  has been shown in previous reports to be a stable fragment from larger clusters. Increasing the vaporization laser power even further, to 160-180 mJ/pulse, results in the mass spectrum shown in Figure 5.4. Here we observe  $Cr_6O_{14}$  (MeCN)<sub>4</sub> with greater intensity than the previous sample as well as some

smaller peaks corresponding to  $Cr_6O_{13}(MeCN)_4$ ,  $Cr_6O_{14}(MeCN)_6$ , and  $Cr_6O_{16}(MeCN)_6$ . For this high power sample there are no indications of clusters with 4 or 5 chromium atoms. The general trend suggested by this mass analysis is that higher laser vaporization powers in the LVFR create larger ligand coated clusters. We also seem to be able to capture some of the same "magic number" clusters sizes seen in gas phase experiments.

Structural characterization of this material has been somewhat difficult. Ideally, crystallization should be possible, and X-ray crystallographic data would unambiguously determine the structure of these materials. Unfortunately, to date, crystallization of coated chromium oxide clusters has not been realized. Therefore we turn to SERS in conjunction with computational analysis to provide some insight into their structure. The computed ground state structures for bare chromium oxide clusters can be seen in Figure 5.5. Computations here are at the BP86/TZVP level of theory, although similar structures have been determined with other density functionals,<sup>16</sup> as well as with much higher levels of theory by Dixon and co-workers.<sup>26</sup> The ground state of the  $Cr_4O_{10}$  clusters has been shown in the literature to be a closed shell singlet and indeed we too find this also be the ground state for this cluster. We find Cr<sub>5</sub>O<sub>13</sub> and  $Cr_6O_{14}$  to have triplet ground states. Computing the structures of chromium oxide clusters complexed to MeCN has proven difficult. The predicted structure of  $Cr_4O_{10}$  (MeCN) can be seen in Figure 5.6. Computations on larger clusters containing 5 or 6 chromium atoms complexed to MeCN have failed to converge. The lowest energy structures for bare chromium oxide clusters is reported to be the cage type structures shown in Figures 5.5 and 5.6. The SERS spectrum of coated chromium oxide clusters can be seen in Figure 5.7. This spectrum was taken by placing a few microliters of our sample on a film of silver nanorods. As the sample dried, the resulting film appeared homogenous and spectra across the entire film consistently showed the features



Figure 5.5. Lowest energy structures for "magic number" chromium oxides. a)  $Cr_4O_{10}$ , b)  $Cr_5O_{13}$ , and c)  $Cr_6O_{14}$ .



Figure 5.6. Computed "cage" structure for  $Cr_4O_{10}(MeCN)$  at the BP86/TZVP level of theory.



Figure 5.7. Experimental SERS spectrum of coated chromium oxide clusters (bottom). Predicted spectra for cage-like  $Cr_4O_{10}$  (middle) and  $Cr_4O_{10}$ (MeCN) (top).

seen in Figure 5.7. These same features were also observed for samples prepared at different times and with varying laser powers. The SERS spectrum of the sample is compared to the predicted spectra for bare and coated  $Cr_4O_{10}$  in Figure 5.7 (these spectra are unscaled). The observed spectrum of these coated clusters is clearly not explained by the predicted spectra for the cage structure of  $Cr_4O_{10}$  or  $Cr_4O_{10}$  (MeCN). Indeed, the largest feature of the experimental spectrum at 800 cm<sup>-1</sup> is not predicted with any intensity for the cage structure. Terminal oxygen stretches (Cr=O) are predicted at 1085 (symmetric) and 1065 (anti-symmetric) cm<sup>-1</sup> for the bare clusters and at approximately 1049 cm<sup>-1</sup> for the coated cluster. The peak measured at 1005 cm<sup>-1</sup> can be assigned to this type of transition although it is observed with much lower intensity than is predicted. This discrepancy in intensity can be attributed to surface effects of the silver nanorod film dampening or selectively enhancing the vibrations of these clusters.<sup>23</sup> Transitions at 573 and 359 cm<sup>-1</sup> can be assigned to skeletal vibrations of the metal oxide core and the width of the bands in this spectrum is most likely due to the distribution of cluster sizes contained within the sample, as shown in its mass spectrum.

Since the traditional cage like structure does not appear to explain our observed SERS spectrum, we turn to alternative higher energy structures. We have already observed changes in the structure of metal oxide clusters due to ligand effects in our previous work on cobalt oxide. In that study bare  $Co_4O_4$  preferred a ring like structure, but with the addition of two or more MeCN ligands a cube structure was more preferential. Therefore, it is reasonable to suggest that the discrepancies between the observed spectrum for chromium oxide and the spectrum predicted for the cage could be explained by another structure. Relative energies of the cage as well as chain and ring structures for  $Cr_4O_{10}$  and  $Cr_4O_{10}$ (MeCN) are displayed in Table 5.1. Computed structures for bare and coated chains and rings can be seen in Figure 5.8. The cage structure

Structure	$Cr_4O_{10}$	Cr <sub>4</sub> O <sub>10</sub> (MeCN)	Cr <sub>4</sub> O <sub>10</sub> (MeCN) <sub>2</sub>
Cage	0	0	0
Chain	+78.9	+57.2	+52.1
Ring	+44.3	+33.1	+43.1

Table 5.1. Relative energy in kcal/mol of cage, chain and ring isomers of bare and coated chromium oxide clusters at the BP86/TZVP level of theory.



Figure 5.8. Chain (left) and ring (right) predicted structures for bare and coated  $Cr_4O_{10}$  clusters.

remains the lowest energy isomer for the bare clusters and for the clusters with one MeCN. The ring and chain structures do, however, become closer in energy to the cage with the addition of one ligand (by approximately 10 kcal/mol). It is likely that these species exist in solution with more than one ligand, and in that case the additional ligands could account for a transition from a cage to another structure. A comparison of predicted spectra for the coated cage, cube and ring versus the experimental spectrum of the sample can be seen in Figure 5.9. As discussed above, the large band observed at approximately 800 cm<sup>-1</sup> is absent from the spectrum of the cage. A feature is predicted in this range for the chain and for the ring. Much of the rest of the spectrum remains the same across the three structures. Our observed SERS spectrum matches most closely with the ring structure. The predicted bands between 700 and 900 cm<sup>-1</sup> for the ring and chain structures are due to Cr<sub>2</sub>O<sub>2</sub> breathing modes which are not present for the cage. This result suggests that these coated chromium oxides clusters have either a chain or ring-like structure with Cr<sub>2</sub>O<sub>2</sub> units. A similar observation has been made for gas phase vanadium oxide clusters by As mis and co-workers.<sup>21</sup> In that work they trapped  $V_{3}O_{6-8}^{++}$  clusters which have been shown to be "magic number" sizes for vanadium oxide. Infrared photodissociation spectra of these bare clusters match well with the traditional cage structures, but when a rare gas tag was added to the clusters (Ar or He) unexplained bands appeared in the spectrum between 700 and 900 cm<sup>-1</sup>. Their computations showed that these bands could be explained by ring or chain structure for these clusters. Indeed, it appears that while the cage structure is the most stable for bare chromium oxide clusters, interaction with ligands (or even atoms) can easily transform these clusters to rings or chains.

As stated above, X-ray crystallographic data for these samples could unambiguously determine the structure of these clusters. Our initial production of coated chromium oxides led



Figure 5.9. Experimental SERS spectrum of coated chromium oxide clusters (bottom). Predicted spectra for  $Cr_4O_{10}$  (MeCN) cage (red), chain (blue) and ring (green).

us to believe this might be possible. This is because the yield of this material is much higher than that of materials previously produced with the LVFR, and we believed that low concentration was a large factor of our inability to crystalize these samples. Despite the large yield of this sample, crystallization attempts have remained fruitless. The purity of these samples may also be the cause of this and so with that in mind we have begun studies using chromatography to separate the components of these samples. Figure 5.10 is a HPLC chromatogram of coated chromium oxide clusters produced with 180 mJ pulses. Similar elution peaks were seen for samples produced at 160 or 200 mJ/pulse, but as of this writing samples made with lower powers have not been investigated. This result does confirm that several components are present in these samples. Further investigation into the identity of these components is currently underway using LC-MS. We hope to observe the same masses shown in the LDI ToF-MS spectra and to see these species separate by size. Purification by separation will ideally lead to a concentrated solution of one cluster size which will hopefully crystalize.

The UV-visible spectrum of these clusters is shown in Figure 5.11. This spectrum is obtained in from a solution of coated clusters in MeCN and is reproducible for samples produced at various laser powers. Intense bands can be seen in the UV with a shoulder extending into the visible region in the spectrum with the largest features observed at 266 and 367 nm. Features in this region have been reported for chromium oxide materials in the literature including supported catalysts<sup>26,27</sup> and ligand-metal complexs.<sup>29,30</sup> These particular transitions at 266 and 367 nm have been assigned to charge transfer bands of  $Cr^{+5}$  or  $Cr^{+6}$  species.

The broad and intense photoluminescence of coated chromium oxide clusters is shown in Figure 5.12. The emission observed here is a result of excitation with 355 nm light, although similar emission was seen with excitation at a large range of UV wavelengths. This profile of



Figure 5.10. Liquid chromatogram of coated chromium oxide cluster solution produce at 180 mJ/pulse.



Figure 5.11. Solution phase UV-visible spectrum of chromium oxide clusters coated and dissolved in MeCN.



Figure 5.12. Photoluminescence spectra of chromium oxide clusters coated by MeCN. differences. Like vanadium oxide, gas phase "magic number" cluster sizes have been captured,

near white light emission from 350 – 600 nm has also observed for both clusters of vanadium and cobalt oxides in the past. Indeed, all ligand coated metal oxide clusters produced with the LVFR so far display this signature emission regardless of ligand, solvent or metal employed. This suggests that this photoluminescence is a result of the small size of these clusters, and is not specific to any particular metal or ligand.

Chromium oxide has proven an interesting system as the coated clusters produced by the LVFR have shown many similarities to materials created in the past but also some stark although in the case of chromium oxide the particular size distribution seems to be tunable by varying the vaporization laser power of the LVFR. The vibrational spectrum of these clusters suggests that their structure is affected by the addition of ligands. While bare cages have long been proposed as the stable structure, the dominant vibration at 800 cm<sup>-1</sup> can only be explained by structures which contain  $Cr_2O_2$  groups such as rings or chains. Cobalt oxide clusters produced by the LVFR have also shown a similar structural transition caused by ligand-oxide core interaction. The emerging picture of these results is that LVFR can produce clusters with stoichiometries that are similar to the gas phase "magic number" sizes, but that the ligand coating process which offers the clusters stability and solubility affects their structure. The UV-visible absorption observed for this material is consistent with that for chromium oxide materials produced by other methods. The near white light photoluminescence of these coated clusters is similar to the emission observed for all oxide clusters produce via the LVFR thus far.

#### Conclusions

Acetonitrile is employed to coat and capture sub-nanometer sized chromium oxide clusters in solution. The stoichiometry of these clusters is analogous to that of "magic number"

gas phase chromium oxide clusters with some small number of ligands attached. Interestingly, the yield of these coated clusters is much greater than in the systems previously studied with the LVFR. For this system, the cluster size distribution which is captured by LVFR is tunable, with larger clusters being produced by higher laser vaporization powers. Cage type structures do not explain the vibrational spectrum of this material even though theory predicts these to be lowest in energy. Ring or chain schemes which contain  $Cr_2O_2$  units are consistent with the spectral features measured for this material, suggesting that the ligand interaction with these oxide cores causes them to change structures. Coated chromium oxide clusters absorb strongly in the UV and electronic transitions were measured that are consistent with chromium oxide materials produced by other methods. This material is found to exhibit broad and intense visible photoluminescence and the emission profile is similar to that of other ligand coated oxides produced via the LVFR. Future work will continue the purification process begun here using HPLC with the goal of producing a sample which will crystallize. A more rigorous characterization of these materials including the measurement of their catalytic and magnetic properties is also planned. Many other sub-nanometer cluster systems such as pure metal, metal carbide and metal silicon are well suited for study using the LVFR and will be the subject of future work.

### References

- 1. Rao, C. N. R.; Raveau, B. Transition Metal Oxides; Wiley-VCH: New York, 1998.
- 2. Weckhuysen, B. M.; Wachs, I. E. Schoonheydt, *R.* A. "Surface chemistry and spectroscopy of chromium in inorganic oxides," *Chem. Rev.* **1996**, *96*, 3327–3350.
- (a) Schwarz, K. "CrO<sub>2</sub> predicted as a half-metallic ferromagnet," *J. Phys. F* 1986, *16*,
   L211–L215. (b) Kamper, K.P.; Schmitt, W.; Guntherodt, G.; Gambino, R. J.; Ruf, R. "CrO<sub>2</sub> A new half-metallic ferromagnet," *Phys. Rev. Lett.* 1987, *59*, 2788–2791. (c) Korotin, M. A.; Anisimov, V. I.; Khomskii, D. I.; Sawatzky, G. A. "CrO<sub>2</sub>: a self-doped double exchange ferromagnet," *Phys. Rev. Lett.* 1998, *80*, 4305–4308.
- Hogan, J. P. "Ethylene polymerization catalysis over chromium oxide," *J. Polym. Sci., Part A: Polym. Chem.* 1970, 8, 2637-2652.
- Schneider, H.; Maciejewski, M.; Kohler, K.; Wokaun, A.; Baiker, A. "Chromia supported on titania. 6. Properties of different chromium oxide phases in the catalytic reduction of no by NH<sub>3</sub> studied by in-situ diffuse reflectance FTIR spectroscopy," *J. Catal.* 1995, *157*, 312-320.
- 6. Boitsov, S.; Riahi, A.; Muzart, J. "Chromium(VI) oxide-catalysed oxidations by tert-butyl hydroperoxide using benzotrifluoride as solvent," *Cr. Acad. Sci. II. C* **2000**, *3*, 747-750.
- Sohn, J. R.; Ryu, S. G. "Redox and catalytic behaviors of chromium oxide supported on zirconia," *Catal. Lett.* 2001, 74, 105-110.
- Bender, M.; Ehrlich, D.; Yakovkin, I. N.; Rohr, F.; Baumer, M.; Kuhlenbeck, H.; Freund, H. J.; Staemmler, V. "Structural rearrangement and surface magnetism on oside surfaces: A temperature-dependent low-energy electron diffraction-electron energy loss spectroscopy study of Cr<sub>2</sub>O<sub>3</sub>(111)/Cr(110)," *J. Phys.: Condens. Matter* **1995**, *7*, 5289-5301.

- Sasaki, S.; Zhang, Y. F.; Yanagisawa, O.; Izumi, M. "Light-induced esr in polycrystalline and thin films of Cr<sub>2</sub>O<sub>3</sub>," *J. Magn. Magn. Mater.* 2007, *310*, 1008-1010.
- Shi, S.; Wysocki, A. L.; Belashchenko, K. D. "Magnetism of chromia from first-principles calculations," *Phys. Rev. B* 2009, 79,104404/1-7.
- 11. a) Deng, H. T.; Kerns, K. P.; Castleman, A. W., Jr. "Formation, structures, and reactivities of niobium oxide cluster ions," *J. Phys. Chem.* 1996, *100*, 13386-13392. b) Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. "Studies of metal oxide clusters: elucidating reactive sites responsible for the activity of transition metal oxide catalysts," *J. Phys. Chem. B* 2002, *106*, 6136-6148 c) Bergeron, D. E.; Castleman, A. W., Jr.; Jones, N. O.; Khanna, S. N. "Stable cluster motifs for nanoscale chromium oxide materials," *Nano Lett.* 2004, *4*, 261-265. d) Castleman, A. W., Jr. "Cluster structure and reactions: Gaining insights into catalytic processes," *Catal. Lett.* 2011, *141*, 1243-1253.
- 12. a) Foltin, M.; Stueber, G. J.; Bernstein, E. R. "On the growth dynamics of neutral vanadium oxide and titanium oxide clusters," *J. Chem. Phys.* 1999, *111*, 9577-9586. d) Matsuda, Y.; Bernstein, E. R. "On the titanium oxide neutral cluster distribution in the gas phase: Detection through 118 nm single-photon and 193 nm multiphoton ionization," *J. Phys. Chem. A* 2005, *109*, 314-319. e) Matsuda, Y.; Bernstein, E. R. "Identification, structure, and spectroscopy of neutral vanadium oxide clusters," *J. Phys. Chem. A* 2005, *109*, 3803-3811. g) Dong, F.; Heinbuch, S.; Bernstein, E. R.; Rocca, J. J. "Mass spectroscopy of neutral metal oxide clusters using a desk-top soft X-ray laser," *Springer Proc. Phys.* 2007, *115*, 463-469. h) Jakubikova, E.; Rappe, A. K.; Bernstein, E. R. "Density functional theory study of small vanadium oxide clusters," *J. Phys. Chem. A* 2007, *111*, 12938-12943.

- 13. a) Griffin, J. B.; Armentrout, P. B. "Guided ion beam studies of the reactions of Fe<sub>n</sub><sup>+</sup> (n=2-18) with O<sub>2</sub>: Iron cluster oxide and dioxide bond energies," *J. Chem. Phys.* 1997, *106*, 4448-4462. c) Griffin, J. B.; Armentrout, P. B. "Guided ion beam studies of the reactions of Cr<sub>n</sub><sup>+</sup> (n=2-18) with O<sub>2</sub>: Chromium cluster oxide and dioxide bond energies," *J. Chem. Phys.* 1998, *108*, 8062-8074. e) Liu, F. Y.; Li, F. X.; Armentrout, P. B. "Guided ion beam studies of the reactions of the reactions of Co<sub>n</sub><sup>+</sup> (n=2-20) with O<sub>2</sub>: Cobalt cluster-oxide and -dioxide bond energies," *J. Chem. Phys.* 2005, *123*, 64304-64319.
- 14. a) France, M. R.; Buchanan, J. W.; Robinson, J. C.; Pullins, S. H.; Tucker, J. L.; King, R. B.; Duncan, M. A. "Antimony and bismuth oxide clusters: Growth and decomposition of new magic number clusters," *J. Phys. Chem. A* 1997, *101*, 6214-6221. b) Molek, K. S.; Jaeger, T. D.; Duncan, M. A. "Photodissociation of vanadium, niobium, and tantalum oxide cluster cations," *J. Chem. Phys.* 2005, *123*, 144313-144313. c) Molek, K. S. Reed, Z. D. Ricks, A.M. Duncan, M.A. "Photodissociation of chromium oxide cluster cations," *J. Phys. Chem. A* 2007, *111*, 8080-8089. d) Dibble, C. J.; Akin, S. T.; Ard, S.; Fowler, C. P.; Duncan, M. A. "Photodissociation of cluster cations," *J. Chem. Phys. A* 2012, *116*, 5398-5404.
- 15. a) Fan, J. W.; Wang, L. S. "Photoelectron spectroscopy of FeO<sup>-</sup> and FeO<sub>2</sub><sup>-</sup> Observation of low-spin excited-states of FeO and determination of the electron affinity of FeO<sub>2</sub>," *J. Chem. Phys.* **1995**, *102*, 8714-8717. d) Sun, Q.; Sakurai, M.; Wang, Q.; Yu, J. Z.; Wang, G. H.; Sumiyama, K.; Kawazoe, Y. "Geometry and electronic structures of magic transition metal oxide clusters M<sub>9</sub>O<sub>6</sub> (M = Fe, Co, and Ni)," *Phys. Rev. B* **2000**, 62, 8500-8507. e) Gutsev, G. L.; Jena, P.; Zhai, H. J. Wang, L. –S. "Electronic structure of chromium oxides, CrO<sub>n</sub><sup>-</sup> and CrO<sub>n</sub> (n = 1-5) from photoelectron spectroscopy and density functional theory calculations,"

*J. Chem. Phys.* **2001**, *115*, 7935-7944. g) Zhai, H. J.; Huang, X.; Waters, T.; Wang, X. B.; O'Hair, R. A. J.; Wedd, A. G.; Wang, L. S. "Photoelectron spectroscopy of doubly and singly charged group VIB dimetalate anions:  $M_2O_7^{2-}$  MM '  $O_7^{2-}$ , and  $M_2O_7^{-}$  (M, M ' = Cr, Mo, W)," *J. Phys. Chem. A* **2005**, *109*, 10512-10520.

- 16. a) Wenthold, P. G.; Gunion, R. F.; Lineberger, W. C. "Ultraviolet negative-ion photoelectron spectroscopy of the chromium oxide negative ion," *Chem. Phys. Lett.* 1996, 258, 101-106. b)
  Gunion, R. F.; DixonWarren, S. J.; Lineberger, W. C.; Morse, M. D. "Ultraviolet photoelectron spectroscopy of molybdenum and molybdenum monoxide anions," *J. Chem. Phys.* 1996, *104*, 1765-1773. c) Ramond, T. M.; Davico, G. E.; Hellberg, F.; Svedberg, F.; Salen, P.; Soderqvist, P.; Lineberger, W. C. "Photoelectron spectroscopy of nickel, palladium and platinum oxide anions," *J. Mol. Spectrosc.* 2002, *216*, 1-14.
- 17. a) Klopcic, S. A.; Moravec, V. D.; Jarrold, C. C. "Photoelectron spectrum of PdO. *J. Chem. Phys.* **1999**, *110*, 10216-10217. b) Yoder, B. L.; Maze, J. T.; Raghavachari, K.; Jarrold, C. C. "Structures of Mo<sub>2</sub>O<sub>y</sub> and Mo<sub>2</sub>O<sub>y</sub> (y=2,3,4) studied by anion photoelectron spectroscopy and density functional theory calculations," *J. Chem. Phys.* **2005**, *122*, 094313-094322. c) Rothgeb, D. W.; Hossain, E.; Kuo, A. T.; Troyer, J. L.; Jarrold, C. C. "Structures of Mo<sub>x</sub>W<sub>3-x</sub>O<sub>6</sub> (x=0-3) anion and neutral clusters determined by anion photoelectron spectroscopy and density functional theory calculations," *J. Chem. Phys.* **2009**, *131*, 044310-044323. d) Mann, J. E.; Waller, S. E.; Rothgeb, D. W.; Jarrold, C. C. "Study of Nb<sub>2</sub>O<sub>y</sub> (y=2-5) anion and neutral clusters using anion photoelectron spectroscopy and density functional theory calculations," *J. Chem. Phys.* **2011**, *135*, 104317-104329.
- 18. a) Pramann, A.; Nakamura, Y.; Nakajima, A.; Kaya, K. "Photoelectron spectroscopy of yttrium oxide cluster anions: Effects of oxygen and metal atom addition," *J. Phys. Chem.*

A 2001, 105, 7534-7540. b) Pramann, A.; Koyasu, K.; Nakajima, A.; Kaya, K.

"Photoelectron spectroscopy of cobalt oxide cluster anions," *J. Phys. Chem. A* **2002**, *106*, 4891-4896. c) Pramann, A.; Koyasu, K.; Nakajima, A.; Kaya, K. "Anion photoelectron spectroscopy of V<sub>n</sub>O<sub>m</sub><sup>-</sup> (n=4-15; m=0-2)," *J. Chem. Phys.* **2002**, *116*, 6521-6528.

- a) Von Helden, G.; Kirilyuk, A.; van Heijnsbergen, D.; Sartakov,B.; Duncan, M. A.; Meijer, G. "Infrared spectroscopy of gas-phase zirconium oxide cluster," *Chem. Phys.* 2000, 262, 31-39. b) Van Heijnsbergen, D.; von Helden, G.; Meijer, G.; Duncan, M. A. "Infrared resonance-enhanced multiphoton ionization spectroscopy of magnesium oxide clusters," *J. Chem. Phys.* 2002, *116*, 2400-2406. c) Van Heijnsbergen, D.; Demyk, K.; Duncan, M.A.; Meijer, G.; von Helden, G. "Structure determination of gas phase aluminum oxide cluster," *Phys. Chem. Chem. Phys.* 2003, *5*, 2515-2519.
- 20. a) Fielicke, A.; Meijer, G.; von Helden, G. "Infrared spectroscopy of niobium oxide cluster cations in a molecular beam: Identifying the cluster structures," *J. Am. Chem. Soc.* 2003, *125*, 3659-3667. b) Fielicke, A.; Meijer, G.; von Helden, G. "Infrared multiple photon dissociation spectroscopy of transition metal oxide cluster cations; Comparison of group Vb (V, Nb, Ta) metal oxide clusters," *Eur. Phys. J.D* 2003, *24*, 69-72. c) Fielicke, A.; Mitric, R.; Meijer, G.; Bonacic Koutecky,V.; von Helden, G. "The structures of vanadium oxide cluster Ethene complexes. A combined ir multiple photon dissociation spectroscopy and DFT calculation study," *J. Am. Chem. Soc.* 2003, *125*, 15716-15717. d) Demyk, K.;van Heijnsbergen, D.; von Helden, G.; Meijer, G. "Experimental study on gas phase titanium and aluminum oxide clusters," *Astron. & Astrophys.* 2004, *420*, 547-552.
- 21. a) Asmis, K. R.; Meijer, G.; Brümmer, M.; Kaposta, C.; Santambrogio, G.; Wöste, L.; Sauer,J. "Gas phase infrared spectroscopy of mono- and divanadium oxide cluster cations," *J.*

*Chem. Phys.* **2004**, *120*, 6461-6470. b) Asmis, K. R.; Sauer, J. "Mass-selective vibrational spectroscopy of vanadium oxide cluster ions." *Mass Spectrom. Rev.* **2007**, *26*, 542-562. c) Feyel, S.; Schwarz, H.; Schröder, D.; Daniel, C.; Hartl, H.; Dobler, J.; Sauer, J.; Santambrogio, G.; Wöste, L.; Asmis, K. R. "Gas-phase infrared photodissociation

spectroscopy of tetravanadiumoxo and oxo-methoxo cluster anions,"

ChemPhysChem 2007, 8, 1640-1647. d) Santambrogio, G.; Brümmer, M.; Wöste, L.;

Dobler, J.; Sierka, M.; Sauer, J.; Meijer, G.; Asmis, K. R. "Gas phase vibrational

spectroscopy of mass-selected vanadium oxide anions," Phys. Chem. Chem. Phys. 2008, 10,

3992-4005. e) Asmis, K. R. "Structure characterization of metal oxide clusters by vibrational spectroscopy: Possibilities and prospects," *Phys. Chem. Chem. Phys.* **2012**, *14*, 9270-9281. f)

Asmis, K. R.; Wende, T.; Bruemmer, M.; Gause, O.; Santambrogio, G.; Stanca-Kaposta, E.

C.; Doebler, J.; Niedziela, A.; Sauer, J., "Structural variability in transition metal oxide

clusters: gas phase vibrational spectroscopy of V3O6-8+," Phys. Chem. Chem.

Phys. 2012, 14, 9377-9388.

- 22. a) Ayers, T. M.; Fye, J. L.; Li, Q.; Duncan, M. A., "Synthesis and Isolation of titanium metal cluster complexes and ligand-coated nanoparticles with a laser vaporization flowtube reactor," *J. Clust. Sci.* 2003, *14*, 97-113. b) Ard, S.; Dibble, C. J.; Akin, S. T.; Duncan, M. A. "ligand-coated vanadium oxide clusters: Capturing gas-phase magic numbers in solution," *J. Phys. Chem. C* 2011, *115*, 6438-6447.
- 23. Chaney, S. B.; Shanmukh, S.; Dluhy, R. A.; Zhao, Y. P. "Aligned silver nanorod arrays produce high sensitivity surface-enhanced Raman spectroscopy substrates," *Appl. Phys. Lett.* 2005, *87*, 031908/1-3.
- 24. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J.

- R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.;
- Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.;
- Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.;
- Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark,
- M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.;
- Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.;
- Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.;
- Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.;
- Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- 25. Schafer, A.; Huber, C.; Ahlrichs, R. "Fully optimized contracted gaussian-basis sets of triple zeta valence quality for atoms Li to Kr," *J. Chem. Phys.* **1994**, *100*, 5829-5835.
- 26. a) Li, S.; Dixon, D. A. "Benchmark calculations on the electron detachment energies of MO<sub>3</sub><sup>--</sup> and M<sub>2</sub>O<sub>6</sub><sup>--</sup> (M = Cr, Mo, W)," *J. Phys. Chem. A* 2007, *111*, 11908-11921. b) Zhai, H.-J.; Li, S.; Dixon, D. A.; Wang, L.-S. "Probing the electronic and structural properties of chromium oxide clusters (CrO3)<sub>n</sub><sup>--</sup> and (CrO3)<sub>n</sub> (n=1-5): Photoelectron Spectroscopy and density functional calculations," *J. Am. Chem. Soc.* 2008, *130*, 5167-5177. c) Li, S.; Dixon, D. A. "Structural and electronic near degeneracy of M<sub>3</sub>O<sub>9</sub><sup>--</sup> (M = Cr, Mo, W)," *J. Chem. Phys. C* 2011, *115*, 19190-19196. d) Li, S.; Zhai, H.-J.; Wang, L.-S.; Dixon, D. A. "Structural and electronic properties of reduced transition metal oxide clusters, M<sub>4</sub>O<sub>10</sub> and M<sub>4</sub>O<sub>10</sub><sup>--</sup> (M = Cr, W), from photoelectron spectroscopy and quantum chemical calculations," *J. Phys. Chem. A* 2012, *116*, 5256-5271.
- 27. Fountzoula, C.; Matralis, H. K.; Papadopoulou, C.; Voyiatzis, G. A.; Kordulis, C. "The influence of the chromium content on the physicochemical properties and the catalytic behavior of CrO<sub>x</sub>/TiO<sub>2</sub> catalysts for the selective catalytic reduction of nitric oxide by ammonia at relatively high temperatures," *J. Catal.* **1997**, *172*, 391-405.
- 28. Khaddar-Zine, S.; Ghorbel, A.; Naccache, C. "EPR and UV-visible spectroscopic studies of alumina-supported chromium oxide catalysts," *J. Mol. Catal. A-Chem.* **1999**, *150*, 223-231.
- 29. Bartholomaeus, R.; Harms, K.; Levina, A.; Lay, P. A. "Synthesis and characterization of a chromium(V) cis-1,2-cyclohexanediolato complex: A model of reactive intermediates in chromium-induced cancers," *Inorg. Chem.* **2012**, *51*, 11238-11240.
- 30. Chatterjee, C.; Chisholm, M. H. "Influence of the metal (Al, Cr, and Co) and the substituents of the porphyrin in controlling the reactions involved in the copolymerization of propylene oxide and carbon dioxide by porphyrin metal(III) complexes. 2. Chromium chemistry," *Inorg. Chem.* **2012**, *51*, 12041-12052.

## CHAPTER VI

# PRODUCTION AND ISOLATION OF LIGAND COATED ALUMINUM CLUSTERS USING A LASER VAPORIZATION FLOWTUBE REACTOR

# Introduction

Nanoparticles on the order of 1 - 100 nm in size are commonly produced in solutions using colloidal suspensions or sol-gel techniques.<sup>1,2</sup> Vapor phase processes also exist.<sup>3,4</sup> The focus here is on a much smaller scale. In this work a laser vaporization flowtube reactor (LVFR) is used to produce and isolate aluminum based material stabilized with small organic ligands, which contain only two or three aluminum atoms.

Aluminum nanoparticles have attracted considerable interest, as they relate to the micron sized particles, which have been commonly used in rocket propellant. This focus on "nanoaluminum" has yielded materials with increased surface area, which enhances the combustion rate of fuel ten times over larger particles.<sup>5,6</sup> Size dependent optical properties<sup>7</sup> and phase transitions<sup>8,9</sup> of aluminum nanomaterials have also been studied.

Smaller aluminum clusters have been investigated in the gas phase. This size regime of <100 atoms is uniquely interesting. Small changes, such as the addition or removal of a single atom, can drastically change the properties of these species. Several groups have explored reactivity of aluminum clusters as a function of size.<sup>10-12</sup> Collision induced dissociation<sup>13</sup> and photodissociation<sup>14</sup> of small clusters have also been investigated. Electronic spectra have been measured on aluminum dimer and trimer cations.<sup>15</sup> Al<sub>7</sub><sup>+</sup>, Al<sub>13</sub><sup>-</sup>, and Al<sub>23</sub><sup>-</sup> have been shown to be

particularly inert and stable.<sup>12,16</sup> This stability is believed to come from shell closings, where the valence electrons from each atom add to unified orbital shells as if the entire cluster were one atom. This type of behavior has been seen in other atomic clusters as well, and is called the spherical jellium model.<sup>17</sup> The structure and bonding of these complexes has been investigated using photoelectron spectroscopy.<sup>18</sup> This system has also been investigated computationally.<sup>19-24</sup> These theoretical studies have largely used density functional theory (DFT) to probe and compare the structure (both geometric and electronic) of small clusters to experiments.

Our previous studies using the LVFR have focused on the synthesis and isolation of ligand coated transition metal oxide clusters.<sup>25</sup> In the past we have shown how small metal oxide clusters can be captured, and how those clusters relate to stable species found in gas phase molecular beam experiments. However, some data suggest that the LVFR can produce coated clusters that vary greatly from gas phase results. Ligand binding and/or reaction with the core cluster has been shown to alter what clusters we collect, as well as the structure of those clusters. Here we show how the LVFR can be used to synthesize and isolate small coated aluminum material, which contains the first non-oxide clusters produced in this way.

#### **Experimental and Theoretical Methods**

The LVFR has been described in detail previously.<sup>25</sup> Coated aluminum clusters are made using the straight configuration of the apparatus (see Chapter II, Figure 2.1). This apparatus uses a Lambda Physik Compex 110 KrF excimer laser that ablates a 1/4 inch aluminum rod in the presence of helium gas. The laser is focused to a 3 x 13 mm rectangle and produces 200-250 mJ pulses at a repetition rate of 100 Hz. Production of aluminum clusters requires much higher laser power than other metals we have studied (V, Co, Cr). Helium gas is injected into the flowtube through a small (~750  $\mu$ m) hole positioned 8 mm away from the metal rod, which results in an

ambient pressure of 5 torr. The inert gas promotes collisions of the small metal clusters produced in the laser plasma. In this work, as well as in previous studies, we find MeCN to complex efficiently to ultra-small clusters created in the LVFR. Although, we have investigated the use of other ligands in the past(tetrahydrofuran, propionitrile, pyridine), we find that cluster material coated with MeCN are easily characterized. Acetonitrile is heated to 60 °C and backed by 5 psi of argon gas. This ligand mixture results in 100 mtorr of particle pressure in the tube. Coated clusters are collected further downstream in a liquid nitrogen trap. Typical run times of six hours produce less than one milligram of white film. This film dissolves in excess MeCN to form a cloudy liquid (Figure 6.1).

Characterization tools for these coated clusters include laser desorption ionization time-of flight mass spectrometry (LDI ToF-MS), surface enhanced Raman spectroscopy( SERS), UVvisible absorption, and fluorescence emission. For an initial characterization, mass spectra are obtained using a home-made time-of-flight instrument, which has been previously described in detail (Chapter II). This apparatus uses UV (355 nm) or green laser pulses (532 nm) from a Nd:YAG laser (New Wave Research, Polaris II) to ionize and desorb the sample. Mass calibration, which is critical for these experiments, is accomplished by adding coronene (300 amu) or  $C_{60}$  (720 amu) to the samples. For SERS spectra, a drop of sample is placed onto a film of Ag nanorods provided by the Dluhy group.<sup>26</sup> A 785 nm diode laser is used to irradiate the sample in these experiments. The spectrum is recorded using a commercial Renishaw InVia Raman Microscope. A low energy per photon laser is required in order to prevent fluorescence of the sample from interfering with the Raman signal. UV-visible absorption spectra are collected using a Shimadzu UV-2401 PC spectrometer, and fluorescence emission spectra are obtained using a SPEX Fluorolog 1692T.



Figure 6.1. Photograph of aluminum sample solution.

Density functional theory (DFT) calculations are performed using the B3LYP functional and the Gaussian 09 program suite.<sup>27</sup> The TVZP basis set, developed by Ahlrichs and co-workers, is employed .<sup>28</sup> Computed structures for the bare clusters of aluminum or aluminum oxides are similar to those reported in the literature. These clusters bound to one or more ligands are also investigated. Excitation energies for bare and coated clusters are estimated using Time-dependent DFT (TD-DFT).

#### **Results and Discussion**

Grey frozen material is observed in the collection flask after thirty minutes of operation, and upon warming to room temperature, it forms a cloudy solution. The solution is filtered, and excess solvent is removed, resulting in a white film. Control experiments where the LVFR is operated with no MeCN result in bulk aluminum oxide which is not soluble in MeCN (see Figure 6.2). The production yield for coated aluminum is approximately 0.5 mg in six hours. This is less than that of chromium oxide, but higher than the yield previously observed for vanadium or cobalt oxide clusters. Characterization of this sample shows similar results when analyzed immediately after capture, after drying/re-solvating, or after several weeks.

Promptly after collection, the sample is analyzed using LDI ToF-MS. A few drops of sample solution are placed on a stainless tip, forming a thin film. Mass spectra are collected by neat desorption of this sample inside the acceleration region of the mass spectrometer. Control experiments are performed by measuring mass spectra of bulk aluminum oxide or aluminum metal suspended in MeCN. The spectrum of pure Al<sub>2</sub>O<sub>3</sub> is shown in Figure 2. Pure aluminum metal displays the same spectrum as it oxidizes rapidly. Representative mass spectra of coated aluminum clusters can be seen in Figures 6.3 and 6.4. Spectra are taken at threshold desorption



Figure 6.2. Mass spectrum of bulk aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) suspended in MeCN.



Figure 6.3. Mass spectrum of acetonitrile coated aluminum and aluminum oxide clusters.



Figure 6.4. Mass spectrum of larger acetonitrile coated aluminum and aluminum oxide clusters.

powers (approximately 500  $\mu$ J/pulse), as higher powers only increase the intensity of low mass peaks (< 100 amu) indicating that they are fragment ions. Features at 81, 143 and 163 amu (Figure 6.3) are assigned to Al<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>(MeCN) and Al<sub>3</sub>(MeCN)<sub>2</sub> respectively.

Although attempts to minimize the presence of oxygen in the system where made, such as removing the outer oxide layer from the aluminum rod and flowing helium for thirty minutes prior to collection, clusters containing oxygen are still captured.  $Al_2O_3$  is the smallest unit of aluminum (III) oxide found in bulk material, and so its capture is not surprising. However, it is encouraging that clusters containing no oxygen are also produced, as these types of species have not been observed in previous LVFR experiments. The presence of oxides in the sample seems to be unavoidable as the surface of aluminum oxidizes rapidly and the operating pressure of the flowtube is relatively high (5 torr). Under different conditions of LVFR operation samples are collected which display mass spectra similar to Figure 6.4. We are still unsure which conditions produce these different samples as the production of one or the other seems quite random. This may be due to small fluctuations in laser power or gas pressure. The degree of surface oxidation on the aluminum rod may also cause this discrepancy. The mass spectrum in Figure 6.4 contains higher mass features, as well as a peak at 163 amu. This peak is consistently found in all samples and, as stated above, is assigned to Al<sub>3</sub>(MeCN)<sub>2</sub>. Assignment of the higher masses is not possible at this time, due to the limited resolution of the mass spectrometer. Many clusters containing aluminum, oxygen and acetonitrile have masses within the widths of these peaks (2-5 amu). There are 23 assignments for the peak observed at 393 amu (see Table 6.1). This problem becomes even more pronounced at higher mass with the peaks at 676 and 1180 amu having 93 and 155 possible assignments, respectively. This issue can hopefully be resolved by using a higher resolution mass spectrometer, which can differentiate between these clusters. Attempts

1,5,7	4,0,7	8,11,0
1,10,5	4,10,3	10,0,3
1,23,0	5,6,4	10,5,1
2,11,4	5,16,0	11,1,2
2,16,2	6,12,1	11,6,0
3,4,6	7,0,5	13,0,1
3,17,1	7,5,2	14,1,0
4,5,5	8,6,2	

Table 6.1. Possible mass assignments containing aluminum, oxygen and acetonitrile for mass  $393 \pm 2$  amu. Assignments listed are of the form X,Y,Z were X = Al, Y = O and Z= MeCN.

thus far to obtain such a mass spectrum have failed as the only high resolution mass spectrometers readily available to us use either low powered  $N_2$  lasers or electrospray for ionization. Neither method seems to ionize our samples. An instrument at the High Magnetic Field Laboratory has sufficient ionization power (Nd:YAG) and mass resolution (ICR) to solve this problem and collaboration has already begun. With this in mind, the interrogation of the properties of coated aluminum clusters in this work concentrates on samples with mass spectra that can be assigned, namely those similar to Figure 6.3.

The capture of a coated aluminum trimer is an unexpected result. Although the bare analog of this species has been seen before in gas phase molecular beams, no reports of its particular stability exist. Indeed, small clusters, like the aluminum trimer, have been shown to be quite reactive,<sup>10</sup> while the most stable clusters adhere to the jellium model  $(Al_7^+, Al_{13}^-, and Al_{23}^{-1})$ , as described above .<sup>12,16,17</sup> We do not capture coated analogs of these jellium clusters. However, it should be noted that there are no small neutral clusters of aluminum which have full shell closings, and we are unsure if clusters grow as neutrals, anions, or cations in the LVFR. It is possible, if clusters grow as neutrals, that selective capture of aluminum clusters relating to the spherical jellium model may be impossible.

SERS has been a productive tool for characterizing these types of coated clusters in the past. Since mass spectral evidence suggests that the samples contain primarily  $Al_3(MeCN)_2$  and  $Al_2O_3(MeCN)$ , comparing their computed spectra to the experimental spectrum of our sample should be enlightening. The SERS spectrum of our material, as well as predicted spectra for the computed structures of these clusters can be seen in Figure 6.5. The theoretical structures for  $Al_3(MeCN)_2$  and  $Al_2O_3(MeCN)$  are calculated at the B3LYP/TZVP level of theory, and are pictured above their respective spectra. These structures were determined by first computing



Figure 6.5. SERS spectrum of coated aluminum nanocluster material (bottom) compared to computed spectra for  $Al_3(MeCN)_2$  (middle) and  $Al_2O_3(MeCN)_1$  (top). Predicted structures for these clusters are shown above their respective spectrum.

structures for bare Al<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> clusters. These species have already been investigated theoretically and experimentally by other groups, and our computations are consistent with those results.<sup>19,20,22-24</sup> Al<sub>3</sub> is an equilateral triangle ( $D_{3h}$ ) with bond distances of 2.54 Å, and Al<sub>2</sub>O<sub>3</sub> hasmetal oxide bond distances of 1.74 and 1.77 Å for terminal and bridging bonds, respectively. Ligand coated analogs are computed by first randomly placing ligands around the bare clusters, followed by iterative energy calculations to find the lowest energy structure. As ligands are added, metal - metal or metal - oxygen bond distances of the clusters are slightly elongated to 2.58 and 1.75 - 1.77 Å, respectively. The SERS spectrum (Figure 6.5) appears to contain peaks predicted for both coated aluminum trimer and oxide. The most intense band in the spectrum is measured at 1395 cm<sup>-1</sup>. This band is also predicted in the computed spectra of both clusters  $(1409 \text{ cm}^{-1} \text{ for the trimer and } 1413 \text{ cm}^{-1} \text{ for the oxide})$ . This peak and the smaller, higher frequency band at 1462 cm<sup>-1</sup> are the result of CH<sub>3</sub> umbrella motions of the ligand (systemic and asymmetric, respectively). The second most intense band is observed at 1005  $\text{cm}^{-1}$ . This peak is best assigned to the CH<sub>3</sub> wag of Al<sub>3</sub>(MeCN)<sub>2</sub> (1017 cm<sup>-1</sup>). The CH<sub>3</sub> wag of the coated oxide is predicted at 1060 cm<sup>-1</sup>, and is not observed in the SERS spectrum. Peaks measured at 1238 and 1135 cm<sup>-1</sup> do not correspond to computed vibration of either cluster. These bands are possibly caused by some containment on the Ag nanorod substrate. Observed peaks between 1000 and 300 cm<sup>-1</sup> are the result of either metal-metal or metal-oxygen vibrations. The transition at 854  $cm^{-1}$  is assigned to the terminal oxygen stretch of the coated oxide (851 cm<sup>-1</sup>), and the peak at  $720 \text{ cm}^{-1}$  is due to bridging oxygen stretch (767 cm<sup>-1</sup>). The band observed at  $383 \text{ cm}^{-1}$  is assigned to a rocking motion of the aluminum trimer and both MeCN ligands, which is predicted at 382  $cm^{-1}$ . Pure aluminum vibrations are expected to fall lower in energy (< 300  $cm^{-1}$ ) than this instrument can measure. It should be noted that predicted frequencies and intensities here are for free clusters, and this spectrum is measured on silver nanorods. The surface enhancement of the nanorods may be responsible for discrepancies in both peak position and intensity. The vibrational spectrum of this material is consistent with the mass spectrum and supports the presence of both species in solution.

The UV-visible absorption and fluorescence emission of coated aluminum clusters can be seen in Figure 6.6. Both of these spectra are quite remarkable as the band width of the features is extremely narrow. In contrast, all materials previously synthesized with the LVFR have exhibited only broad peaks in their absorption and emission spectra. It is likely that this behavior is due to the small size of the clusters or relative homogeneity of the samples. The intense bands at 302 and 338 nm are predicted reasonably well by TD-DFT calculations on the coated aluminum trimer. The computed transitions at 308.59 and 333.84 nm (Table 6.2) are within six nm of the measured features. There are no electronic transitions predicted for bare aluminum trimer or Al<sub>2</sub>O<sub>3</sub>(MeCN) in this range, but it must be noted that bare Al<sub>2</sub>O<sub>3</sub> has a predicted transition at 334.36 nm, which matches the peak measured at 338 nm. The addition of ligands to Al<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> does change their electronic structure, although not in a systematic way. The fluorescence spectrum of this material displays a broad emission with an overlaying structure. The emission in Figure 6.6 results from excitation with 302 nm light, which corresponds to the most intense peak in the UV-visible spectrum. The same spectral features are observed using wavelengths corresponding to any of the peaks in the 280-350 nm range. Excitation with other frequencies does not result in the emission shown in Figure 6.6. The bands in the emission spectrum have consistent spacing of approximately 1080 or 1470 cm<sup>-1</sup> (Figure 6.7). These spacings correspond to the most intense vibrational modes observed in the SERS spectrum, suggesting that the structure in the emission is due to two or more vibrational progressions. A

Table 6.2. Excitation energies for Al <sub>3</sub> (MeCN) <sub>2</sub> , Al <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> (MeCN), and Al <sub>2</sub> O <sub>3</sub> estimated using
time-dependent DFT. Computed oscillator strengths are in parenthesis. Only transitions with
predicted oscillator strengths >0.01 are shown.

Al <sub>3</sub> (MeCN) <sub>2</sub>	Al <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> (MeCN)	$Al_2O_3$
651.98 nm (0.0198)	395.87 nm (0.0285)	294.60 nm (0.0878)	334.36 nm (0.0136)
640.15 nm (0.0439)	364.51 nm (0.0255)	263.69 nm (0.0128)	287.44 nm (0.0635)
501.61 nm (0.0994)	209.06 nm (2.1511)	262.71 nm (0.0300)	265.81 nm (0.0382)
486.73 nm (0.1762)	203.34 nm (0.0268)	256.18 nm (0.0359)	263.22 nm (0.0258)
478.58 nm (0.2299)	165.81 nm (0.2034)	221.63 nm (0.128)	263.14 nm (0.0166)
461.53 nm (0.0221)			243.49 nm (0.1343)
354.44 nm (0.0432)			216.57 nm (0.1031)
333.89 nm (0.0500)			
314.80 nm (0.1167)			
308.59 nm (0.0694)			



Figure 6.6. UV-visible spectrum of aluminum nanocluster material (bottom). Fluorescence spectrum of this material resulting from excitation with 302 nm light (Middle). Electronic spectrum of jet-cooled gas phase aluminum trimer measured by Morse and co-workers (top).<sup>15</sup>



Figure 6.7. Fluorescence spectrum of coated aluminum nanoclusters in wavenumbers with peak spacings in blue.

similar spectrum has been observed by Morse and co-workers.<sup>15</sup> The resonant two-photon ionization spectrum they measured for gas phase aluminum trimer can also be seen in Figure 6.6.Our spectrum is blue shifted with respect to theirs, but this may be due to ligand effects on aluminum trimer. In any case, it is remarkable that the spectra for our coated trimer and the gas phase trimer are so similar.

## Conclusions

Ligand coated aluminum and aluminum oxide nanoclusters are produced, captured, and isolated using a LVFR. Acetonitrile stabilizes and renders these clusters soluble. The selective capture of coated aluminum trimer is remarkable, as this cluster is much smaller than traditional nanoparticles, and has not been observed to form preferentially in the gas phase. The SERS spectrum of this material has evidence for both Al<sub>2</sub>O<sub>3</sub>(MeCN) and Al<sub>3</sub>(MeCN)<sub>2</sub>, which is consistent with the mass spectral analysis. The UV-visible spectrum for this cluster material is interesting, as it displays sharp bands, which correspond to electronic transitions of Al<sub>3</sub>(MeCN)<sub>2</sub>. The fluorescence emission of the sample is broad and intense and contains vibrational structure. Until now the LVFR has been used to produce only oxide clusters, but this study shows it is possible to produce interesting pure metal clusters. It should be feasible in the future to produce other non-oxide materials in the LVFR, such as metal carbides, metal nitrides or metal silicon clusters.

# References

- Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J.; "Recent advances in the liquid-phase syntheses of inorganic nanoparticles," *Chem. Rev.* 2004, *104*, 3893-3946.
- Gvishi, R. "Fast sol-gel technology: from fabrication to applications," J. Sol-Gel Sci. Technol. 2009, 50, 241-253.
- M. S.; El-Shall, W.; Slack, W.; Vann, D.; Hanley, D. "Synthesis of nanoscale metal-oxide particles using laser vaporization condensation in a diffusion cloud chamber," *J. Phys. Chem.* 1994, *98*, 3067-3070.
- 4. R. C.; Flagan, M. M. Lunden, "Particle structure control in nanoparticle synthesis from the vapor phase," *Mat. Sci. Eng. A-Struct.* **1995**, *204*, 113-124.
- Rai, A.; Lee, D.; Park, K. H.; Zachariah, M. R. "Importance of phase change of aluminum in oxidation of aluminum nanoparticles," *J. Phys. Chem. B.* 2004, *108*, 14793-14795.
- Martirosyan, K. S.; Zyskin, M. "Reactive self-heating model of aluminum spherical nanoparticles," *App. Phys. Lett.* 2013, *102*, 053112/1-4.
- Chan, G. H.; Zhao, J.; Schatz, G. C.; Van Duyne, R. P. "Localized surface plasmon resonance spectroscopy of triangular aluminum nanoparticles," *J. Phys. Chem. C* 2008, *112*, 13958-13963.
- Alavi, S.; Thompson, D. L. "Molecular dynamics simulations of the melting of aluminum nanoparticles," *J. Phys. Chem. A* 2006, *110*, 1518-1523.
- 9. a) Starace, A. K.; Cao, B.; Judd, O. H.; Bhattacharyya, I.; Jarrold, M. F.; "Melting of size-selected aluminum nanoclusters with 84-128 atoms," *J. Chem. Phys.* 2010, *132*, 34302/1-9.
  b) Aguado, A.; Jarrold, M. F. "Melting and freezing of metal clusters," *Annu. Rev. Phys. Chem.* 2011, *62*, 151-172.

- a) Hanley, L.; Anderson, S. L. "Reactions of bare aluminum cluster ions," *Chem. Phys. Lett.* 1986, 129, 429-432. b) Ruatta, S. A.; Hanley, L.; Anderson, S. L. "size-dependent barriers for reaction of aluminum cluster ions with oxygen," *Chem. Phys. Lett.* 1987, 137, 5-9. c) Parent, D. C.; Anderson, S. L. "Chemistry of metal and semimetal cluster ions," *Chem. Rev.* 1992, 92, 1541–1565.
- a) Jarrold, M. F.; Bower, J. E. "The reactions of mass selected aluminum cluster ions, Al<sub>4-25</sub><sup>+</sup> with oxygen," *J. Chem. Phys.* 1986, *85*, 5373 -5376. b) Leslie, K. L.; Shinholt, D.; Jarrold, M. F. "Reactions of CO<sub>2</sub> on solid and liquid Al<sub>100</sub><sup>+</sup>," *J. Phys. Chem. A* 2013, *117*, 1053-1058.
  c) Leslie, K. L.; Jarrold, M. F. "Dehydrogenation of benzene on liquid Al<sub>100</sub><sup>+</sup>," *J. Phys. Chem. A* 2013, *117*, 2075-2081.
- 12. . a) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. "Thermal metal cluster anion reactions behavior of aluminum clusters with oxygen," *J. Chem. Phys* 1989, *91*, 2753-2755.
  b) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. "Aluminum cluster reactions," *J. Chem Phys.* 1991, *94*, 1093-1101. c) Reber, A. C.; Khanna, S. N.; Roach, P. J.; Woodward, W. H.; Castleman, A. W., Jr. "Reactivity of aluminum cluster anions with water: origins of reactivity and mechanisms for H<sub>2</sub> release," *J. Phys. Chem. A* 2010, *114*, 6071–6081. d) Woodward, W. H.; Eyet, N.; Shuman, N. S.; Smith, J. C.; Viggiano, A. A.; Castleman, A. W., Jr. "Aluminum cluster anion reactivity with singlet oxygen: evidence of Al<sub>9</sub><sup>-</sup> stability," *J. Phys. Chem. C* 2011, *115*, 9903–9908.
- Hanley, L.; Ruatta, S. A.; Anderson, S. L. "Collision-induced dissociation of aluminum cluster ions fragmentation patterns, bond-energies, and structures for Al<sub>2</sub><sup>+</sup>-Al<sub>7</sub><sup>+</sup>," *J. Chem. Phys.* 1987, 87, 260-268.
- 14. Ray, U.; Jarrold, M. F.; Bower, J. E.; Kraus, J. S. "Photodissociation spectroscopy of

aluminum clusters - Al<sub>3</sub><sup>+</sup> - Al<sub>6</sub><sup>+</sup>," *Chem. Phys. Lett.* **1989**, *159*, 2614-2623.

- a) Fu, Z. W.; Lemire, G. W.; Hamrick, Y. M.; Taylor, S.; Shui, J. C.; Morse, M. D.
  "Spectroscopic studies of the jet-cooled aluminum trimer," *J. Chem. Phys.* 1988, 88, 3524-3531. b) Fu, Z. W.; Lemire, G. W.; Bishea, G. A.; Morse, M. D. "Spectroscopy and electronic-structure of jet-cooled Al<sub>2</sub>," *J. Chem. Phys.* 1990, *93*, 8420-8441.
- 16. a) Bergeron, D. E.; Castleman, A. W., Jr.; Morisato, T.; Khanna, S. N. "Formation of Al<sub>13</sub>Γ : Evidence for the superhalogen character of Al<sub>13</sub>," *Science* 2004, *304*, 84-87. b) Bergeron, D. E.; Roach, P. J.; Castleman, A. W., Jr.; Jones, N.; Khanna, S. N. "Al cluster superatoms as halogens in polyhalides and as alkaline earths in iodide salts," *Science* 2005, *307*, 231-235.
  c) Castleman, A. W., Jr.; Khanna, S. N. "Clusters, superatoms, and building blocks of new materials," *J. Phys. Chem. C* 2009, *113*, 2664–2675. d) Melko, J. J.; Castleman, Jr., A. W. "Photoelectron imaging of small aluminum clusters: quantifying s-p hybridization," *Phys. Chem. Chem. Phys.* 2013, *15*, 3173-3178.
- 17. Deheer, W. A. "The physics of simple metal-clusters Experimental aspects and simplemodels," *Rev. Mod. Phys.* **1993**, *65*, 611-676.
- 18. a) Desai, S. R.; Wu, H. B.; Rohlfing, C. M.; Wang, L. S. "A study of the structure and bonding of small aluminum oxide clusters by photoelectron spectroscopy: Al<sub>x</sub>O<sub>y</sub><sup>-</sup> (x=1-2, y=1-5)," J. *Chem. Phys.* **1997**, *106*, 1309-1317. b) Li, X.; Wu, H. B.; Wang, X. B.; Wang, L. S. "S-p hybridization and electron shell structures in aluminum clusters: A photoelectron spectroscopy study," *Phys. Rev. Lett.* **1998**, *81*, 1909-1912. c) Akola, J.; Manninen, M.; Hakkinen, H.; Landman, U.; Li, X.; Wang, L. S. "Photoelectron spectra of aluminum cluster anions: Temperature effects and ab initio simulations," *Phys. Rev. B* **1999**, *60*, 11297/1-4. d) Akola, J.; Manninen, M.; Hakkinen, H.; Landman, U.; Li, X.; Wang, L. S. "Aluminum

cluster anions: Photoelectron spectroscopy and ab initio simulations," *Phys. Rev. B* **2000**, *62*, 13216/1-12.

- Jones, R. O. "structure and bonding in small aluminum clusters," *Phys. Rev. Lett.* 1991, 67, 224-227.
- Schultz, N. E.; Staszewska, G.; Staszewski, P.; Truhlar, D. G. "Validation of theoretical methods for the structure and energy of aluminum clusters," *J. Phys. Chem. B* 2004, *108*, 4850-4861.
- 21. Noya, E. G.; Doye, J. P. K.; Calvo, F. "Theoretical study of the melting of aluminum clusters," *Phys. Rev. B* 2006, *73*, 125407/1-6.
- 22. Sun, J.; Lu, W. C.; Wang, H.; Li, Z. S.; Sun, C. C. "Theoretical study of Al<sub>n</sub> and Al<sub>n</sub>O (n=2-10) clusters," *J. Phys. Chem. A* 2006, *110*, 2729–2738.
- Mitin, A. V. "Accurate theoretical IR and Raman spectrum of Al<sub>2</sub>O<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> molecules," *Struct. Chem.* 2011, 22, 411-418.
- 24. a) Rao, B. K.; Jena, P. "Evolution of the electronic structure and properties of neutral and charged aluminum clusters: A comprehensive analysis," *J. Chem. Phys.* 1999, *111*, 1890-1905. b) Burgert, R.; Schnoeckel, H.; Grubisic, A.; Li, X.; Stokes, S. T.; Bowen, K. H.; Gantefor, G. F.; Kiran, B.; Jena, P. "Spin conservation accounts for aluminum cluster anion reactivity pattern with O<sub>2</sub>," *Science* 2008, *319*, 438-442. c) Ko, Y. J.; Shakya, A.; Wang, H.; Grubisic, A.; Zheng, W.; Goetz, M.; Gantefoer, G.; Bowen, K. H.; Jena, P.; Kiran, B.
  "Electronic structure and properties of isoelectronic magic clusters: Al<sub>13</sub>X (X=H, Au, Li, Na, K, Rb, Cs)," *J. Chem. Phys.* 2010, *133*, 124308/1-6.
- 25. a) Ayers, T. M.; Fye, J. L.; Li, Q.; Duncan, M. A., "Synthesis and isolation of titanium metal cluster complexes and ligand-coated nanoparticles with a laser vaporization flowtube

reactor," *J. Clust. Sci.* **2003**, *14*, 97-113. b) Ard, S.; Dibble, C. J.; Akin, S. T.; Duncan, M. A. "Ligand-coated vanadium oxide clusters: capturing gas-phase magic numbers in solution," *J. Phys. Chem. C* **2011**, *115*, 6438-6447.

- Chaney, S. B.; Shanmukh, S.; Dluhy, R. A.; Zhao, Y. P. "Aligned silver nanorod arrays produce high sensitivity surface-enhanced raman spectroscopy substrates," *Appl. Phys. Lett.* 2005, *87*, 031908/1-3.
- 27. Frisch, M. J. et. al., Gaussian, Inc., Wallingford CT, 2009.
- 28. Schafer, A.; Huber, C.; Ahlrichs, R. "Fully optimized contracted gaussian-basis sets of triple zeta valence quality for atoms Li to Kr," *J. Chem. Phys.* **1994**, *100*, 5829-5835.

#### CHAPTER VII

#### CONCLUSIONS

The production and characterization of new and interesting nano-scale materials is an exciting and active area of research. Metal and metal oxide nanoparticles on the order of hundreds of atoms have long been studied due to their interesting magnetic, catalytic, and optical properties. We have developed a process for the production of much smaller particles or clusters. These nanoclusters are produced using a laser vaporization flowtube reactor (LVFR), and contain only 10 - 30 atoms making them some of the smallest particles ever synthesized.

Vanadium oxide clusters coated with tetrahydrofuran (THF) or acetonitrile (MeCN) are described in Chapter III. These samples contain coated clusters, which are analogues to "magic number" clusters seen previously in gas phase experiments. Using mass spectrometry and infrared spectroscopy to characterize these material

ls, it was determined that clusters coated with THF react with the ligand, which replaces terminal oxygen atoms of the core oxide. In contrast, MeCN coated clusters remain intact. These clusters exhibit intense and broad fluorescence.

In Chapter IV cobalt oxide clusters complexed to MeCN are described. Although studies show small gas phase clusters form with little preference for particular size, we collect primarily  $Co_4O_4(MeCN)_6$ .  $Co_4O_4$  has been produced by others using inorganic synthesis and has been implicated in water splitting. This is due to its similarity to the Mn<sub>4</sub>O<sub>4</sub> core of Photosystem II. By comparing Raman spectroscopy to theoretical spectra of  $Co_4O_4(MeCN)_6$ , we find that it forms a cube, while the bare cluster likely grows as a ring. This structural transition is predicted to take place when more than two ligands are added. The size selective capture of particularly stable or "magic number" clusters of chromium oxide is discussed in Chapter V. Here, the MeCN coated clusters are produced with much higher yield than in previous LVFR studies. With careful tuning of the vaporization laser, it is possible to selectively produce coated nanoclusters containing 3 - 6 chromium atoms. While these clusters share the same stoichiometry as "magic number" clusters seen in gas phase experiments, their structure cannot be the traditional "cage." Raman spectra of these samples contain a large feature at 800 cm<sup>-1</sup>, which can only be explained by structures with  $Cr_2O_2$  groups. It is likely that these clusters form rings or chains.

In Chapter VI the production of coated aluminum clusters, including the first non-oxide, are discussed. Mass spectral analysis of this material reveals that Al<sub>3</sub>(MeCN)<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>(MeCN) are present. Predicted vibrations for both these complexes appear in the sample's Raman spectrum. Although efforts were made to remove oxygen in the system, it appears that both metal clusters and oxides are produced. Capture of coated aluminum trimer is surprising, as it does not follow the jellium model. UV-visible spectrum and fluorescence emission of this sample is remarkable, due to the very sharp features they contain. Vibrational structure is observed in the emission spectra, which is quite similar to the electronic spectrum previously measured for the bare gas phase trimer.

Substantial progress has been made, not only in the production of several new materials, but also in the understanding of what types of materials can be made using the LVFR. In spite of this several challenges remain for the future of this experiment. First and foremost, no means of analyzing the clusters as they grow in the flowtube have yet been successful. Although it is sometimes possible, through trial-and-error, to reproduce the exact conditions required by some of these systems, parameters such as laser fluence, flow rate and gas concentrations can change

slightly over time. Having real-time feedback, such as mass spectral analysis, could solve this issue.

Attempts to analyze cluster distribution in the flowtube using the in-line time-of-flight instrument, built prior to my arrival, have been largely unsuccessful (see Figure 7.1). This is due to the difficulty of getting clusters into the photoionization region of the mass spectrometer (ArF excimer). Even with a small aperture (1 mm), the 5 torr running condition of the LVFR causes the pressure in the mass spectrometer to increase to non-operable ranges (1x10<sup>-5</sup> torr). It is possible to measure mass spectra with the flows substantially lower (< 100 mtorr), but even so, clusters grown in the LVFR have never been seen in the in-line mass spectrometer. Commercial high pressure gas analyzers exist which can continuously detect up to 300 amu and sample 1 torr of pressure (Standford QMS series). These systems use differential pumping and capillary inlets to achieve this. The most profound advancement for the LFVR project would be to use one of these systems (or to build something similar) which would substantially increase the ability to reproduce certain materials, as well as provide insight into the growth process.

Characterization of LFVR grown materials has been an evolving process. Using mass spectrometry, vibrational spectroscopy and computations, we have developed a method of determining the contents of our cluster samples. Future work should concentrate on scaling up the LVFR process so that higher yields can be obtained. In addition to more material, a purer sample, obtained using some form of chromatography, would also be beneficial. A concentrated, pure sample could be characterized in a much more rigorous fashion. Magnetic and catalytic properties of these coated clusters could be obtained, which might render them useful for many applications.



Figure 7.1. In-line mass spectrometer attached to the LVFR.