## LIGAND-COATED METAL AND METAL-OXIDE CLUSTERS

by

## SCOTT T. AKIN

(Under the Direction of Michael A. Duncan)

#### ABSTRACT

Ultra-small metal and metal-oxide clusters are produced in the gas phase with laser vaporization, coated with ligands, and captured in solution with the use of a laser vaporization flowtube reactor. Their properties were investigated with mass spectrometry, numerous spectroscopic methods, and computational chemistry. Observed chromium oxide clusters coated with acetonitrile ligands have stable metal-oxide stochiometries previously observed in gas phase experiments. Production and capture of aluminum clusters yields aluminum trimer with acetonitrile ligands as the primary clusters. Small aluminum oxides and larger aluminum clusters are also observed. Separate gas phase X-ray studies were performed to investigate cluster-ligand interactions. Ligand addition to cobalt clusters revealed drastic quenching of magnetic moments for both benzene and carbonyl ligands.

INDEX WORDS: Metal Clusters, Metal-Oxide Clusters, Metal-Ligand Interactions

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SCOTT T. AKIN

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# SCOTT T. AKIN

Major Professor: Michael A. Duncan

Committee:

Gary Douberly Todd Harrop

Electronic Version Approved:

Suzanne Barbour Dean of the Graduate School The University of Georgia August 2016

# DEDICATION

This dissertation is dedicated to my family and friends. A special thanks to my wife Laura who makes the real money while I toil in grad school.

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### CHAPTER I

#### INTRODUCTION

Metal clusters and nanoparticles have unique electronic, optical, magnetic, and chemical properties that cannot be deduced based on the properties of the corresponding bulk material.<sup>1-9</sup> These unique properties play a significant role in catalysis, chemical sensors, fuel cells, magnetic materials, and other applications.<sup>1-17</sup> Theoretical advancements allow for density functional theory (DFT) studies of large metal clusters,<sup>18</sup> but high level *ab initio* methods remain out of reach for these systems. The focus of this dissertation is the production and characterization of small (<50 atoms) ligand-coated metal and metal-oxide clusters through the use of a laser vaporization flowtube reactor (LVFR) and gas phase x-ray spectroscopy of cobalt cluster cations with ligands.

Production of metal nanoparticles goes back over 100 years to Faraday's colorful suspensions of gold nanoparticles.<sup>19</sup> Since this time, numerous metal and metal-oxide nanoparticles have been produced in solution using precipitation, microemulsions, micelle/reverse micelle, and sol-gel techniques,<sup>20-31</sup> with more recent work producing a variety of particles in the 1–10 nm size range. More conventional inorganic synthesis methods are also effective for certain species, including the broad class of polyoxometalates (POMs)<sup>32-37</sup> and some small sub-nanometer metal clusters, but such methods are largely limited to noble metal clusters.<sup>38-42</sup> Although solution phase synthesis is more common, some nanoclusters and nanoparticles have been produced with gas phase methods.<sup>43-49</sup>

Gas phase clusters have been studied for over five decades, showing important, and often surprising, results. Enhanced cluster stability due to electronic shell closings was observed in 1984 for sodium and potassium clusters.<sup>50,51</sup> Not long after, buckminsterfullerene ( $C_{60}$ ) was discovered, possessing a unique stability from it's highly symmetric truncated icosahedron geometry.<sup>52</sup> Since this time, other gas phase clusters have been observed to occur in unusually large abundances. Reactions of aluminum clusters with oxygen produced primarily  $Al_{13}^{-53-55}$ ,  $S_{13}^{-55}$ showing this particular cluster to be more stable than other aluminum clusters. Attempts to use early first row transition metals for dehydrogenation reactions of hydrocarbons instead produced metal carbide clusters of the form M<sub>8</sub>C<sub>12</sub><sup>+</sup> known as "met-cars".<sup>56,57</sup> Subsequent work discovered larger metal carbide clusters ( $M_{14}C_{13}^+$ ) forming a 3 x 3 x 3 cube, <sup>58–60</sup> and these clusters were later discovered in circumstellar environments.<sup>61</sup> Beyond the initial observations of cluster stability and abundance, much work has been done to probe additional cluster properties. Ionization potential, reactivity, bonding, geometry, and electronic structure have all been probed over the last number of years.<sup>62-65</sup> The results demonstrate that clusters offer a unique opportunity to explore properties in a way that cannot be accessed otherwise.

Smalley and coworkers studied carbon clusters formed from laser ablation of graphite in 1985, in the process discovering  $C_{60}$  (buckminsterfullerene).<sup>52</sup> Krätschmer and Huffman<sup>66</sup> later isolated  $C_{60}$  from carbon soot, finding  $C_{60}$  to be soluble in benzene while the soot was insoluble. Other interesting gas phase clusters, however, currently remain confined to the gas phase. Since their discovery, attempts were made to isolate metal carbide clusters in hopes of recreating the success of  $C_{60}$ . However, the fortunate solubility of  $C_{60}$  does not apply to metal carbide clusters (and many other gas phase clusters), and despite the remaining interest, metal carbide and other clusters have not been definitively isolated or collected in solution. The ability to capture gas

phase clusters in solution represents an opportunity to investigate novel sub-nanometer and nanometer clusters.

It has been shown that fullerenes are readily soluble in organic solvents and are stable enough to be separated with chromatography. Such characteristics are not expected of transition metal and transition metal-oxide clusters, as they would likely have minimal solubility in common solvents. Andres and coworkers<sup>43</sup> first demonstrated a technique for synthesizing gold nanoparticles, using an over source to produce gold atoms in the gas phase. El-Shall and coworkers have used laser vaporization followed by condensation techniques to produce a number of small ligand-coated metal-oxide nanoparticles.<sup>46,47</sup> The use of laser vaporization allows for the study of a wider variety of metals, and the LVFR has been previously used by our lab to produce ligand-coated metal-oxide particles in order to produce these small clusters in solution.<sup>67-69</sup>

The combination of gas phase growth and solution phase capture allows for production and collection of ultra-small ligand-coated clusters in the LVFR. These ultra-small clusters are smaller than typical nanoparticles possessing hundreds to thousands of atoms but larger than most inorganic molecules containing up to a few central metal atoms. Gas phase laser vaporization is used for the formation of small naked clusters (<50 atoms) that can possess nonbulk stochiometries and oxidation states. The distribution of clusters is not mass-selected, but gas phase mass spectrometry has shown that the formation of metal-oxide and metal-carbide clusters often produces a small number of preferred stochiometries with strong bonding (3–5 eV).<sup>1,2,4,6</sup> Consequently, the cluster distribution in the LVFR is comprised predominantly of strongly bonded stable stochiometries. As bond dissociation is unlikely, gas phase interactions with ligand

molecules produce ligand-coated clusters which are subsequently captured in a liquid nitrogen cold trap (78 K).

The first LVFR result was production and isolation of titanium and titanium oxide clusters coated with tetrahydrofuran (THF) and ethylenediamine (en).<sup>67</sup> In both cases, laser desorption time of flight mass spectrometry (LDI-TOF-MS) was performed to probe stoichiometries. Observed Ti(en)<sup>+</sup> cluster stoichiometries of Ti(en)<sub>3</sub><sup>+</sup>, Ti<sub>2</sub>(en)<sub>5</sub><sup>+</sup>, and Ti<sub>3</sub>(en)<sub>7</sub><sup>+</sup>. Control experiments were performed to ensure that these were formed in the LVFR and not in the mass spectrometer during laser desorption. Using THF in place of ethylenediamine produced clusters of the stoichiometry Ti<sub>x</sub>O<sub>y</sub>(THF)<sub>z</sub>. The oxide formation likely occurs from a reaction between titanium and THF (although trace oxidation of the titanium rod could also provide a source of oxygen). Observed masses in LDI-TOF-MS were attributed to clusters grown and captured in solution after careful control. Larger masses of the formula Ti<sub>x</sub>O<sub>x+2</sub>(THF)<sub>2x</sub> were observed at increased laser desorption power in the LDI-TOF-MS. These may represent larger polymer-like chains produced in the LVFR, although one cannot rule out the LDI process as the cause of formation.

Also produced and isolated in the LVFR system were vanadium oxide clusters, coated with THF and acetonitrile (MeCN).<sup>68</sup> LDI-TOF-MS revealed stoichiometries (V<sub>3</sub>O<sub>6</sub>, V<sub>4</sub>O<sub>9</sub>, and V<sub>5</sub>O<sub>12</sub>) with acetonitrile ligands forming V<sub>x</sub>O<sub>y</sub>(MeCN)<sub>z</sub> clusters whose metal-oxide cores were first observed in gas phase studies of V<sub>x</sub>O<sub>y</sub> clusters.<sup>70</sup> Production of V<sub>x</sub>O<sub>y</sub>(THF)<sub>z</sub> clusters leads to the observation of primarily one cluster size, V<sub>3</sub>O<sub>4</sub>(THF)<sub>3</sub>. V<sub>3</sub>O<sub>4</sub>(THF)<sub>3</sub> represents an analog of the gas phase cluster V<sub>3</sub>O<sub>7</sub> with the oxygen in THF replacing accessible terminal oxygens. IR spectra of both species were recorded, with IR of V<sub>x</sub>O<sub>y</sub>(MeCN)<sub>z</sub> exhibiting terminal metal-

oxygen stretches, while such stretches in  $V_xO_y(THF)_z$  were not evident. These results were consistent with the assignments from LDI-TOF-MS.

Metal clusters and their transitions to solution phase chemistry increase the ability to use such clusters in practical applications. However, fundamental gas phase studies are still needed and useful, as experimental observations in the gas phase are able to probe isolated clusters. Xray absorption spectroscopy (XAS) has been performed on free cation clusters to probe molecule-to-bulk changes and electronic states.<sup>71-74</sup> More recently, the application of X-ray Magnetic Circular Dichroism (XMCD) to gas phase cation clusters can measure the spin and orbital momenta. This has allowed for studies of cluster magnetic properties.<sup>75-78</sup> and ground state assignments of a number of metal dimer cations.<sup>79-81</sup>

This work concentrates on accessing different clusters in to potentially open avenues for new cluster based materials. The application of fundamental understanding from previously observed gas phase clusters allows for cluster capture in solution through ligand coordination. In tandem with LVFR experiments, x-ray absorption and XMCD studies in the gas phase are performed to study fundamental metal cluster – ligand interactions.

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## CHAPTER II

### EXPERIMENTAL SETUP

The laser vaporization flowtube reactor (LVFR) apparatus has been described previously<sup>1</sup> and successfully used to produce and capture ligand-coated clusters and particles in solution.<sup>1-3</sup> The current configuration of the LVFR is shown in Figure 2.1. A laser vaporization source is chosen over discharge or sputtering due to its general applicability and use for production of pure metal, oxide, carbide, etc. clusters.<sup>4–5</sup> The main disadvantage of laser vaporization is a lower throughput that some other methods, but this issue is addressed with the use of a high repetition rate laser with high power/pulse and high energy photons. This is paramount for efficient gas phase cluster production that yields up to milligrams of cluster material for analysis and characterization. The excimer laser (Coherent LPXpro 240F) output is focused to a roughly 1–3 x 12 mm rectangular spot, to balance laser fluence and ablation area. The laser power is fixed for a given synthesis run, but different power levels (60-260 mJ/pulse) are used for different experiments. The metal rod is rotated slowly by a motor during the ablation process. Argon or helium gas (with 1–10% oxygen for metal-oxide production) is continuously expanded through a 750 µm hole positioned above the metal rod. The flowing gas passes over the length of the rotating metal rod perpendicular to the intersection of the laser pulse, entraining the vaporized metal in while providing collisional quenching and cooling. The pressure in this region ranges from 2–15 torr during cluster production. The stainless steel six-way cross is water cooled externally to provide additional cooling in the cluster growth region. Nascent metal and metaloxide clusters are grown in this first region, prior to passing through a first aperture (13 mm diameter Aperture 1).

The region between apertures 1 and 2 is the passivation zone, where gas phase ligands are introduced as direct vapor entrained in argon, with an oven source, or as an aerosol via a nebulizer. The use of apertures 1 and 2 is critical as it slows the flow, promoting additional collisional cooling of the clusters and increased collisions for ligand capture. Without both apertures, little to no soluble material is produced. The gas flow ultimately continues through aperture 2 into a liquid nitrogen (78 K) cooled trap. The trap consists of a two neck round bottom flask with 5 mm glass beads and a round glass stem. The stem forces all gas flow to the bottom of the round bottom flask and improves trapping efficiency as gas phase material comes into contact with the cooled glass beads and condenses before being pumped away. The round bottom flask is separated from an Edwards E40 mechanical pump by two additional liquid nitrogen traps in order to prevent back streaming of oil into the experiment. The flask containing the collected cluster material is back-filled with argon, disconnected from the flow system, and allowed to warm to room temperature. Production of material varies with different metal systems, but can occur at rates of up to three milligrams/hour.

Collected cluster samples are characterized with a number of methods. The first stage of sample analysis employs laser desorption ionization (LDI) and electrospray ionization (ESI) time of flight (TOF) mass spectrometry (MS). Careful use of two different ionization methods and control experiments serves to confirm that the clusters are intrinsic to the solution and not simply produced in the MS process. LDI-MS is performed with a custom-built TOF-MS<sup>6</sup> using a Nd:YAG laser operating at the second (532 nm; green) or third (355 nm; UV) harmonic. Typically both green and UV result in the same or similar mass spectra. ESI-MS is performed

with a Mariner Biospectroscopy Workstation and is generally in agreement with the LDI results, though some minor differences can occur. Transmission electron microscopy (TEM) is also performed (FEI Tecnai 20) to observe or rule out larger nanoparticles. Small stoichiometric clusters are often not visible through the available TEM systems, but larger nanoparticles over 2 nm in diameter can be readily observed.

After confirmation of sub-nanometer clusters in solution, multiple different spectroscopic methods are performed for chemical insight. Use of a simple tabletop UV-Vis instrument (Shimadzu UV-2600) provides an absorption spectrum which can be compared to the bulk bandgap, the nanoparticle bandgap, and experimental/theoretical gas phase cluster transitions. Other optical spectroscopy measurements include fluorescence spectroscopy (Shimadzu RF-5301C), infrared spectroscopy (Nicolet 6700 FT-IR), and surface-enhanced Raman spectroscopy (SERS) using a Renishaw InVia Raman Microscope with specially prepared silver nanorod substrates.<sup>7</sup> HPLC experiments are also investigated (Spectra System SCM1000/P4000/UV1000 with a SUPELCOSIL LC-18 column) using a detector set at absorption wavelengths selected from the UV-visible spectra. Computational chemistry studies are performed in conjunction with experimental spectroscopy. Density functional theory (DFT) methods performed in Gaussian 09<sup>8</sup> predict relative energies of isomers and their respective infrared and raman spectra, which are useful in determining the cluster structure. Time dependent DFT (TD-DFT) allows for prediction of electronic excited states which can be observed in solution using UV-Vis spectroscopy. Unfortunately, computational studies on metal and metal-oxide clusters are difficult and are largely restricted to DFT methods.

The experimental apparatus for LDI-TOF-MS is displayed in Figure 2.2. The basic principles of TOF-MS were described previously by Wiley and McLaren.<sup>9</sup> Cluster samples are

deposited onto a probe tip and inserted into the mass spectrometer. Mass analysis in this LDI-TOF-MS requires ionization of the sample and separation of the ions in time. A pulsed laser (New Wave Research, Polaris II operated at 532 or 355 nm) is used for ionization of the deposited films. The ionization process for these samples is unclear. Direct photoionization from the absorption of one photon is unlikely, as most molecules have ionization potentials 9-12 eV and visible/UV photons are 2-6 eV. Multiphoton ionization (MPI) is possible as the use of a pulsed laser provides a large number of photons in a short amount of time. The underlying metal surface can absorb photons and, if the work function is overcome, eject electrons. These electrons are then accelerated back towards the positive repeller plate and can be slammed into the thin film causing electron impact ionization. It is also possible to have detachment of electrons in the ionization process, and these electrons would also be accelerated back towards the repeller plate. Other ionization mechanism involving reactions are also possible and cannot be discounted. The acceleration region of the mass spectrometer consists of the repeller plate (8–15 kV; Bertan 205B-20R), the draw-out grid (2–14 kV; Bertan 205B-20R), and a ground plate. The repeller plate is solid while the draw-out grid and ground plates have screen covered holes that allow for ion transmission. The fields produced from parallel plates held at constant voltages are described Equation 1:

$$E = (V_1 - V_2)/L$$
 Eq. 1

The difference in voltage between the two plates is divided by the length separating the two plates to give the field (often in V/cm or kV/cm). When the repeller and draw-out grid voltages are positive, positive ions are pushed down the flight tube. After the acceleration region, an einzel lens (2–10 kV; Bertan 205B-10R) is used to radially focus the ion packet. Deflection plates (200–1000 V; Bertan 205A-3R) are used to steer the ion packet left and right. Ions then

travel to a reflectron (Bertan 205B-20R) consisting of a stack of rings. Positive high voltage is applied to the ring farthest from the repeller. Each ring is connected to other rings by a resitor, and the voltage increases as the ions travel further into the reflectron. Eventually, the ions are turned away from the reflectron and towards the detector. Ions are detected using an electron multiplier tube (Hamamatsu R-595). The signal is amplified (Stanford Research Systems SR445A) and collected using a digital oscilloscope (LeCroy Waverunner LT342). Data is transferred to a PC where home-made software is used to analyze the TOF mass spectra. Analysis of mass spectra requires that ions of different mass (more specifically, mass to charge ratio) are separated in time. Ions are imparted with kinetic energy in the acceleration stage, and the energy is related to ion velocity by Equation 2:

$$KE = \frac{1}{2} mv^2$$
 Eq. 2

Assuming all ions have the same kinetic energy, ions of heavier mass will travel slower and ions of lighter mass will travel faster. All ions travel approximately the same distance (depending on where in the acceleration region an ion is formed), and ion signal recorded in time can then be related back to the mass. Because of uncertainties in the kinetic energies of all ions produced and the inability to measure the flight distance of ions accurately enough, two peaks in the mass spectrum are assigned as known values. This is typically done with sodium and potassium ions (m/z = 23 and 39) and unknown peaks are determined using Equations 3 and 4.

$$m_k v_k^2 = m_u v_u^2 Eq. 3$$

Here the kinetic energies of the known (k) and unknown (u) ions are assumed to be the same (Equation 3). As velocity is a function of distance/time, Equation 4 is used to relate the known

mass, flight time of the unknown ion, and flight time of the known ion to determine the mass of the unknown ion.

A schematic view of the experimental setup is shown in Figure 2.3. A previous iteration of this instrument has been described in great detail.<sup>10</sup> A liquid nitrogen cooled CW magnetron gas aggregation source is used to produce cluster ions. Use of a continuous magnetron source is required to reach appropriate ion densities in the trap. Cluster ions are then guided through a hexapole ion guide. Gas or the ambient vapor pressure above a volatile liquid is added into the hexapole ion guide via a leak valve. Collisions of cluster ions with a desired ligand molecule produce cluster ion complexes which are size selected in a quadrupole mass filter. Ions are then focused with an electrostatic ion lens and turned 90° with the use of a quadrupole deflector. Ions are collected in a liquid helium cooled radiofrequency quadrupole ion trap. This trap resides within the bore of a 5T liquid helium cooled magnet. X-ray radiation from the Bessy II beamline intersects the trapped ions causing fragmentation, and parent and fragment ions are extracted into a time-of-flight mass spectrometer (TOF-MS). X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) spectroscopy are performed on the trapped ions by recording a given fragment ion yield as a function of photon energy. An X-ray photodiode (GaAsP) mounted on-axis behind the ion trap is used to record total photon flux during experiments.

A standard magnetron gas aggregation source is used for cluster production. A 2 inch circular metal target is evaporated by argon (99.9999% purity) sputtering and propagated away from the target by helium (99.9999% purity) buffer gas introduced at the target. Cluster growth occurs by gas phase collisions in a liquid nitrogen cooled aggregation region. Adjustments to helium flow, aggregation length, and pressure allow for control of the cluster size distribution,

from single atoms to clusters containing tens of thousands of atoms. This continuous source operates at around  $10^{-2}$  mbar (7.5<sup>-3</sup> torr) and produces both neutral and charged species. Cations exit the variable diameter aperture and are guided through the use of the hexapole ion guide. Neutral clusters are prevented from entering the ion guide by orienting the cluster source exit aperture off axis. After the hexapole ion guide, a home-made quadrupole mass filter (up to 2,000 amu) is used for cluster mass selection. This mass filter offers a mass resolution (m/ $\Delta$ m) of 50.

After mass selection, the ion path is bent  $90^{\circ}$  and focused into an ion trap by the use of an electrostatic lens. The entrance aperture of the trap is held at a slightly lower potential than the pulsed exit aperture potential to allow for continuous filling of the trap. The trap housing and electrodes are cooled to 4–6 K with liquid helium, and trapping is further promoted by collisions with helium buffer gas ( $10^{-4}$  to  $10^{-3}$  mbar). This results in typical ion temperatures of 10-30 K, as RF heating ensures that cluster temperature never reaches the actual trap temperature. Ion packets are then extracted in a TOF-MS by pulsing of the exit aperture potential (typically at 1 kHz). Based on the physical dimensions of the trap and typical voltages used, the cluster ion density in the trap reaches approximately 5 x  $10^{8}$ /cm<sup>-3</sup> (the space charge limit for this trap). The cluster ion packet resides along the center axis of the quadrupole ion trap, where a tunable soft xray beam is intersected with the trapped clusters. The X-ray beam is monochromatic with variable polarization. Based on the number of atoms/cluster, atomic cross section, cluster ion density, interaction length, and photon flux, approximately  $1 \ge 10^5$  daughter ions per second are produced in the experiment. As daughter ions spend some time in the trap, secondary daughter ions can also be formed. Such ions are present at up to  $10^2$  ions/second and therefore account for a maximum of 0.1% of the recorded XAS. Bunches of parent ions and product ions are extracted from the ion trap by a pulsed exit aperture potential, and are detected by a reflectron time-of-

flight mass spectrometer with a mass resolution of  $m/\Delta m = 3000$  that operates in the inhomogeneous stray field of the superconducting solenoid and therefore is mounted in-line with the ion trap for maximum transmission.

To obtain ion yield spectra as a measure of X-ray absorption, time-of-flight mass spectra are recorded for a given photon helicity  $\sigma$  with a total data acquisition time of 8–24 s per photon energy step, and spectra are normalized to the incident photon flux. The XMCD asymmetry is corrected for the elliptically polarized (circular polarization degree of 90%) soft X-ray beam.

X-ray absorption spectroscopy (XAS) involves excitation of core electrons. In this work,  $2p_{1/2}$  and  $2p_{3/2}$  electrons in cations are excited to unfilled d orbitals. An example X-ray spectrum is shown in Figure 2.4. This transition is labeled as "L", and the "edge" can be either L<sub>3</sub> or L<sub>2</sub> depending on whether the excited electron is  $2p_{1/2}$  and  $2p_{3/2}$ . These transitions are considered to be atom specific as similar transitions on different atoms are generally separated by tens to hundreds of eV. After promotion of a 2p electron into a 3d orbital, Auger decay occurs and yields a doubly charged ion. Coulomb forces within the dication lead to fragmentation, which is detected as a function of photon energy.

X-ray magnetic circular dichroism (XMCD) spectroscopy is the result of the difference of two X-ray absorption spectra. These two spectra are taken with opposite circularly polarized xrays (often referred to as positive/negative or left/right), and an example is shown in Figure 2.4. When recorded in a magnetic field, the difference of the positive and negative circularly polarized spectra result in a difference spectrum known as the XMCD (shown in Figure 2.4). Use of the XMCD sum rules<sup>11</sup> result in Equation 5:

$$m_{l}/m_{s} = (2/3)(\int L_{3}(\sigma^{+} - \sigma^{-}) + \int L_{2}(\sigma^{+} - \sigma^{-}))/(\int L_{3}(\sigma^{+} - \sigma^{-}) - \int L_{2}(\sigma^{+} - \sigma^{-}))$$
Eq. 5

Spectra taken with positive and negative circularly polarized light are denoted  $\sigma^+$  and  $\sigma^-$ . The ratio of the orbital to spin magnetic moments is proportional to the integrated area at the L<sub>3</sub> edge and L<sub>2</sub> edges divided by difference of the L<sub>3</sub> and L<sub>2</sub> areas. The measurement of the orbital to spin ratio is exact and can be used to derive magnetic moments. Such values for L and S are given by Equations 6 and 7:

$$L = (4/3)(n_h)(\int L_3 + L_2(\sigma^+ - \sigma^-))/(\int L_3 + L_2 L_3(\sigma^+ + \sigma^-))$$
 Eq. 6

$$S = (6n_h)(6 \int L_3 L_3(\sigma^+ - \sigma^-) - 4 \int L_3 + L_2(\sigma^+ - \sigma^-)) / (\int L_3 + L_2 L_3(\sigma^+ + \sigma^-))$$
Eq. 7

Here  $n_h$  represents the number of unoccupied d orbitals and the resulting values are in  $\mu_B$ /atom. This measurement at the L-edge probes the d orbitals and results in spin and orbital magnetic moments.

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Figure 2.1. Schematic view of the current LVFR configuration.



**Figure 2.2**. Schematic for home-made LDI-TOF-MS in reflectron mode. Ion beam is shown with the red dashed line, and the laser beam is shown with the dark blue line.



**Figure 2.3**. This schematic shows the instrumental apparatus for X-ray cluster spectroscopy at the UE52-PGM beamline at Bessy II. Clusters are grown with a magnetron sputter source and cation clusters are guided through a hexapole ion guide. Gas phase collisions with molecules in the hexapole creates ligand-coated metal cluster cations. These ions are then mass selected and guided into an ion trap. X-ray light intersects the trapped ion packet and daughter ions are extracted into a TOF-MS for and monitored as a function of photon energy.



**Figure 2.4**. L-edge XAS of  $Co_3^+$  is shown in the top spectrum. The middle spectrum shows spectra recorded with negative (red) elliptically polarized light and positive (blue) elliptically polarized light. The difference between the negative and positive traces represents the XMCD of the cluster and is shown in the bottom spectrum.
## CHAPTER III

# SYNTHESIS AND SPECTROSCOPY OF ULTRA-SMALL LIGAND-COATED CHROMIUM OXIDE CLUSTERS

## Introduction

Transition-metal-oxide nanoparticles have diverse properties and widespread applications in catalysis, chemical sensors, fuel cells, magnetic storage, and electronic materials.<sup>1-13</sup> Typical oxide particles in the nanometer size regime are produced in solution using precipitation, microemulsions, micelle/reverse micelle, and sol-gel techniques.<sup>14-25</sup> More conventional inorganic synthesis methods are also effective for certain species, including the broad class of polyoxometalates (POMs).<sup>26-31</sup> Although solution synthesis is more common, some nanoclusters and nanoparticles have been produced with gas phase methods.<sup>32-38</sup> Laser vaporization is a wellknown method to produce gas phase oxide clusters in the small size range,<sup>39</sup> and the properties of these systems have been investigated with both experiments and theory.<sup>40.46</sup> In recent work, we have demonstrated how the laser vaporization method can be combined with ligand addition and trapping methods to capture gas phase clusters and transfer them into solution.<sup>47-49</sup> Here we use these methods to produce small chromium oxide clusters and to investigate their properties.

Chromium oxide nanoparticles and clusters have been studied extensively in solution, on surfaces, and in the gas phase. Ligand-free clusters have been studied with infrared spectroscopy in matrices<sup>50</sup> and in the gas phase using mass spectrometry,<sup>51</sup> photodissociation,<sup>52</sup> collision induced dissociation,<sup>53</sup> and photoelectron spectroscopy.<sup>54-62</sup> Computational studies have been

applied to these systems by several groups.<sup>56,57,59,60,62,63-65</sup> Perhaps most intriguing are the strong preferences for certain specific stoichiometries in the small clusters detected in mass spectrometry. Growth and decomposition patterns repeatedly produce the  $Cr_2O_4^+$ ,  $Cr_3O_6^+$ ,  $Cr_3O_7^+$ , and  $Cr_4O_{10}^+$  ion species, and the  $CrO_3$ ,  $Cr_2O_5$  and  $Cr_4O_{10}$  species are often eliminated as neutrals in photodissociation experiments.<sup>52</sup> The  $Cr_4O_{10}$  species is especially conspicuous, as it is the most prominent species in the clusters that grow in the source and is detected repeatedly in both ion and neutral forms in dissociation processes.<sup>42,52</sup> These experiments suggest these species are more stable than other cluster sizes, and it is therefore intriguing to consider if such species might be isolated in macroscopic quantities.

Our laboratory uses a laser vaporization flowtube reactor (LVFR) to produce gas phase clusters, ligand coat them via gaseous reactions, and then to capture these species in solution.<sup>47,49</sup> Earlier studies in our group employed the LVFR to produce and capture titanium, titanium oxide, and vanadium oxide nanoclusters using ethylenediamine, tetrahydrofuran (THF), and acetonitrile (MeCN) as ligands.<sup>47,48</sup> More recent studies have shown that this same methodology can produce larger nanoparticles of silver coated with ligands rather than the usual surfactants.<sup>49</sup> Most relevant for the present work is our study of vanadium oxide clusters. In gas phase molecular beam experiments, vanadium oxide clusters exhibited a strong preference for the specific V<sub>2</sub>O<sub>4</sub><sup>+</sup>, V<sub>3</sub>O<sub>7</sub><sup>+</sup>, V<sub>4</sub>O<sub>9</sub><sup>+</sup> and V<sub>5</sub>O<sub>12</sub><sup>+</sup> cation stoichiometries.<sup>66</sup> Gas phase infrared studies indicated that these species formed cage structures.<sup>67,68</sup> LVFR studies were able to isolate corresponding ligand-coated vanadium oxide clusters.<sup>48</sup> With acetonitrile as the ligand, the same specific oxide stoichiometries seen in the gas phase were isolated as ligand-coated species in solution, whereas studies with THF as the ligand led to oxygen substitution reactions on the cluster surfaces.

coating. Another insight from these studies is that the cluster stability is apparently not strongly dependent on charge when comparing neutrals and cations. Cation clusters were identified as stable in the gas phase, but neutral ligand-coated clusters having those same stoichiometries were isolated in solution.<sup>48</sup> The present chromium oxide clusters have much in common with the previous vanadium oxide system. Strong preferences have been detected for specific stoichiometries in the gas phase work,<sup>52</sup> which may carry over into the species which can be isolated. As shown below, small chromium oxide clusters can indeed be isolated in solution, and the ligand-coating process preserves the same stoichiometries believed to be stable in the gas phase.

#### Experimental

Ligand-coated chromium oxide clusters are produced by laser vaporization in a specially designed flow reactor.<sup>47,48</sup> A high repetition rate (100–400 Hz) KrF excimer laser (248 nm; Lambda Physik Compex 102 or Coherent LPXPro 240) is focused to a 3 x 12 mm rectangle on the surface of a rotating chromium rod sample mounted at the beginning of the flowtube. The laser power is fixed for a given synthesis run, but different power levels (100–180 mJ/pulse) are used for different experiments. The rod has a continuous stream of helium buffer gas seeded with 5–10% oxygen flowing over its surface during ablation. The gas mixture at 40 psi is expanded through a 750 µm hole positioned 8 mm above the intersection of the laser with the metal rod. The ambient pressure in the flowtube was varied in the range of 2–15 Torr. Just after the vaporization point, nascent clusters pass through a 20 cm length section of flowtube designed for collisional cooling. Following this, acetonitrile vapor entrained in argon is injected to the gas flow. Ligand mixing and ligand-cluster reactions occur in another section of flowtube (20 cm

length), after which the cluster/ligand mixture is condensed in a trap at 78 K. The trap is filled with glass beads to ensure that the gas mixture interacts with many cold surfaces before the flow exits to the vacuum pump. The flask containing the icy mixture collected is back-filled with argon, disconnected from the flow system, and allowed to warm to room temperature, producing a brown solution.

The initial analysis of the collected material is done using laser desorption and electrospray ionization mass spectrometry.<sup>69</sup> For laser desorption measurements, the cluster solution is applied to a solid probe tip, dried in air, and then injected into a homemade time-offlight mass spectrometer. Laser desorption employs a pulsed Nd: YAG laser at 532 nm (New Wave Research Polaris II). To rule out cluster growth in the laser desorption process, blank mass spectra are measured for combined metal powder/ligand samples that did not pass through the reactor. Electrospray ionization studies use a commercial instrument (Mariner Biospectrometry Workstation) and a solution of pure acetonitrile or 50/50 water/acetonitrile. Optical spectroscopy measurements include UV-visible absorption (Shimzadzu UV-2600), fluorescence spectroscopy (Shimadzu RF-5301C), infrared spectroscopy (Nicolet 6700 FT-IR), and surface-enhanced Raman spectroscopy (SERS) using a Renishaw InVia Raman Microscope with specially prepared silver nanorod substrates.<sup>70</sup> HPLC experiments are also investigated (Spectra System SCM1000/P4000/UV1000 with a SUPELCOSIL LC-18 column) using a detector set at absorption wavelengths selected from the UV-visible spectra. To investigate the possible formation of larger nanoparticles, the samples here are also examined with TEM measurements (FEI Tecnai 20).

Computational studies were conducted using density functional theory (DFT) and the BP86 functional as implemented in Gaussian09.<sup>71</sup> These calculations employed the TZVP basis set. Vibrations in predicted Raman spectra are presented without scaling.

#### **Results and Discussion**

Brown solid material is evident in the collection flask after as little as 20 minutes of LVFR operation. This material consists of ligand-coated clusters, frozen excess ligand, trace nanoparticles and insoluble bulk oxides. After warming to room temperature a brown solution is observed and any insoluble bulk material is filtered out. In order to determine whether small clusters or larger particles are present, both mass spectrometry and transmission electron microscopy (TEM) are performed. Control LVFR experiments where no acetonitrile ligand is added produce only bulk insoluble material. Sample analysis (mass spectrometry, UV-visible, etc.) is the same when performed immediately after collection and at later dates (in some cases up to a year later).

Positive ion laser desorption ionization mass spectrometry (LDI-TOF-MS) is performed on the samples collected from the LVFR. Figure 3.1 exhibits a representative mass spectrum of the samples showing chromium oxide clusters with acetonitrile ligands. To carefully rule out bulk oxides or bulk stoichiometry nanoparticles, control experiments were performed with bulk oxide or nanoparticles mixed with ligand on the probe tip. Such samples do not produce mass spectra resembling those shown here. Additionally, mass spectra generated from LVFR control study samples (ligand-only or cluster-only) do not produce the observed spectra. Observed peaks correlate to clusters seen in gas phase experiments or similar stoichiometries with one or more ligands. As the metal ligand bonding is expected to be weaker than that of the metal oxygen

bonding, any fragmentation would likely result in the loss of one or more ligand molecules. We do not observe a loss of ligands with increasing laser power, suggesting that fragmentation in the desorption process is minimized. The observed stoichiometries include magic number chromium oxide cores of 4,10 and 6,14 with attached ligands. Other observed clusters are stoichiometries seen previously in gas phase experiments but were not as prominent. These clusters have stoichiometries of 1,3; 1,4; 2,4; 3,3; 3,7; 4,11; 5,13; 5,14; 5,15; 6:13 and all have between one and four coordinated ligands. This mixture of chromium oxide clusters is not unexpected, as laser desorption has been shown to produce a variety of chromium oxide stoichiometries.

Various conditions of the LVFR were optimized to maximize cluster production, with minor changes in conditions leading to more or less efficient collection of cluster material. Figure 3.2 shows mass spectra from three different samples produced with three different energies of the vaporization laser in the LVFR. The mass spectra were recorded at similar conditions (laser power, wavelength, etc.). Samples produced with a "high" laser power (160–180 mJ) preferentially produce larger clusters than samples produced at "moderate" laser powers (120–140 mJ) and larger still than samples produced at "low" laser powers (100 mJ), though all laser powers produce multiple clusters. This result is not unexpected, as higher laser powers likely lead to more metal ablation in the gas phase, yielding more collisions and growth of larger clusters.

In addition to LDI-MS, ESI-MS (Figure 3.3) was also performed to sample clusters directly from solution. The clusters observed using ESI-MS are similar to those seen with LDI-MS. Core clusters containing 4,10; 5,13; and 6,14 stoichiometries are observed, both with and without ligands. Smaller clusters (1,3; 1,4; 2,4; and 3,7) seen with LDI are not observed using ESI. In electrospray ionization, a solution is dispersed into an aerosol via a capillary with a

potential difference (generally 1-2 kV for ESI-MS shown here). Solvent evaporation from aerosol droplets leads to smaller more highly charged droplets that are eventually fragmented by Coulomb forces. In many cases, ESI favors protonated ionic species or sodium/potassium adducts over molecular ions, and the details of ion formation are still in question for ESI-MS. The ionization mechanism for LDI is discussed previously in Chapter II. Both methods are complex and have no universally agreed upon ionization mechanism. In the case of chromium oxide clusters with acetonitrile ligands, these two methods produce similar but different mass spectra. The lack of observation of small clusters in ESI-MS may be due to the higher ionization energies of these smaller clusters and a softer ionization in ESI. However, ESI produces stochiometries that on average contain fewer ligands than those detected with LDI. As protonation of these clusters is not observed in these mass spectra, observed stochiometries using ESI may be limited to clusters that undergo fragmentation and loss of one or more ligands. Such fragmentation is not generally expected for ESI-MS, but spectra shown here exhibit relatively less intense peaks that require more averaging (one to two orders of magnitude) than those in the LDI-MS.

Additionally, clusters containing 9,22 and 10,24 cores, larger than those observed in LDI-MS, are detected using ESI. Clusters larger still, ranging from 11,27 to 15,37, are evident upon additional averaging (Figure 3.4). In addition to confirming the same or similar clusters with a different ionization method, the ESI-MS instrument offers better mass resolution. Consequently, the peaks are resolved well enough to record the isotope distributions. The 14,34 cluster is presented as a representative example, and the observed isotope distribution matches perfectly to that simulated using IsoPro  $3.1^{72}$  (Figure 3.5). ESI-MS collected in negative ion mode reveal clusters of the form (CrO<sub>3</sub>)<sub>n</sub><sup>-</sup> with no observed ligands (Figure 3.6). Naked anion clusters of bulk

stoichiometry may result from fragmentation of cluster material or trace nanoparticles formed in the LFVR. Figure 3.7 shows TEM images of chromium oxide nanoparticles formed in LVFR experiments. Images were recorded for undiluted samples, and the amount of nanoparticles observed represent a small fraction of the cluster material. Clusters observed with MS are too small to be seen with this TEM instrument.

To investigate cluster geometries and electronic states we have performed computational studies on chromium oxide clusters. Previous work has been performed on small chromium oxide clusters.<sup>56,57,59,60,62,63-65</sup> Calculations here were performed to find minimum energy structures in Gaussian 09<sup>70</sup> for the 4,10; 5,12; and 6,14 clusters at the BP86/TZVP level. We find cage structures to be the lowest energy isomers with singlet, quintet, and septet spin, respectively. Total and relative energies for singlet through nonet isomers of all three cluster sizes can be found in the Tables 3.1–3.3, and Figure 3.8 shows the lowest energy cage, chain, and ring structures for the 4,10; 5,12; and 6,14 clusters with relative energies shown in kcal/mol. Optical absorption spectra from time dependent DFT (TD-DFT) and Raman spectra were also predicted and will be discussed later in combination with the appropriate experimental results. Optical absorption spectra generated from TD-DFT were broadened by 0.4 eV, and predicted Raman spectra were given a linewidth of 50 cm<sup>-1</sup>.

UV-visible spectra of  $Cr_xO_y(MeCN)_z$  clusters were recorded in acetonitrile (top of Figure 3.9). The two most intense peaks occur at 265 and 365 nm, with a weak shoulder feature at 460 nm and a broad, weak feature around 675 nm. A large amount of photoelectron spectroscopy (PES) has been performed by L. S. Wang and coworkers on naked, mass-selected gas phase chromium oxide anion clusters.<sup>56-62</sup> These studies probe the electron affinity of the anion cluster and the electronic states of mass-selected neutral clusters. Here we compare the gas phase PES

results for individual naked clusters with the observed UV-visible transitions for our distribution of acetonitrile coated clusters in solution. Stick spectra representing observed PES transitions for the 1,3; 2,4; 3,8; and 4,10 clusters are shown in the bottom of Figure 3.9, and Table 3.4 displays all observed PES transitions with those correlating to solution phase transitions shown in bold. All of the cluster sizes studied have HOMO-LUMO transitions (labeled as X to A in PES studies) at wavelengths (970 to 2,400 nm) longer than those observable in the UV-visible spectrometer (200 to 800 nm). The 4,10 neutral cluster has its second transition (X to B) at 1380 nm, while other cluster sizes have second transitions from 610 to 730 nm. Features from 610 to 730 nm most closely match the weak 675 nm feature in the UV-visible spectrum. The 610 nm PES transition is not observed in our UV-visible spectra. This lack of observation may be caused by ligand addition to clusters, which has been shown to effect the transition energies and intensities.<sup>72</sup> Additionally, the 610 nm transition may be overshadowed by other transitions. The X to C transitions in PES occur from 550 to 390 nm for all of the clusters shown in Table 4. These transitions are in good agreement with the first two features observed in the UV-visible spectrum, a weak shoulder at 460 nm and a peak centered at roughly 365 nm. Higher energy transitions (including those that would correlate to the 265 nm peak seen in UV-visible spectra) are not observed in the PES work due to limitations imposed by the photon energy used. Considering the width observed in many of the PES spectra and the distribution of cluster sizes, the observed absorption in solution displays unsurprising broadness in observed peaks. Additionally, TD-DFT optical absorption spectra of 4,10; 5,12; and 6,14 match well with the observed UV-visible spectra (Figure 3.10). All three predicted spectra exhibit two strong peaks between 240 and 355 nm, and the 5,12 cluster exhibits a weaker features around 420 nm. Lower energy transitions at 515, 570, and 695 nm are also observed, and the average of these spectra

result in one broad, weak feature at 555 nm. This difference represents 0.4 eV, which is likely due to error from TD-DFT calculations and changes caused by ligand interactions.

Excitation with 355 nm produces a broad fluorescence (bottom of Figure 3.11), ranging from 370 to 520 nm, and centered at 445 nm. The 355 nm excitation falls directly on the first peak in the UV-visible absorption, which itself is relatively broad from approximately 330 to 400 nm. The broad fluorescence does have two sharp features on the high energy side at 400 and 420 nm in addition to a shoulder at 470 nm. These features may correlate to strong emission from a specific cluster size. Such a broad emission is not unexpected for a sample containing a mixture of many cluster sizes. This emission is expected to occur from excitation of the metal-oxide core, as seen previously in ligand-coated vanadium oxide clusters.<sup>47</sup>

As separation of these clusters would be ideal for studying properties of individual clusters instead of mixtures, HPLC was performed on the microliter scale as a proof of principle (Figure 3.12). Detecting at 259 nm, which falls on the higher energy peak, at least six different clusters were separated from each other using HPLC, though none were baseline resolved. This is consistent with multiple ligand-coated clusters existing in solution. The total retention time of the clusters in the column was between 1 ½ and 3 minutes. Future efforts to better separate and isolate these clusters will hopefully provide pure samples which can allow x-ray crystallography studies, providing improved structural information.

SERS of  $Cr_xO_y(MeCN)_z$  samples performed on silver nanorods (Figure 3.13) exhibits a number of broad peaks between 200 and 1,000 cm<sup>-1</sup>. The width of these peaks may be due to contributions from a number of different clusters or low lying isomers (Tables 3.1–3.3). The observed peaks at 360, 570, 800, and 900 cm<sup>-1</sup> correspond to terminal metal-oxide bending modes, symmetric Cr-O-Cr modes, asymmetric Cr-O-Cr modes, and terminal metal-oxide

stretching modes, respectively. Predicted Raman spectra of any one individual bare cluster do not fully explain the observed SERS spectra. However, the predicted Raman spectra for the lowest energy isomers of the 4,10; 5,12; and 6,14 clusters exhibit peaks that begin to reproduce the observed spectra (Figure 3.13). Figures 3.14, 3.15, and 3.16 show cage, chain, and ring structures for all three of these clusters compared to SERS. The predicted spectra are for uncoated clusters only, and it has been shown that ligand interactions can induce large structural changes to metal-oxide clusters.<sup>73</sup> None of the predicted spectra for higher energy structures match the observed SERS spectrum better than those predicted for the lowest energy structures, and it is likely that the acetonitrile ligands do not drastically change the metal-oxide core structure. The least well reproduced feature is the external M-O stretch that occurs around 1050 cm<sup>-1</sup>. The intensity of this feature should decrease drastically for larger cluster sizes, as external oxygen atoms become a relatively small fraction of the total oxygen atoms in the cluster. Additionally, this stretching mode should be most perturbed by ligand coating. A small peak observed in this region is likely due to both perturbation of this terminal oxide stretch and the presence of larger clusters containing nine to 15 metal atoms, (as observed in the ESI-MS). The amplification of intensity that occurs in SERS can also enhance different modes preferentially,<sup>74-</sup> <sup>76</sup> although it is difficult to predict which modes will be most affected. The methyl rocking motion of acetonitrile also occurs in this region above 1,000 cm<sup>-1</sup>. Although this mode is expected to be IR active and Raman inactive, both cluster-ligand interaction and SERS effects can turn on such modes. Weak methyl deformation modes around 1400 cm<sup>-1</sup> are observed in SERS, and higher energy acetonitrile stretches correlating to the C-N stretch and symmetric and asymmetric C-H stretches were observed at 2,390, 2,870, and 2,930 cm<sup>-1</sup> (Figure 3.17), confirming the presence of ligand coating. The peak observed around 1,600 cm<sup>-1</sup> does not match

any expected metal-oxide or acetonitrile modes for Raman or IR and is attributed to a combination of lower energy modes. Control experiments of pure acetonitrile on SERS substrates produced no spectra, as the acetonitrile quickly evaporates from the surface. Predicted spectra for bulk oxide stoichiometry clusters were generated using previously determined structures<sup>59</sup> These clusters of the form  $(CrO_3)_n^-$  (n=1–5) have ring structures (Figure 3.18) that do not match the observed SERS spectra, further suggesting that the  $(CrO_3)_n^-$  stochiometries observed in negative mode ESI-MS are not characteristic of clusters in solution and stem from cluster or particle fragmentation.

Ligand-coated chromium oxide clusters were also produced in the LVFR using a 10 Hz Nd:YAG laser at 532 nm. As expected, the 10 Hz ablation laser produces much less cluster material (by at least an order of magnitude). Figure 3.19 shows SERS of these samples, which match almost perfectly with the samples synthesized using the high repetition rate 248 nm excimer laser. LDI-MS of samples produced with 532 nm are also consistent with those produced using 248 nm.

## Conclusions

Chromium oxide clusters have been produced and ligand-coated with acetonitrile using the LVFR. The combination of spectrometry and spectroscopy in conjunction with theoretical methods confirms the presence of these clusters in solution. Observed cluster stochiometries are reminiscent of those seen in previous gas phase. Acetonitrile ligand coating produces minimal changes to both the electronic transitions and the metal-oxide core structure. Broad emission spectra are similar to those seen in similar ligand-coated vanadium oxide clusters. The use of HPLC to separate clusters provides the possibility for future work in which a single cluster can be isolated in solution.

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**Figure 3.1**. Positive ion LDI-TOF-MS of  $Cr_xO_y(MeCN)_z$  performed with 532 nm desorption laser. Observed clusters are identical or similar to those seen in previous gas phase work. All clusters are seen with one to four acetonitrile ligands.



**Figure 3.2**. Positive ion LDI-TOF-MS of  $Cr_xO_y(MeCN)_z$  cluster samples synthesized with different LVFR laser vaporization energies. Observed clusters show a preference for larger clusters with increasing pulse energy.



**Figure 3.3**. Positive ion ESI-TOF-MS of  $Cr_xO_y(MeCN)_z$ . Observed clusters are similar to those seen in the LDI-MS. Larger clusters with 9,22 and 10,24 cores are also seen here. Peaks labeled with an \* contain no chromium atoms based on isotope patterns.



**Figure 3.4**. Higher mass range positive ion ESI-TOF-MS of  $Cr_xO_y(MeCN)_z$ . Larger clusters ranging from 11,27 to 15,34 cores are evident with increased averaging when compared to Figure 3.3.



**Figure 3.5**. Positive ion ESI-TOF-MS of (top) and the simulated isotope distribution using IsoPro (bottom) for the 14,34,0 cluster.



**Figure 3.6**. Negative ion ESI-TOF-MS of  $Cr_xO_y(MeCN)_z$ . Clusters of the form  $(Cr_xO_y)_n^-$  are observed with no ligands.



**Figure 3.7**. TEM images of  $Cr_xO_y(MeCN)_z$  clusters show trace amounts of nanoparticles. The scale scale bar shown in the bottom left represents 100 nm in length.

**Table 3.1**.  $Cr_4O_{10}$  total energy in hartrees and relative energies in kcal/mol at the BP86/TZVP level for singlet through nonet spin states. Energies are corrected for zero-point vibrational energy. Lowest energy isomer in bold.

	2S+1	Total Energy (Hartrees)	Relative Energy (kcal/mol)	
Cage	1	-4931.654504	0.0	
Cage	3	-4931.629479	+15.7	
Cage	5	-4931.609859	+28.0	
Cage	7	-4931.521021	+83.8	
Cage	9	-4931.423664	+144.9	
Chain	1	-4931.531662	+77.1	
Chain	3	-4931.540301	+71.7	
Chain	5	-4931.550616	+65.2	
Chain	7	-4931.486949	+105.1	
Chain	9	-4931.413393	+151.3	
Ring	1	-4931.585735	+43.2	
Ring	3	-4931.590885	+39.9	
Ring	5	-4931.589213	+41.0	
Ring	7	-4931.512172	+89.3	
Ring	9	-4931.425027	+144.0	

**Table 3.2**.  $Cr_5O_{12}$  total energy in hartrees and relative energies in kcal/mol at the BP86/TZVP level for singlet through nonet spin states. Energies are corrected for zero-point vibrational energy. Lowest energy isomer in bold.

	2S+1	Total Energy (Hartrees)	Relative Energy (kcal/mol)	
Cage	1	-6126 864405	+13.9	
Cage	3	-6126.878252	+5.2	
Cage	5	-6126.886551	0.0	
Cage	7	-6126.872734	+8.7	
Cage	9	-6126.797364	+56.0	
Chain	1	-6126.792688	+58.9	
Chain	3	-6126.816908	+43.7	
Chain	5	-6126.816410	+44.0	
Chain	7	-6126.815189	+44.8	
Chain	9	-6126.741993	+90.7	
Ring	1	-6126.748095	+86.9	
Ring	3	-6126.784646	+63.9	
Ring	5	-6126.776335	+69.2	
Ring	7	-6126.786251	+62.9	
Ring	9	-6126.710890	+110.2	

**Table 3.3**.  $Cr_6O_{14}$  total energy in hartrees and relative energies in kcal/mol at the BP86/TZVP level for singlet through nonet spin states. Energies are corrected for zero-point vibrational energy. Lowest energy isomer in bold. The nonet cage A and singlet ring structures did not converge.

	2S+1	Total Energy (Hartrees)	Relative Energy (kcal/mol)	
<u> </u>	1	7201 010770	204.4	
Cage A	1	-/321.818//3	+204.4	
Cage A	3	-7321.871949	+171.0	
Cage A	5	-7321.863033	+176.6	
Cage A	7	-7321.872455	+170.7	
Cage A*	9	-	-	
Cage B	1	-7322.138674	+3.6	
Cage B	3	-7322.086302	+36.5	
Cage B	5	-7322.103807	+25.5	
Cage B	7	-7322.144483	0.0	
Cage B	9	-7322.138570	+3.7	
Chain	1	-7322.043611	+63.3	
Chain	3	-7322.081048	+39.8	
Chain	5	-7322.078728	+41.3	
Chain	7	-7322.084378	+37.7	
Chain	9	-7322.088749	+35.0	
Ring	1	-	-	
Ring	3	-7322.027942	+73.1	
Ring	5	-7322.036683	+67.6	
Ring	7	-7322.028170	+73.0	
Ring	9	-7322.033365	+69.7	



**Figure 3.8**. The lowest energy cage, chain, and ring isomers are shown for 4,10; 5,12; and 6,14 cluster sizes at the BP86/TZVP level. Relative energies are shown in kcal/mol. The two cage structures shown for the 6,14 cluster are Cage A (+170.7) and Cage B (+0.0).



**Figure 3.9**. The UV-visible spectra of  $Cr_xO_y(MeCN)_z$  exhibits absorption throughout visible and UV wavelengths. Stick spectra for 1,3 (red), 2,4 (blue), 3,8 (green), and 4,10 (purple) shown at the bottom indicat observed transitions from PES work by Wang and coworkers (c.f. Table 3.4).

Cluster	$X \rightarrow A$ (eV/nm)	$\begin{array}{l} X \rightarrow B \\ (eV/nm) \end{array}$	$\begin{array}{l} X \rightarrow C \\ (eV/nm) \end{array}$	$\begin{array}{l} X \rightarrow D \\ (eV/nm) \end{array}$
1,3 2,4 3,8	0.95/ 1300 1.28/ 970 0.51/ 2400	<b>1.75/ 710</b> <b>1.86/ 670</b> 2.03/ 610	2.95/ 420 2.78/ 450 2.26-2.76/ 550-450	3.44/ 360 3.25/ 380
4,10	0.68/1800	0.96/1300	3.14/ 390	

**Table 3.4**. Observed transitions of neutral chromium oxide clusters from PES. Transitions in bold are those correlating to observed peaks in solution phase UV-visible of  $Cr_xO_y(MeCN)_z$ .


**Figure 3.10**. UV-visible spectra of  $Cr_xO_y(MeCN)_z$  (top; black) are shown in comparison with TD-DFT predicted transitions for the 4,10; 5,12; and 6,14 lowest energy cage structures at the BP86/TZVP level (red). The average of these three predicted spectra is shown at the bottom (blue).



**Figure 3.11**. UV-visible spectra of  $Cr_xO_y(MeCN)_z$  (top) and fluorescence spectra excited with 355 nm (bottom).



Figure 3.12. HPLC of  $Cr_xO_y(MeCN)_z$  with 259 nm detection.



**Figure 3.13**. SERS of  $Cr_xO_y(MeCN)_z$  (top trace in black) exhibits a number of metal-oxygen modes from approximately 250 to 1,000 cm<sup>-1</sup>. Individual Raman spectra predicted for the lowest energy isomers of the 4,10; 5,12; and 6,14 clusters are shown in the middle three traces (red). The average predicted Raman spectrum of these three clusters is shown in the bottom trace (blue). All structures and spectra are calculated at the BP86/TZVP level.



**Figure 3.14**. SERS of  $Cr_xO_y(MeCN)_z$  (top trace in black) exhibits a number of metal-oxygen modes from approximately 250 to 1,000 cm<sup>-1</sup>. Individual Raman spectra predicted for the lowest energy isomers of the 4,10 cage, chain, and ring clusters are shown in the middle three traces (red). All structures and spectra are calculated at the BP86/TZVP level.



**Figure 3.15**. SERS of  $Cr_xO_y(MeCN)_z$  (top trace in black) exhibits a number of metal-oxygen modes from approximately 250 to 1,000 cm<sup>-1</sup>. Individual Raman spectra predicted for the lowest energy isomers of the 5,12 cage, chain, and ring clusters are shown in the middle three traces (red). All structures and spectra are calculated at the BP86/TZVP level.



**Figure 3.16**. SERS of  $Cr_xO_y(MeCN)_z$  (top trace in black) exhibits a number of metal-oxygen modes from approximately 250 to 1,000 cm<sup>-1</sup>. Individual Raman spectra predicted for the lowest energy isomers of the 6,14 cage, chain, and ring clusters are shown in the middle three traces (red). All structures and spectra are calculated at the BP86/TZVP level.



Figure 3.17. Full range SERS of  $Cr_xO_y(MeCN)_z$  exhibiting both lower energy metal-oxygen mode and higher energy acetonitrile modes.



**Figure 3.18**. SERS of  $Cr_xO_y(MeCN)_z$  (top trace in black) compared to predicted Raman spectra for  $(Cr_xO_y)_n^-$  (n = 1–5) clusters. Theoretical spectra are predicted at the BP86/TZVP level.



**Figure 3.19**. SERS of  $Cr_xO_y(MeCN)_z$  produced with a 400 Hz, 248 nm excimer vaporization laser (top) and with a 10 Hz, 532 nm, Nd:YAG (bottom) vaporization laser exhibit the same main features.

# CHAPTER IV

#### PRODUCTION AND ISOLATION OF LIGAND-COATED ALUMINUM CLUSTERS

# Introduction

Aluminum nanoparticles are interesting for a number of applications including propulsion, explosives, and catalytic hydrogen evolution.<sup>1-6</sup> Smaller aluminum clusters have been studied in the gas phase,<sup>7-26</sup> and these reactivity and spectroscopic studies have been compared to computational chemistry.<sup>27-34</sup> Aluminum cluster based materials are proposed to form new three-dimensional periodic table elements.<sup>35-40</sup> Larger aluminum nanoparticles are synthesized with more traditional wet chemical methods,<sup>41-45</sup> but these methods have not yet been extended to clusters in the sub-nanometer size range. Small ligand-coated metal-oxide clusters have been synthesized with gas phase laser vaporization and captured in solution using the LVFR apparatus.<sup>46,47</sup> Here we apply these methods to capture ligand-coated aluminum clusters in solution.

Early work on small aluminum clusters included reactions, collision induced dissociation and photodissociation.<sup>8-19</sup> Size dependent melting for aluminum clusters has been reported by Jarrold.<sup>20</sup> Photoionization and photoelectron spectroscopy (PES) provided insight into ionization energies, electron affinities, electronic states, and vibrational frequencies.<sup>21-26</sup> In conjunction with these studies, several groups have performed computational studies.<sup>27-34</sup> More recently, aluminum clusters have been proposed for cluster based materials. Specifically, the Al<sub>13</sub><sup>-</sup> cluster is of unique interest as it is produced in greater abundance than other competing clusters<sup>35-40</sup> and

is relatively inert with regards to oxidation.<sup>14-18</sup> The high abundance and stability of this cluster are attributed to a 40 valence electron shell closing described by the jellium model.<sup>48</sup> The  $Al_{13}^{-}$ cluster is considered to be a part of the superatom class that has been proposed to be a stable building block for the previously mentioned cluster assembled materials.<sup>35-40</sup> While this has been observed in gas phase experiments,<sup>40</sup> such clusters have not been produced in macroscopic quantities. Work by Schnöckel and coworkers lead to the synthesis of ligand-coated aluminum clusters through the use of a heated oven source and condensation apparatus.<sup>43-44</sup> In this work, heated aluminum with temperatures around 1,000°C is reacted with halides and ultimately condensed with ligands such as N(SiMe<sub>3</sub>)<sub>2</sub>. This process produces a variety of clusters ranging from those containing a few aluminum atoms to those with >50 atoms.

As cluster properties can change drastically with size and environment, the subnanometer regime of aluminum clusters merits investigation. Propulsion and explosion applications of aluminum nanoparticles depend heavily on a high surface area to volume ratio. As clusters have a higher surface area to volume ratio than nanoparticles, the use of aluminum clusters in these areas could provide major progress. For clusters in this size range (generally < 50 atoms), new and interesting properties are often unique to each individual cluster. In order to apply these properties to solve modern problems, such clusters must be produced in macroscopic quantities. Here we produce aluminum clusters through gas phase laser vaporization followed by ligand coating with acetonitrile and collection in solution.

#### Experimental

Ligand-coated aluminum and aluminum oxide clusters are produced by laser vaporization<sup>7,49</sup> in a specially designed fast flowtube reactor described previously.<sup>46,47</sup> An

aluminun metal rod mounted with a continuous flow of argon or helium buffer gas over its surface is ablated with a high repetition rate (100 Hz) KrF excimer laser (248 nm; Lambda Physik Compex 102) with high energy pulses (200–260 mJ). The pressure in the flowtube is about 10 torr. No oxygen is added to the gas flow, and steps are taken to prevent the formation of oxide clusters. Prior to use, the aluminum rod is polished to remove the outer layer of oxides. Prior to cluster collection, the aluminum rod is treated with laser vaporization in the presence of flowing buffer gas for 30 minutes serves to remove surface oxides and to purge trace oxygen from the LVFR. Just after the vaporization point, nascent clusters pass through a section of flowtube (20 cm length) designed for collisional cooling; immediately after this acetonitrile vapor is injected to the gas flow. After another section of flowtube (20 cm length) to allow for ligand mixing and reaction with metal clusters, the cluster/ligand mixture is condensed in a trap at 78 K. The flask containing the icy mixture collected is disconnected from the flow system and allowed to warm to room temperature, producing a clear colorless solution.

For mass spectrometry analysis, the cluster solution is applied to a solid probe tip of a specially designed laser desorption time-of-flight mass spectrometer.<sup>50</sup> Laser desorption time of flight (LDI-TOF) mass spectra are collected under a variety of conditions and desorption laser wavelengths (Nd:YAG laser at 532 and 355 nm). To rule out cluster growth in the laser desorption process, blank mass spectra are measured for metal and ligand combined samples that did pass through the reactor. The cluster solution is studied with UV-visible absorption spectrometry (Shimadzu UV-2600), fluorecence spectroscopy (Shimadzu RF-5301C), and surface-enhanced Raman spectroscopy (SERS) using specially prepared silver nanocluster substrates.<sup>51,52</sup>

Computational studies were conducted using density functional theory (DFT) and the B3LYP functional as implemented in Gaussian03.<sup>53</sup> These calculations employed the TZVP basis set.<sup>54</sup> Vibrations in predicted Raman spectra are presented without scaling.

#### **Results and Discussion**

LVFR production of acetonitrile coated aluminum clusters (Al/MeCN) results in a small amount of grey frozen material. After warming this material to room temperature, a light grey solution is obtained (Figure 4.1). Some amount of insoluble material is present, and filtering removes a white film. Subsequent analysis shows this to be bulk aluminum oxide, Al<sub>2</sub>O<sub>3</sub>. Attempted cluster production with no ligand present results entirely in Al<sub>2</sub>O<sub>3</sub> production and no material that is soluble in acetonitrile. Synthesis of Al/MeCN is less efficient than other ligandcoated clusters produced with the LVFR, yielding less than 0.1 mg/hour.

To rule out cluster formation due to laser vaporization within the mass spectrometer, control experiments were performed to measure the mass spectra of Al<sub>2</sub>O<sub>3</sub> suspended in MeCN. Figure 4.2 shows an LDI-TOF mass spectrum (532 nm desorption laser) which contains mass peaks such as Al<sub>2</sub>O<sub>3</sub><sup>+</sup> and Al<sub>5</sub>O<sub>6</sub><sup>+</sup>. All of the observed clusters are heavily oxidized and there is no evidence of ligand coating. Interestingly, a mass spectrum of pure aluminum metal suspended in MeCN displays the same mass spectrum as that of Al<sub>2</sub>O<sub>3</sub> in MeCN, as the aluminum metal oxidizes rapidly. On the other hand, mass spectra of Al/MeCN samples produced by the LVFR reveal a number of cluster stoichiometries seen in Figure 4.3. Observed clusters are of the form Al<sub>x</sub>O<sub>y</sub>(MeCN)<sub>z</sub><sup>+</sup> (denoted as x,y,z) and include both pure aluminum and aluminum oxide clusters. The most intense peak at m/z=81 is assigned to the aluminum trimer cation, 3,0,0. Peaks observed at m/z=122 and 163 correspond to 3,0,1 and 3,0,2, respectively. In addition to the pure

aluminum trimer, a number of aluminum oxide species are detected. The presence of aluminum oxides is unsurprising due to the highly exothermic formation of Al<sub>2</sub>O<sub>3</sub>. The most prevalent aluminum oxide cluster is 2,3,1 though other small oxides are also observed.

Figure 4.4 displays the mass spectrum of larger aluminum clusters (m/z 200 to 1,200) from an Al/MeCN sample. The first prevalent peak observed in this mass spectrum is still the 3,0,2 cluster seen in Figure 4.3. Higher mass peaks at m/z = 393, 542, 676, and 1180 are consistently observed in the mass spectra. However, the resolution of the LDI-TOF-MS currently prohibits unequivocal assignment of the mass spectra. The resolution of the larger m/z peaks often leads to an uncertainty of +/-2 amu. The assignment of m/z = 393 produces 23 different possible assignments from the combination of aluminum, oxygen, and acetonitrile. Some possible assignments are very unlikely, such as 1,23,0 or 3,17,1. Unfortunately, even with elimination of unreasonable stochiometries, a number of possible assignments remain. Shown in Figure 4.4 are some possible assignments that represent either pure aluminum clusters or clusters with minimal oxidation and an appropriate number of acetonitrile ligands. Pure metal clusters have been shown to follow the jellium model for electron counting, and such an approach can be applied here. Table 4.1 shows some possible assignments with electron counts. No electron counts for these peaks correlate exactly jellium model electronic shell closings. However, some assignments are close, and acetonitrile ligands could donate electrons to provide a shell closing. Higher resolution mass spectra (available with the electrospray ionization time-of-flight mass spectrometer used in Chapter III) are still needed for definitive assignments. Though the ambiguity of the larger cluster assignments is unfortunate, the ligand-coated capture of small aluminum clusters in solution (particularly that of the aluminum trimer) is clear. This result is

somewhat unexpected, as small aluminum clusters have been shown to be highly reactive,<sup>11</sup> and this cluster passivation is almost certainly due to the ligand coating.

Before discussing the SERS spectra, the theoretical work on aluminum and aluminum oxide clusters should be addressed. Other groups have theoretically investigated such clusters,<sup>27-34</sup> and our results for the 3,0,0 and 2,3,0 cluster are consistent with those previously determined. The aluminum trimer is an equilateral triangle ( $D_{3h}$ ) with a doublet ground state. The main aluminum oxide cluster (2,3,0) forms a "kite" structure with a triplet ground state. Calculations with acetonitrile ligands were carried out by Jon Maner, and the results can be found in Appendix A. Figure 4.5 shows the lowest energy isomer for the two ligand-coated clusters. It is to these ligand-coated clusters that SERS spectra are compared in the next paragraph.

Al/MeCN SERS spectra up to 2,000 cm<sup>-1</sup> taken at "lower" and "higher" laser power (black traces in Figure 4.6) show evidence for the aluminum trimer clusters and the bulk stoichiometry Al<sub>2</sub>O<sub>3</sub> clusters. Spectra recorded with higher laser power produce better signal to noise than those recorded with lower laser power, and higher power spectra also reveal additional peaks. The theoretical spectra for the 3,0,3 (blue) and 2,3,2 (red) clusters are shown below the SERS spectra. While the aluminum trimer is readily evident we do not actually observe the 3,0,3 cluster in mass spectra. However, the capture of aluminum trimer in solution and detection with MS suggest significant passivation from acetonitrile ligands. This is most likely in a fully ligated (3,0,3) cluster, and computed ligand binding energies show that the third acetonitrile binds more strongly than the first or second (7.5, 4.4, and 8.1 kcal/mol, respectively). Comparison of the lower power SERS spectrum to the predicted 3,0,3 spectrum shows a decent match. Expected transition at 370, 940, 1035, and 1400 cm<sup>-1</sup> have correlating observed transitions at 380, 960, 1005, and 1395 cm<sup>-1</sup>. These transitions are assigned to the rocking motion

of the aluminum trimer and acetonitrile ligands, the symmetric/asymmetric C-C stretch, the CH<sub>3</sub> wag, and the CH<sub>3</sub> umbrella motion. Actual aluminum-aluminum modes are too low to be measured with this SERS setup, and these assignments do not rule out the presence of oxide clusters. The observed 610 cm<sup>-1</sup> transition in the lower power SERS spectrum can be assigned to the 2,3,2 cluster, which is predicted to have a symmetric aluminum oxide stretch at 595 cm<sup>-1</sup>. Comparison of the higher power SERS spectrum to that of the 3,0,3 cluster further shows that the 3,0,3 cluster cannot fully explain the SERS spectrum. This is not surprising, as Al/MeCN samples are expected to contain a mixture of clusters, and the previously discussed mass spectra show exactly this. The appearance of a peak at 855 cm<sup>-1</sup> matches well with the predicted aluminum-oxygen stretch predicted at 870 cm<sup>-1</sup>. Other peaks in this region, such as that at 715 cm<sup>-1</sup>, are likely due to other aluminum-oxide stretches.

The full SERS spectra (Figure 4.7; 300–3,200 cm<sup>-1</sup>) show higher energy acetonitrile vibrations assigned to the symmetric/asymmetric C-N stretch (2255 and 2275 cm<sup>-1</sup>) and the symmetric/asymmetric CH<sub>3</sub> stretch (2870 and 2928 cm-1) in the higher power SERS. These higher energy vibrations match well with those predicted for the 3,0,3 cluster. Unlike other observed acetonitrile vibrations, the predicted frequencies for the 3,0,3 and 2,3,2 C-N stretches differ by over 150 cm<sup>-1</sup>. This difference is attributed to the dissimilarity in binding energies of acetonitrile for pure aluminum (7.5, 4.4, and 8.1 kcal/mol for acetonitrile ligands to Al<sub>3</sub>) compared to those of aluminum oxide clusters (21.9 and 16.3 kcal/mol for acetonitrile ligands to Al<sub>2</sub>O<sub>3</sub>). Because of this clear difference in predicted frequencies, we are able to assign these acetonitrile vibrations to the 3,0,3 cluster and not the 2,3,2 species. The discrepancy between the expected and observed transitions is generally less than 30 cm<sup>-1</sup> and can be accounted for by the expected error of DFT calculations (up to 30 cm<sup>-1</sup> even in lower frequency modes) and possible

SERS shifts (up to 10 cm<sup>-1</sup>).<sup>55</sup> The observed spectra are not fully explained by these two clusters, and the combination of small oxides and larger unassigned clusters are most likely responsible for the additional SERS features. However, it is clear that the Al/MeCN samples contain both pure aluminum clusters with acetonitrile ligands and some smaller amount of aluminum oxide clusters.

The UV-visible absorption and fluorescence emission spectra for Al/MeCN are shown in Figure 4.8. The absorption spectrum is shown in blue (top), and four fluorescence spectra with excitation wavelengths of 288 nm (purple), 302 nm (cyan), 323 (blue) and 338 nm (red) are shown below the absorption trace. The UV-visible absorption spectrum shows sharp intense features at 302 and 338 nm, and the fluorescence spectra exhibit the same emission pattern for all four excitation wavelengths. All of these spectra exhibit a few peaks with narrower peak widths than those previously observed for LVFR cluster samples. However, both mass spectrometry and SERS have shown the Al/MeCN sample is comprised of multiple different clusters. To reconcile this, it is suggested that the unique absorption and fluorescence patterns are characteristic of predominantly one or two clusters, with the two most likely candidates being ligand-coated aluminum trimer and  $Al_2O_3$ . The fluorescence spectra are identical with different excitation wavelengths corresponding to the observed UV-visible transitions, meaning that the spectra should be attributed to one specific cluster. Initial theoretical attempts with TD-DFT did not reproduce the observed UV-visible spectrum, and these results are also inconsistent with previous aluminum trimer spectra obtained by Morse and coworkers.<sup>21</sup> TD-DFT work is ongoing to determine which cluster is responsible for this unique spectrum.

In Figure 4.9 we show the UV-visible and fluorescence spectra from Figure 4.8 plotted in wavenumbers. Shown in this manner, the vibrational structure is readily evident. Resolved

vibrational spacings are approximately 950 and 1,370 cm<sup>-1</sup>, which are expected MeCN vibrations (the C-C stretch and CH<sub>3</sub> umbrella, respectively) for the Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub> clusters. We also see a spacing of 3,610 cm<sup>-1</sup>, which is assigned to a combination band, as a number of combinations of lower modes could combine to produce this frequency. Identical fluorescence spectra with different excitation wavelengths and vibrational progressions correlating to acetonitrile vibrations further suggest that these spectra are the result of one aluminum cluster with acetonitrile ligands.

# Conclusions

Ligand-coated aluminum and aluminum oxide clusters on the sub-nanometer scale have been produced and captured in solution using the LVFR apparatus. Ligand coating of acetonitrile renders the aluminum trimer stable in solution. Both mass spectrometry and SERS show evidence for the ligand-coated aluminum trimer and the presence of aluminum oxide clusters. Unique UV-visible and fluorescence spectra are tentatively assigned to the ligand-coated aluminum trimer, as it is the most abundant cluster collected in this experiment. Though the presence of oxides is undesired, these results show that the ligand-coated capture of reactive clusters is possible with this technique.

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Figure 4.1. Photograph of Al/MeCN sample in acetonitrile.



**Figure 4.2**. The positive ion LDI-TOF-MS (532 nm desorption laser) of bulk aluminum oxide powder ( $Al_2O_3$ ) suspended in MeCN solution shows only aluminum oxide clusters with no acetonitrile.



**Figure 4.3**. Positive ion LDI-TOF-MS of Al/MeCN sample. Aluminum trimer is observed with up to two ligands. Al<sub>2</sub>O<sub>3</sub> with one acetonitrile ligand is also observed. Other small, partially oxidized aluminum clusters with up to two ligands are detected in lesser amounts.



**Figure 4.4**. Positive ion LDI-TOF-MS of the Al/MeCN sample in the higher mass range. The aluminum trimer is again observed with two ligands. Larger mass clusters are observed for m/z of 393, 542, 676, and 1180; however, the stochiometries of these clusters are not able to be confidently assigned due to both mass coincidences and mass resolution.

electrons.			
m/z	Assignment	Electron Count	
	(x,y,z)	(Al/Al+MeCN)	
163	3,0,2	9/13	
202	10.0.1	20/41	
392	13,0,1	39/41	
393	10,0,3	30/39	
394	7,0,5	21/31	
540	20.0.0		
540	20,0,0	60/60	
541	17,0,2	51/55	
542	14,0,4	42/50	
543	11,0,6	33/45	
544	8,0,8	24/40	
675	25,0,0	75/75	
676	22,0,2	66/70	
677	19,0,4	57/65	
678	16,0,6	48//60	
679	13,0,8	39/55	
1178	33,0,7	99/113	
1179	30,0,9	90/108	
1180	27,0,11	81/103	
1181	24,0,13	72/98	
1182	21,0,15	63/93	

**Table 4.1**. Possible assignments for larger  $Al_xO_y(MeCN)_z$  clusters. Electrons are counted for the pure aluminum core and for the aluminum core with donation of two electrons per acetonitrile ligand. Jellium model shows enhanced stability for cluster sizes with 8, 20, 40, 58, and 92 electrons.



**Figure 4.5**. Lowest energy isomers of the 3,0,3 and 2,3,2 clusters at the B3LYP/TZVP level of theory.



**Figure 4.6**. The top two traces (black) show SERS of Al/MeCN at "lower" and "higher" Raman laser powers up to 2,000 cm<sup>-1</sup>. Spectra collected with higher laser powers exhibit better signal to noise and more peaks than can be explained by one cluster size. Theoretical spectra for  $Al_3(MeCN)_3$  and  $Al_2O_3(MeCN)_2$  are shown in blue and red, respectively.



**Figure 4.7**. The top two traces (black) show SERS of Al/MeCN at "lower" and "higher" Raman laser powers. Spectra collected with higher laser powers exhibit better signal to noise and more peaks than can be explained by one cluster size. Theoretical spectra for Al<sub>3</sub>(MeCN)<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>(MeCN)<sub>2</sub> are shown in blue and red, respectively.



**Figure 4.8**. The UV-visible absorption spectra for Al/MeCN sample is shown in blue (top). Three fluorescence spectra with excitation wavelengths of 288 nm (purple), 302 nm (cyan), 323 nm (blue) and 338 nm (red) are below the absorption trace. The fluorescence spectra exhibit the same emission pattern for all four excitation wavelengths.



**Figure 4.9**. Al/MeCN absorption (top, blue) and fluorescence (bottom, red) from Figure 4.4 are shown here in cm<sup>-1</sup>. The vibrational spacings in both spectra correlated to vibrational modes observed in the SERS spectra (Figure 4.3).

# CHAPTER V

# SIZE-DEPENDENT LIGAND QUENCHING OF FERROMAGNETISM IN CO<sub>3</sub>(BENZENE)<sub>n</sub><sup>+</sup> CLUSTERS STUDIED WITH XMCD SPECTROSCOPY

### Introduction

The magnetism of transition metal clusters and nanoparticles has significant potential applications in areas such as magnetic storage or spintronics.<sup>1-2</sup> Measurements of cluster magnetic properties have been conducted on isolated clusters in the gas phase<sup>3-13</sup> and for clusters supported on surfaces.<sup>14-18</sup> The seminal work on magnetic moments of neutral metal clusters employed Stern-Gerlach deflection experiments in molecular beams.<sup>3-13</sup> Unfortunately, these experiments suffer from limited angular resolution and difficulties cooling the small metal clusters into their lowest states. However, recent work has applied X-ray magnetic circular dichroism (XMCD) spectroscopy to trapped and cooled gas phase metal cluster *ions*.<sup>19-26</sup> Unlike Stern-Gerlach experiments on neutrals, this approach yields magnetic moments that can be separated into spin and orbital components.<sup>27,28</sup> In the present study, we extend these new measurements to study the effects of benzene ligand coating on cobalt cluster ions.

The magnetic moments of small clusters or nanoparticles may be enhanced significantly compared to that observed for the same material in the bulk.<sup>1</sup> Per-atom spin moments for clusters may be 50% higher than bulk moments, while their orbital moments may be an order of magnitude greater.<sup>1,19,20,22,29-31</sup> Electron delocalization and crystal-field effects are responsible for the lower bulk magnetic moments. Small transition metal atom clusters in the gas phase are
superparamagnetic and may have both spin and orbital contributions to their magnetism.<sup>3-13,26</sup> Significant orbital angular momentum is possible because the atoms in such clusters are mostly on the surface, with low coordination. The trends in magnetism for isolated metal clusters of different sizes have been well studied, as well as their temperature dependence.<sup>3-26,28-33</sup> Cobalt, iron and nickel clusters have been featured throughout this work because of their expected large magnetic moments. However, applications require materials distributed on surfaces or suspended within inert solids or films, raising questions about metal-support interactions. Consequently, atoms and small clusters of these metals have been investigated on several surfaces using a variety of techniques.<sup>29-47</sup> Small neutral cobalt clusters have been studied with Stern-Gerlach experiments and found to have magnetic moments in the range of 2  $\mu$ B/atom.<sup>4-9,11</sup> The spin and orbital magnetic moments of the smallest cation clusters of cobalt (8–22 atoms) have only recently been reported, with  $\mu_s$  and  $\mu_L$  values of 2.0–2.7 and 0.4–1.0  $\mu_B$  per atom, respectively.<sup>19,22</sup> The cobalt dimer cation has also been measured, with  $\mu_s$  and  $\mu_L$  values of 3 and 1  $\mu_B$  per atom.<sup>26</sup>

Ligand interactions and their effects on the magnetism of neutral clusters have also been investigated.<sup>48-53</sup> Such studies are of interest as naturally occurring metal clusters are coordinated, and chemistry involving metal clusters often occurs in the solution phase. In general, the greater coordination of ligated clusters is expected to reduce their orbital magnetic moment, but ligand effects on spin moments are also possible. Thus, ligand addition often reduces magnetic moments, but in some cases it has been found to enhance the magnetism. Knickelbein has investigated ligand effects on neutral nickel clusters with added carbon monoxide, oxygen and hydrogen, as well as iron clusters coated with hydrogen.<sup>51-53</sup> All three ligands reduced the magnetism of nickel clusters,<sup>51,52</sup> but hydrogen enhanced the magnetism of

iron clusters.<sup>52</sup> In additional experiments, Stern-Gerlach measurements were conducted on a variety of transition metal-benzene clusters, including those believed to have multiple-decker sandwich structures or those with multi-metal cores and adsorbed benzene.<sup>54-56</sup> Whereas, magnetic moments in the  $1.9 - 2.5 \mu_B$ /atom range were observed for naked cobalt clusters, those with adsorbed benzene had significantly reduced moments. However, such measurements were applied to neutrals and it was not possible to separate the orbital versus spin components of the magnetic moments or to correlate the ligand effect with the specific electronic structure of the system. Various computational studies have also been performed on metal-benzene systems, predicting both enhanced or quenched magnetic moments in different systems.<sup>58-65</sup> Here we use XAS and XMCD spectroscopy in conjunction with computational work to study the cobalt-benzene system, focusing on  $Co_3^+$  with different numbers of attached benzene ligands.

#### Experimental

 $Co_m(bz)_n^+$  clusters are produced and studied in the Nanocluster Trap endstation at the BESSY II beamline UE52-PGM shown in Figure 5.1.<sup>66</sup> Co<sub>m</sub><sup>+</sup> clusters produced with a magnetron source are interacted with benzene vapor in the hexapole ion guide region of the instrument to form  $Co_m(bz)_n^+$  species (mass spectrum shown in Figure 5.2). These ions are mass selected and held in a cryogenic ion trap at 3–4 K. X-ray absorption causes dissociation, producing both Co<sup>+</sup> and benzene<sup>+</sup> ions, along with additional smaller organic ions resulting from the fragmentation of benzene (mass spectrum shown in Figure 5.3). The combined intensities of all of these ions were recorded as a function of photon energy to produce XAS spectra.

#### **Results and Discussion**

Figure 5.4 shows the resulting XAS spectra for the  $Co_3(bz)_n^+$  (n = 0–3) complexes. The red dashed lines mark the onsets of the L<sub>3</sub> edge (779 eV) and the L<sub>2</sub> edge (792 eV) for the ligand-free  $Co_3^+$  cluster. Clusters with an increasing number of benzenes exhibit additional intensity in the second, higher energy L<sub>3</sub> peak. The L<sub>3</sub> edge for  $Co_3(bz)_3^+$  continues this trend with an even greater intensity in the second L<sub>3</sub> peak and the appearance of a third L<sub>3</sub> feature, suggesting a change in the oxidation state of the  $Co_3^+$  core. However, the onset of the  $Co_3(bz)_3^+$  L<sub>3</sub> edge occurs at 780.3 eV, a large shift of 1.3 eV from the onset for  $Co_3^+$ . This large shift is attributed to increased bonding which leads to a delocalization of 3*d* orbitals. Consequently, 2*p*-3*d* Coulomb repulsion weakens, and this increases the transition energy from 2*p* to 3*d* orbitals (the initial probed transition), leading to a blue-shift in the absorption onset.<sup>66</sup> As expected for the spin-orbit split L<sub>3</sub> and L<sub>2</sub> edges,<sup>68</sup> the trend in the L<sub>2</sub> edge mirrors that of the L<sub>3</sub> with a second feature becoming more prominent with the addition of one and two benzenes. Again the addition of the third benzene produces greater intensity in the second peak and the appearance of a third feature.

Figure 5.5 shows the XAS of  $Co_3(bz)_n^+$  (n = 0–3) with red traces representing spectra recorded with negative elliptically polarized light and blue traces representing spectra recorded with positive elliptically polarized light. The difference between the negative and positive traces represents the XMCD of the cluster. Figure 5.6 shows the XMCD spectra, taken from the difference of the positive and negative circularly polarized spectra (Figure 5.5). The XMCD spectra for n = 0–2 are similar, exhibiting a strong negative dichroism at the L<sub>3</sub> edge followed by a weaker positive dichroism at the L<sub>2</sub> edge. In stark contrast to this,  $Co_3(bz)_3^+$  exhibits virtually no dichroism, indicating that it has no net magnetic moment.

The determination of spin and orbital moments from XMCD is dependent upon the ratio of the spin to orbital angular momenta, the number of unoccupied d orbitals (holes), and the

cluster temperature. From the integrated intensities of the  $L_3$  and  $L_2$  edges and the application of the XMCD sum rules,<sup>27,28</sup> we determine the ratios of the spin to orbital angular momenta in these clusters. With the spin/orbital ratio measured, the number of holes and the cluster temperature must be adjusted using chemical and physical insight. The number of holes in the *d* orbitals is assigned as 2 holes/cobalt atom, and a temperature of 17–27 K was used for all cluster sizes. The assignment of 2 holes in the d orbitals represents a local  $d^8$  configuration for all three cobalt atoms, and this assignment is consistent with the theoretical results from Truhlar and coworkers (Appendix B). The temperature range is consistent with other ions produced and measured using this instrument.<sup>20-26</sup> While the measurement of the spin/orbital ratio is generally described as "exact," the actual measurement derives from the difference of two spectra recorded with opposite polarization. Consequently, the noise observed in the XMCD process is the square of the noise recorded in the individual spectra. This problem is exacerbated for larger clusters that exhibit more fragmentation channels, thus decreasing the signal to noise for a given channel. In the case of larger pure metal clusters, this issue is overcome by increased absorption strength. For a cluster like  $Co_3(bz)_3^+$ , the number of fragmentation channels increases drastically while the cobalt absorption remains constant. The uncertainty in the spin/orbital ratio and the possible range of cluster temperatures can result in more than one potential assignment for spin and orbital angular momentum. Figure 5.7 shows the measured spin/orbital ratio and the possible assignments for these clusters based on the aforementioned factors.

Figure 5.8 shows the cluster size dependence of the spin and orbital angular momenta for n = 0-3. The XMCD spectra for n = 0-2 exhibit the same orbital to spin ( $\mu_L/\mu_S$ ) ratio of approximately  $\frac{1}{2}$  (shown in Figure 5.7). No such ratio is determined for Co<sub>3</sub>(bz)<sub>3</sub><sup>+</sup>, as this cluster has no magnetic moment. For the n = 0-2 clusters, the values of  $\mu_S$  and  $\mu_L$  are 6 and

approximately 3  $\mu$ B, respectively. As the error bars for Co<sub>3</sub>(bz)<sub>2</sub><sup>+</sup> are relatively large, it is not possible determine its ground state with certainty. However,  $\mu_{\rm S} = 6$  is the more likely choice, as it would not require a spin flip from Co<sub>3</sub>(bz)<sup>+</sup> to Co<sub>3</sub>(bz)<sub>2</sub><sup>+</sup>. Lastly, Co<sub>3</sub>(bz)<sub>3</sub><sup>+</sup> shows no significant dichroism at the L<sub>3</sub> or L<sub>2</sub> edge, indicating that  $\mu_{\rm S} = 0$  and  $\mu_{\rm L} = 0$ . These assignments are consistent with theoretical predictions. Figure 5.9 shows the XAS spectra for Co<sub>3</sub>(bz)<sub>3</sub><sup>+</sup> and Co<sub>4</sub>(bz)<sub>4</sub><sup>+</sup>. The XAS spectrum for Co<sub>4</sub>(bz)<sub>4</sub><sup>+</sup> appears quantitatively similar to that of Co<sub>3</sub>(bz)<sub>3</sub><sup>+</sup>, suggesting that benzene induced quenching of cobalt clusters may occur for cluster sizes other than Co<sub>3</sub><sup>+</sup>.

Computational studies were conducted at the DFT/M06-L/Def2-TZVP level to investigate the geometry and electronic structure of these complexes. Other levels of DFT were also investigated for comparison (Appendix B). Table 1 shows the relative energies in kcal/mol for all cluster sizes for singlet through nonet spin states, and the lowest energy isomers for each cluster size are shown in Figure 5.8. For n = 0-2 clusters, the septet states are much lower than all but the triplet states, which are 1.6 to 3.2 kcal/mol higher in energy. The most stable structures for  $Co_3(bz)^+$  and  $Co_3(bz)_2^+$  both have  $C_1$  symmetry with septet spin states. For n = 3, the singlet and triplet states are almost indistinguishable in energy, with the singlet lying only 0.2 kcal/mol lower than the triplet. The fully coordinated  $Co_3(bz)_3^+$  also has  $C_1$  symmetry, but its predicted spin state is an open-shell singlet. These predicted spin states agree completely with the assigned spins from the XMCD spectra. The interaction between individual cobalt atoms and benzene is  $\eta^6$  for all structures. Although these two states are close in energy, the singlet state is predicted to be lower and agrees with the assignment from the XMCD spectra.

Theory predicts a local electron configuration of  $4s^{2/3}3d^8$  with two *s* electrons distributed over three orbitals for all three cobalt atoms for each cluster size. The  $3d^8$  configuration could be

a local low spin or high spin state for each cobalt atom, as shown in Figure 5.10. Local high spin on each cobalt atom with ferromagnetic coupling is more energetically favorable for n = 0-2, giving septet and triplet as the two lowest spin states with the septet states lower by 1.0-3.2 kcal/mol. As with the XAS and XMCD spectra, the theory shows a large change in the electronic structure for  $Co_3(bz)_3^+$ . Whereas septet and triplet are the two lowest isomers for n = 0-2 clusters, the n = 3 cluster has a singlet lowest predicted state followed by the triplet state only 0.2 kcal/mol higher in energy.

#### Conclusions

This study shows a sudden and large (9  $\mu$ B) ferromagnetic quenching of magnetic moments for the Co<sub>3</sub><sup>+</sup> cluster through the addition of benzene ligands. Cobalt-benzene cluster ions of the form Co<sub>3</sub>(bz)<sub>n</sub><sup>+</sup> (n = 0–3) were produced in the gas phase, mass-selected, and cooled in a cryogenic ion trap at 3–4 K. Using XMCD as a probe, we determine that Co<sub>3</sub>(bz)<sup>+</sup> and Co<sub>3</sub>(bz)<sub>2</sub><sup>+</sup> both preserve the spin and orbital magnetic moments of Co<sub>3</sub><sup>+</sup> ( $\mu$ <sub>S</sub> = 6  $\mu$ B and  $\mu$ <sub>L</sub> = 3  $\mu$ B), while Co<sub>3</sub>(bz)<sub>3</sub><sup>+</sup> has a  $\mu$ <sub>S</sub> = 0 and  $\mu$ <sub>L</sub> = 0 ground state, with quenched spin and orbital magnetic moments. Computational studies on multi-atom transition metal clusters are notoriously problematic, as these systems possess many electronic states lying close in energy. Experimental measurements of magnetism are likewise challenging, as multiple states may be populated under experimental conditions. In this particular case, DFT calculations predict at most two relatively close electronic states, with the lowest predicted state matching the assignment from the low temperature XMCD measurements for all clusters sizes. The XMCD method described here provides the potential to more clearly elucidate the magnetic properties of metal nanoclusters and to reveal the effects of their local molecular environments.

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**Figure 5.1**. This schematic shows the Nanocluster Trap endstation for X-ray cluster spectroscopy at the UE52-PGM beamline of Bessy II. The cluster ion beam travels from bottom right to top left (blue). Clusters are grown with a magnetron sputter source and cation clusters are guided through a hexapole ion guide. Gas phase collisions (shown here with a benzene reservoir) in the hexapole create ligand-coated metal cluster cations. These ions are then mass selected and guided into an ion trap. X-ray light (purple) intersects the trapped ion packet and daughter ions are extracted into a TOF-MS for and monitored as a function of photon energy.



**Figure 5.2**. The mass spectrum recorded with magnetron sputtering of a cobalt target followed by addition of benzene vapor to the hexapole ion guide exhibits cobalt clusters from n=1 to n=6 with and without attached benzene molecules.



**Figure 5.3**. Observed fragmentation pattern for  $Co_3(bz)_3^+$ . Trapped cluster ions fragment after absorption of 780 eV X-rays.



**Figure 5.4**. XAS of  $Co_3(bz)_n^+$  (n = 0–3). Increasing coordination of benzenes produces a blue shift and an increase in observed peaks. The dashed red lines show the onset of the L<sub>3</sub> and L<sub>2</sub> absorption for  $Co_3^+$ .



**Figure 5.5**. XAS of  $Co_3(bz)_n^+$  (n = 0–3). Red traces represent spectra recorded with negative elliptically polarized light and blue traces represent spectra recorded with positive elliptically polarized light. The difference between the negative and positive traces represents the XMCD of the cluster.



**Figure 5.6**. XMCD spectra for  $Co_3(bz)_n^+$  (n = 0–3). The spectra for the n = 0–2 species show a large negative dichroism at the L<sub>3</sub> edge and a small positive dichroism at the L<sub>2</sub> edge. The n = 3 species exhibits no dichroism indicating quenched magnetic moments.



**Figure 5.7**. The measured ratio of orbital to spin for  $\text{Co}_3(\text{bz})_n^+$  (n = 0–3) is shown at the bottom (diamonds) with error bars. Possible spin magnetic moments are shown at the top (squares). Spin moments are calculated using the orbital/spin ratio, the number of holes (2), and the temperature. When the orbital/spin ratio and the number of holes are fixed, the temperature can be adjusted to produce quantized results. The most likely spin moments are  $\mu_S = 6 \mu_B$  for n = 0–2 and  $\mu_S = 0 \mu_B$  for n = 3, which agrees with theoretical predictions at the M06-L/Def2-TZVP level (shown in red).



**Figure 5.8**. Spin (black) and orbital (red) angular momenta from XMCD spectra for  $Co_3(bz)_n^+$  (n = 0–3). Theoretical structures shown as insets have septet (n = 0–2) and singlet (n = 3) spin states. Structures are optimized at the M06-L/Def2-TZVP level.



**Figure 5.9**. XAS of  $Co_3(bz)_3^+$  and  $Co_4(bz)_4^+$ . The XAS spectrum for  $Co_4(bz)_4^+$  appears quantitatively similar to that of  $Co_3(bz)_3^+$ , suggesting that benzene induced quenching of cobalt clusters may occur for cluster sizes other than  $Co_3^+$ .

$\text{Co}_3(\text{bz})_n^+$	Singlet	Triplet	Quintet	Septet	Nonet
0	24.1	1.6	25.6	0.0	15.0
1	12.8	3.2	9.4	0.0	22.8
2	11.8	1.0	8.6	0.0	30.2
3	0.0	0.2	7.8	4.8	65.9

**Table 5.1**. Relative energies of  $Co_3(bz)_n^+$  in kcal/mol for singlet through nonet spin-states at the M06-L/Def2-TZVP level. Computed ground states are shown in bold.



**Figure 5.10**. Local electronic structures of  $Co_3^+$ . Singlet and quintet states each have one low spin (0) atom while triplet and septet states have only high spin (-1,+1) atoms.

## CHAPTER VI

# EXPERIMENTAL AND THEORETICAL X-RAY ABSORPTION SPECTRA OF COBALT CARBONYL CLUSTER CATIONS

## Introduction

Transition metals form well known complexes with carbonyls which are ubiquitous throughout inorganic and organometallic chemistry,<sup>1-3</sup> with applications to catalysis and industrial processes.<sup>4-5</sup> Metal carbonyl bonding provides a classic example of metal-ligand interactions throughout chemistry and is generally probed with infrared (IR) spectroscopy.<sup>1-3,6-10</sup> These systems have also been studied with IR spectra in rare gas matrices<sup>10</sup> and investigations of metal carbonyl cations have been investigated with gas phase mass spectrometry<sup>11-12</sup> and IR photodissociation spectroscopy.<sup>13</sup> As IR studies have long been the benchmark for studying metal-carbonyl bonding, many theoretical studies have been performed to investigate geometries, electronic structure, and metal-ligand bonding.<sup>10,14-17</sup> However, theoretical calculations involving transition metals often require density functional theory (DFT) due to computational costs. As DFT often struggles with relative energies of electronic states, information on electronic structure is not as well characterized. Here we investigate cobalt carbonyl cluster cations of the form Co(CO)<sub>n</sub><sup>+</sup> (n = 1–5) and Co<sub>2</sub>(CO)<sub>8</sub><sup>+</sup>, Co<sub>3</sub>(CO)<sub>10</sub><sup>+</sup>, and Co<sub>4</sub>(CO)<sub>12</sub><sup>+</sup> with X-ray absorption spectroscopy (XAS) in order to probe the electronic structure of these clusters in the gas phase.

The bonding in transition metal carbonyl systems is characterized by  $\sigma$  donation from the carbonyl to the metal and  $\pi$  back-bonding form the overlap of *d* orbitals on the metal with  $\pi$ 

antibonding orbitals of the CO. This back-bonding depends heavily on the number of *d* electrons available. The competition and synergism between  $\sigma$  donation and  $\pi$  back-bonding has been well studied in the condensed and gas phase with IR spectroscopy,<sup>1-3,6-10</sup> where the change in electron density of the anti-bonding orbitals can be observed through shifts in the CO stretch frequency.

Although IR studies probing bonding in metal carbonyl are the most prevalent, electronic spectroscopy of metal carbonyls have been investigated. Photoelectron spectroscopy (PES) of metal cluster anions has been performed and yields information about the ground electronic states of neutral clusters.<sup>18-20</sup> X-ray absorption has been used to study supported metal carbonyl species.<sup>21</sup> Stern-Gerlach deflection experiments on neutral transition metal clusters have long been used to measure total magnetic moments.<sup>22-32</sup> Ligand addition to metal clusters generally reduces magnetic moments but has also been shown to enhance magnetism in some cases. Knickelbein investigated ligand effects on neutral nickel and iron clusters, finding the addition of carbonyl ligands to reduce cluster magnetic moments.<sup>33-35</sup>

Cobalt carbonyl cation complexes produced in a laser vaporization source were investigated with photodissociation, IR spectroscopy, and DFT.<sup>36,37</sup> The first coordination sphere around Co<sup>+</sup> is five carbonyl ligands. Co(CO)<sub>n</sub><sup>+</sup> (n = 1–4) complexes were all found to have triplet ground states, but the 18 electron Co(CO)<sub>5</sub><sup>+</sup> was found to have a singlet ground state.<sup>36</sup> Here XAS and DFT/ROCIS investigations of these clusters are presented in an effort to confirm the ground state assignments of the Co(CO)<sub>n</sub><sup>+</sup> (n = 1–5) clusters. Co<sub>2</sub>(CO)<sub>8</sub><sup>+</sup>, Co<sub>3</sub>(CO)<sub>10</sub><sup>+</sup>, and Co<sub>4</sub>(CO)<sub>12</sub><sup>+</sup> clusters have also been investigated with IR spectroscopy,<sup>37</sup> but the ground electronic states were not able to be clearly determined for all of these species. These larger clusters are also studied with XAS to gain further insight into their ground electronic states.

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

The Nanocluster trap at the UE52-PGM endstation of Bessy II has previously been described in detail.<sup>38</sup> See the Chapter VI for an overview of this instrument. The formation of previous cobalt benzene clusters required benzene vapor leaked into the hexapole ion guide. In the case of cobalt carbonyl clusters, a carbon monoxide gas tank is connected to the hexapole ion guide via a regulator and a leak valve. Cluster collisions with carbon monoxide in the hexapole lead to cobalt carbonyl clusters. These ions are mass selected and held in a cryogenic ion trap at 3–4 K. X-ray absorption causes dissociation, producing both Co<sup>+</sup> and CO<sup>+</sup> ions. The combined intensities of all of these ions were recorded as a function of photon energy to produce XAS spectra.

DFT calculations were carried out in ORCA<sup>39</sup> at the B3LYP<sup>40</sup>/Def2-TZVP<sup>41</sup> level to determine structures and relative energies of  $Co(CO)_n^+$  (n = 1–5) complexes. This system has previously been investigated with DFT methods,<sup>36</sup> and the singlet and triplet states were found to be the two lowest states for all clusters investigated. Structures found at the B3LYP/Def2-TZVP level were then used for DFT/Restricted Open Shell Configuration Interaction (ROCIS) calculations in order to predict L-edge spectra.<sup>42</sup> The DFT/ROCIS method uses the adequate description of molecular orbitals found from DFT and applies a rigorous multiplet structure and spin-orbit coupling effects that result from configuration interaction methods. Such calculations have been used for mononuclear transition metal complexes<sup>43</sup> and produce good agreement with experimental spectra. DFT/ROCIS calculations are parameterized to perform best for first row transition metals using B3LYP/Def2-TZVP results. Calculations here employed 50 to 100 roots to ensure saturation of involved excitations. Though DFT/ROCIS calculations offer good predictive value for L-edge spectra, there is a significant systematic shift for all spectra that is unique to each first row transition metal. Consequently, all displayed theoretical spectra are shifted by 20.7 eV.<sup>42</sup> This shift arises from shortcomings of DFT to accurately describe core electrons.

## **Results and Discussion**

The XAS spectra of  $Co(CO)_n^+$  (n = 1–5) complexes are shown in Figure 6.1. The onset of the  $L_3$  edge for the n = 1 species is approximately 778 eV, which is almost the same as that of the free cobalt ion.<sup>38</sup> This value doesn't change for the n = 2,3 species, although the lowest energy  $L_3$  peak does narrow significantly and the higher energy  $L_3$  peaks begin to increase in intensity. These quantitative changes continue for the n = 4 species, which also exhibits a shift of approximately 0.5 eV. Upon completion of the first coordination sphere, the XAS spectrum for  $Co(CO)_{5^+}$  has an extremely large 3.5 eV shift of the L<sub>3</sub> edge. This shift is larger than the roughly 2.5 eV shift observed from free Co<sup>+</sup> to bulk cobalt.<sup>38</sup> Significant shifts in the onset energy arise due to delocalization of d orbitals, though such a large shift is unusual. Delocalization of dorbitals causes 2p-3d Coulomb repulsion to weaken, and this increases the transition energy from 2p to 3d orbitals (the initial probed transition), leading to a blue-shift in the absorption onset.<sup>38</sup> As expected for the spin-orbit split  $L_3$  and  $L_2$  edges, the trends in the  $L_2$  edge mirror that of the  $L_3$  with a large shift for the n = 5 species and a second feature becoming more prominent with the increasing addition of carbonyls. Though the  $L_2$  edge behaves similarly to the  $L_3$  edge the overall shift at the L<sub>2</sub> edge from n = 1 to n = 5 is only 1.5 eV, less than half the observed L<sub>3</sub> shift. Such a results requires that the spin-orbit coupling of the 2p electrons changes significantly, which has been predicted to occur with large changes in symmetry.<sup>44</sup>

Figure 6.2 shows the Co(CO)<sup>+</sup> XAS spectrum (black) and the predicted DFT/ROCIS spectra for the triplet (red) and singlet (blue) species. Both structures are  $C_{xv}$ , and theory at the B3LYP/Def2-TZVP level predicts the triplet to be much lower in energy than the singlet (+51.1 kcal/mol). Table 6.1 shows the relative energies for the n = 1–5 species calculated in this work, and Table 6.2 shows the relative energies for the n = 1–5 species calculated previously.<sup>36</sup> The predicted DFT/ROCIS spectrum for the triplet species matches the experimental spectrum much better than that for the singlet. The triplet spectrum L<sub>2</sub> edge onset more closely matches that observed in the experiment while the singlet spectrum is blue shifted relative to the experiment. Additionally, the singlet spectrum predicts an L<sub>2</sub> peak with nearly identical intensity to that of the first L<sub>3</sub> peak while the triplet spectrum exhibits an intensity ratio that better matches the experimental results. The assignment of a triplet ground state is in agreement with the previous IR spectroscopy that also observed a triplet for this species. Both the triplet and singlet spectra underestimate the spin-orbit coupling, and this trend extends to the remainder of the calculations discussed here.

XAS of Co(CO)<sub>2</sub><sup>+</sup> (black) and the accompanying triplet (red) and singlet (blue) theoretical spectra (Figure 6.3) show roughly the same results as that for the Co(CO)<sup>+</sup> species. The triplet ( $D_{\infty h}$ ) structure is much lower in energy than the singlet (+48.4 kcal/mol) and the predicted spectrum more closely matches the onset energy of the experimental spectrum and better represents the peak intensities. The singlet ( $D_{\infty h}$ ) spectrum is blue shifted and predicts a large intensity in the L<sub>2</sub> edge that is not seen in the experimental spectrum. Unlike the previous cluster size, Co(CO)<sub>2</sub><sup>+</sup> has peaks around 786 and 802 eV that are observed in the triplet spectrum but may be exhibited in the higher energy singlet spectrum. Figure 6.4 displays the experimental spectrum of Co(CO)<sub>3</sub><sup>+</sup> (black) and the accompanying triplet (red; C<sub>2v</sub>) and singlet (blue; C<sub>2v</sub>)

theoretical spectra. Comparison of the experimental spectrum to the theoretical spectra yields the same observations as those for the  $Co(CO)_2^+$  cluster, with the main difference being increased intensity in the 786 and 802 eV features in the experimental spectrum and a small feature in the triplet spectrum that correlates to the observed 786 eV peak. For the n = 2,3 clusters, observation of a triplet state agrees with previous IR spectroscopy.

The experimental spectrum of  $Co(CO)_{4}^{+}$  (Figure 6.5, black) is blue shifted by 0.5 eV when compared to the n = 1–3 species, and the higher energy L<sub>3</sub> and L<sub>2</sub> peaks are relatively more intense. Like the previous clusters, the triplet species (C<sub>2v</sub>) is considerably lower in energy than the singlet (+8.4 kcal/mol; D<sub>4h</sub>), and the predicted triplet spectrum matches the experimental spectrum better than that of the singlet. The match between experimental and theoretical spectra is not as obvious here as in other clusters, but the progressively larger blue shift of the theoretical singlet spectrum in conjunction with the triplet predicted to be the lowest energy isomer suggests that the measured species does belong to triplet Co(CO)<sub>4</sub><sup>+</sup>.

Theory predicts triplet ground states for  $Co(CO)_n^+$  (n = 1–4) clusters, but the 18 electron  $Co(CO)_5^+$  species is predicted to be a singlet ground state with a triplet state 4.2 kcal/mol higher in energy. Previous gas phase IR in conjunction with DFT assigns a singlet ground state for this species as well,<sup>36</sup> but the singlet and triplet species were found to be close in energy and the predicted IR spectra were not distinctly different. Figure 6.6 shows the experimental XAS spectrum (black) along with the singlet (blue; D<sub>3h</sub>) and triplet (red; C<sub>4v</sub>) spectra predicted with DFT/ROCIS. The experimental spectrum is highly shifted compared to those of previous clusters. The predicted singlet spectrum is blue shifted 2 eV relative to the experimental spectrum matches well with the absorption onset, the predicted singlet state clearly matches the

experimental spectrum better, exhibiting the same number of peaks with reasonable intensities and energies. Additionally, the predicted singlet spectrum shows a reduced spin-orbit coupling of 13.7 eV, which is very close to the reduced spin-orbit coupling of 14 eV observed in the experimental spectrum. The 18 electron  $Co(CO)_{5}^{+}$  species was previously determined to be a singlet ground state, and here experimental XAS and theoretical DFT/ROCIS spectra confirm this assignment.

Larger cobalt carbonyls  $Co_2(CO)_{8^+}$ ,  $Co_3(CO)_{10^+}$ , and  $Co_4(CO)_{12^+}$  have also been studied with IR spectroscopy and DFT calculations.<sup>37</sup> As with the smaller clusters, some electronic state assignments are relatively clear while others remain difficult. Theory at the B3LYP/6-31+G(d)level<sup>37</sup> predicts a quartet state for  $Co_2(CO)_8^+$  that is lower than the doublet state by only 0.9 kcal/mol. The IR spectrum is not conclusive, but the authors did assign a doublet ground state. Theory for  $Co_3(CO)_{10}^+$  predicts a quintet state to be lower than a singlet state by 25.5 kcal/mol. For this cluster, the IR spectrum clearly shows a singlet state and not the quintet state that was predicted to be much lower in energy. Two doublet structures were found for  $Co_4(CO)_{12}^+$  that differ by only 1.4 kcal/mol. Unfortunately, these two doublet structures have similar theoretical spectra. The experimental spectrum for this cluster more closely matches the lower energy doublet, which the authors assigned to be the observed ground state. XAS of these clusters are shown in Figure 6.7 with the  $Co(CO)_5^+$  spectrum, and all of these fully coordinated clusters exhibit similar spectra. The most intense feature for all four of these clusters is the L<sub>3</sub> peak around 785 eV, though the absorption onset does undergo a red shift with increasing cluster size. Small free cobalt cluster cations have an absorption onset around 778 eV,<sup>38</sup> while the clusters with carbonyls shown here are blue shifted to 780 eV. This change is not as drastic as that seen for  $Co(CO)_5^+$ , but such a shift still implies a large delocalization of d orbitals. While the L<sub>3</sub> peaks change somewhat, the  $L_2$  peaks show almost no change from one spectrum to another. From the shape of the spectra and the blue shift of the absorption edge, it can be concluded that these clusters have low spin ground states, which is consistent with the previous IR and theoretical work.<sup>37</sup> Future work including DFT/ROCIS calculations and XMCD spectroscopy will shed further light on this subject.

### Conclusions

 $Co(CO)_{n}^{+}$  (n=1–5) complexes were formed using a magnetron sputtering source and investigated with x-ray absorption spectroscopy (XAS) at the cobalt L-edge. Theoretical XAS spectra were predicted using the Restricted-Open-Shell Configuration Interaction with single excitations based on density functional theory (DFT/ROCIS). Comparison of XAS and predicted spectra suggests primarily high spin (triplet) complexes for n=1–4 and a low spin (singlet) complex for n=5.  $Co_2(CO)_{8}^{+}$ ,  $Co_3(CO)_{10}^{+}$ , and  $Co_4(CO)_{12}^{+}$  clusters were also investigated with XAS. Assignments without XMCD and/or DFT-ROCIS are tentative, but XAS spectra for all three multiple metal clusters suggest delocalization of *d* orbitals and low spin ground states.

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**Figure 6.1**. The XAS of  $Co(CO)_n^+$  (n = 0–5) are shown for an increasing number of carbonyl ligands. Increasing coordination produces an increase in observed peaks and a 3.5 eV blue shift for the onset of  $Co(CO)_5^+$ .



**Figure 6.2**. The XAS of  $Co(CO)^+$  (black) is shown compared to theoretical DFT/ROCIS spectra for the triplet (red) and singlet (blue) states.



**Figure 6.3**. The XAS of  $Co(CO)_2^+$  (black) is shown compared to theoretical DFT/ROCIS spectra for the triplet (red) and singlet (blue) states.



**Figure 6.4**. The XAS of  $Co(CO)_3^+$  (black) is shown compared to theoretical DFT/ROCIS spectra for the triplet (red) and singlet (blue) states.



**Figure 6.5**. The XAS of  $Co(CO)_4^+$  (black) is shown compared to theoretical DFT/ROCIS spectra for the triplet (red) and singlet (blue) states.



**Figure 6.6**. The XAS of  $Co(CO)_5^+$  (black) is shown compared to theoretical DFT/ROCIS spectra for the singlet (blue) and triplet (red) states.



**Figure 6.7**. The XAS of  $Co(CO)_5^+$ ,  $Co_2(CO)_8^+$ ,  $Co_3(CO)_{10}^+$ , and  $Co_4(CO)_{12}^+$  are qualitatively similar. The absorption onset undergoes a red shift with increasing cluster size.

#### CHAPTER VII

#### CONCLUSIONS

The macroscopic synthesis of clusters previously confined to the gas phase is an exciting area of research. The laser vaporization flowtube reactor (LVFR) was used to produce ultra-small ligand-coated metal and metal-oxide clusters and capture them in solution. Their properties were investigated with mass spectrometry, numerous spectroscopic methods, and computational chemistry, and this method shows promise to synthesize new and unique cluster materials of a variety of elements. Gas phase X-ray studies were performed to investigate cluster-ligand interactions, and ligand addition to cobalt clusters revealed drastic quenching of magnetic moments for both benzene and carbonyl ligands. When and why ligand induced quenching occurs is still not well understood, but future experiments can continue to investigate these interactions with hopes of uncovering insight and eventually predictive ability.

Gas phase chromium oxide clusters were coated with acetonitrile ligands and capture in solution. The production of this cluster material is relatively efficient, and HPLC separation provides a future opportunity for isolation of individual clusters in solution. Vibrational spectroscopy reveals cage-like metal-oxide structures. Additionally, these clusters exhibit a broad visible fluorescence.

While the LVFR has been used to produce a number of metal-oxide clusters, Al/MeCN clusters represent the first non-oxide clusters produced with this method. Despite greater intensity of other jellium model clusters in gas phase experiments, the aluminum trimer with

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acetonitrile ligands is the most prevalent aluminum cluster collected in solution. Surface enhanced Raman spectroscopy reveals the presence of aluminum trimer and small aluminum oxide clusters, but UV-visible and fluorescence spectroscopy exhibit remarkable sharp features that are attributed to the aluminum trimer.

Cobalt trimer cation was studied with X-ray absorption and X-ray magnetic circular dichroism (XMCD) spectroscopies. Addition of one or two benzene molecules produces little change in the X-ray absorption spectra and no change in the spin or orbital angular momenta for these clusters. Addition of a third benzene molecule results in large changes in the absorption spectrum (attributed to significant delocalization of d orbitals) and sudden and complete quenching of the cobalt trimer cation to form singlet  $Co_3Bz_3^+$ .

A combination of X-ray absorption spectra and density functional theory of cobalt cation carbonyls confirm the triplet state species for unsaturated clusters and the expected 18 electron singlet ground state for  $Co(CO)_5^+$ . Cobalt dimer, trimer, and tetramer cations are all known to be high spin systems with large magnetic moments. A full coordination sphere of carbonyl ligands produces only low spin cobalt carbonyl clusters.

Future LVFR efforts will be directed towards production and isolation of metal-carbide, metal-silicon, and other interesting clusters previously observed in the gas phase. With the use of a new 400 Hz excimer laser, LVFR cluster material can now be produced in large enough quantities to fully characterize and investigate. Use of HPLC separation should allow for techniques such as NMR and X-ray crystallography. While laser vaporization is a widely applicable technique, collection of cluster material using the LVFR varies drastically in efficiency from on system to another. Future efforts will be made to determine the causes of this (instrumental conditions, choice of ligand, etc.) in hopes that Al/MeCN and other cluster

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materials can be produced in larger amounts. Preliminary work has been conducted on metal oxy-carbide nanoparticles which represent a new and unusual nano-material, and further studies could potentially expand from clusters to include additional unique nano-materials

### APPENDIX A

#### AL/MECN THEORY BY JON MANER

All calculations were done with DFT-B3LYP level of theory with TZVP basis set. Redundant bond lengths and angles have been omitted. The frequencies reported in the supporting information have not been scaled. The energies have been corrected for ZPVE but not BSSE.

Table A1. The calculated total and relative energies of acetonitrile using B3LYP/TZVP.

	Total Energy (Hartrees)	Relative Energy (kcal/mol)
Acetonitrile	-132.753299	0.0



**Figure A1**. The calculated structure of acetonitrile using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

390.1 (0.3), 390.7 (0.4), 930.3 (1.3), 1060.2 (2.7), 1060.4 (2.7), 1407.8 (3.5), 1472.6 (12.8),

1473.7 (12.7), 2360.8 (10.5), 3050.7 (2.1), 3125.7 (0.4), 3127.2 (0.4)

Structure		Total Energy (Hartrees)	Relative Energy (kcal/mol)
Al <sub>3</sub>	$^{2}A_{1}'(D_{3h})$ $^{4}A_{2}(C_{2v})$	-727.241299 -727.236054	0.0 +3.3
		2.540 60.00	

Table A2. The calculated total and relative energies of Al<sub>3</sub> isomers using B3LYP/TZVP.

**Figure A2**. The calculated structure of the Al<sub>3</sub> ( ${}^{2}A_{1}' D_{3h}$ ) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

227.4 (2.9), 227.4 (2.9), 339.9 (0.0)



**Figure A3**. The calculated structure of the Al<sub>3</sub> (<sup>4</sup>A'') isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

123.8 (1.5), 275.1 (13.1), 295.7 (1.5)



Table A3. The calculated total and relative energies of Al<sub>3</sub>(MeCN) isomers using B3LYP/TZVP.

**Figure A4**. The calculated structure of the Al<sub>3</sub>(MeCN) (<sup>2</sup>A) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

11.8 (0.1), 22.8 (5.6), 26.1 (3.1), 94.5 (1.9), 105.6 (1.0), 193.9 (0.6), 246.9 (3.9), 294.7 (6.1), 357.2 (0.1), 392.7 (0.1), 405.5 (14.8), 940.7 (33.8), 1037.0 (6.8), 1039.9 (7.1), 1401.0 (26.8), 1454.2 (13.0), 1460.0 (13.1), 2261.3 (390.8), 3030.7 (13.7), 3101.7 (0.4), 3108.2 (1.1)



**Figure A5**. The calculated structure of the Al<sub>3</sub>(MeCN) ( $^{4}$ A) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

14.6 (1.6), 21.7 (0.0), 30.2 (2.7), 101.7 (1.8), 104.0 (1.9), 144.3 (0.6), 207.4 (4.4), 268.6 (2.1), 319.6 (4.7), 337.4 (6.4), 397.5 (0.4), 934.7 (55.5), 1028.9 (22.1), 1043.6 (6.4), 1400.9 (38.4), 1454.1 (16.4), 1461.9 (12.4), 2202.0 (692.4), 3022.0 (35.9), 3088.4 (9.4), 3105.8 (0.4)



**Table A4**. The calculated total and relative energies of Al<sub>3</sub>(MeCN)<sup>+</sup> isomers usingB3LYP/TZVP.

**Figure A6**. The calculated structure of the  $Al_3(MeCN)^+$  (<sup>3</sup>A) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

15.2 (0.0), 20.4 (2.1), 30.8 (1.3), 96.6 (5.2), 100.1 (2.0), 168.2 (3.6), 228.6 (18.6), 239.3 (15.6), 400.3 (12.9), 410.1 (0.3), 415.2 (0.8), 950.4 (0.2), 1043.1 (8.6), 1044.2 (10.2), 1396.9 (0.8), 1443.7 (18.3), 1444.2 (17.4), 2321.9 (51.0), 3037.3 (31.0), 3118.6 (9.6), 3119.7 (9.7)



**Figure A7**. The calculated structure of the  $Al_3(MeCN)^+$  (<sup>1</sup>A) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

12.0 (0.0), 38.0 (6.8), 39.8 (1.7), 118.7 (4.9), 128.6 (0.6), 204.3 (3.2), 293.8 (13.6), 324.0 (12.8), 402.0 (0.1), 423.3 (0.4), 957.2 (0.0), 1039.7 (8.9), 1044.8 (12.8), 1395.9 (0.6), 1440.5 (17.8), 1444.7 (17.8), 2319.6 (31.4), 3035.8 (30.0), 3116.8 (9.7), 3118.3 (12.6)



**Table A5**. The calculated total and relative energies of Al<sub>3</sub>(MeCN)<sub>2</sub> isomers usingB3LYP/TZVP.

**Figure A8**. The calculated structure of the  $Al_3(MeCN)_2$  (<sup>2</sup>A) isomer, using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

14.8 (1.3), 30.4 (9.5), 31.9 (0.0), 34.8 (0.0), 41.9 (0.5), 102.6 (25.6), 103.9 (10.5), 112.2 (1.0), 125.6 (0.0), 162.3 (1.3), 223.0 (0.2), 258.5 (27.0), 297.5 (93.5), 323.2 (22.2), 363.1 (0.3), 371.6 (0.1), 373.1 (0.0), 397.2 (2.1), 924.8 (122.3), 938.8 (43.3), 1009.4 (74.5), 1023.8 (13.4), 1045.6 (0.0), 1045.8 (10.7), 1398.4 (71.5), 1402.0 (38.3), 1457.4 (1.1), 1458.8 (20.3), 1459.6 (0.0), 1459.9 (21.7), 2175.7 (974.0), 2213.5 (674.0), 3013.0 (83.6), 3077.9 (12.3), 3079.0 (0.6), 3098.0 (0.7)



**Table A6**. The calculated total and relative energies of  $Al_3(MeCN)_2^+$  isomers using B3LYP/TZVP.

**Figure A9**. The calculated structure of the  $Al_3(MeCN)_2^+$  (<sup>1</sup>A) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

19.1 (0.2), 19.3 (0.3), 23.0 (4.9), 30.5 (8.7), 43.1 (0.8), 44.0 (0.0), 103.8 (6.1), 110.7 (0.0), 114.2 (0.0), 142.0 (0.0), 200.0 (5.0), 216.3 (1.8), 328.7 (16.7), 395.7 (21.4), 396.5 (10.2), 418.7 (2.8), 447.2 (5.8), 948.7 (2.1), 950.4 (0.0), 1041.8 (14.9), 1042.4 (0.7), 1048.3 (3.5), 1398.8 (1.0), 1399.3 (0.1), 1446.9 (0.1), 1450.5 (4.2), 1450.5 (29), 2318.4 (0.2), 2320.5 (1.7), 3039.1 (5.2), 3117.9 (0.0), 3122.0 (0.1), 3122.1 (15.8)



**Figure A10**. The calculated structure of the  $Al_3(MeCN)_2^+$  (<sup>3</sup>B) isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

12.3 (3.9), 17.1 (0.0), 17.4 (0.2), 22.8 (5.7), 30.4 (0.1), 32.9 (0.3), 91.1 (1.9), 93.5 (1.5), 94.0 (1.1), 109.0 (7.9), 182.8 (10.9), 187.3 (3.0), 295.1 (0.4), 305.5 (14.3), 390.0 (0.3), 397.5 (0.5), 403.2 (1.1), 410.3 (0.6), 416.3 (2.0), 944.6 (5.3), 945.2 (1.2), 1043.7 (1.1), 1044.2 (15.2), 1045.6 (0.0), 1046.0 (14.6), 1399.1 (1.7), 1399.7 (0.4), 1449.0 (10.6), 1450.9 (0.0), 1450.9 (32.4), 2309.3 (6.8), 2310.4 (4.8), 3039.5 (16.8), 3039.6 (3.4), 3119.7 (7.3), 3119.7 (3.8), 3120.4 (0.3), 3120.4 (11.6)



**Table A7**. The calculated total and relative energy of Al<sub>3</sub>(MeCN)<sub>3</sub> using B3LYP/TZVP.

**Figure A11**. The calculated structure of  $Al_3(MeCN)_3$  using B3LYP/6-311+G(d,p). They are followed by the predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

17.6 (0.0), 23.6 (1.1), 24.9 (13.7), 25.1 (0.2), 25.9 (15.0), 34.9 (0.0), 37.2 (0.9), 52.1 (0.8), 55.0
(0.2), 111.4 (0.0), 111.6 (3.5), 123.9 (0.0), 124.2 (2.1), 140.1 (0.6), 141.9 (1.3), 201.5 (0.2),
229.8 (1.7), 242.2 (1.4), 248.6 (15.5), 260.4 (41.9), 301.3 (2.3), 352.4 (2.6), 353.1 (2.5), 355.9
(9.4), 358.9 (9.4), 369.5 (0.8), 380.1 (0.2), 927.4 (51.8), 931.9 (135.8), 1026.8 (2.1), 1028.3
(9.9), 1038.4 (6.4), 1039.5 (6.3), 1041.1 (5.4), 1042.0 (0.2), 1398.4 (53.2), 1401.4 (105.4),
1403.4 (10.5), 1460.6 (2.3), 1461.8 (29.3), 1461.9 (2.5), 1462.3 (9.2), 1463.3 (1.8), 2185.4
(610.7), 2212.2 (1642.6), 2244.1 (320.4), 3016.3 (48.3), 3017.0 (105.4), 3023.9 (53.7), 3080.2
(2.7), 3080.7 (0.6), 3087.7 (2.0), 3088.1 (2.5), 3092.0 (0.7), 3096.8 (0.0)



**Table A8**. The calculated total and relative energy of Al<sub>3</sub>(MeCN)<sub>3</sub><sup>+</sup> using B3LYP/TZVP.

**Figure A12**. The calculated structure of  $Al_3(MeCN)_3^+$  using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

14.7 (11.4), 16.7 (8.1), 21.8 (4.8), 21.9 (4.1), 22.7 (1.5), 23.6 (0.6), 38.9 (0.0), 39.6 (0.0), 40.6 (0.0), 85.4 (0.8), 101.7 (0.0), 106.6 (2.9), 106.8 (2.8), 128.2 (0.0), 128.4 (0.0), 145.8 (0.0), 237.2 (9.5), 238.0 (9.2), 381.2 (23.6), 381.4 (24.6), 392.5 (0.1), 394.2 (0.0), 394.4 (0.0), 408.9 (0.0),

419.1 (0.3), 419.2 (0.5), 487.5 (0.0), 945.3 (1.8), 945.3 (2.0), 946.4 (0.0), 1045.6 (5.8), 1045.8 (15.8), 1045.9 (5.6), 1049.6 (5.8), 1049.8 (0.2), 1050.0 (16.1), 1401.0 (2.8), 1401.7 (0.0), 1452.4 (13.9), 1452.5 (13.1), 1452.6 (20.3), 1454.8 (14.3), 1455.0 (12.0), 1455.0 (19.6), 2326.4 (9.4), 2326.5 (9.9), 2329.3 (0.0), 3041.6 (4.5), 3041.6 (2.6), 3119.7 (2.0), 3119.7 (5.6), 3119.9 (5.8), 3123.4 (3.6), 3123.5 (5.2), 3123.6 (4.5)

	Structure	Total Energy (Hartrees)	Relative Energy (kcal/mol)
Al <sub>2</sub> O <sub>3</sub>	${}^{3}\mathrm{B}_{2}$	-710.721471	0.0
	${}^{1}A_{1}$	-710.687766	21.1

Table A9. The calculated total and relative energies of Al<sub>2</sub>O<sub>3</sub> isomers using B3LYP/TZVP.



**Figure A13**. The calculated structure of the  $Al_2O_3(^3B_2)$  isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).



**Figure A14**. The calculated structure of the  $Al_2O_3(^1A_1)$  isomer using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

161.1 (0.6), 235.0 (12.6), 370.6 (109.3), 449.8 (1.9), 450.8 (62.1), 514.7 (2.3), 859.0 (4.3), 893.5 (90.2), 1036.7 (6.1)



**Table A10**. The calculated total and relative energies of Al<sub>2</sub>O<sub>3</sub><sup>+</sup> using B3LYP/TZVP.

**Figure A15**. The calculated structure of  $Al_2O_3^+$  using B3LYP/TZVP, followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

 $141.1\ (0.2),\ 156.3\ (13.8),\ 355.7\ (158.1),\ 465.2\ (0.0),\ 554.6\ (61.4),\ 624.1\ (109.9),\ 859.2\ (68.5),$ 

861.5 (120.4), 930.7 (99.6)

Structure	Total Energy (Hartrees)	Relative Energy (kcal/mol)
Al <sub>2</sub> O <sub>3</sub> (MeCN) <sub>2</sub> <sup>1</sup> A	-976.285520	0.0

Table A11. The calculated total and relative energies of  $Al_2O_3(MeCN)^+$  isomers using B3LYP/TZVP.



**Figure A16**. (a) The calculated structure of the  $Al_2O_3(MeCN)_2$  (<sup>1</sup>A) isomer using B3LYP/TZVP. (b) is a rotated view of (a) showing bonds and angles out of  $Al_2O_2$  plane. The structure is followed by its predicted frequencies (cm<sup>-1</sup>) and IR intensities (shown in parentheses, km/mol).

15.8 (0.3), 20.9 (10.4), 31.5 (0.8), 40.3 (0.4), 41.0 (16.5), 49.8 (2.2), 100.8 (7.7), 155.8 (1.0), 164.3 (8.9), 169.0 (6.4), 206.0 (15.7), 238.9 (8.2), 248.0 (18.1), 281.0 (3.7), 375.5 (160.8), 388.6 (7.6), 390.6 (39.5), 407.6 (0.3), 410.9 (8.1), 425.3 (83.1), 491.6 (54.9), 536.3 (2.7), 901.0 (3.3), 950.3 (141.7), 954.3 (0.4), 964.5 (71.2), 1016.6 (12.7), 1036.7 (8.4), 1041.3 (10.4), 1046.2 (21.0), 1064.1 (4.4), 1398.1 (24.0), 1403.0 (0.9), 1447.7 (16.7), 1449.4 (16.2), 1463.5 (14.9), 1465.5 (13.2), 2332.7 (718.6), 2376.8 (22.5), 3038.2 (0.1), 3042.4 (5.7), 3117.1 (1.6), 3117.2 (5.1), 3118.3 (6.3), 3127.7 (0.0)

## APPENDIX B

# $CO_3(BZ)_n^+$ THEORY BY KAINING DUANMU

Tuble D1. Relative chergies (Real mor) of singlet unough nonet spin states of Co3.	Table B1. Relative energ	gies (kcal/mol) of singlet th	rough nonet spin states of Co <sub>3</sub> <sup>+</sup> .
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Functional	Singlet	Triplet	Quintet	Septet	Nonet
MOGI	24.1	16	25.6	0.0	15.0
MU0-L	24.1	1.0	23.0	0.0	13.0
M08-SO	12.2	1.1	11.7	0.0	26.9
SOGGA11-X	17.5	0.4	17.0	0.0	20.8
B97-3	16.8	0.1	16.7	0.0	19.8
ωB97X-D	16.6	0.8	16.3	0.0	25.1
mPW1B95	16.7	0.6	16.6	0.0	20.3

Spin State	Energy (kcal/mol)	Mulliken Spin Density (Co atom 1, 2, 3)	<s<sup>2&gt;</s<sup>
M06-L			
Singlet	24.1	0.00, -2.27, 2.27	3.11
Triplet	1.6	-2.27, 2.24, 2.02	4.15
Quintet	25.6	-0.27, 2.14, 2.13	7.05
Septet	0.0	1.99, 2.07, 1.94	12.08
Nonet	15.0	2.40, 2.80, 2.80	20.07
M08-SO			
Singlet	12.2	0.01, 2.08, -2.09	3.06
Triplet	1.1	-2.10, 2.05, 2.05	4.08
Quintet	11.7	-0.05, 2.02, 2.03	7.06
Septet	0.0	2.01, 2.00, 1.99	12.08
Nonet	26.9	3.44, 2.28, 2.28	20.11
SOGGA11-X			
Singlet	17.5	0.00, 2.07, -2.07	3.02
Triplet	0.4	-2.09, 2.04, 2.04	4.03
Quintet	17.0	-0.04, 2.02, 2.02	7.02
Septet	0.0	2.00, 2.00, 2.00	12.04
Nonet	20.8	2.33, 3.34, 2.34	20.11
<b>B97-3</b>			
Singlet	16.8	-0.02, -2.10, 2.13	3.03
Triplet	0.1	-2.13, 2.07, 2.07	4.04
Quintet	16.7	2.06, 2.05, -0.11	7.04
Septet	0.0	1.99, 2.00, 2.00	12.04
Nonet	19.8	2.33, 2.84, 2.84	20.12
<b>ωB97X-D</b>			
Singlet	16.6	2.10, -2.13, 0.03	3.03
Triplet	0.8	-2.11, 2.06, 2.05	4.04
Quintet	16.3	-0.09, 2.05, 2.04	7.04
Septet	0.0	1.99, 2.00, 2.00	12.05
Nonet	25.1	2.34, 2.61, 3.04	20.12
mPW1B95			
Singlet	16.7	-0.18, -2.04, 2.22	3.04
Triplet	0.6	-2.15, 2.07, 2.07	4.05
Quintet	16.6	-0.05, 2.03, 2.03	7.02
Septet	0.0	2.00, 2.02, 1.98	12.05
Nonet	20.3	2.33, 2.56, 3.11	20.12

Table B2. Energies, spin densities, and  $\langle S^2 \rangle$  of  $Co_3^+$ .

Spin State	Energy (kcal/mol)	Mulliken Spin Density (Co atom 1, 2, 3)
M06-L		
Singlet	12.8	-0.39, -2.13, 2.52
Triplet	3.2	1.76, -2.16, 2.43
Quintet	9.4	-0.78, 2.38, 2.38
Septet	0.0	1.52, 2.26, 2.28
Nonet	22.8	2.19, 2.86, 2.86
M08-SO		
Singlet	15.3	-0.02, 2.12, -2.09
Triplet	0.9	-2.12, 2.00, 2.12
Quintet	14.7	-0.09, 2.05, 2.04
Septet	0.0	1.96, 2.02, 2.02
Nonet	33.0	2.79, 2.78, 2.33

**Table B3.** Energies and spin densities of  $Co_3(bz)^+$  in different spin states at the M06-L and M08-SO level.

Spin State	Energy (kcal/mol)	Mulliken Spin Density (Co atom 1, 2, 3)
M06-L		
Singlet	11.8	-2.55, 1.34, 1.34
Triplet	1.0	-2.06, 1.82, 2.28
Quintet	8.6	0.00, 1.64, 2.40
Septet	0.0	2.30, 1.89, 1.89
Nonet	30.2	2.36, 2.36, 3.24
M08-SO		
Singlet	29.2	-3.55, 1.76, 1.76
Triplet	0.3	-2.11, 2.03, 2.08
Quintet	13.7	-0.07, 1.99, 2.08
Septet	0.0	2.03, 1.98, 1.98
Nonet	23.4	3.50, 2.24, 2.24

**Table B4.** Energies and spin densities of  $Co_3(bz)_2^+$  in different spin states at the M06-L and M08-SO level.
Spin State	Energy (kcal/mol)	Mulliken Spin Density (Co atom 1, 2, 3)
M06-L		
Singlet	0.0	-2.16, 1.13, 1.13
Triplet	0.2	-1.92, 1.96, 2.02
Quintet	7.8	1.66, 1.31, 1.31
Septet	4.8	2.07, 2.04, 2.04
Nonet	65.9	2.44, 2.18, 2.18
M08-SO		
Singlet	36.9	-2.48, 1.29, 1.29
Triplet	0.0	-2.13, 2.09, 2.06
Quintet	42.3	1.53, 1.29, 1.29
Septet	1.2	1.93, 2.05, 2.05
Nonet	79.5	2.33, 2.26, 2.26

**Table B5.** Energies and spin densities of  $Co_3(bz)_3^+$  in different spin states at the M06-L and M08-SO level.