The Pennsylvania State University

The Graduate School

Department of Chemistry

CLUSTERS: ADDRESSING MATERIAL AND ENVIRONMENTAL ISSUES

A Dissertation in

Chemistry

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2008
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ABSTRACT

The present thesis work is part of a continuing effort in the Castleman group to study the physical and chemical properties of clusters as they relate to materials and the environment. With regards to materials, metal-based clusters are synthesized in the gas phase in order to identify uniquely stable species. Just as atoms or molecules are the building blocks of matter in nature, our group envisions the synthesis of future cluster-assembled materials (CAMs) built with clusters. By varying the size and composition of a cluster by even one atom, the electronic properties can be dramatically changed. A general introduction of the cluster chemistry and physics pertinent to this thesis work is presented in Chapter 1.

Anion photoelectron spectroscopy is the experimental technique utilized in this work to study metal and metal-based clusters. A home-built instrument was employed, and descriptions of its components are presented in Chapter 2. This instrument was used to study a series of Al\textsubscript{n}Bi\textsuperscript{−} (n = 1-5) clusters. As explained in Chapter 3, experimental data was combined with theoretical work from our collaborators in order to show that the introduction of a bismuth atom to aluminum clusters creates uniquely stable clusters. One of these, Al\textsubscript{3}Bi, is demonstrated be an all-metal aromatic cluster. Another cluster, Al\textsubscript{5}Bi, is shown to be stabilized by the jellium model. The findings are a practical example of how small changes in size and/or composition of a cluster give rise to exciting properties. Based on the results, a relationship is drawn between the aromatic and jellium models herein, and potential for use in CAMs is briefly discussed.

In Chapter 4, niobium carbide clusters of the form Nb\textsubscript{3}C\textsubscript{n}− (n = 5-10) are investigated with similar methods in order to elucidate the formation of larger metal-carbon clusters, most notably the niobium Met-Car (Nb\textsubscript{8}C\textsubscript{12}). When the experimental data is merged with theory from our collaborators, isomers with various structural motifs are identified. Structures of tri-niobium carbide clusters are proposed to follow two general trends. One structural trend of Nb\textsubscript{3}C\textsubscript{n}−
clusters features a triangular niobium unit at the cluster core. The second structural motif entails a single carbon atom that links to all three metal atoms, and C2 units that bridge the individual niobium atoms. Nice agreement between the experimental and computational results is shown, lending credence to our findings. Comparisons are drawn between the results presented here and previous theoretical and experimental studies of small niobium carbide clusters.

The last study presented in this work does not deal with materials, but rather environmental chemistry. In Chapter 5, reactions of formic acid (HCOOH) and protonated water clusters of the form H⁺(H₂O)ₙ (n = 3-27) are examined in a fast-flow reactor under well-defined thermal conditions. The product distributions of H⁺(H₂O)ₙ(HCOOH)ₘ show that nucleation occurs with these clusters on a molecular scale more easily than both pure water and methanol-water clusters do under similar conditions. Calculations are performed using the Thompson liquid drop model to interpret the experimental results. The findings are also in good agreement with recent theoretical work regarding a “cooperative bonding” effect with formic acid molecules and water. The atmospheric implications of this study are briefly discussed. A summary of all the results from this thesis work is presented in Chapter 6.
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Chapter 1

Introduction

In the community of physical chemistry, clusters can be generally defined as a group of atoms or molecules that coalesce when brought together. The forces that bind cluster constituents include weak van der Waals contacts, metal bonding, and strong ionic bonds, to name a few. Clusters are an intermediate form of matter that bridge the gas and condensed phases. The degree of aggregation in a system that can be regarded as a cluster is not rigorously defined, but is commonly comprised from as few as two and as many as several thousand entities. With small changes in geometry, stoichiometry, and charge, the properties of a cluster can change dramatically with respect to its bulk phase counterpart. The focus of this work is twofold. One aspect is to exploit and understand the unique stability of certain clusters to serve as building blocks for a new class of materials with tailored properties. The second facet in this thesis is to investigate the formation and properties of weakly bound clusters to comprehend the change of a system from the gaseous to the condensed state, specifically regarding heterogeneous nucleation in the atmosphere.

1.1 Ultraviolet Photoelectron Spectroscopy of Metal Clusters

The first sections of this thesis work involve the application of ultraviolet photoelectron spectroscopy to study metal and metal-carbide clusters. Since a portion of this work involved the design, construction, and operation of a home-built PES apparatus, Chapter 2 consists of an explanation and description of the components of our instrument.
Photoelectron spectroscopy (PES) is a powerful technique in that it studies molecular orbitals in a direct fashion. The specific type of spectrometer used in the present studies, a “magnetic bottle time-of flight” electron analyzer, was first introduced by Kruit and Read. When photons of sufficient energy interact with free anionic clusters, electrons are ejected from occupied molecular orbitals in the outer valence shell(s). These photoelectrons have energies, abundances, and angular distributions characteristic of the molecular orbitals from which they originate. The quantity most directly measured in anion photoelectron spectroscopy is the binding energy (BE) of electrons from the individual occupied orbitals.

A useful way of viewing this method is through an approximation known as Koopmans’ theorem, which assumes that each BE is equal in magnitude to an orbital energy. Under this assumption, the photoelectron spectrum of a molecule would be a direct representation of the molecular orbital energy diagram. A simple schematic for this one-photon process is shown in Figure 1. Furthermore, changes in the molecular geometry caused by removal of one electron from each orbital could be revealed, as well as the character of the orbitals (bonding, antibonding, or nonbonding) and how their bonding power is localized in the molecule.
Anion PES involves transitions from the anionic ground state to the corresponding neutral cluster’s ground and excited states. When the experimental results are combined with calculations using density functional theory, which were performed by our collaborators at Virginia Commonwealth University, important information can be gained. First, the electron affinity (EA) of the neutral cluster is close to the BE of the highest-energy electron of the anionic species. Second, the experimentally-determined photoelectron spectrum is a fingerprint of the electronic structure of the neutral cluster. Third, the energy gap between the highest occupied molecular orbital and lowest occupied molecular orbital (the HOMO-LUMO gap), can oftentimes be directly measured in the experiment.

In the past decade, the concept of aromaticity to explain the electronic structure of organic molecules has been extended to include metal cluster systems as well. The most notable example, Al₄⁻, was discovered through an experimental and theoretical examination of MAL₁⁻ (M = Li, Na, or Cu) clusters. The calculated molecular orbitals, shown in Figure 1.2,
provided evidence that \( \text{Al}_4^{2-} \) favors a cyclic, planar structure with two delocalized \( \pi \) electrons. The delocalized \( \pi \) bonding, present in the HOMO in Figure 1.2, is reminiscent of the aromatic bonding present in benzene (\( \text{C}_6\text{H}_6 \)), with bonding above and below the molecular plane. Further studies revealed that the extent of delocalization in \( \text{Al}_4^{2-} \) includes \( \sigma \) electrons as well (HOMO-1 and HOMO-2 in Figure 1.2), accounting for its three-fold aromaticity (one pair of \( \pi \) electrons and two pairs of \( \sigma \) electrons).

![Figure 1-2: The calculated molecular orbitals for Al\(_4^{2-}\). Adapted from reference 10.](image)

Direct evidence of another all-metal aromatic cluster, Al\(_3\)Bi, is presented in the current thesis study. It is isoelectronic with Al\(_4^{2-}\) (14 valence electrons), and has a cyclic, planar structure. The Al\(_3\)Bi cluster has been found to exhibit both \( \pi \) and \( \sigma \) aromaticity, and has better prospects for synthesis into a cluster-assembled material (CAM). Because it is electronically neutral, it has no need for counter-ion or ligand support, and may be found to be stable under ambient conditions.
A second aluminum bismuth cluster with enhanced stability, Al\textsubscript{5}Bi, was also found during the present work. This cluster exhibits stability through the Jellium model, which has been used to describe the unique stability of super atoms.\textsuperscript{6, 12, 13} The Al\textsubscript{5}Bi cluster also shows potential for being made into a CAM. Chapter 3 discusses the discovery of both Al\textsubscript{3}Bi and Al\textsubscript{5}Bi through joint experimental and theoretical studies, and establishes connections between aromatic and Jellium stability.

1.2 Ultraviolet Photoelectron Spectroscopy of Niobium Carbide Clusters

Among the ever-growing array of clusters with enhanced stability lies the family of metallocarbohedrynes (Met-Cars). The first member of the Met-Car class of clusters, Ti\textsubscript{8}C\textsubscript{12}, was discovered in the Castleman group.\textsuperscript{14} Since that first discovery, the family of clusters comprising of 8 early transition metals and 12 carbon atoms assembled into a cage-like structure has come to include Ti, Zr, Hf, V, Nb, Cr, Mo, and Fe.\textsuperscript{15} Furthermore, binary Met-Cars can be prepared from the above metals, with the same metal to carbon stoichiometry remaining unchanged. In addition to being uniquely stable, other interesting properties of Met-Cars include delayed ionization,\textsuperscript{16} low ionization potentials relative to their individual constituents,\textsuperscript{17} and prospects for pollution abatement.\textsuperscript{18}

One active area of current study is the investigation of the exact geometry and formation mechanisms of the Met-Car. Chapter 4 of this thesis involves the continuation of our group’s studies to elucidate one member of the Met-Car family, Nb\textsubscript{8}C\textsubscript{12}. Photoelectron spectroscopy is well-suited as a structural characterization technique towards these means. We first conducted a joint experimental and theoretical study (with our collaborators at VCU) of di-niobium carbide clusters.\textsuperscript{19} The results of this study showed that Nb may easily substitute for C atoms in small cluster sizes, namely that linear chains of Nb\textsubscript{2}C\textsubscript{n\textsuperscript{-}} clusters can form just as those found previously
for $C_n^-$ clusters. The study in Chapter 4 entails tri-niobium carbide clusters. While no evidence of pure carbon-like geometric clusters was found, evidence of particular structural motifs was discovered. It is anticipated that the findings presented in this thesis work will aid in the development of methods to produce bulk quantities of the Met-Car.

1.3 Protonated Water Cluster Reactions as a Model for Heterogeneous Nucleation

The final part of this thesis work deals with clusters as a model for chemical processes that occur in the atmosphere. Specifically, the study of water clusters links the study of clouds and condensation processes with gas-phase chemical reactions. Aerosols play a crucial role as centers for the formation of cloud condensation nuclei (CCN), which in many cases are formed by nucleation. A proposed mechanism for their formation is ion-induced nucleation. The Castleman group has performed extensive studies of ion-molecule reactions relating to those in our environment. The experimental study in Chapter 5 is the latest extension of those studies, namely the reactions of protonated water clusters with formic acid under thermal conditions.

Figure 1-3: Schematic diagram of the fast-flow reaction apparatus. Adapted from reference 28.
The experimental apparatus used to study reactions of protonated water clusters with formic acid is shown in Figure 1.3. The details of the experimental components and conditions are given in Chapter 5. Protonated water clusters of the form $\text{H}^+(\text{H}_2\text{O})_n$ ($n = 3-27$) are reacted with formic acid (HCOOH) under well-defined conditions. From these studies, it was determined that the formic acid-water complexes studied have a high propensity to undergo nucleation, particularly when compared to pure water clusters. Experimental evidence indicates that the presence of formic acid in water clusters allows for the facile propagation of hydrosopic growth on the molecular scale. The results are put into context with theoretical findings in previous literature regarding a cooperative bonding effect in neutral formic acid-water clusters of small sizes $[(\text{H}_2\text{O})_n(\text{HCOOH}), n = 1-3]$ by Vaida et al. Additionally, an implementation of the classical Thompson charged liquid drop model is used to understand the experimental results from a thermodynamic standpoint. Chapter 5 also includes a discussion of some possible implications of the findings towards atmospheric nucleation processes.

1.4 References


27. Yang, X.; Castleman, A. W., Jr., Large protonated water clusters $\text{H}^+(\text{H}_2\text{O})_n$ ($n > 60$): the production and reactivity of clathrate-like structures under thermal conditions. *J. Am. Chem. Soc.* 1989, 111, (17), 6845-6846.


Chapter 2

Experimental Details of Anion Photoelectron Spectroscopy (PES)

2.1 Experimental Overview

The technique of anion PES involves the interrogation of a mass-selected beam of negative ions by a fixed-frequency light source, and analysis of the kinetic energies of photodetached electrons. The energy-conserving relationship between the photon energy and the kinetic energy of the detached electrons is expressed in Equation 2.1.

\[ KE = h\nu - BE - E_{vib.,rot}^* \]  

(2.1)

The photon energy is represented by \( h\nu \); the measured kinetic energy of the electron is \( KE \), the binding energy of the electron is represented by \( BE \), and \( E_{vib.,rot}^* \) represents the internal energy, which includes vibrational and rotational states. Photoelectron spectroscopy, when applied to gas-phase molecules, provides direct evidence of molecular orbital theory.\(^1\) In a simplified picture, the binding energy of a photodetached electron is the orbital energy that the electron occupied. With high resolution, one can gain detailed spectroscopic information, such as the energies of vibrational states.\(^2\) Photoelectron spectroscopy is a powerful technique that can contribute to the understanding of the electronic structure of atoms, molecules, bulk solids, surfaces, and clusters. The study of clusters is of main importance in this work.

The study of negative ions with PES is advantageous for several reasons. First, since clusters generally are formed with a distribution of sizes, negative ions allow for size-selectivity. This is accomplished using a Wiley-McLaren time-of-flight (TOF) assembly.\(^3\) Second, anions generally have low binding energies, which allows for the use of visible and ultraviolet lasers for
photodetachment. Neutral clusters often have high binding energies and require higher photon energies for ionization. Third, and most importantly, performing PES on negative clusters yields electronic and spectroscopic information about the electron affinities of neutral clusters, which often are of most interest.

In order to perform PES experiments on clusters, in particular metal clusters over a wide size range (between 10 and 2000 amu), the instrument used must have the following attributes. First, a cluster source that can generate a variety of clusters in the ground state is essential. This is accomplished with laser vaporization (LAVA) source coupled with supersonic expansion of the gas-phase clusters. Second, the instrument must have size-selective capabilities with high resolution. Our time-of-flight assembly allows the selection and resolution of species from highly complex, mixed clusters. Third, high sensitivity is vital, particularly with cluster systems. This is due to the nature of cluster studies, which generally do not include number densities as high as atomic gas and condensed phase experiments.\(^4,5\) A magnetic bottle photoelectron spectrometer, which has high collection efficiency relative to other PES methods, meets this criterion. Fourth, a photodetachment laser must be pulsed to produce photons with high enough energy to probe tightly-bound electrons. An XeCl excimer laser that produces photons with 4.03 eV (308 nm) of energy was used in the experiments discussed herein.

The magnetic bottle time-of-flight photoelectron apparatus that incorporates the above characteristics was constructed during the present thesis work. It has been designed mainly for the study of metal clusters, mixed-metal clusters, and metal-nonmetal clusters. The first signal from photodetached electrons came in September, 2004, and the first manuscript from anion PES experiments was published on November 30, 2006.\(^6\) Thus far, three graduate students have earned their Doctorate degrees designing, constructing, and performing experiments on the apparatus in its current configuration. The following sections will describe the instrument in greater detail.
2.2 Experimental Setup

A schematic of the experimental apparatus is shown in Figure 2-1. The main components include a pulsed laser vaporization cluster source, a Wiley-McLaren TOF mass spectrometer, and a magnetic bottle TOF photoelectron analyzer. A detailed description of each of these major components follows.

Figure 2-1: The magnetic bottle photoelectron spectrometer coupled with a laser vaporization supersonic cluster source and a time-of-flight mass spectrometer.

Pulsed Laser Vaporization Cluster Source

Anionic clusters are generated via a laser vaporization (LAVA) plasma reactor. This type of source is capable of generating pure metal, mixed-metal, and metal-nonmetal clusters with a
large enough abundance for photodetachment studies. It has been machined from stainless steel, and is depicted in Figure 2-2.

Figure 2-2: The pulsed laser vaporization cluster source.

The source produces species at a repetition rate of 10 Hz. A sequence of events that are activated through timed transistor-transistor logic pulses from a home-built pattern generator and a Stanford™ delay generator (DG 535). The first event in each sequence is a square pulse applied to the pulsed valve (General Valve Series 9) shown in Figure 2-2. The duration of the square pulse can vary between 250 μs and 400 μs, depending on the product distribution required for a given experiment. The timed logic pulse is delivered to a solenoid containing a magnetic
armature. When activated, the armature in the pulsed valve is lifted, and gas enters the reaction region. A stagnant pressure of 40-60 psi of either pure helium or a mixture of helium and methane is expanded into the vacuum through an orifice of 800 μm.

The second timed event causes light from a pulsed laser (10 Hz) to ablate the metal (or mixed-metal) rod during the pulsed valve opening. The metal rod is continuously translating back and forth and rotating at 1 rpm. The second harmonic (532 nm) of a Nd³⁺:YAG (yttrium aluminum garnet) laser (Spectra Physics Indi Series) is tightly focused to about 1 mm and aligned perpendicularly to the pulsed valve. Energies used range from 5-20 mJ/pulse. The stagnation pressure in the pulsed valve, the duration of the pulse valve opening, the arrival of the laser light, and the power of the photon packet are all optimized for each particular cluster of study in the photodetachment experiment.

Clusters are produced when the laser-induced plasma is cooled by the carrier gas pulse from the pulsed valve. The packet of clusters that forms is made up of both electrically charged and neutral species. The mixture of He and cluster species undergoes a supersonic expansion and is skimmed to form a collimated cluster beam in the time-of-flight extraction region. Before the beam is skimmed, however, it travels through a cylindrical expansion nozzle. Several different nozzles are used, with lengths that vary from 2-5 cm and inner-diameters from 3-6 mm. Longer nozzles allow more collisions to take place during the expansion, and subsequently cause large cluster formation. The short expansion nozzles are well-suited for the production of very small clusters and atomic ions.

*Time-of-flight Mass Spectrometer*

The collimated cluster beam enters the extraction region portion of the (TOF) mass spectrometer, shown in Figure 2-3. When the cluster species of interest arrives between two
TOF grids, an electronic trigger pulse (the third timing event) is sent to two Behlke\textsuperscript{TM} high-speed transistor switches. These switches are each connected to TOF 1 and TOF 2, and charged with high voltages simultaneously. Typical voltages are shown in Figure 2-3, but are sometimes varied to change the focusing conditions of the cluster beam. In order to study anionic species, a higher negative potential is placed on TOF 1. Anionic clusters are abruptly directed towards the field-free region for study, cationic species are directed towards TOF 1, and neutral species are not affected by the field and are pumped away. The anionic clusters then pass through a series of three Einzel lenses, the second of which is given a constant voltage. The lenses are used to both collimate the cluster beam and prevent space-charge effects.

![Figure 2-3: The extraction region portion of the time-of-flight mass spectrometer.](image)

The kinetic energy imparted to anions by the applied field is given by the relation:

\[ KE = qE_z \]  \hspace{1cm} (2.2)
The kinetic energy \((KE)\) is dependent on the charge of the ion \((q)\), the distance traveled by the ions within the extraction region \((s)\) in the direction of the applied field, and the magnitude of the field \((E_s)\). Relating Equation 2.2 to the non-relativistic definition of kinetic energy gives:

\[
qsE_s = \frac{mv^2}{2}
\]  

\[(2.3)\]

From Equation 2.3, it is apparent that the velocity \((v)\) of an ion is inversely proportional to the square of its mass \((m^2)\). The field-free region, defined as the distance \((d)\) from TOF 3 to an electron multiplier, is 245 cm. Because all ions travel the same distance and are imparted with the same amount of kinetic energy, their masses are identified based on the time \((t)\) it takes them to reach the detector, which is shown by:

\[
t = d \sqrt{\frac{m}{2qsE_s}}
\]  

\[(2.4)\]

The detector used is a Chevron-mounted multichannel plate (MCP) electron multiplier. A digital oscilloscope (LeCroy) records each event when an ion strikes the face of the detector. A personal computer is then used to convert the file to a format suitable for analysis and calibration with Equation 2.4.

**Magnetic Bottle TOF Photoelectron Analyzer**

The method of electron collection using a “magnetic bottle” was first introduced by Kruit and Read.\(^7\) Approximately 143 cm from the extraction region described above, cluster anions are interrogated by a pulsed ultraviolet laser. The laser used is an excimer laser with a wavelength of 308 nm (4.03 eV) and a typical energy of 45 mJ/pulse. The moment a cluster of interest arrives in the magnetic bottle region, a pulse of light interacts with it. The photodetachment laser beam is not focused in order to avoid multi-photon ionization. Figure 2-4 depicts the magnetic bottle
time-of-flight analyzer. The blue circle represents the location of interaction (photodetachment), where the laser beam is perpendicular to the axis of the bottle. Beneath the interaction region is a permanent, conical magnet which exerts an inhomogeneous magnetic field of $\sim 1$ Tesla. Above the interaction region is a solenoid made up of a 1.8 m stainless steel tube wrapped with nine sections of 24 AWG copper wires. The inner-diameter of the solenoid is 4 in. A variable current (4-12 Amperes) is passed through the sections, which are wired in parallel, generating an essentially homogeneous field of 1 mT. The magnetic field lines are shown for both the permanent magnet and solenoid in Figure 2-4.

Figure 2-4: The magnetic bottle time-of-flight analyzer.
The magnetic flux lines determine both the collection efficiency and final cyclotron radius, which must be smaller than the detection area at the top of Figure 2-4. Once an electron is photodetached from an anion, its trajectory is parallelized to the plane of the magnetic bottle irrespective of its initial velocity vector.\(^4\) The magnetic field exerts a force on the electron that is proportional to its velocity and charge, given by
\[
\vec{F} = e \vec{v} \times \vec{B}
\]
(2.5)
where \(\vec{F}\) is the force, \(e\) is the elementary charge \((e = 1.6 \times 10^{-19} \text{ C})\), \(\vec{v}\) is the velocity, and \(\vec{B}\) is the magnetic field. The direction of \(\vec{F}\) is defined by the cross product of \(\vec{v} \times \vec{B}\), and when the velocity vector makes an angle \((\theta)\) with \(\vec{B}\), the force is given by
\[
\vec{F} = e \vec{v} \vec{B} \sin \theta.
\]
(2.6)
The velocity vector direction is always perpendicular to the force vector, therefore when an electron moves through the magnetic field \((\vec{B})\), the trajectory of the electron is altered without any change in its kinetic energy.

If an electron is initially emitted at an initial angle \((\theta)\) to the axis of the magnetic bottle \((z)\), it undergoes a helical motion in the strong magnetic field \((\vec{B}_i)\). The frequency of the electron motion is given by
\[
\omega_i = e \frac{\vec{B}_i}{m}
\]
(2.7)
where \(m\) is the mass of the electron. The radius of the orbit, or cyclotron radius, is
\[
r_i = \frac{\vec{v} \sin \theta_i}{\omega_i}
\]
(2.8)
and the initial angular momentum ($\vec{L}_i$) of the circular motion is

$$\vec{L}_i = \frac{m^2 v^2 \sin^2 \theta_i}{e B_i}. \quad (2.9)$$

The change in magnetic field with $z$ is adiabatic, which means that the field change experienced by the electron is negligible in the course of one helical revolution. Thus, the angular momentum is conserved, and it follows that the final angle ($\theta_f$) of the low magnetic field ($\vec{B}_f$) region is given by

$$\frac{\sin \theta_f}{\sin \theta_i} = \left(\frac{\vec{B}_f}{\vec{B}_i}\right)^{1/2}. \quad (2.10)$$

For the instrument used for this thesis, an electron ejected perpendicularly to the magnetic bottle axis ($\theta_i = 90^o$) has a final angle ($\theta_f$) equal to $1.8^o$.

The adiabatic invariance can also be stated by combining Equation 2.8 and Equation 2.10 to give

$$\frac{r_f}{r_i} = \left(\frac{\vec{B}_i}{\vec{B}_f}\right)^{1/2}. \quad (2.11)$$

The final cyclotron radius of an electron detached with a kinetic energy of 1.0 eV is ~1.0 mm, which is far less than the 15 mm radius of our MCP detector at the end of the magnetic bottle.

Calibration of the electron energies is performed with the collected spectra of the Cu$^-$ anion, for which the transitions are well-characterized. The transitions that are accessible from our XeCl excimer laser (4.03 eV) are from the anion ground state ($^1S_0, 3d^{10}4s^2$) to the neutral ground state ($^2S_{1/2}, 3d^{10}4s^1$) and the first two excited states of Cu ($^2S_{5/2}, 3d^94s^2$ and $^2S_{3/2}, 3d^94s^2$). These states have binding energies of 1.235, 2.617, and 2.869 eV, respectively.
Photoelectron spectra are collected by measuring the intensity of electron count as a function of electron time-of-flight. The measured electron time-of-flight is converted to kinetic energy by using Equation 2.4, and then to binding energy by using Equation 2.1. The resolution of the instrument is determined from the full width at half maximum for the low binding energy copper transition at 1.235 eV, and is less than 200 meV. The methods described in this chapter allow the assignment of discrete binding energies to each measured flight time.

2.3 References


Chapter 3

Al$_n$Bi Clusters: Transitions Between Aromatic and Jellium Stability

3.1 Abstract

An experimental and theoretical study of bismuth-doped aluminum clusters in the gas phase has revealed two particularly stable clusters, namely Al$_3$Bi and Al$_5$Bi. We show that their electronic structure can be understood in terms of the aromatic and “Jellium” models, respectively. Negative ion photodetachment spectra provide a fingerprint of the electronic states in Al$_n$Bi$^-$ ($n = 1 - 5$) anions, while theoretical investigations reveal the nature of the electronic orbitals involved. Agreements between the experimental and computational energies validate the subsequent theoretical results. The findings show that the all-metal Al$_3$Bi cluster with 14 valence electrons is a cyclic, planar structure with a large ionization potential of 7.08 eV, a low adiabatic electron affinity of 1.41 eV, and a large gap of 1.69 eV between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap). The Al$_3$Bi cluster has molecular orbitals reminiscent of aromatic systems, and is a neutral cluster with no need for counter-ion or ligand support. A slightly larger cluster, Al$_5$Bi, has 20 valence electrons and is another highly stable, compact structure, with a large ionization potential of 6.51 eV and a large HOMO-LUMO gap of 1.15 eV. This cluster’s stability is rooted in a Jellium electronic shell closing. The formation of stable species using aromatic bonding allows us to extend the idea of cluster-assembled materials built out of stable clusters with Jellium shell closings (superatoms), to include ones involving aromatic building blocks.
3.2 Introduction

The electronic structure and the chemical behavior of small metal clusters can be fundamentally different from the bulk, where the electronic states are well described by band theory. Metal clusters, which feature both finite size and structural flexibility, inherently have a unique relationship between geometry and electronic states. When the structure and electronic states are manipulated, the stability and chemical characteristics can be tuned through ways that are generally inaccessible in the bulk phase.\(^1\)-\(^3\) For clusters of free-electron metals, a model is commonly used in which the nuclei and innermost electrons form a positively charged core with an essentially uniform potential. Valence electrons from individual atoms in the cluster are then subjected to this uniform potential, and a Jellium electronic shell structure emerges. A Jellium shell structure has specific stable numbers in electron configurations (2, 8, 18, 20\(\ldots\)) that differ from either the atomic series (2, 10, 18\(\ldots\)), or the bulk system.\(^4\), \(^5\) This model accounts for the stability of numerous simple and compound metal clusters with electron counts leading to closed electronic shells. In aluminum clusters, which have three valence electrons per atom, this model explains the observed stability and chemical inertness of Al\(_{13}^\text{-}\), which contains 40 valence electrons. The model also explains the high electron affinity of Al\(_{13}\), with 39 valence electrons, because the highest occupied molecular orbital (HOMO) needs one \(p\)-like electron to complete its shell.\(^6\) We have previously demonstrated, both experimentally and theoretically, the superhalogen character of Al\(_{13}\) in anionic species formed by combining it with a halogen atom.\(^7\), \(^8\) Our current investigations are focused on identifying particular clusters that display enhanced stability.\(^9\), \(^10\)

A different concept to explain electronic stabilization, aromaticity, has been applied to organic systems for over a century\(^11\), \(^12\) as a way to describe stable molecules with delocalized bonding. Organic molecules that are conjugated, cyclic, planar, and contain \((4n + 2)\pi\) electrons are traditionally classified as aromatic. Recent studies by Wang, Boldyrev, and coworkers have
extended aromaticity to include all-metal anionic molecules, most notably the Al$_4^{2-}$ dianion. An experimental and theoretical examination of MAL$_i^{-}$ (M = Li, Na, or Cu) clusters provided evidence that Al$_4^{2-}$ favors a cyclic, planar structure with two delocalized $\pi$ electrons. Further studies revealed that the extent of delocalization in Al$_4^{2-}$ includes $\sigma$ electrons as well, accounting for its three-fold aromaticity (one pair of $\pi$ electrons and two pairs of $\sigma$ electrons). Boldyrev et al. calculated resonance energies for all-metal aromatic systems and found unusually high values of 48 kcal/mol for Na$_2$Al$_4$ and 21 kcal/mol for Na$_2$Ga$_4$ (compared to 20 kcal/mol in benzene, the most well-known aromatic molecule). Previous experimental studies of all-metal aromatic clusters investigated species that are isoelectronic with Al$_4^{2-}$, including X$_4^{2-}$ where X is B, Ga, In, or Tl, mixed valence isoelectronic species MAl$_3^{-}$, where M is Si, Ge, Sn, or Pb, and triatomic aromatics of the form X$_3^{-}$, where X is B, Al, Ga. Additionally, studies on similar mixed systems, including theoretical work on Al$_3$As and experiments involving Al$_3$P have also been reported.

Recent reviews of all-metal aromaticity written by Boldyrev, Wang and coworkers provide a comprehensive guide to work reported in the literature.

The above examples of Jellium and aromatic clusters show that, depending on the electron count and the number of atoms, the electron gas has the potential to stabilize clusters through different mechanisms. Clusters with 2, 8, 18, 20, … valence electrons favor a compact geometry and lead to stability via a Jellium-like model, whereas clusters with $(4n + 2)\pi$ electrons favor a planar arrangement and aromatic stability. It would be ideal to find a system where the electron count could be varied to fit either of the two scenarios, and then to demonstrate how the geometric arrangements and the electronic states in the same system adapt for stabilization. In the present work, we demonstrate this unusual possibility in Al$_n$ clusters doped with a single Bi atom. The valence electron configuration of Al is 3s$^2$ 3p$^1$, and that of Bi is 6s$^2$ 6p$^3$. Pure aluminum clusters are known to undergo a transition from a monovalent to a trivalent state in small sizes.
Depending on the contributions of $s$ and $p$ electrons, Al$_3$Bi would correspond to either a 6 $p$ electron system in a planar configuration, or a 14 valence electron cluster with a compact structure that favors $s$-$p$ mixing. A valence configuration of 6 makes it isoelectronic with Al$_4$$^{2-}$, with six $p$-electrons that exhibit aromatic bonding. This may imply that Al$_3$Bi should have a planar structure and enhanced energetic stability.

If the stability of Al$_3$Bi is caused by the combination of $p$-electrons in a planar structure, then naturally the addition or removal of one electron would cause destabilization and geometric distortion. For example, adding one electron to the neutral Al$_3$Bi cluster to form Al$_3$Bi$^-$ (7 $p$ electrons, 15 total) should drive the system away from aromatic stability and a planar geometry. The Al$_3$Bi$^-$ cluster, with a non-planar, more compact structure, will consequently have a smaller HOMO-LUMO gap, indicative of lower stability. With negative ion photodetachment spectra, where the peaks in the photoelectron spectrum sample the valence electronic states of the neutral cluster in the anionic ground state geometry, this structural transition can be directly probed. The addition of two electrons, however, to Al$_3$Bi would make an Al$_3$Bi$^{2-}$ cluster with 8 $p$ and 16 total electrons. We demonstrate theoretically that the addition of electrons to an aromatic bonding scheme causes the molecular orbitals to become reminiscent of a Jellium scheme. This is performed in order to describe the interplay between aromaticity and the Jellium model in understanding bonding in metal clusters.

In Al$_3$Bi, another potential Jellium situation arises. Each Al contributes 3 valence electrons, while Bi contributes 5 valence electrons. The cluster therefore contains a total of 20 valence electrons corresponding to a closed Jellium shell, and it would be expected to have a symmetric and compact three dimensional geometry with a large HOMO-LUMO gap. This shows that, with the right geometry and electron count, both aromaticity and Jellium closings can be achieved for many permutations of metals and non-metals in the periodic table. In both types of stability, the valence electrons of individual atoms in a given cluster combine for cooperative
bonding effects. Aluminum clusters doped with bismuth atoms are thus an ideal system in which the interplay between aromaticity and Jellium stability can be observed.

In this work we carry out a synergistic effort combining experimental data with first principles electronic structure studies from S. N. Khanna et al. from Virginia Commonwealth University to demonstrate these two differing facets of the electron gas. For the experimental component, we use negative ion photodetachment spectroscopy as a probe of the electronic states. A comparison between the experimental photoelectron spectra and the calculated spectra of anions provides a fingerprint of the neutral electronic states, with the caveat that the neutral species are probed in the anionic geometry. The experimentally observed species are then examined theoretically with established “pointers” that prove both energetic stability and chemical hardness. Energetic stability is demonstrated by a large calculated energy gain when a cluster forms from a stoichiometry with one less atom, and a small energy gain when one additional atom binds to the cluster. Chemical hardness is the resistance to change in electron number or deformation of the electron cloud and is tested by the size of the HOMO-LUMO gap, as a large gap indicates inertness. Both the experimental and computational parts of the present study are essential for a complete picture of the clusters investigated.

We have previously proposed that selected clusters exhibiting Jellium stability could be described as “superatoms,” asserting that clusters of a given element can have chemical and electronic properties resembling those of another atom in the periodic table.\textsuperscript{7,8,24} A new type of chemistry, one involving clusters taking on the role of atoms as the basic building blocks, is already possible. The ability to identify and synthesize inert clusters using aromaticity allows us to have even more building blocks at our disposal in the creation of cluster-assembled materials.
3.3 Experimental and Computational Methods

Experiments were performed with a magnetic bottle photoelectron spectroscopy apparatus that has been described in detail in Chapter 2. A laser vaporization supersonic cluster beam source synthesizes anionic clusters of interest. Two methods were successful in creating Al\textsubscript{n}Bi\textsuperscript{−} clusters. The first made use of two adjacent rods of pure aluminum and bismuth that met at the laser’s focal point. A second method used a thin layer of bismuth coated on an aluminum rod. In both cases helium was used as the carrier gas with stagnation pressures between 50 and 75 psi. Negative ions were extracted and mass analyzed with a Wiley-McLaren time-of-flight mass spectrometer.\textsuperscript{25} Mass-selected anions of interest were interrogated by a laser beam from an excimer laser (308 nm) in a magnetic bottle time-of-flight electron analyzer, where photodetached electrons were detected according to their kinetic energies. Electronic spectra were calibrated based on the known spectra of Bi\textsuperscript{−}.\textsuperscript{26}

In order to interpret our experimental findings, our collaborators from Virginia Commonwealth University (VCU) performed theoretical calculations. First-principle electronic structure studies on the anion, neutral and cation forms of Al\textsubscript{n}Bi (\textit{n} = 1-6) clusters were performed within the density functional formalism,\textsuperscript{27} employing the Perdew, Burke and Ernzerhof generalized gradient approximation.\textsuperscript{28} The actual calculations were carried out using the deMon\textsuperscript{2k} software.\textsuperscript{29} The electronic orbitals and eigenstates were determined by using a linear combination of Gaussian atomic type orbitals molecular orbital approach. For Al they employed the DFT optimized DZVP basis set,\textsuperscript{30} and the Bi atom was described using the 23 electron scalar relativistic effective core potential proposed by B. Metz \textit{et al}.\textsuperscript{31} in combination with the correlation consistent aug-cc-pVDZ valence basis set.\textsuperscript{32} In order to avoid the calculation of four-center electron repulsion integrals, a variational fitting of the Coulomb potential was employed.\textsuperscript{33,34} The auxiliary density was expanded in primitive Hermite Gaussian functions using the GEN-
A2 auxiliary function set for Al, and the GEN-A2* auxiliary function set for Bi. The exchange-correlation potential was calculated with the orbital density. The numerical integration of the exchange-correlation energy and potential were performed on an adaptive grid, and a half-numeric integrator was employed for the effective core potential (ECP) integrals. In order to determine the ground state geometries, the configuration space was sampled by starting from several initial configurations and spin states. All the structures were fully optimized in redundant coordinates without symmetry constraints, and resulting ground states were ascertained via a frequency analysis. The methodology was first tested via studies on pure neutral and anionic aluminum clusters Al$_n$ with $n = 1$-6. The geometries and ground state spin multiplicities of these clusters have been previously investigated, and the results agree with those investigations. The calculated vertical detachment energies (VDE) for the Al$_n$ series ($n = 2$-6) showed very good agreement with respect to the experimental values. Additionally, they correctly predicted the ground state spin multiplicity of the Bi atom as a quartet, and the electron affinity was calculated to be 0.85 eV, in good agreement with the experimental value of 0.95 eV. The molecular geometries and orbitals were plotted using the Schakal and Molden software, respectively.

3.4 Results and Discussion

Photoelectron spectra of Al$_n$Bi$^-$ ($n = 1$-5) taken at 308 nm are presented on a binding energy scale in Figure 3-1. The electron binding energies of anionic clusters deduced by photodetachment correspond to the electron affinities of the neutral clusters. The spectrum of an anionic cluster that has a closed electronic shell is predicted to display a dominant peak that corresponds to a doublet neutral state formed via a one-electron detachment channel. The spectrum of an open shell cluster anion, corresponding to a doublet state, may show two dominants peaks due to singlet and triplet final states in the neutral species. The anionic ground
states of Al,Bi clusters with an odd number of electrons were calculated to be doublet states, so two peaks were predicted. This prediction is borne out in the experimental spectra of AlBi and Al2Bi\(^-\). The energies of the features correspond to the HOMO-LUMO gap of the neutral species in the anionic geometry. The ground states of Al2Bi\(^-\) and Al4Bi\(^-\), on the other hand, are singlet states, so a single peak was predicted in the experimental spectrum for each of the clusters. The higher energy peaks observed for those clusters, as well as Al5Bi\(^-\), correspond to removal of electrons from deeper states and are not accurately described within the current density functional framework. The resolution of our instrument was not high enough to see individual features in the spectrum for Al3Bi\(^-\). One quantity that can be observed for all species is the adiabatic electron detachment energy (AEDE), which is taken from the leading edge of the low energy features in the photodetachment spectra. This measurement corresponds to the adiabatic electron affinity, which measures the difference in energy between the ground state of the anion and the ground state of the neutral species. All features in the photoelectron spectra were present for different source conditions and photodetachment laser powers, therefore no unambiguous evidence of structural isomers was found. However, theoretical calculations by Khanna et al. revealed isomers that are likely to account for the minor peaks at low energies in the spectra for Al2Bi\(^-\) and Al3Bi\(^-\). Further details of the theoretical results are presented below.
Table 3-1 compares the theoretical adiabatic electron affinities (EA) with the experimental adiabatic electron detachment energies (AEDE). We have also listed the ionization potential (IP) and the calculated HOMO-LUMO gap in the neutral species. The calculated gap for the clusters that have an odd number of electrons represents the difference in energy between the singly-occupied upper valence orbital and the lowest unoccupied level in the opposing (majority or minority) spin manifold. If one considers the uncertainty in experimental
measurements, the calculated EA are in very good agreement with the experimental AEDE, with a maximum difference of 15% for AlBi. For Al3Bi, the experimental value of 1.62 eV for the AEDE of the anion agrees well with the calculated EA of the neutral species (within 10%). The photodetachment spectrum of Al3Bi− (Figure 3-1) shows two peaks, with a gap of 0.58 eV. As is described in more detail below, the theoretical studies of the singlet neutral Al3Bi cluster in the anion geometry predict a HOMO-LUMO gap of 0.52 eV, also in agreement with the experimental value of 0.58 (see Figure 3-1). Theoretical evidence of the stability of Al3Bi and Al5Bi emerges from Table 3-1. Specifically, Al3Bi has the largest HOMO-LUMO gap of the series, as well as the lowest EA. Al3Bi also has a large HOMO-LUMO gap, as well as a high IP when compared to Al5Bi.

Table 3-1: Experimental adiabatic electron detachment energies (AEDE) of AlnBi− clusters along with calculated electron affinities (EA), ionization potentials (IP), and HOMO-LUMO gap values for the AlnBi clusters (n = 1-6). All values are given in eV.

<table>
<thead>
<tr>
<th>#Al atoms</th>
<th>AEDE (exp.)</th>
<th>EA (theo.)</th>
<th>IP</th>
<th>HOMO-LUMO Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.59 ± 0.07</td>
<td>1.94</td>
<td>6.75</td>
<td>0.46</td>
</tr>
<tr>
<td>2</td>
<td>1.97 ± 0.05</td>
<td>2.06</td>
<td>7.04</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>1.62 ± 0.07</td>
<td>1.41</td>
<td>7.08</td>
<td>1.69</td>
</tr>
<tr>
<td>4</td>
<td>2.05 ± 0.05</td>
<td>2.19</td>
<td>6.19</td>
<td>0.57</td>
</tr>
<tr>
<td>5</td>
<td>2.02 ± 0.09</td>
<td>2.17</td>
<td>6.51</td>
<td>1.15</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>2.21</td>
<td>6.04</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Figure 3-2 shows the calculated ground state geometries of anionic, neutral, and cationic AlnBi (n = 1-6) clusters. The primary focus of the calculations was to examine the electronic structure and stability of neutral Al3Bi, which we suspected would show signs of aromaticity. The ground state of neutral Al3Bi was indeed found to have a planar structure. Furthermore, the electronic states showed a large HOMO-LUMO gap of 1.69 eV.
To further probe its bonding character, we investigated the nature of the molecular orbitals. A molecular orbital analysis of Al$_3$Bi (Figure 3-3) attests to its true aromatic makeup. Figure 3-3(A) shows that the three most energetic occupied orbitals, the (A1) HOMO, (B1) HOMO-1, and (B2) HOMO-2, respectively, are all delocalized. The HOMO has $\sigma$ delocalization from the $p_{x,y}$ atomic orbitals oriented radially toward the center of the ring. The electron density lies in the center of the Al$_3$Bi ring and around the perimeter. The HOMO-1 is a delocalized $\pi$ orbital from the atomic $p_z$ orbitals perpendicular to the plane of the ring, which results in electron density delocalization above and below the ring, similar to benzene. The third delocalized orbital, HOMO-2, is of the $\sigma$-type, caused by overlap between the atomic $p_{x,y}$ orbitals oriented tangentially around the ring. In this orbital, the two electrons are delocalized between the atoms in the heterocyclic unit. These results are similar to those found for Al$_4^{2-}$ and other all-metal, aromatic tetramer anions.$^{10,12-13}$
Figure 3-3: One-electron levels, isosurfaces (isovalue = 0.001 a.u.), and symmetries of the molecular orbitals for the 14-electron Al₃Bi cluster at the neutral ground state geometry (A), at the C₃ anion ground state geometry (B), and at the compact C₃ᵥ geometry (C). The continuous lines represent occupied levels, the dotted lines correspond to single unfilled states, the degeneracy is marked next to each level and the arrows indicate the majority (up) and minority (down) spin states.

There are, however, slight distortions in the symmetry of Al₃Bi when compared to the delocalized orbitals calculated for the more-symmetric Al₄²⁻, but since the Pauling electronegativity difference between bismuth (1.9) and aluminum (1.5) is small,⁴¹ the extent of delocalization in Al₃Bi is still substantial. This can be seen from a vantage point above the ring in the HOMO-1 in Figure 3-4.
Aromatic stability is linked to the filling of molecular $\sigma$ and $\pi$ orbitals, and will disappear if any additional electrons are present. A study of the electronic structure of the Al$_3$Bi$^-$ anion demonstrates this. Figure 3-2 shows that Al$_3$Bi$^-$, unlike Al$_3$Bi, has a ground state structure that is non-planar. This geometric distortion significantly affects the electronic structure. Figure 3-3(B) plots the one-electron levels and molecular orbitals of Al$_3$Bi in the ground state geometry of Al$_3$Bi$^-$. The most apparent difference in the electron levels in the non-planar geometry is the stabilization of the delocalized $\pi$ orbital. In the planar geometry this orbital has B1 symmetry and is degenerate with the HOMO, as seen in Figure 3-3(A). When the geometry is altered in Figure 3-3(B), the $\pi$ molecular orbital is converted to the HOMO-1 with A’ symmetry, and is substantially lower in energy than the HOMO. Furthermore, the calculated HOMO-LUMO gap of the neutral species in the non-planar geometry is reduced to 0.52 eV (from 1.69 eV in the planar configuration). The reduced gap can be observed experimentally in the anion photodetachment spectrum (Figure 3-1), as the peaks in each photoelectron spectrum probe the electronic structures of the neutral species in the anion geometries. The experimental value for the HOMO-LUMO gap of Al$_3$Bi in the anionic, non-planar geometry is 0.58 eV, shown by the separation
between the peaks in the spectrum for Al$_3$Bi$^-$ (Figure 3-1). It should be noted that the calculated HOMO-LUMO gap of the ground state of Al$_3$Bi$^-$ itself is only 0.72 eV.

In order to examine the effects of geometry on the electronic structure of Al$_3$Bi further, the planar ground state structure was forced into a theoretical compact geometry. Figure 3-3(C) shows the one-electron levels and molecular orbitals of Al$_3$Bi in a pyramidal C$_{3v}$ geometry. In this compact structure, the seven orbitals (14 electrons) re-arrange themselves into an electronic structure that roughly resembles the energy levels and geometries within an open shell Jellium framework. As 18 electrons are needed for a shell closing, the addition of 4 more electrons to the system would satisfy a complete Jellium configuration. The molecular orbital diagram, shown in Figure 3-3(C), depicts both the occupied and unoccupied levels of the pyramidal Al$_3$Bi. The LUMO is almost degenerate with the HOMO, and the addition of four electrons would occupy the LUMO and LUMO+1 levels. In the 14-electron system shown, the energy gap between the LUMO+1 and the LUMO+2 is greater than 2 eV. It is reasonable to assume that if the LUMO and LUMO+1 in Figure 3-3(C) were filled, an Al$_3$Bi cluster with C$_{3v}$ geometry and 18 electrons could be stable within a Jellium framework.
Figure 3-5: One-electron levels, isosurfaces (isovalue = 0.001 a.u.), and symmetry of the molecular orbitals for the Al$_3$Bi cluster (A), for the Al$_3$Bi$^-$ cluster anion (B), and for the Al$_3$Bi$^{2-}$ cluster dianion (C). The superscripts indicate spin multiplicity, the continuous lines represent occupied levels, the dotted lines correspond to single unfilled states, the degeneracy is marked next to each level and the arrows indicate the majority (up) and minority (down) spin states. Optimized ground state geometries and symmetries of the neutral, anionic and dianionic Al$_3$Bi cluster are given respectively in the panels (D) and (E) and (F). Bond lengths are given in Angstroms.

Above we have shown how the addition of electrons to Al$_3$Bi can drive the cluster system away from aromatic stability and towards Jellium stability. In Al$_3$Bi, the 6 electrons occupying the $p$-states lead to the aromatic stability, shown in Figure 3-3(A). Furthermore, the inner core states are well-separated in energy from the three levels nearest to the delocalized orbitals. With the separation between deeper $s$-states and the upper valence manifold in mind, we added two
extra electrons to the neutral Al₃Bi cluster in order to examine if the set of 8 outer valence electrons would be near-degenerate, and consequently lead to a stable, 8 valence electron cluster within the Jellium scheme that has a large HOMO-LUMO gap. The examination of the electronic and geometric structures would then indicate the mechanism(s) for stabilization, similar to the study of Al₃Bi in a pyramidal geometry above. **Figure 3-5** shows the evolution of the one-electron levels, molecular orbitals, and ground state geometries of the neutral, anion, and dianion forms of the Al₃Bi cluster. With each electron that is added to the neutral cluster, rearrangement/reordering of the electronic energy levels occurs, as would be expected for a system moving away from aromatic stability and towards Jellium stability. In **Figure 3-5(A)** the (B1) HOMO-1 in the neutral Al₃Bi, responsible for \( \pi \) aromaticity, is energetically degenerate with the (A1) HOMO. **Figure 3-5(B)** shows that the (B1) HOMO-1 orbital in Al₃Bi is displaced in Al₃Bi⁻, where it becomes the (A') HOMO-3. There is at least 0.5 eV separating this \( \pi \) orbital from the HOMO in Al₃Bi⁻. Since the displaced orbital is lower in energy, it is expected to contribute less to the overall valence makeup of the anionic cluster. Adding a second electron further displaces this orbital, which now becomes the (B1) HOMO-3 in **Figure 3-5(C)**. In the dianion, the difference in energy between the (B2) HOMO and (B1) HOMO-3 is well over 1 eV. These results show that just adding electrons to Al₃Bi is not enough to achieve a Jellium-like electronic shell structure. First, the HOMO-LUMO gap is only 0.73 eV, which is not a large value when compared to the HOMO-LUMO gap of a cluster with true Jellium stability, such as Al₁₃⁻ (1.87 eV).⁴² Second, the geometry of the Al₃Bi²⁻ dianion is planar, as seen in **Figure 3-5(F)**. The two-dimensional geometry is a result of the Coulomb repulsion between the extra electrons. The molecular geometry of Al₃Bi²⁻ is at odds with the requisite Jellium compact geometry. As a consequence, a less-than-expected increase in the HOMO-LUMO gap is seen, and the molecular orbitals of Al₃Bi²⁻ do not approach the electronic structure predicted by the Jellium model.⁴³
Despite the results seen with the above approach, an additional study of adding electrons without the aforementioned Coulomb repulsion was performed. The mechanism(s) of stability for the Al$_3$Bi$_2^-$ in a compact geometry was investigated with the use of adding alkali metal atoms to the cluster. The role of each additional alkali atom was to donate the requisite electrons without modifying the overall charge. To this effect, we studied the isoelectronic sixteen-electron Al$_3$BiNa` and Al$_3$BiNa$_2$ clusters, in which each Na atom is expected to contribute an electron to the upper manifold because of its low ionization potential. The results are shown in Figure 3-6, which presents the one-electron levels, molecular orbitals, and ground state geometries of the Al$_3$Bi, Al$_3$BiNa`, and Al$_3$BiNa$_2$ clusters. Interestingly, in the Al$_3$BiNa` cluster, the Na atom is above the plane in the ground state structure, and the Al$_3$Bi plane becomes bent as shown in Figure 3-6(E). Because of this condensed geometry, the molecular orbitals rearrange dramatically to produce orbitals beginning to resemble a three-dimensional electron gas, seen in Figure 3-6(B). The resulting HOMO-LUMO gap for the anion is 0.78 eV, which is larger than the gap observed for Al$_3$Bi$_2^-$ (0.73 eV). Since the electron count is the same for both Al$_3$Bi$_2^-$ and Al$_3$BiNa`, the enhancement in stability of the latter can be attributed to its compact geometry. The addition of another Na atom to form Al$_3$BiNa$_2$ further deforms the structure, shown in Figure 3-6(F), with one Na atom above the heterocyclic Al$_3$Bi unit, and the other on top of an Al-Bi bond. In Figure 3-6(C), it is clear that the valence molecular orbitals are more delocalized in Al$_3$BiNa$_2$ than those in Al$_3$Bi$_2^-$ (Figure 3-5(C)). Contrary to Al$_3$Bi$_2^-$, the four uppermost doubly-occupied energy levels in Al$_3$BiNa$_2$ group together to accommodate 8 electrons and, in turn, enhance the stability of the sixteen-electron cluster. This is evinced by a large HOMO-LUMO gap of 1.12 eV. From these findings we deduce that the mechanism(s) for a cluster to approach Jellium stabilization will only occur with a proper electron count and a compact geometry, while aromatic stabilization in these small clusters will only occur with a proper electron count and planar geometry.
Figure 3-6: One-electron levels, isosurfaces (isovalue = 0.001 a.u.), and symmetries of the molecular orbitals for the Al₃Bi cluster (A), for the anionic Al₃BiNa⁻ cluster (B), and for the Al₃BiNa₂ cluster (C). The superscripts indicate spin multiplicity, the continuous lines represent occupied levels, the dotted lines correspond to single unfilled states, the degeneracy is marked next to each level and the arrows indicate the majority (up) and minority (down) spin states. Optimized ground state geometries and symmetries of the Al₃Bi, of the anionic Al₃BiNa⁻ and of the Al₃BiNa₂ clusters are given respectively in the panels (D) and (E) and (F). Bond lengths are given in Angstroms.

An independent test of aromatic behavior is the Nucleus-Independent Chemical Shift (NICS), proposed by Schleyer and co-workers.⁴⁴ It provides a magnetic criterion to mirror the ring current and hence, identify aromaticity. Systems with negative NICS values tend to be
aromatic, while systems with positive NICS values may be classified as antiaromatic. Khanna et al. calculated the NICS values using the same theoretical model in the Gaussian 03 program.\textsuperscript{45} It was found that Al\textsubscript{3}Bi gives rise to a large, negative NICS value at the center of the ring (-32.19 ppm), and this value increased as the NICS value was calculated above the plane, again affirming the aromatic character. This was also true for the charged clusters, Al\textsubscript{3}Bi\textsuperscript{-} and Al\textsubscript{3}Bi\textsuperscript{+}, although the neutral had the most negative NICS value. These results are presented in Table 3-2.

Table 3-2: Nucleus-Independent Chemical Shift (NICS) values of Al\textsubscript{3}Bi\textsuperscript{+}, Al\textsubscript{3}Bi, and Al\textsubscript{3}Bi\textsuperscript{-} in ppm. A ghost atom was placed at the ring center in the molecular plane, and 0.5, 1.0, and 1.5 Å above the plane, respectively. For the cases of non-planar systems (Al\textsubscript{3}Bi\textsuperscript{-}), the values below the plane are also reported.

<table>
<thead>
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<th>NICS(0.5)</th>
<th>NICS(1.0)</th>
<th>NICS(1.5)</th>
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<td>-12.3</td>
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<td>-31.25</td>
<td>-25.62</td>
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<tr>
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<td>-21.27</td>
<td>-19.64</td>
<td>-14.44</td>
</tr>
<tr>
<td>Al\textsubscript{3}Bi\textsuperscript{- below}</td>
<td>-14.08</td>
<td>-11.65</td>
<td>-9.15</td>
<td></td>
</tr>
</tbody>
</table>

To further emphasize the correlation between Al\textsubscript{3}Bi and Al\textsubscript{4}\textsuperscript{2-}, the vibrational modes of alkali metal interactions were examined. The clusters Al\textsubscript{4}Li\textsuperscript{-} and Al\textsubscript{4}Li\textsubscript{2} have been previously found to exhibit floppy modes, due to the large fluxionality of the Li atom(s).\textsuperscript{46} These modes lead to low vibrational frequencies for Al\textsubscript{4}Li\textsuperscript{-} and Al\textsubscript{4}Li\textsubscript{2} of 96 and 63 cm\textsuperscript{-1}, respectively, corresponding to movement of the lithium atom(s). For Al\textsubscript{4}Li\textsuperscript{-}, the frequency of 96 cm\textsuperscript{-1} represents the Li atom hopping to the corners and back to the position on top of the ring center, and in Al\textsubscript{4}Li\textsubscript{2} the vibrational frequency of 63 cm\textsuperscript{-1} is a consequence of the collective motions between Li atoms. In our case, vibrational frequencies of 40.3 and 27.9 cm\textsuperscript{-1} were found, corresponding to the movement of the Na atom(s) in Al\textsubscript{3}BiNa\textsuperscript{-} and Al\textsubscript{3}BiNa\textsubscript{2}, respectively, indicating a comparable fluxional nature in these clusters.
Figure 3-7 shows the molecular orbitals and electron levels for Al₃Bi, which has a suitable geometry and electron count for a completely filled shell described by the Jellium model. The orbitals are consistent with what is expected for a 20-electron cluster that exhibits Jellium stabilization, which ideally has a 1s², 1p⁶, 1d¹⁰ and 2s² electronic configuration. As mentioned above for Al₃Bi in a hypothetical C₃ᵥ symmetry, the lowest energy occupied orbital (A’) in Al₅Bi represents the Jellium 1s² level, and the next three levels make up the Jellium 1p⁶. The 1d¹⁰ and 2s² levels in Al₅Bi are mixed, but there are enough electrons to fully occupy both states. Of the six upper-valence orbitals, the (A’) HOMO-3 in Figure 3-7 has the most character from the Jellium 2s² level. This is implicit from its distorted spherical shape. The rest of the six upper valence orbitals have the most d-character. As shown in Figure 3-2, the structure is three-dimensional and compact, meeting the requirement for Jellium stability. The electron count (20) combined with a compact, three-dimensional geometry makes the stable Al₅Bi a possible superatom candidate.
Figure 3-7: One-electron levels, isosurfaces (isovalue = 0.001 a.u.), and symmetries of the molecular orbitals for the 20-electron Al₅Bi cluster. The superscript indicates spin multiplicity, the continuous lines represent occupied levels, the dotted lines correspond to single unfilled states, the degeneracy is marked next to each level and the arrows indicate the majority (up) and minority (down) spin states.

As an added test for the stability of Al₃Bi and Al₅Bi, we examined the energetics of formation for AlₙBi clusters. One method employed was to examine the gain in energy as successive Al atoms are added to a Bi atom. Another method was to calculate the binding energy of a Bi atom to Alₙ (n = 1-6) clusters. The results of these investigations are shown in Figure 3-8. Note that in both cases, Al₃Bi and Al₅Bi emerge as uniquely stable. Considering the energy
gains from Al atom addition, there are large values for the formation of Al₃Bi and Al₅Bi from their preceding sizes, and only small gains in energy in growing to the next size. Additionally, it is shown in Figure 3-8 that a Bi atom binds more strongly to Al₃ and Al₅, again indicating the enhanced stability of these particular mixed clusters.

![Graph](image)

**Figure 3-8:** Calculated removal energies (in eV) for aluminum ($\Delta E_{Al}$) and bismuth ($\Delta E_{Bi}$) from the neutral AlₙBi clusters.

The present study demonstrates the delicate relationship that electron count and molecular geometry have in stable cluster systems. Our measures of stability include electron affinities, ionization potentials, HOMO-LUMO gaps, and formation energies. Within a Jellium picture, it has been shown that clusters with both exactly the number of electrons needed to fill
the electronic shells, and a condensed geometry are extremely stable and chemically inert.Clusters that have stability described by the Jellium model may be regarded as superatoms, resembling atoms of the periodic table. The inclusion of aromaticity as a free electron gas-like stabilizing force suggests that parallels may be drawn between the two mechanisms. Aside from the more conventional Jellium shell closings (2, 8, 18, 20 ...), occurring with compact geometries, additional shell closings exist for planar arrangements (i.e. 2, 6, 10, 14 ...) that can be described with aromaticity. It is intriguing that there is an all-metal system, namely Bi-doped Al clusters, in which the atoms can combine to form an aromatic, inert species (Al$_3$Bi) at one size, and a filled-shell Jellium cluster (Al$_5$Bi) at another size. While superatoms have demonstrated their use towards becoming building blocks in a new type of chemistry, all-metal aromatic clusters should be included as another important constituent.

### 3.5 Conclusions

The combination of anion photoelectron spectroscopy and theoretical computations from VCU has allowed the study of bismuth-doped aluminum clusters. Low adiabatic electron detachment energies were observed for both Al$_3$Bi, an all-metal aromatic cluster, and Al$_5$Bi, a Jellium superatom candidate. These species also exhibited large HOMO-LUMO gap sizes, a further testament to their unique stability, and give insight into how electron shell counts and/or closings work synergistically with geometry. We have shown that the planar Al$_3$Bi and the three-dimensional, compact Al$_5$Bi exhibit the type of stability that can be exploited in the construction of cluster-based materials.

Furthermore, benzene is well-known for its ability to form sandwich complexes M(C$_6$H$_6$)$_2$, and we believe the planar Al$_3$Bi might behave in a similar fashion. We also envision the capability of forming three-dimensional metal clusters that display unique properties derived
from aromatic behavior. It would be interesting to study the reactivity of Al₃Bi, similar to those performed on other small mixed-metal clusters. A neutral all-metal aromatic may retain its geometric and electronic structure when undergoing electrophilic substitution reactions, much like benzene. While the electronic and geometric structures indicate that Al₃Bi is a Jellium cluster, future reactivity studies will be required to demonstrate that it is indeed a superatom. Because of their unique stability, the all-metal aromatic Al₃Bi and the potential superatom Al₅Bi show promise for being stable in condensed phases. It is hoped that the relationship between different mechanisms for electron stability will lead to the design of materials with novel chemical and magnetic properties.

3.6 References

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4.1 Abstract

Experimental photoelectron spectroscopy combined with computational results show that tri-niobium carbide clusters Nb_3C_n^+ (n = 5-10) are stable in multiple isomeric forms. All structures found are three-dimensional, with some clusters preferentially forming Nb_3 triangular units, and others favoring Nb-C bonding. We provide evidence of a C_2 bridging unit being important in most ground state structures, and discuss a possible formation mechanism for Nb_3C_n^+ clusters.

4.2 Introduction

Metal carbide clusters show excellent potential for the synthesis of cluster-based materials with unique, tailored properties. Metallocarbohedrenes (Met-Cars), with stoichiometry M_8C_{12} with M being one or more of several early transition metals, are of particular interest towards these means due to their enhanced stability. Metallofullerenes and metal carbide nanocrystals have also been shown as important potential precursors to future nanomaterials. Thus far, the structures and growth mechanisms for many of these metal carbide clusters are not well understood. In particular, the electronic structure of metal carbide clusters must be characterized in order to understand their unique properties that differ from both their atomic and bulk counterparts.
The Met-Car was first observed in our research group during experiments of the dehydrogenation of methane by titanium.\textsuperscript{1} Its discovery has not only identified a new class of metal carbide clusters, but has motivated a number of investigations to elucidate the physical features of metal carbide clusters, including structural and electronic properties.\textsuperscript{3} An important finding was that the Met-Car exhibits distinctive trends in ionization potential as well as electron affinity.\textsuperscript{3,6-8} Muckerman and co-workers have shown its enhanced catalytic properties for pollution abatement through density functional calculations,\textsuperscript{9} and we have observed substantial delayed electron emission characterizing ionization of the Met-Car.\textsuperscript{6,8} In order to gain more insight into the evolution of nanoscale properties, we have continued our studies of potential building blocks of the Met-Car though interrogation of their electronic structures via anion photoelectron spectroscopy.\textsuperscript{10,11}

Photoelectron spectroscopy (PES) of mass-selected anions is an experimental technique that is well-suited for studying the electronic properties of clusters in the gas phase. This technique also has the ability to distinguish between isomers not seen though standard mass spectrometric methods. Anion PES involves a single-photon ionization event, and thus allows one to gain information about the energetics of the neutral cluster ground and lower-excited states. With this technique we have recently taken on studies of vanadium carbide clusters\textsuperscript{10} as well as di-niobium carbide clusters.\textsuperscript{11} In the present work, we focus on the tri-niobium carbide series of clusters, Nb\textsubscript{3}C\textsubscript{n} \textsuperscript{- (n = 5-10). Our group has shown previously that variations in source conditions can produce niobium carbide versions of both cubic nanocrystalline structures and Met-Cars.\textsuperscript{12} This study continues our efforts toward the ability to identify and synthesize nanoscale, cluster-based materials.

Some additional previous work on niobium-carbon interactions already exists. Wang and co-workers have made an extensive study of the electronic and vibrational properties of mono-niobium carbide clusters, NbC\textsubscript{n} \textsuperscript{- (n = 2-7).\textsuperscript{13} Using anion photoelectron spectroscopy, they
observed two structure types: NbC$_2^-$ and NbC$_3^-$ were shown to have cyclic structures, NbC$_6^-$ and NbC$_7^-$ to have linear structures, and NbC$_3^-$ and NbC$_4^-$ to display evidence of both cyclic and linear isomers. Metha et al. recently studied niobium carbide clusters of stiochiometries Nb$_3$C$_n$ ($n = 1$-$4$) and Nb$_4$C$_n$ ($n = 1$-$6$) with photoionization efficiency spectroscopy and found excellent agreement with structures determined from density functional theory.\textsuperscript{14} Jarrold and co-workers performed ion mobility experiments that showed fullerenes have the ability to incorporate niobium atoms by carbon replacement.\textsuperscript{4,15} Most notably, Harris and Dance performed an extensive density functional investigation of Nb$_3$C$_y$ isomers and discovered a variety of structural motifs.\textsuperscript{16} Niobium interacts with carbon covalently in the bulk phase to form a refractory material, and along with zirconium carbide, it is used as a refractory coating in nuclear reactors.

The present study of Nb$_3$C$_n^-$ clusters continues our interest in the versatility of niobium carbides as well as the future synthesis of cluster-based materials.

In this work, we present photoelectron spectra of carbon-rich tri-niobium carbide clusters Nb$_3$C$_n^-$ ($n = 5$-$10$) obtained at 308 nm. We also incorporate density functional theory calculations by our collaborators (Khanna \textit{et al.} at Virginia Commonwealth University) to identify stable isomers that are synthesized in our laser vaporization source. Our results show the ability of tri-niobium carbide clusters to form multiple stable isomers, specifically structures which are stabilized through Nb-C bonding and others that favor Nb-Nb bonds.

\textbf{4.3 Experimental and Computational Methods}

The experiments of tri-niobium carbides Nb$_3$C$_n^-$ ($n = 5$-$10$) were carried out using a mass spectrometer, based on the design first conceived by Wiley and McLaren,\textsuperscript{17} in tandem with a magnetic bottle time-of-flight (MB-TOF) PES apparatus, the details of which have been described in Chapter 2.\textsuperscript{10} In short, Nb$_3$C$_n^-$ anions are created with a pulsed laser vaporization
supersonic cluster beam source at a frequency of 10 Hz. The second harmonic of a Nd:YAG laser is focused down to a 2 mm spot on a pure niobium rod (0.25-in diameter) that is simultaneously rotating and translating *in vacuo*. A mixture of methane seeded in helium gas, with a typical pressure of 3-5 atm, is delivered in a short and intense pulse by a pulsed molecular beam valve mounted perpendicularly to the niobium rod. The CH$_4$ in the helium carrier gas reacts with niobium and cools in the laser-induced plasma to form Nb$_{m}$C$_{n}$ clusters. The anionic clusters are extracted at 90° with a high voltage pulse (0.7-1.5 keV) and detected downstream with multi-channel plates. Clusters of interest were subjected downstream to a pulsed XeCl$_2$ excimer laser (308 nm) in a magnetic bottle. The magnetic bottle, first employed by Kruit and Read,\textsuperscript{18} consists of a strong magnetic field from a permanent magnet (in our case 1.2 Tesla) opposing a weak field due to a solenoid (1 mT, 70-in in length). Photoelectrons are collected and detected with a Z-stack electron detector. Photoelectron spectra were obtained at a repetition rate of 10 Hz, and were background-subtracted. The electron-TOF spectra were converted to binding energy by calibration with the well-known Cu$^-$ spectra, obtained during the same experiment.

In order to determine the structures, Khanna *et al.* performed first principle electronic structure investigations in a generalized gradient approximation (GGA) within the density functional formalism.\textsuperscript{19} The actual calculations were performed using the deMon2k software package.\textsuperscript{20} A variational fitting of the Coulomb potential was employed to avoid the calculation of four-center electron repulsion integrals.\textsuperscript{21,22} The numerical integration of the exchange-correlation energy and potential was performed on an adaptive grid.\textsuperscript{23} The functional proposed by Perdew, Burke, and Ernzerhof was used to incorporate the exchange and correlation effects.\textsuperscript{24} For the carbon atoms a DZVP basis set was used,\textsuperscript{25} while the Nb atom was described using the 13-electron scalar quasi-relativistic electron core potential (QECP) proposed by Andrae *et al.*\textsuperscript{26} in combination with the LANL2DZ valence basis set.\textsuperscript{27} An auxiliary density was used for both C and Nb. The auxiliary density was expanded in primitive Hermite Gaussian functions using the
A2 auxiliary function set for carbon atoms and the GEN-A2* auxiliary function set was used for niobium. A half-numeric integrator was employed for the ECP integrals\textsuperscript{28} In order to avoid getting trapped in local minima of the potential energy surfaces, multiple initial configurations were used and their geometries were fully optimized.

4.4 Results and Discussion

The photoelectron spectra of Nb\textsubscript{3}C\textsuperscript{n}− (n = 5-10) at 308 nm (4.03 eV) are presented in Figure 4-1(A-F) with binding energy (in eV) plotted on the abscissa. As identified via theoretical calculations by our collaborators below, these spectra portray electronic transitions from the anions to the ground state, and in some cases low-lying excited states, of the neutral product species. Vibrational “hot bands” account for the width of many features in the spectra for the polyatomic isomers. However, our instrument is not capable of resolving these features, so they are not specifically reported. Our instrument is able to mass-select clusters to study, but is unable to separate structural isomers of individual masses. As seen in Figure 4-1, there are multiple prominent features in the photodetachment spectra for individual tri-niobium clusters, which is indicative of multiple structural isomers present in the molecular beam. This can be attributed to the laser vaporization cluster source. The source is capable of generating isomers that are higher in energy than the “coldest,” ground state structures, and in many cases their individual detachment energies are detected in the spectra.
Figure 4-1: Anion photoelectron spectra of Nb$_3$C$_n^-$ ($n = 5$-$10$) clusters at 308 nm.
Table 4-1 gives the measured adiabatic electron detachment energy (AEDE) and vertical electron detachment energy (VEDE) for each experimentally observed anionic cluster isomer. The AEDE is determined from a linear regression of the “leading edge” of the peak at low binding energy, and the VEDE by the most intense point in a given feature.

Table 4-1: Experimental (Exp.) adiabatic electron detachment energies (AEDE) and vertical electron detachment energies (VEDE) for Nb$_3$C$_n^-$ observed features. The experimental uncertainty for each measurement is 0.2 eV.

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Figure 4-2 depicts calculated stable structures that are relevant to the experimental findings. Many bonding arrangements were considered, but only three-dimensional structures were found to be energetically favorable for tri-niobium carbide clusters Nb$_3$C$_n^-$ ($n = 5-10$). The atomization energy (A.E.), the energy required to separate each structure into its individual
atoms, is listed for each structure, and is used as a general measure of stability. The vertical detachment energy (VDE) is also listed for comparison with the photoelectron spectra. The VDE represents the energy (in eV) for a vertical transition from the anion electronic ground state to the neutral species with the same geometry.

Figure 4-2: Structures of calculated isomers of Nb$_3$C$_n^-$ ($n = 5$-10) clusters. Written beneath each isomer are the atomization energies (AE), spin states, and vertical electron detachment energies (VDE).

![Figure 4-2: Structures of calculated isomers of Nb$_3$C$_n^-$ ($n = 5$-10) clusters. Written beneath each isomer are the atomization energies (AE), spin states, and vertical electron detachment energies (VDE).](image)

The experimental detachment spectrum of Nb$_3$C$_5^-$ is shown in Figure 4-1(A). We observe two features. The dominant peak corresponds to an AEDE of 1.88 eV and a VEDE of 2.30 eV. The measured vertical detachment energy (VDE) is in close agreement with the theoretical structure in Figure 4-2(A) having a VDE of 2.26 eV. This cluster with C$_{2v}$ symmetry
contains a three-membered niobium ring, where each niobium atom is bonded to the others. The niobium atoms are separated by 2.6 Å, making an equilateral triangle. One of the carbon atoms caps the triangular niobium unit, and the other four carbons take bridging positions, with Nb-C-C-Nb bonding units. This latter type of metal carbon bonding seems important in Met-Car precursors, where the MC2 unit is thought to be a major building block.12 The tail in the major feature at low binding energies is either due to hot bands of excited vibrational states within the ground electronic state of the isomer in Figure 4-2(A) or the presence of the isomer shown in Figure 4-2(B). This isomer of Nb3C5− is absent of Nb-Nb bonding, and has a theoretical VDE of 1.70 eV. Due to overlap with the main feature, it is difficult to ascertain if that isomer is present. Because the triangular niobium structure in Figure 4-2(A) is calculated to be more stable than that in Figure 4-2(B) by 0.95 eV, it is most likely that the low binding energy “tail” is a result of excited vibrational states of the structure in Figure 4-2(A).

Nb3C6− is the smallest member of the triniobium carbide series studied in which there is clear evidence of multiple isomers. The photoelectron spectrum in Figure 4-1(B) has multiple features that potentially correspond to several different isomeric forms of the cluster. The most stable theoretical structure, given in Figure 4-2(C), most likely corresponds to the high binding energy feature in the spectrum at 3.03 eV. The calculated VDE for the structure in Figure 4-2(C) is 2.79 eV. This isomer contains only Nb-C and C-C bonds. The most intense feature for Nb3C6− is observed experimentally at 2.47 eV, and is within experimental uncertainty to the energy of the theoretical structure in 2(D). As seen for the dominant isomer for Nb3C5−, there is a central triangular Nb3 unit. This also holds true for the theoretical structure in Figure 4-2(E), for which the theoretical VDE of 2.07 eV is close to the experimental value of 2.20 eV. Due to overlap of this peak with the major feature at 2.47 eV, however, the observed feature is poorly resolved. All three Nb-Nb bonds in Figure 4-2(E) have a calculated length of 2.7 Å. This isomer is reminiscent of the “wheel” structural motif found by Harris et al. in calculated structures of
neutral Nb$_2$C$_y$ clusters. It comes as no surprise that the small differences in binding energies for these isomers correspond to subtle structural differences. Finally, the minor feature with an observed VEDE of 1.74 eV indicates the small presence of the structure in Figure 4-2(F), which contains two Nb-Nb bonds.

**Figure 4-1(C)** shows the spectrum of Nb$_3$C$_7^-$ at 308 nm, and is one of the least convoluted photoelectron spectra in the triniobium carbide series studied. Additionally, this cluster stoichiometry consistently has the highest abundance in our mass spectra. The observed VEDE of 3.31 eV is close to the calculated value of 3.40 eV for the most stable isomer based on atomization energy. One may envision this isomer as the addition of one bridging carbon atom to the most stable structure found for Nb$_3$C$_6^-$ in Figure 4-2(C), forming a third Nb-C-C-Nb subunit. This structure is also absent of bonds between the niobium atoms. The low binding energy peak has an observed VEDE of 2.33, which lies in good agreement with the theoretical value of 2.25 eV for the structure in Figure 4-2(H). This isomer features a triangular Nb$_3$ motif, similar to the calculated structures for Nb$_3$C$_6^-$ in Figure 4-2(D-E).

**Figure 4-1(D)** gives the experimental photoelectron spectrum of Nb$_3$C$_8^-$.

**Figure 4-2(I)** shows the most stable theoretical structure with a VDE of 3.34, which is observed experimentally as the high binding energy peak at 3.36 eV. This three-dimensional, compact structure contains a triangular Nb$_3$ unit. The feature at 2.99 eV VEDE might correspond with the calculated energy of 3.29 for the structure in Figure 4-2(J), and is akin to the structures in Figure 4-2(C) (Nb$_3$C$_6^-$) and Figure 4-2(G) (Nb$_3$C$_7^-$). The commonality lies in the “capping” carbon atom and the Nb-C$_n$-Nb bridges between the metal atoms. The low energy, low intensity feature observed has a VEDE of 2.18 eV, and is most likely evidence of a relatively small abundance of the isomer in Figure 4-2(K) which has calculated vertical detachment energies of 2.23 eV and 3.04 eV.

The photoelectron spectrum for Nb$_3$C$_9^-$ is shown in Figure 4-1(E). The most prominent feature is observed to have a VDE of 2.97 eV. The theoretical structure shown in Figure 4-2(L)
is calculated to have a VDE of 3.10 eV. Although this is not the most stable isomer based on its calculated atomization energy, its prominence in the spectra suggests that it has a relatively large abundance. The structure also features a “capping” carbon atom that is bonded to each of the three niobium atoms, in accordance with structural isomers calculated for Nb$_3$C$_n^-$ ($6 \leq n \leq 8$). The low binding energy feature with low intensity is attributed to the structure shown in Figure 4-2(M), with a calculated VDE of 2.31 eV. This structure is only 0.13 eV more stable in terms of atomization energy, and has a triplet spin state. Because of its high spin state, it is predicted to have an additional peak in the photoelectron spectrum, namely an M+1 VDE. The M+1 feature is calculated to be at 3.89 eV, which is beyond our detection capabilities because of its close proximity to our photodetachment limit of 4.03 eV. It should be noted that Figure 4-2(N) shows the most stable structure from calculations; however the associated VDE of 3.96 is also too high for our spectrometer to detect. None of the stable structures found for Nb$_3$C$_9^-$ contain all-metal bonds.

Figure 4-1(F) shows the experimental photoelectron spectrum at 308 nm of Nb$_3$C$_{10}^-$. Three features are observed: one broad feature with a VEDE of 2.79 eV, and two sharper peaks at 3.24 and 3.42 eV, respectively. The most stable theoretical structure is given in Figure 4-2(O). The calculated VDE of the Nb$_3$C$_{10}^-$ isomer is 3.56 eV, which is in reasonable agreement with the high binding energy feature in the experimental section. Furthermore, the structure follows the types seen for smaller cluster anions in Figures 4-2(C), (G), (K), and (L), featuring a central unit of one carbon atom and three niobium atoms, with the carbon atom at the cap of a triangular pyramid. The second-most stable structure in Figure 4-2(P) contains a triangular Nb$_3$ unit with carbon atoms making up the rest of the three-dimensional structure. The sharp peak at 3.24 eV might be evidence of this isomer. The broad feature at low binding energy in the experimental spectrum can be attributed to the structure in Figure 4-2(Q). The calculated atomization energy of this isomer is 1.99 eV lower than the most stable structure for Nb$_3$C$_{10}^-$ (Figure 4-2(O)), and
has a triplet spin state. While many geometries were considered for this anionic cluster, the one shown in Figure 4-2(Q) was the only one with a calculated VDE that was below 3 eV. Thus, it is most likely only formed under high-energy plasma conditions in our laser vaporization source.

To summarize, the upper-valence electronic states of a series of Nb$_3$C$_n^-$ ($n = 5-10$) clusters were observed in photoelectron spectroscopy experiments, and first-principle electronic structure calculations were performed to aid in the assignment of the collected spectra. Most of the tri-niobium clusters studied showed evidence of multiple isomers, specifically Nb$_3$C$_n^-$ with $n = 6-10$. These findings are in agreement with previous experimental studies of both mono-niobium and di-niobium carbide clusters.$^{11,13}$ Zhai et al. found evidence of two isomers in both NbC$_4^-$ and NbC$_5^-$.

The authors attributed the low binding energy features in photoelectron spectra to cyclic isomers, and higher binding energies to linear isomers. We have previously examined di-niobium carbide in our laboratory, and the findings suggested a similar trend. Both linear and three-dimensional isomers were found for Nb$_2$C$_n^-$ where $n = 4-9$, with the exception of Nb$_2$C$_8^-$, where evidence of only one, three-dimensional structure was observed. Each of the aforementioned examinations suggest that a niobium atom can substitute for a carbon atom in linear structures, mostly due to similarities between the electronic structures of pure carbon clusters of small sizes with mono- and di-niobium clusters.

In the current study we propose two major structural motifs as well. In contrast to smaller niobium carbide clusters studied, there is no evidence of linear structures for anionic tri-niobium carbide clusters from calculations. All Nb$_3$C$_n^-$ clusters synthesized in our laser vaporization source are three-dimensional structures. Tri-niobium carbide anionic cluster structures have been found to generally follow two major trends. One structural motif involves a central Nb$_3$ unit, in which the three niobium atoms are bound in a planar triangle. These isomers are referred to as triangular types. In the second general type, there are no metal-metal bonds, but the central unit
is a triangle pyramid, where a carbon atom “caps” the three niobium atoms in a pyramid arrangement. These isomers are referred to as capped types.

The $\text{Nb}_3\text{C}_n^-$ clusters with five, six, seven, eight, and ten carbon atoms have stable isomers of the triangular type. In $\text{Nb}_3\text{C}_5^-$ and $\text{Nb}_3\text{C}_8^-$, the Nb$_1$-containing isomers are the most stable structures found based on calculated atomization energy. Additionally, there is excellent agreement between theory and experiment for the triangular isomers, shown in Figure 4-3. For comparison, one larger discrepancy between the experimental and theoretical vertical electron detachment energies is in the low binding energy isomer for $\text{Nb}_3\text{C}_6^-$, pictured in Figure 4-2(E), for which the calculated energy is within 6% of the experimental value (2.07 eV compared to 2.20 eV, respectively).

![Graph showing experimental (open squares) and theoretical (open diamond) values of VDE for $\text{Nb}_3\text{C}_n^-$ clusters with a triangular $\text{Nb}_3$ unit as a function of $n$.](image)

**Figure 4-3**: Graph showing experimental (open squares) and theoretical (open diamond) values of VDE for $\text{Nb}_3\text{C}_n^-$ clusters with a triangular $\text{Nb}_3$ unit as a function of $n$.

**Figure 4-4** charts the experimental and theoretical vertical detachment energies of capped $\text{Nb}_3\text{C}_n^-$ isomers, where a C atom resides on the face of the $\text{Nb}_3$ triangular unit. This structure type is favored for $\text{Nb}_3\text{C}_6^-$, $\text{Nb}_3\text{C}_7^-$, $\text{Nb}_3\text{C}_9^-$, and $\text{Nb}_3\text{C}_{10}^-$. The largest discrepancy for these isomers is for $\text{Nb}_3\text{C}_8^-$, where the experimental vertical detachment of 2.99 eV lies within
10% of the theoretical value. These structures for Nb$_3$C$_n^-$ ($n = 6$-$10$) clusters have experimental and theoretical vertical electron detachment energies above 2.75 eV, suggesting that these isomer types have higher electron affinities than their aforementioned isomer counterparts.

Figure 4-4: Graph showing experimental (open squares) and theoretical (open diamond) values of VDE for Nb$_3$C$_n^-$ clusters with a carbon-capped Nb$_3$ unit as a function of $n$.

Harris and Dance performed an extensive density functional theory investigation of neutral and cationic niobium carbide clusters, but for tri-niobium carbides only considered Nb$_3$C$_3$ and Nb$_3$C$_4$ stiochiometries. They found Nb$_3$ units in equilateral and isosceles triangles, with the most stable isomer for Nb$_3$C$_3$ containing the Nb atoms in an approximately equilateral triangle, and containing single C atom bridges. The structures they found had Nb-Nb bond distances that ranged from 2.6 to 3.1 Å for the neutral clusters. The carbon-rich triangular Nb$_3$C$_n^-$ clusters in the current study have similar calculated distances ranging from 2.6 to 3.0 Å. Dryza et al. obtained similar results from their studies of Nb$_3$C$_n$ ($n = 1$-$4$) clusters. Their DFT studies concluded that Nb$_3$C and Nb$_3$C$_2$ had lowest-energy isomers which contained an Nb$_3$ triangular unit. For Nb$_3$C$_3$, their calculated lowest-energy structure contained one C atom on the face of the Nb$_3$ unit (similar
to the capped type in the present study), and single carbon atoms bound across the Nb-Nb edges. They also found a lowest-energy isomer for Nb$_3$C$_4$ that has one C atom bound to the face of the triangular Nb$_3$ unit and the remaining C atoms bound across separate Nb-Nb edges. Based on their combined experimental and theoretical results, Metha and coworkers suggested that carbon-carbon bonding is energetically stable for Nb$_3$C$_n$ clusters when $n > 3$. The results from the present study are in general agreement.

The most stable structures for the majority of the Nb$_3$C$_n^-$ clusters studied include C$_2$ units that bridge between Nb atoms. Stability is determined by the calculated atomization energies (AE), which are given below each structure in Figure 4-2. The Nb$_3$C$_5^-$ cluster in Figure 4-2(A) has two of the bridging C$_2$ units, as well as a fifth C atom that is located on the face of a triangular Nb$_3$ unit. In going to the ground state structure (highest AE) for Nb$_3$C$_6^-$ in Figure 4-2(C), the Nb atoms are further separated and the additional C atom forms a third bridge between Nb atoms when compared with the aforementioned Nb$_3$C$_5^-$. When an additional carbon is added to form Nb$_3$C$_7^-$, the favored position is in creating a third C$_2$ bridging unit where a single carbon atom becomes positioned in Nb$_3$C$_6^-$ (see Figure 4-2(G)). In Nb$_3$C$_8^-$, the calculated structure with the highest AE in Figure 4-2(I) does not follow the same structural pattern as smaller Nb$_3$C$_n^-$ clusters. However, the calculated isomer shown in Figure 4-2(J) is similar to the ground state structure for Nb$_3$C$_7^-$, with the additional carbon atom altering one of the C$_2$ bridges and causing one Nb atom to have a coordination number of four. The isomer for Nb$_3$C$_8^-$ in Figure 4-2(J) is calculated to be less than 0.5 eV higher in energy than that in Figure 4-2(I). It is therefore reasonable that both isomers are stable and present in our experiments. In going to Nb$_3$C$_9^-$, the most stable conformation in Figure 4-2(N) has two C$_2$ bridging units. Moreover, the structure in Figure 4-2(L), which has a lower AE by only 0.25 eV, contains one C$_2$ unit and creates a second tetra-coordinated Nb atom when compared to the Nb$_3$C$_8^-$ isomer in Figure 4-2(J). Finally, the
most stable isomer for Nb₃C₁₀⁻ shown in Figure 4-2(O) is a symmetric structure with one C atom on the face of the triangular Nb₃ unit and each Nb atom bonded to three other carbon atoms.

Based on our combined experimental and theoretical results, we find that the formation mechanisms of Nb₃Cₙ⁻ (n = 5-10) clusters favor structures that have the three niobium atoms positioned in a triangular arrangement. Furthermore, a “capping” carbon that is positioned at the face of the triangular unit is present in lowest or near-lowest energy isomers. As carbon atoms are added to this four-atom unit, C₂ bridging units are favored. These findings are in good agreement with the previous theoretical and experimental studies of Nb₃Cₙ clusters. Further understanding of the formation mechanisms of Nb₃Cₙ clusters may come from theoretical and experimental PES studies of systems involving four or more niobium atoms. Additionally, IR photodissociation spectroscopy for metal carbide clusters, similar to those performed by Duncan et al., may yield complementary data that provide further insight into which isomers have the lowest electronic temperatures, as well as the ones that feature C₂ bridging units in the successive growth of clusters.

4.5 Conclusions

In conclusion, our joint experimental and theoretical studies have elucidated the electronic and geometric properties of carbon-rich tri-niobium cluster anions. We show evidence of multiple isomers, the presence of which are a consequence of high-temperature species formed from our laser vaporization source. The data suggests that the preferred structure for Nb₃Cₙ⁻ clusters involves a triangular Nb₃ unit with a single carbon atom bound to a face. Additional carbon atoms preferably form C₂ bridging units between metal atoms. Additional studies involving niobium-carbide systems with greater numbers of metal atoms will aid in the goal of
understanding the formation mechanisms of the Met-Car for its eventual condensed phase synthesis.

4.6 References


14. Dryza, V.; Addicoat, M. A.; Gascooke, J. R.; Buntine, M. A.; Metha, G. F., Threshold Photoionization and Density Functional Theory Studies of the Niobium Carbide Clusters Nb$_3$C$_n$ ($n = 1-4$) and Nb$_4$C$_n$ ($n = 1-6$). *J. Phys. Chem. A* **2008**.


5.1 Abstract

The hydration of formic acid molecules with protonated water clusters \([H^+(H_2O)_n, n = 3-27]\) is examined using a fast-flow reactor operated at temperatures below 150 K under well-defined thermal conditions. Analysis of the observed products reveals a propensity of the formic acid-water complexes studied to undergo nucleation, particularly when compared to pure water cluster cations. A noticeable absence of any “magic numbers” in the formic acid-water cluster distribution is explained by the ability of formic acid to alter the hydrogen-bonding network in protonated water clusters. We present experimental evidence that the presence of formic acid in water clusters allows for the facile propagation of hydroscopic growth on the molecular scale. The results are put into context with theoretical findings in previous literature regarding a cooperative bonding effect in neutral formic acid-water clusters of small sizes \([(H_2O)_n(HCOOH), n = 1-3]\). Additionally, an implementation of the Thompson model is used to understand the experimental results from a thermodynamic standpoint. We discuss some possible implications of these findings towards atmospheric nucleation processes.

5.2 Introduction

A nucleation process that is influenced by the presence of an ion, atom, or foreign molecule of different chemical composition from the bulk nucleating phase is deemed
heteromolecular nucleation.\textsuperscript{1} In contrast to homogeneous nucleation, the heteromolecular case is affected by additional forces on the molecular scale that may facilitate the formation of prenucleation clusters. In the atmosphere, it is likely that the formation of particles from low-volatility gases occurs from the growth of molecular clusters that involve two or more different chemical species.\textsuperscript{2} It has been proposed that atmospheric nucleation events are in reality heterogeneous nucleation events that originate with “prenucleation embryos” such as cluster ions, neutral clusters formed by ion-ion recombination, or small embryos formed from heteromolecular nucleation involving extremely low volatility products of gas-phase reactions.\textsuperscript{3,4} The embryos that are made up of preexisting clusters of molecules are often so small in size and number that they have not been measured. For example, Hoppel \textit{et al.} predicted that a cluster with a radius of 1 nm could act as a nucleus for the condensation of sulfuric acid and water at 60\% relative humidity and a sulfuric acid concentration of only 1.2 ppb, which is well below the concentrations required for homogeneous nucleation.\textsuperscript{5}

An increasing amount of attention has been given to carboxylic acids as important chemical constituents in the atmosphere.\textsuperscript{2,6-11} Formic acid is one of the most ubiquitous of the organic acids in both the aqueous and gaseous phases of the troposphere, as well as in aerosol particles.\textsuperscript{7} While much attention has been paid to the contributions of mineral acids as the dominant factors of acid-base chemistry in precipitation, HCOOH also contributes a significant amount to acid deposition over broad regions of North America,\textsuperscript{10} South America,\textsuperscript{6} and Europe.\textsuperscript{12} In fact, formic acid concentrations in the eastern United States have been measured to range from a few ppb to as high as 44.6 ppb.\textsuperscript{11,13} Organic material may be a major contributor to cloud condensation nuclei (CCN) formation, and if so it would be very valuable to further develop an understanding of the relationship between organic emissions and cloud droplet concentrations.\textsuperscript{14} Despite a great deal of recent investigation, the mechanisms that are involved in sustaining the proportionate concentration of HCOOH in our atmosphere are generally unknown.
An elegant theoretical study by Vaida and coworkers brought new insight into the role of HCOOH in aerosol formation mechanisms by modeling the structures of a single formic acid molecule with up to three water molecules. The results of their investigation revealed a so-called “cooperative bonding effect” that takes place in small formic acid-water complexes. The most energetically stable structure found at the B3LYP/6-311++G(d,p) level for formic acid with three water molecules [HCOOH-(H2O)3] contained water-water hydrogen bonds that were shorter than those for their calculated pure water tetramer [(H2O)4]. Additionally, they found that the binding energy (D0) of the aforementioned lowest-energy formic acid-water complex was lower in energy than the isolated monomers by 26.3 kcal mol\(^{-1}\), as compared to the water tetramer whose energy was only 18.6 kcal mol\(^{-1}\) lower than four isolated water molecules. Their findings concluded that formic acid has the ability to make water bond more strongly to itself in the four-molecule size regime. The authors postulated that the hydrated acid complexes studied could grow more easily on a molecular level than their pure water counterparts.

In the present work, ion-molecule reactions of protonated water clusters with formic acid are studied under well-defined thermal conditions and the reaction products are carefully examined. The results show that reactions of pure protonated water clusters [H+(H2O)\(_n\)] with formic acid molecules [HCOOH] lead to the formation of mixed-cluster ions having the general form H+(H2O)\(_n\)(HCOOH)\(_m\). There is a particular focus on the oft-studied clathrate-like structure, which for protonated water cluster ions is observed for H+(H2O)\(_{21}\). The results are compared with the formation of both pure protonated water clusters as well as methanol-water clusters, which have been examined in previous work published by our group. It was found that formic acid molecules, unlike methanol, do not replace water molecules in protonated clusters. Instead, there is evidence that the introduction of formic acid molecules to protonated water clusters causes the propagation of hydroscopic growth (nucleation) on the molecular scale. The experimental results
are discussed within the context of the findings by Vaida et al. for small, neutral formic acid-water complexes.\textsuperscript{15} Some possible atmospheric implications are also discussed.

5.3 Experimental Details

The experiments were performed in a flow tube reactor apparatus, a schematic of which is shown in Chapter 1 (Figure 1-3). Protonated water clusters are produced by discharging a mixture of helium and water vapor in a high pressure “poor man’s” source. The pure water clusters are then entrained in helium carrier gas down the flow tube at a continuous flow rate of 7000 scem (standard cubic centimeters per minute) through a 3 mm aperture, where they undergo multiple collisions with He atoms and become thermalized. A preset concentration of formic acid vapor in helium is introduced approximately 30 cm downstream of the source by a reactant gas inlet.\textsuperscript{18} The pressure of the flow tube, including the reaction region, is maintained between 0.27 and 0.33 Torr. Protonated water cluster ions and neutral formic acid molecules are allowed to interact for several milliseconds before a small fraction of both reactant and product ions are sampled through a 1000 $\mu$m orifice. The distance between the reactant gas inlet and orifice is \textasciitilde71 cm. Four electrostatic lenses guide the ions through a quadrupole mass filter before they are detected with a channeltron electron multiplier. Cold temperatures necessary for the formation of water clusters are achieved by circulating liquid nitrogen around the flow tube wall. The temperature of the flow tube is held constant with an accuracy of \textpm1 K, with typical values between 145 and 170 K.
5.4 Results and Discussion

Typical protonated water cluster distributions at two different temperatures are shown in Figure 5-1. Water cluster distributions under thermal conditions, which were first reported in our laboratory, are sensitive to the temperature of the flow tube. The H+(H2O)21 cluster clearly stands out at both temperatures shown in Figure 5-1, as has been seen in previous experimental studies. Specifically, clusters having smaller numbers of water molecules have higher relative abundances at T = 161 K, while larger protonated water clusters are more easily formed at T = 149 K; compare spectra shown in Figure 5-1(A) and Figure 5-1(B).

Figure 5-1: Mass spectra of H+(H2O)n at (A) T = 161 K and (B) T = 149 K.
In order to more clearly identify magic numbers in a thermal cluster distribution, we use intensity ratios, which relate the spectral abundance of two particular cluster sizes. Intensity ratios ($R$) are generally defined as $R = I[n]/I[n+1]$. These ratios are not very sensitive to temperature change, and allow for facile determinations of magic numbers. Figure 5-2 shows the intensity ratio plots for water cluster distributions in Figure 5-1(A) and Figure 5-1(B), where $R = I[H^+(H_2O)_n]/I[H^+(H_2O)_{n+1}]$. While a comparison of both spectra in Figure 5-1 show a shift in distribution of $H^+(H_2O)_n$ clusters for each temperature, a distinct magic number at $n=21$ is seen for both $R$ distributions in Figure 5-2, indicating that this cluster ion is particularly stable. This also holds true to a lesser extent for $n=28$.

![Figure 5-2: Intensity Ratio $R = I[H^+(H_2O)_n]/I[H^+(H_2O)_{n+1}]$ for distributions of water clusters at $T=161$ K (▲) and 149 K (■).](image)
Upon the introduction of formic acid vapor through a reactant gas inlet (RGI) in the flow tube, ion-molecule reactions take place. The cationic products observed have the general form $\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})_m$. **Figure 5-3(A-D)** shows the mass distributions of cationic water cluster reactions with neutral formic acid addition at flow rates of 12.5, 25, 50, and 125.5 sccm, respectively. Pure water cluster peaks $[\text{H}^+(\text{H}_2\text{O})_n]$ are marked as “W$_n$,” and formic acid-water clusters $[\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})_m]$ are marked as “W$_n$F$_m$.” Only a few selected species are labeled to avoid congestion, but every mass peak corresponds to either a pure water cluster ion or a formic acid-water cluster ion containing up to three formic acid molecules.

**Figure 5-3**: Mass spectra of $\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})_m$ obtained after the addition of 12.5 sccm HCOOH (A), 25 sccm HCOOH (B), 50 sccm HCOOH (C), and 125.5 sccm HCOOH (D). $W_n = \text{H}^+(\text{H}_2\text{O})_n; W_nF_m = \text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})_m$. 
At a formic acid flow rate of 12.5 sccm, as shown in Figure 5-3(A), the water clusters (labeled as $W_n$) are still relatively abundant in the mass spectrum. With increasing formic acid flow, higher order products from the reaction are generated. The spectra shown in Figures 3(B-D) were collected at flow rates of 25, 50, and 125.5 sccm, respectively. At the highest flow rate studied, only trace amounts of pure water clusters are seen, and mixed formic acid-water molecules with up to three formic acid molecules dominate. We do not consider the clusters containing four formic acid molecules, because the mass difference between a pure water cluster and a formic acid-water cluster that contains four formic acid molecules is less than 4 amu. This small mass difference between $\text{H}^+(\text{H}_2\text{O})_n$ and $\text{H}^+(\text{H}_2\text{O})_{n-10}(\text{HCOOH})_4$ makes it difficult to both identify these products as well as measure their respective intensities.

With the intention of ascertaining if the structures of $\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})$ clusters correspond to those expected for pure water clusters, the intensity ratios were plotted for each mass spectrum in Figure 5-3. Figure 5-4(A-D) shows the intensity ratios for ion reactants $[\text{H}^+(\text{H}_2\text{O})_n]$ and the ion products of the form $\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})$ at formic acid flow rates of 12.5, 25, 50, and 125.5 sccm, respectively. For each concentration of formic acid, the pure water reactant ions showed a magic peak at $\text{H}^+(\text{H}_2\text{O})_{21}$. Conversely, the clusters containing one formic acid molecule do not show significant intensity ratio values for either clusters containing 21 total molecules $[\text{H}^+(\text{H}_2\text{O})_{20}(\text{HCOOH})]$ or the product from an association reaction of HCOOH with the pure water 21-mer $[\text{H}^+(\text{H}_2\text{O})_{21}(\text{HCOOH})]$. This is somewhat surprising, given results from previous water studies in our lab.
Figure 5-4: Intensity Ratio for pure water cluster distributions $R = I[H^+(H_2O)_n]/I[H^+(H_2O)_{n+1}]$ (■) and water-formic acid clusters $R = I[H^+(H_2O)_m(HCOOH)_n]/I[H^+(H_2O)_{n+1}(HCOOH)_m]$ (▲) at formic acid flow rates of 12.5 (A), 25 (B), 50 (C), and 125.5 sccm (D). In all cases, there is one formic acid molecule attached to each water cluster size ($m = 1$).

Water clusters are expected to undergo three possible reaction channels with neutral molecules: proton transfer; switching; and association. A proton transfer channel is not seen for the reactions of protonated water clusters and formic acid in this study, since protonated formic acid clusters of the form $H^+(HCOOH)_n$ are not detected under the current experimental conditions. In the case of a switching mechanism, a formic acid molecule would replace a water molecule in the protonated cluster. If switching occurred for all sizes studied, the intensity ratio $R$ of the $H^+(H_2O)_{20}(HCOOH)$ peak would be equal to that for $H^+(H_2O)_{21}$, which is also clearly not the case. An association channel, where a formic acid molecule links to a protonated water molecule through intermolecular forces, is not clearly evident, either. An association mechanism would show the $H^+(H_2O)_{21}(HCOOH)$ intensity ratio to be the same as that for $H^+(H_2O)_{21}$. 
To better understand the formation mechanism(s) of formic acid-water clusters, the product intensity ratios for $\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})_m$ were compared to the products from $\text{H}^+(\text{H}_2\text{O})_n(\text{CH}_3\text{OH})_m$ ($m = 1\text{--}4$ in both cases). Figure 5-5(A-B) shows the $R$ values for mixed methanol-water and formic-acid water clusters, respectively. It is evident that the ratios for methanol-water clusters in Figure 5-5(A) are strikingly similar to those of the pure water cluster cations in Figure 5-2. All of the $\text{H}^+(\text{H}_2\text{O})_n(\text{CH}_3\text{OH})_m$ clusters where $m + n = 21$ have $R$ values over 1.3. These results are the same as those found from a previous study from our group.\textsuperscript{16, 17}

It was found previously that up to eight methanol molecules could replace water molecules in the clathrate-like structure, keeping the arrangement of the hydrogen bonding network intact.

![Figure 5-5: Intensity Ratio for pure water-methanol cluster distributions $R=\frac{I[\text{H}^+(\text{H}_2\text{O})_n(\text{CH}_3\text{OH})_m]}{I[\text{H}^+(\text{H}_2\text{O})_{n+1}(\text{CH}_3\text{OH})_m]}$ (A) and water-formic acid clusters $R=\frac{I[\text{H}^+(\text{H}_2\text{O})_n(\text{HCOOH})_m]}{I[\text{H}^+(\text{H}_2\text{O})_{n+1}(\text{HCOOH})_m]}$ (B) at a flow rate of 150 sccm for $m = 1$ (■), 2 (▲), 3 (●), and 4(♦).]
For formic acid-water clusters in Figure 5-5(B), there are no outstanding $R$ values evident for the sizes under examination. Both methanol and formic acid have a hydroxyl group that is able to hydrogen bond, so one might expect similar behavior (i.e. a switching mechanism) for each neutral, organic reactant. There is a difference, however, between formic acid and methanol in the rest of their structures. The carbonyl oxygen in HCOOH is able to accept hydrogen bonds, whereas the methyl group on CH$_3$OH can not. If one envisions a methanol molecule substituting for a water molecule on the perimeter of a water cluster’s hydrogen bonding network, the nonpolar methyl group would protrude. Furthermore, the methyl group can replace a “dangling” hydrogen atom in a pure cationic water cluster without significantly altering the clathrate-like structure. In the case of a formic acid molecule, however, the protruding, polar carbonyl oxygen can accept hydrogen bonds from other molecules that impinge upon the mixed cluster. Moreover, the carbonyl oxygen may lie close enough in proximity to other water molecules in the structure to form more hydrogen bonds within the existing network. The formic acid may both shorten and strengthen the hydrogen bonding network between the water molecules themselves, in accordance with the findings of Vaida et al. in small formic acid-water cluster systems.$^{15}$ If the magic character of the protonated water 21-mer is caused by structural stability, a single formic acid molecule might alter the arrangement of the hydrogen bonding network dramatically, thereby disrupting the stable clathrate-like structure.

Calculations have been performed to gain a better understanding of the free energy of formation of an embryo of a stable phase and critical nucleus. The classical formulation for liquid drop formation developed by Thompson is often used to evaluate the free energy of formation ($\Delta G$) of a cluster of $n$ molecules under a given super-saturation ratio ($p/p^0$).$^{24,25}$ The free energies of the $n$th cluster is given by

$$\Delta G_{0,n} = -nRT \ln \left( \frac{p}{p^0} \right) + 4\pi N r^2 \sigma + \left( \frac{q^2 N}{2} \right) \left( 1 - \frac{1}{r} \right) \left( 1 - \frac{1}{r_i} \right),$$  \hspace{1cm} (5.1)
where $p^0$ is the vapor pressure of the condensing molecules at the temperature $T$ of the system, $N$ is Avogadro’s number, $r$ is the radius of the droplet, $\sigma$ is the surface tension, $\varepsilon$ is the bulk permittivity, and $r_i$ is the ionic radius. The necessary values for the various terms are available from a number of different sources and are summarized in Table 5-1.\textsuperscript{26-29}

Table 5-1:  Parameters Used in Charged Liquid Drop Calculations for Water and Formic Acid

<table>
<thead>
<tr>
<th>parameters\textsuperscript{a}</th>
<th>water\textsuperscript{b}</th>
<th>formic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, K</td>
<td>317</td>
<td>317</td>
</tr>
<tr>
<td>$M$, g mol\textsuperscript{-1}</td>
<td>18.015</td>
<td>46.005</td>
</tr>
<tr>
<td>$\sigma$, g s\textsuperscript{-2}</td>
<td>68.72</td>
<td>35.06\textsuperscript{c}</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>72.60</td>
<td>49.80\textsuperscript{d}</td>
</tr>
<tr>
<td>$\rho$, g cm\textsuperscript{-3}</td>
<td>0.992</td>
<td>1.19\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See text; cgs units where applicable. \textsuperscript{b} From ref. 31. \textsuperscript{c} From ref. 29. \textsuperscript{d} From ref. 30. \textsuperscript{e} From ref. 28.

This equation has three terms: The first term accounts for the free energy of vaporization of the condensing molecules (the vapor pressure term), the second stands for the work done in changing the surface area upon condensation of additional molecules about an ion cluster (the surface term), and the third term signifies the change in field energy due to the condensation of a dielectric film about the ion (the dielectric term). Nucleation will only take place when the super-saturation ratio ($p/p^0$) is greater than unity. When this occurs, the barrier to nucleation becomes finite, and the critical cluster size is decreased as super-saturation is increased.

Figure 5-6 shows the individual contributions of the three terms in the Thompson equation (vapor pressure, surface, and dielectric) and the free energy change per molecule in terms of droplet radius for pure water (A) and pure formic acid (B) at temperature $T = 317$ K and a super-saturation ratio $p/p^0 = 1.5$. At very small sizes (small $r$), the vapor pressure and surface terms are close to zero, and the dielectric term is the dominant factor in determining the free
energy. In the cases of water and formic acid, the volume of the ion itself is assumed to be very small when compared to the bulk volume. Since the effect of the charge from the ion is also very small beyond the first few ligand molecules, its radius \((r_1)\) is ignored in these calculations. As the radius of a classical droplet grows, the dielectric term diminishes and the interplay between the vapor pressure and surface terms control the overall free energy.

Figure 5-6: The free energy change \(\Delta G_{0,n}\) with respect to droplet radius \((r)\) from Equation (1) for pure water (A) and pure formic acid (B) at \(T = 317\) K and a super-saturation ratio \(p/p^0 = 1.5\). The blue curve is the contribution from the surface term, the green curve is the contribution from the vapor pressure term, the purple curve represents the dielectric term, and the red curve is the total free energy. The function for \(\Delta G_{0,n}\) goes through a maximum at the critical radius, \(r^*\). At this size, the free energy of formation for a critical nucleus \((\Delta G_{W}^{*}\) for water and \(\Delta G_{F}^{*}\) for formic acid) can be evaluated.
It is interesting that at the same temperature and super-saturation ratio, the curves for \(\Delta G_{0,n}\) are quite different for water (Figure 5-6(A)) and formic acid (Figure 5-6(B)). For a pure formic acid droplet, the free energy barrier for nucleation is \(~596.7 \text{ kJ mol}^{-1}\), and for water the barrier is \(~975.4 \text{ kJ mol}^{-1}\). It should also be noted that the critical radius, the radius that corresponds to \(\Delta G^*\) (the local maximum) is not significantly changed. The critical drop radius is found to be 2.52 nm for formic acid and 2.32 nm for water.

The Thompson liquid drop model does not explicitly account for structural effects in clusters, so deviations can occur for specific molecular interactions. This is mainly because the model is based on bulk solvent properties. Our experimental results show that cluster structure, such as the magic number for the cationic water 21-mer, is an important factor that is unaccounted for in our calculations. However, the model has been shown to fit experimental data reasonably well for the thermodynamic properties of hydrated clusters containing monovalent ions.\(^{30-33}\) The continuous Thompson model is useful in the present work to provide insight into the heterogeneous nucleation that we have observed with formic acid-water clusters.

The findings suggest that as formic acid molecules are added to the pure, protonated water cluster system in our experiments, the free energy function for pure water begins to approach that for formic acid. In other words, with each formic acid molecule addition, the critical radius does not change significantly while the corresponding free energy barrier for nucleation may become lower at relatively low super-saturation ratios. To an extent, this correlates our findings on a molecular scale to large sizes that are involved in the co-clustering of formic acid and water in the atmosphere. Moreover, the facile nucleation of formic acid-water clusters may be part of the reason that proportionate concentrations of formic acid are maintained in the atmosphere. Further evaluation of thermodynamic values, such as enthalpy and entropy, will allow a more detailed, quantitative understanding of this phenomenon.
5.5 Conclusions

In summary, the results from the present study give evidence that formic acid molecules have an appreciable interaction with protonated water clusters. This is most likely due to the ability of formic acid to take part in hydrogen bonding with its hydroxyl group as well as its carbonyl oxygen. These findings are in alignment with those of Vaida et al. They found that, due to a “cooperative bonding effect,” the introduction of a formic acid molecule to small water clusters can induce a change in the hydrogen bonding network. Specifically, the hydrogen bond distances between the water molecules themselves become shortened. The lack of a stable clathrate-like structure containing formic acid in our experiments suggests that the stable network of hydrogen bonding within an \( \text{H}^+\text{(H}_2\text{O})_{21} \) molecule is disrupted with just a single formic acid molecule, contrary to the effects of a methanol molecule addition. Furthermore, the overall shape of the cluster distributions we observe for formic acid-water clusters is similar to what would be expected for nucleation about ions. The steady-state concentrations of the formic acid-water clusters begin to increase continuously only after the finite free energy barrier is overcome, which gives rise to the upturn in the mass spectra seen in Figures 5-3(C-D). A comparison of the free energies for both pure water and formic acid as modeled by the classical Thompson equation shows that this barrier is significantly higher for water. Our findings demonstrate that as formic acid molecules are added to a pure water cluster, the barrier is lowered, and nucleation can more easily occur. More work is needed to better understand the structure of prenucleation clusters, as well as more detailed statistical mechanical methods for calculating the thermodynamic properties. Future studies of larger carboxylic acids, such as acetic acid (also present in the atmosphere) may aid in the understanding of the transport processes of organic acids in the atmosphere.
5.6 References


Chapter 6

Concluding Remarks

Studies of clusters with implications for both materials science and environmental science have been presented. Anion photoelectron spectroscopy experiments, when combined with theory, are a useful tool to both identify uniquely stable clusters and obtain valuable electronic information. The discoveries of Al$_3$Bi and Al$_5$Bi add to the ever-increasing number of clusters that may someday be used to synthesize cluster-assembled materials. The Al$_3$Bi cluster was shown to be a cyclic, planar, all-metal aromatic molecule. The added feature of this cluster is that it is electronically neutral, as opposed to the great majority of other metal aromatic clusters. The Al$_5$Bi cluster has been shown to be extremely stable. It has a closed electronic shell, according to the jellium model, and is a potential superatom. Future studies of the reactivity of these clusters will be required to understand how these clusters can be synthesized into the bulk.

Anion photoelectron spectroscopy was also used to understand the formation processes of niobium carbide clusters. The combined experimental and theoretical results show that the preferred structures for Nb$_3$C$_n$ clusters involve a triangular Nb$_3$ unit with a single C atom bound to a face. Moreover, the other carbon atoms tend to form C$_2$ bridging units between metal atoms. The structures of tri-niobium carbide clusters may have similar motifs as those in the Met-Car, particularly the presence of C$_2$ units. Further experiments of niobium carbide clusters may lead to the ability to synthesize transition metal carbide materials with properties that are hitherto unknown.

Atmospherically relevant experiments focusing on formic acid-water clusters were performed in a fast-flow reactor. Protonated water clusters of the form H$^+$ (H$_2$O)$_n$ ($n = 3-27$) were subjected to various concentrations of formic acid vapor. The products suggest that when formic
acid molecules bond to water clusters, the hydrogen bonding network between the water molecules is disrupted. This was shown by the intensity ratios of the product distributions for pure water, methanol-water, and formic acid-water complexes. While the 21-molecule clathrate structure is dominant in pure water clusters and methanol-water clusters, it is not a major product when formic acid molecules bond with water. Formic acid does, however, enable nucleation with protonated water clusters at unexpectedly small sizes. This was understood in part with classical liquid drop model calculations. The chemistry in the atmosphere that sustains proportionate concentrations of organic acids, including formic acid, in the atmosphere is not well understood. Additional experiments involving the interactions of carboxylic acids with water clusters will provide more insights into acid deposition in the environment.
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