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**PHOTOELECTRON SPECTROSCOPY INVESTIGATIONS
ON THE STABILITY, ENERGETICS, AND DYNAMICS
OF GAS-PHASE P-BLOCK CLUSTERS**

A Dissertation in

Chemistry

by

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ABSTRACT

Through the use of mass spectrometry and photoelectron spectroscopy, as well as theoretical calculations, the studies within this dissertation investigate the geometric and electronic structures of small clusters of p-block elements. There is a focus on identifying cluster stoichiometries that exhibit enhanced stability, as part of a synergistic collaboration to build assembled nanomaterials out of cluster building blocks. Further, the work in this dissertation reveals the guiding principles governing cluster behavior in the small size regime and various theoretical models are used to rationalize the enhanced stability of certain clusters.

Investigations of Al_nX ($n = 1-6$, $\text{X} = \text{As}, \text{Sb}$) clusters establish that Al_3As and Al_3Sb are planar, all-metal, aromatic molecules, while Al_5As and Al_5Sb are spherical clusters that possess large energy gaps due to closed electronic shells. The stability of these molecules is subtly affected by the identity of the non-aluminum atom, and this leads to a tunability of cluster properties. These ideas are developed through additional studies on lead-indium clusters, in which it is shown that both aromatic and closed electronic shell species are present, but that lead often drives the geometries towards close-packed arrangements. Thus, by controlling the amount of lead within the cluster, one can control the geometry. Additionally, within the lead-indium system a thorough investigation of Pb_2In_2 and PbIn_3^- reveals new rules for all-metal aromaticity, showing that despite large electronegativity differences of the constituent atoms and different

geometric arrangements, aromatic character can be preserved in heavy p-block clusters, in contrast to the lighter aluminum analogs.

To further explore the behavior of the heavy p-block clusters, experiment and theory are used to reveal remarkable similarities in the electronic structures of Pb_xSb_y^- and Bi_xSn_y^- clusters. It is found that the energy and ordering of electrons within these clusters is not affected by the identity of the nuclear core. Thus, the properties of one cluster (or assembled material) may be mimicked through a substitution of different elements.

Finally, this dissertation describes the invention of a new method for determining the angular momentum character of molecular orbitals. Photoelectron imaging experiments coupled with calculations reveal the degree of s - p hybridization in the valence electrons of small aluminum clusters. The Al_3^- cluster possesses a large degree of s - p hybridization, while Al_4^- is completely unhybridized. Further, the degree of hybridization continues to vary markedly for larger clusters. This work represents the first demonstration of an experimental technique that can directly probe the level of hybridization within molecular orbitals.

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Chapter 1

Introduction

“What would the properties of materials be if we could really arrange the atoms the way we want them...I can’t see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do.”

-Richard P. Feynman¹

1.1 Clusters

The focus of this dissertation is the experimental investigation of small molecules in the gas-phase. These species, henceforth referred to as clusters, may be defined as having any number of atoms (from two to tens of thousands), provided that they exhibit properties different than their corresponding bulk material. This makes the field of cluster research rich and diverse, bridging the gap between the sub-nanometer dimensions of single atoms and the macroscopic world of bulk materials. For instance, while bulk gold is known for its inert behavior, small gold clusters react readily and have shown promise in nanocatalysis.² Alternatively, bulk aluminum happens to oxidize readily, yet Al_{13}^- clusters have shown a peculiar resistance to oxygen etching.³

In this dissertation the studies are restricted to small clusters of less than ten atoms. This resides in the angstrom size regime, where there are stark variations in the properties of two clusters that differ by just one atom. This is due to the quantum confinement of electrons, the finite density of states, and the high percentage of atoms at

the cluster surface. This is quite different than the macroscopic world of bulk materials, where free electrons are accurately described by band theory and geometries are explained by crystal structure. By studying clusters, fundamental insight can be gained into their physics and chemistry, and it is hoped that this will lead to practical applications. A good example of this is in chemisorption and catalysis, where it has been shown that metal clusters model bulk catalytic active sites, and gaining a fundamental knowledge of the chemistry of the isolated cluster can lead to new catalytic materials.⁴ Results like this and others^{5,6} encourage the study of cluster phenomena for exploring a variety of potential applications.

1.2 Cluster Assembled Materials

Take a small cluster with a unique and fundamentally interesting property. Gather several of these clusters up into a material, and the overall characteristics of the material may be a reflection of the isolated cluster's properties. Change the cluster building block by just one atom and the overall properties of the assembled material are altered, achieving a truly tailored material design. The prospect of achieving these cluster assembled materials (CAMS) has gathered much attention,^{7,8} and Figure 1 illustrates three examples of materials that could be created from cluster building blocks.

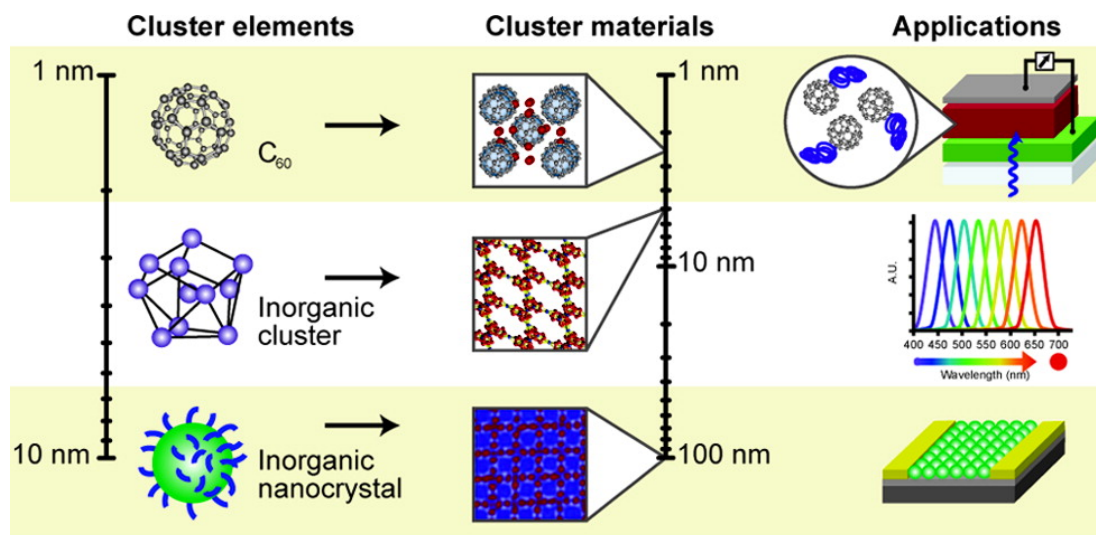


Figure 1.1 Examples of cluster building blocks, nanoassemblies, and materials with tailored properties. Reprinted from reference 8.

However, the realization of cluster assembled materials is far from trivial for the following reasons:

- i) It may be difficult to identify clusters with unique and desirable properties.
- ii) It may be difficult to bring just two, let alone thousands, of the identical cluster building blocks together without disrupting their inherent properties or undergoing agglomeration.
- iii) The integrity of the cluster assembly as a whole may become completely lost when introduced to an outside substance.

These issues are at the heart of the current efforts to design CAMS, and there are many teams working to attack these problems with promising results.⁹⁻¹³

The studies presented within this dissertation focus on the first step of realizing cluster assembled materials, i.e. characterizing cluster properties and identifying stable clusters that may be candidates for assembly into nanomaterials. Along the way, there

will be fundamental information gained on the chemical bonding picture within these small clusters, and how and why some clusters are stable while others are not. Though “stable” can be a broad term, it is used here to describe a cluster that meets certain criteria that may help prevent problems ii and iii above. These criteria can include resistance to oxygen reactivity, large energy gaps between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap), or large electron detachment energies.

The clusters investigated within this dissertation all belong to the p-block of the periodic table, and more specifically to groups III, IV, and V. These groups of the periodic table have led to some revolutionary materials of the past century, perhaps most notably semiconductors, fullerenes, and carbon nanotubes. It is largely because of these materials that there is further interest in groups III, IV, and V, and the experiments detailed here focus on some of the lesser-known family members of these groups, as well as unique combinations of different elements. It is hoped these studies will elucidate the subtle chemistry of p-block elements and identify candidates for building blocks of new nanomaterials.

1.3 Outline of the Dissertation

The remainder of this dissertation begins with an overview of the current state of cluster physics in Chapter 2. Next, the experimental setup employed to investigate the properties of clusters is described in Chapter 3. The first study is detailed in Chapter 4, which describes an experiment on Al_nX ($n = 1-6$; $\text{X} = \text{As}, \text{Sb}$) clusters, applying theoretical models to account for cluster stability. In Chapter 5, two unique clusters are investigated that yield insight into the chemical bonding picture of small clusters. Next, a

comprehensive study of lead-indium clusters is presented in Chapter 6. In Chapter 7, geometric and electronic structure similarities are revealed and rationalized in bismuth-tin and lead-antimony clusters. Chapter 8 investigates *s-p* hybridization in small aluminum molecules and details a novel approach to assigning angular momenta to experimentally observed molecular orbitals. Finally, some concluding remarks are made that summarize the findings of this dissertation and outline future directions.

1.4 References

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Chapter 2

Background

“the many-body problem is still far from trivial...at a much lower level are the “hook and crook” approaches so dear to experimentalists who usually cannot wait for accurate theoretical predictions.”

-Walter A. de Heer¹

2.1 Introduction

The birth of the field of clusters has presented a new challenge for physical chemists to both explain experimental observables and provide a fundamental description of cluster behavior (e.g. reactivity, dynamics, or electronic, geometric, and magnetic properties). This chapter is designed to present a sufficient background to the concepts of cluster physics that will be applied to future chapters, and so will principally deal with the description of electronic and geometric effects in small metal clusters, as well as topics on the interaction of light and matter that are pertinent to the experiments performed. Furthermore, instead of providing a rigorous description of the quantum-mechanical treatment of these effects (though they will be briefly discussed), concentration will be placed on classical or semi-classical explanations, painting the “physical picture” that is so important to an experimental chemist’s understanding.

2.2 The Jellium Model

2.2.1 The Spherical Jellium Model

Electrons govern chemistry, and it is of central importance to experimentally determine their energy and organization within a molecule. Further, there is a need to develop models that account for such findings, which in turn can be used to predict chemistry. In 1984, Knight, de Heer, Clemenger, Saunders, Chou, and Cohen made the first experimental observation of a pattern in the electronic structure of clusters.² By flowing an inert gas over hot sodium metal, and then through a nozzle into vacuum, they were able to create a large variety of sodium clusters. Their mass spectrum is shown in Figure 2.1.

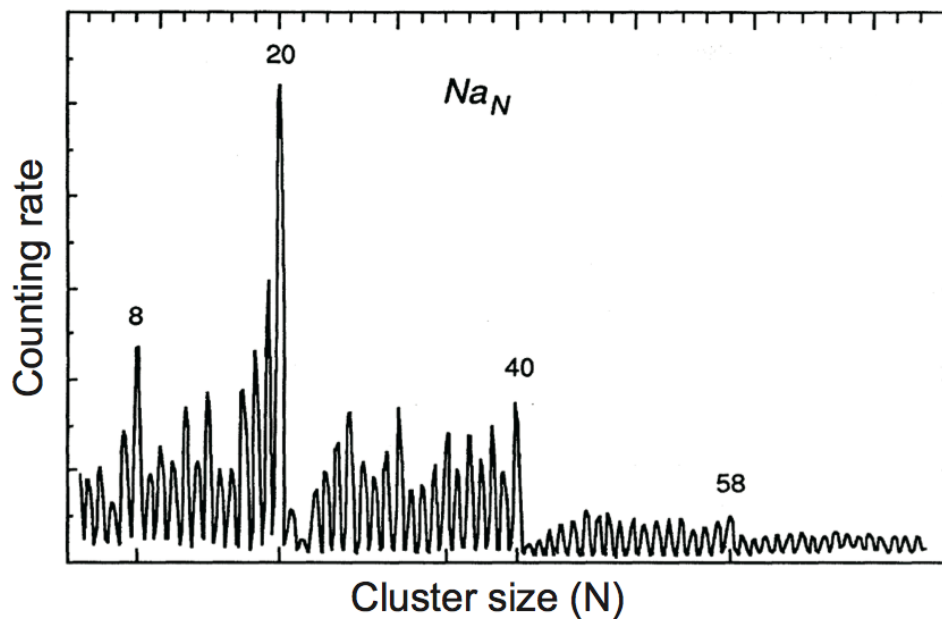


Figure 2.1 Mass spectrum of sodium clusters created by Knight et al. Reprinted from reference 2.

It is immediately apparent that some clusters are created more favorably than others. Most notable are the clusters that are much more intense than their neighbors, for example Na_8 , Na_{20} , Na_{40} , and Na_{58} . These clusters, termed “magic” clusters, all have a sharp drop-off at the next cluster size (e.g. for Na_{40} there is almost no Na_{41} produced). These observations immediately brought about questions as to why some clusters were preferentially created, and why other sizes were not created at all. Knight et al. attributed these findings to the presence of an electronic shell structure, a concept somewhat analogous to the closed valence shells in noble gas atoms. Since a sodium atom has a single valence electron, the observed magic clusters have 8, 20, 40, and 58 electrons, respectively. However, these numbers are different than the traditional closed shells of the noble gas atoms, since by definition clusters have more than one nuclear core. The explanation for the electronic shell structure observed by Knight et al. can be thought of as treating the entire cluster as one positive nucleus, or “jelly”, with the valence electrons delocalized around this potential. The jellium model has since been applied to numerous metal systems with great results.³⁻⁷

2.2.2 Derivation of the Jellium Shell Structure

To more rigorously account for the electronic shell closings observed in the jellium model, quantum mechanics can be applied. Here, the notation of Brack will be adopted.⁸ An exact quantum-mechanical treatment of a cluster can be accomplished by solving the time-independent Schrödinger equation:

$$\mathcal{H}\psi = E\psi \quad 2.1$$

to obtain the eigenstates ψ and eigenenergies E . For a neutral cluster of N nuclear cores and Z electrons per atom, the Hamiltonian can be exactly defined as:

$$\mathcal{H} = \sum_{\alpha=1}^N \left\{ \frac{\mathbf{P}_{\alpha}^2}{2M} + \sum_{i=1}^Z \frac{\mathbf{p}_{\alpha i}^2}{2m} + \sum_{\beta=1}^N \left[\frac{1}{2} \frac{(Ze)^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} + \sum_{i=1}^Z \left(-\frac{Ze^2}{|\mathbf{r}_{\beta i} - \mathbf{R}_{\alpha}|} + \frac{1}{2} \sum_{j=1}^Z \frac{e^2}{|\mathbf{r}_{\alpha i} - \mathbf{r}_{\beta j}|} \right) \right] \right\} \quad 2.2$$

where M , $\mathbf{P}$, and $\mathbf{R}$ are the mass, momenta, and location, respectively, of the nuclear cores, and m , $\mathbf{p}$, and $\mathbf{r}$ are the mass, momenta, and location of the electrons from atom α . The summations are indexed by α and β over all N atoms, and by i and j over all NZ electrons. The first two terms in Equation 2.2 represent the kinetic energy of the nuclei and electrons, respectively. The remaining three terms account for the repulsions among the nuclei, the attractions between the nuclei and electrons, and the repulsions among the electrons, respectively. Substituting Equation 2.2 into 2.1 represents one of the most elegant equations in physics, but currently it is impossible to analytically solve for any system beyond $N = 1$ and $NZ = 1$ (e.g. H, He^+ , Li^{2+}), which is quite unfortunate for the field of clusters. Luckily, there are some approximations that can be used to simplify Equation 2.2 to the point where it may be solved for some cluster systems. For proof that the approximations are justified, the reader is referred to numerous works.^{1,8,9}

The first simplification is a fundamental principle of physical chemistry known as the Born-Oppenheimer approximation,¹⁰ which states that since the mass of the nuclei is large enough compared to that of an electron, they may be treated separately in the Hamiltonian. To think of it classically, an electron is flying around so quickly that the

slow-moving nucleus is essentially frozen, and thus their dynamics are not intertwined. This approximation allows terms that are pertinent to the electronic structure in Equation 2.2 (i.e. terms two, four, and five) to be separated and dealt with alone within an electronic Hamiltonian.

However, further simplification is still needed. This can be accomplished by treating the w valence electrons quantum-mechanically, while combining the core electrons in with the nuclei, creating an ion with a positive w charge. This helps reduce the calculation tremendously, and works well even for clusters where the valence electrons are not strongly delocalized.⁸ The resulting electronic Hamiltonian can be represented by:

$$\mathcal{H}_{electronic} = \sum_{i=1}^{wN} \left\{ \frac{\mathbf{p}_i^2}{2m} + \sum_{\alpha=1}^N V_{ps}(|\mathbf{r}_i - \mathbf{R}_\alpha|) + \frac{1}{2} \sum_{j(\neq i)=1}^{wN} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right\} \quad 2.3$$

where the first term is the kinetic energy of the valence electrons, the middle term represents the interaction between the valence electrons and the ionic core, and the last term is the coulombic repulsion between the valence electrons. While the kinetic energy of the valence electrons can be calculated, terms two and three of Equation 2.3 represent considerable difficulties and must be approximated even further. Luckily, the last term of the electronic Hamiltonian has been the focus of entire fields of theoretical chemistry (e.g. Density Functional Theory (DFT) and Hartree-Fock),¹¹⁻¹³ with a basic strategy being that the electron-electron interactions can be incorporated into an average potential. This average potential is known as the mean-field approximation, where each valence electron

is treated as moving independently from the other valence electrons, responding only to the average field.

For very small molecules with few electrons, the above approximations allow for the calculation of geometric and electronic structure. However, even for small clusters the middle term in Equation 2.3, $V_{p,s}(|\mathbf{r}_i - \mathbf{R}_\alpha|)$, known as the pseudopotential, becomes difficult to solve. Here, the observations in Figure 2.1 led to a vastly valuable approximation. Knight et al. were able to reproduce the shell closings quantum-mechanically by employing a spherically symmetric pseudopotential referred to as the jellium potential. The ionic cores, which contain the nuclei and the core electrons, are neglected and instead approximated as a uniform positive field that extends over a finite distance r_0 , which is assumed to be the boundary of the cluster dimensions. For a spherical cluster of N atoms, Knight et al. chose the potential $V_{ps}(\mathbf{r})$, where:

$$V_{ps}(\mathbf{r}) = -\frac{V_0}{1 + e^{(r-r_0)/\epsilon}} \quad 2.4$$

Here, r_0 is the effective radius of the spherical cluster and ϵ is an adjustable parameter that can account for slight variations of the potential at the edge of the sphere. V_0 will depend on the elemental identity of the cluster, and can be thought of as the depth of the potential well described by the sum of the Fermi energy and the work function of the bulk (See Figure 2.2).

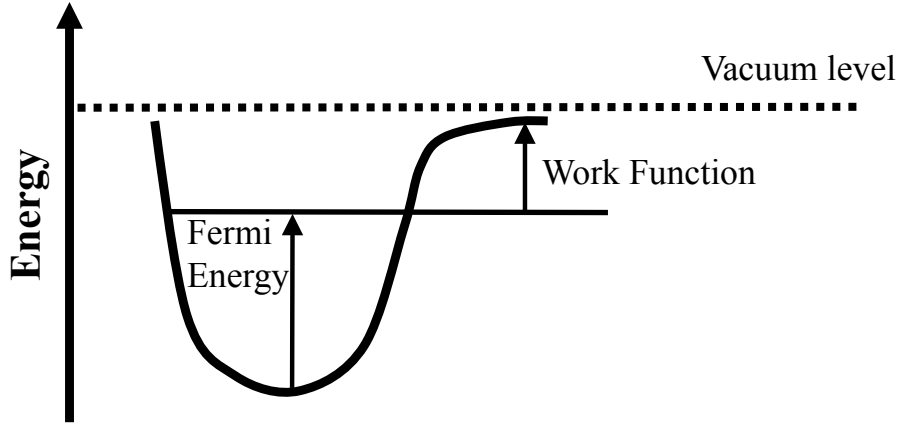


Figure 2.2 Illustration of the potential well depth used for V_0 in Equation 2.4. The exact values will depend on the element under consideration.

With Equation 2.4 substituted into Equation 2.3, the electronic Hamiltonian is complete, and the Schrödinger equation can be solved numerically. This is precisely what Knight et al. accomplished, finding that the eigenvalues yield discrete energy levels with angular momenta L , and $2(2L+1)$ degeneracy. The first ten levels are as follows:

$$1s^2, 1p^6, 1d^{10}, 2s^2, 1f^{14}, 2p^6, 1g^{18}, 2d^{10}, 3s^2, 1h^{22} \quad 2.5$$

where the familiar notation for the electronic shells of atoms is adopted, with the principal quantum number first, followed by the angular momentum of the shell, and the total number of electrons in the shell is superscripted. The total electronic energy of the cluster can thus be found by summing the eigenvalues of all the occupied states.

When considering sodium clusters, where each atom has one valence electron, clusters that differ by one atom also differ by one valence electron. Thus, the difference in energy between two adjacent clusters is determined by the eigenvalue of the new state

the extra valence electron occupies. Because there are discrete energy levels with angular momenta L and $2(2L+1)$ degeneracy, there is a large jump in energy in going from one full level to opening the next shell. For example, to fill the first four levels of Equation 2.5 requires 20 electrons, while to start the fifth level requires a 21st electron. Thus, Na_{20} is much more energetically favorable than Na_{21} , resulting in an intense peak in the mass spectrum of Figure 2.1, followed by a sharp drop-off. The peaks for Na_8 , Na_{40} , and Na_{58} can be similarly explained. These special numbers of electrons are referred to as magic numbers, and have since been used to explain many experimental observations, both in mass spectra and elsewhere.¹⁴⁻¹⁷ The majority of the remaining intensity variations in Figure 2.1 can be explained with the methods in Section 2.2.3.

It is important to note that since the initial success of Knight et al., much work has been done to model the pseudopotential, from square potentials to the Woods-Saxon potential to self-consistent potentials. For a detailed discussion that is beyond the scope of this dissertation, the reader is referred to the literature.^{8,18} The overall conclusions of these efforts are still basically the same as the original findings by Knight et al.,² namely that certain magic numbers correspond to electronic closed shells in clusters, and clusters with closed shells exhibit an enhanced stability. This conclusion is the basis for certain findings of cluster stability within this dissertation, and we shall refer to stable clusters with these closed shells as “jellium clusters”.

2.2.3 The Clemenger-Nilsson Model

The shells listed in Equation 2.5 assume that the cluster is spherical, but this is often far from the case for clusters of two to perhaps more than 50 atoms. Non-spherical

geometries can be explained by Jahn-Teller distortion, wherein it is more energetically favorable for the cluster to adjust the position of the nuclei to account for only partially filled electronic shells. For example, imagine that the $1p^6$ shell, which consists of the three degenerate p-orbitals p_x , p_y , and p_z , is only partially occupied with two electrons, and these two electrons lie in the p_z orbital. The cluster will deform such that the arrangement of the nuclei is in the shape of an ellipsoid with the major axis in the z-direction (i.e. the prolate structure in Figure 2.3). This can be thought of as matching the positively charged core potential to the negatively charged electron density. This lowers the total energy of the cluster, as the previously degenerate orbitals are split to raise the energy of the unoccupied orbitals (p_x , p_y) and lower the energy of the occupied orbitals (p_z). If there are four electrons out of the six possible in the p-shell, the cluster will adopt the oblate geometry shown in Figure 2.3. These ideas can be extended to the other shells; the p-shell is used as the example as it is conceptually the easiest to understand.

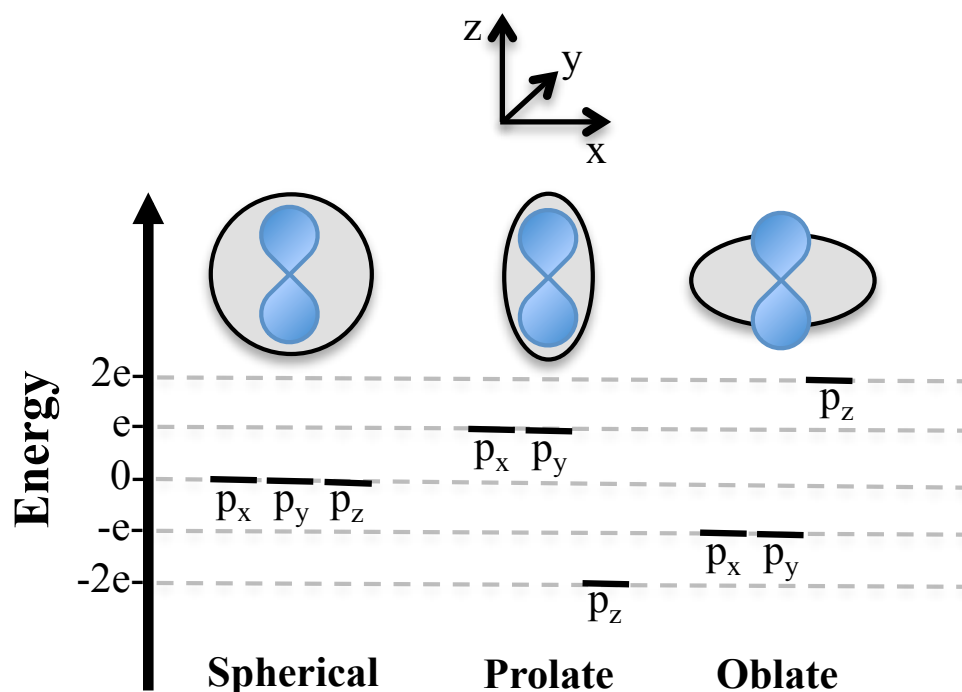


Figure 2.3 Illustration of Jahn-Teller distortion resulting in the splitting of previously degenerate electron orbitals. Here, only the p_z orbital is shown for clarity. The energy unit e is arbitrary.

To deal with this behavior, Keith Clemenger in 1985 adopted a theory developed by Sven Gösta Nilsson that had originally been designed for distortions in nuclei,¹⁹ but instead applied it to clusters. This became the Clemenger-Nilsson model and it can explain the smaller variations in intensity of non-magic numbers in Figure 2.1 (e.g. the relatively large intensity of Na_{14} or Na_{26}).²⁰ Clemenger accomplished this by introducing a distortion parameter, δ , that accounts for how prolate or oblate the cluster may be. The resulting “sub-shell” closings are depicted in Figure 2.4 as a function of δ .

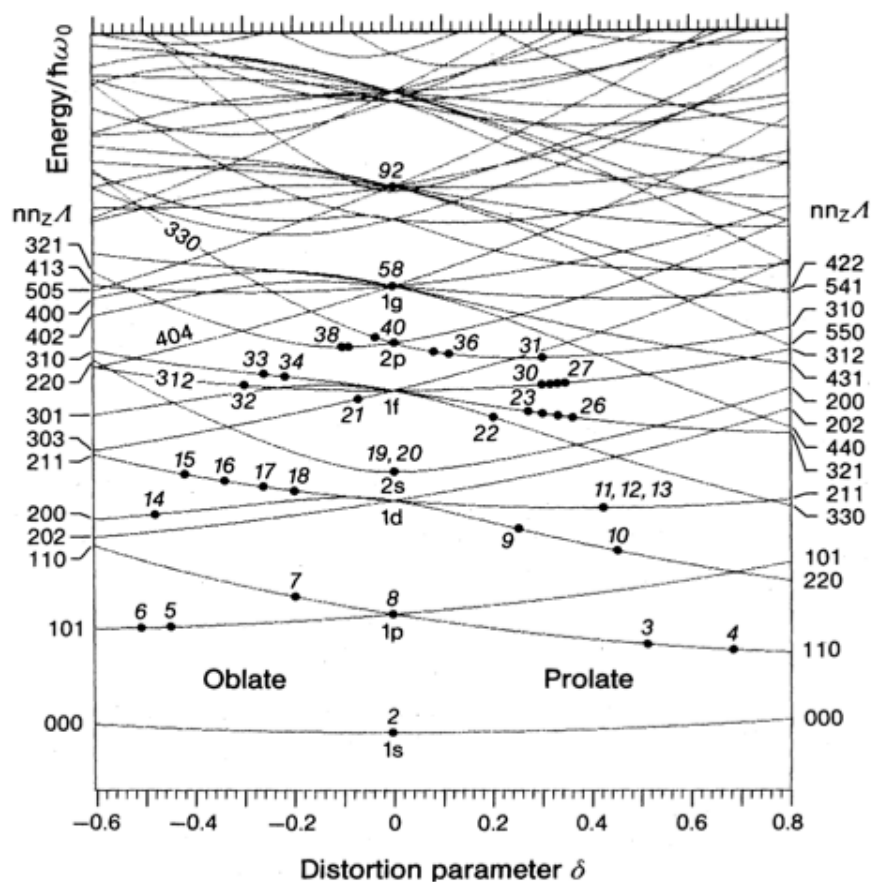


Figure 2.4 Graph of the energies calculated by the Clemenger-Nilsson model as a function of the distortion parameter. Sub-shell closings are shown as bold points in the figure. Reprinted from reference 20.

2.2.4 The Two-step Spherical Jellium Model

A second assumption in the original model by Knight et al. is homoatomicity, meaning that the cluster consists of only one element. This is not always true, and the majority of the work in this dissertation involves heteroatomic species, as they provide for more possibilities in tuning cluster properties. The applicability of the jellium model to heteroatomic clusters is difficult, but is justified when the elements have similar inherent properties (e.g. electronegativity, atomic radius). There have been attempts to

modify the jellium model for heteroatomic clusters, most notably by Janssens, Neukermans, and Lievens.²¹ They introduced a two-step spherical jellium model, wherein the jellium pseudopotential is modified to account for a heteroatom placed in the center of an otherwise homoatomic cluster. This seems justifiable, since a single dopant atom is frequently located at the center of the cluster.²²⁻²⁴

The two-step spherical jellium model comes in two variations, one in which the central heteroatom is more electronegative than the surrounding atoms, and one in which the heteroatom is less electronegative. The pseudopotentials used are shown in Figure 2.5 along with the resulting magic numbers for closed shells. Although the pseudopotentials are somewhat trivial, they have shown success in predicting shell closings in heteroatomic clusters.^{21,25}

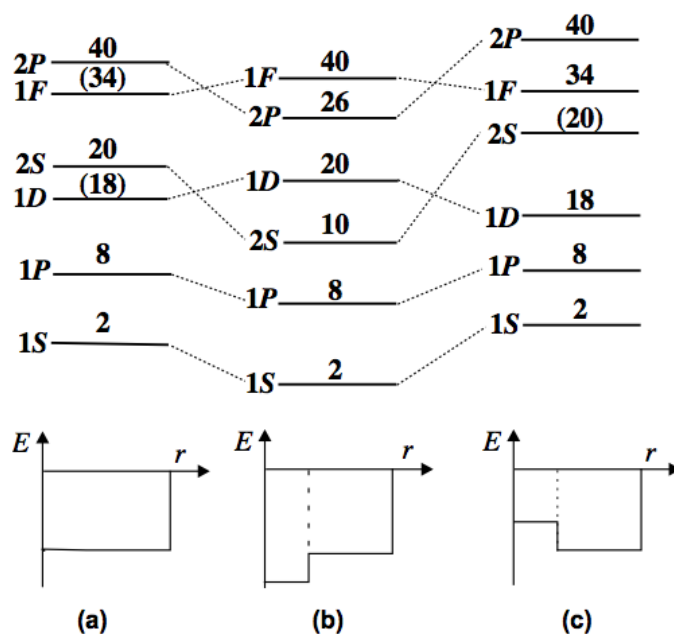


Figure 2.5 Shell closings and pseudopotentials in (a) a standard jellium potential, (b) a potential where the central heteroatom is more electronegative, and (c) a potential where the central heteroatom is less electronegative. Reprinted from reference 21.

2.3 Aromaticity in Metal Clusters

2.3.1 Definition of Aromaticity

While the jellium model has shown success in explaining many experimental observations, it cannot account for all the complex behavior of metal clusters. A second model that will be used to describe cluster stability throughout this dissertation is aromaticity. Historically, aromaticity was first used to describe benzene and its derivatives that exhibited a lack of reactivity and possessed an “aroma”. It has since been applied to many organic molecules that have cyclic, conjugated, planar geometries and possess $(4n + 2) \pi$ electrons according to Hückel’s rule.²⁶ Traditionally, an aromatic molecule has p-orbitals perpendicular to the plane of the ring-structure, which overlap to form a delocalized ring of electrons known as a π -bond (Figure 2.6); this delocalization acts to stabilize the cluster (see Section 2.3.3).

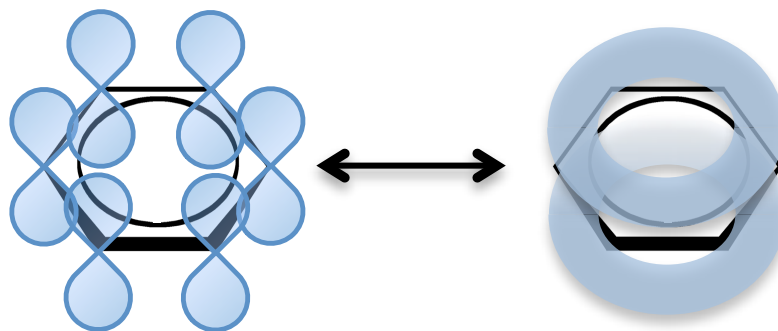


Figure 2.6 Schematic of the overlap of p-orbitals above and below the ring to create π molecular orbitals in benzene.

Aromatic behavior is not limited to p-orbitals and π -bonds, and there are cases of σ -aromaticity and δ -aromaticity, which can arise from the overlap of s-, p-, or d-

electrons.²⁷ Additionally, with the discovery of fullerenes has come a new concept of three-dimensional aromaticity, where the Hückel rule is satisfied for $2(n + 1)^2$ electrons.²⁸ However, these concepts will not be covered in this dissertation as they are not pertinent to the experimental findings; if interested, the reader is referred to detailed discussions in the literature.²⁷⁻²⁹ Instead, the more traditional form of aromaticity will be discussed and how it can account for experimental observations in metal clusters.

2.3.2 All-metal Aromaticity

The seminal work by Li et al.³⁰ was the first to show that aromaticity can be extended to gas-phase *metallic* clusters by identifying the first all-metal aromatic cluster in Al_4^{2-} . Magnetic bottle photoelectron spectroscopy experiments (see Section 3.4) were used to investigate a series of MAl_4^- clusters ($\text{M} = \text{Li}, \text{Na}, \text{Cu}$). When coupled with theoretical calculations it was shown that the M-atom effectively becomes a cation that sits atop the Al_4^{2-} subunit. Like benzene, Al_4^{2-} was found to possess a cyclic, planar structure and satisfy the Hückel rule with two electrons delocalized in a π -bond (i.e. $n = 0$ in $(4n + 2)$). Since this initial discovery, all-metal aromaticity has been extended to many other systems, and is now firmly established as a model to account for the enhanced stability shown by metal clusters that meet certain rules.³¹⁻³⁴ Our lab was the first to show experimental proof of a gas-phase *neutral* all-metal aromatic cluster.³⁵ This finding sparked our interest because it is analogous to the neutral aromatics that make up sandwich-compounds,³⁶ and thus represent a viable route to assembled materials.

2.3.3 Derivation of the Hückel rule

Although originally derived by Hückel using a simple linear combination of atomic orbitals (LCAO) method, the Hückel rule can be justified as a solution to the Schrödinger equation (Equation 2.1) for a particle on a circular ring. The ring is representative of the electron density in a π -bond as visualized in Figure 2.6. For a particle of mass m on a ring of radius R , it is convenient to adopt cylindrical coordinates, and thus the Hamiltonian in Equation 2.1 becomes:

$$\mathcal{H} = -\frac{\hbar^2}{2mR^2} \left(\frac{d^2}{d\phi^2} \right) \quad 2.6$$

where $\hbar$ is the reduced Planck's constant and ϕ is the azimuthal angle used in a cylindrical coordinate system. Correspondingly, the Schrödinger equation becomes:

$$-\frac{\hbar^2}{2mR^2} \left(\frac{d^2\psi}{d\phi^2} \right) = E\psi \quad 2.7$$

which has the solutions:

$$\psi_{(\phi)} = Ae^{\pm ik\phi} \quad 2.8$$

where A is a constant, i is the imaginary number, and k is a dimensionless quantity. Since increasing the azimuthal angle by 2π represents the same point on the ring, it follows that:

$$e^{ik\phi} = e^{ik(\phi+2\pi)} \quad 2.9$$

which is only true for $k = 0, \pm 1, \pm 2, \dots$. Thus, the eigenenergies are:

$$E = \frac{\hbar^2 k^2}{2mR^2} \quad \text{for } k = 0, \pm 1, \pm 2, \dots \quad 2.10$$

This means that the first energy level of the molecule is singly degenerate, and all the remaining energy levels are doubly degenerate. For the lowest n levels, $4n + 2$ electrons result in a closed set of molecular orbitals with all electrons paired (i.e. Hückel's rule). This is the most energetically stable electronic structure, and it is helpful (though not strictly correct) for the experimentalist to think of these as closed shells, analogous to the jellium model.

2.4 The Geometric Structure of Clusters

2.4.1 Geometric Closed Shells

The experimental observations of Knight et al. described in Section 2.2 were successfully explained by electronic shell closings. So it was quite surprising when this model failed to explain the variations at larger sizes. One example is shown in Figure 2.7.³⁷ Although it is not the first example ever identified, it is pertinent to the discussion of sodium clusters above. The spectrum shows that at very large sizes (i.e. in the thousands to tens of thousands of atoms) there are certain clusters that are preferably created in experiments. Because these experiments involve ionizing neutral clusters and detecting the resulting cations, the minima in Figure 2.7 correspond to neutral clusters with high ionization potentials, and thus represent the more stable clusters (or magic numbers, to adopt from the terminology in Section 2.2).

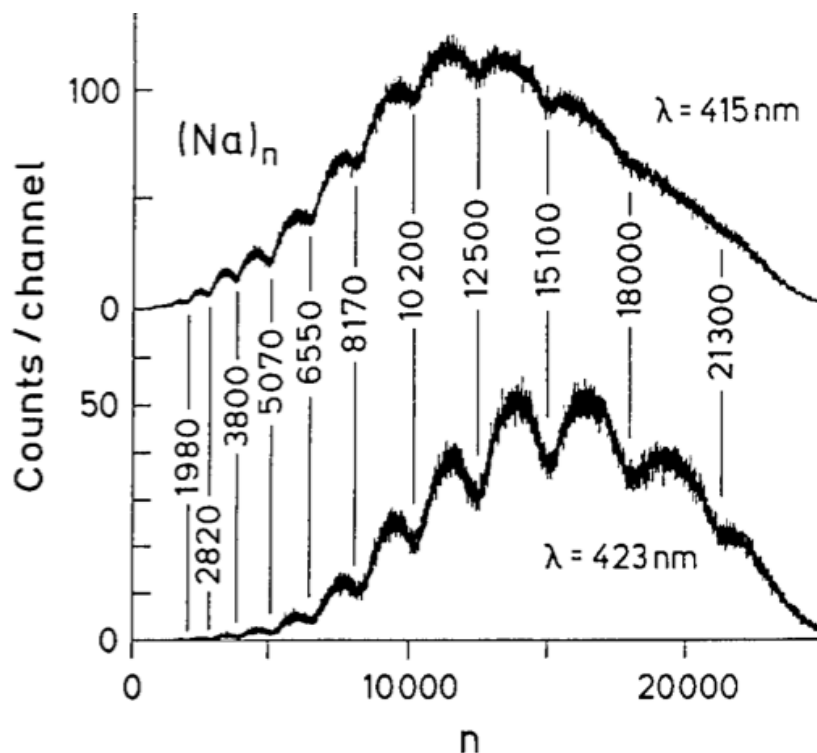


Figure 2.7 Experimental mass spectrum of large sodium cationic clusters, where the minima result from neutral clusters with high ionization potentials, and thus correspond to magic numbers. Reprinted from reference 37.

The minima observed in Figure 2.7 cannot be explained by electronic closed shells. Instead, each minimum corresponds to *geometric* closed shells, or shells of atoms. As the size of the cluster increases, the additional atoms must take some position inside the cluster, or add to some part of the cluster's surface. The total energy of the cluster becomes very dependent on the volume and total surface area of the cluster, and there is a competition to minimize both. The optimum geometry is a sphere, but since each atom itself is spherical, the cluster as a whole cannot have a smooth surface. It is useful to imagine the packing of spheres into nearly spherical shapes, where the surfaces are

truncated into distinct faces. The most optimal near-spherical geometry was first identified by Alan Mackay in 1962, and is known as the Mackay icosahedron.³⁸ This shape has 20 distinct faces and 12 vertices (think of a 20-sided die), with five-fold rotational symmetry and a very low surface energy. The smallest number of atoms that can create this shape is 13, with one atom at each vertex and one atom in the center. In fact, the amazing stability of the Al_{13}^- cluster previously identified in our lab³⁹ is in part due to this ideal geometry of high symmetry (note: it also corresponds to an electronic closed shell). The next Mackay icosahedron can be built from the 13-atom cluster by simply adding another layer of atoms to the surface. Like an onion, each successive layer corresponds to a certain number of atoms in a close-packed arrangement on the surface of the preceding layer. The formula for the number of atoms N it takes to create each shell S is:

$$N = \frac{10}{3}S^3 - 5S^2 + \frac{11}{3}S - 1 \quad 2.11$$

which leads to geometric shells consisting of 1, 13, 55, 147, 309,... atoms. It is customary to ignore the first shell, as this corresponds to a single atom. When extrapolated to $S = 9-19$, the numbers correspond to the 11 minima labeled in Figure 2.7. The numbers are not exact because it is difficult to experimentally assign the exact minimum for such large cluster sizes, but they are very close and are assumed correct.

2.4.2 Geometric versus Electronic Shells

The preference for cluster stability to be governed by electronic or geometric effects is dependent on numerous factors, and in actuality it is always a competition between the two. At small sizes, where there are discrete energy levels and the electrons are subjected to quantum confinement (i.e. the diameter of the cluster is on the order of the wavelength of the electron wave function), the organization of electrons tends to be the determining factor. As the cluster grows in size, the molecular orbitals evolve into bands, where the energy levels are almost continuous (see Figure 2.8). In this case, there is no great energetic benefit to have a certain number of valence electrons, and thus there is no electronic closed shell structure. At this point the geometric shell structure, or organization of the actual atoms, becomes the determining factor in minimizing the total cluster energy.

While this transition from electronic to geometric shells occurs at large sizes in most metals, such as sodium, there are certain metals, such as lead,⁴⁰ that strongly prefer close-packed geometries even in the few-atom size regime, as will be discussed in Chapter 6. Thus, the degree to which the cluster is governed by electronic or geometric shells depends on the identity of the constituent atoms. More specifically, some determining factors are the number of valence electrons, the size of the nuclei, and the energy gap between the s, p, and/or d electrons.

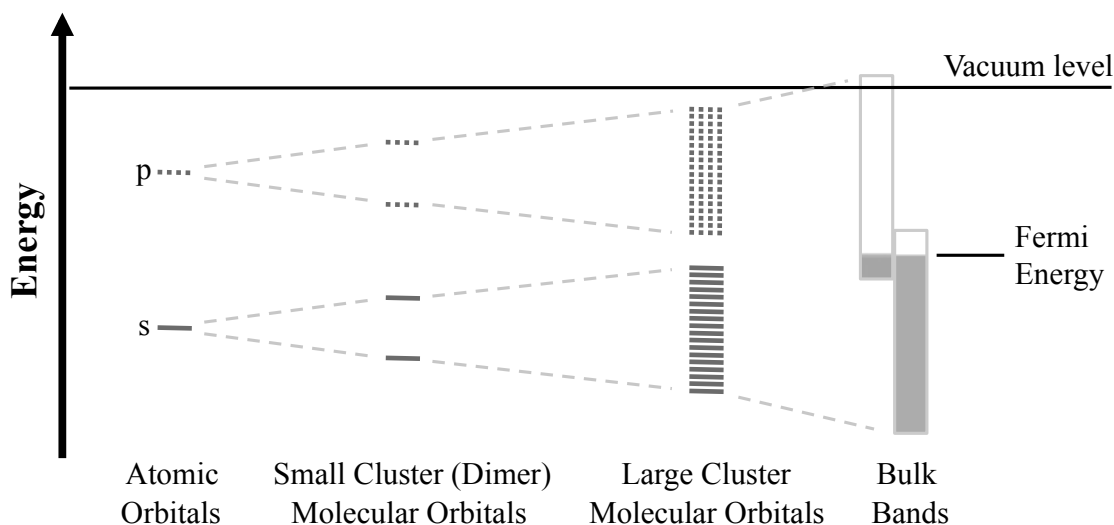


Figure 2.8 The evolution from atomic orbitals to molecular orbitals to bulk electronic bands, and the associated density of states. Fully occupied states are shown as solid lines or filled bands, while unoccupied levels are shown as dashed lines or empty bands. The completely filled s-state and the empty p-state shown are typical of a group II element, such as magnesium.

2.5 Principles of Photoelectron Spectroscopy

The interaction of light and matter can result in the absorption, emission, or scattering of electromagnetic radiation. By carefully studying the original and/or resulting radiation, an experimentalist can gain valuable information about both the light and the matter. This is a general approach of any spectroscopy. Within this dissertation, the discussion will be restricted to absorption of light by clusters, and the subsequent ejection of electrons. These “photoelectrons” can be studied by photoelectron spectroscopy, where the experimental observables are the kinetic energy (Section 2.5.1), abundance (Section 2.5.2), and anisotropy (Section 2.5.3) of the detached photoelectrons. These parameters offer a window into both the electronic and geometric structure of the parent cluster.

2.5.1 The Photoelectric Effect

Shine monochromatic light at matter, and if the photon energy is above some threshold, then there is a possibility for the ejection of photoelectrons. In the bulk, the threshold is known as the work function, while in atoms it is known as the ionization energy, I . The kinetic energy, E , of the resulting photoelectron detached from an atom is then:

$$E = h\nu - I \quad 2.12$$

where $h\nu$ is the photon energy. Increasing the intensity of the light does not affect the energy of the photoelectron since light has discrete quanta, a deduction that earned Albert Einstein the Nobel Prize. In actuality, the modern techniques of multiphoton ionization, above-threshold ionization, and intensity moderated strong-field effects can actually affect photoelectron energy,⁴¹⁻⁴⁴ but are beyond the scope of this dissertation.

2.5.2 Photodetachment Cross Section

If the photon energy is less than the ionization energy, then no photodetachment can occur. However, if the photon energy is more than the ionization energy, photodetachment *may* occur. This “likelihood” that an atom will absorb the photon and eject a photoelectron is known as the cross section for photodetachment. The cross section depends on numerous factors, for example at very high photon energies Compton scattering may be favored over photon absorption.⁴⁵ The derivation of the differential cross section for photodetachment is beyond the scope of this dissertation, and for a good

guide the reader is referred to the literature.^{46,47} The differential cross section, $\partial\sigma$, for detaching a photoelectron into the solid angle $\partial\Omega_{\mathbf{k}}$ is:

$$\frac{\partial\sigma}{\partial\Omega_{\mathbf{k}}} = \frac{4\pi^2}{c} h\nu |D_{\mathbf{k}}^{IF}(\theta, \phi)|^2 \quad 2.13$$

where $h\nu$ is the photon energy of the radiation, $D^{IF}(\theta, \phi)$ represents the photoelectron matrix element, $\mathbf{k}$ is a vector quantity denoting the energy and direction of the photoelectron, and the solid angle is defined in terms of spherical coordinates and is set equal to $\sin\theta d\theta d\phi$. Averaging over all orientations of the molecule and directions of the laser polarization, the total cross section can be found:

$$\sigma = \frac{8\pi^2}{3c} h\nu \int \sin\theta d\theta d\phi \overline{|D^{IF}(\theta, \phi)|^2} \quad 2.14$$

The matrix element $D^{IF}(\theta, \phi)$ in Equations 2.13 and 2.14 depends on the polarization of the incoming radiation, the initial wave function of the system with N electrons, the final wave function of the system with $N-1$ electrons, and the final photoelectron wave function. Accurately determining this parameter is a focus of many theoretical groups.⁴⁸⁻⁵⁰ For an experimentalist, the quantities of interest that can be varied are the photon energy and the polarization of the radiation, while monitoring total photodetachment signal.

2.5.3 Photoelectron Angular Distributions

The angular dependence in Equation 2.13 suggests that if one could measure the angle of the ejected photoelectron, some information about the *initial* wave function of

the electron within the atom could be obtained. It can be shown^{51,52} that for one-photon photodetachment using linearly polarized light, the differential cross section in Equation 2.13 can be normalized and reduced to:

$$I_{\theta} = \frac{1}{4\pi} [1 + \beta P_2(\cos\theta)] \quad 2.15$$

where I_{θ} refers to the photoelectron angular distribution, θ is the angle between the radiation polarization vector and the photoelectron vector, $P_2(\cos\theta)$ is the second order Legendre polynomial, and β is the anisotropy parameter, which contains information about the angular momenta of the initial and final photoelectron. The anisotropy parameter is limited to any value between -1 and +2, since I_{θ} cannot be negative. For the experimentalist, there are three different types of observations. An anisotropy parameter of -1 leads to a $\sin^2\theta$ distribution, a value of +2 leads to a $\cos^2\theta$ distribution, and a value of 0 leads to an isotropic distribution (i.e. no angular dependence).

To further understand the anisotropy parameter, it is important to note that a photon has one unit of angular momentum. Thus, when the initially bound electron absorbs a photon, it necessarily changes its angular momentum value by one (i.e. $l_{\text{final}} = l_{\text{initial}} \pm 1$). It has been shown⁵¹⁻⁵³ that the final photoelectron can be described as a superposition of partial waves where both $l_{\text{initial}}+1$ and $l_{\text{initial}}-1$ angular momenta states are represented. Strictly defined, the anisotropy parameter β depends on the relative cross sections of these partial waves ($\sigma_{l\pm 1}$), and the phase shift between these waves ($\delta_{l+1} - \delta_{l-1}$), such that:

$$\beta = \frac{l(l-1)\sigma_{l-1}^2 + (l+1)(l+2)\sigma_{l+1}^2 - 6l(l+1)\sigma_{l-1}\sigma_{l+1}\cos(\delta_{l+1} - \delta_{l-1})}{(2l+1)[l\sigma_{l-1}^2 + (l+1)\sigma_{l+1}^2]} \quad 2.16$$

where l is the angular momentum quantum number for the initial electron. For an electron originating in an s-orbital, l is equal to zero, and Equation 2.16 is reduced to $\beta = 2$. Thus, for photodetachment from an s-orbital an experimentalist should always measure a $\cos^2\theta$ distribution. To think of it another way, there is no option for an initial electron with $l = 0$ to lose one unit of angular momentum upon photon adsorption since l must be greater or equal to zero. Therefore, the ejected photoelectron must leave looking like a p-orbital, which indeed has a $\cos^2\theta$ distribution. For photodetachment from a p-orbital, where $l = 1$, there is no simple interpretation. The photoelectron leaves the cluster with an angular momentum of zero or two, *or* a combination of both. An accurate description of the photoelectron⁵¹⁻⁵³ is a superposition of the $l = 0$ and $l = 2$ partial waves, and the relative weights of these partial weights are described in Equation 2.16 by σ_{l+1} and σ_{l-1} . Further, the two partial waves can interfere with each other constructively or destructively. This term is represented in Equation 2.16 by $\delta_{l+1} - \delta_{l-1}$ and for complete constructive interference is equal to zero, or equivalently 2π . For a complete destructive interference the phase shift is π , and for a partial interference exactly between constructive and destructive it is $\frac{\pi}{2}$, or equivalently $\frac{3\pi}{2}$. By varying the weights of σ_{l+1} and σ_{l-1} in Equation 2.16, and separately the phase shift, any value between the limits -1 and 2 can be obtained for β . This is depicted in Figure 2.9, which shows the possible values of β as a function of the relative cross sections of the partial waves. Three curves are shown, representing the three limiting values of phase shift. In actuality an infinite number of

curves would exist, corresponding to all possible phase shifts. The top plot is for photodetachment from a p-orbital, while the bottom plot is for photodetachment from a d-orbital. A similar plot constructed for photodetachment from an s-orbital would be a horizontal line at $\beta = 2$, since only the σ_{l+1} channel is possible and there can be no phase shift.

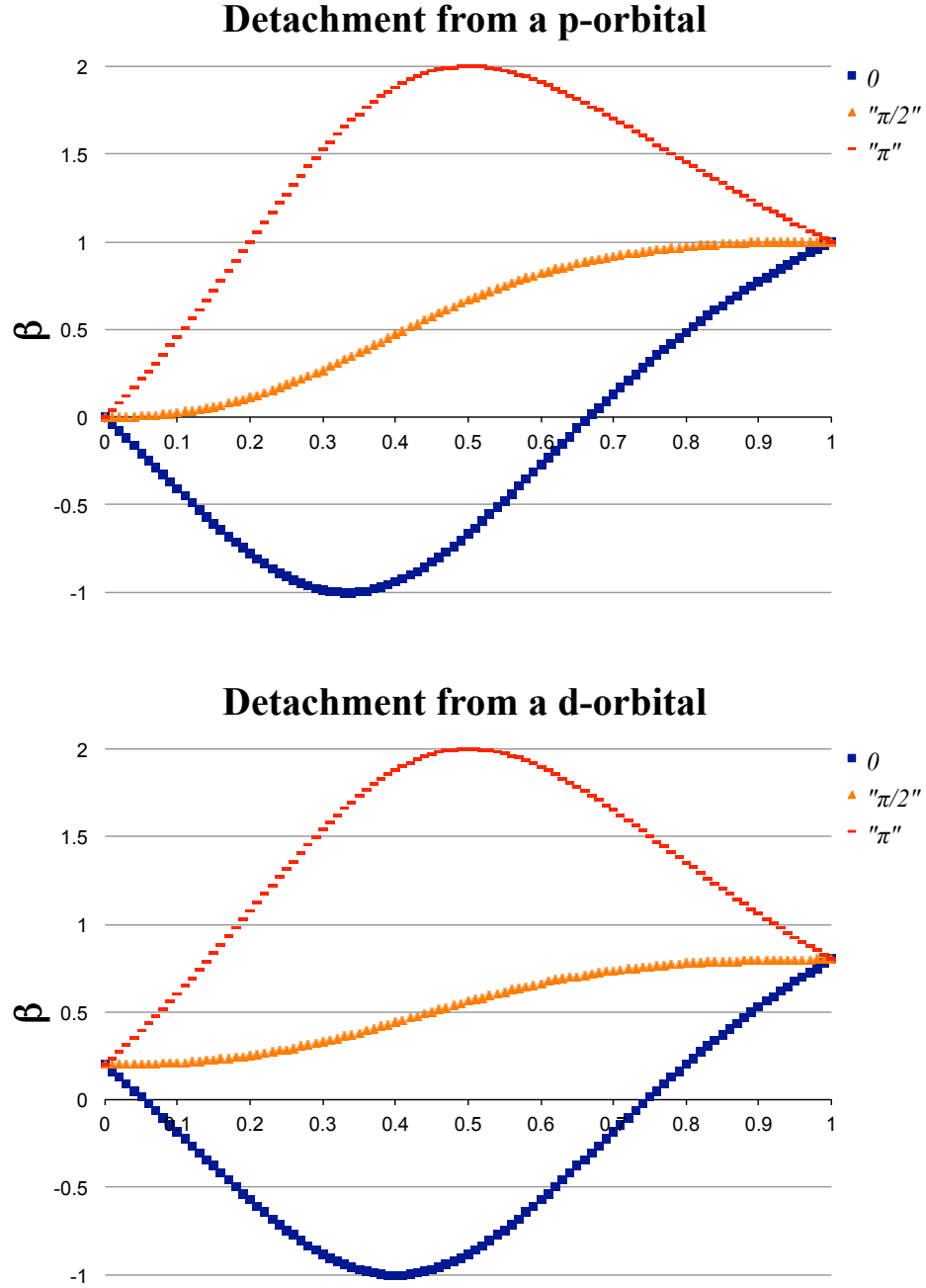


Figure 2.9 Plots of the anisotropy parameter as a function of channel preference, where 0 on the x-axis represents a complete preference for the lower angular momentum partial wave (e.g. $\sigma_{l+1} = 0\%$, $\sigma_{l-1} = 100\%$) and 1 on the x-axis represents a complete preference for the higher angular momentum partial wave. The red, orange, and blue plots denote the cases where the phase shift between the partial waves is π , $\pi/2$, and 0, respectively.

2.5.4 Extension to Molecular Clusters

The experimental observables described in the previous three subsections have been constructed for atomic species. For describing molecules the situation is complicated because i) there is no spherical symmetry in a molecule and so there are orientation effects, ii) there are vibrational and rotational degrees of freedom in molecules, and iii) angular momentum is not a good quantum number for molecular orbitals.

For the kinetic energy of an electron detached from a molecule, Equation 2.12 becomes:

$$E_{electron} = h\nu - I - \Delta E_{vib} - \Delta E_{rot} \quad 2.17$$

where ΔE_{vib} and ΔE_{rot} represent any vibrational or rotational excitation of the core upon ionization. For the photodetachment cross section of molecules, Equations 2.13 and 2.14 remain unchanged, as molecular orientation effects are already taken into account. However, the wave functions describing the initial and final states do become more complicated.

For photoelectron angular distributions from molecules, Equations 2.15 and 2.16 are no longer valid, as they rely on the values of angular momenta for atomic orbitals. Although molecular orbitals are constructed out of atomic orbitals, their angular momenta cannot be represented by the atomic angular momentum quantum number l . Thus, the various partial waves and their interference effects that makeup the photoelectron wave packet are extremely difficult, if not impossible, to disentangle for molecular

photodetachment. For the experimentalist, the situation is usually reduced to qualitative arguments, although there are new methods for trying to determine some quantitative information (see Chapter 8, and pertinent references⁵⁴⁻⁵⁶).

2.5.5 The Photoelectron Spectrum

The studies conducted within this dissertation concern metal cluster anions. This is principally for three reasons. First, charged clusters can be manipulated with electrostatic lenses, while neutrals cannot. Second, anions usually have lower ionization energies than neutrals or cations, frequently in the range of a few electronvolts; this permits the use of radiation in the visible or UV range. Third, as will be shown in this section, a photodetachment experiment on an anion yields information about both the anion and the resulting neutral.

For an anionic cluster, Equation 2.17 is valid. According to Koopmans' approximation⁵⁷ the ionization energy, I , can refer to the energy necessary for the removal of electrons from any molecular orbital within the anion:

$$I = -\varepsilon \tag{2.18}$$

where ε is the orbital energy. This means that photoelectron spectroscopy can be used to map out the molecular orbital energies of a cluster (provided the energies are less than the photon energy of the radiation used). This equivalently maps out the cluster's electronic structure. The resulting photoelectron spectrum is a plot of the number of electrons detached that possess a given kinetic energy, where each peak corresponds to a binding

energy of an electron to the parent cluster. The intensity of the peak in the spectrum is related to the photodetachment cross section covered in Section 2.5.2. For the experimentalist, it is easiest to relate the intensity of the peak to the occupancy of the molecular orbital (i.e. an orbital with one electron will provide half the signal of an orbital with two paired electrons), though this is not the only determining factor.⁵⁸

Unfortunately, photodetachment from one molecular orbital can lead to many possible photoelectron energies. This is because, as Equation 2.17 notes, the rotational and vibrational level populations within a given electronic state can affect the measured photoelectron kinetic energy. Traditionally, it is common to refer to photoelectron signal that originates from a certain molecular orbital as a “band”, even though this band may contain a progression of smaller peaks (i.e. a vibrational or rotational progression of photoelectron energies). To better explain this process, please refer to Figure 2.10, and note that since rotational splittings are generally smaller than the resolution of photoelectron experiments,⁵⁹ they are ignored here, and only the vibrational levels are shown.

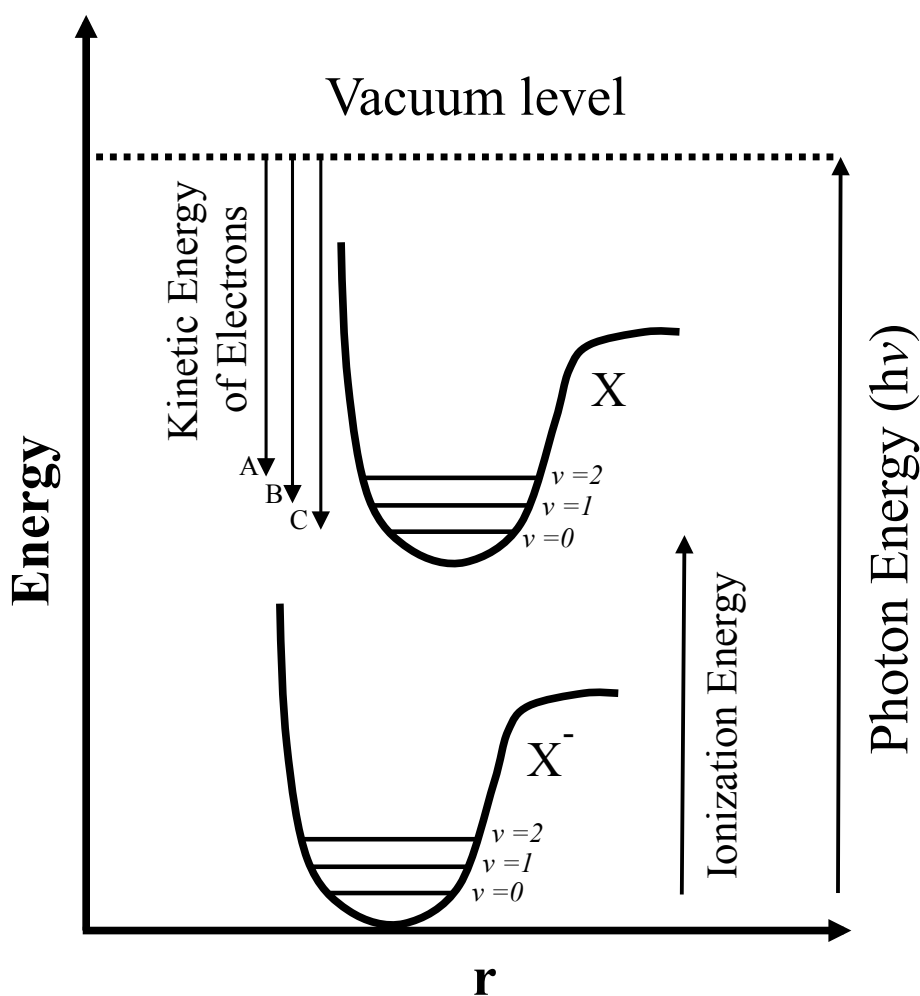


Figure 2.10 Electronic states with vibrational sublevels of a metal cluster anion X^- and the corresponding neutral X . The quantities pertinent to photoelectron spectroscopy experiments are shown as arrows. Conservation of energy ensures that the sum of the ionization energy, the change in vibrational sublevel, and the kinetic energy of the photoelectron must equal the photon energy ($h\nu$).

The multiple arrows (A, B, C) for kinetic energy of the photoelectrons shown in Figure 2.10 represent a spectral band, since they are all a result of photodetachment from the same orbital. At first guess, one may expect the intensity of A, B, and C to be equal, or perhaps that C will always be the most intense since it corresponds to the ground state

of the neutral. However, the exact intensities are dependent on the overlap of the initial and final state wavefunctions, known as the Frank-Condon overlap. This is due to the fact that the excitation in an electronic transition is extremely short compared to vibrational motion, and so the favorable transitions are those where the nuclei have not changed place. This can be explained by imagining a vibrating anion that instantly loses an electron. Since the nuclei have not moved, the remaining neutral will start a vibration that is consistent with the position of the nuclei.

The situation is further complicated if the vibrational sublevels of the original anion are significantly populated. In this case, a myriad of possible transitions result, which tends to broaden the photoelectron band. Luckily, modern experimental techniques can prepare “cold” anions to reduce this effect, and we will proceed as if only the ground state vibrational level is occupied. Figure 2.11 illustrates the Frank-Condon overlap, and shows the resulting photoelectron peak intensities that make up one photoelectron band.

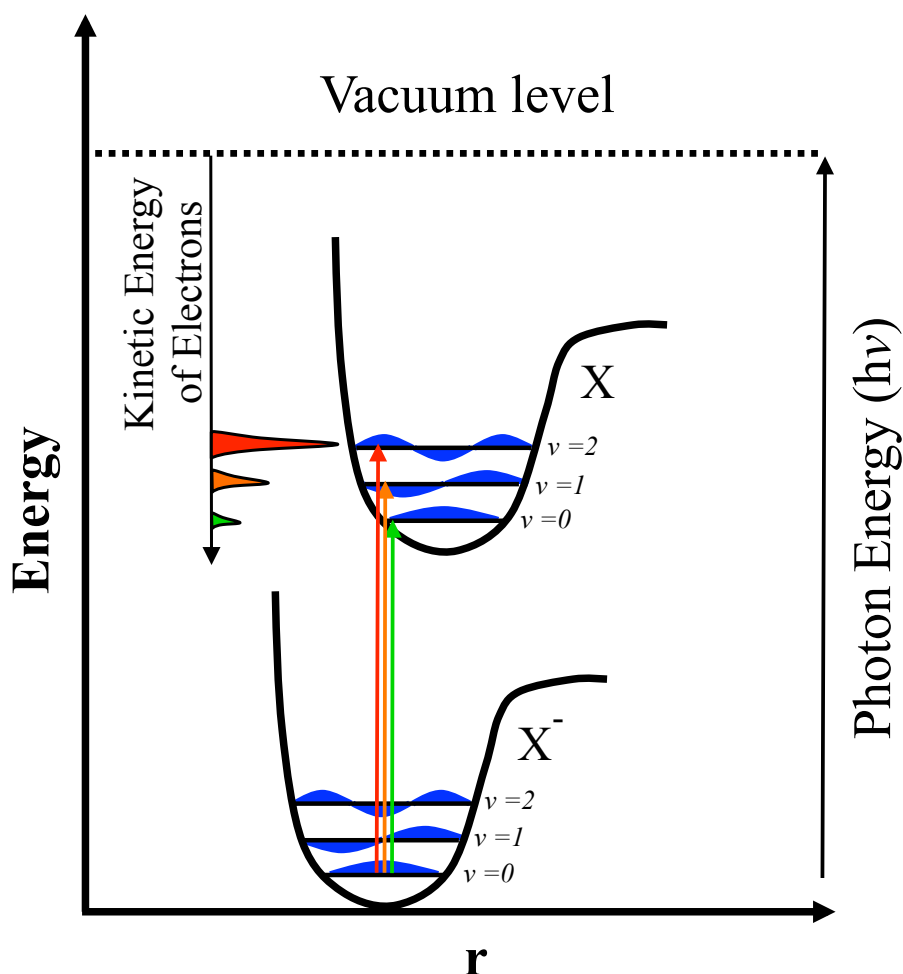


Figure 2.11 Illustration of the Frank-Condon principle, where better overlap between the initial and final state wave functions leads to more intense photoelectron peaks. All peaks shown are part of one photoelectron band, corresponding to photodetachment of a single electronic state.

The red arrow in Figure 2.11 is referred to as the vertical detachment energy (VDE). When experimental resolution is better than the vibrational splittings, the VDE corresponds to the most intense peak within a band. However, often times the experimental resolution is insufficient to resolve the vibrational progression, and in these cases the VDE is taken as the band's maximum intensity. The green arrow in Figure 2.11

represents the minimum amount of energy needed to detach an electron from the ground vibrational state. In other words, this is the binding energy of an electron to the neutral ground state, and so it is referred to as the electron affinity (EA). This will always be the peak with the highest kinetic energy within a band, provided the vibrational progression is resolved. When experimental resolution is not sufficient, an extrapolation to baseline of the edge of the photoelectron band is taken to reflect this energy.

The VDE and EA are important experimental observables, as they allow a comparison with theory to establish accurate calculations of ground state geometries (see chapters 4-7). For small clusters, where the geometries of the anion and neutral can be very different, large vibrational progressions can be possible and the EA can be difficult to accurately assign. For larger clusters, the geometries are usually quite similar between the anion and neutral and thus the VDE and EA are almost identical.

2.6 References

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Chapter 3

Experimental Details

3.1 Introduction

All of the experiments within this dissertation were performed on one instrument. This instrument, however, is quite complex and over the years has been built, modified, and upgraded to suit the goals of past and present researchers within our lab. Due to its complexity, it is convenient to separate the instrument into four main components, each of which has a specific goal and unique principles of operation, as discussed in the following sections. The first component is the cluster source, which is responsible for creating the clusters and delivering them into vacuum. The second component is a mass spectrometer, which separates and identifies the anions by mass-to-charge ratio. The third component is the magnetic bottle photoelectron spectrometer, which includes a photodetachment region and the subsequent collection and separation of electrons by kinetic energy. The final component is the velocity map imager photoelectron spectrometer. Like the magnetic bottle, it includes a photodetachment region and collects and separates electrons, but does so based on kinetic energies and angular distributions. While the principles governing the operation of the instrumentation are described within this chapter, minor details that are pertinent to a particular experiment are presented within each of Chapters 4-8. For a visual guide, the location and relative size of the various instrument components are shown in Figure 3.1 (note: some components enlarged for clarity). More detailed images of the components are presented within each section. Additionally, the pumping scheme for the vacuum system is briefly described at the end of the chapter.

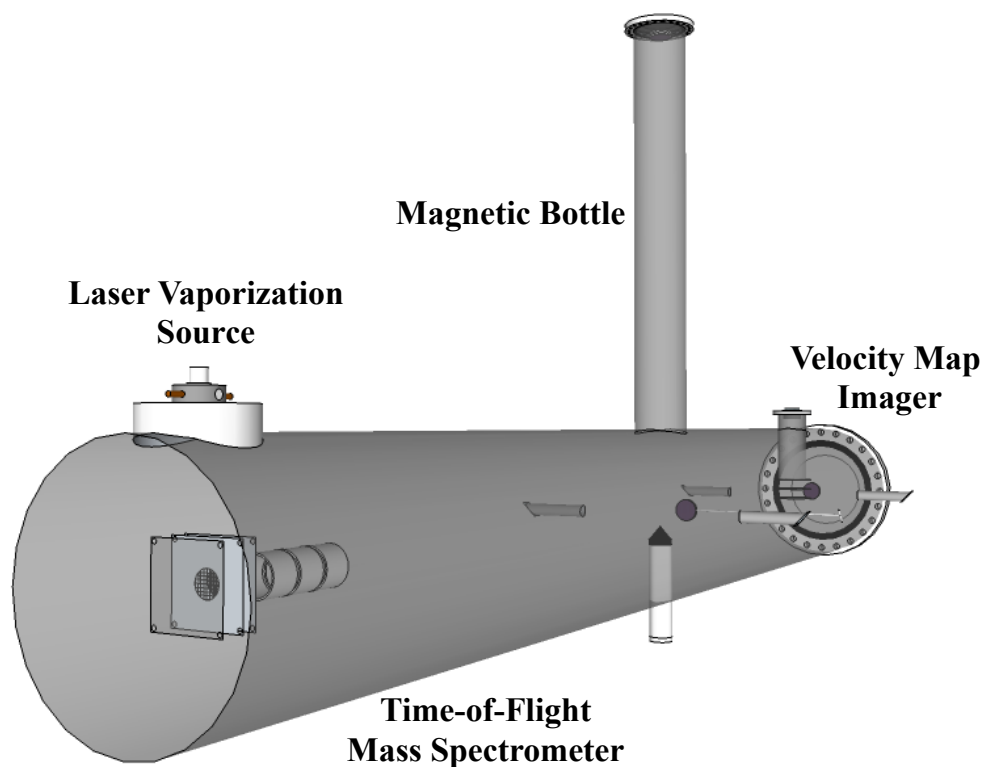


Figure 3.1 Schematic of the instrument used for all experiments. Relative sizes and locations of the components are inexact, and instead reflect rough estimations.

3.2 The Cluster Source

The possibility of using laser radiation to vaporize metal within a mass spectrometer chamber was first shown in 1966 by a team of researchers at Penn State.¹ In 1981, Richard Smalley at Rice University combined this laser vaporization technique, or LaVa for short, with existing pulsed supersonic nozzle technology.² The result was a technique for the facile production of large amounts of cold metal clusters, which quickly became a popular method of cluster production.³⁻⁵ Consequently, Smalley's design became known as the LaVa source, even though it was not the first to use lasers for metal

vaporization.¹ Since 1981, the LaVa source has been employed by many groups for cluster production, and thus has been subjected to many modifications.³⁻⁵ The source used in our laboratory is largely based on the design Smalley published in 1981.² Shown in Figure 3.2, our cluster source consists of a stainless-steel housing with two perpendicular channels (i.e. along the x- and y-axis) that are intersected by a third perpendicular channel, which is slightly offset (i.e. just off the z-axis). The first channel houses a metal rod, which consists of either a pure metal or an alloyed mixture, depending on the goal of the particular study. This rod fits through an ultra-torr fitting so that approximately half the rod is within the source, and half is outside the instrument. This setup allows for an external stepper motor, which can translate and rotate the metal rod at variable speeds. A rotation of about 1 rpm is typically used to ensure a fresh part of the rod is presented to each laser pulse. The second channel within the LaVa source is entirely empty and allows for the passage of a laser beam employed to ablate the metal rod target. This channel is sealed by an entrance window, which consists of a quartz slide oriented at Brewster's angle,⁶ and an exit window, which is a quartz disc flush against an o-ring seal. The exit window is a bit of a misnomer, as the laser never reaches it, provided the metal rod is present. However, the exit window is important, as it allows for simple laser alignment when the metal rod is removed. The last channel is slightly offset from the first two. It is open at one end (into the instrument) and connected to a pulsed valve at the other end through an o-ring fitting. The pulsed valve consists of a solenoid, spring, metal arm, and a Teflon plug. When a direct current is supplied to the solenoid it lifts a metal arm, breaking the Teflon seal and opening a pinhole. This allows for the precise delivery of a gas into the LaVa source.

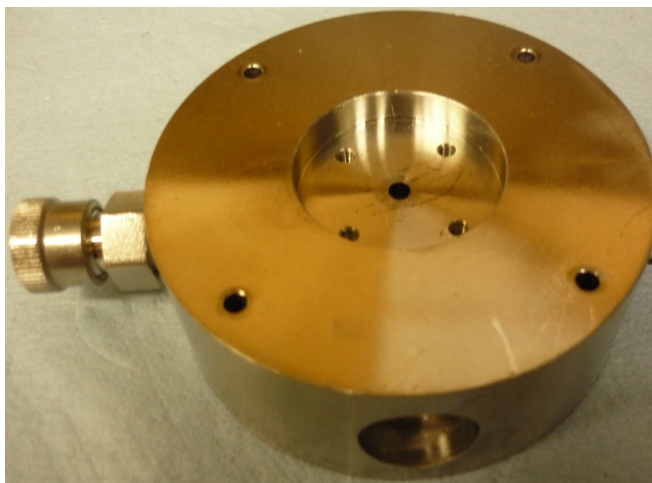


Figure 3.2 Picture of the LaVa source used. The metal rod is inserted through the ultra-torr fitting displayed on the left side of the image. The pulsed valve (not shown) is attached to the top of the source, while the ablation laser would enter through the opening shown at the bottom of the image.

The experiment is conducted at a repetition rate of 10 Hz, and begins when the second harmonic (532 nm) of a neodymium doped yttrium aluminum garnet laser (Spectra Physics INDI-50) is focused onto the translating and rotating metal rod. This creates a plasma, where the vaporized metal becomes entrained in a pulse of inert “carrier” gas (usually helium) delivered from the pulsed valve at a corresponding 10 Hz. The precise timing (to the microsecond) of the laser and gas pulse can be varied by the researcher; optimum conditions have been found for laser ablation near the end of the gas pulse. Backing pressures of gas on the order of several atmospheres are used, which results in a gas pulse of sufficient density to first recombine the electrons and ions within the plasma, and subsequently cool the excited atoms to room temperature through collisions. Importantly, the resulting packet is actually a mix of atoms, ions, and electrons

at this point. As the cooled atoms begin to condense and form clusters, some cold electrons attach to the neutral species, creating anionic clusters.⁷ The end result is a packet that contains anions, cations, and neutrals. Before this packet enters the main vacuum chamber it encounters a nozzle, which is attached to the LaVa source and can be changed to allow the use of nozzles with various lengths and channel diameters. The longer the metal atoms remain in a confined channel, the more time they have to cool and condense, and so the size of the clusters can be somewhat controlled by varying the nozzle dimensions. However, if the channel is too long, metal clusters may have enough time to reach the walls of the nozzle and be lost.⁸

At the end of the nozzle, the clusters are introduced to a high-vacuum chamber ($10^{-8} - 10^{-7}$ torr). The expansion from the high pressure source through a relatively large orifice (i.e. one in which the diameter is much greater than the mean free path of the gas) results in many collisions between the clusters and the inert carrier gas. This effectively cools the clusters vibrationally, rotationally, and electronically, which is ideal for spectroscopy experiments. As the molecules leave the source and enter the vacuum chamber they accelerate, and the translational energy of the beam after expansion is quite high, though the relative velocity spread within the ensemble becomes low. The low velocity spread is due to the fact that any slow moving molecules within the beam are “sped-up” by faster moving ones, and vice versa. Also, molecules with velocity directions perpendicular to the beam will collide and either be directed entirely out of the beam or start moving parallel to the beam. Thus, the random kinetic energy is redistributed to a large “forward” velocity with a very narrow spread. Because the translational speed is much greater than the local speed of sound, the expansion is dubbed

supersonic expansion. Typical rotational temperatures of the clusters after supersonic expansion are on the order of 10 K, while vibrational temperatures are on the order of 50 K.⁹ The translational temperature of the *distribution* within the beam can be much less than 10 K, even though the translational energy of the beam as a whole can be quite high.⁹ For a further description of the velocity distributions, temperatures, and Mach numbers the reader is referred to the seminal work by Anderson and Fenn,¹⁰ as well as a good review by Levy.¹¹

The LaVa source is oriented directly above the entrance to the mass spectrometer, where the middle portion of the beam emerging from the nozzle is centered between the time-of-flight electrodes. The space between the end of the nozzle and the start of the time-of-flight electrodes is on the order of a few inches, which allows sufficient time for the beam to expand to collision-free conditions while also creating a spatial spread of the beam in the shape of a cone. This spatial spread of the beam between the time-of-flight electrodes can be a problem for mass spectrometer resolution, and so a skimmer is placed before the entrance to the mass spectrometer to collimate the beam. The end result is a well-collimated, collision-free, low temperature cluster beam that is ideal for photoelectron spectroscopy.

While the LaVa source is extremely robust and able to create clusters of almost any metal, there is often an art to mastering the experimental conditions. Thus, no exact numbers are given here for nozzle dimensions, carrier gas pressure, laser power, etc. These values differ from experiment to experiment, and depend on the inherent properties of the metal to be studied and the cluster size desired by the researcher. Finding the right

combination of all the experimental variables can be a daunting task, and cluster production is often the limiting factor in performing the experiments.

3.3 Time-of-Flight Mass Spectrometry

The purpose of the mass spectrometer is to separate and identify ions based on their mass-to-charge ratio. An ion with charge q subjected to an electric field $\mathcal{E}$ for a distance l gains a kinetic energy:

$$KE = q\mathcal{E}l \quad 3.1$$

corresponding to a velocity:

$$v = \sqrt{\frac{2q\mathcal{E}l}{m}} \quad 3.2$$

where m is the mass of the ion. This means that ions given an initial “push” from an electric field into a field free region will separate in time based on their mass-to-charge ratio. Thus, the time, t , it takes an ion to go through a field free region of distance D is:

$$t = \frac{D}{\sqrt{\frac{2q\mathcal{E}l}{m}}} \quad 3.3$$

The time-of-flight mass spectrometer makes use of these equations to subject a group of ions to an electric field, which accelerates the ions into a field free region. Since all ions of the same charge gain the same kinetic energy, heavier ions will have a lower velocity, and therefore a longer flight time, than lighter ions. However, this assumes the ions all

travel the same distance l through the initial electric field. In actuality there will always be a spread of initial positions, so that some ions will start closer to the field free region, and will therefore gain less energy before entering it. These same ions, though, will have a shorter total distance (i.e. field region plus field free region) to cover before reaching the end of the field free region. The competing effects are effectively offset at some particular distance, when the ions that start farther back exactly catch up to the ions that start at the front, and the ions are “focused”. Knowing precisely where this point is located can be easy theoretically, but difficult to control experimentally. By introducing a second field region and adjusting the two electric fields, the focus can be moved.¹² This allows for a detector to be placed at a certain distance within the field free region and the experimentalist can adjust the voltages until the ions are focused at this point. This arrangement was first proposed by Wiley and McLaren in 1955,¹² and is the basis for our spectrometer.

The clusters leave the source, pass through a skimmer, and are directed into the mass spectrometer, which is oriented perpendicular to the cluster beam. A collinear arrangement is not favorable, as the high transverse speed of the molecular beam would limit the maximum achievable resolution of the spectrometer. Thus, the clusters are introduced perpendicularly down into the spectrometer, between the first two electrodes of the extraction region. The first time-of-flight electrode, henceforth referred to as TOF1, is provided with a large negative potential (for example -1500 V), while the second electrode, referred to as TOF2, is at a less negative potential (for example -1350 V), and the third electrode is kept grounded. Thus, in the first stage the clusters are accelerated by a potential difference of about 150V, while in the second they are

accelerated by a potential difference of about 1350V. After the third electrode they enter the field free region and eventually impinge on a detector. As mentioned above, the exact voltages can be adjusted to maximize the focusing conditions, which often change from experiment to experiment. TOF1 and TOF2 are separated by 1.6 cm, while TOF2 and the grounded electrode are one cm apart. TOF2 and the grounded electrode have one cm apertures to allow the clusters to pass through them, and are covered with mesh (45 by 45 holes per inch) to ensure uniform fields, though the mesh is still highly transmissive to the ion flight.

As the ions pass the grounded electrode they enter an einzel lens, which consists of three cylindrical lenses, where the first and last lens are grounded and the middle lens is held at a large negative voltage (for example -700 V). This helps focus the ions in the directions perpendicular to the major axis of the spectrometer. Additionally, horizontal and vertical deflectors are included to allow for steering of the ion beam. The vertical deflector is quite important, as the initial downward velocity of the cluster beam from the source is large. The result of these optics is, ideally, a spatially focused beam travelling exactly horizontal down the center of the instrument. The field free region is about 1.5 meters and ends with two microchannel plates in a chevron arrangement for cluster detection. The detector is mounted on a rotating and translating arm, such that the angle and position can be optimized from outside the instrument. This also allows the detector to be completely moved out of the path of the ions, so that the ions may travel further down the instrument to the velocity map imaging region described in Section 3.5.

The front plate of the detector is grounded in order to preserve the field free region, while the back of the second plate is held at +2200 V. The anions crash into the

detector, resulting in a cascade of electrons, which is amplified and sent to a digital oscilloscope (LeCroy 9304A). The mass spectrum, an example of which is shown in Figure 3.3, can be saved to a personal computer for data analysis through a GPIB interface. The spectrum is a plot of counts versus time-of-flight. The time can be recalculated into mass-to-charge ratio based on Equation 3.3 above, but it is much more reliable to use a calibration. This is accomplished by gaining a spectrum of a known distribution of ions, where a linear plot of mass versus the time squared gives an accurate scaling factor.

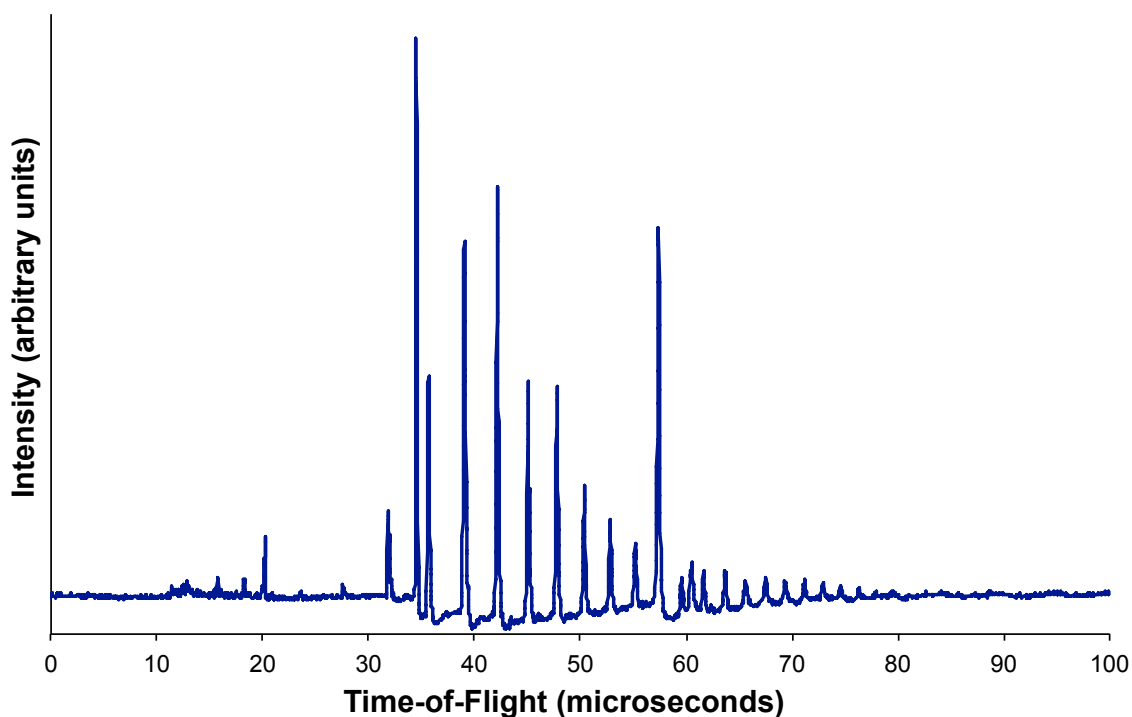


Figure 3.3 Example mass spectrum of aluminum clusters, showing a distribution of sizes and their corresponding time-of-flights before reaching the detector.

The experimentalist must carefully control the timing of the various parts of the mass spectrometer to yield reliable flight times. In our experiment, the voltages on the time-of-flight electrodes are governed by high-voltage solid-state switches, which deliver a square wave pulse of adjustable width to the electrodes. A typical width is on the order of 200 μ s, with a very fast rise time to ensure uniform field during extraction of the anions. The electrode voltages must be pulsed, otherwise the cluster packet entering from the skimmer would be extracted before reaching the center of the mass spectrometer, and crash into the walls of the electrodes. There is an ideal delay time between when the ions are created in the LaVa source and when the TOF electrodes are pulsed. This time corresponds to the moment when a majority of the cluster packet reaches the center of the extraction region. An example extraction and the resulting ion trajectories are shown in Figure 3.4, as modeled with SIMION 8.0.¹³ The trajectories of 50 ions are shown, assuming the cluster packet is a Gaussian-like distribution of ions centered at the center of the extraction region. As can be seen, some ions do impact on the TOF electrodes themselves, but most pass through and are focused slightly.

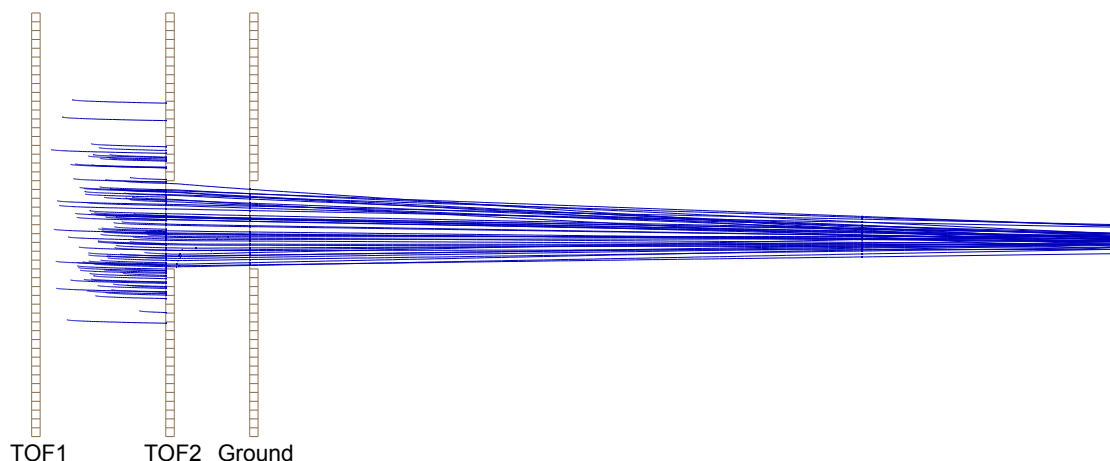


Figure 3.4 Simulation of ion trajectories when the TOF electrodes have been pulsed at the optimum time (i.e. when the cluster packet arriving from the source region is centered around the axis of extraction).

Concurrent with the pulse of the electrodes, the oscilloscope is also triggered, setting time zero on the spectrum. The middle lens of the einzel stack, and the subsequent deflector plates, can be held at a static voltage, but must be adjusted often to maximize the total ion throughput to the detector.

3.4 Magnetic Bottle Photoelectron Spectroscopy

The time-of-flight mass spectrometer spatially separates ions into ion packets, where each packet consists of a small spread of identical mass-to-charge ratio ions. While this allows for the identification of the ion packets as discussed above, it is also ideal for photoelectron spectroscopy experiments. As the packet travels down the spectrometer and becomes isolated, it can be intersected with a laser at a photodetachment region,

where the laser timing is simply matched to the corresponding flight time of the ion packet. In our magnetic bottle experiments, the photodetachment laser is a 308 nm beam from an unpolarized XeCl excimer laser (Lambda Physik LPX 100), which enters and exits the instrument through quartz slides oriented at Brewster's angle.⁶

In principle, photoelectrons detached from the cluster ions could be detected using a microchannel plate oriented at one angle off the axis of the mass spectrometer, where the energy of the electrons, E , corresponds to the time, t , it takes them to traverse the distance d , such that:

$$E = \frac{1}{2} m_e \left(\frac{d}{t} \right)^2 \quad 3.4$$

where m_e is the mass of the electron. Indeed, photoelectron spectroscopy experiments were performed in this manner for many years.¹⁴ However, this method suffers from low photoelectron signal. One reason is that only a limited number of anionic clusters can be forced into the photodetachment region before the coulombic repulsion is too great. This is known as the space-charge limit, and for a typical photodetachment region of one cubic centimeter this limit corresponds to about 1000 anionic clusters.¹⁵ Assuming single electron detachment, which is valid for the laser intensities used, only 1000 total electrons can be detected. In addition, the photodetached electrons have an angular distribution, as discussed in Section 2.5.3, and so only a small fraction of the total number of photoelectrons can reach the detector for a given laser pulse. This can be somewhat improved by using lasers polarized at the magic angle,¹⁶ but is still far from perfect. For the researcher, a setup that could collect all of the electrons regardless of

their energy or angle would be ideal, especially since it is not always trivial to create a strong ion beam corresponding to the maximum number density of the space-charge limit.

The solution to this problem was first obtained by Kruit and Read in 1983,¹⁷ when they used an inhomogeneous magnetic field to parallelize an angular distribution of electrons into a directed beam. The design was based on standard principles used in magnetic mirrors and magnetic bottles, giving the current technique its namesake. The original design by Kruit and Read collected all electrons over 2π steradians, but has since been modified by groups^{18,19} to collect over the full solid angle of 4π steradians; our design is based on these modifications.

To examine the principles of operation, imagine an electron photodetached in a magnetic field. The electron will feel a force, $\mathbf{F}$, given by:

$$\mathbf{F} = e\mathbf{v} \times \mathbf{B} \quad 3.5$$

where $\mathbf{v}$ is the velocity of the electron, e is the elementary charge, and $\mathbf{B}$ is the magnetic field. This force induces the electron to spiral around the magnetic field line. As it travels from an area of high to low magnetic field, the force in Equation 3.5 necessarily decreases, and thus the electron's transverse velocity decreases. Due to conservation of angular momentum, the longitudinal velocity of the electron must then increase correspondingly. This can be visualized in Figure 3.5 as the unspiraling and parallelizing of the electrons as they move from the high field to the low field region.

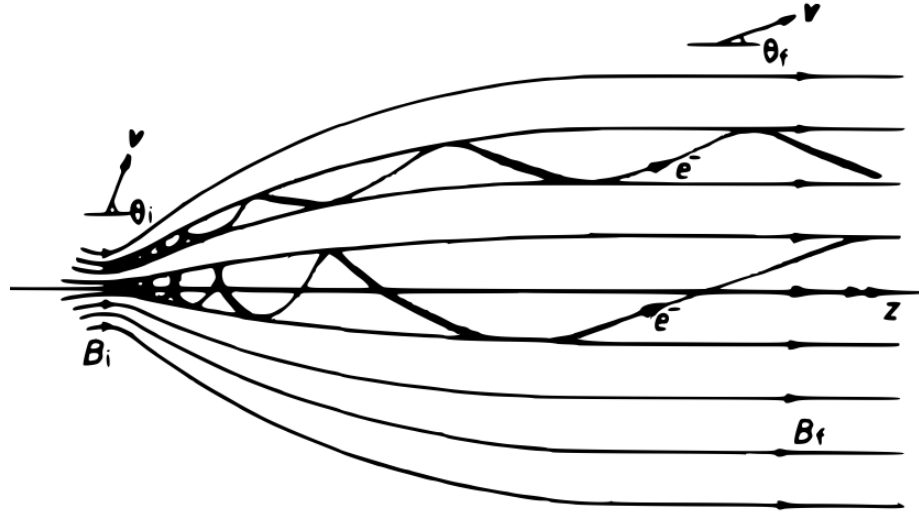


Figure 3.5 Diagram of the parallelization of ejected electrons as they travel away from the photodetachment region towards the detector. Reprinted from reference 17.

More specifically, a photodetached electron that is emitted at an initial angle θ_i , with a velocity v , charge e , and mass m , in the presence of an initial magnetic field B_i , undergoes helical motion where the angular frequency, ω , is:

$$\omega = \frac{eB_i}{m} \quad 3.6$$

and the initial radius of orbit, r_i , is:

$$r_i = \frac{v \sin \theta_i}{\omega} \quad 3.7$$

The corresponding angular momentum, l_i , of the electron's motion is:

$$l_i = r_i^2 m \omega = \frac{m^2 v^2 \sin^2 \theta_i}{eB_i} \quad 3.8$$

Since angular momentum is conserved (i.e. $l_i = l_f$), the parallelization of the electrons can be expressed as:

$$\frac{\sin^2 \theta_f}{\sin^2 \theta_i} = \frac{B_f}{B_i} \quad 3.9$$

In our experiment, an initial field of 1.2 T is created by a conical rare-earth magnet, while the final field of 0.001 T is created by a solenoid. Thus, even for an electron ejected initially at 90° away from the detector, its final angle becomes 1.7° according to Equation 3.9. This parallelization results in a near 100% collection efficiency of the magnetic bottle.

The electrons travel away from the photodetachment region and traverse a length of 1.75 meters in a drift tube, which is shielded with μ -metal sheets to prevent stray magnetic fields from deflecting the electrons. At the end of a drift tube three microchannel plate detectors are mounted in a Z-stack configuration, with the back plate held at +4000 V. The high-voltage, and number of microchannel plates, is necessary to obtain a sufficient gain in detection from so few electrons. Similar to ion detection in the mass spectrometer, the output signal is amplified and sent to an oscilloscope. The oscilloscope is timed to start precisely when the photodetachment laser intersects the cluster beam, which can be estimated with a photodiode placed near the interaction region. Thus, the times of the electron flights can be measured and related back to their kinetic energy according to Equation 3.4. Usually though, the kinetic energies of the electrons are determined by a calibration, measuring the flight times of electrons ejected from an ion with known detachment energies. The most common ion used for calibration

is atomic bismuth due to its facile synthesis, large range of detachment energies, and lack of vibrational or rotational states. At the photon energies used in our experiments, photodetachment of electrons from the bismuth anion leads to three possible transitions, which correspond to electron binding energies of 0.947 eV, 2.363 eV, and 2.861 eV. These three photodetachment channels should produce three peaks with kinetic energies derived from Equation 2.12. By plotting these kinetic energies as a function of the inverse of the measured electron time-of-flight squared (in accordance with the relationship shown in Equation 3.4), the experimentalist can derive a linear calibration curve to use for all subsequent measurements.

3.5 Velocity Map Imaging

The magnetic bottle photoelectron spectrometer benefits from excellent collection efficiency but has one major drawback. It wastes the angular information contained in the distribution of the photodetached electrons. As discussed in Section 2.5.3 the photoelectron angular distribution is valuable because it can reveal information about the angular momentum state of the orbital from which photodetachment occurs. Charged particle imaging, first employed by Chandler and Houston in 1987 for the detection of photodissociation fragments,²⁰ allows for measurement of the energy and angular distribution simultaneously. This is accomplished by using electric fields to project a distribution of charged particles onto a position-sensitive detector, yielding a two-dimensional image of the original three-dimensional momentum distribution. The detector usually consists of microchannel plates coupled to a phosphor screen, which can be photographed using a digital camera. Although originally used for ions, the imaging

technique can be used for the detection of photodetached electrons. Measurement of an electron on a position sensitive detector collapses the electron wavefunction to a point. After a large number of repetitions, the two-dimensional projection of the three-dimensional probability density of the wavefunction can be mapped out. Additionally, provided that the applied field is exactly perpendicular to the face of the detector, the velocity distribution can be attained. Thus, imaging can yield the energetic and angular information of photodetached electrons.

For a point source of electrons, this technique works perfectly. However, experimentally this is impossible, as the intersection of a photodetachment laser with an ion packet of non-negligible volume leads to multiple electron sources. With the original imaging design, this yields a blurry image corresponding to the overlap of various distributions. In 1997, Eppink and Parker discovered that a unique arrangement of electrodes drastically reduced the image blurring.²¹ (The actual discovery was made during “down-time” waiting for the machining of new electrodes, a valuable lesson for experimentalists.) The initial longitudinal spread of electrons is corrected for by using three electrodes (similar to the Wiley-McLaren setup discussed in Section 3.3), while the transverse spread is corrected for by using open circular electrodes (i.e. no wire meshes), which create transversally inhomogeneous fields. By carefully adjusting the electric fields used, one can create the exact inhomogeneous electric field needed to funnel all electrons with the same velocity vector onto the same point on the position sensitive detector. This is shown in Figure 3.6, which is a simulation of electron trajectories from three different positions, conducted in SIMION 8.0.¹³ The positions are chosen to reflect different parts of the ion packet as it traverses (i.e. from top to bottom in the figure)

across the photodetachment region. This new experimental design was dubbed “velocity map imaging” and allowed for high-resolution images of the momentum-space distribution of the electrons in the plane of the detector.

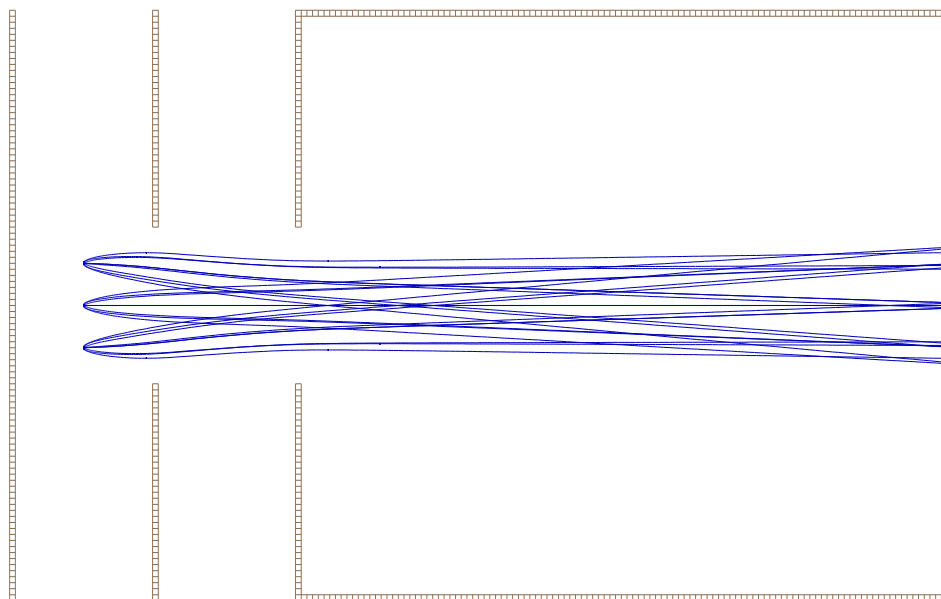


Figure 3.6 Simulation of electron trajectories from three positions within the photodetachment region. Electrons with the same initial speed and direction are mapped to the same point on the detector.

By using a laser with a polarization parallel to the face of the detector, the angular distribution of the photodetached electrons will be cylindrically symmetric. This is important because it allows the original three-dimensional photoelectron angular distribution to be reconstructed from the two-dimensional projection through the use of an inverse integral transformation, termed the Abel inversion.²² The result is equivalent to a two-dimensional slice through the center of the three-dimensional distribution, which allows for the complete recovery of the original angular distribution. However, the Abel

inversion does not deal with experimental noise very well, and thus there has been much work to mathematically treat this problem.²³⁻²⁶ One of the most widely used methods is the basis set expansion method (BASEX),²⁴ which takes the experimental image and represents it as an expansion in a basis set of functions that are “well-behaved”, meaning they are more easily treated in the Abel inversion. This method has since been improved upon by simply using polar coordinates for the functions, in a method known as pBASEX.²⁵

The Abel-inverted image allows all the angular and energetic information to be extracted in a straightforward manner. Integrating over all angles at a particular radius from the image center yields a total intensity. The intensity can be plotted as a function of the radius to yield a spectrum, which can be converted into a typical photoelectron spectrum by calibration (see discussion in Section 3.4). The angular distribution of a given radius can be fit according to Equation 2.15 and the anisotropy parameter can be extracted. An example of a raw image and the corresponding reconstructed image (using BASEX) and photoelectron spectrum are shown in Figure 3.7.

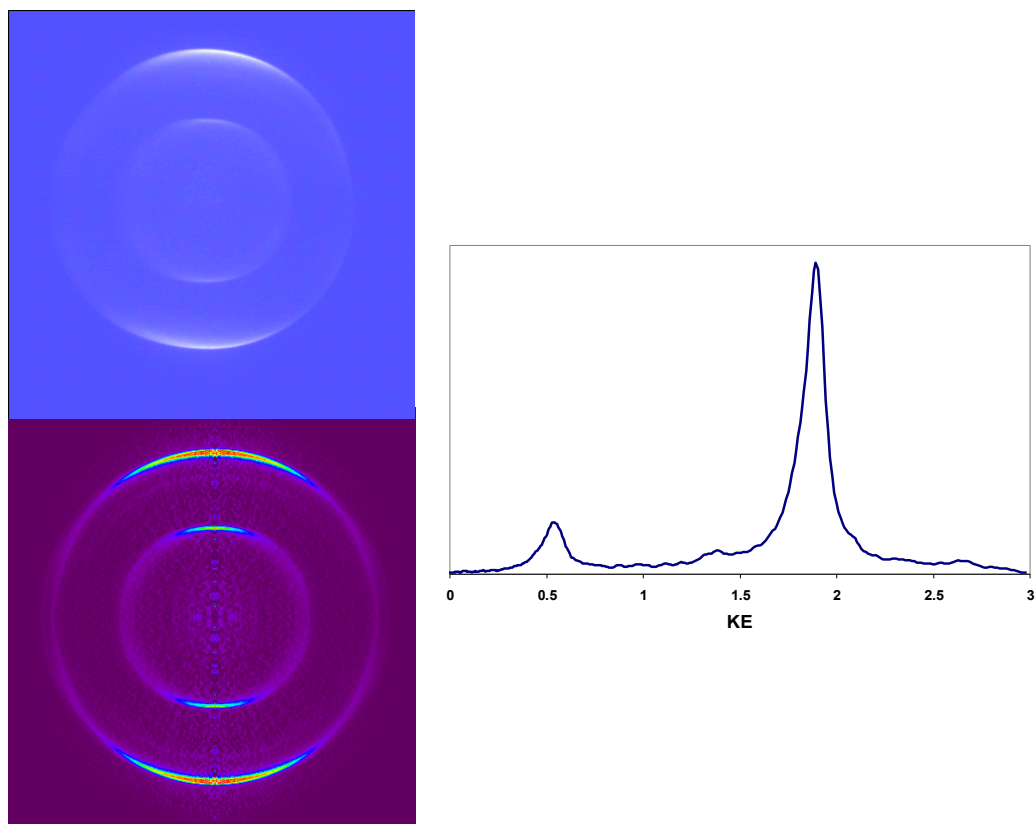


Figure 3.7 An example of a raw image (top, left) along with the corresponding BASEX reconstructed image (bottom, left) and resulting photoelectron spectrum (right) shown on a kinetic energy (KE) scale. The raw image was obtained from the multiphoton photodetachment of xenon atoms.

In our experiment, the velocity map imaging region is housed inside of a μ -metal shield to prevent stray magnetic fields from deflecting photodetached electrons. The cluster beam enters the region via a hole in the μ -metal shield, delivering the ions between the first two electrodes of the three-electrode design of Eppink and Parker.²¹ An identical hole on the other side of the μ -metal shield allows the ions to pass through the photodetachment region so that the researcher can monitor the anion distribution on a detector. The anion detector (Burle Electro-Optics bipolar detector) contains microchannel plates, a scintillator, and a photomultiplier tube, and yields better total gain

than a traditional microchannel plate stack. This is needed, as the mass spectrometer region is extended by about one meter relative to the magnetic bottle section, resulting in better resolution but poorer total ion signal. The μ -metal shield also has two other holes to allow the photodetachment laser to proceed into and out of the photodetachment region. The laser (Spectra Physics GCR-3) can be utilized at the 2nd (532 nm) or 3rd (355 nm) harmonic. The laser enters and exits the instrument through quartz windows oriented at Brewster's angle⁶ to minimize scattering.

Inside the velocity map imaging assembly, the first electrode, known as the repeller, is pulsed in order to ensure only electrons from the photodetachment event are sampled. The pulse is on the order of a few microseconds before and after the laser arrival, which ensures a uniform field is present during photodetachment. The voltage is pulsed from ground to approximately -180 V, and is supplied using a fast switch (Directed Energy PVM-4210) with a 25 nanosecond rise time. The second electrode is kept at ground potential, while the third electrode is attached to a flight tube and has a static voltage of about +420 V, though the experimenter must often adjust this to ensure maximum image resolution. At the end of the flight tube there are two microchannel plates. The front plate is held at the same voltage as the flight tube, while the rear plate is pulsed (using a fast switch identical to the one described above) from +1600 V to +2100 V for a period of about one microsecond, covering a few hundred nanoseconds before and after the electron arrival time. This pulsing greatly reduces the amount of stray electrons in the final captured image. After the microchannel plates there is a phosphor screen, which is maintained at +5200 V. Thus, the original electron that impinges on the microchannel plate is amplified and delivered to a phosphor screen, which lights up. A

window mounted on the same flange as the phosphor screen allows the image to be captured by a digital camera (LaVision Imager Intense CCD) mounted outside the instrument on a movable stage. The CCD sensor within the camera is cooled via Peltier cooling to reduce dark current. To prevent stray light from the room interfering with the image, the whole assembly is enclosed with curtains. The images the camera captures are transported to a personal computer, where they are reconstructed and analyzed as discussed previously. A schematic of the VMI assembly is shown in Figure 3.8, while the power supplies and timing controls are shown in Figure 3.9.



Figure 3.8 Schematic of the velocity map imaging setup. From bottom to top: the repeller electrode, the grounded electrode, the extractor electrode mounted on the flight tube, the microchannel plate and phosphor screen stack, the end flange, and the window.



Figure 3.9 The stack of power supplies and timing generators. From bottom to top: the timing generator responsible for gating the repeller and microchannel plates, the power supply for the microchannel plate (+1600 V), the power supply for the pulsed portion of the microchannel plate (left, +2100 V) and the power supply for the flight tube (right, +420 V), the power supply for the phosphor screen (+5200 V), and the power supply for the anion detector.

3.6 Vacuum System

The maintenance of high-vacuum is often the most strenuous job of an experimentalist. In our instrument there are no less than fifteen pumps operating at a given time, and the maintenance of these pumps is a great concern. To avoid venting the

entire instrument whenever something must be adjusted internally, the instrument is separated by gate valves into three regions. The first region consists of the LaVa source plus approximately two-thirds of the mass spectrometer length. This region has the largest volume and requires two diffusion pumps and one turbomolecular pump (each backed by a mechanical pump) to maintain pressures in the low 10^{-7} torr range. The second region consists of the magnetic bottle, and requires two turbomolecular pumps and one diffusion pump (each backed by a mechanical pump) to maintain pressures slightly lower than the first region. The third region consists of the velocity map imager. It is by far the smallest region, and uses one turbomolecular pump (backed by a mechanical pump) and one cryopump to maintain pressures in the mid to low 10^{-8} torr range. To monitor pressures in each region, ion gauges are used, while thermocouples monitor the pressures in the mechanical pump lines. Each of the gauges is wired into a safety box, so that when vacuum is lost and the pressure spikes above a predetermined threshold, any electronics in use (e.g. TOF electrodes or microchannel plates) are automatically turned off. Figure 3.10 displays the readouts for the ion gauges and thermocouples, as well as the safety box. For a nice description of the pumps and gauges used, as well as many matters pertinent to vacuum instrumentation, the reader is referred to an invaluable guide.²⁷

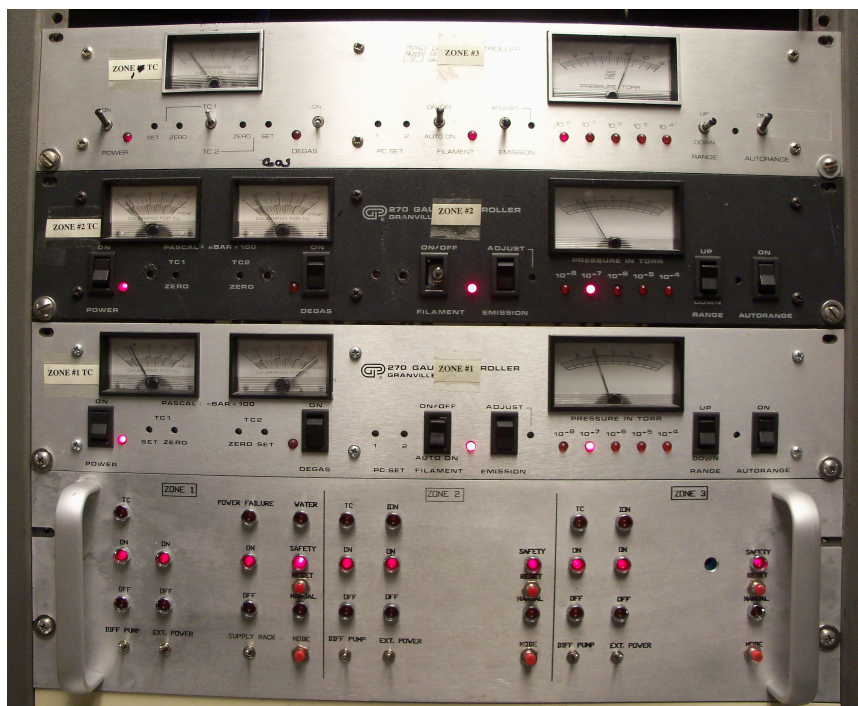


Figure 3.10 From bottom to top: the safety box, the readouts of the thermocouples and ion gauge of the first region, the readouts of the thermocouples and ion gauge of the second region, and the readouts of the thermocouple and ion gauge of the third region.

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Chapter 4

Combined Experimental and Theoretical Study of Al_nX ($n = 1-6$; $\text{X} = \text{As}, \text{Sb}$) Clusters: Evidence of Aromaticity and the Jellium Model

4.1 Introduction

Finite-sized metal clusters have been shown to possess unique properties, as compared with their bulk and atomic counterparts.¹⁻³ This phenomenon has initiated a wealth of studies that are aimed at exploring the possibility of cluster assembled nanomaterials in which the material's properties are derived from the cluster building blocks.⁴⁻⁶ One approach in this area involves the use of doped metal clusters, where one or more heteroatoms are incorporated into an existing metal cluster framework.⁷⁻⁹ This demands a new understanding of the geometry and electronic structure but provides greater freedom in designing cluster building blocks. As a result, there has been interest in exploring doped or mixed-metal clusters in an attempt to identify stable cluster motifs and explore simple models that may explain their stability. One example, recent work in our lab on bismuth-doped aluminum clusters, revealed two especially stable clusters, Al_3Bi and Al_5Bi .⁸ Although these clusters differ by just two aluminum atoms, they are substantially different in geometry and electronic structure, and each requires a theoretical model to account for its stability.

The first model, aromaticity, has historically been applied to organic systems that are cyclic, planar, and contain $(4n + 2) \pi$ electrons.^{10,11} Only recently has this concept been extended to all-metal systems, with the seminal work of Li et al. on Al_4^{2-} , studied experimentally and theoretically as MAl_4^- ($\text{M} = \text{Li}, \text{Na}, \text{or Cu}$).¹² This work has been

extensively discussed in the literature and prompted a number of subsequent theoretical and experimental studies.¹³⁻¹⁶ The reader is directed to reviews on the subject for a more comprehensive description.^{17,18} Work in our lab on Al_3Bi yielded the first experimental evidence of a neutral all-metal aromatic species, providing an attractive candidate for assembly.⁸

A second model in the realm of metal clusters is the jellium model, in which valence electrons in the cluster respond to a uniform background potential, and electronic shell closings are seen at certain sizes.¹⁹ This model has been applied to aluminum clusters in our lab,²⁰ explaining the stability and inertness of Al_{13}^- , and has prompted our investigation of superatoms as candidates for cluster assembled materials.²¹⁻²⁴ More recently, the jellium model has been adapted and applied to doped metal clusters.²⁴⁻²⁶ For example, we recently explained the stability of Al_5Bi , which has a compact geometry and 20 valence electrons, within the jellium model.⁸

In this chapter, the Al_nSb and Al_nAs systems are investigated. Note that antimony, arsenic, and bismuth belong to group V of the periodic table, which also contains nitrogen and phosphorus. Earlier studies indicate that Al_3N has a planar D_{3h} ground state with a central nitrogen atom surrounded by three aluminum atoms.^{27,28} Al_3P has competing geometries: a D_{3h} structure similar to that of Al_3N and a C_{2v} structure with atoms forming a distorted rhombus.^{29,30} Al_3As possesses a planar C_{2v} ground state,^{31,32} and Al_3Bi has a planar C_{2v} ground state stabilized by its aromatic character.⁸ This evolution in behavior could be due to electronic effects. For example, aluminum has an electronegativity of 1.61, whereas nitrogen has an electronegativity of 3.04, compared with 2.19, 2.18, 2.05, and 2.02 for phosphorus, arsenic, antimony, and bismuth,

respectively.³³ Therefore, a study of Al_3As and Al_3Sb could highlight the role of electronegativity on the nature of bonding as one dopes with different elements of the same group.

Through a collaborative study using photoelectron spectroscopy (PES) and first principles electronic structure calculations, the Al_nX ($n = 1-6$, $\text{X} = \text{As}, \text{Sb}$) systems are explored. There is evidence of two neutral all-metal aromatics (Al_3Sb and Al_3As) and two jellium stabilized clusters (Al_5Sb and Al_5As). Also, the individual cluster properties, such as HOMO-LUMO gap, ionization potential, and binding energy, are investigated as a function of different heteroatom doping.

4.2 Experimental and Computational Details

The experimental portion of the current study was carried out with a magnetic bottle photoelectron spectroscopy apparatus that has been described in detail in Chapter 3 and in the literature.³⁴ A laser vaporization supersonic cluster beam source synthesizes anionic clusters of interest. Al_nAs or Al_nSb clusters were created in the gas-phase by placing a thin coating of arsenic or antimony on a pure aluminum rod. Helium was used as the carrier gas with stagnation pressures of about 50 psi. Negative ions were extracted and mass analyzed with a Wiley-McLaren time-of-flight mass spectrometer.³⁵ Mass-selected anions of interest were then interrogated by an unfocused, unpolarized laser beam from an excimer laser (308 nm) in a magnetic bottle analyzer, where photodetached electrons are analyzed according to their kinetic energies. The electronic spectra were calibrated on the basis of the known spectra of Bi^- .

To aid in both the assignment of the spectra and the determination of electronic properties, collaborators have carried out first-principles electronic structure investigations on the anionic, neutral, and cationic forms of Al_nX ($n = 1-6$, $\text{X} = \text{As}, \text{Sb}$) clusters. These calculations were performed within the density functional formalism³⁶ and employed the Perdew, Burke, and Enzerhof generalized gradient functional for the exchange and correlation effects.³⁷ Both the aluminum and arsenic atoms were described using a DZVP basis,³⁸ whereas for antimony atoms, a 23 relativistic effective core potential proposed by Metz et al.³⁹ in combination with the correlation consistent aug-cc-pVTZ basis set was used.⁴⁰ The GEN-A2 auxiliary function set for Al and As and the GEN-A2* auxiliary function set for Sb were used. The actual calculations used the deMon2k software package.⁴¹ To determine the ground state geometries for the clusters studied, several initial geometries and spin states were attempted and fully optimized without constraints, and the minima were ascertained with a frequency analysis.

4.3 Results and Discussion

Figure 4.1 shows the photoelectron spectra of the Al_nAs^- and Al_nSb^- ($n = 1-5$) clusters taken with a 308 nm laser. The spectra of the previously published Al_nBi^- series are included for comparison.⁸ The peaks in the spectra of Figure 4.1 denote transitions from the anion to ground and excited electronic states of the neutral. In the case of a singlet anionic species (i.e., Al_2X^-), only one primary peak is expected in the spectrum, corresponding to the transition to the lowest doublet neutral state. Alternatively, the spectrum of a doublet anionic species (i.e., Al_3X^-) will possess at least two primary features, corresponding to transitions to the lowest singlet and triplet states of the neutral

and are labeled as $M - 1$ and $M + 1$ vertical detachment energy (VDE), respectively. Additional shoulders or peaks in the spectrum may be present because of hot band excitation or the removal of electrons from deeper states, leading to the neutral cluster in excited electronic states.

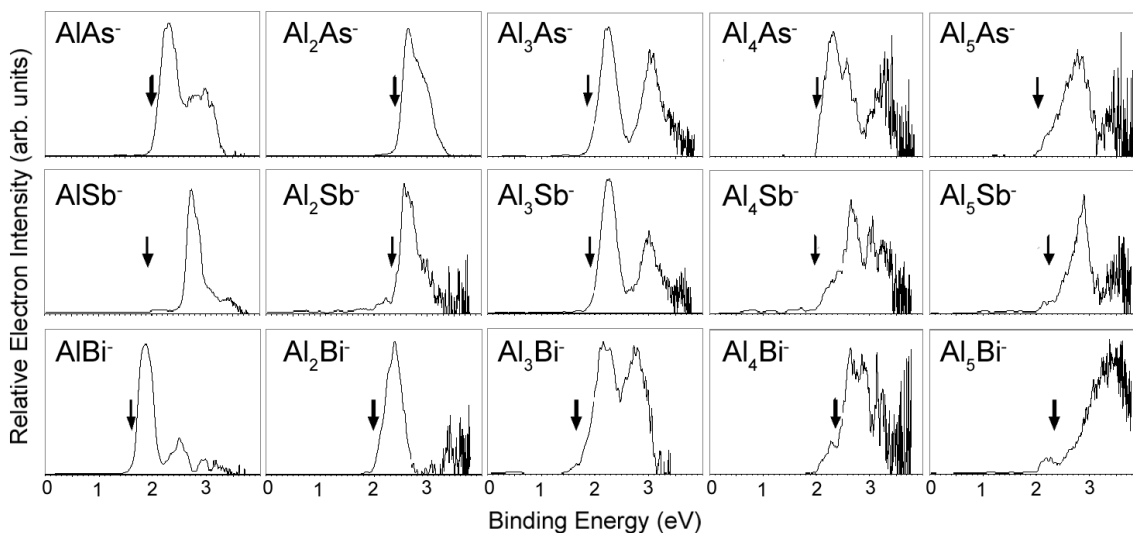


Figure 4.1 Photoelectron spectra at 308 nm for Al_nAs^- , Al_nSb^- , and Al_nBi^- clusters ($n = 1-5$). Black arrows denote experimental adiabatic detachment energies.

In assigning experimental quantities, the peak maximum is taken as the VDE, which is thereby assigned for every major peak in the spectrum; the adiabatic detachment energy (ADE) is obtained by extrapolation of the leading edge of the first peak. Tables 4.1 and 4.2 list the experimentally determined VDEs and ADEs for the Al_nAs^- and Al_nSb^- series, respectively. These assignments are a particularly useful test of theoretically proposed structures and bonding mechanisms, as shown below.

Table 4.1 Experimental adiabatic detachment energies (ADE) and vertical detachment energies (VDE) of Al_nAs^- ($n = 1-5$) clusters. Calculated ADEs and VDEs of Al_nAs^- ($n = 1-6$) clusters. Calculated vertical electron affinities (VEA), adiabatic ionization potentials (IP), and HOMO-LUMO gap (HL gap) values for the ground state Al_nAs ($n = 1-6$) clusters. All values are in units of eV.

#Al atoms	ADE (exp.)	ADE (theo.)	VDE (exp.) ^a	VDE M - 1 (theo.) ^b	VDE M + 1 (theo.) ^b	VEA (theo.)	IP (theo.)	HL gap (theo.)
1	1.96±0.07	1.97	2.32,2.75	2.70	2.00	1.93	7.37	0.23
2	2.39±0.07	2.29	2.66		2.34	2.01	7.23	0.70
3	1.85±0.09	1.74	2.19,2.99	1.98	2.86	1.41	7.34	1.86
4	1.98±0.08	1.92	2.29		2.38	1.82	6.30	0.56
5	2.03±0.11	2.07	2.74	2.43	2.64	1.64	6.65	1.12
6	---	2.25	---		2.46	2.00	6.17	0.55

a) Experimental VDEs have an uncertainty of ± 0.05 eV.

b) For theoretical VDEs, transitions to both the lower ($M - 1$) and higher ($M + 1$) spin states are listed where appropriate.

Table 4.2 Experimental adiabatic detachment energies (ADE) and vertical detachment energies (VDE) of Al_nSb^- ($n = 1-5$) clusters. Calculated ADEs and VDEs of Al_nSb^- ($n = 1-6$) clusters. Calculated vertical electron affinities (VEA), adiabatic ionization potentials (IP), and HOMO-LUMO gap (HL gap) values for the ground state Al_nSb ($n = 1-6$) clusters. All values are in units of eV.

#Al atoms	ADE (exp.)	ADE (theo.)	VDE (exp.) ^a	VDE M - 1 (theo.) ^b	VDE M + 1 (theo.) ^b	VEA (theo.)	IP (theo.)	HL gap
1	1.89±0.07	2.02	2.13,2.75	2.73	2.05	1.98	6.99	0.21
2	2.34±0.1	2.16	2.57		2.34	1.90	7.09	0.84
3	1.88±0.09	1.76	2.27,2.99	2.00	2.90	1.44	7.18	1.73
4	1.96±0.12	1.94	2.62		2.45	1.88	6.29	0.62
5	2.21±0.10	2.17	2.87	2.54	2.64	1.63	6.58	1.17
6	---	2.19	---		2.74	1.96	6.15	0.52

a) Experimental VDEs have an uncertainty of ± 0.05 eV.

b) For theoretical VDEs, transitions to both the lower ($M - 1$) and higher ($M + 1$) spin states are listed where appropriate.

In Figures 4.2 and 4.3, the calculated ground state geometries are provided for the anionic, neutral, and cationic Al_nAs and Al_nSb ($n = 1-6$) clusters with bond lengths given in angstroms. Of the clusters examined in this work, previous studies have been performed by Archibong and St-Amant on the neutral and anionic Al_3As cluster at the B3LYP and CCSD(T) levels using the 6-311+G(2df) basis set.³¹ Additionally, with the same basis set, Guo and Wu calculated the ground state structures of the neutral and anionic Al_3As cluster with pure and hybrid exchange correlation functionals.³² Both groups calculated a planar C_{2v} ($^1\text{A}_1$) ground state; the results in Figure 4.2 agree.

For the calculated structures in Figures 4.2 and 4.3, it was found that cluster anions Al_nX^- ($\text{X} = \text{As}$ and Sb) with an even number of aluminum atoms were singlet states, and the theoretical VDE for each is provided in the corresponding table. For the odd aluminum cluster anions, doublet ground states were calculated. The corresponding theoretical vertical detachment energies were determined by calculating the energy difference between the ground state geometry of the anion with multiplicity M and the neutral cluster with the anion geometry in $M + 1$ and $M - 1$ multiplicity states. Considering only the lowest energy state of a given multiplicity, this results in one value for clusters with an even number of aluminum atoms, and two VDEs for clusters with an odd number of aluminum atoms, for reasons discussed above. Furthermore, the theoretical adiabatic detachment energies for Al_nAs and Al_nSb clusters are provided in Tables 4.1 and 4.2, respectively. These are obtained by calculating the energy difference between the ground state geometry of the anion and the ground state geometry of the neutral cluster.

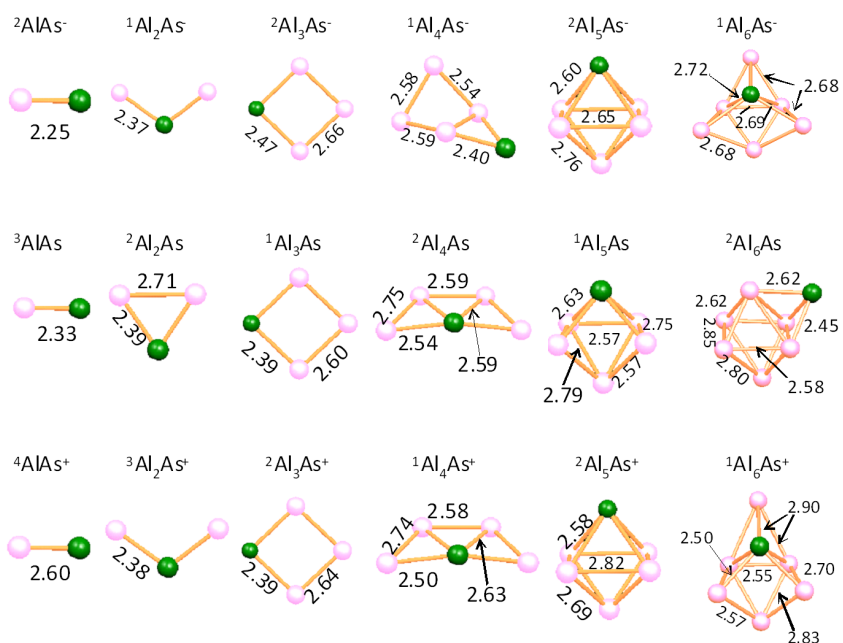


Figure 4.2 Optimized geometries of anionic, neutral, and cationic Al_nAs clusters ($n = 1-6$). The superscripts indicate the spin multiplicities. Bond lengths are given in angstroms.

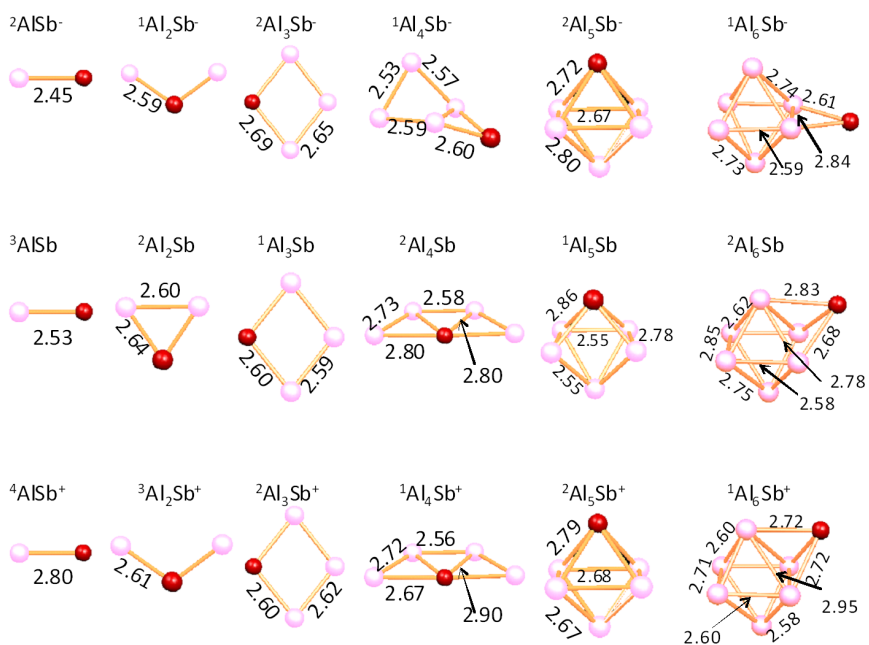


Figure 4.3 Optimized geometries of anionic, neutral, and cationic Al_nSb clusters ($n = 1-6$). The superscripts indicate the spin multiplicities. Bond lengths are given in angstroms.

The theoretical ADEs agree very well with experiment, showing a maximum deviation of 7%. Additionally, the calculated VDEs are in fair agreement with the experimental values, differing at most by 14%. These results suggest confidence in the ground state structures predicted. Also provided in Tables 4.1 and 4.2 are the vertical electron affinities (VEAs) calculated as the energy difference between the neutral ground state and the anion species at the neutral's ground state geometry, adiabatic ionization potentials (IP) calculated as the energy difference between the neutral and cationic ground states, and HOMO-LUMO gaps of the neutral clusters.

It is important to note that in general low AEA or VDE of a cluster in a series is indicative of the stability of the neutral species. Such a comparison will hold provided the anionic series does not exhibit marked variations in stability. A better approach that avoids this problem is to look at the VEA of the cluster. In this case, the energy gain by the addition of an extra electron to the neutral ground state without relaxing the geometry will truly test the stability of the neutral species.

The remainder of this discussion is focused on the Al_3X and Al_5X clusters because they are the most interesting cases. In a previous publication, Al_3Bi and Al_5Bi were identified as an aromatic and a jellium stabilized cluster, respectively.⁸ A motivating factor for the current work was to explore if analogous species were present upon doping with arsenic or antimony instead of bismuth. Consulting Figure 4.1, it is clear that the photoelectron spectra are quite similar for each of the Al_3X^- clusters. The first peak is located at nearly the same binding energy for each cluster and has approximately the same width. The second peak lies at the same energy for Al_3As^- and Al_3Sb^- and slightly lower energy for Al_3Bi^- . In going down the series from As to Sb to Bi, the gap in the

photoelectron spectra decreases (0.80, 0.72, and 0.58 eV); the calculated HOMO-LUMO gap follows this same trend (1.86, 1.73, and 1.69 eV). Additional similarities between Al_3Bi and the clusters in this chapter are found when looking at the removal energies and ionization potentials. The removal energy (R.E.) is used as a criterion for stability and is defined as the amount of energy required to remove one aluminum atom from the cluster:

$$\text{R.E. (Al)} = E(\text{Al}_{n-1}\text{X}) + E(\text{Al}) - E(\text{Al}_n\text{X})$$

Figure 4.4A shows a plot of removal energies for the Al_nAs and Al_nSb neutral clusters, with the actual values given in Table 4.3. Notice that there is a peak for both the antimony- and arsenic-doped clusters (though less pronounced for arsenic) at $n = 3$ when compared with their nearest neighbors. This result is much like that of the aromatic bismuth-doped cluster, Al_3Bi , which showed enhanced stability as well. As an additional criterion for stability, the embedding energy (E.E.) was calculated, defined as the gain in energy as the dopant atom (As or Sb) is added to the pure aluminum cluster:

$$\text{E.E.} = E(\text{Al}_n) + E(\text{As,Sb}) - E(\text{Al}_n(\text{As,Sb}))$$

Figure 4.4B shows a plot of the E.E. for the Al_nAs and Al_nSb clusters; the specific values are listed in Table 4.3. There is a maximum for both Al_3As and Al_3Sb when compared with their nearest neighbors, attesting for their stability. Additionally, the VEAs of 1.41 and 1.44 eV for Al_3As and Al_3Sb are the lowest ones in their respective series. Furthermore, the adiabatic ionization potential is quite high at 7.34 and 7.18 eV for Al_3As and Al_3Sb , respectively. These values are larger than the high ionization potential calculated for Al_3Bi (7.08 eV) and are an indicator of the stability of the neutral clusters. The calculated removal energies, embedding energies, low VEAs, high calculated ionization potentials, and large HOMO-LUMO gaps (Tables 4.1, 4.2, and 4.3) all point to

the special stability of Al_3As and Al_3Sb , much like that of Al_3Bi . These factors and the similar experimental spectra are convincing indicators that Al_3As and Al_3Sb also possess aromatic character analogous to the Al_3Bi cluster.

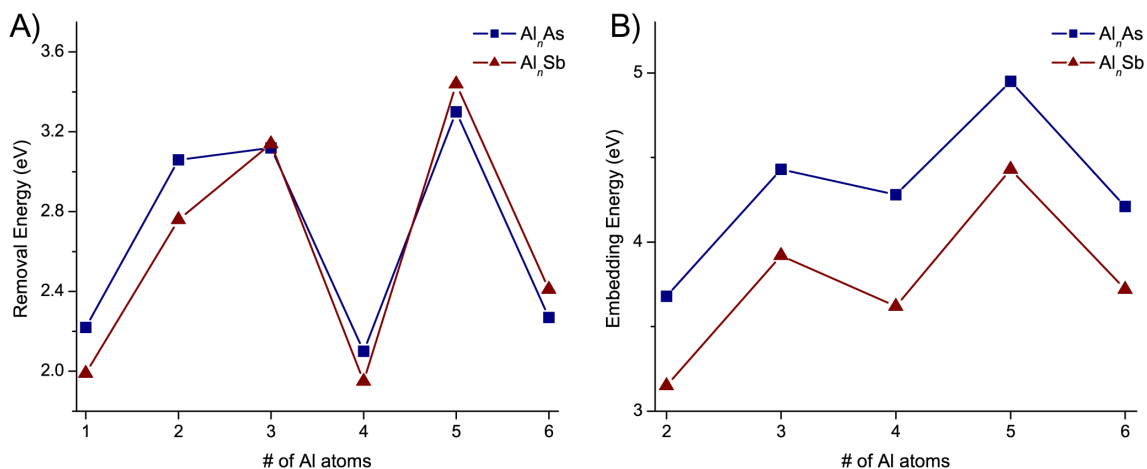


Figure 4.4 Calculated aluminum removal energies (A) and embedding energies (B) for the neutral Al_nAs and Al_nSb clusters.

Table 4.3 Calculated removal and embedding energies for the neutral Al_nAs and Al_nSb series. All values are in eV.

n	Removal Energy		Embedding Energy	
	Al_nAs	Al_nSb	Al_nAs	Al_nSb
1	2.22	1.99		
2	3.06	2.76	3.68	3.15
3	3.12	3.14	4.43	3.92
4	2.10	1.95	4.28	3.62
5	3.30	3.44	4.95	4.43
6	2.27	2.41	4.21	3.72

To ensure that the concept of aromaticity is applicable, we examined whether these new clusters met criteria associated with all-metal aromaticity. Indeed, the calculated ground state structures for the Al_3As and Al_3Sb clusters are cyclic and planar

with C_{2v} symmetry, as seen in Figures 4.2 and 4.3, respectively. The bond lengths are nearly equivalent in the case of the antimony-doped cluster, whereas in the arsenic-doped cluster, they differ by 0.21 Å. Furthermore, the aromatic nature of these clusters is illustrated when calculating the molecular orbitals for the ground state structures. For both Al_3As and Al_3Sb clusters, the one electron energy levels, isosurfaces, and symmetries of the molecular orbitals are shown in Figure 4.5. For clarity, an enlarged top down view of the molecular orbitals is shown in Figure 4.6.

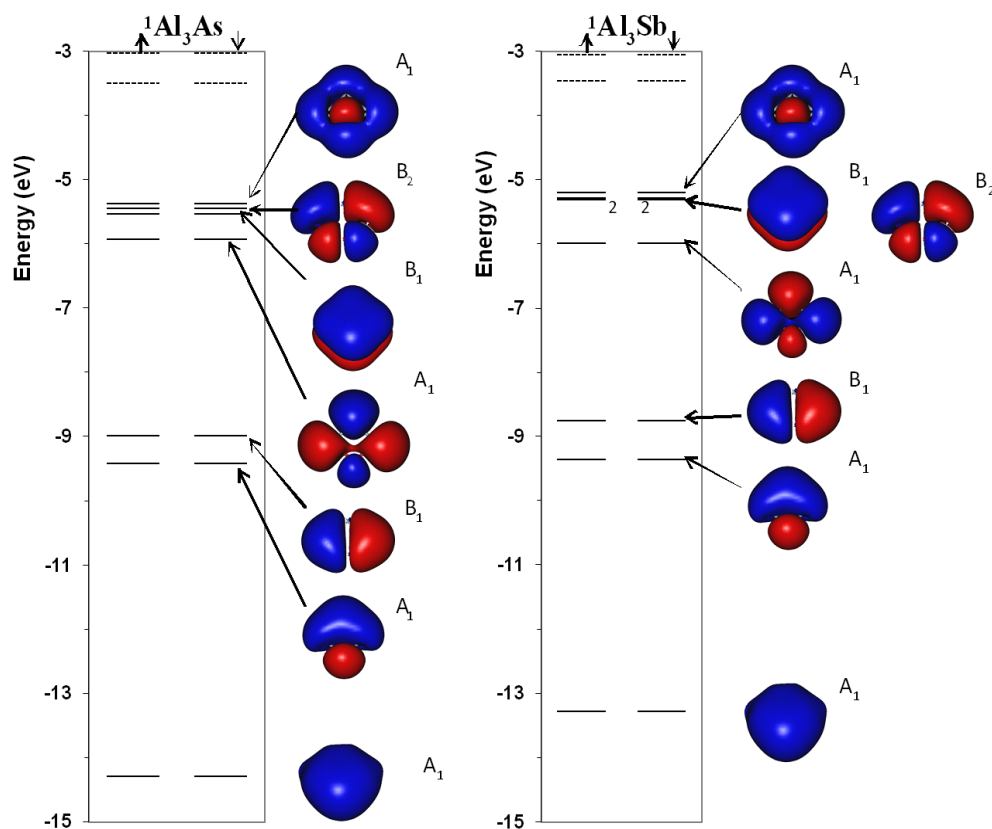


Figure 4.5 One electron energy levels, isosurfaces (isovalue = 0.01 au), and symmetries of the molecular orbitals for the neutral Al_3As and Al_3Sb clusters. The superscripts indicate the spin multiplicities. The continuous lines are occupied states, the dashed lines represent unoccupied levels. The levels are singly degenerate unless otherwise noted. The up and down arrows at the top of the figure indicate the majority (up) and minority (down) spin states, respectively.

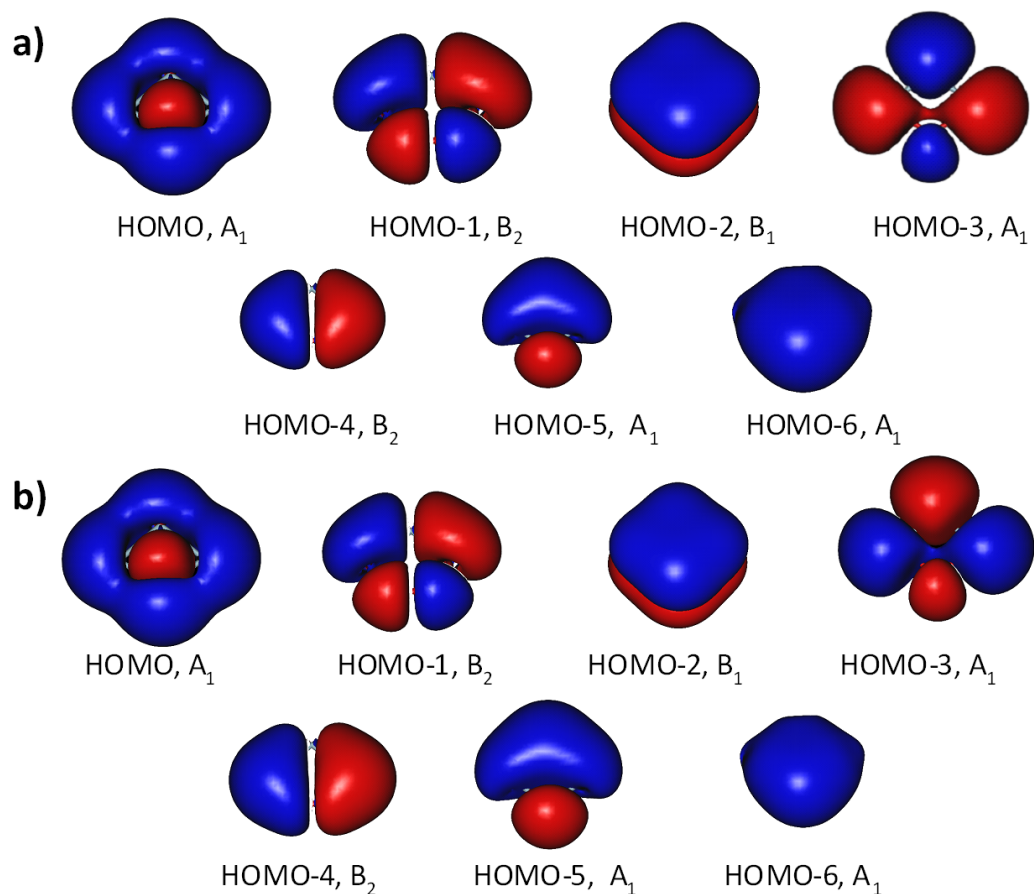


Figure 4.6 Top down view of the molecular orbitals with symmetry for the a) Al_3As and b) Al_3Sb clusters. Note the strong similarities in shape, order, and symmetry.

In both the arsenic- and antimony-doped cases, the molecular orbitals are similar to those of the aromatic Al_3Bi cluster, with some rearrangement in ordering. For Al_3As and Al_3Sb , the HOMO-2 orbital is a delocalized π orbital with two electrons, satisfying the $(4n + 2)$ π electron rule for aromaticity. Additionally, the HOMO and HOMO-1 orbitals are σ delocalized orbitals resulting from the radially and tangentially oriented $p_{x,y}$ orbitals, respectively. These findings are reminiscent of the orbitals observed¹² for the homoatomic species Al_4^{2-} . However, in the case of Al_3Bi and the work presented here, electron density is slightly concentrated on the more electronegative atom.

An additional pointer to aromaticity is the concept of nucleus-independent chemical shift (NICS), developed by Schleyer et al.⁴² In this method, a ghost atom is used to report the chemical shift felt at certain points in relation to a ring structure. Negative chemical shifts result from the induced diamagnetic ring current in the presence of an external magnetic field and thus denote aromatic character. Positive chemical shifts result from paramagnetic ring currents and denote antiaromatic character. The NICS values (Figure 4.7) have been calculated using the same theoretical model, namely, the PBE functional employing the DZVP basis set for Al and As, and a 23 electron scalar relativistic effective core potential and aug-cc-pVTZ basis set for Sb, within the Gaussian03 program.⁴³

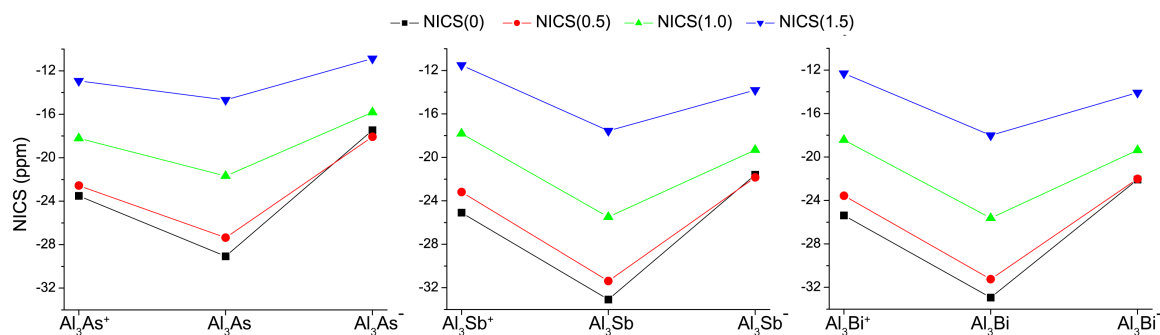


Figure 4.7 Nucleus-Independent Chemical Shift (NICS) values of cationic, neutral, and anionic Al₃As and Al₃Sb in ppm. Previous results for Al₃Bi are shown for comparison. The NICS values are calculated at the position of a ghost atom placed at the ring center in the molecular plane, and 0.5, 1.0, and 1.5 Å above the plane, respectively.

We find that both Al₃As and Al₃Sb have large, negative NICS values at the center of the ring of -29.07 and -33.08 ppm, respectively, and agree closely with our previous findings for Al₃Bi with a NICS value of -32.93.8 These values increased as the NICS value was calculated above the plane, affirming the aromatic character. This was also true

for the charged Al_3As^+ , Al_3As^- , Al_3Sb^+ , Al_3Sb^- , Al_3Bi^+ , and Al_3Bi^- clusters, although the neutral Al_3As , Al_3Sb , and Al_3Bi species had the most negative NICS values, as shown in Figure 4.7. In addition, the NICS values for the neutral Al_2Bi , Al_2Sb , and Al_2As clusters are shown in Table 4.4. These clusters have moderately negative NICS values that increase to nearly zero at 1.5 Å above the ring, a trend that is not representative of aromatic behavior.

Table 4.4 Nucleus-Independent Chemical Shift (NICS) values for $\text{Al}_3\text{As}^{+/0/-}$, $\text{Al}_3\text{Sb}^{+/0/-}$, $\text{Al}_3\text{Bi}^{+/0/-}$, Al_2As , Al_2Sb , and Al_2Bi in ppm. The NICS values are calculated at the position of a ghost atom placed at the ring center in the molecular plane, and 0.5, 1.0, and 1.5 Å above the plane, respectively.

	NICS(0)	NICS(0.5)	NICS(1.0)	NICS(1.5)
Al_3As^+	-23.51	-22.56	-18.21	-12.93
Al_3As	-29.07	-27.35	-21.68	-14.68
Al_3As^-	-17.47	-18.08	-15.83	-10.87
Al_3Sb^+	-25.09	-23.19	-17.82	-11.51
Al_3Sb	-33.08	-31.38	-25.48	-17.56
Al_3Sb^-	-21.6	-21.84	-19.32	-13.81
Al_3Bi^+	-25.38	-23.56	-18.43	-12.3
Al_3Bi	-32.93	-31.25	-25.62	-18.01
Al_3Bi^-	-22.07	-22	-19.37	-14.08
Al_2As	-21.82	-19.89	-11.16	-2.51
Al_2Sb	-14.89	-13.81	-8.07	-1.05
Al_2Bi	-11.41	-10.55	-6.16	-0.39

Although there is some debate about the applicability of NICS values in predicting aromaticity,^{16,44,45} the results for Al₃As and Al₃Sb are in agreement with what one would expect for an aromatic species (significantly negative). Although NICS values do not rigorously assign the degree of aromaticity, the neutral all-metal aromatic cluster with the most negative (aromatic-like) NICS value is Al₃Sb, followed by Al₃Bi and Al₃As. This is also the ordering of the equivalency of bond lengths if one consults Figures 4.2 and 4.3 and reference 8. The least negative NICS value and the least equivalent bond lengths in Al₃As may be a function of the electronegativity difference between aluminum (electronegativity 1.61) and the heteroatom, which is greatest in the case of arsenic (difference in electronegativity, $\Delta\text{EN} = 0.57$). This is illustrated if we examine the delocalized π orbital across the series, which appears to become more displaced (lower in energy) relative to the HOMO as the electronegativity difference is increased. For example, in Al₃Bi ($\Delta\text{EN} = 0.41$), the delocalized π orbital is the HOMO-1 and is energetically degenerate with the HOMO.⁸ However, in Al₃As and Al₃Sb, the delocalized π orbital is the HOMO-2 and is displaced more in the arsenic-doped case ($\Delta\text{EN} = 0.57$) than the antimony-doped case ($\Delta\text{EN} = 0.44$). When the π orbital is lower in energy, it is expected to contribute less to the overall valence character of the cluster. As discussed above, using nitrogen as the dopant atom (electronegativity 3.04, $\Delta\text{EN} = 1.43$), Al₃N adopts a planar D_{3h} structure with no evidence of aromaticity.^{27,28} We can conclude that whereas large differences in electronegativity may lead to a more ionic bonding scheme (Al₃N), in the case of Al₃As, Al₃Sb, and Al₃Bi, the electronegativity difference is not enough to disrupt the aromaticity. This agrees with similar findings for doped aromatic anions.¹⁴

Next, the Al_5As and Al_5Sb clusters were explored for evidence of enhanced stability, and whether they could be rationalized within the jellium model, analogous to previous findings for the Al_5Bi cluster. Consulting Tables 4.1 and 4.2, the Al_5As and Al_5Sb clusters display significant HOMO-LUMO gaps (above 1.1 eV), attesting to their stable nature. We expected that these clusters would exhibit properties similar to those of the jellium cluster Al_5Bi . This can be seen experimentally in Figure 4.1, which contains the photoelectron spectra for the Al_5X^- clusters. For Al_5Bi^- , the small feature at 2.15 eV was attributed to an isomer, whereas the shoulder feature at 2.60 eV is a separate, reproducible feature from the large peak at 3.35 eV. Considering these assignments, the three Al_5X^- spectra show a strong resemblance, with first detachment peaks in the Al_5As^- and Al_5Sb^- spectra at 2.74 and 2.87 eV, respectively. These assignments are in agreement with the theoretically predicted values, provided in Tables 4.1 and 4.2. There seems to be an additional feature at higher energy, similar to Al_5Bi^- , but the spectra are too noisy to assign accurately a VDE for this feature. The small shoulders present in both the Al_5As^- and Al_5Sb^- spectra are attributed to hot band excitation.

Although the PES spectra show similarities among these species, using the jellium model to account for the stability of Al_5As and Al_5Sb requires more strict observations. Jellium species have a 3D, compact geometry with an appropriate number of valence electrons to complete a jellium closed shell. The calculated structures for Al_5As and Al_5Sb display a 3D geometry, as shown in Figures 4.2 and 4.3, respectively. The agreement between the experimental and theoretical detachment energies discussed above confirm the geometries. Furthermore, the total number of valence electrons is 20, with three electrons from each aluminum and five electrons from the heteroatom. This

number of valence electrons corresponds to a jellium closed shell with a configuration of $1s^2$, $1p^6$, $1d^{10}$, and $2s^2$. It can be seen that the molecular orbitals for Al_5As and Al_5Sb display this ordering (Figure 4.8), although with mixing of the $1d^{10}$ and $2s^2$ states. Therefore, the molecular orbital picture, the compact geometry, and the valence electron count establish Al_5As and Al_5Sb as two jellium-type clusters with filled electronic shells.

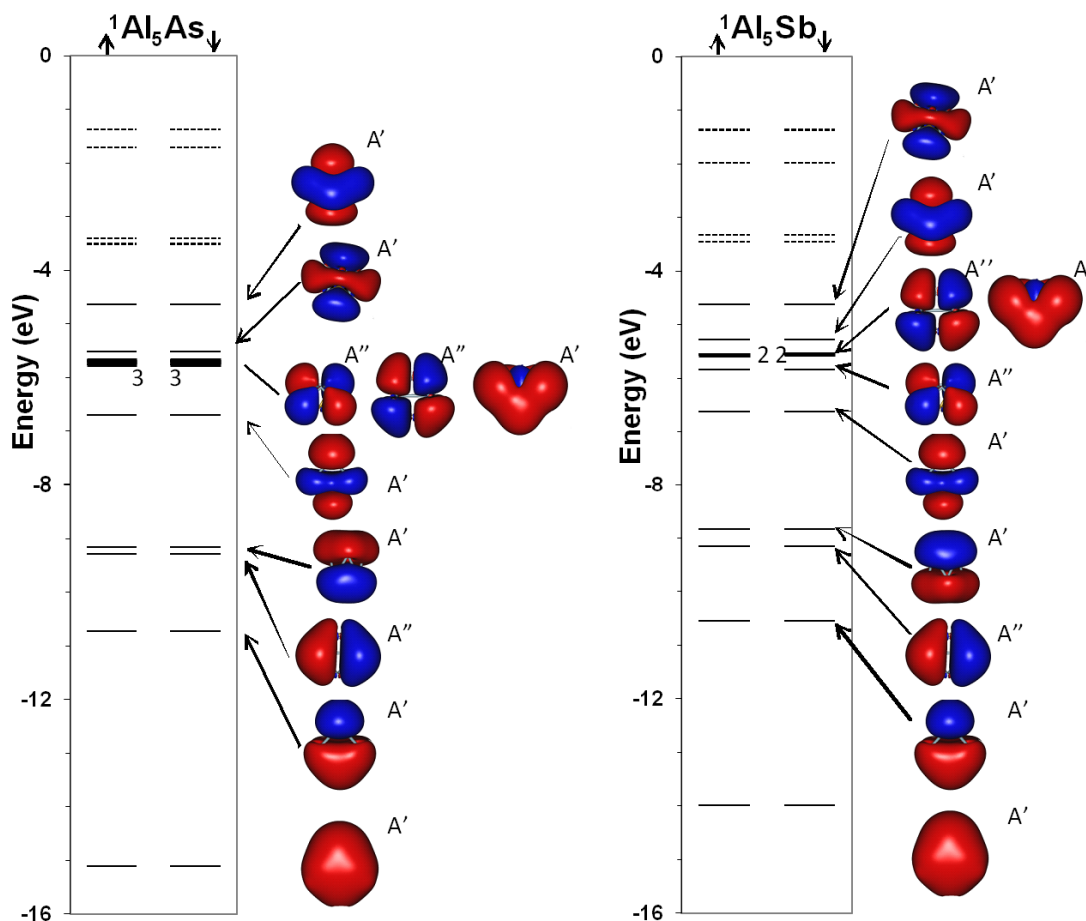


Figure 4.8 One electron energy levels, isosurfaces (isovalue = 0.01 au), and symmetries of the molecular orbitals for the neutral Al_5As and Al_5Sb clusters. The superscripts indicate the spin multiplicities. The continuous lines are occupied states, the dashed lines represent unoccupied levels. The levels are singly degenerate unless otherwise noted. The up and down arrows at the top of the figure indicate the majority (up) and minority (down) spin states, respectively.

The special stability of Al_5As and Al_5Sb is further supported by calculating the removal and embedding energies, VEA, adiabatic ionization potential, as well as the HOMO-LUMO gaps (Tables 4.1 and 4.2). Note that the Al_5As and Al_5Sb removal and embedding energies (Figure 4.4 and Table 4.3) are higher, the VEAs are lower, and the ionization potentials are higher (Tables 4.1 and 4.2), as compared with the Al_4X and Al_6X species. The HOMO-LUMO gaps of Al_4As , Al_4Sb , Al_6As , and Al_6Sb are also substantially smaller than those for Al_5As and Al_5Sb .

4.4 Conclusions

This chapter demonstrates that stable neutral clusters can be synthesized by combining an atom from the group V elements with aluminum atoms. In particular, it is demonstrated that Al_3As and Al_3Sb are highly stable species with planar structures and whose molecular orbitals possess radial σ , tangential σ , and π aromatic character. The aromatic nature of the clusters is further confirmed by the large negative NICS values. The behavior of Al_3As and Al_3Sb as well as that of our previously published Al_3Bi contrasts with that of Al_3N , which has a planar D_{3h} structure. It is believed that the difference lies in the electronegativity, where the high electronegativity of nitrogen leads to a more ionic bond. The new stable species (Al_3As and Al_3Sb) share aromatic characteristics with organic species like benzene. Therefore, it may be possible to form complexes conventionally produced in metal-organic systems using the all-metal aromatic clusters. Additionally, the studies have revealed two closed-shell species, namely, Al_5As and Al_5Sb . These clusters have a valence count of 20, and their stability can be rationalized within a jellium framework as resulting from a closed electronic shell.

Future work should examine the nature of nanomaterials that could be formed through assemblies of these different cluster motifs.

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Chapter 5

Resilient Aromaticity in Lead-Indium Clusters

5.1 Introduction

Metal clusters are the focus of many current experimental and theoretical research efforts due to the interesting phenomena that emerge by altering just one atom's presence, location, or identity.¹⁻⁵ Of specific importance is the development of a foundation for understanding how electronic and geometric structures, and hence chemical reactivity, vary with cluster size, which would presumably allow for the predictability of a cluster's behavior in a given environment. This has naturally led to the consideration of clusters as building blocks for the tailored design of nanoscale materials via a "bottom-up" approach.⁶⁻⁹ Although creating cluster assembled materials (CAMS) is a complex task, it is clear that the necessary first step in this process is to identify suitable clusters that i) contain a useful characteristic and ii) show promise for retaining that property in an assembled material. Even this first step is far from trivial, but is greatly aided by the use of pertinent models to help characterize and classify the behavior of metal clusters.

One such model, all-metal aromaticity, has proved valuable in describing the stability of a new class of clusters.^{10,11} Historically, aromaticity has been used to describe the class of organic molecules with conjugated, cyclic, planar geometries and $(4n+2)$ π valence electrons.^{12,13} Recent studies by Wang et al. have shown that this concept can be applied to explain structural and electronic characteristics of all-metal species.¹⁰ Numerous experimental and theoretical studies have since followed to expand on this notion, resulting in several "all-metal aromatics".¹⁴⁻²⁰ It is of interest with regards to

cluster assembled materials whether this new class of metal clusters may provide suitable candidates for building blocks. Although the answer is still unclear, these all-metal aromatics satisfy the conditions described above, as they i) frequently possess a large gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap), comparable to those of C_{60} and Al_{13}^- of 1.72 eV²¹ and 1.87 eV,²² respectively, and ii) behave similarly to organic molecules that have been assembled into sandwich compounds.²³

In the current chapter, two new all-metal aromatic species are identified through a joint experimental and theoretical effort, namely $PbIn_3^-$ and Pb_2In_2 . These clusters were part of an extensive study of $PbIn_y$ ($y = 1-7$), Pb_2In_y ($y = 1-6$), Pb_3In_y ($y = 1-5$), Pb_4In_y ($y = 1-3$), and Pb_xIn ($x = 1-5$) clusters, which will be the focus of Chapter 6 of this dissertation. In identifying aromatic species, we have focused on heterogeneous clusters for two major reasons. First, they may provide more opportunity for assembly due to different elemental properties at cluster vertices. Second, and more pertinent to the present investigation, it is still unclear how applicable all-metal aromaticity is to heterogeneous clusters. Here, $PbIn_3^-$ and Pb_2In_2 are particularly good test cases, as they have the same number of outer-shell electrons as many other all-metal aromatics, but consist of only heavy p-block elements, where *s-p* hybridization is significantly reduced. In this chapter it is shown that even in heavy metal aromatics, the bonding motifs are representative of all-metal aromaticity. In fact, the aromaticity in the present case seems more insensitive to elemental differences than in the lighter aluminum-based aromatics of Chapter 4. Additionally, $PbIn_3^-$ and Pb_2In_2 are found to possess large HOMO-LUMO gaps of 1.34 and 1.45 eV, respectively, making them candidates for CAMS.

5.2 Experimental and Computational Details

The experimental portion of this chapter was conducted employing a magnetic bottle photoelectron spectroscopy apparatus described in Chapter 3 and in the literature.²⁴ Pb_xIn_y^- clusters were formed within a laser vaporization source by ablating a 50:50 molar ratio Pb-In molded rod. Helium was used as a carrier gas (55 psi) and the anionic clusters produced were analyzed using Wiley-McLaren time-of-flight mass spectrometry.²⁵ Species of interest were mass selected and subjected to an unpolarized excimer laser pulse (308 nm) within a magnetic bottle analyzer. Photodetached electrons were detected according to their kinetic energies and calibrated with the known spectrum of Bi^- .²⁶

To aid in both the assignment of the spectra and the determination of electronic and geometric properties, collaborators have carried out first-principles electronic structure investigations on the anionic and neutral forms of PbIn_3 and Pb_2In_2 . The calculations were performed within the density functional theory (DFT) formalism.²⁷ The exchange correlation interactions were treated by the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof.²⁸ The actual calculations were carried out using the linear combination of Gaussian type orbitals DFT code deMon2k.²⁹ Both the In and Pb atoms were described using the 3 and 22 electron scalar relativistic effective core potentials (ECP) proposed by Ingel-Mann et al.³⁰ and Metz,³¹ respectively. The corresponding relativistic ECP basis set for In,³⁰ and the correlation consistent aug-cc-pVDZ basis set for Pb³² were used. The GEN-A2* auxiliary function set was used for both In and Pb atoms. The ground state cluster geometries were determined by fully optimizing various initial geometries and spin configurations without symmetry constraints.

5.3 Results and Discussion

Figure 5.1 displays the photoelectron spectra of PbIn_3^- and Pb_2In_2^- obtained at 308 nm (4.0 eV). The spectra are plotted on a binding energy scale. The peaks represent electronic transitions from the anion to ground and excited states of the neutral species. For each spectrum we extract two experimental quantities, which prove important in establishing a cluster's electronic and geometric structure. These quantities are the adiabatic detachment energy (ADE), obtained by extrapolating the leading edge of only the first peak in the spectrum, and the vertical detachment energy (VDE), obtained for each peak by taking the energy of the peak maximum. In Figure 5.2, the calculated ground state structures of both the anionic and neutral forms of the PbIn_3 and Pb_2In_2 clusters are provided. The ADE for each species is calculated by the energy difference between the anion and neutral in their respective ground state geometries. The VDE is obtained by calculating the energy difference between the ground state anion and the neutral frozen in the corresponding anion's geometry.

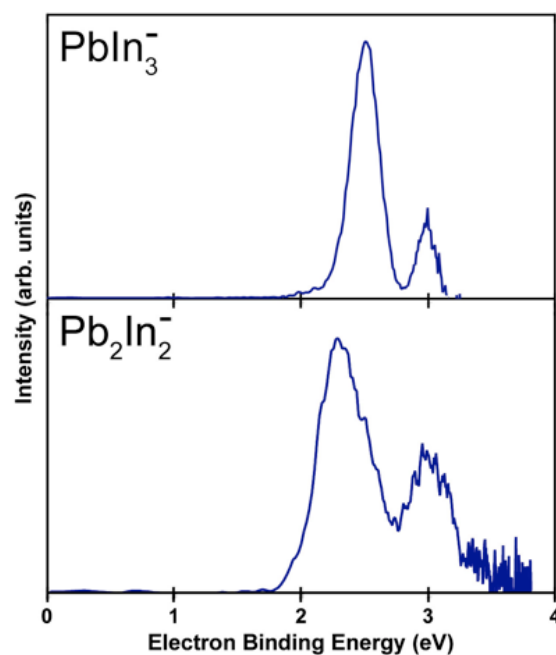


Figure 5.1 Photoelectron spectra at 308 nm for PbIn_3^- and Pb_2In_2^- .

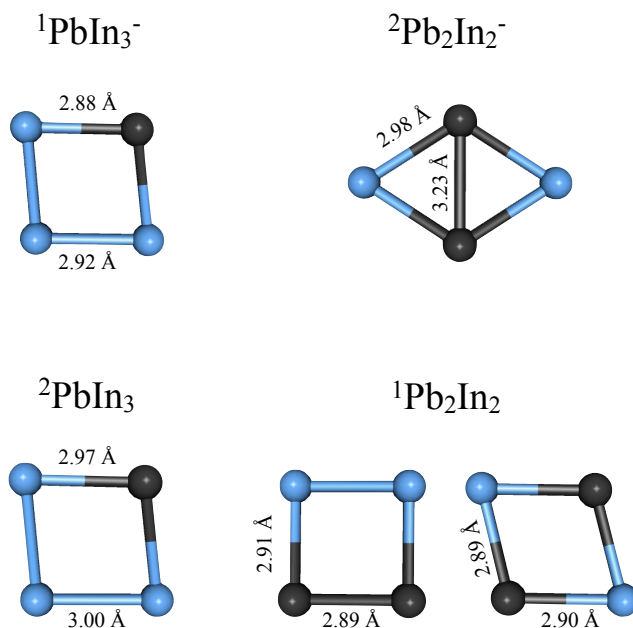


Figure 5.2 Ground state optimized geometries of anionic and neutral PbIn_3 and Pb_2In_2 . Bond lengths are given in angstroms. The darker (grey) spheres represent the Pb atoms, and the lighter (blue) spheres represent the In atoms. For the Pb_2In_2 cluster, the two geometries shown represent the two nearly-degenerate structures.

Table 5.1 lists the experimental and theoretical values of ADE and VDE, as well as the HOMO-LUMO gap, which are discussed later. As previously noted, there is only one ADE for each species, while there can be multiple VDEs, which correspond to different resolved peaks in the spectrum. The theoretical VDEs are assigned for transitions from the anion with a multiplicity M to the neutral with multiplicity $M\pm 1$. Thus, for the singlet PbIn_3^- only the $M+1$ value is listed theoretically. However, there are two experimental VDEs listed; the second peak in the experimental spectrum (VDE 2) is a result of the removal of a deeper lying electron, resulting in a neutral cluster in an excited state. For Pb_2In_2^- both the $M-1$ (singlet) and the $M+1$ (triplet) VDE are listed theoretically, and these two peaks are observed in the experimental spectrum.

Table 5.1 Experimental and theoretical adiabatic detachment energies (ADE), experimental and theoretical vertical detachment energies (VDE) to neutral states of $M+1$ and $M-1$ spin multiplicities, and calculated HOMO-LUMO gaps (H-L gap) of the neutral and anionic PbIn_3 and Pb_2In_2 clusters. The superscripts indicate the M spin multiplicity. The relative energy of the low lying energy isomer for Pb_2In_2 is also given. All values are given in units of eV.

	E_{rel}	ADE	ADE	VDE 1	VDE 2	VDE Theo.		H-L gap
		Exp.	Theo.	Exp.	Exp.	($M-1$)	($M+1$)	
$^1\text{PbIn}_3^-$		2.21±0.08	2.21	2.52±0.04	3.00±0.06		2.30	1.34
$^2\text{PbIn}_3$								0.17
$^2\text{Pb}_2\text{In}_2^-$		1.86±0.10	1.80	2.30±0.08	2.94±0.10	2.01	2.55	0.55
$^1\text{Pb}_2\text{In}_2$								1.45
$^1\text{Pb}_2\text{In}_2$	0.002							1.10

A comparison of the theoretical and experimental values for ADE results in excellent agreement, with the values deviating by 0% and 3% for PbIn_3^- and Pb_2In_2^- , respectively. Further, the theoretical VDEs vary by 9% for PbIn_3^- and 13% for both Pb_2In_2^- transitions, representing a fair agreement. This is on par with previous studies, where deviations of VDEs are in a similar range.^{17,19} These results represent strong evidence that the geometries shown in Figure 5.2 are correct.

The first pointers that PbIn_3^- and Pb_2In_2 possessed enhanced stability can be directly found from their experimental spectra and the measured values of ADE. In general a low ADE signifies stability of the neutral species, while a high ADE represents stability of the anion; to quantify “low” and “high” ADE values, one customarily compares clusters within a single series. Figure 5.3 and Figure 5.4 depict both the experimental and theoretical ADE values for the PbIn_y^- ($y = 1-7$) and Pb_2In_y^- ($y = 1-6$) series, respectively. Since we will more thoroughly explore the photoelectron spectra and theoretical assignments of PbIn_y and Pb_2In_y clusters in a later chapter, only the information pertinent to the aromatic clusters is provided here. The plot of ADEs in Figure 5.3 is peaked at PbIn_3^- , while the plot in Figure 5.4 has a minimum at Pb_2In_2^- for the theoretical ADE and a near minimum for the experimental ADE. Thus, it is comparatively difficult to remove an electron from PbIn_3^- , while it is comparatively easy to remove an electron from Pb_2In_2^- . Although these findings are not sufficient to conclude a special stability for these clusters, it led us to further investigate the electronic and geometric structure of PbIn_3^- and Pb_2In_2 .

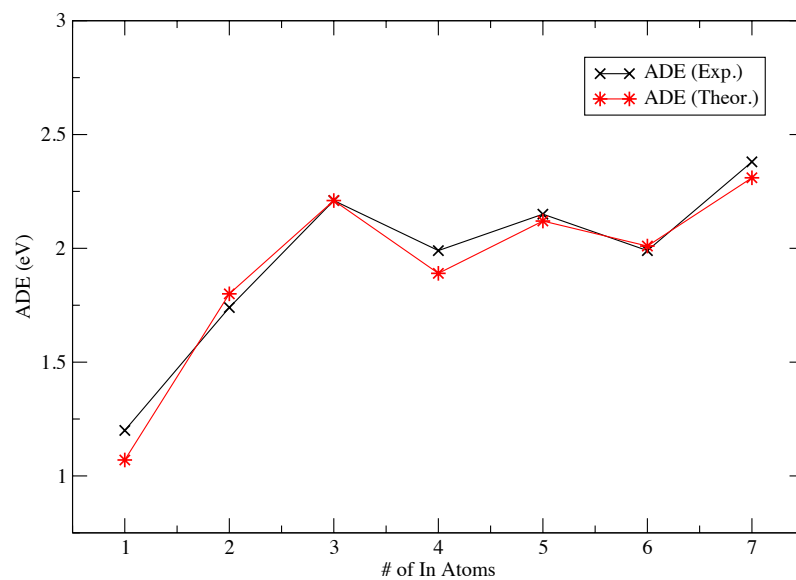


Figure 5.3 Adiabatic detachment energies of the PbIn_y^- ($y = 1-7$) series. The dark (black) X symbols represent the experimentally determined values, and the light (red) asterisks represent the theoretically calculated values. The connecting lines are shown as guides.

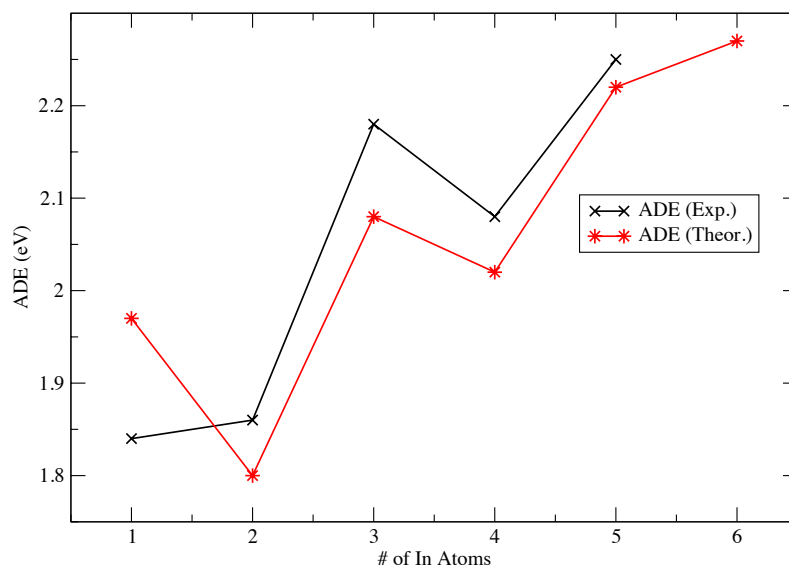


Figure 5.4 Adiabatic detachment energies of the Pb_2In_y^- ($y = 1-6$) series. See caption of Figure 5.3.

We subsequently calculated the HOMO-LUMO gap, and the amount of energy gained (ΔE_{In}) when successive In atoms bind to a Pb^- and Pb_2 :

$$\Delta E_{\text{In}} = E(\text{Pb}_x\text{In}_{y-1}) + E(\text{In}) - E(\text{Pb}_x\text{In}_y).$$

Here $E(\text{Pb}_x\text{In}_{y-1})$, $E(\text{In})$, and $E(\text{Pb}_x\text{In}_y)$ are the total ground state energies of the species. Large HOMO-LUMO gaps of 1.34 eV and 1.45 eV were determined for PbIn_3^- and Pb_2In_2 , respectively, and a maximum in ΔE_{In} was found for PbIn_3^- in the PbIn_y^- series and Pb_2In_2 in the Pb_2In_y series, as shown in Figure 5.5 and Figure 5.6. These findings led us to conclude that there was indeed some unique behavior in PbIn_3^- and Pb_2In_2 .

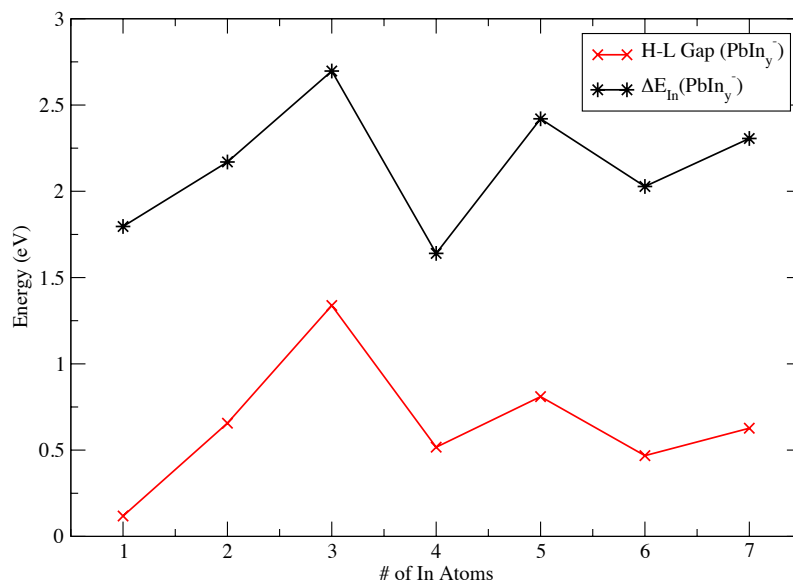


Figure 5.5 The calculated HOMO-LUMO gaps (H-L Gap) and In gain energies (ΔE_{In}) for the PbIn_y^- ($y = 1-7$) series. The light (red) X symbols represent the values for the HOMO-LUMO gaps, and the dark (black) asterisks represent the indium removal energies. The connecting lines are shown as guides.

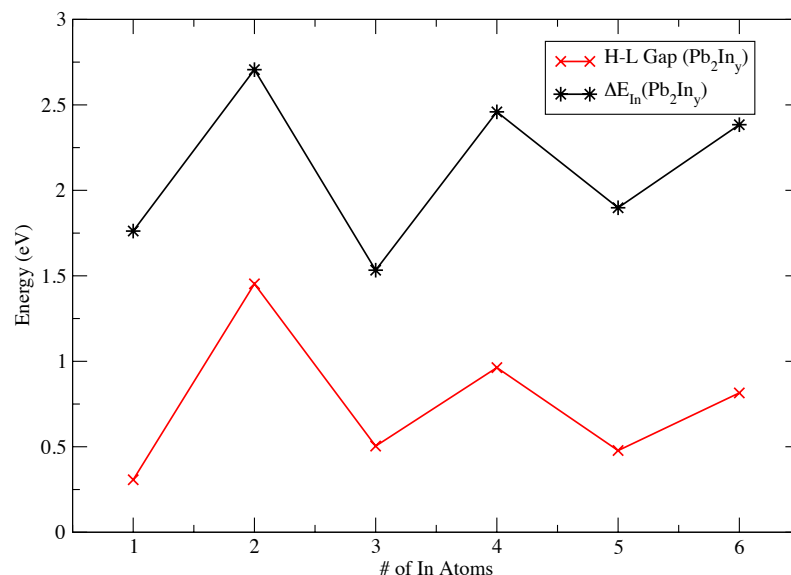


Figure 5.6 The calculated HOMO-LUMO gaps (H-L gap) and In gain energy (ΔE_{In}) for the Pb_2In_y ($y = 1-6$) series. See caption of Figure 5.5.

Since both of these clusters are isoelectronic to the all-metal aromatics Al_3X ($\text{X} = \text{As, Sb, Bi}$)^{17,19}, Ga_3Bi ¹⁸, and In_3Bi ²⁰ we have recently studied, we sought to explore if these clusters satisfied criteria of all-metal aromaticity. First PbIn_3^- is described, as it is analogous to our previous studies, and subsequently the more interesting Pb_2In_2 is described. As seen in Figure 5.2, the calculated geometry of PbIn_3^- is cyclic and planar with C_{2v} symmetry, with nearly-equivalent bond lengths of 2.88 Å for the Pb-In bond and 2.92 Å for the In-In bonds. This structure is common to heterogeneous all-metal aromatics, in which the usual cyclic and planar behavior is still present but with slightly uneven bond lengths due to elemental differences in electronegativity.¹⁷⁻²⁰ The structure of the neutral PbIn_3 cluster is quite similar to PbIn_3^- , which results in sharp peaks in the photoelectron spectrum. However, the bond lengths are shorter in PbIn_3^- than PbIn_3 , and in fact the 2.88 Å bond of PbIn_3^- is the shortest of any Pb-In bond in the calculations,

except for the dimer anion. This behavior is reminiscent of the shorter conjugated bonds in benzene and other conventional aromatic species.

To further investigate the aromatic character of PbIn_3^- the one electron energy levels, isosurfaces, and symmetries of the molecular orbitals have been calculated, as shown in Figure 5.7. The three highest occupied orbitals are all delocalized p-orbitals, with the HOMO representing the familiar π delocalized orbital and satisfying the $4n+2$ π electron rule ($n = 0$). Both the HOMO-1 and HOMO-2 have σ delocalization, resulting from the overlap of p-orbitals radially and tangentially, respectively.

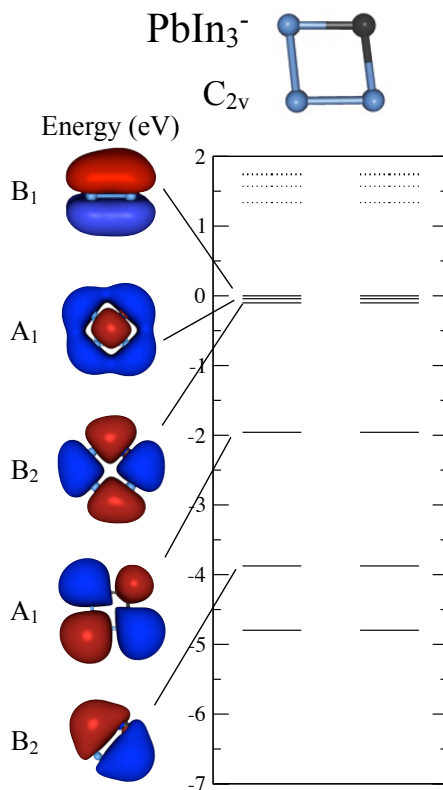


Figure 5.7 One electron energy levels, isosurfaces (isovalue = 0.01 au), and symmetry of the molecular orbitals for the anionic PbIn_3^- cluster. The continuous lines are occupied states and the dashed lines represent unoccupied levels. Energy is in units of eV.

This progression in the molecular orbitals is similar to other all-metal aromatics we have studied. In the cases of Al_3As and Al_3Sb the π delocalized orbital was the HOMO-2, while it was the HOMO-1 in Al_3Bi . However, in PbIn_3^- the π delocalized orbital is the HOMO, which makes a greater contribution to the valence character of the cluster. In fact, the ordering of the molecular orbitals is the same¹⁰ as that of the prototypical all-metal aromatic Al_4^{2-} . Thus, even in heavier non-aluminum based systems this aromatic bonding scheme is still preserved. It is important to note that there are slight distortions of the electron density in heterogeneous all-metal aromatics due to the differing elemental electronegativities, as can be seen in the molecular orbital picture in Figure 5.7. The difference in electronegativity between lead and indium is 0.55, a value similar to that found in the aromatic Al_3As (0.57), which was discussed in Chapter 4 as being near the threshold allowed while still retaining the cyclic, planar structure.¹⁹ For example, studies of Al_3P , which has an electronegativity difference of 0.58, have shown there are competing geometries for the ground state, one of which is non-cyclic.³³ In the case of PbIn_3^- the closest non-planar isomer is significantly higher (0.72 eV) than the ground state, revealing that even with a significant difference in electronegativity the cluster still strongly prefers the aromatic structure. This energy difference of 0.72 eV can be considered an energetic measure of aromaticity, as it indicates the energy gained in forming a resonant structure, *vis. a vis.* a compact three-dimensional structure.

To further confirm the aromatic character of PbIn_3^- and Pb_2In_2 the nucleus independent chemical shift (NICS) values have been calculated. This procedure, developed by Schleyer et al.,³⁴ attempts to quantify aromaticity by examining the cluster's response to a magnetic field. An aromatic molecule should possess a ring current in the

presence of an external magnetic field, and this current should induce a secondary magnetic field in opposition to the external field. In the calculation, a ghost atom is placed at the center of the cluster and the magnetic shielding at this point is measured. Aromatic clusters should possess negative NICS values, while antiaromatic clusters possess positive NICS values. For example, the NICS value calculated for benzene is -9.7 ppm.³⁴ In addition to NICS values, the magnetic susceptibility tensor χ is often used as a probe of aromaticity. The magnetic susceptibility tensor is the cluster's response to an applied magnetic field in three Cartesian coordinates, and can be written as a rank 2 tensor. The susceptibility tensor can be split into in-plane χ_{ip} and out-of-plane χ_{op} components, the difference of which is the magnetic susceptibility anisotropy $\Delta\chi$, generally used as a measure of aromaticity in hydrocarbons. Similar to NICS, aromatic clusters possess negative magnetic susceptibility and magnetic susceptibility anisotropy values, indicating a diamagnetic response to the applied magnetic field. For instance, the calculated $\Delta\chi$ value for benzene is -64.14 cgs-ppm, which is in good agreement with the previously reported value of -62.5 cgs-ppm³⁵. The NICS and magnetic susceptibility calculations were both performed using the same theoretical model, namely the PBE functional employing identical basis sets as mentioned in Section 5.2 for both In and Pb using the Gaussian03 software package.³⁶ The ground state geometries were re-optimized prior to the NICS and magnetic susceptibility calculations. The NICS results are displayed in Table 5.2. The value of -27.42 ppm for PbIn_3^- reinforces the conclusion of aromatic character. The magnetic susceptibility calculations show χ_{ip} and χ_{op} values of -202.00 and -31.92 cgs-ppm, respectively. This yields a magnetic susceptibility anisotropy $\Delta\chi$ value of -170.08 cgs-ppm for PbIn_3^- , confirming aromatic character.

Table 5.2 Nucleus-independent chemical shift (NICS) values of $^1\text{PbIn}_3^-$ and $^1\text{Pb}_2\text{In}_2$ in ppm. The NICS values are calculated by placing a ghost atom at the ring center in the molecular plane and at 0.5, 1.0, and 1.5 Å above the plane.

Distance (Å)	NICS (ppm)		
	$^1\text{PbIn}_3^-$	$^1\text{Pb}_2\text{In}_2$ (C_{2v})	$^1\text{Pb}_2\text{In}_2$ (D_{2h})
0.0	-27.42	-28.69	-32.34
0.5	-26.61	-27.52	-31.26
1.0	-23.56	-23.83	-27.09
1.5	-18.51	-18.19	-20.34

Also shown in Table 5.2 are the NICS values for Pb_2In_2 of -28.69 ppm and -32.34 ppm for the C_{2v} and D_{2h} structures, respectively. If one imagines Pb to behave as In^- , then Pb_2In_2 neutral should behave similarly to PbIn_3^- . This is found in the NICS calculations, as the values for both isomers of Pb_2In_2 are similar to the value for PbIn_3^- , differing at most by 4.92 ppm. The magnetic susceptibility anisotropy calculations indicate that both the C_{2v} and D_{2h} structures exhibit aromatic character, possessing $\Delta\chi$ values of -138.28 and -109.68 cgs-ppm, respectively. However, analyzing the in-plane and out-of-plane components provided useful information on the behavior of aromaticity in these species. Interestingly, the χ_{ip} components are almost identical at -189.87 and -189.85 cgs-ppm for the C_{2v} and D_{2h} structures, respectively; the χ_{op} components were measured as -51.59 and -80.17 cgs-ppm, respectively. Despite the large $\Delta\chi$ value for the C_{2v} structure, the out-of-plane component of the D_{2h} structure indicated a larger current. The larger χ_{op} value for the D_{2h} structure is due to the alternating Pb-In bonds, allowing for a larger current. On the other hand, the Pb-Pb bond of the C_{2v} structure leads to a smaller χ_{op} value, due to the

mismatched electronegativities and thus uneven electron delocalization around the cluster plane. Another criterion for aromatic character, generally used for conjugated hydrocarbons, is the resonance energy.³⁷ Zhan et al have recently extended the criterion to pure metal clusters³⁸ and have calculated the resonance energy for Al_4^{2-} . However, there is considerable ambiguity in extending this definition to heteroatomic, metallic systems.

The aromatic character in Pb_2In_2 is much more interesting when examining the ground state geometries and molecular orbitals for this species. Figure 5.8 displays the ground state geometry and low lying isomer for this species. The two structures with C_{2v} and D_{2h} symmetry are nearly energetically degenerate, differing by just 0.002 eV. The structure for the anion is more similar to the D_{2h} isomer, with alternating lead and indium atoms. If the isomer for Pb_2In_2 (D_{2h}) was the true ground state structure, meaning there were no close lying isomers, we would expect sharp peaks in the experimental spectrum due to little vibrational progression in the detachment features. Consulting Figure 5.1, it is apparent that the spectrum of Pb_2In_2^- is much less resolved than that of PbIn_3^- . This led us to believe that there could be a much larger geometry difference between the anion and neutral of Pb_2In_2^- than for PbIn_3^- . Hence, we believe the experimental spectrum lends support to the calculations here, that there are competing, nearly-degenerate C_{2v} and D_{2h} structures for Pb_2In_2 . This is quite surprising; the structure with alternating Pb-In bonds was expected to be favored for an aromatic structure. There is a better chance at delocalization if the more electronegative lead atoms are on opposite sides of the ring structure. However, when the orbital diagrams were calculated, shown in Figure 5.8, the molecular orbital picture is nearly identical between the Pb_2In_2 structures. This is

especially true for the HOMO through HOMO-2, which are the orbitals that primarily contribute to the valence character of the cluster. These orbitals represent the π delocalized orbital and two σ delocalized orbitals, and in each case the delocalization is fairly uniform. Therefore, it would seem that in heavy metal aromatics the electronegativity differences and location of the heteroatoms play a smaller role than expected in governing the electronic structure and geometry. The important point here is that the valence count and number of atoms is almost solely responsible for the appearance of all-metal aromaticity.

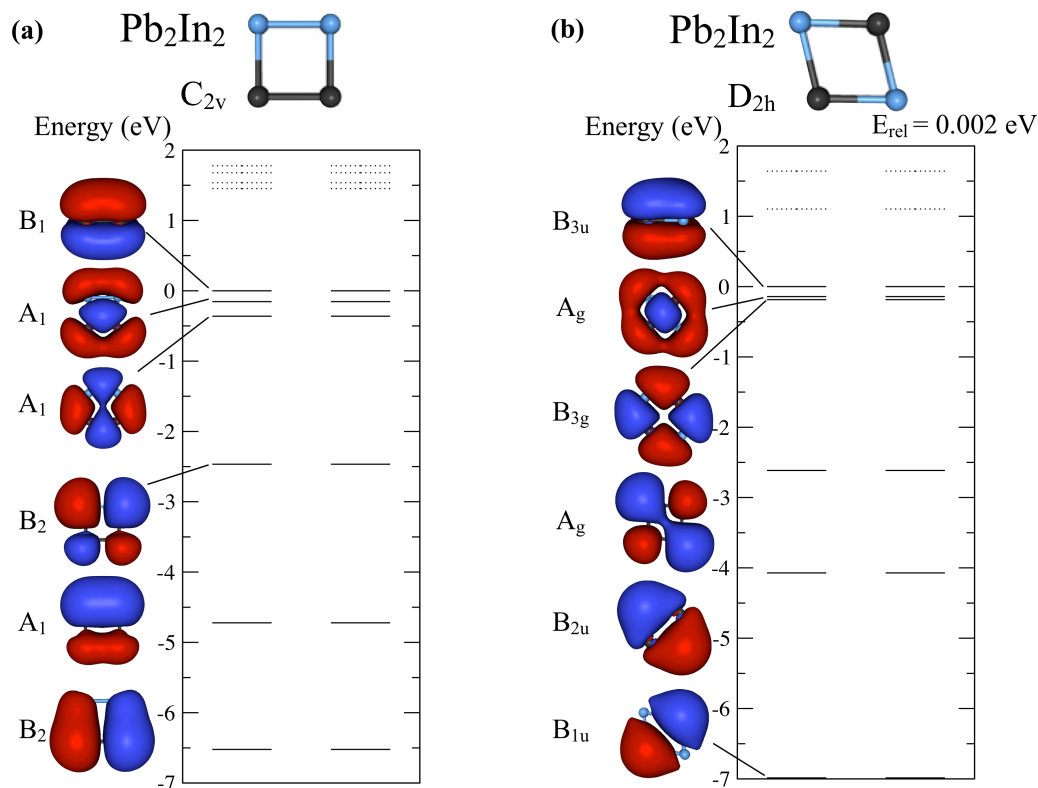


Figure 5.8 One electron energy levels, isosurfaces (isovalue = 0.01 au), and symmetry of the molecular orbitals for (a) the neutral Pb_2In_2 ground state and (b) its lowest energy isomer. The continuous lines are occupied states and the dashed lines represent unoccupied levels. Energy is in units of eV.

Consequently, heavy metal aromatics may be an ideal candidate for CAMS. The electron delocalization and cyclic, planar structures seem resilient to changes in atomic location or identity, maintaining their highly aromatic character; however, we have shown that their HOMO-LUMO gaps do change. Therefore, we may be able to significantly tune these gaps by substituting different heavy metal atoms while still retaining the aromaticity. This is in contrast to previous studies, where the aromaticity has been shown to be quite sensitive to changes in atomic composition.^{15,19}

5.4 Conclusions

Through a collaborative approach of photoelectron spectroscopy and first-principles electronic structure calculations, the stability of two specific clusters are attributed to all-metal aromaticity. Both the PbIn_3^- and Pb_2In_2 clusters were shown to have planar, C_{2v} ground state geometries. Additionally, we found large HOMO-LUMO gaps of 1.34 and 1.45 eV, respectively, and large formation energy gains, indications of high chemical inertness and energetic stability. The low ADE value for Pb_2In_2^- and high ADE value for PbIn_3^- are indicative of a high energetic stability for Pb_2In_2 and PbIn_3^- , respectively. The aromatic nature of these planar clusters is shown through the delocalized orbitals in the HOMO through HOMO-2 states, the largely negative NICS values of -27.42 ppm for PbIn_3^- and -28.69 ppm for Pb_2In_2 , and the largely negative magnetic susceptibility values. Conversely to previous studies, the aromaticity is preserved despite a large electronegativity difference between the heteroatoms. Further, in the case of Pb_2In_2 it was shown that the arrangement of atoms within the planar structure can be varied without disrupting the aromatic character.

5.5 References

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Chapter 6

Anion Photoelectron Spectroscopy and First-Principles Study of Pb_xIn_y Clusters

6.1 Introduction

The prospect of nanomaterials with tailored properties has encouraged a wealth of studies in cluster science.¹⁻⁷ This is due to the unique possibility of a bottom-up approach, where clusters with desirable characteristics are assembled into a functional material. This goal is far from trivial; chief among the problems is the challenge of retaining the interesting cluster properties when assembling them into a bulk material. One route to overcome this problem is to identify clusters that exhibit an enhanced stability. The driving forces of stability in clusters are commonly attributed to geometric^{8,9} and electronic^{10,11} effects (See Chapter 2). Generally, the electronic effects dominate at small sizes, where the quantum confinement leads to electronic shells with large spacing between the shells, while the geometric effects dominate at large sizes. For example, experiments in our group have shown that small anionic aluminum clusters exhibit the magic species Al_{13}^- , Al_{23}^- , and Al_{37}^- , whose stability arises from filled electronic shells.¹² For aluminum clusters in the size range of 200-15000 atoms, on the other hand, the oscillations in the mass spectra can be associated with filling of geometrical shells of octahedral shape.¹³

The electronic closed shells have been rationalized within a confined nearly free electron gas (NFEG) where the valence electrons respond to a spherical, smeared-out, positive background potential.¹⁰ This model has even been adopted for heteroatomic

species, in which new magic numbers emerge depending on the nature of the heteroatom.¹⁴ A theoretical understanding of stable heteroatomic species is intriguing in light of cluster assembled materials (CAMS), as heteroatomic clusters present advantages over homoatomic clusters in the design of cluster assemblies. For example, the charge state of a cluster, for a given size, can easily be manipulated by exchanging one atom for an atom with a different number of valence electrons. Additionally, partial charges due to elemental differences within heteroatomic clusters may present easier opportunity for assembly using counteranions or ligands. These variations are particularly important in view of the recent findings¹⁵⁻²⁵ that planar or caged metallic clusters can undergo electronic stabilization through aromaticity, a concept that has been applied to organic systems for over a century 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 have extended aromaticity to include all-metal clusters, most notably the Al_4^{2-} dianion,¹⁵ and it has recently been shown that Al_3X ($\text{X} = \text{As}, \text{Sb}, \text{Bi}$), Ga_3Bi , and In_3Bi clusters also exhibit stabilization due to aromaticity.¹⁹⁻²²

In the current chapter, a large variety of Pb_xIn_y anionic and neutral clusters are examined. Although experimental^{26,27} and theoretical²⁸ work on similar group III-IV clusters have been reported, the lead-indium clusters examined here represent an intriguing choice of study due to the stark contrast in the behavior of pure lead and pure indium clusters. For instance, previous studies provide a mass spectrum of lead clusters where closed electronic shells and close-packed structures govern the enhanced stability, and thus spectral abundance, at certain sizes.²⁹⁻³¹ The result is far different in pure indium

clusters, where the electronic shell structure is dominant for the presence of magic species.³²⁻³³ It is unclear how the properties of mixed lead-indium clusters will evolve with size, and whether their stability will be dominated by geometric or electronic effects, or perhaps both. Using a combination of photoelectron spectroscopy and first-principles calculations, it is demonstrated here that both factors are important in lead-indium clusters. In fact, numerous clusters are identified with enhanced stability suitable for CAMS candidates, including electronic closed-shell species, all-metal aromatics, and close-packed clusters.

6.2 Experimental and Computational Details

Experimental photoelectron spectra were obtained with a magnetic bottle photoelectron spectroscopy apparatus that has been described in Chapter 3 and in the literature.³⁴ The Pb_xIn_y^- clusters were produced in a laser vaporization supersonic cluster beam source, using a 1/4" 50:50 molar ratio lead-indium molded rod as the target. Helium was used as the carrier gas with stagnation pressures of around 50 psi. The resulting anions were extracted and mass analyzed with a Wiley-McLaren time-of-flight mass spectrometer.³⁵ Mass-selected anions of interest were then interrogated by an unfocused, unpolarized laser beam from an excimer laser (308 nm) in a magnetic bottle analyzer, where photodetached electrons are analyzed according to their kinetic energies. The electronic spectra were calibrated based on the known spectra of Bi^- .³⁶

To aid in both the assignment of the spectra and the determination of geometric and electronic properties, first-principles electronic structure calculations were carried out by collaborators on both neutral and anionic forms of the Pb_xIn_y clusters. The calculations

were performed within the density functional theory (DFT) formalism³⁷ with the exchange and correlation interactions treated by the generalized gradient approximation as proposed by Perdew, Burke, and Ernzerhof.³⁸ The In atoms were described using a 3 electron scalar relativistic effective core potential (ECP) and corresponding basis set, as proposed by Igel-Mann et al.³⁹ The Pb atoms were described using a 22 electron relativistic ECP proposed by Metz⁴⁰ and the correlation consistent aug-cc-pVDZ basis set.⁴¹ The GEN-A2* auxiliary function set were used for both In and Pb atoms. The actual calculations were performed using the linear combination of Gaussian type orbitals DFT software package deMon2k.⁴² To determine the ground state geometries of the clusters, various initial geometries and spin states were attempted and fully optimized without symmetry constraints. A frequency analysis was carried out to reinforce the ground state structures.

6.3 Results and Discussion

Figure 6.1 shows collected photoelectron spectra of Pb_xIn_y^- clusters obtained at 308 nm (4.0 eV) and plotted on a binding energy scale. Each peak represents an electronic transition from the anion ground state to the neutral ground state (band X) and higher neutral excited states (A, B, etc.). For each resolved peak the peak maximum is assigned as the vertical detachment energy (VDE) and the leading edge of the first peak is the adiabatic detachment energy (ADE). In some cases, multiple electronic transitions may lie within a single experimental peak (i.e. the spacing between electronic states is less than the resolution of the instrument). In these cases, experimental VDEs are still assigned as the peak maximum for each resolved peak. However, it is important to note

that the sequential experimentally-determined VDEs listed may not be sequential energetic states.

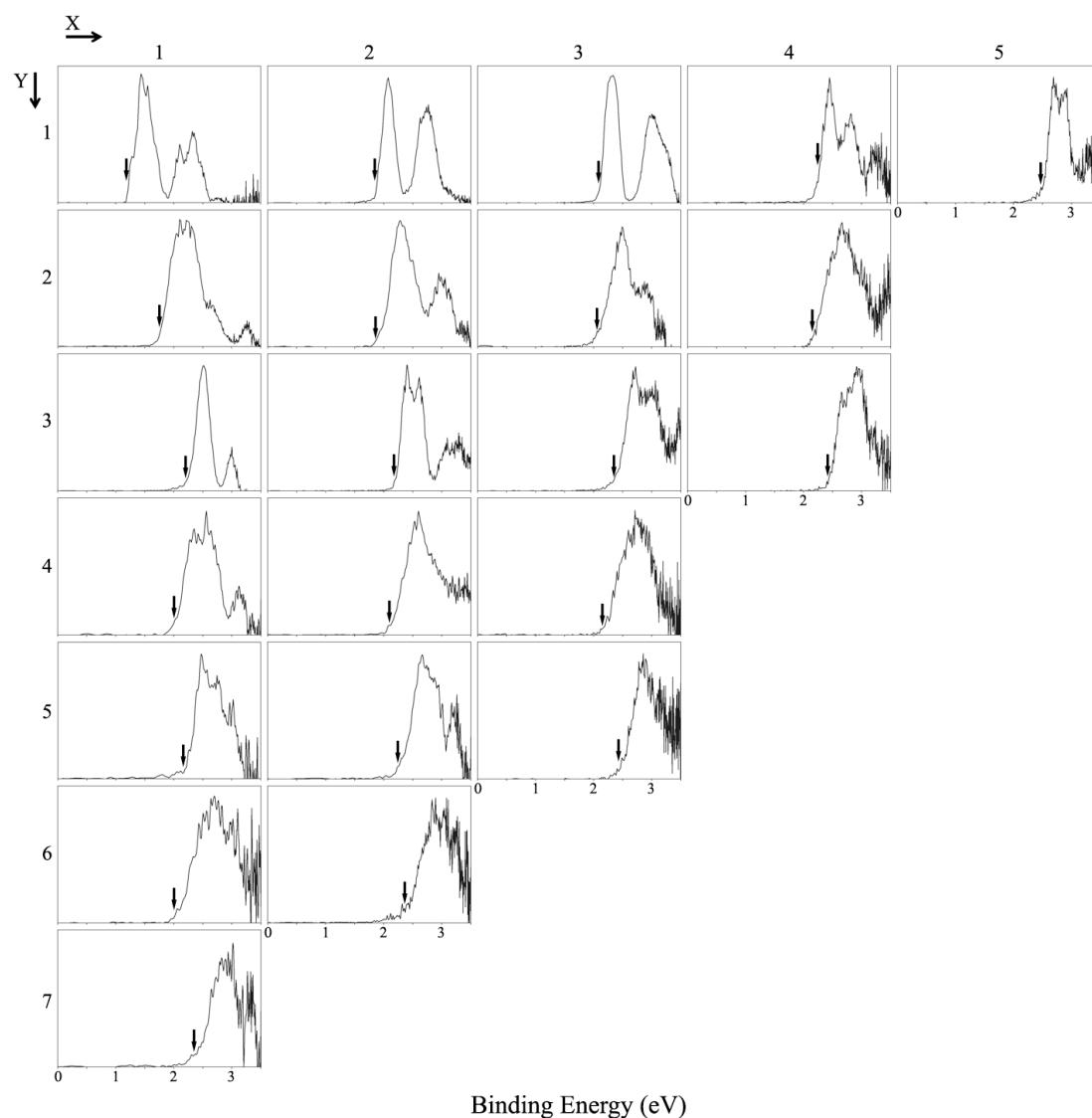


Figure 6.1 Photoelectron spectra of Pb_xIn_y^- clusters. The rows represent increasing lead concentration from left to right ($X = 1-5$), while the columns represent increasing indium concentration from top to bottom ($Y = 1-7$). The black arrows within each spectrum represent the experimental ADE.

Tables 6.1-6.3 show the experimental quantities compared with calculated values. The calculated VDE values are obtained by taking the energy difference between the anion ground state geometry (with multiplicity M) and the neutral cluster in the anion geometry (with multiplicity $M+1$ or $M-1$). The ADE values are calculated by taking the energy difference between the anion ground state geometry and the neutral ground state geometry. Good agreement between the experimental and calculated values of VDE and ADE represents confidence in both the experimental spectra and the ground state geometries found.

Table 6.1 Experimental and theoretical VDEs to the neutral ground state, band X, and to higher excited states of the neutral species, bands A, B, and C. Adiabatic electron detachment energies (ADE) and calculated HOMO-LUMO gaps (H-L gap) of the neutral and anionic PbIn_y ($y = 1 - 7$) species. The superscripts indicate the spin multiplicity. The relative energies of the low lying energy isomers are also given. All values are given in units of eV.

	E_{rel}	Band	VDE Exp.	VDE Theo.	ADE Exp.	ADE Theo.	H-L gap
$^3\text{PbIn}^-$		X	1.43	1.10	1.20	1.07	0.12
		A	2.10	2.13			
		B	2.32				
		C	2.77				
$^4\text{PbIn}$							0.98
$^2\text{PbIn}_2^-$		X	2.10	1.80	1.74	1.80	0.66
		A	2.62	2.70			
		B	3.26				
$^3\text{PbIn}_2$							0.39
$^1\text{PbIn}_3^-$		X	2.52	2.30	2.21	2.21	1.34
		A	3.00				
$^2\text{PbIn}_3$							0.17
$^2\text{PbIn}_4^-$		X	2.35	2.14	1.99	1.89	0.52
		A	2.56	2.38			
		B	3.12				
$^1\text{PbIn}_4$							1.24
$^1\text{PbIn}_5^-$	0	X	2.47	2.17	2.15	2.12	0.81
		A	2.75				
		B	3.02				
	0.013			2.33 3.24		2.11	0.86
$^2\text{PbIn}_5$							0.44
$^2\text{PbIn}_6^-$		X	2.70	2.31 2.42	1.99	2.01	0.47
$^1\text{PbIn}_6$							0.92
$^1\text{PbIn}_7^-$		X	2.82	2.42	2.38	2.31	0.63
$^2\text{PbIn}_7$							0.30

Table 6.2 Experimental and theoretical VDEs, ADEs, and calculated H-L gaps of the neutral and anionic Pb_2In_y ($y = 1 - 6$). See caption of Table 6.1.

	E_{rel}	Band	VDE Exp.	VDE Theo.	ADE Exp.	ADE Theo.	H-L gap
$^1\text{Pb}_2\text{In}^-$		X	2.08	2.04	1.84	1.97	0.86
		A	2.73				
$^2\text{Pb}_2\text{In}$							0.31
$^2\text{Pb}_2\text{In}_2^-$		X	2.30	2.01	1.86	1.80	0.55
		A	2.94	2.55			
$^1\text{Pb}_2\text{In}_2$							1.45
$^1\text{Pb}_2\text{In}_3^-$		X	2.40	2.16	2.18	2.08	0.71
		A	2.61				
		B	3.09				
$^2\text{Pb}_2\text{In}_3$							0.50
$^2\text{Pb}_2\text{In}_4^-$		X	2.60	2.25 2.56	2.08	2.02	0.53
$^1\text{Pb}_2\text{In}_4$							0.96
$^1\text{Pb}_2\text{In}_5^-$	0	X	2.66	2.45	2.25	2.22	0.90
		A	3.17				
	0.022			2.52		2.19	0.94
$^2\text{Pb}_2\text{In}_5$							0.48
$^2\text{Pb}_2\text{In}_6^-$		X	2.89	2.56 2.68	2.37	2.27	0.34
$^1\text{Pb}_2\text{In}_6$							0.82

Table 6.3 Experimental and theoretical VDEs, ADEs, and calculated H-L gaps of the Pb_3In_y ($y = 1 - 5$), Pb_4In_y ($y = 1 - 3$) and Pb_5In neutral and anionic clusters. See caption of Table 6.1.

	E_{rel}	Band	VDE Exp.	VDE Theo.	ADE Exp.	ADE Theo.	H-L Gap
$^1\text{Pb}_3\text{In}^-$		X	2.33	2.13	2.09	2.00	0.95
		A	3.00				
$^2\text{Pb}_3\text{In}$							0.63
$^2\text{Pb}_3\text{In}_2^-$		X	2.49	2.33	2.06	1.86	0.38
		A	2.87	2.57			
$^1\text{Pb}_3\text{In}_2$							1.23
$^1\text{Pb}_3\text{In}_3^-$		X	2.72	2.59	2.35	2.28	1.08
		A	3.01				
$^2\text{Pb}_3\text{In}_3$	0						0.58
	0.004						0.56
$^2\text{Pb}_3\text{In}_4^-$	0	X	2.71	2.45	2.16	2.06	0.43
				2.56			
	0.024			2.42		2.03	0.36
$^1\text{Pb}_3\text{In}_4$	0						0.91
	0.002						1.07
$^1\text{Pb}_3\text{In}_5^-$		X	2.85	2.64	2.43	2.59	1.12
$^2\text{Pb}_3\text{In}_5$							0.37
$^1\text{Pb}_4\text{In}^-$	0	X	2.44	2.51	2.24	2.42	1.43
		A	2.82				
		B	3.18				
	0.025			2.54		2.40	1.12
$^2\text{Pb}_4\text{In}$							0.38
$^2\text{Pb}_4\text{In}_2^-$	0	X	2.66	2.32	2.14	2.01	0.51
				2.59			
	0.037			2.46		1.97	0.57
				2.51			
$^1\text{Pb}_4\text{In}_2$							1.06
$^1\text{Pb}_4\text{In}_3^-$		X	2.65	2.52	2.40	2.39	1.10
		A	2.91				
$^2\text{Pb}_4\text{In}_3$	0						0.39
	0.042						0.50
$^1\text{Pb}_5\text{In}^-$		X	2.69	2.37	2.48	2.55	1.50
		A	2.92				
		B	3.29				
$^2\text{Pb}_5\text{In}$							0.55

The anion and neutral ground state geometries for the first series of clusters, PbIn_y ($y = 1-7$), are shown in Figure 6.2. In addition, a low lying energy isomer was found for PbIn_5^- and is shown next to the ground state structure. Most of the even- and odd-electron systems were found to have a singlet and doublet multiplicity, respectively. The only exceptions were PbIn^- , PbIn , and PbIn_2 , which were found to possess a triplet, quartet, and triplet multiplicity, respectively. For $y < 4$ the geometries for both anion and neutral clusters are planar. The transition from 2-D to 3-D happens at $y = 4$, with PbIn_4^- possessing a planar structure and PbIn_4 possessing a structure similar to PbIn_3 , but with an extra indium atom attached to the lead at about 90° off the plane, making it a 3-D structure. Above $y = 4$, the clusters clearly favor a compact, 3-D geometry. In all cases the lead atom seems to prefer to bind to multiple indium atoms, as expected by comparison of the calculated PbIn bond strength (2.08 eV) to that of In_2 (1.18 eV).

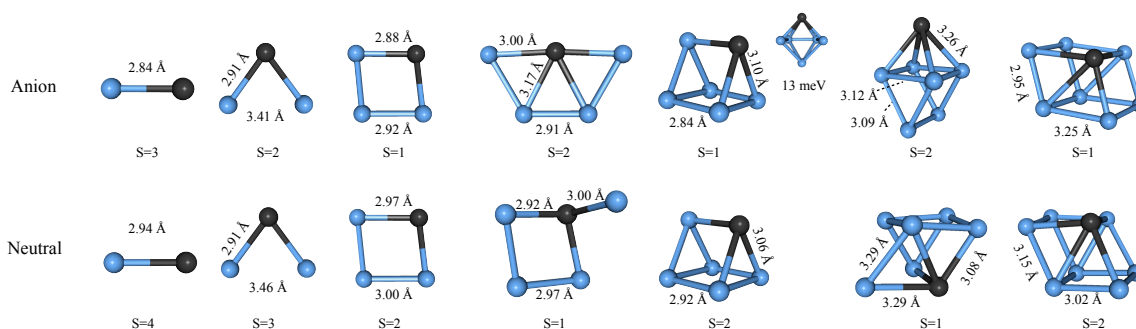


Figure 6.2 Optimized geometries of anionic and neutral PbIn_y clusters ($y = 1-7$). Bond lengths are given in angstroms and spin multiplicities are denoted below each cluster. The black spheres represent lead atoms, while the blue spheres represent indium atoms. A low lying energy isomer is shown as an inset of PbIn_5^- , and it has a relative energy 13 meV above the ground state.

Figure 6.3 depicts the anion and neutral ground state geometries for the second series of clusters, Pb_2In_y ($y = 1-6$). Low lying energy isomers were found in the cases of Pb_2In_2 and Pb_2In_5^- , and are shown next to the corresponding ground state structures. For this cluster series all even-electron systems were found to possess singlet multiplicities while all odd-electron systems were found to have doublet multiplicities. The transition from 2-D to 3-D again appears around five atoms, i.e. $y = 3$ for the Pb_2In_y series. At this size, the clusters adopt a planar structure similar to that of PbIn_4^- . Starting at Pb_2In_4 the clusters favor a compact, 3-D geometry, again similar to the previous series. It is interesting to note that in all cases except one (the Pb_2In_5^- ground state) the Pb-Pb bond remains intact, a consequence of the larger Pb_2 bond strength (2.43 eV) as compared to the PbIn bond strength (2.08 eV). In Figure 6.4 the anion and neutral geometries for the Pb_3In_y ($y = 1-5$) series are provided; only singlet and doublet multiplicities were found for the even- and odd-electron systems, respectively, and isomers are shown where appropriate. As expected, in most of the series the lead atoms prefer to bind with each other due to the higher bond strength. Further, the Pb_3 triangle is present in all of the species that contain more lead atoms than indium atoms.

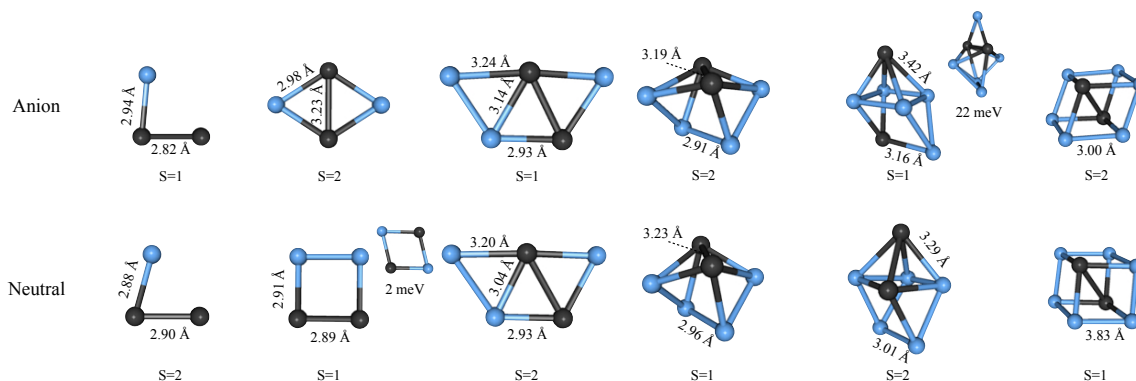


Figure 6.3 Optimized geometries of anionic and neutral Pb_2In_y clusters ($y = 1-6$). Bond lengths are given in angstroms and spin multiplicities are denoted below each cluster. The black spheres represent lead atoms, while the blue spheres represent indium atoms. Low lying energy isomers are shown as insets to respective ground states, with their relative energy listed in meV.

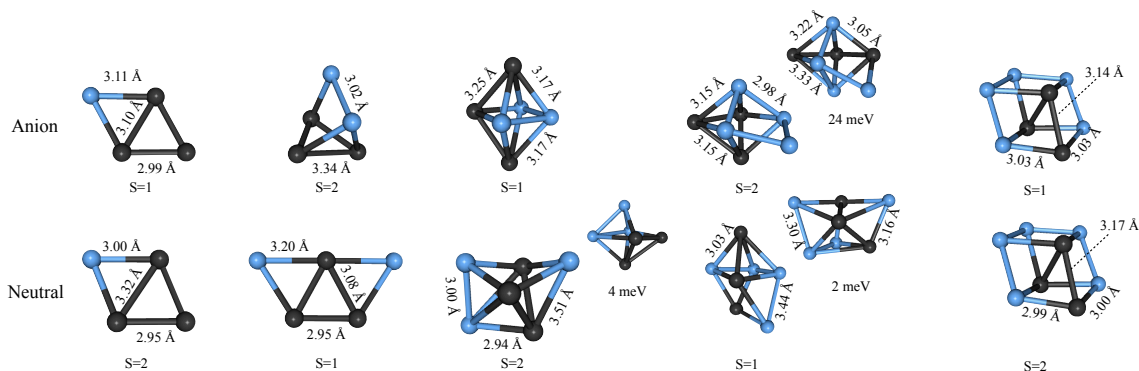


Figure 6.4 Optimized geometries of anionic and neutral Pb_3In_y clusters ($y = 1-5$). Bond lengths are given in angstroms and spin multiplicities are denoted below each cluster. The black spheres represent lead atoms, while the blue spheres represent indium atoms. Low lying energy isomers are shown as insets to respective ground states, with their relative energy listed in meV.

Figure 6.5 shows the ground state geometries and low lying isomers for the anionic and neutral Pb_4In_y clusters ($y = 1-3$); all even electron systems are singlet states and all odd electron systems are doublet states. Each cluster in this series is three dimensional, and the ground state geometries are reminiscent of pure lead clusters.³¹ The

optimized anion and neutral geometries for the last series, Pb_xIn ($x = 1-5$), are displayed in Figure 6.6. A low lying energy isomer was found for Pb_4In^- and is shown next to the ground state structure. As previously mentioned the PbIn anion and neutral possess triplet and quartet multiplicities, respectively. However, the remaining anions and neutrals in this series have singlet and doublet multiplicities, respectively. As was found for the PbIn_y and Pb_2In_y series, the transition to a 3-D geometry occurs at five atoms in the Pb_xIn series. The indium atom appears to bond to as few lead atoms as possible, with no ground state geometry possessing more than two indium-lead bonds. As in the case of the Pb_2In_y series, this is a consequence of the larger Pb_2 bond strength as compared to the PbIn bond strength.

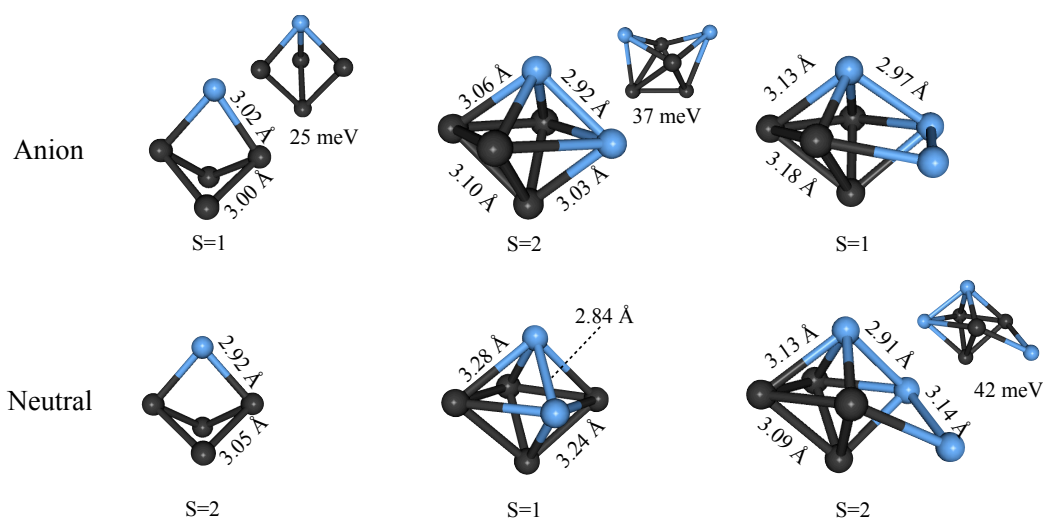


Figure 6.5 Optimized geometries of anionic and neutral Pb_4In_y clusters ($y = 1-3$). Bond lengths are given in angstroms and spin multiplicities are denoted below each cluster. The black spheres represent lead atoms, while the blue spheres represent indium atoms. Low lying energy isomers are shown as insets to respective ground states, with their relative energy listed in meV.

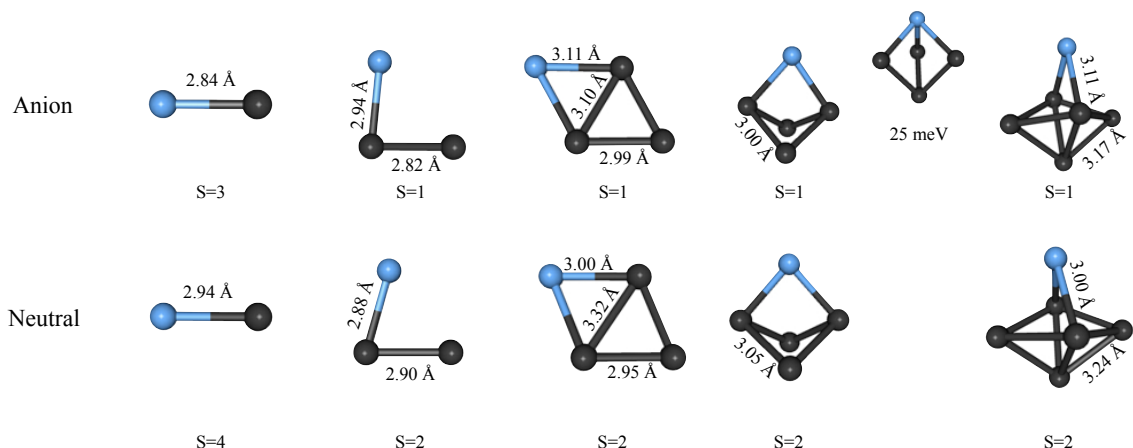


Figure 6.6 Optimized geometries of anionic and neutral Pb_xIn clusters ($x = 1-5$). Bond lengths are given in angstroms and spin multiplicities are denoted below each cluster. The black spheres represent lead atoms, while the blue spheres represent indium atoms. A low lying energy isomer is shown as an inset of Pb_4In^- , and it has a relative energy 25 meV above the ground state.

In order to investigate the stability of a particular cluster one can consult multiple pieces of evidence. The first is the ADE, an experimental and theoretical pointer to stability. In general a low ADE signifies stability of the neutral, as it is “easy” to remove an electron from the anion, while a high ADE signifies stability of the anion, as it is “difficult” to remove an electron from the anion to produce the neutral. Since it is not possible to set a universal threshold for high or low ADE, it is customary to compare clusters within a series. Figure 6.7 shows the trend in ADE for each of the PbIn_y^- , Pb_2In_y^- , Pb_3In_y^- , Pb_4In_y^- , and Pb_xIn^- series in panels A-E, respectively. The black X’s represent the experimental data, while the red asterisks represent the calculated values. The lines are shown as guides. The agreement between experiment and theory is evident, providing confidence for the calculated ground state structures. In the first four panels one might expect an oscillation of ADE values due to the even-odd electron counts of the species. In

some sense this is observed, but there are exceptions that point to enhanced stability of certain clusters, which are discussed later. There is no oscillation in the last panel, as each cluster anion possesses an even number of electrons.

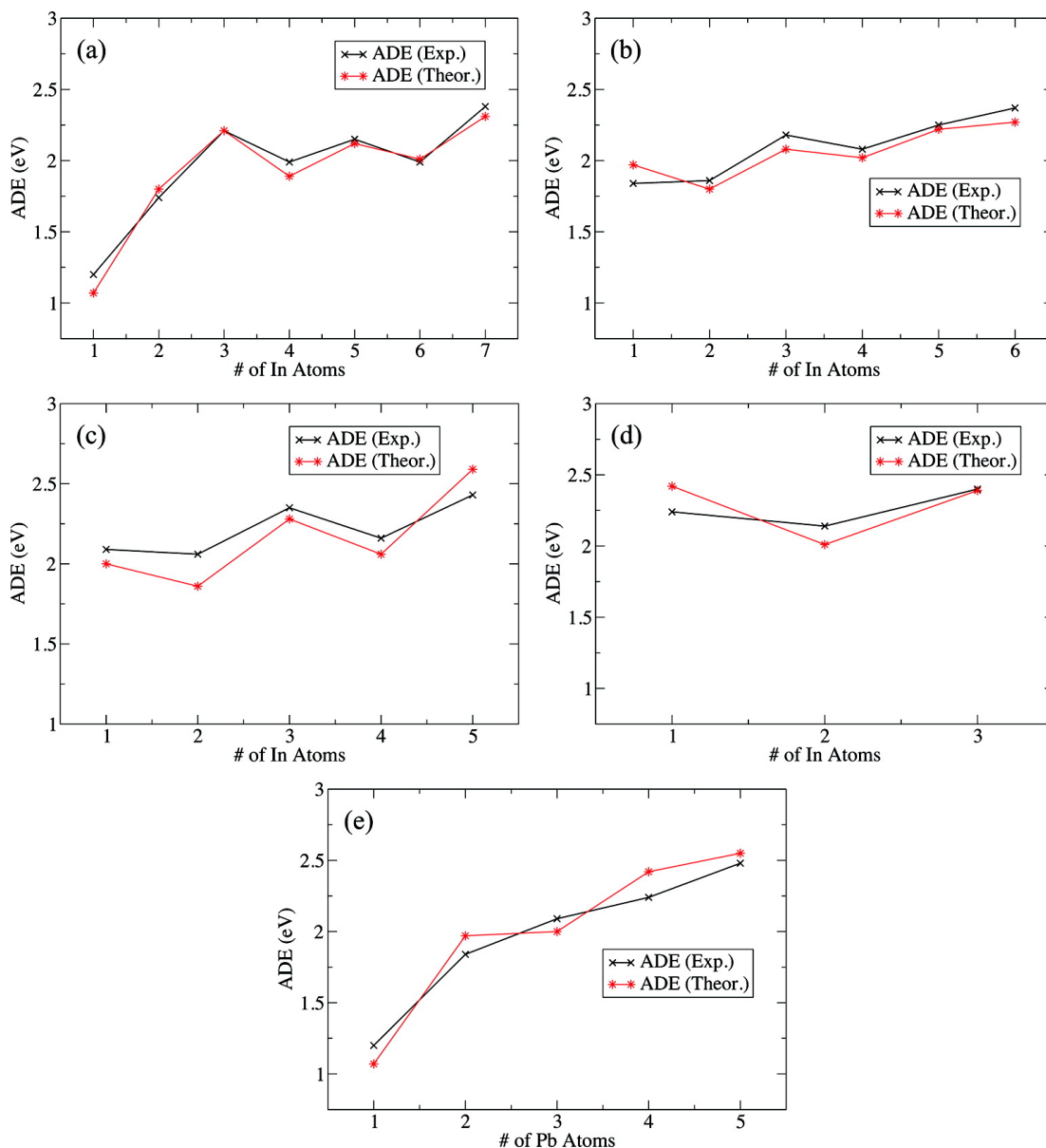


Figure 6.7 Trends in experimental adiabatic detachment energy (black), calculated adiabatic detachment energy using deMon2k (red). The PbIn_y , Pb_2In_y , Pb_3In_y , Pb_4In_y , and Pb_xIn cluster series are shown in panels (a) – (e), respectively.

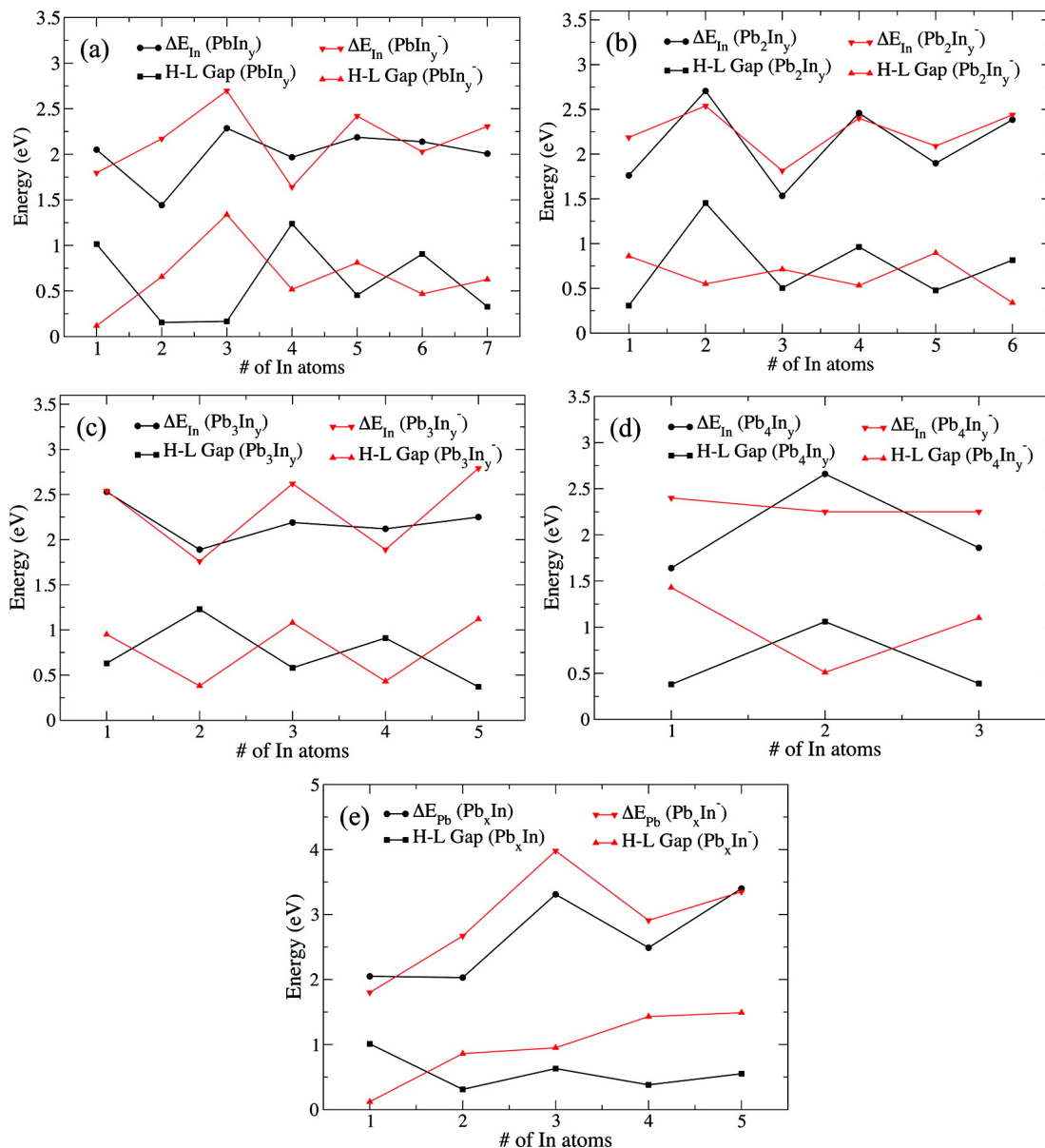


Figure 6.8 Trends in HOMO-LUMO gap (black squares for neutral species, red triangles up for anion species) and energy gain (black circles for neutral species, red triangles down for anion species). The neutral and anion PbIn_y , Pb_2In_y , Pb_3In_y , Pb_4In_y , and Pb_xIn cluster series are grouped and shown in panels (a) – (e), respectively.

An additional investigation of stability is performed by calculating the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO); a large gap indicates chemical stability. The trends in

HOMO-LUMO gap for each of the cluster series are depicted in Figure 6.8. Also displayed are values of energy gain, which is an indicator of energetic stability. The energy gain upon adding indium atoms (1) or lead atoms (2) to a given species is defined as:

$$\Delta E_{\text{In}} = E(\text{Pb}_x\text{In}_{y-1}) + E(\text{In}) - E(\text{Pb}_x\text{In}_y)$$

$$\Delta E_{\text{Pb}} = E(\text{Pb}_{x-1}\text{In}_y) + E(\text{Pb}) - E(\text{Pb}_x\text{In}_y)$$

Here $E(\text{Pb}_x\text{In}_y)$, $E(\text{Pb}_x\text{In}_{y-1})$, and $E(\text{Pb}_{x-1}\text{In}_y)$ are the total ground state energies of the respective clusters, while $E(\text{In})$ and $E(\text{Pb})$ are the ground state energies of the indium and lead atoms, respectively. An indicator of stability is if a large gain in energy occurs when a cluster forms from a stoichiometry with one less atom.

For panels (a)-(d) the indium energy gain is plotted, and for panel (e) the lead energy gain is plotted. Similarly to the trends in ADE, there is some evidence of an even-odd alternation within a series, for example the indium energy gain in panel (b). These alternations have frequently been used to explain cluster stability within a series, where clusters with even numbers of electrons exhibit enhanced stability.^{43,44} However, there are a handful of observations within the present study that demanded further investigation, and the remainder of the discussion is devoted to them.

First, the two clusters identified as possessing aromatic character in a previous chapter are summarized.⁴⁵ Consulting Figure 6.7, panel (a) has a peak at PbIn_3^- , while panel (b) has a minimum at Pb_2In_2^- for the theoretical ADE value and a near minimum for the experimental ADE value, suggesting enhanced stability for both PbIn_3^- and the neutral Pb_2In_2 cluster. These clusters also exhibit significant calculated HOMO-LUMO gaps of 1.34 eV for PbIn_3^- and 1.45 eV for Pb_2In_2 . These gaps are fairly high noting that

an Al_{13}^- , previously identified as a highly stable species, has a HOMO-LUMO gap of 1.87 eV. To probe the origin of their stability, one can examine the molecular orbitals. The molecular orbitals were found to have two delocalized σ and one delocalized π orbitals, which is common in all-metal aromatic systems.^{15,17} These clusters are isoelectronic to the aromatic Al_3X ($\text{X} = \text{As}, \text{Sb}, \text{Bi}$) species of Chapter 4,^{19,20} an investigation that also revealed the closed-shell species Al_5X ($\text{X} = \text{As}, \text{Sb}, \text{Bi}$). The stability of these species was rationalized within the NFEG framework, where certain sizes possess magic numbers of valence electrons that lead to filled electronic shells. Thus, if the aromaticity found in the Al_3X species was preserved in the isoelectronic Pb_xIn_y^- species, we were curious if the Pb_xIn_y^- series possessed stabilized clusters similar to the Al_5X species. As indium and aluminum are part of the same group, the isoelectronic species of Al_5X would be In_5Pb^- , with Pb^- acting as the neutral X atom ($\text{X} = \text{As}, \text{Sb}, \text{Bi}$).

To find evidence of NFEG character in PbIn_5^- we first looked to pointers of enhanced stability and examined the trend in ADE within the PbIn_y^- series. Consulting Figure 6.7(a) it can be seen that there is a peak for this species, but it cannot be distinguished from the even-odd alternation discussed previously. Likewise, the trend in HOMO-LUMO gap or indium gain energy in panel (a) of Figure 6.8 does not provide concrete support. An additional requirement of a NFEG-stabilized cluster is a compact 3-D geometry. For the Al_5X clusters studied in Chapter 4, the species all possess similar compact structures. The calculations on the ground state structure for PbIn_5^- resulted in competing compact geometries corresponding to a triangular prism (the ground state) and a distorted triangular antiprism (an isomer with a relative energy 13 meV above the

ground state). The triangular antiprism is very similar to the structures seen in Al_5X clusters, while the ground state “tent-like” triangular prism is slightly less compact. To investigate which of these structures is produced in the experiment, one can compare the experimental values of ADE and VDE with the calculated values for each of the different isomers. The ADE comparison is inconclusive; the two structures are so nearly degenerate that the calculated ADE values would only change by 13 meV, much less than the experimental uncertainty of the ADE values. However, for the VDE measurements, the calculated values for the more compact structure are closer to the experimental values. While the more compact structure is in better agreement with the peak positions, we can not definitively say that only this structure is produced, as both states may be sampled at once. Indeed, the experimental spectrum of PbIn_5^- may possess features of both.

Although we conclude that both structures for PbIn_5^- are likely present, they do have a common origin of stability. To explore this, the one electron energy levels and isosurfaces of the molecular orbitals were calculated, as shown in Figure 6.9. The orbitals are consistent with a 20-electron NFEG closed shell, which ideally consists of a $1s^2$, $1p^6$, $1d^{10}$, and $2s^2$ configuration. The $1d^{10}$ and $2s^2$ levels are mixed, but this is often the case with the heteroatomic clusters previously studied.^{19,20} The compact structure has orbital symmetries and ordering very similar to the Al_5X clusters of Chapter 4, while the “tent-like” structure has orbitals that are ordered differently. Thus, the correct electron count, geometry, and orbital picture of the compact structure are more suitable to a classification within the NFEG framework. It should be noted that the peaks at $y = 3$ and $y = 5$ in the ADE values, seen in Figure 6.7(a), could be interpreted as a stable PbIn_4 species.

However, the non-compact geometry (Figure 6.2) and electron count of 16 do not fit the NFEG model. Additionally, upon inspection of the neutral series in Figure 6.8(a), a peak is observed in the HOMO-LUMO gap, but a decrease in the gain energy for the PbIn_4 structure is seen. Unlike PbIn_5^- , this species does not meet the criteria of stability within the NFEG model.

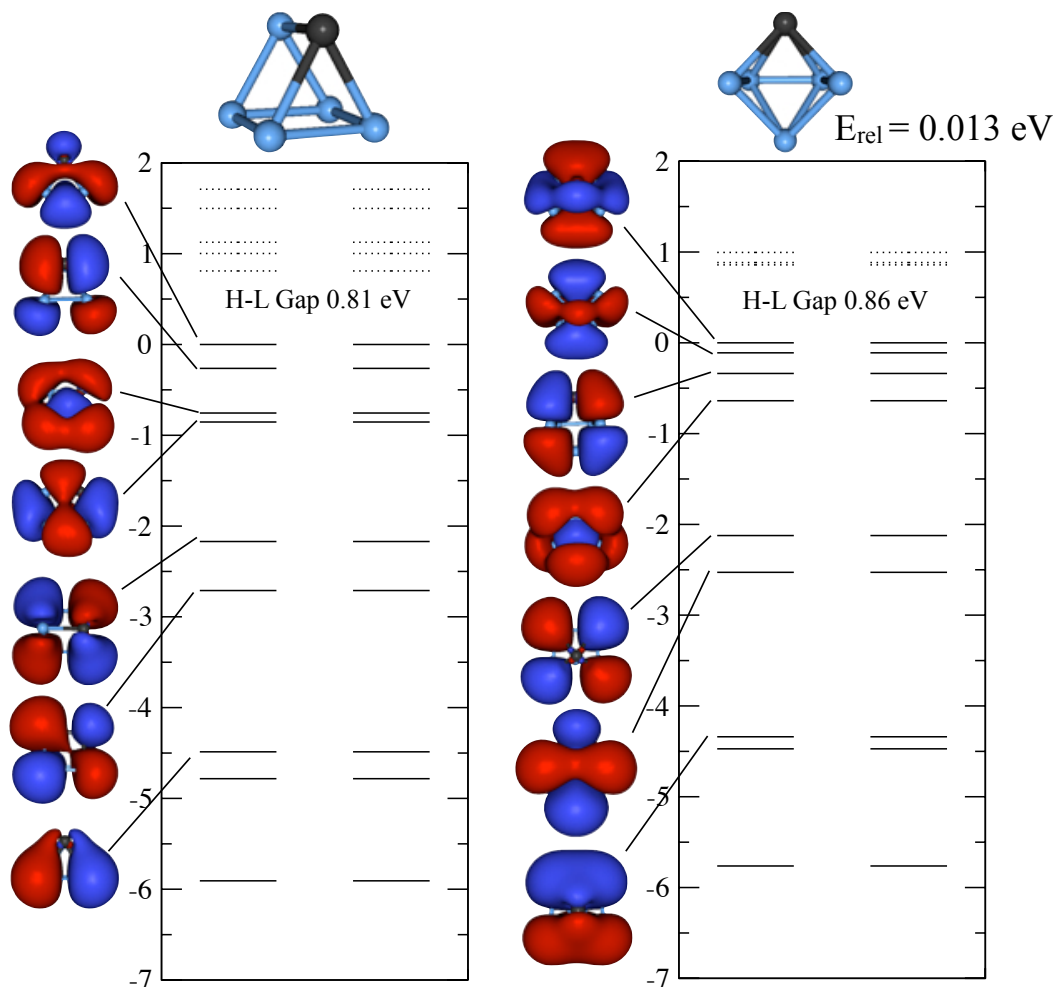


Figure 6.9 One electron energy levels and isosurfaces (isovalue = 0.01 au) of the molecular orbitals for the isomers of PbIn_5^- . The continuous lines are occupied states, the dashed lines represent unoccupied levels. The HOMO-LUMO gap is labeled as H-L gap and the relative energy of the low lying isomer is given in eV.

Additionally, Pb_2In_4 has been identified as a NFEG species. This cluster piqued our interest as it displayed evidence of enhanced stability across all the criteria measured. First, consulting the plotted experimental and theoretical values of ADE in Figure 6.7(b), there is a definitive step at Pb_2In_4^- , indicating a lower detachment energy than the neighboring species. While this initially signifies stability of the neutral counterpart, Pb_2In_4 , there is always the chance that the stability/instability of other clusters within the series affects the interpretation. For example, an enhanced stability of Pb_2In_3^- would affect the interpretation of the “low” Pb_2In_4 value. However, Figure 6.8(b), which displays additional criteria for stability, reveals no evidence of enhanced stability for either the neutral or anionic Pb_2In_3 cluster. Rather, the plots reinforce the enhanced stability of Pb_2In_4 , as it has the highest HOMO-LUMO gap and indium gain energy in the Pb_2In_y series, except for the aromatic Pb_2In_2 cluster. In fact, when considering all of the anionic and neutral clusters in the Pb_2In_y series, Pb_2In_4 has the second highest HOMO-LUMO gap (0.96 eV). These pointers of stability, along with the ADE, establish the enhanced stability of Pb_2In_4 .

One might expect this behavior, and subsequently classify Pb_2In_4 as a NFEG species, merely because it has the same valence count as PbIn_5^- (20-electron jellium closed shell). Indeed, it was already shown in Chapter 5 that a Pb atom may substitute for In^- and still retain a similar electronic structure.⁴⁵ However, examining the ground state geometry of Pb_2In_4 in Figure 6.3, the structure is not reminiscent of the compact octahedral-like geometry found for the isomer of PbIn_5^- and other heteroatomic, six-atom, NFEG species.^{19,20} This is likely due the increasing lead concentration, as pure lead clusters are known to transition towards close packed geometries near this size range.⁴²

To further investigate Pb_2In_4 , the electron energy levels and isosurfaces of the molecular orbitals were calculated, as shown in Figure 6.10. The ordering of the orbitals is characteristic of previous heteroatomic NFEG species identified, where the 20-electron configuration of $1s^2$, $1p^6$, $1d^{10}$, and $2s^2$ is maintained with a mixing of the $1d^{10}$ and $2s^2$ states.^{19,20} Thus, the electronic structure supports the classification of Pb_2In_4 as a NFEG species.. It is interesting to note that the findings in Chapter 5 for Pb_2In_2 demonstrated a similar behavior, in which an aromatic electronic structure was retained despite an unexpected ground state geometry.⁴⁵ These results reinforce the notion that lead-indium clusters have competing driving forces of stability, in which both electronic shell closings characteristic of indium clusters and the geometric packing effects typically seen in lead clusters are responsible for governing the behavior of the mixed clusters.

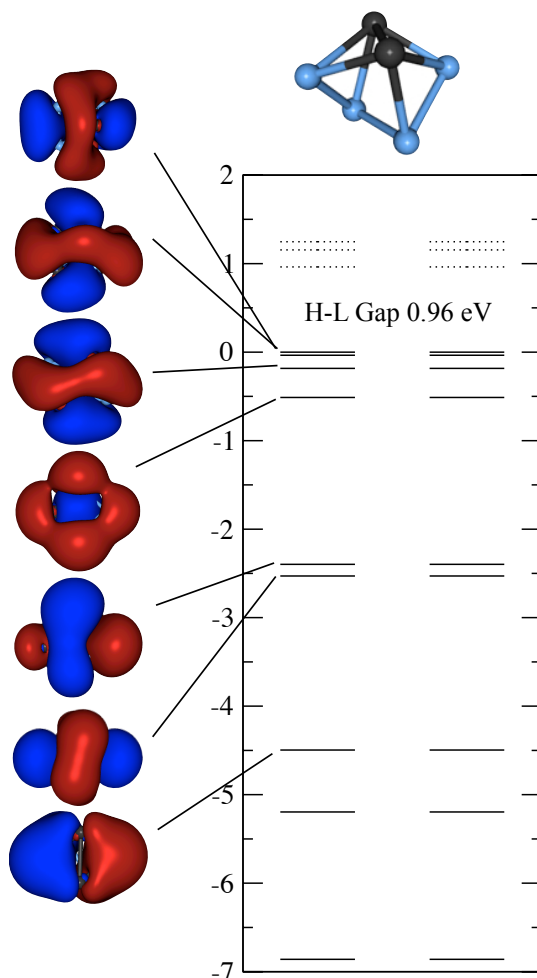


Figure 6.10 One electron energy levels and isosurfaces (isovalue = 0.01 au) of the molecular orbitals for Pb_2In_4 . The continuous lines are occupied states, the dashed lines represent unoccupied levels. The HOMO-LUMO gap is labeled as H-L gap.

Lastly, an interesting behavior was noted in the Pb_3In_2 cluster. The anion possesses the lowest ADE in the Pb_3In_y^- series, signifying a stability of the corresponding neutral cluster. Additionally, the HOMO-LUMO gap of this cluster is the highest (1.23 eV) of any neutral or anionic species in the Pb_3In_y series. The geometry of Pb_3In_2 , depicted in Figure 6.4, is found to be planar, quite different from the Pb_3In_2^- three-dimensional geometry. In fact, all of the five-atom, lead-rich clusters studied here are

three-dimensional with the exception of Pb_3In_2 . Instead, this cluster has a geometry similar to the indium-rich, five-atom clusters calculated. This observation led to the calculation of molecular orbitals for Pb_3In_2 , as shown in Figure 6.11. The HOMO-3 is immediately evident as a π -delocalized orbital, a characteristic of aromatic clusters. Although our past studies of all-metal aromaticity have been limited to four-atom species,^{19-22,45} the Pb_3In_2 cluster satisfies many of the criteria of all-metal aromatics; it possesses a two-dimensional geometry, satisfies Hückel's rule, and has a large HOMO-LUMO gap of 1.23 eV. Further, many of the all-metal aromatics previously studied have both σ and π aromaticity. In the present study, one can see signatures of the σ -like aromaticity in the HOMO, HOMO-1, and HOMO-2. For example, σ -like aromaticity is seen in the HOMO and HOMO-1 from a combination of radially and tangentially oriented p-orbitals, while in the HOMO-2 it is a result of only the radially oriented p-orbitals. Thus, the Pb_3In_2 cluster displays the aromatic characteristics typically found in all-metal aromatics.

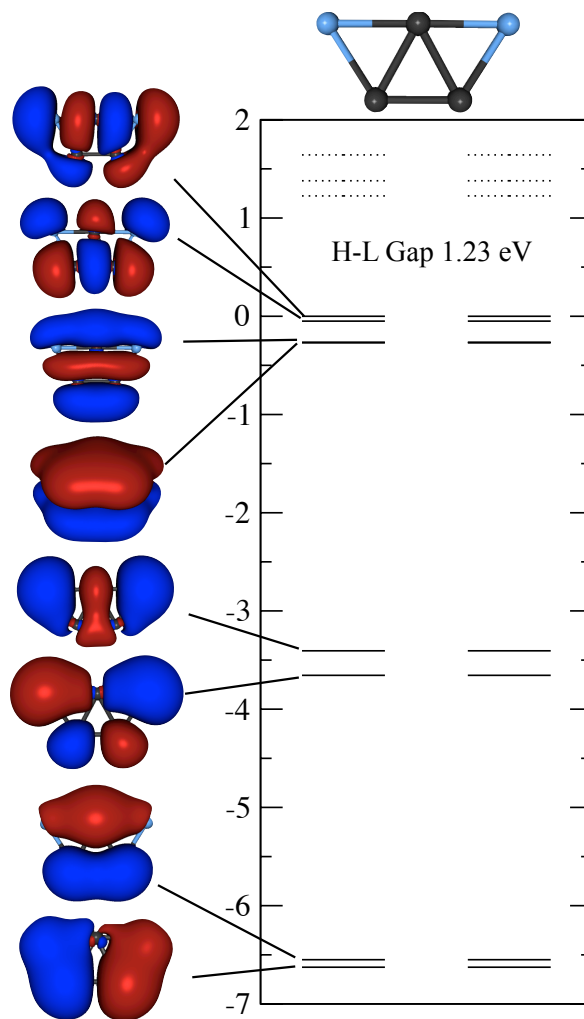


Figure 6.11 One electron energy levels and isosurfaces (isovalue = 0.01 au) of the molecular orbitals for Pb_3In_2 . The continuous lines are occupied states, the dashed lines represent unoccupied levels. The HOMO-LUMO gap is labeled as H-L gap.

6.4 Conclusions

In this chapter photoelectron spectroscopy and first-principles electronic structure calculations were used to examine a variety of anionic and neutral Pb_xIn_y clusters. The ground state geometries, adiabatic detachment energies, vertical detachment energies, HOMO-LUMO gaps, and indium or lead removal energies are provided. Among the

Pb_xIn_y series, numerous clusters were found to exhibit enhanced stability, which provide suitable candidates for cluster assembled materials. Specifically, electronic closed-shell species were found (PbIn₅⁻ and Pb₂In₄), all-metal aromatics were identified (PbIn₃⁻, Pb₂In₂, and Pb₃In₂ with significant HOMO-LUMO gaps of 1.34, 1.45, and 1.23 eV, respectively), and many examples of close-packed clusters were shown. Finally, it is found that both the geometric effects commonly found in pure lead clusters, as well as electronic effects seen in pure indium clusters, govern the stability of mixed lead-indium clusters.

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Chapter 7

Electronic Structure Similarities in Pb_xSb_y^- and Sn_xBi_y^- Clusters

7.1 Introduction

While nanoscale clusters have served as valuable models for investigating various fundamental molecular interactions,¹ with the growth of nanoscience they are gaining increased interest as systems with practical applications.² This is particularly evident in clusters of the p-block elements, where the discovery of C_{60} has led to a new field of materials in fullerenes and carbon nanotubes, while III-V semiconductor materials have led to numerous modern electronics. Recently, our lab has started to explore the new area of cluster assembled materials, which allows the fine tuning of material properties based on the characteristics of the constituent cluster building blocks.³ In this realm, heteroatomic p-block clusters have proven to be especially interesting, as their heteroatomic nature provides a facile route to manipulating the charge state and size of the cluster building blocks, while changing the electronic structure in a predictable way.⁴ This has led to many new clusters being identified as suitable candidates for assembly into nanomaterials.⁵ One intriguing class of clusters, termed “superatoms”, have been shown to mimic the properties of elements.⁶ These superatoms offer many possibilities in designing new materials based on traditional rules of chemistry. Recently, in some systems it has been found that the electronic structure between atoms and molecules⁷ may be comparable, providing new superatoms on the basis of parallel electronic structures. Separately, similarities have been observed in reactivity studies, where neutral systems

are shown to possess the same structural features and radical oxygen centers as their charged counterparts.⁸ These findings have encouraged us to search for similar electronic structures in other species. The p-block clusters provide a good opportunity to explore this phenomenon because of their facile synthesis in experiment^{4,5} and their promise for success in the realm of cluster assembled materials.³ Additionally, the current applications of materials built from p-block elements already carry importance and span a broad range of disciplines.⁹

In this chapter, photoelectron spectroscopy experiments and theoretical calculations are used to explore electronic structure similarities between Pb_xSb_y^- and Sn_xBi_y^- clusters. These IV-V elements are next to each other on the periodic table, and so equivalent stoichiometries lead to equivalent valence electron counts. However, the results indicate that some of these clusters also have similar electronic structures and analogous ground state geometries. An additional focus of the present chapter is to determine what factors govern when similarities persist and when they break down. The experimental and theoretical results indicate that the electronic structure is quite sensitive to changing the total number of valence electrons. Further, theoretical calculations depict how changing the ground state geometry can affect the electronic structures. Although these findings may be expected, it was also found that the electronic structures of unrelated clusters can be similar, provided the valence electron count and geometric structures are analogous. In fact, there is a substantial body of work in the literature involving photoionization or electron induced dissociation experiments on heteroatomic clusters,^{10,11} where comparable mass spectra distributions point to similar geometric structures and growth patterns (even for Pb_xSb_y and Sn_xBi_y clusters).¹² Perhaps the best

example is the work by Recknagel et al.,¹¹ which concludes that the stability of the post-transition elements is governed by the number, not the origin, of the electrons. However, all of these studies would be strengthened by a detailed probing of the electronic structure, which photoelectron spectroscopy (PES) can provide. While PES experiments on electronic structure similarities are well known among homoatomic clusters with similar electron counts¹³ or heteroatomic clusters that share a common element (such as Al_xP_y , Ga_xP_y , and In_xP_y species),¹⁴ the work presented here is the first to provide a detailed investigation into the similarities of the electronic structures in heteroatomic clusters that possess *no shared elements*.

7.2 Experimental and Computational Details

The experimental apparatus employed in this study has been described in Chapter 3 and in the literature.¹⁸ In brief, Pb_xSb_y^- or Sn_xBi_y^- clusters were created by ablating a 50:50 molar ratio Pb-Sb or Sn-Bi rod, respectively, within a laser vaporization source. The focused, second harmonic of a Nd:YAG laser (532 nm) was used for the ablation, while helium was used as a carrier gas. Both charged and neutral clusters were created, but for the present study only the anions were extracted and subsequently analyzed in a Wiley-McLaren time-of-flight mass spectrometer.¹⁹ Mass selected clusters of interest were subjected to a pulsed 308 nm excimer laser, and photodetached electrons were analyzed within a magnetic bottle photoelectron spectrometer.²⁰ The kinetic energy distribution of the electrons was calibrated using the known²¹ electron spectrum of Bi^- . The structural properties of anionic bimetallic trimers and tetramers as well as the theoretical photoelectron spectra were determined using density functional theory (DFT)

with the hybrid PBE0 functional²² as implemented in Turbomole 6.0.²³ Relatively large triple zeta valence atomic basis sets containing polarization and diffuse functions (def2-TZVP)²⁴ were employed in combination with the Stuttgart-Dresden relativistic effective core potentials.²⁵ The first peak in the photoelectron spectrum, corresponding to the vertical detachment energy (VDE), has been calculated as the energy difference between the neutral and anionic ground electronic states in the anionic geometry, as obtained from time-dependent DFT. The higher peaks have been obtained by adding the transition energies between the ground and excited electronic states of the neutral species to the VDE of the first peak. Since in this approach the transition dipole moments for ionization are not available, the intensities have been assigned to a constant value of 1 and subsequently convoluted with a Lorentzian function where the full width of the peak at half maximum is 0.2 eV.

7.3 Results and Discussion

Figure 7.1 depicts the experimental and theoretical results on the trimer systems PbSb_2^- and SnBi_2^- . Both clusters have 9 valence p-electrons and our calculations indicate that they have analogous C_{2v} ground state geometries, with no low-lying isomers (within 0.9 eV). Thus, these clusters can be considered isoelectronic.¹⁵ Consideration of the experimental results in Figure 7.1 (panel I) reveals that both PbSb_2^- and SnBi_2^- have a comparable “fingerprint” of their electronic structure. These similarities are also apparent when comparing the theoretical photoelectron spectra of PbSb_2^- and SnBi_2^- . The features in the theoretical spectra corresponding to singlet and triplet states of the neutral are labeled blue and red, respectively. Additionally, each peak, or group of peaks, is labeled

corresponding to the molecular orbital, or group of molecular orbitals, from which photodetachment occurs. The occupation, energy, and isosurface plots of the associated molecular orbitals for PbSb_2^- and SnBi_2^- are depicted in panel II.

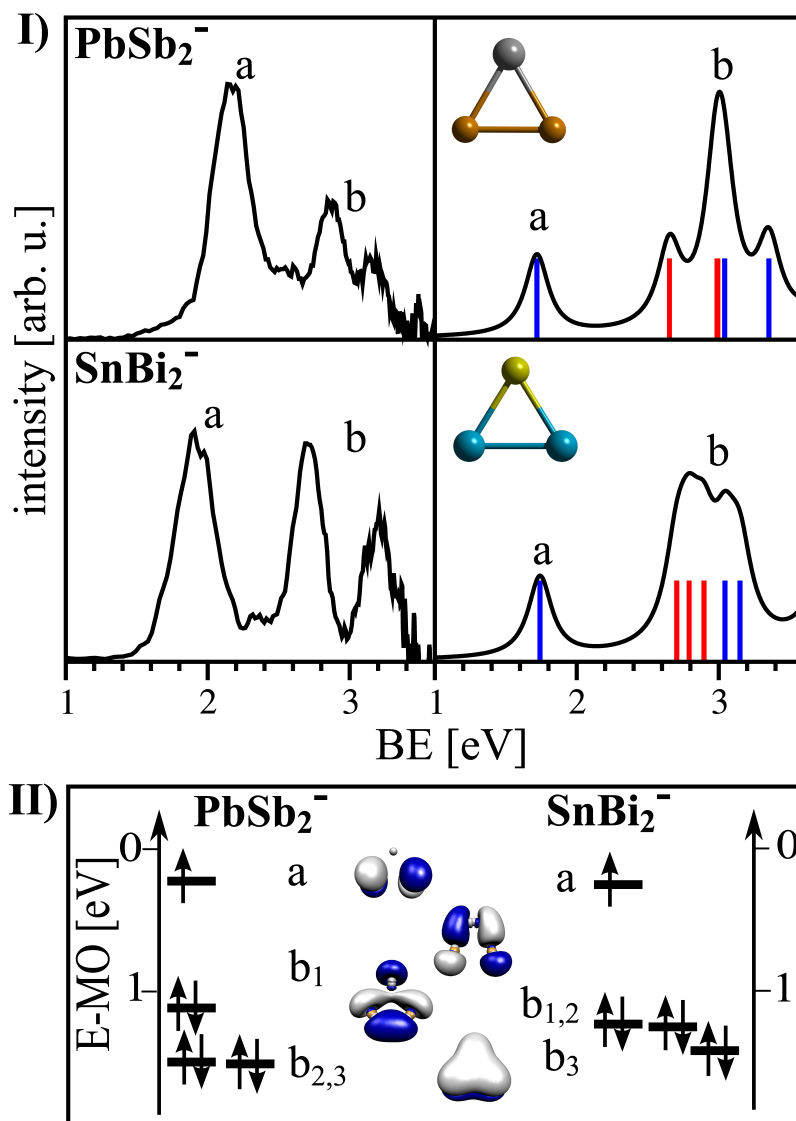


Figure 7.1 I) Experimental (left) and theoretical (right) photoelectron spectra on a binding energy (BE) scale for PbSb_2^- and SnBi_2^- . Peaks in the theoretical spectra corresponding to singlet and triplet states of the neutral are labeled blue and red, respectively. II) Calculated energies of the molecular orbitals (E-MO) in eV and isosurface plots. In order to simplify the picture, the energies of alpha and beta spin orbitals were averaged.

For each peak in the experimental and theoretical spectra, we assign a vertical detachment energy value, which can be found in Table 7.1. Additionally, the onset of the first feature in an experimental spectrum is extrapolated to baseline for the assignment of an adiabatic detachment energy (ADE). This method is traditionally used to provide a valid estimation of the true ADE when the vibrational progression is not well-resolved.^{14,16}

Although the similarities in electronic structures of PbSb_2^- and SnBi_2^- are visible in the experimental spectra, it is through theory that we can establish the degree of equivalence. There is a close correspondence between the two theoretical spectra in Figure 7.1, where the features labeled (a) are a nearly identical match, and features (b) possess equivalent groups of transitions with slightly different peak splittings. These splittings are a consequence of the small energetic differences in the molecular orbital energies, as shown in panel II. Thus, this results in slightly different energies for the transitions visualized in the photoelectron spectra. In addition to the parallels in photoelectron spectra, the molecular orbitals of PbSb_2^- and SnBi_2^- are equivalent. These similarities are a function of the clusters possessing identical valence electron counts and analogous geometric structures. Additionally, it is important to note that the heteroatomic clusters studied here are comprised of similar elements (i.e. heavy group IV-V elements) so that the character of valence electrons in these clusters are the same. The reluctance to hybridize s- and p-electrons in these heavy elements¹⁷ leads to the highest occupied molecular orbitals (HOMOs) being predominantly built from atomic p-orbitals.

Table 7.1 Experimental adiabatic detachment energy (ADE) and experimental and theoretical vertical detachment energy (VDE) assignments for the 9 p-electron trimer species, in units of eV.

ADE Exp.		VDE Exp.		VDE Theo.	
PbSb ₂ ⁻	SnBi ₂ ⁻	PbSb ₂ ⁻	SnBi ₂ ⁻	PbSb ₂ ⁻	SnBi ₂ ⁻
1.78	1.58	2.16	1.90	1.72	1.74
		2.85	2.71	2.65	2.79
		3.15	3.21	3.01	3.04
				3.35	

To examine if the similarities in electronic structure are confined to the trimer species, we have also undertaken investigations into the tetramer Pb₂Sb₂⁻ and Sn₂Bi₂⁻ systems. A detailed comparison of the experimental and theoretical spectra is provided in panel I of Figure 7.2. The experimental spectra exhibit a strong likeness, each with four detachment features and similar VDE values (see Table 7.2). These four features are also present in the theoretical spectra, while the fifth feature shown in the theoretical spectrum is not seen in experiment since it is near the limit of our photodetachment energy. As was observed in the trimers, the small energy differences in the molecular orbital energies shown in panel II lead to slight variations in peak splittings of the theoretical photoelectron spectra. However, qualitatively these spectra are quite similar, and the molecular orbitals that are responsible for photodetachment are equivalent for Pb₂Sb₂⁻ and Sn₂Bi₂⁻, and are depicted in panel II. The similar orbitals and electronic structures are again a function of identical valence counts (11 p-electrons), analogous geometries, and similar elemental compositions.

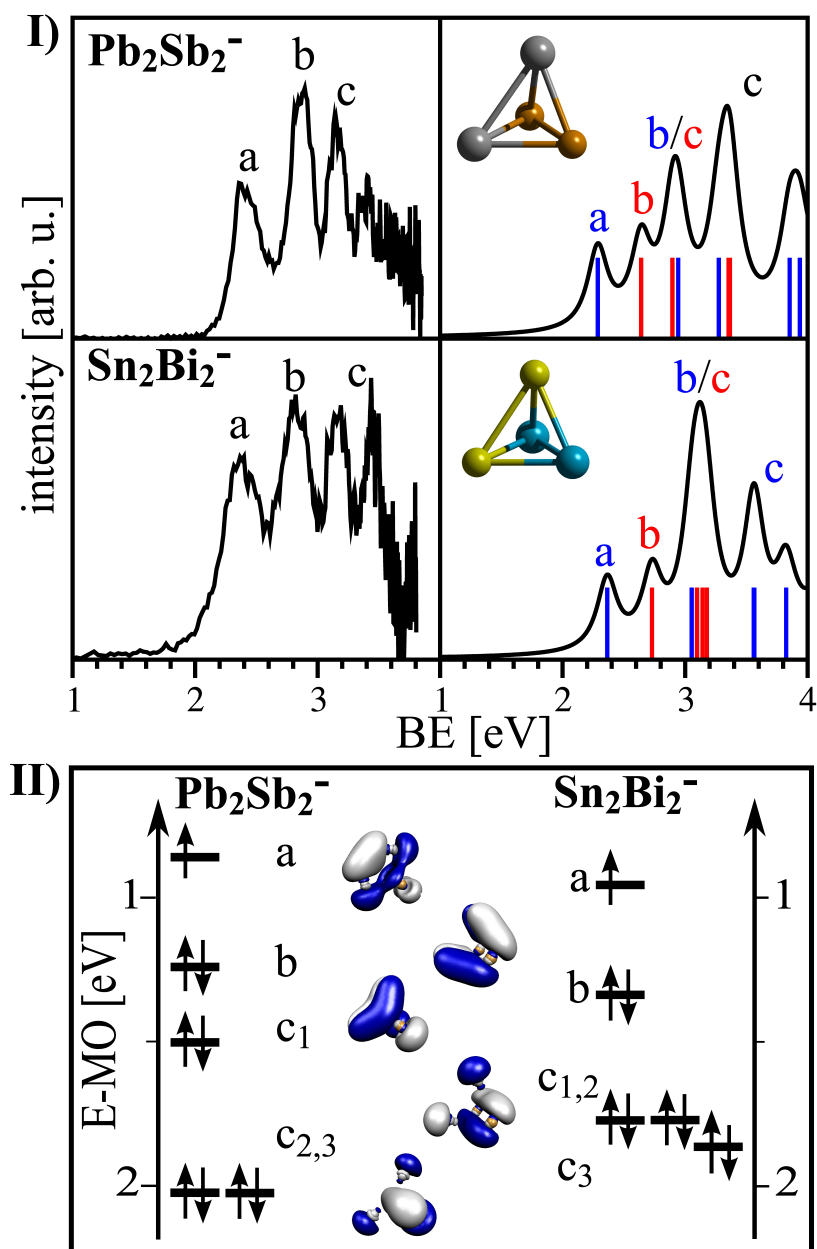


Figure 7.2 I) Experimental (left) and theoretical (right) photoelectron spectra on a binding energy (BE) scale for Pb_2Sb_2^- and Sn_2Bi_2^- . Peaks in the theoretical spectra corresponding to singlet and triplet states of the neutral are labeled blue and red, respectively. II) Calculated energies of the molecular orbitals (E-MO) in eV and isosurface plots. In order to simplify the picture, the energies of alpha and beta spin orbitals were averaged.

Table 7.2 Experimental adiabatic detachment energy (ADE) and experimental and theoretical vertical detachment energy (VDE) assignments for the 10, 11, and 12 p-electron tetramer species, in units of eV.

10 p-electron tetramers					
ADE Exp.		VDE Exp.		VDE Theo.	
Pb ₃ Sb ⁻	Sn ₃ Bi ⁻	Pb ₃ Sb ⁻	Sn ₃ Bi ⁻	Pb ₃ Sb ⁻	Sn ₃ Bi ⁻
2.24	2.48	2.57	2.81	2.38	2.62
		2.92	3.02		
		3.40	3.31	3.20	3.27
		3.62	3.63	3.65	3.85
11 p-electron tetramers					
ADE Exp.		VDE Exp.		VDE Theo.	
Pb ₂ Sb ₂ ⁻	Sn ₂ Bi ₂ ⁻	Pb ₂ Sb ₂ ⁻	Sn ₂ Bi ₂ ⁻	Pb ₂ Sb ₂ ⁻	Sn ₂ Bi ₂ ⁻
2.12	1.99	2.36	2.38	2.29	2.36
		2.89	2.82	2.64	2.73
		3.14	3.19	2.91	3.12
		3.41	3.44	3.34	3.56
				3.90	3.82
12 p-electron tetramers					
ADE Exp.		VDE Exp.		VDE Theo.	
PbSb ₃ ⁻	SnBi ₃ ⁻	PbSb ₃ ⁻	SnBi ₃ ⁻	PbSb ₃ ⁻	SnBi ₃ ⁻
2.38	2.25	2.75	2.60	2.68	2.61
		3.13	2.87	3.79	3.29
			3.50		3.67

Next, in order to investigate the effects of the valence count on electronic structure, we have obtained experimental and theoretical spectra for the 10 and 12 p-electron tetramer clusters. This is accomplished by substituting one of the tetramer atoms

with an element containing one additional, or one less, valence electron. For example, by replacing one of the antimony atoms in Pb_2Sb_2^- with a lead atom, the valence p-electron count is changed from 11 to 10. The resulting experimental and theoretical spectra for the 10 p-electron systems of Pb_3Sb^- and Sn_3Bi^- are shown in Figure 7.3, while the 12 p-electron systems of PbSb_3^- and SnBi_3^- can be found in Figure 7.4. The calculated ground state structures for the 10 p-electron systems in Figure 7.3 are analogous and the species exhibit similar spectra; equivalent conclusions can be drawn from the 12 p-electron systems. Note that the shoulder feature for each experimental spectrum in Figure 7.3 is attributed to hot band excitation, which is characteristic for clusters under comparable experimental conditions.¹⁶ The molecular orbitals of Pb_3Sb^- and Sn_3Bi^- are equivalent in shape, and are featured in panel II. This observation, along with the similar spectra, represents another example of the analogous behaviors described above for the trimers and 11 p-electron tetramers. However, when one compares the spectra of the 10 p-electron tetramers to that of the 11 p-electron tetramers in Figure 7.2, there is no correspondence. This is a direct result of the open versus closed shell nature of these species, and depicts the delicate nature of the electronic structure and its strict dependence on valence electron count. The 12 p-electron systems in Figure 7.4 are also quite different than the 11 p-electron systems. An interesting point is that there is some degree of similarity between the spectra of the 12 p-electron and 10 p-electron systems, as these are both closed shell species, with only slightly different geometries. With the additional occupied molecular orbital in the 12 p-electron system, the HOMO-4 of the 10 p-electron system becomes the HOMO-5 of the 12 p-electron system and is pushed down in energy and out of the range of the experiment. As a result, similarities persist in the

electronic structures of the 10 and 12 p-electron systems, although if the spectra were carried out to five eV, an additional peak should be observed for the 12 p-electron system that is not found in the 10 p-electron system.

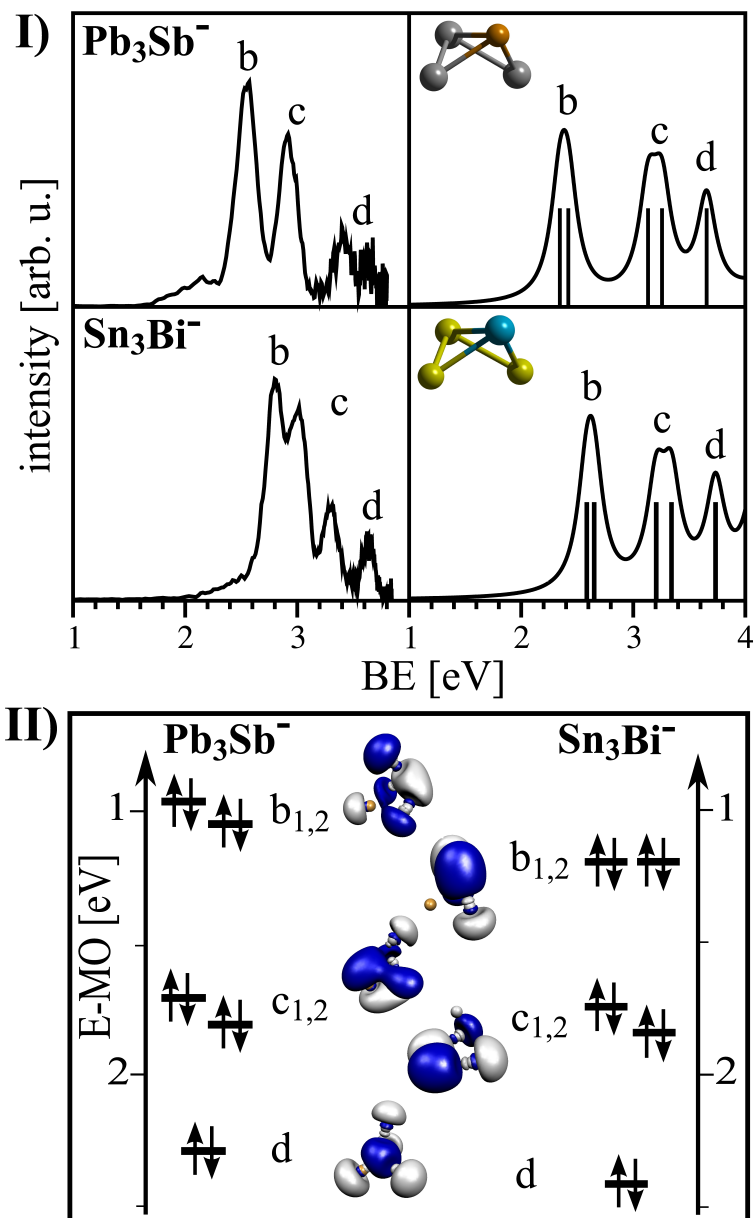


Figure 7.3 I) Experimental (left) and theoretical (right) photoelectron spectra on a binding energy (BE) scale for the 10 p-electron tetramers Pb_3Sb^- and Sn_3Bi^- . II) Calculated energies of molecular orbitals (E-MO) in eV and isosurface plots.

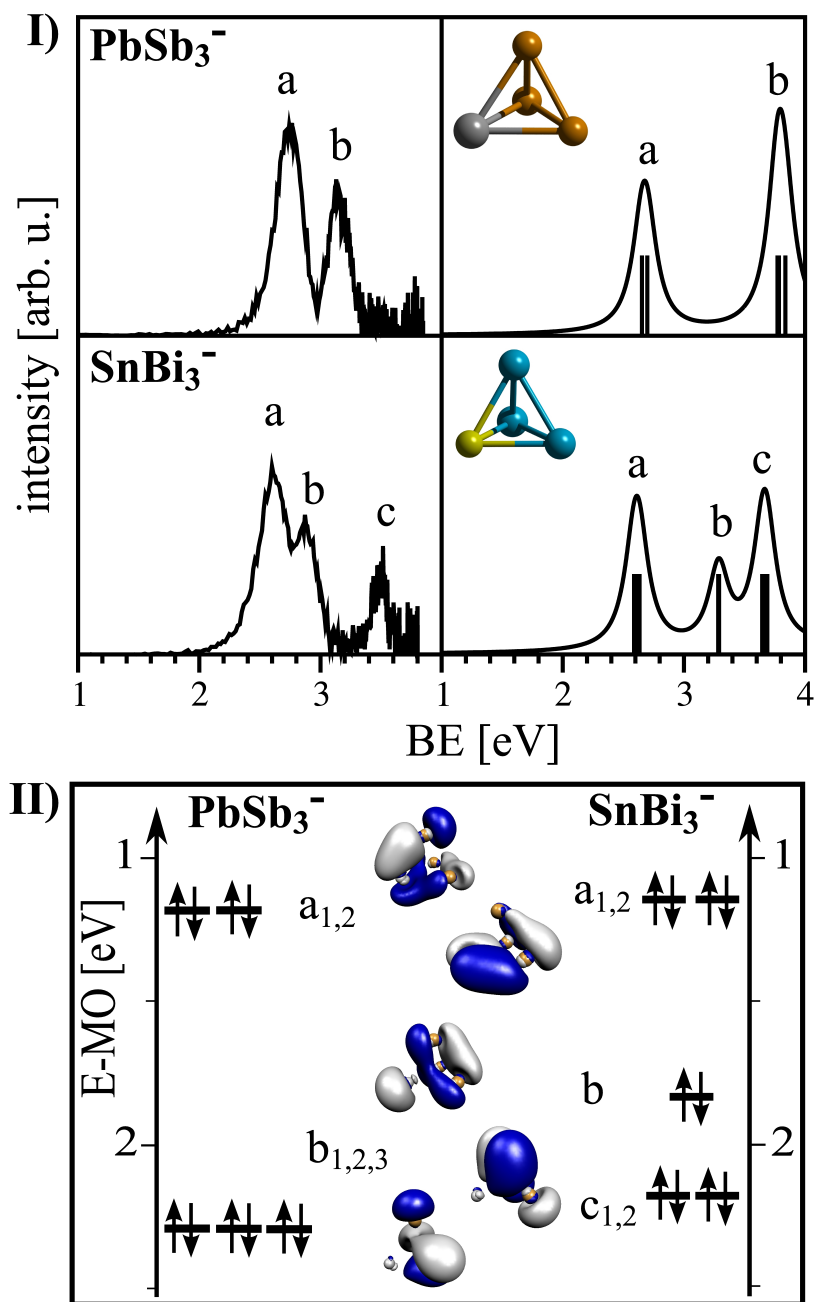


Figure 7.4 I) Experimental (left) and theoretical (right) photoelectron spectra on a binding energy (BE) scale for the 12 p-electron tetramers PbSb_3^- and SnBi_3^- . II) Calculated energies of molecular orbitals (E-MO) in eV and isosurface plots.

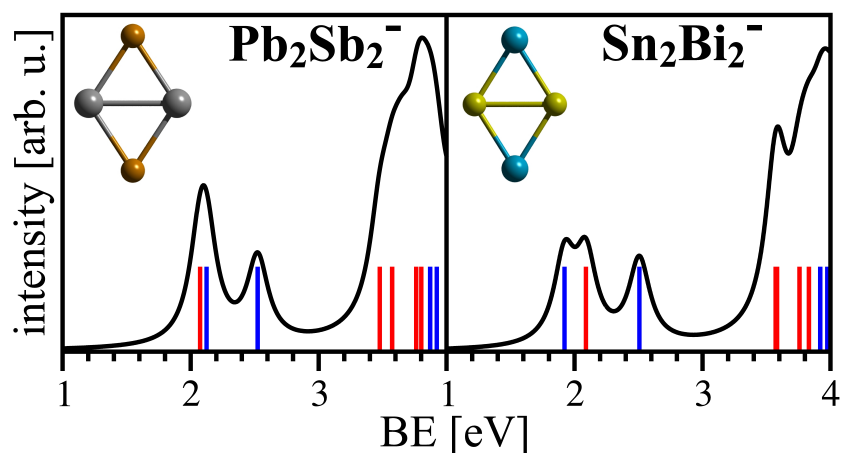


Figure 7.5 Theoretical photoelectron spectra on a binding energy (BE) scale for the 11 p-electron tetramers Pb_2Sb_2^- and Sn_2Bi_2^- in planar geometries. Peaks in the theoretical spectra corresponding to singlet and triplet states of the neutral are labeled blue and red, respectively.

Having investigated the effect of electron count on the electronic structure, we now turn to a study on the role of geometry. Figure 7.5 depicts the theoretical spectra of the Pb_2Sb_2^- and Sn_2Bi_2^- clusters in a planar geometry. These two-dimensional structures are 0.92 and 0.75 eV, respectively, higher in energy than the three-dimensional structures in Figure 7.2. At these energies, the two-dimensional structures are clearly not produced in our experiment, but from theory they do allow for an examination of geometric effects on electronic structure. Because the two planar clusters still share identical valence counts and analogous geometries, the two calculated spectra in Figure 7.5 are quite similar. While there is a slight shift in the first singlet state, the remaining transitions possess nearly a one-to-one correspondence in energy. However, when comparing the spectra of the two-dimensional clusters in Figure 7.5 with the three-dimensional Pb_2Sb_2^- and Sn_2Bi_2^- clusters in Figure 7.2, there is no correspondence, even though the valence count is identical. For example, the region between 2.6 eV and 3.4 eV lacks any

transitions in the case of the planar geometries (Figure 7.5), while the same region in the spectra of the tetrahedral geometries (Figure 7.2) possesses at least five transitions. These observations illustrate the crucial nature of geometry on a cluster's spectroscopic patterns, and thus its electronic structure.

7.4 Conclusions

The work presented here shows both experimental and theoretical evidence that similarities in heteroatomic clusters can extend further than geometric structures or cluster growth patterns¹⁰⁻¹², into similarities in the actual electronic structure. This leads to exciting possibilities. The principal of electronic structure mimics being built up to larger systems presents new avenues for creating cluster assembled materials by either i) replacing traditional building blocks with less expensive mimics or ii) providing minor alterations of electronic structure to existing building blocks, leading to materials with slightly different, and therefore tunable, properties. It is hoped that these materials can be directly applied in energetic, electronic, and optical applications.

7.5 References

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Chapter 8

Photoelectron Imaging of Small Aluminum Clusters: Quantifying *s-p* Hybridization

8.1 Introduction

Small metal clusters have been shown to possess properties that are unique from their bulk and atomic counterparts.¹⁻³ This has led to a new field of cluster physics aimed at understanding how the properties arise, and how they change with cluster size. One of the great successes of the field has been the jellium model,⁴ which has been used to account for the electronic shell structure of various metal clusters.⁵⁻⁷ This model assumes that the arrangement of atoms and core electrons within the cluster can be replaced by a spherical distribution of positive charge, in which highly delocalized valence electrons exist. The result is an electronic structure that consists of a series of electronic shells, where closed shells lead to an enhanced stability. This simple model works wonderfully in describing monovalent metal clusters (e.g. Na and Cu),^{8,9} and has even been applied to multivalent clusters as well.¹⁰⁻¹² However, for many multivalent clusters there have been strong deviations from the jellium model observed, though this is partly due to the fact that multiply charged ionic cores cannot be approximated in the same way as singly charged cores.¹³

Perhaps the most widely discussed multivalent system is aluminum clusters, on which experimental and computational studies have debated the applicability of the jellium model.¹⁴⁻¹⁷ While bulk aluminum is well-described as a free-electron metal, atomic aluminum has a $3s^2 3p^1$ electron configuration where the *s*- and *p*-orbitals are

separated by a substantial energy gap,¹⁸ and thus the atom is essentially monovalent. Clusters can bridge this gap between atomic and bulk aluminum. As the cluster grows in size the molecular orbitals, built from the atomic *s*- and *p*-orbitals, should eventually evolve into bands, and at some distinct cluster size merge. It is assumed that the jellium model may only be applied to sizes above this *s-p* hybridization.^{15,16} A central question to cluster science is then: at what size does this occur? Put another way, when do the aluminum atoms within the cluster transition from a monovalent state (one valence *p*-electron) to a trivalent state with hybridized orbitals? Experimentally, attempts have been made to answer this question through anion photoelectron spectroscopy with conflicting results.¹⁹⁻²¹ The *s-p* hybridization is assumed to take place when photodetachment peaks from the *s* band and *p* band begin to overlap, which is estimated to occur at Al₉,¹⁹ somewhere above Al₈,²⁰ or Al₆.²¹ Meanwhile, at least three theoretical studies have argued that substantial *s-p* mixing is present at Al₄,²²⁻²⁴ while others conclude the crucial size is Al₇,²⁵ and still others suggest Al₈.²⁶

An experimental technique that is suited to answer the question of *s-p* hybridization in aluminum clusters is photoelectron imaging. In this technique, the angular distribution of photodetached electrons provides information about the molecular orbital from which photodetachment occurred. The photoelectron angular distribution for a one-photon process is given by:

$$1 + \beta \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \quad 8.1$$

where β is the anisotropy parameter that fully describes the distribution. Emission from an s-orbital yields a β value of +2, while emission from a p-orbital (or higher angular momentum state) results in two partial waves that can interfere to yield any β value between -1 and +2. Thus, a photoelectron that yields a β value other than +2 must be from a non-s-orbital. In this manner, the angular momentum character of the parent molecular orbital can be qualitatively probed.

In this chapter, the photoelectron imaging technique is used to probe the electronic structure of small aluminum cluster anions. The binding energy information obtained is not new, and closely reproduces existing measurements in the literature.¹⁹⁻²¹ However, this study is the first to investigate the photoelectron angular distributions of aluminum clusters. The experiments reveal β values that can be used for qualitative arguments about the angular momentum states of the parent molecular orbitals, therefore providing a measurement of s- or p-character. Additionally, high-level calculations are performed and a calibration method is invented that allows for a *quantitative* comparison between the experimentally measured β values and the calculated atomic orbital contributions to the molecular orbitals.

8.2 Experimental and Computational Details

The experiments were conducted on the instrument that is described in Chapter 3 and in the literature.^{27,28} The aluminum clusters were created by laser ablation of an aluminum rod in the presence of a helium carrier gas at stagnation pressures of 50-60 psi. The anions created were extracted and analyzed by a time-of-flight mass spectrometer.²⁹ Anions of interest were intersected by the third harmonic of a Nd:YAG laser (355 nm)

within a velocity map imaging apparatus, and photodetached electrons were collected and imaged on a phosphor screen. The images were captured by a CCD camera and averaged over approximately 20,000 laser shots. The original three-dimensional distributions were reconstructed from these raw images using the BASEX software.³⁰ Energy calibrations were performed using the known spectrum of the bismuth anion.³¹

Geometry optimizations were performed within the Gaussian 03 program,³² employing a functional and basis set based on the results of an exhaustive study by Truhlar et al.³³ They identified the PBE0 hybrid density functional³⁴ and the 6-311+G(3d2f) basis set³⁵ as the most reliable combination for calculations on small aluminum-based molecules. In our calculations, computational limits restricted our choice to a PBE0/6-311+G(3d1f) combination, which only differs from the method suggested by Truhlar et al. by one *f* function. Starting structures and multiplicities for the aluminum clusters were based on recent findings in the literature³⁶⁻³⁸ and subsequently the geometries were reoptimized. A frequency analysis was conducted to check the reliability of the ground state structures. Electronic state energies were also calculated at the same level as the geometry optimizations. Molecular orbitals are plotted with an isosurface value of 0.02. Atomic orbital angular momentum coefficients of the orbitals were obtained via a population analysis, as described by Peppernick et al.³⁹

8.3 Results and Discussion

While the anisotropy parameter in Equation 8.1 is easily predicted for detachment from an s-orbital as discussed in the introduction, it is much more difficult to predict for orbitals with higher angular momentum quantum numbers. Originally shown by Bethe,⁴⁰

and subsequently extended to many-electron systems by Cooper and Zare,⁴¹ the anisotropy parameter can be predicted for photodetachment from any angular momentum state. Doing so allows for a comparison with experimental results to both rationalize experimental observations and support calculated parameters of the bound electron (e.g. orbital angular momentum). The exact relationship is defined as:

$$\beta = \frac{l(l-1)R_{l-1}^2 + (l+1)(l+2)R_{l+1}^2 - 6l(l+1)R_{l-1}R_{l+1}\cos(\delta_{l+1} - \delta_{l-1})}{(2l+1)[lR_{l-1}^2 + (l+1)R_{l+1}^2]} \quad 8.2$$

where l is the angular momentum quantum number, $(R_{l\pm 1})$ are the relative cross sections of the partial waves, and $(\delta_{l+1} - \delta_{l-1})$ is the phase shift between these waves. Therefore, in order to predict an experimentally measured anisotropy parameter there are three distinct variables: angular momentum, partial wave cross section, and partial wave phase shift.

The first variable is the angular momentum quantum number of the orbital from which photodetachment occurs. It is important to note that in molecules, where there is no spherical symmetry, angular momentum is not a good quantum number. However, recent results indicate that the angular momentum character of the valence orbitals in metal clusters is well approximated by atomic angular momentum quantum numbers.^{39,42,43} Adopting the methodology of Peppernick et al.,³⁹ the angular momentum of a molecular orbital can be estimated using the atomic orbital angular momentum coefficients calculated by density functional theory. For example, for photodetachment from a molecular orbital that is 80% s-like and 20% p-like, the total anisotropy parameter, β_{Total} , may be partitioned and summed together as follows:

$$\beta_{Total} = 0.8(\beta_{l=0}) + 0.2(\beta_{l=1}) \quad 8.3$$

Since theoretically the anisotropy parameter from the $l = 0$ state is always +2, the problem is reduced to solving for the $\beta_{l=1}$ term. Unfortunately, to accomplish this, one must also be able to predict the relative cross sections of the partial waves and the phase shifts between those waves. Recently, detailed modeling of the phase shifts have shown that for electrons with kinetic energies above about one eV, the phase shift is almost always 0.⁴⁴ This leads the $\cos(\delta_{l+1} - \delta_{l-1})$ part of the last term in Equation 8.2 to be unity, and only one variable remains to be dealt with, namely the cross sections of the partial waves.

It is well established that the cross sections have an energetic dependence, and according to Wigner⁴⁵ the cross sections $R_{l\pm 1}$ are proportional to the energy E as follows:

$$R_{l\pm 1} \propto E^{l\pm 1 + \frac{1}{2}} \quad 8.4$$

Thus, at very low kinetic energies the lower detachment channel is favored. However, this is not a strict relationship that can be used for accurate calculations of the cross sections. Instead, it is proposed here that the relative cross sections of the partial waves may be determined based on an experimental calibration method, where a curve of relative cross section value versus electron kinetic energy is established from previous results. It is important to stress that the relative cross section values discussed in this methodology are not the results of rigorous quantum-mechanical calculations, but instead are assigned as fractions that sum to unity (i.e. $R_{l+1} + R_{l-1} = 1$).

The data points that make up the calibration correspond to a series of ions we have previously measured experimentally.⁴⁶ The electron kinetic energies of these ions were measured directly,⁴⁶ while the cross section values are determined from the measured anisotropy parameters as follows. Assuming an equation analogous to Equation 8.3 is obtained for each molecular orbital through calculations, and also assuming that only electrons whose kinetic energy is above one eV are used (i.e. the phase shift is 0), the anisotropy parameter in Equation 8.2 is only a function of the cross sections. By experimentally determining the anisotropy parameter,⁴⁶ one can solve for the cross sections necessary to reproduce this anisotropy parameter.

For example, a previous result⁴⁶ for BiIn^- yielded an experimental anisotropy parameter equal to 0.61 for an electron with a kinetic energy of 1.63 eV. The calculated molecular orbital has 99% p-character, so effectively the total anisotropy is equal to the $\beta_{l=1}$ term in Equation 8.3. By substituting 0.61 in for β and 1 for l in Equation 8.2, and assuming the phase shift is 0, R_{l+1} must be equal to 0.84 and R_{l-1} must be equal to 0.16 (i.e. $1 - 0.84$). Therefore, a point on the calibration plot is placed at (0.84, 1.63). Repeating this process for several photodetached electrons, whose kinetic energy is each above one eV, results in a calibration curve that may be used to determine the partial wave cross sections of any electron, given the kinetic energy can be accurately measured. It is expected that the curve would fail for electrons below one eV, as the phase shifts of the partial waves may begin to play a role. The calibration curve is shown in Figure 8.1, where a power regression was chosen as a best-fit line due to the known dependence expressed in Equation 8.4. Although some points are below the proposed cutoff of one

eV, they were included to increase the statistical reliability of the curve, and because the phase shifts should still be very close to zero at these energies.⁴⁴

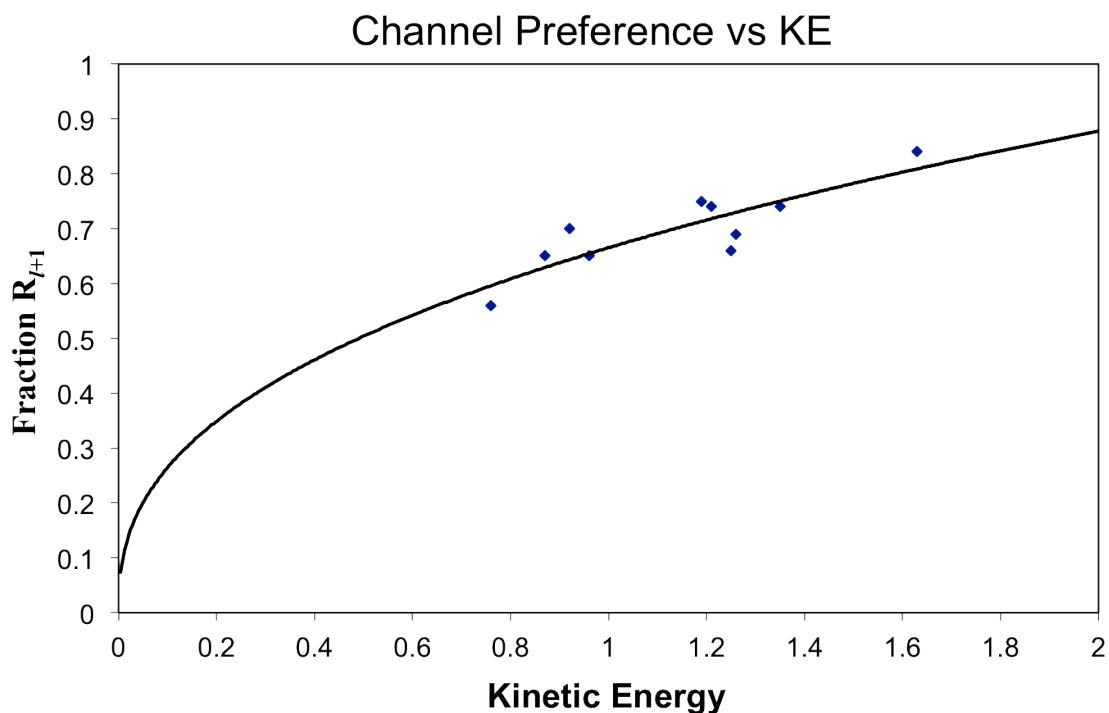


Figure 8.1 The calibration curve of the fraction of the photodetached electron described by the $l + 1$ partial wave as a function of electron kinetic energy.

This curve was created for the purpose of trying to predict the anisotropy parameters of aluminum clusters, and the remarkable agreement that will be shown below is an *ex post facto* justification of the preceding discussion. Figure 8.2 displays the reconstructed velocity map image and corresponding photoelectron spectrum measured for the Al_3^- cluster. Additionally, the results of the calculations are shown, displaying the ground state geometry and molecular orbitals (showing atomic orbital contributions) of the HOMO through the HOMO-3. The spacing of the energy levels are also shown. Due

to the energy of the laser used, electrons can only be photodetached from the levels marked A and B, which show up in the image and spectrum with the corresponding energy splitting. Because both the photoelectron spectrum and the calculated ground state geometry are nearly identical to previously published results,^{19-26, 36-38} they are not further discussed, and neither detachment energies nor bond lengths/angles are presented. (See Appendix of this dissertation for a detailed comparison of one species with the literature).

Feature B is a shoulder to feature A, and attempts to extract reproducible β values (i.e. deviations less than ± 0.2) were unsuccessful, so only feature A, which corresponds to the HOMO, is considered in the discussion of anisotropy parameters. The experimentally measured β value for feature A is 1.06, while the kinetic energy was determined to be about 1.7 eV. Employing the calibration curve, this kinetic energy corresponds to partial waves that are described as consisting of 83% $l + 1$ character. Using this value, and assuming the phase shift is 0, any p-character in the HOMO would yield a β value of 0.58 according to Equation 8.2. Consulting the results of our calculated molecular orbitals, the HOMO consists of 71% p-character and 28% s-character (the remaining one percent is a negligible contribution of higher angular momentum states). Thus, using an equation analogous to Equation 8.3, the total predicted β value would be:

$$\beta_{Total} = 0.28(\beta_{l=0}) + .71(\beta_{l=1}) = 0.28(2) + 0.71(0.58) = 0.97 \quad 8.5$$

which agrees nicely with the measure value of 1.06. This is the real power of the calibration method; that is, to confirm the atomic orbital percentage contributions of the calculated molecular orbitals. Similar to conventional photoelectron spectroscopy where

measured electron affinities or vertical detachment energies can be used to confirm proposed ground state structures, the calibration method here allows for a quantitative comparison that can confirm theoretically proposed atomic orbital angular momentum contributions. For Al_3^- , the good agreement reinforces the theoretically proposed angular momentum character of the HOMO of 28% s-character and 72% p-character, therefore yielding experimental proof of the degree to which the HOMO is *s-p* hybridized.

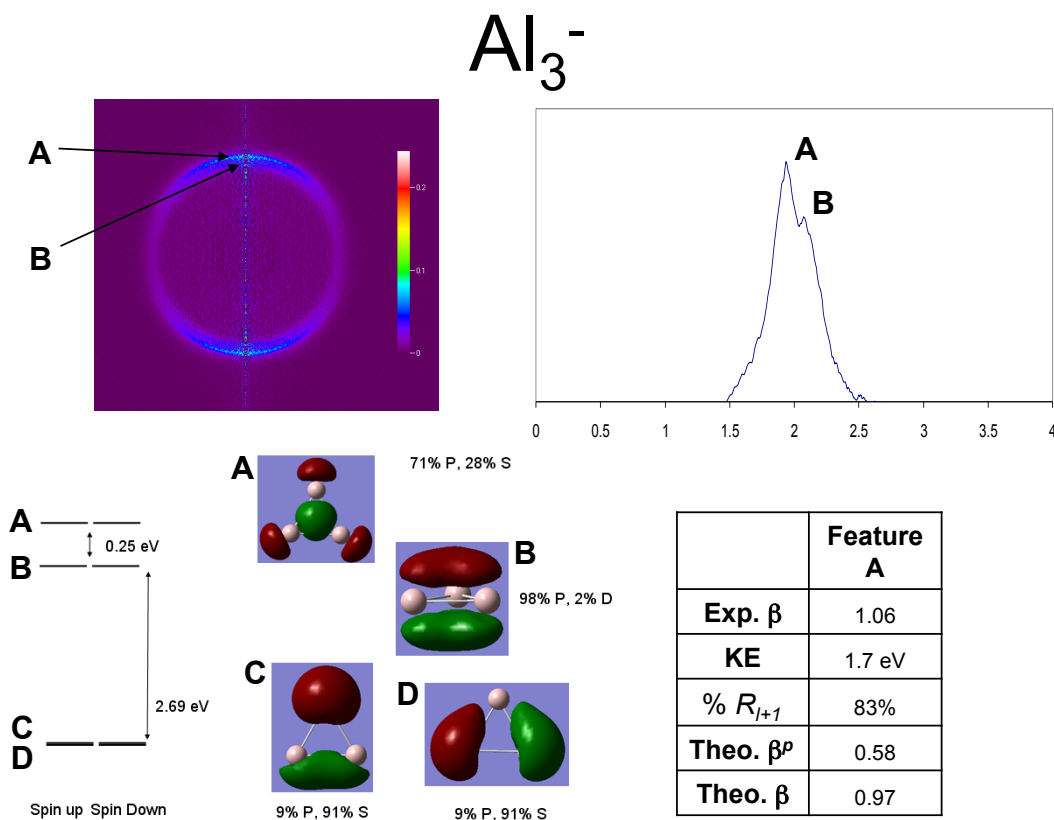


Figure 8.2 Reconstructed velocity map image (top left) and photoelectron spectrum on a binding energy scale with units of eV (top right) for Al_3^- . The corresponding calculated geometry, electronic energy levels, and molecular orbital isosurfaces with atomic orbital percentages (bottom left) as well as a table of experimental and theoretical anisotropy parameters (bottom right) are also provided. The resolved features A and B are labeled in the image and the spectrum, and correspond to photodetachment from the HOMO and HOMO-1. Only feature A yielded a reproducible anisotropy parameter.

An analogous discussion for each of the remaining aluminum clusters can be made, but is avoided in favor of briefly highlighting the important conclusions. Two features are fully resolved in the image and spectrum of Al_4^- , although a small shoulder to feature A is reproducible and likely corresponds to the molecular orbital labeled B. The fully resolved features (A and D) correspond to detachment from the HOMO and HOMO-3. As an odd-electron system, the spin up and spin down levels are split, but essentially the HOMO, HOMO-1, and HOMO-3 are doubly occupied, while the HOMO-2 is singly occupied. Attempts to extract reproducible β values for features B, C, and D were unsuccessful due to low signal or poor resolution, so only feature A, which corresponds to the HOMO, is considered. Employing the calibration for the 1.4 eV kinetic energy electron, any p-character in the HOMO would yield a β parameter of 0.32. Since the HOMO is found to be 99% p-like, this corresponds to the total β parameter. The value of 0.32 matches the experimental value of 0.31 closely, confirming the molecular orbital picture.

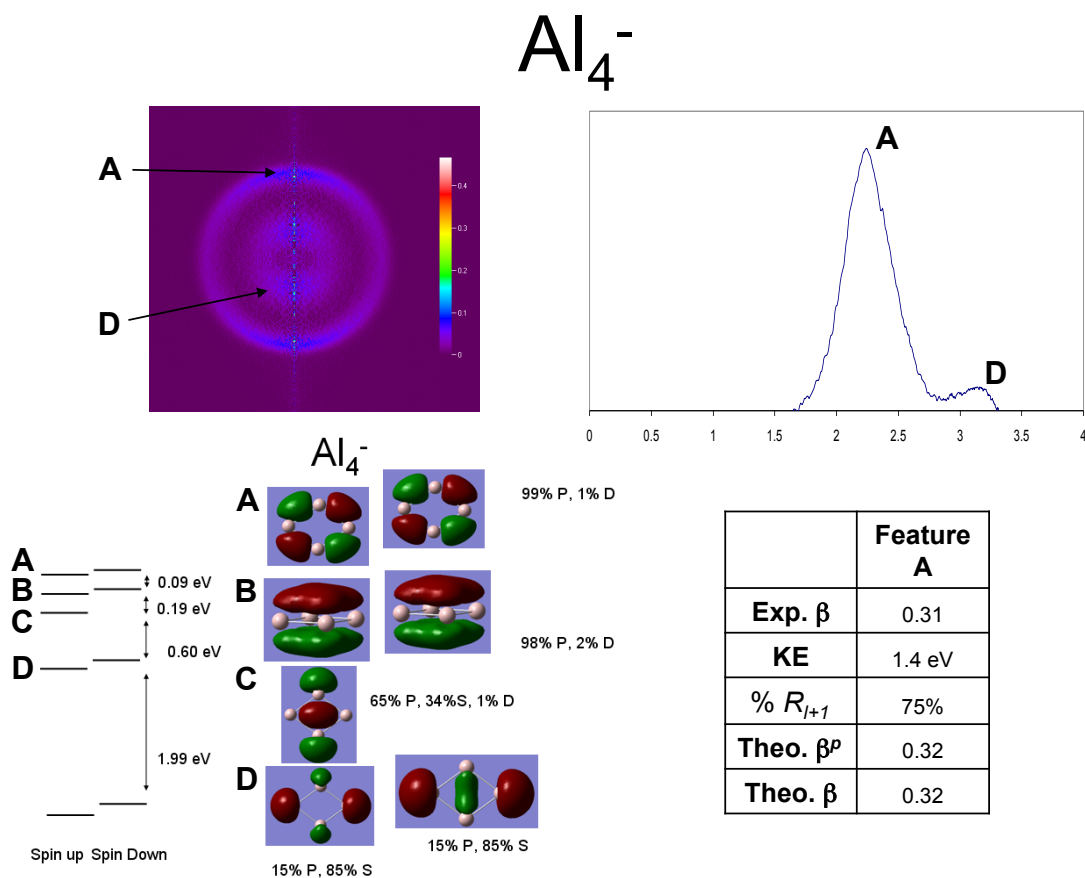


Figure 8.3 Reconstructed velocity map image (top left) and photoelectron spectrum on a binding energy scale with units of eV (top right) for Al_4^- . The corresponding calculated geometry, electronic energy levels, and molecular orbital isosurfaces with atomic orbital percentages (bottom left) as well as a table of experimental and theoretical anisotropy parameters (bottom right) are also provided. The resolved features A and D are labeled in the image and spectrum, and correspond to photodetachment from the HOMO and HOMO-3, respectively. Only feature A yielded a reproducible anisotropy parameter.

The molecular orbitals of Al_5^- and Al_6^- begin to become densely spaced, so in the interest of clarity the calculated energy levels and isosurface plots of the molecular orbitals are left out of Figure 8.4. Each image and spectrum has two well-resolved features and anisotropy parameters were obtained for both. For Al_5^- , the features labeled A and B correspond to detachment from the HOMO and HOMO-1, respectively. The

HOMO corresponds to a molecular orbital with 90% p-character and 9% s-character, while the HOMO-1 is 84% p-character and 16% s-character. With kinetic energies of 1.35 eV and 0.98 eV the β values are predicted to be 0.47 and 0.33 for the HOMO and HOMO-1, respectively. The corresponding experimentally determined values are 0.46 and 0.59, respectively. Thus, the *s-p* hybridization of the HOMO is confirmed. The experimental and predicted β values for the HOMO-1 differ slightly, but are in fair agreement, which suggests the calculated molecular orbitals are qualitatively correct. Perhaps the difference in β values is due to the fact that the kinetic energy of this feature (0.98 eV) may lead to a non-zero phase shift, which is admittedly unaccounted for.

For Al_6^- the calculations show that there are three groups of molecular orbitals within about 0.1 eV of the HOMO, which our experiment is unable to resolve. However, all of these calculated orbitals are almost identical in *s-p* character, with each having at least 97% p-character. Since electrons photodetached from any of these orbitals would have similar energies and similar angular momentum values, there should also be similar β values. Feature A contains all of these orbitals, and the experimental β value on average within this peak is 0.12. Using the calibration, the predicted β value for any of the close-lying molecular orbitals is about -0.07. This is in qualitative agreement, lending credence to the calculated orbital compositions. The discrepancy could be due to the kinetic energy of this feature (0.89 eV), which may lead to phase shift effects. Feature B corresponds to detachment from the HOMO-3, which has 62% p-character and 36% s-character, and has a kinetic energy of just 0.47 eV. Attempting the calibration method for such a low kinetic energy fails, as is expected since the phase shift is likely no longer 0. The predicted β value is -0.01, which is far from the experimentally measured value of

0.69. This reinforces the importance of only applying the calibration to electrons of sufficient kinetic energy.

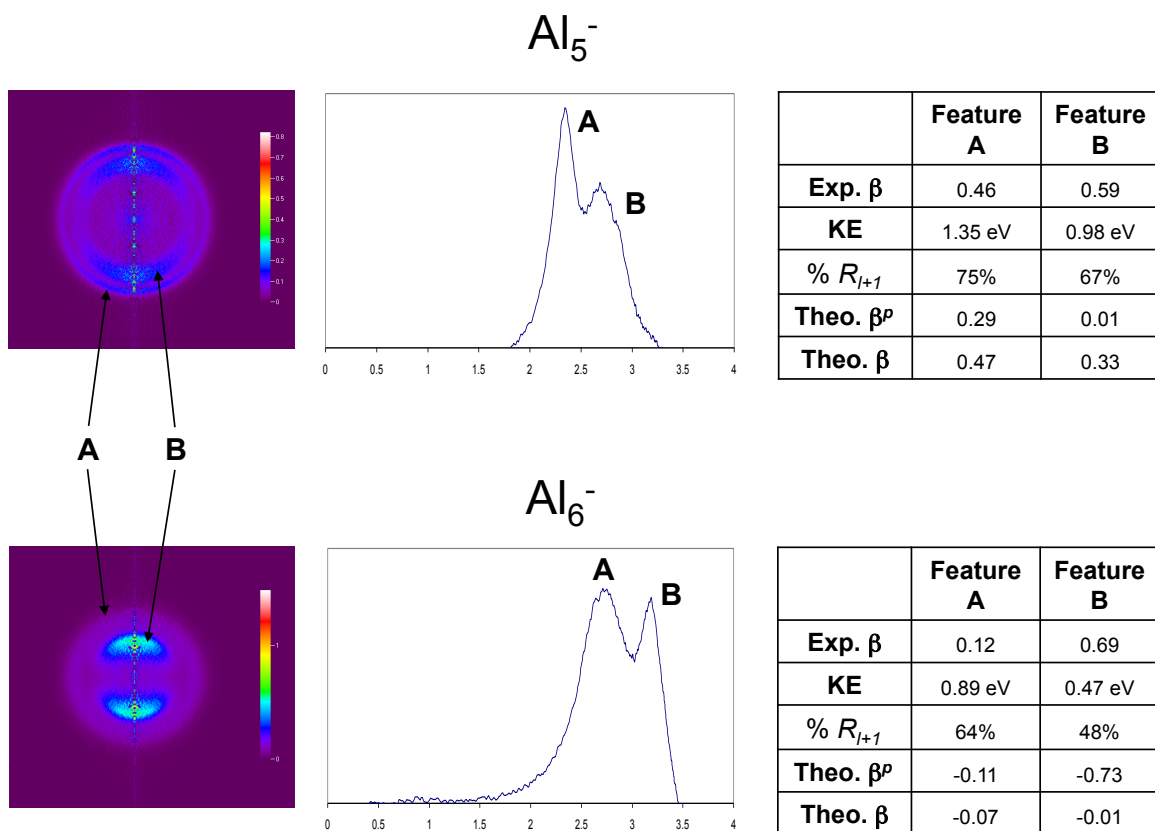


Figure 8.4 Reconstructed velocity map image (left), photoelectron spectrum on a binding energy scale with units of eV (middle), and table of experimental and theoretical anisotropy parameters (right) for Al_5^- and Al_6^- .

It has been shown that the calibration method can successfully predict β values for electrons with kinetic energies near or above one eV, which allows one to trust the calculated molecular orbital compositions. Thus, the now-affirmed values of angular momentum contributions can yield insight into the s - p hybridization of small aluminum

clusters. Examining the HOMOs across the series of clusters, the percentage of p-character goes from 71% in Al_3^- to essentially 100% in Al_4^- , then back down to 90% in Al_5^- , and finally back up again to 97% in Al_6^- . It is interesting to note that for the odd-electron systems, the HOMOs are essentially entirely p-like, or unhybridized, while for the even-electron systems the HOMOs have some degree of *s-p* hybridization. Moreover, this is also the case for any molecular orbitals near the HOMO, except for the HOMO-1 of Al_3^- . The fact that there is any *s-p* hybridization at all in these small sizes is interesting, considering previous experimental conclusions.¹⁹⁻²¹ Beyond that, the finding that the HOMO of Al_3^- , the smallest cluster studied here, has the largest degree of hybridization is quite surprising. To answer the question posed in the introduction of this chapter, *s-p* hybridization begins to occur in aluminum clusters as small as Al_3^- , not Al_9^- , Al_8^- , or Al_6^- as previously thought. However, the hybridization does not continue, and should really be evaluated on a size-by-size basis. Perhaps the better question to ask now is at what size does hybridization set in without disappearing again. This may yield a better evaluation of the size at which complete metallic-like nature is established and thus when one may use the jellium model (or other models that rely on free-electron character) to justify observations of stability. To answer this question would require extending the current study to a large range of aluminum cluster sizes, which is a current research effort in our lab.

8.4 Conclusions

In this chapter, velocity map imaging experiments and theoretical calculations were performed on small aluminum clusters. Experimental photoelectron spectra

reproduce results in the literature and new experimental data is obtained on the photoelectron angular distributions of aluminum clusters. The invention of a new calibration method is shown to work well for predicting anisotropy parameters based on calculated molecular orbital compositions. It is hoped that this proof of concept study may allow the method to be extended to other systems. In addition, the test case of small aluminum clusters studied here has yielded a quantitative measure of the s - p hybridization present in the highest occupied molecular orbitals. The smallest cluster investigated is found to have the largest degree of s - p mixing, in contrast to previous experimental results. It is also shown that the s - p hybridization does not suddenly appear at a critical cluster size, but instead evolves quite drastically as aluminum atoms are added one by one.

8.5 References

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Chapter 9

Summary of Findings and Current Research Directions

Through the use of mass spectrometry and photoelectron spectroscopy, the work within this dissertation has investigated the geometric and electronic structures of p-block clusters. There also has been a focus on testing theoretical models in an attempt to rationalize cluster behavior. Further, various clusters have been identified that possess unique stability based on experimentally and theoretically determined parameters, and these species have been proposed as suitable candidates for cluster assembled materials. A summary of all findings is given in this chapter, with a focus on observations that conflict with the current understanding of cluster physics and the new questions that have been raised.

In Chapter 4 studies on Al_nX clusters ($n = 1-6$, $X = As, Sb$) were discussed. Al_3As and Al_3Sb were found to be stable clusters with HOMO-LUMO gaps of 1.73 eV and 1.86 eV, respectively. These species were found to have cyclic structures, as well as molecular orbitals that exhibit π delocalization. Further criteria were met to justify these clusters as all-metal aromatics, and the elemental identity of the dopant atom was found to subtly affect the electronic structure and degree of aromaticity. Also within Chapter 4, Al_5As and Al_5Sb were found to have closed electronic shells, leading to an enhanced stability that was rationalized within the jellium model. Thus, it has been shown that the difference of just two aluminum atoms brings about substantial changes in both the geometry (two-dimensional to three-dimensional transition) and the electronic structure

(aromatic to closed jellium shells) of Al_nX clusters. This is an intriguing finding, as jellium closed shells and aromaticity have traditionally been treated throughout the cluster community as separate, mutually exclusive theoretical models. For instance, aromaticity has been confined to the light p-block elements such as carbon, while jellium closed shells best describe free-electron metals such as sodium or magnesium. We are beginning to show that some systems (i.e. doped aluminum clusters) possess examples of both types of clusters, which allow us to investigate where these models overlap. An important question for future studies is if a cluster can be identified that fits both models, and if the effects will be compounded to lead to a further enhancement of stability.

The studies discussed in Chapter 5 involve two particularly stable lead-indium clusters, namely PbIn_3^- and Pb_2In_2 . Both clusters were classified as all-metal aromatics that have large HOMO-LUMO gaps of 1.34 and 1.45 eV, respectively. The large difference in electronegativity between lead and indium does not destroy the aromaticity, as was previously hypothesized. In addition, the Pb_2In_2 cluster was found to have competing C_{2v} and D_{2h} geometries for its ground state; however, the electronic structures corresponding to these geometries were quite similar and in both geometries the aromaticity was preserved. These observations led to the conclusion that the atomic arrangement or identity of the atoms within the planar geometry is not crucial in heavy p-block clusters for maintaining aromaticity. This is in stark contrast to some of the conventional ideas of aromaticity in organic chemistry. We have shown that heavy-element clusters do not require equal bond lengths or a symmetric delocalization of electrons to reap the benefits of aromaticity, though they do need to be planar and satisfy Hückel's rule. To bridge the gap to assembled materials, efforts have been underway to

try to build sandwich architectures out of these all-metal aromatics, analogous to the inorganic structures built from a metal ion and two aromatic hydrocarbon rings. In fact, unpublished work within our lab has demonstrated that gas-phase clusters can be synthesized in which a nickel or iron atom sits atop a planar, aromatic, all-metal Al_4 ring, reminiscent of the half-sandwich complexes known in organometallic chemistry.

In Chapter 6, a comprehensive study of Pb_xIn_y clusters containing up to 5 lead atoms and up to 7 indium atoms was discussed. Through monitoring experimental and theoretical parameters, two families of stable clusters were identified that may find use in cluster assembled materials. PbIn_3^- , Pb_2In_2 , and Pb_3In_2 exhibited stability that was linked to aromatic character identified in their molecular orbitals. On the other hand, PbIn_5^- and Pb_2In_4 exhibited enhanced stability associated with filled electronic shells within a confined nearly free electron gas. Overall, the findings revealed that mixed lead-indium clusters have two distinct driving forces, electronic shell closings reminiscent of pure indium clusters and geometric packing effects observed in pure lead clusters. The presence of geometric packing effects for systems this small in size is surprising. Traditionally, it has been thought that clusters containing a few atoms are governed by purely electronic effects, since they possess a finite density of states; however, in lead-indium clusters this is not the case. Further, we have shown that one can control the geometric effects by altering the percentage of lead in mixed lead-indium clusters, delivering a tunability that could prove valuable in designing cluster building blocks.

The investigations presented in Chapter 7 involve the geometric and electronic structure of small Pb_xSb_y^- and Sn_xBi_y^- clusters investigated by photoelectron spectroscopy measurements and theoretical methods. PbSb_2^- and SnBi_2^- were found to possess

remarkably similar spectroscopic patterns, reflecting correlations in their electronic nature that are a result of their isovalence and common geometries. Analogous findings were presented for Pb_2Sb_2^- and Sn_2Bi_2^- . Further, altering the total valence count, and separately the geometry, were shown to substantially affect the spectroscopic patterns. It was also shown that the electronic structure correspondence is preserved regardless of the elemental composition, so long as the total p-valence count is the same and the geometries are alike. This represents an extension of the conventional concepts of periodicity, in which elements of similar valence configuration are grouped into columns. Instead, elements from different columns may be combined to yield similarities in chemistry, given the overall valence count is preserved. These findings support the prospect of replacing traditionally expensive materials with those comprised of entirely different elements. Thus, it will be important to continue this type of work, building up to larger and larger cluster sizes in an attempt to bridge the gap between the cluster and bulk size regimes.

In Chapter 8, the invention of a unique calibration method for determining the angular momentum of molecular orbitals was presented. As both a proof of concept and to resolve a debated topic in the literature, the model was applied to small aluminum clusters. Photoelectron imaging experiments and high-level calculations (shown in the Appendix) were conducted on Al_n^- clusters ($n = 3-6$). The calibration method was shown to successfully predict the anisotropy in the photodetached electron's angular distribution, yielding insights into the angular momentum state of the parent molecular orbital. The highest occupied molecular orbitals of the small aluminum clusters were found to contain varying degrees of *s-p* mixing, with Al_3^- containing the “most

hybridized” orbital and Al_4^- containing the “least hybridized” orbital. Thus, in aluminum clusters it was found that there is no critical size where hybridization sets in and remains. Similar to other cluster properties, *s-p* hybridization was shown to evolve as aluminum clusters grow in size, and it was concluded that the amount of free electron character within a cluster must be treated on a size-by-size basis. This work has helped clarify a thoroughly debated topic in the literature concerning *s-p* hybridization in aluminum clusters, and in principle this study can be extended to other elements as well.

Finally, although not formally covered within this dissertation, a current project within the lab warrants some brief comments. One main focus is extending the photoelectron imaging experiments into the time-resolved domain, which would allow for some understanding of cluster dynamics. By using a femtosecond laser instead of a nanosecond laser for photodetachment, the evolution of the photoelectron wave packet can be observed. This is done by using two separate femtosecond laser beams, namely a pump beam and a probe beam. While in conventional photoelectron spectroscopy the laser energy is sufficient to detach an electron, in pump-probe photoelectron spectroscopy the energy of the pump beam is not large enough to overcome the electron binding energy. Instead, the pump beam is used to reach an excited state, from which a delayed probe beam can complete the photodetachment. By delaying the arrival time of the probe beam, snapshots of the excited state dynamics can be followed. As the excited cluster redistributes the energy, the properties of the electrons are expected to change, which should be observable in both the kinetic energy and angular distribution of the photodetached electrons. Using time-resolved photoelectron imaging we can experimentally determine the various ways that a molecule can store and release energy

through the manipulation of electrons. Thus, pursuing a study of the relaxation of various orbitals using femtosecond velocity map imaging will open up a new avenue to exploring the deep world of chemical dynamics.

Appendix

Al_3^- Calculations and Comparison with Literature Values

The calculations discussed in Chapter 8 are supported by their close resemblance to findings in the literature. Here, the example of Al_3^- is investigated in detail as a proof. Table A.1 shows the bond lengths, bond angles, and vibrational frequencies calculated by Truhlar et al.¹ for the ground state of Al_3^- . The PBE0 hybrid density functional² and the 6-311+G(3d2f) basis set³ were used, as they were previously found to best reproduce experimental data.⁴ The symmetry of the cluster was identified as D_{3h} .

Table A.1 Results of Truhlar et al. on the ground state of Al_3^- . Bond lengths (in units of Angstroms), bond angles, and the vibrational frequencies (in units of cm^{-1}) are shown. Adapted from reference 1.

	Bond Lengths	Bond Angles	ν_1	ν_2	ν_3
Al_3^-	2.508	60°	373	246	246

The results of our calculations using the PBE0 hybrid density functional² and the 6-311+G(3d1f) basis set³ are shown in Figure A.1. The ground state of the cluster has D_{3h} symmetry, as found by Truhlar et al. The bond length we calculated of 2.509 is very close to the value obtained by Truhlar et al., and the bond angle of 60° is identical to their results. The vibrational frequencies we calculated are 374, 247, and 246 cm^{-1} , reproducing the values found by Truhlar et al. quite well. Small discrepancies in the bond lengths and vibrational frequencies are due to the fact that computational limits restricted

our calculations to employ a basis set with one less f function. Table A.2 provides the atomic coordinates obtained from the Gaussian 03 output file.⁵

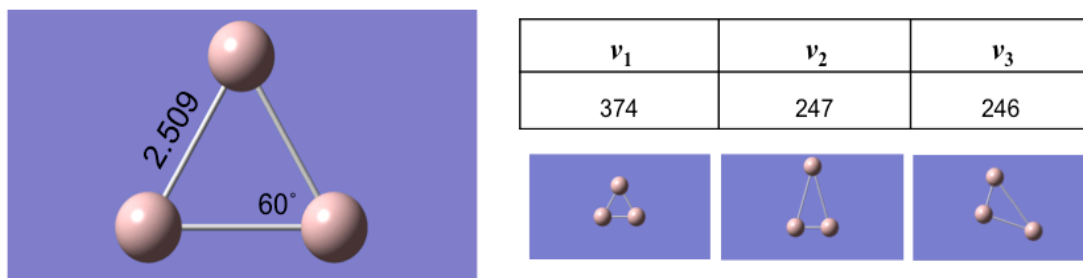


Figure A.1 Results of our calculations on the ground state of Al_3^- . Bond lengths (in units of Angstroms), bond angles, and the vibrational frequencies (in units of cm^{-1} with corresponding snapshots of the vibrations) are shown.

Table A.2 Cartesian coordinates (in units of Angstroms) for the three aluminum centers as obtained from the Gaussian 03 output file.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	13	1.254550	-0.724300	0.000000
2	13	0.000000	1.448620	0.000000
3	13	-1.254550	-0.724320	0.000000

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AWARDS

- Research Associateship, National Research Council, *2011-2012*.
- Apple Fellowship Award, The Pennsylvania State University, *2010-2011*.
- Graduate Student Travel Award, The Pennsylvania State University, *2010*.
- Geiger Fellowship Award, The Pennsylvania State University, *2009-2010*.
- Graduate Student Award, The Pennsylvania State University, *2007*.
- Graduate Student Fellowship, The Pennsylvania State University, *2006*.

PRESENTATIONS

- Characterization and Deposition of Clusters for Nanoscale Materials, The Cluster-Surface Interactions Workshop, *2010*.
- Photoelectron Spectroscopy of III-V Mixed Metal Systems, Gordon Conference on Photoions, Photoionization, and Photodetachment, *2010*.
- Study of III-V Semiconductor Clusters Using Anion Photoelectron Spectroscopy, APS Division of Atomic, Molecular, and Optical Physics, *2008*.
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