Theoretical discovery of shape reactivity relationships in aluminum nanoclusters

Katharine Witkin Corum

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THEORETICAL DISCOVERY OF SHAPE REACTIVITY RELATIONSHIPS IN ALUMINUM NANOCUSTERS

by

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

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Thesis Supervisor: Assistant Professor Sara E. Mason
CREDENTIAL OF APPROVAL

PH.D. THESIS

This is to certify that the Ph.D. thesis of

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To Charlotte and Petunia
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ABSTRACT

Keggin-based aluminum nanoclusters have been noted to be efficient sorbents for the adsorption of arsenic, copper, lead, and zinc from water. Obtaining a molecular-level understanding of the adsorption processes associated with these molecules is of fundamental importance and could pave the way for rational design strategies for water treatment. Furthermore, due to their size and the availability of experimental crystal structures, Al nanoclusters are computationally tractable at the atomistic modeling level.

The adsorption of contaminants onto metal-oxide surfaces with nanoscale Keggin-type structural topologies has been established, but identification of the reactive sites and the exact binding mechanism are lacking. In more common surface studies the two main factors that affect reactivity have been found to be charge and functional group identity. Since Al nanoclusters each have a distinct shape we introduce the effects of shape as a third factor. In all the work presented in this dissertation, it is extremely apparent that the shape of the aluminum particle plays the most important role in nanoparticle reactivity studies.

We first focus on the reactivity of three aluminum polycations: 

\[ [\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+} \quad (\text{Al}_{13}), \quad [\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+} \quad (\text{Al}_{30}), \quad \text{and} \]

\[ [\text{Al}_{32}\text{O}_8(\text{OH})_{60}(\text{H}_2\text{O})_{30}]^{20+} \quad (\text{Al}_{32}). \]

Using outer-sphere adsorption of sulfate and chloride as probe adsorbents, density functional theory (DFT) calculations determined that the reactivity can be represented as a function of particle topology, and not functional group identity or charge. Further exploring the shape-reactivity relationship of Al$_{30}$ we reveal that cations and anions have opposing trends and ion reactivity can be generalized. It is determined that all cations favor the adsorption sites on the caps of Al$_{30}$ and all anions
favor adsorption in the beltway (middle) region. This result is supported by the visualization of the electrostatic potential of Al₃₀ and three-dimensional induced charge density maps. The middle of the cluster is more positive than the caps, and this promotes anion adsorption in the beltway and cation adsorption on the caps.

Next we explore the reactivity of co-adsorption (outer-sphere anions and inner-sphere cations) onto Al₃₀ through a collaborative approach. Al₃₀ with two surface-bound Cu²⁺ cations (Cu₂Al₃₀-S) was experimentally crystallized in the presence of disulfonate anions; however, in the Cu₂Al₃₀-S structure the cations bind to the beltway region of the cluster. Using DFT we determined that the counter anions play a key (and governing) role in the crystallization of Cu₂Al₃₀-S. This result that outer-sphere adsorption dictates inner-sphere adsorption does not appear in surface calculations, it is unique to Keggin studies.

Seeing that all anions favor adsorption to the beltway region and all cations favor adsorption to the cap region we set out to determine if any reactivity patterns can be reversed. In order to do this inner-sphere As(V) and P(V) adsorption is modeled onto Al₃₀ through another collaborative approach. The experimental crystal structure of (TBP)₂[Al₂(μ₄-O₈)(Al₂₈(μ₂-OH)₅₆(H₂O)₂₆)]¹⁴⁺ (where TBP = t-butylphosphonate (CH₃)₃CPO₃) has been synthesized, and using DFT calculations we can alter the R-group of P(V) or the DFT As(V) analogue to see if the inner-sphere anion ever prefers to bind to the cap region instead of the beltway. We observe that no matter the intrinsic properties of the R-group the anion always prefers to bind to the beltway region, which once again shows that the shape-reactivity relationship plays a major role in Keggin based structure reactivity.
Since As(V) is such a harmful ion we extend our As(V) adsorption studies to aluminum surfaces. As(V) has been experimentally shown to bind to aluminum surfaces in a bidentate binuclear configuration. By modeling a variety of configurations we can confirm and explain that the bidentate binuclear configuration is most stable due to the least amount of strain on the As(V) atom. Aluminum surfaces are common DFT models to study but are computationally expensive, due to this fact some people choose to model small Al octahedral cluster models instead. Comparing the reactivity of both systems we see a significant difference in energy magnitudes and ranges and can conclude that small Al octahedral cluster models cannot take place of aluminum surfaces.

All in all, the work presented in this dissertation provides an important contribution in our understanding of Keggin based Al compounds. Keggin based compounds are very sparsely studied computationally and this work helps to fill a knowledge gap. Hopefully the insights obtained from this work can help guide future Keggin based studies.
PUBLIC ABSTRACT

Clean water is essential to everyday life and finding cheap and efficient ways to purify water is extremely valuable. Small aluminum clusters have been shown to be more efficient at adsorption based water remediation strategies than aluminum surfaces. These aluminum clusters have been shown to be sufficient in removing harmful and toxic ions from water such as arsenic, copper, and lead. However, there are just a handful of studies that point to which aluminum particles are most effective at removing these harmful ions but there is even less knowledge about how the adsorption process is occurring.

Typically with surface studies the two main factors that affect reactivity are charge and functional group identity but we introduce a third factor, shape, and discover that the shape of the aluminum particle plays the most important role in reactivity studies. Surfaces are flat and uniform throughout but large aluminum nanoclusters have different topography which leads to unique ion adsorption. We choose to mainly focus on the large aluminum nanocluster \( \text{Al}_{30} \) in order to make connections with experimental studies. We model the reactivity of a variety of cations and anions and consider co-adsorption affects. We conclude that the shape of \( \text{Al}_{30} \) determines if the ion will adsorb to the middle or the ends of the aluminum nanocluster. We also compare the reactivity of aluminum clusters to aluminum surfaces and conclude that they cannot be substituted for the other due to their inherent structural differences.
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1. INTRODUCTION

With clean water being a necessity to life there will always be a need for finding new ways for water purification that are inexpensive and more efficient than previous methods. Aluminum nanoparticles are known to exhibit high reactivity towards polyoxoanion species and are frequently used in coagulation-coprecipitation and adsorption based water remediation methods; however, there is not much knowledge about these aluminum nanoparticles regarding the identity, shape, and reactivity. Recently polyaluminum chloride (PACl) has been shown as a successful wastewater treatment substance to purify water by removing harmful ions and carcinogens such as arsenic, natural organic matter, and other toxic metals.\(^1\text{-}^3\) PACl is composed of a variety of smaller aluminum clusters such as \([\text{Al}_2(\text{OH})_2]^{4+}\), \([\text{Al}_3(\text{OH})_4]^{5+}\), \([\text{Al}_8(\text{OH})_{20}]^{4+}\), and \([\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}(\text{Al}_{13})\) that can bind together to make larger aluminum clusters such as \([\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}\) (Al\(_{30}\)).\(^4\text{-}^5\) PACl can also be prepared with an enrichment of Al\(_{30}\) and is known as PACl\(_{30}\).

Poorly-crystalline aluminum oxyhydroxide nanoparticles with Keggin-type structural features are considered some of the most effective materials for adsorption of toxic heavy metals, radionuclides, and oxyanions.\(^6\text{-}^7\) Several previous studies have demonstrated that the 1 nm \(\varepsilon\)-Al\(_{13}\) clusters perform well in clarifying water sources, but chemical agents containing the 2 nm Keggin-type Al\(_{30}\) species improves the removal efficiency of contaminants over a broader dosage and pH range, these two Keggin-type structures are shown in Figure 1.1.\(^1\text{-}^2\text{,}^8\)
Figure 1.1. Polyhedral representation of the Al\textsubscript{13}, Al\textsubscript{30}, and Al\textsubscript{32} nanoclusters.

Conceptually, the high reactivity of the Al nanoclusters has been rationalized through structure-reactivity relationships that were developed for extended mineral surfaces and based on Pauling’s rules of inorganic crystal stability.\textsuperscript{9} Mineral-water interfaces are well-defined models for geochemical systems and have been studied using a broad range of approaches. Experimentally, it is prohibitive to extract information about interfacial energetics. Theoretical studies using methods such as density functional theory (DFT) and \textit{ab initio} molecular dynamics (AIMD) can help to fill in the conceptual gap between macroscopic experiments and molecular understanding. However, information from atomistic modeling currently trails the information obtained from over a decade of experimental studies of hydrated single-crystal surfaces (see, for example, Catalano et al.,\textsuperscript{10} Fenter et al.,\textsuperscript{11} Fenter and Sturchio,\textsuperscript{12} Eng et al.,\textsuperscript{13} Catalano,\textsuperscript{14} Rosso et al.,\textsuperscript{15} Abadia et al.\textsuperscript{16}).

In the absence of more robust chemical modeling, bond-valence theory has been a popular and useful means of mapping experimental information about adsorption to structure-property relationships. The bond-valence model as formulated by Brown relates bond length to bond strength through the bond valence $s$ of atom type $i$.\textsuperscript{17}
model is parametrized such that the sum over $s_i$ for each atom should equal its formal valence, where $s_i=(R/R_0)^{-N}$, $R$ is the observed bond length while $R_0$ and $N$ are fitted bond valence parameters. When applied to mineral-water interfaces, bond-valence theory shows that the relative saturation of exposed oxygen functional groups varies based on the coordination of O to the metal cations of the surface, as well as the protonation state. The conceptual result born out of bond-valence theory is that functional group type is a key predictor of mineral surface reactivity.\textsuperscript{18} In a review by Brown and Calas\textsuperscript{19} they discuss the oxygen functional groups exposed as “long-term docking stations,” as the formation of (partially covalent) inner-sphere adsorption complexes. On the other hand, outer-sphere adsorption is considered to be relatively weak on mineral-water interfaces. In outer-sphere adsorption, the adsorbate maintains its waters of hydration, and interacts with the surface through long range electrostatic forces and hydrogen bonding. Figure 1.2 shows a cartoon of inner-sphere and outer-sphere adsorption.

Figure 1.2. Inner-sphere (IS) and outer-sphere (OS) adsorption onto an Al surface. In inner-sphere adsorption a bond is being made to the surface while in outer-sphere adsorption the adsorbate is being bound through electrostatics and hydrogen bonding interactions.
In order to form inner-sphere complexes, bonds are broken in the substrate and adsorbate, new bonds are formed between the substrate and the adsorbate, and the energy changes associated with the formation are strongly dependent on the details of the adsorption geometry. On the other hand, outer-sphere adsorption is based on electrostatic interactions and is thought to be described by a relatively smooth potential energy surface. Thus, while it is straight-forward to generate models for outer-sphere adsorption in different starting geometries, designing structural models for inner-sphere adsorption involves bond breaking and bond making, variability in the number of bonds formed, and if or how the adsorbing functional groups deprotonate.

The Al nanoclusters discussed in this dissertation contain different types and numbers of functional groups. The Al$_{13}$ molecule has two types of exposed doubly bridging ligands ($\mu_2$-OH) and twelve equivalent bound water molecules ($\eta$-H$_2$O). Al$_{30}$ and Al$_{32}$ are comprised of two $\delta$-Al$_{13}$ Keggin units, [Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ (Al$_{13}$) connected by four Al linkers, $\varepsilon$-Al$_{13}$, Al$_{30}$, and the Al$_{32}$ nanocluster are shown in Figure 1.1.20,21 Three Al atoms that make up one of the four Al trimers on the $\varepsilon$-Keggin rotate $60^\circ$ in order to form the $\delta$-Keggin. There are three surface functional group categories in the Al$_{30}$ and Al$_{32}$ molecule – bound water molecules ($\eta$-H$_2$O), doubly bridging ligands ($\mu_2$-OH), and triply-bridging ligands ($\mu_3$-OH).7,22-24 The Al$_{32}$ molecule contains two additional Al atoms compared to the Al$_{30}$ molecule but contains the same types of oxygen functional groups. The existence of numerous distinct functional groups on the surface of the Al Keggin molecules has been highlighted as an argument for adopting these species as geochemical models and will further be discussed in Chapter 4.
Further Keggin computational studies are needed due to the fact that there are a limited number of studies focused at modeling reactivity and underlying physical properties of Keggin based compounds. Currently the majority of Keggin studies published are experimentally focused. Computational Keggin based studies are trailing behind experimental studies and therefore this leaves a large knowledge gap; filling in this research gap is necessary to better understand Keggin based compounds. The research goals in this dissertation are:

1. To determine how particle topography affects the reactivity of Al$_{13}$, Al$_{30}$, and Al$_{32}$.
2. To determine reactivity trends of cation adsorption, anion adsorption, and co-adsorption onto Al$_{30}$.
3. To determine how the reactivity of alumina surfaces compare to Al hydroxylated clusters.

This dissertation focuses on understanding the reactivity of Al structures. Since we are establishing a better comprehension of Al Keggin nanoclusters future studies can explore other metals like Fe, which will be discussed in chapter 9.

1.1 Dissertation Overview

The focus of this dissertation is to establish reactivity patterns of aluminum hydroxide nanoparticles and alumina surfaces. Specifically the spotlight will be on the unique reactivity of the Al$_{30}$ nanoparticle in order to make experimental connections and to bridge the knowledge gap between experiments and theory. This is done using a collaborative approach; manipulating experimental crystal structures into molecular structures in order to model and explain the reactivity of Keggin based compounds.
In Chapter 2 computational methods will be discussed. DFT is a well-established method and is considered the gold standard in materials computation. This dissertation will go into details about the DFT software used in all my projects, DMol\textsuperscript{3}\textsuperscript{,25,26} and how this software treats certain aspects of the calculations. In all of the calculations it was determined that the Al systems needed to be modeled in aqueous conditions and an implicit solvation model was used. This chapter explains the details of the conductor like screening model (COSMO).\textsuperscript{27}

In order to validate the computational methods and parameters chosen a variety of methods and parameters were tested and are described in Chapter 3. All good modeling approaches start with benchmarking and since the computational research of Al nanoclusters is extremely limited there are few studies to compare with and thus we need to perform our own benchmarking. After testing different methods, basis sets, and functionals we believe our methods are sufficient in modeling the reactivity of Al nanoclusters.

In Chapter 4, the aim is to directly assess how shape of each cluster affects adsorption trends on Al\textsubscript{13}, Al\textsubscript{30}, Al\textsubscript{32}, and briefly compare the nanoclusters with alumina surfaces (\(\alpha\)-Al\textsubscript{2}O\textsubscript{3}), by using DFT calculations and AIMD. Outer-sphere adsorption of SO\textsubscript{4}\textsuperscript{2\textendash} and Cl\textsuperscript{−} was modeled in order to sample the potential energy surfaces of the four Al systems. SO\textsubscript{4}\textsuperscript{2\textendash} and Cl\textsuperscript{−} were chosen as representative probe adsorbates based on their common use in crystallization experiments. Additionally, these ions allowed us to compare reactivity trends as a function of adsorbate size/charge, and can be considered an analog for contaminant polyoxoanions such as selenate and molybdate. From our results we see that the reactivity suggests that the shape of the clusters, and not just the number
and type of functional groups or charge, plays an important role in its adsorption processes.

Plots of the electrostatic potential ($V_{el}$) mapped onto the charge density of the molecule revealed that the unique “hourglass” shape of Al$_{30}$ and Al$_{32}$ gives rise to more positive values in the beltway and less positive values at the caps compared to $\varepsilon$-Al$_{13}$. Choosing Al$_{30}$ as our main Al nanocluster of interest we can go on to study inner-sphere cation reactivity. Al$_{30}$ was selected in order to connect DFT calculations with experimental crystal structures.

Chapter 5 reports studies of inner-sphere Cu$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ adsorption and shows opposite adsorption trends compared to anion (SO$_{4}^{2-}$ and Cl$^{-}$) adsorption. These trends are also in agreement with the electrostatic potential in that the caps of Al$_{30}$ are least positive which promotes inner-sphere cation reactivity.\textsuperscript{28}

Chapter 6 focuses on using DFT calculations to rationalize the crystal structure of an Al$_{30}$ Keggin species with two surface-bound Cu$^{2+}$, referred to as Cu$_2$Al$_{30}$-S. The crystallization was done in the presence of disulfonate ions (2,6-NDS), and the structure exhibited Cu$^{2+}$ bound to Al$_{30}$ in a corner-sharing bidentate fashion, while the sulfonate groups had an outer-sphere relationship to the molecule. DFT modeling of inner-sphere Cu$^{2+}$ adsorption and outer-sphere SO$_{4}^{2-}$ adsorption (as a simplified approximation to the bulky 2,6-NDS counter ions used in the experiment) was carried out. Outer-sphere adsorption is generally thought of as a weak interaction but the reaction energies associated with the outer-sphere adsorption of SO$_{4}^{2-}$ were relatively large compared to the reactivity of Cu$^{2+}$. When co-adsorption was modeled, the preferred structure had both Cu$^{2+}$ and SO$_{4}^{2-}$ adsorbed in the beltway, congruent with the crystal structure and suggests
that the strong outer-sphere adsorption controlled the co-adsorption site preference. The variation in the Cu$^{2+}$/SO$_4^{2-}$ adsorption energies as a function of molecular topography, specifically between the beltway and caps, was greater than 1 eV per ion, despite the fact that all of the inner-sphere adsorption geometries involved two η-H$_2$O groups. These results suggest once again that reactivity factors other than oxygen functional group identity govern the DFT energy trends.$^{29}$

In Chapter 7 we extend our collaborative research of Al$_{30}$ reactivity to include phosphate and arsenate adsorption. The experimental crystal structure of tert-butylphosphonic acid adsorbing to Al$_{30}$ (TBP$_2$Al$_{30}$) exhibits inner-sphere adsorption, again in the beltway region of the molecule. DFT calculations were carried out comparing adsorption configurations involving functional groups of common oxygen coordination and protonation, but varying location on the Al$_{30}$ surface. DFT energies showed that adsorption in the beltway versus the caps was preferred by 0.27-0.53 eV per adsorbate, spanning five phosphates, organophosphates, and their As(V) analogs. These oxyanions ultimately bind to Al$_{30}$ in an inner-sphere fashion, yet seem to be governed by the same electrostatic factors as the outer-sphere adsorption of SO$_4^{2-}$. The fact that both inner-sphere and outer-sphere anion reactivity is preferred in the beltway region is indicative of an adsorption mechanism in which there is an initial formation of an outer-sphere ion pair followed by ligand exchange to form the final product.$^{30}$

In Chapter 8, inner-sphere arsenate adsorption is modeled on Al surfaces as well as fictitious Al clusters. Surface studies are a common focus of geochemical research and there is no shortage of arsenate adsorption studies currently published.$^{31-37}$ We model arsenate adsorption on three different alumina surfaces and one small aluminum cluster.
Even though many extended x-ray adsorption fine structure studies (EXAFS) and computational studies find that arsenate binds in a bidentate binuclear (BB) or corner sharing configuration, we test three different configurations for arsenate adsorption on each of the three surface models and two different configurations on the small Al cluster to ensure a variety of sites are studied. Surface studies can be computationally expensive due to the large number of atoms needing to be modeled, so alternatively some studies prefer to use small hydroxylated metal octahedral clusters. We take the opportunity to systematically compare As adsorption on periodic slab models and small cluster models. In current literature, this slab/cluster debate already exists in theoretical surface science, but has not been put under such scrutiny in geochemical surface science. We observe that the reactivity range and magnitude significantly differs between the surface and the clusters due to their inherent structural.
2. THEORETICAL BACKGROUND

2.1 Introduction

Typically chemistry is thought to occur in a wet lab mixing chemicals, conducting experiments, and synthesizing or analyzing new products; computational chemistry uses theoretical chemistry and computer programs to explain and interpret reactions/ideas that cannot be seen or understood at the atomistic level by experimentalists. Computational chemistry can also make predictions about systems for which there is no experimental data and can provide guidance for future experiments. Theory can be used to understand the behavior of materials in order to associate reactivity with physical properties, and to derive structure-reactivity relationships. These calculations can attempt to describe the system in terms of electronic structure by using quantum mechanics and the many-body time-independent, non-relativistic Schrödinger equation given by;

\[ \hat{H}\Psi = E\Psi \] (2.1)

Equation 2.1 can be used to calculate the ground state energy of a collection of electrons. In equation 2.1 \( \hat{H} \) is the Hamiltonian operator, \( \Psi \) is the wave function, and \( E \) is the energy of the state \( \Psi \). In order to solve equation 2.1 one only needs to provide the atomic coordinates and atomic types. Everything else about the system is determined by the various terms in the Hamiltonian operator. The Hamiltonian operator can be broken down into its kinetic and potential energy/Coulombic components based on the interactions between the electrons (el) and/or nuclei (n) and can be written as equation 2.2.

\[ \hat{H} = T_n + T_{el} + V_{n-n} + V_{n-el} + V_{el-el} \] (2.2)

In equation 2.2, the first two terms on the right hand side represent the kinetic energy of the nuclei \( T_n \) and the electrons \( T_{el} \), and the last three terms represent the Coulombic
interactions. The last three terms represent the interactions between the nucleis \((V_{n\cdot n})\), nuclei and electron \((V_{n\cdot e})\), and the electrons \((V_{e\cdot e})\). We can simplify equation 2.2 by removing two terms to arrive at the electronic form of the Hamiltonian operator, equation 2.3.

\[
\hat{H}_{el} = T_{el} + V_{n\cdot el} + V_{el\cdot el} \tag{2.3}
\]

Based off of the Born-Oppenheimer approximation, we can explain why we only need an electronic form of the Hamiltonian operator \((\hat{H}_{el})\). The Born-Oppenheimer approximation assumes that the motions of the electrons and nucleis can be separated.\(^{38}\) The forces of the nucleis and electrons are similar in magnitude; however, the mass of the nuclei is about \(10^4\) times larger than the mass of an electron. Since the mass of the nuclei is significantly larger, the nuclei has a much smaller velocity than the electrons. Due to the large velocity difference we can treat the nuclei as being stationary, and thus the \(V_{n\cdot n}\) term contributes only as a constant in the total energy, and can be ignored. In our main method, Density Functional Theory, the electronic energy is a function of electron density and will be explained further in the next section.

### 2.2 Density Functional Theory

Density functional theory (DFT) is considered the theoretical gold standard in materials modeling. It is a quantum mechanical method used to calculate the electron density of atoms, molecules, and materials; and was initially based off of Hohenberg and Kohn’s two theorems.\(^{39}\)

1. The ground-state energy from Schrödinger’s equation is a unique functional of the electron density.
2. The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation. The Hohenberg and Kohn theorems require that the density corresponds to some ground state antisymmetric wave functions. This is correct for the true electron density but may not be the case for other trial densities. While the Hohenberg-Kohn formulation of DFT suggests that in theory the density contains all information needed, it offers no practical way to obtain it; this realization results in the knowledge that approximations need to be made in order to solve for the energy of the system. This practical DFT method was developed by Kohn and Sham in 1965. \(^\text{40}\) The Kohn-Sham DFT method employed maps the problem of real, interacting electrons onto a simplified problem of fictitious electrons experiencing an effective potential. In going from the real system to the fictitious one, all of the unknown contributions to the total energy are placed into the exchange-correlation term, \(E_{xc}\). In this way, the energy can be expressed as shown in equation 2.4.

\[
E[\rho] = E_{\text{known}}[\rho] + E_{xc}[\rho]
\]  

2.4

In equation 2.4, the electronic energy is broken down into two components, a known energy and the unknown energy, \(E_{xc}\). DFT is not an exact method since all components are not exactly known; with all the unknowns compromising the \(E_{xc}\) term. If we knew the exchange-correlation term then DFT would be exact, however, since we do not know this term it must be approximated. All the DFT error arises from how the \(E_{xc}\) term is treated. We can further break down the known energy term from equation 2.4 and arrive at equation 2.5.

\[
E_{\text{known}}[\rho] = T[\rho] + V[\rho] + V_H[\rho]
\]  

2.5
In equation 2.5, $T_s[\rho]$ is the kinetic energy of non-interacting electrons, $V[\rho]$ is the interaction between the electron and the nuclei, and $V_H[\rho]$ is the Coulomb repulsion between the electron and the total electron density. $T_s[\rho]$ can be defined as shown in equation 2.6.

$$T_s[\rho] = -\frac{\hbar^2}{2m} \nabla^2$$  \hspace{1cm} 2.6

In equation 2.6 $\hbar$ is Planck’s constant divided by $2\pi$ and $m$ is the mass. Combining equations 2.4, 2.5, and 2.6 with the Schrödinger equation we arrive at the one-electron Schrödinger equation for the Kohn-Sham system, equation 2.7.

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V[\rho] + V_H[\rho] + V_{XC}[\rho] \right] \phi_i = \epsilon_i \phi_i$$  \hspace{1cm} 2.7

In equation 2.7 $\epsilon_i$ is the orbital energy of the corresponding Kohn-Sham orbital, $\phi_i$. Equation 2.7 shows the Hartree potential depends on the electron density ($\rho$), but the electron density depends on the single electron wave function, equation 2.8.

$$\rho(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2$$  \hspace{1cm} 2.8

In order to find the total energy of our system we need to solve for $\phi_i$ and the electron density simultaneously, and this is done through an iterative process depicted in Figure 2.1. In order to initiate the process initial trial $\phi_i$ are defined (this is a guess often based on a linear combination of atomic orbitals or other chemical intuition). These $\phi_i$ are plugged into equation 2.8 to get a trial density. This trial density is used to construct the Hartree operator and solve for the eigenvalues in equation 2.7. Lastly, new $\phi_i$ are determined and a total energy is calculated. The new $\phi_i$ are used to construct the Hartree potential and the process is repeated again. This process is repeated until our criterion is met; the number of iterations can be controlled in the calculations by setting a convergence criterion.
Figure 2.1. A flow chart depicting the iterative cycle used in DFT.

2.3 Exchange Correlation Functional

The exchange-correlation term is a problem in DFT because it is unknown and thus approximated. The two most widely used approaches to solve for this unknown term are the local density approximation (LDA)\cite{lda} and the generalized gradient approximation (GGA).\cite{gga1,gga2,gga3} Colloquial the LDA method has been more commonly used; in LDA the exchange-correlation energy per electron is approximated as a function of the local charge density. The local energy terms are generated by integrating the energy density at various values assumed by the electronic density. LDA can determine the exact exchange energy for homogeneous systems by using equation 2.9 but is still an approximation for heterogeneous systems and that energy is calculated using equation 2.10, where equation 2.10 is a function of $\rho$. 
For both homogenous and heterogeneous systems the exchange correlation is still an approximation. The exchange correlation part includes the kinetic and Coulombic correlation energy and a self-interacting correlation. The LDA exchange-correlation treats these unknowns as parameters of a more complicated function.

While LDA has been very successful for many systems it does have some limitations, especially in bulk metals, molecules, semiconductors, ionic crystals, and weak inter-molecular bonds such as hydrogen bonding. Binding energies have been overestimated by 20-30% and energy barriers in diffusion are sometimes nonexistent. There is no unique and obvious way to improve LDA since the limitations drastically vary.

The second common exchange-correlation method is GGA. GGA depends on the density as well as the magnitude of the gradient of the density. GGA has been shown to improve binding and atomic energies as well as bond lengths and angles. The GGA functional is designed using equation 2.11.

\[
E_{xc}^{GGA}[\rho] = \int d^3\vec{r} f(\rho(\vec{r}))\nabla \rho(\vec{r})
\]

There is also a limit for the accuracy that GGA can obtain. This is due to the fact that the non-locality is not fully taken into account for the exchange term. Also the GGA functionals struggle to solve for the self-interaction present in the Hartree terms.
2.4 Basis Sets

In order to perform the calculations a mathematical representation for the one-electron orbital needs to be selected. The one-electron wave function is expanded by using a generic basis set described by orbitals φ_α. The Kohn-Sham orbitals can then be rewritten as equation 2.12.

\[
\varphi_j(\vec{r}) = \sum_{\alpha=1}^{M} c_{j\alpha} \phi_\alpha(\vec{r})
\]

In equation 2.12 c_{j\alpha} are the expansion coefficients of wave function j summed over all the basis functions up to the size of basis set M. The energy dependent wave functions are solutions to the time-independent Schrödinger equation. However, only the energies for which the solutions are normalized are allowed and these energies are the eigenvalues that form a discrete set. In order to solve for the eigenvalues the energies must satisfy Schrödinger’s equation. Therefore, a correctly designed basis set only requires a few (at most) energy-dependent basis functions which are solved iteratively.

The program used for all calculations is DMol^3, developed by Delley.\textsuperscript{25,26} DMol^3 uses a numerical atom-centered basis set which is the most straightforward basis set type. For this type of basis set the one-electron wave functions are expanded in terms of atomic orbitals that are solutions to the atomic problem centered on the atomic nuclei. The main disadvantage for this type of basis set is that the Hamiltonian and overlap matrix elements have to be fully computed numerically and thus is more computationally costly.

The basis set chosen in this dissertation is the double-numeric polarization (DNP) basis set. Calculations using the DNP basis set have been shown to result in good geometry agreement compared to calculations that used larger basis sets, but are computationally faster than larger atomic basis set.\textsuperscript{45} The DNP basis set uses approximately two atomic orbitals for each one occupied with a polarization function.
For example the polarization on hydrogen is 2p and the polarization on carbon is 3d. The DNP basis set is comparable to the Gaussian basis set 6-31G**, which is commonly used in the computational chemistry community.

2.5 Conductor-Like Screening Model

The materials modeled in this dissertation naturally occur in aqueous environments, and therefore we need to include aqueous effects in our computational models. The solvation model implemented in DMol\(^3\) is the Conductor-like Screening Model also known as COSMO developed by Klamt and Schüürmann.\(^{27}\) In this solvation model the solute molecules form a cavity within the dielectric continuum of permittivity that represents the solvent. The DMol\(^3\) code offers a variety of solvents but only water is used in this work; the dielectric constant for water is 78.54. In COSMO the charge distribution of the solute polarizes the dielectric medium. A schematic is shown in Figure 2.2 for formaldehyde.

![Figure 2.2](image.png)

Figure 2.2. A cartoon of what occurs when COSMO is used for a formaldehyde molecule. The blue background and blue arrows represents the polarizable solvent (dielectric continuum) and the white represents the cavity. The cartoon was adapted from Materials Studio.
In the cartoon formaldehyde is shown in a cavity that represents the molecular surface. Around the cavity there are screening charges. These screening charges result from the meeting of the cavity and the dielectric continuum. The large blue arrows are the polarization of the solvent.

When COSMO is implemented there are electrostatic interactions between molecules in solution and these interactions can be described using the Poisson-Boltzmann equation. The Poisson-Boltzmann equation is a differential equation first proposed by Louis George Gouy in 1910 then enhanced by David Leonard Chapman in 1913. Besides being able to model effects of solvents on different structures it can also be used to find Coulomb interactions of a single charge in molecules, determine ionic density distributions, and find ion-ion correlations. Depending on the area of research the Poisson-Boltzmann equation is also known as the Gouy-Chapman equation, the Debye-Hückel theory, and the Derjaguin-Landau-Verwey-Overbeek (DLVO) equation.

To derive the Poisson-Boltzmann equation we can start with the Poisson equation, equation 2.13.

\[ \nabla^2 \psi = -\frac{\rho}{\varepsilon \varepsilon_0} \tag{2.13} \]

In equation 2.13 the electrostatic potential depends on the charge density, \( \rho \). \( \varepsilon \) is the dielectric constant of the solvent and \( \varepsilon_0 \) is the permittivity of free space. When there is not any charge density present the electric field (E), equation 2.14 can be substituted into equation 2.13 to derive equation 2.15.

\[ E = -\nabla \rho \tag{2.14} \]

\[ \nabla \cdot E = \frac{\rho}{\varepsilon \varepsilon_0} \tag{2.15} \]
However, when the charge density depends on the potential, the Poisson equation (equation 2.13) becomes much harder to solve so the relationship of concentration and charge potential is used to overcome this problem. By using the Boltzmann law, the concentration can be written as equation 2.16.

\[ c = c_0 e^{-ze\phi/kT} \]  
\[ 2.16 \]

In equation 2.16, \( c \) is the concentration, \( c_0 \) is the concentration of the bulk, \( z \) is the ion’s valence charge, \( e \) is the elementary charge of a single electron, \( k \) is the Boltzmann’s constant, and \( T \) is the temperature. Equation 2.16 can be related to charge density in equation 2.17.

\[ \rho = F \sum_i z_i c_i e^{-z_i e\phi/kT} \]  
\[ 2.17 \]

In equation 2.17, \( F \) is the Faraday constant, \( z_i \) are the valence charges, and \( c_i \) are the concentrations. Assuming the ion concentrations are independent from one another, equation 2.17 can be substituted into equation 2.13 to derive the Poisson-Boltzmann equation, equation 2.18.

\[ \nabla^2 \phi = \frac{2z^2 eFc_0}{kT\varepsilon_0} \phi \]  
\[ 2.18 \]

The way equation 2.18 is written assumes \( e^{-e\phi/kT} \) is very small and can be equal to \( 1 - e\phi/kT \).

### 2.6 Mulliken Population Analysis

Charge population analysis is used in order to explain reactivity trends by estimating the partial atomic charge for each atom. There are a variety of charge population analysis schemes, and the one that DMol^3 uses is called Mulliken, which is one of the most widely used schemes developed by Robert S. Mulliken. In order to
assign the atomic charge a spatial region around the atoms need to be defined. Mulliken population analysis assigns charge to an atomic center on the basis of the total electron density. This scheme is based on the linear combination of atomic orbitals and the wave function of the molecule. This scheme is computationally inexpensive and available in most types of software. A major limitation with the Mulliken population analysis is that it is extremely basis set dependent so all calculations must be done with the same basis set in order to compare values.

2.7 Electrostatic Potential

One of the most useful analysis tools used in this dissertation is the visualization of the electrostatic potential. The electrostatic potential can be obtained from the charge density by solving equation 2.19.

\[
\nabla^2 V(\vec{r}) = 4\pi \rho(\vec{r})
\]

2.19

The Al nanoclusters modeled all have a high positive charge and the electrostatic potential shows the more positive and less positive regions of the clusters. The electrostatic potential allows us to predict and explain reactivity trends in this dissertation.

2.8 Induced Charge Density Analysis

In DFT the total density and deformation density can be visualized but are usually not extremely informative. In order to study the bonding and/or electrostatic interactions the induced charge density can be calculated and visualized. The induced charge density, \( \Delta \rho \), is calculated using equation 2.20.

\[
\Delta \rho = \rho_{\text{ion}+\text{Al}} - \rho_{\text{Al}} - \rho_{\text{ion}}
\]

2.20
In equation 2.20, $\rho_{\text{ion+Al}}$ is the charge density from the ion adsorbed onto the Al cluster of interest, $\rho_{\text{Al}}$ is the charge density from the Al cluster, and $\rho_{\text{ion}}$ is the charge density from just the ion(s) in their same geometry as if there were adsorbed onto the Al clusters.
3. DFT BENCHMARKING

One of the challenges in modeling Keggin based aluminum structures is that there are only a limited number of other Keggin studies to compare our methods too; so we need to first perform a variety of benchmarking studies. The benchmarking in this chapter is adapted from two published works with permissions obtained. The first part is adapted from the supporting information of *Langmuir* [Abeysinghe, Corum, Neff, Mason, and Forbes (2013) Contaminant Adsorption on Nanoscale Particles: Structural and Theoretical Characterization of Cu$^{2+}$ Bonding on the Surface of Keggin-Type Polyaluminum (Al$_{30}$) Molecular Species, 29, 14124-14134]. Copyright 2013, American Chemical Society. The second part is adapted from the supporting information of *Chemical Communications* [Fairley, Corum, Johns, Unruh, Basile, de Groot, Mason, and Forbes (2015) Isolation and Characterization of the [Ga$_2$Al$_{18}$O$_8$(OH)$_{36}$(H$_2$O)$_{12}$]$^{8+}$ Cluster: Cationic Variations on the Wells-Dawson Topology, 51, 12467-12469]. Copyright 2015.

3.1 Method Testing

In this dissertation all calculations are done using DMol$^3$. DMol$^3$ is a density functional theory commercial software package that can model molecular or periodic structures developed by Delley.\textsuperscript{25,26} DMol$^3$ combines computational speed with accuracy of quantum mechanical methods. It contains the COSMO solvation model and uses an atom-centered grid as its atomic basis. Even though DMol$^3$ combines computational speed with accuracy it is quite an expensive package so many other modelers choose more common packages like Gaussian.\textsuperscript{48} There are limited computational studies on
Keggin based structures, so in order to prove that our methods are sufficient we performed benchmarking calculations comparing DMol³ with Gaussian.

We explore DFT simulations on molecular aqueous species related to the crystal structure formed by experiment by comparing DMol³ calculations at the DFT-GGA+COSMO level to calculations using the Gaussian computational package, employing a DFT-PBE0 exchange-correlation functional and the PCM solvation model⁴⁹,⁵⁰ using the TZVP basis set.⁵¹,⁵² While the GGA exchange-correlation functional employed is local, the PBE0 functional is a hybrid design which uses a combination of Hartree-Fock exchange and DFT calculations. The other computational details of the two sets of methods (COSMO vs. PCM solvent, etc.) are comparable. We find that the optimized structures are in complete structural agreement and we find that there is also excellent agreement between the differences in total energies. We compare two Al₃₀ structures with Cu(II) adsorbed in different configurations (more structural details in Chapter 6) and find that there is a relative energy difference of 0.12 eV between two Cu(II) adsorbed Al₃₀ structures for the DMol³/DFT-GGA+COSMO method compared to Gaussian/DFT-PBE0+PCM. Thus the relative energetics do not show strong model dependence in this case.

3.2 Molecular Nanoparticle vs. Crystal Structure

Another aspect we need to verify is if our molecular nanoparticle calculations are sufficient instead of modeling the many atom crystal structure. To do this, the periodic calculations of δ-Al₁₃ (Na-δ-[Al₁₃O₄(OH)₂₄(H₂O)₁₂][SO₄]₄·19H₂O) and ε-Al₁₃ ((ε-[Al₁₃O₄(OH)₂₄(H₂O)₁₂][SO₄]₃·16H₂O), two formula weights are in one unit cell) were modelled. The model geometries were based on the crystal structures of δ-Al₁₃ and ε-Al₁₃
reported by Rowsell and Johansson.\textsuperscript{53,54} The experimental crystal structures do not necessarily contain H atoms so we use a bond valence program as detailed in the introduction to add H atoms to the DFT models. The \(\delta\)- and \(\varepsilon\)-\text{Al}_{13} nanoparticles are shown in Figure 3.1 In order to efficiently optimize the coordinates for the periodic \(\delta\)- and \(\varepsilon\)-\text{Al}_{13} structures, the positions of the oxygen atoms in the water molecules were constrained in the crystal structure, while all other coordinates of the structures were fully relaxed. In all cases, the angles of the experimental crystal structures were used, while the lattice constants and atomic positions were optimized. The lattice constants of the tridecamer Al species were optimized in DMol\textsuperscript{3} using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{42} using a 2\(\times\)2\(\times\)2 Monkhorst-Pack (MP) \(k\)-point grid. An example of a periodic and molecular input file is shown in Appendix A. For the \(\varepsilon\)-\text{Al}_{13} species, the optimized bulk lattice constants were determined to be (with percent error from experiment in parentheses) \(a = 14.1800 \text{ Å (0.0%)}\), \(b = 11.5000 \text{ Å (0.0%)}\), and \(c = 18.0846 \text{ Å (+2.0%)}\) and are in agreement with the experimental \(\varepsilon\)-\text{Al}_{13} crystal.\textsuperscript{54} There is also agreement between the theoretical lattice constants determined for \(\delta\)-\text{Al}_{13}, the results being \(a = 13.8153 \text{ Å (-2.0%)}\), \(b = 15.0402 \text{ Å (0.0%)}\), and \(c = 16.1857 \text{ Å (+2.0%)}\).\textsuperscript{53} Bond distances from the tetrahedral Al atom to the four oxygen atoms are tabulated for the periodic and molecular structure and compared to the experimental structures in Table 3.1 for \(\varepsilon\)-\text{Al}_{13} and Table 3.2 for the \(\delta\)-\text{Al}_{13} species. At most the bond distances differ by 1.80%; we can conclude that there is excellent structural agreement between both the periodic structure and the molecular structure. Since we will be introducing disorder to the crystal structure in order to study reactivity we use the molecular form instead of the periodic crystal structure.
Figure 3.1. The DFT models of the delta and epsilon Keggin structures. The delta Keggin is on the left while the epsilon Keggin is on the right. The tetrahedral cation is shaded yellow. Aluminum, oxygen, hydrogen, and sodium are shown in turquoise, red, gray, and purple.

Table 3.1. Details of the experimental and theoretical $\varepsilon$-$\text{Al}_{13}$ Keggin geometries in terms of the tetrahedral Al-O distances. The experimental $\varepsilon$-$\text{Al}_{13}$ crystal structure results are listed first then the theoretical periodic and molecular model for $\varepsilon$-$\text{Al}_{13}$. The numbers in parentheses are the percent difference between the DFT Model and the corresponding experimental structure.

<table>
<thead>
<tr>
<th>(Å)</th>
<th>$\varepsilon$-$\text{Al}_{13}$ Crystal$^{54}$</th>
<th>DFT Periodic Model $\varepsilon$-$\text{Al}_{13}$</th>
<th>DFT Molecular Model $\varepsilon$-$\text{Al}_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-O₁</td>
<td>1.844</td>
<td>1.879 (1.90)</td>
<td>1.828 (-0.87)</td>
</tr>
<tr>
<td>Al-O₂</td>
<td>1.843</td>
<td>1.842 (-0.054)</td>
<td>1.814 (-1.57)</td>
</tr>
<tr>
<td>Al-O₃</td>
<td>1.837</td>
<td>1.841 (0.22)</td>
<td>1.804 (-1.80)</td>
</tr>
<tr>
<td>Al-O₄</td>
<td>1.845</td>
<td>1.877 (1.73)</td>
<td>1.814 (-1.68)</td>
</tr>
</tbody>
</table>

Table 3.2. Details of the experimental and theoretical $\delta$-$\text{Al}_{13}$ Keggin geometries in terms of the tetrahedral Al-O distances. The experimental $\delta$-$\text{Al}_{13}$ crystal is listed first then the theoretical periodic and molecular model for $\delta$-$\text{Al}_{13}$. The numbers in parentheses are the percent difference between the DFT Model and the corresponding experimental structure.

<table>
<thead>
<tr>
<th>(Å)</th>
<th>$\delta$-$\text{Al}_{13}$ Crystal$^{53}$</th>
<th>DFT Periodic Model $\delta$-$\text{Al}_{13}$</th>
<th>DFT Molecular Model $\delta$-$\text{Al}_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-O₁</td>
<td>1.821</td>
<td>1.845 (1.32)</td>
<td>1.847 (1.43)</td>
</tr>
<tr>
<td>Al-O₂</td>
<td>1.788</td>
<td>1.800 (0.67)</td>
<td>1.804 (0.89)</td>
</tr>
<tr>
<td>Al-O₃</td>
<td>1.798</td>
<td>1.811 (0.72)</td>
<td>1.806 (0.61)</td>
</tr>
<tr>
<td>Al-O₄</td>
<td>1.790</td>
<td>1.792 (0.11)</td>
<td>1.806 (0.89)</td>
</tr>
</tbody>
</table>
Another test that was done for each project was to test the basis set cutoff radius. The basis set cutoff value allows us to specify the use of real-space cutoffs in the calculations. This test was done in all projects and for all projects it was determined that a cutoff radius of 3.5 Å was sufficient. As shown in Table 3.3, the basis set cutoff radius for the δ-Al$_{13}$ Keggin was tested by monitoring the tetrahedral Al-O bond length for a cutoff radius of 3.50-4.75 Å.

Table 3.3. Tetrahedral Al-O bond distances for all cutoff values for δ-Al$_{13}$ Keggin.

<table>
<thead>
<tr>
<th>Cutoff radius (Å)</th>
<th>δ-Al$_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50</td>
<td>1.842</td>
</tr>
<tr>
<td>3.75</td>
<td>1.846</td>
</tr>
<tr>
<td>4.00</td>
<td>1.849</td>
</tr>
<tr>
<td>4.25</td>
<td>1.846</td>
</tr>
<tr>
<td>4.50</td>
<td>1.846</td>
</tr>
<tr>
<td>4.75</td>
<td>1.849</td>
</tr>
</tbody>
</table>
4. SHAPE-REACTIVITY RELATIONSHIPS IN AL NANOCLUSTERS

Keggin-based aluminum nanoclusters have been shown to be efficient sorbents for the removal of arsenic and other harmful ions from water. Obtaining a molecular-level understanding of the adsorption processes associated with these molecules is of fundamental importance, and could pave the way for rational design strategies for water treatment. We use DFT calculations to determine reactivity as a function of particle topography, using sulfate and chloride as adsorption probes onto $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al$_{13}$), $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}$ (Al$_{30}$), and $[\text{Al}_{32}\text{O}_8(\text{OH})_{60}(\text{H}_2\text{O})_{30}]^{20+}$ (Al$_{32}$), and briefly compare the nanoparticle results to aluminum surfaces for sulfate adsorption. The DFT trends in adsorption energy suggest that the apparent shape-reactivity relationship supersedes reactivity predictions based on oxygen functional group type alone. This chapter has been adapted from the paper that was submitted to the journal *Water Research*, February 2016 [Corum and Mason, *Shape-Reactivity Relationships in Aluminum Nanoclusters*].

4.1 Introduction

Al-based materials are known to exhibit high reactivity towards polyoxoanion species such as arsenate, and therefore are frequently used in coagulation-coprecipitation and adsorption based water remediation. Studies point to the utility of the Keggin-based aluminum hydroxide nanocluster $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}$ (Al$_{30}$) in the efficient removal of arsenic from water. Mertens et al. have been prime investigators in researching the removal of inorganic sodium arsenate from contaminated water samples. In a recent study, the reactivity of several Al-based sorbents was compared by measuring the uptake
capacity of arsenic, specifically As(V). The materials tested included Al$_{30}$ solution, Al$_{30}$ enriched polyaluminum chloride (PACl$_{30}$), polyaluminum granulate (PAG), and the natural Al mineral phase, gibbsite. The pure Al$_{30}$ and PACl$_{30}$ showed similar As uptake efficiency, suggesting that the Al$_{30}$ content of PACl$_{30}$ is responsible for its reactivity towards the contaminant, but with the advantage of lower cost. All of the nanocluster sorbents adsorbed at least 93% of arsenic from solutions of initial arsenic concentration ranging from 0.133-0.667 mmol/L, while the gibbsite sample only decreased the As(V) concentration by 50%. While Al nanoclusters can adsorb contaminants at a variety of pH conditions it has been shown that PACl$_{30}$ efficiency is highest near neutral pH, making it an excellent candidate for the purification of natural waters.$^{1,2,8}$

It is easy to see why, in conjunction with high reactivity noted in the literature, the importance of functional group number and type is assumed to govern the reactivity of Al nanoclusters. The Al$_{13}$ molecule has two types of exposed doubly bridging ligands ($\mu_2$-OH) and twelve equivalent bound water molecules ($\eta$-H$_2$O). Al$_{30}$ and Al$_{32}$ are comprised of two $\delta$-Al$_{13}$ Keggin units, [Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ (Al$_{13}$) connected by four Al linkers.$^{20,21}$ There are three surface functional group categories in the Al$_{30}$ and Al$_{32}$ molecule – bound water molecules ($\eta$-H$_2$O), doubly bridging ligands ($\mu_2$-OH), and triply-bridging ligands ($\mu_3$-OH).$^{22-24}$ The Al$_{32}$ molecule contains two additional Al atoms on the Al$_{30}$ molecule but contains the same types of oxygen functional groups. Indeed, the existence of numerous distinct functional groups on the surface of the Al Keggin molecules has been highlighted as an argument for adopting these species as geochemical models.$^{7,22}$
The Keggin structural motif common to the Al nanoclusters studied here is of general interest to a wide range of chemistry beyond adsorption. For example, Furrer et al has studied aluminum flocs and have found that the Al flocculants that precipitate from streams contain a significant amount of Al(O)$_4$, which is the building blocks of the $\varepsilon$-Al$_{13}$ Keggin. The ferrihydrite structure of Michel et al. based on pair distribution function analysis exhibits similarities to the $\delta$-Keggin structure. More recently, an $\alpha$-Keggin Fe$_{13}$ cluster was characterized by Sadeghi et al., providing further evidence that the growth of both natural and synthetic phases proceeds by aggregation of clusters. The Keggin motif in prenucleation clusters has also been observed in Nb-polyoxometalate systems. These examples of broad interest in Keggin clusters provides further motivation for modeling studies aimed at assigning their reactivity to underlying physical properties.

In this chapter, we aim to directly assess how shape affects adsorption trends on Al$_{13}$, Al$_{30}$, and Al$_{32}$, compared to aluminum surfaces, using DFT calculations and AIMD. We model outer-sphere adsorption of SO$_4^{2-}$ and Cl$-$ to sample the potential energy surfaces of the three Al nanoclusters. SO$_4^{2-}$ and Cl$-$ are chosen as representative probe adsorbates based on their common use in crystallization experiments. Additionally, these ions allow us to compare reactivity trends as a function of adsorbate size/charge, and can be considered an analog for contaminant polyoxoanions such as selenate and molybdate.

### 4.2 Computational and Theoretical Methods

AIMD simulations and DFT geometry optimizations are carried out using the DMol$^3$ package developed by Delley, with aqueous effects accounted for by the conductor-like screening model (COSMO). The AIMD trajectories are used to search
for minimum energy adsorption configurations, which allows for a better sampling of the potential energy surface than through static DFT calculations alone. AIMD simulations were carried out in the \((N, V, T)\) ensemble with trajectories of 1000 steps of 0.463 fs. The temperature was set at 330 +/− 2K and controlled by using the Nosé-Hoover chain (NHC)\(^{60,61}\) method. The inversion symmetry of \(\text{Al}_{30}, \text{Al}_{32}\), and the alumina surface is maintained in the adsorbed systems by modeling two anions with atomic coordinates that are also related by inversion symmetry.

Select configurations of \(\text{SO}_4^{2−}\)/Cl− adsorption at distinct positions (in terms of molecular topography) were then subjected to DFT geometry optimization. The geometry optimization calculations were carried out at the GGA-PBE\(^{42}\) level with a structural convergence criterion of 0.03 eV/Å. A DNP numerical atom-centered basis set (with a cutoff radius of 3.5 Å) was used to expand the single electron orbitals. Further details of the computational optimization methods (including prior benchmarking and convergence studies) are reported in other work as well as Chapter 3.\(^{28,29,62}\)

In order to use probe adsorbates to sample the potential energy surface of the Al nanoclusters, it is necessary to model the isolated molecular form. Molecular Al nanocluster geometries are generated based on the experimental crystal structures of \(\text{Al}_{13}, \text{Al}_{30},^{20}\) and \(\text{Al}_{32}.^{21}\) Protonation states of the exposed oxygen functional groups are determined based on a bond-valence analysis. The molecular structures are then embedded in the COSMO continuum solvent model (with a dielectric constant of 78.54 to simulate water), and fully optimized at the DFT level. The average bond distances between the tetrahedral Al and the four bound O atoms for all three aluminum nanoparticles are tabulated and compared to the experimental structure in Table 4.1,
showing excellent structural agreement between the modeled molecular structure and the experimental crystal structure.

Table 4.1. Average tetrahedral bond length (in \( \text{Å} \)) comparison between the DFT optimized nanoparticles and the experimental crystal structures.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>( \text{Al}_{13} )</th>
<th>( \text{Al}_{30} )</th>
<th>( \text{Al}_{32} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>1.815</td>
<td>1.824</td>
<td>1.824</td>
</tr>
<tr>
<td>Experimental</td>
<td>1.838(^{54})</td>
<td>1.797(^{20})</td>
<td>1.805(^{21})</td>
</tr>
</tbody>
</table>

The aluminum surfaces used for comparison in this chapter are only briefly introduced here, but are the focus and therefore much more thoroughly discussed in Chapter 8. Using the alpha-numeric surface stoichiometry naming scheme of Lo et al.,\(^{63}\) we model five different alumina surfaces but only discuss sulfate adsorption on the C3 and A3 (1102) surface, due to the fact that these surfaces make up the reactivity extremes. These structures are shown in Figure 8.1. These surfaces differ in their topmost layer. The C3 surface has a missing layer of Al cations compared to the A3 surface, and both surfaces are capped with hydroxyls. With these differences, the C3 and A3 slabs consist of 12 and 14 O layers and 6 and 8 Al layers, respectively. All surfaces have 25 Å of vacuum space separating the periodic images along the z direction.

Two adsorption configurations (for each adsorbate) were fully optimized for \( \text{Al}_{13} \) and \( \text{Al}_{30} \) and three configurations were fully optimized for \( \text{Al}_{32} \). The initial adsorption configurations for all three molecules are shown schematically in Figure 4.1. The two adsorption configurations for \( \text{Al}_{13} \) are labeled \( \text{A}_{13} \) and \( \text{B}_{13} \). The configurations for \( \text{Al}_{30} \) have the adsorbate located in the beltway of the cluster, labeled \( \text{A}_{30} \), or at the caps of the cluster, \( \text{B}_{30} \). The \( \text{Al}_{32} \) adsorption configurations were based off of the \( \text{Al}_{30} \) configurations. In the \( \text{A}_{32} \) and \( \text{B}_{32} \) configurations, the adsorbates are in the beltway region (which is now
partially blocked by the additional Al atoms relative to Al$_{30}$), and in the C$_{32}$ configuration the adsorbates are above the molecular caps.

Figure 4.1. The initial outer-sphere adsorption configurations for SO$_4^{2-}$/Cl$^-$ on Al$_{13}$, Al$_{30}$, and Al$_{32}$. The small a and b on Al$_{30}$ represents the two different protonation sites on Al$_{30}$ while the large A and B represents the adsorption configurations. The Al$^{3+}$ cations are represented by the blue, turquoise, and green polyhedrons.

The 18+ form of the Al$_{30}$ molecule was shown to be unstable by vibrational analysis, while several stable 16+ isomers were found.$^{29}$ Therefore, in modeling adsorption on Al$_{30}$, we have the additional consideration of which 16+ isomer(s) to consider. While not exhaustive, we chose two 16+ Al$_{30}$ isomers on which to model adsorption, in which two (symmetry-related) η-H$_2$O groups are deprotonated. In one Al$_{30}^{16+}$, the deprotonated η-H$_2$O groups are in the beltway, labeled as “a”, and in the other, the deprotonated η-H$_2$O groups are at the cap sites, labeled as “b”, also shown in Figure 4.1. The difference in the DFT total energy of the two 16+ isomers is 0.86 eV, and there is evidence that Al$_{30}$ starts to deprotonate at pH~5.3.$^{64}$ Therefore, we consider both deprotonation states as possible starting points for subsequent adsorption. The two deprotonation sites, a and b, and two adsorption configurations, A and B, results in 4
possible configurations: A\textsubscript{a30}, B\textsubscript{b30}, A\textsubscript{b30}, and B\textsubscript{a30}. The A\textsubscript{a30} structure is where the beltway sites are deprotonated to form the 16+ molecule and outer-sphere adsorption is at the beltway, the B\textsubscript{b30} structure is where the cap sides are deprotonated to form the 16+ molecule and outer-sphere adsorption is at the caps, the A\textsubscript{b30} structure is where the cap sites are deprotonated to form the 16+ molecule and outer-sphere adsorption is at the beltway, and the B\textsubscript{a30} structure is where the beltway sites are deprotonated to form the 16+ molecule and outer-sphere adsorption is at the caps.

DFT reaction energies, $E_{\text{rxn}}$, are calculated based on Scheme 4.1 using the total energy information for each reactant and product species, weighted by the appropriate stoichiometric coefficients. In forming (SO\textsubscript{4})\textsubscript{y}---Al\textsubscript{x} and Cl\textsubscript{y}---Al\textsubscript{x}, Al\textsubscript{x} interacts electrostatically with the anion species, where x equals the number of Al atoms: x=13, 30, and 32 and y=1 or 2 depending on the number of ions adsorbing to the molecule. In order to calculate values of $E_{\text{rxn}}$ by Scheme 4.1, the following molecular aqueous species were modeled: Al\textsubscript{13}, Al\textsubscript{30}, Al\textsubscript{32}, SO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-}, SO\textsubscript{4}---Al\textsubscript{13}, Cl---Al\textsubscript{13}, (SO\textsubscript{4})\textsubscript{2}---Al\textsubscript{30}, Cl\textsubscript{2}---Al\textsubscript{30}, (SO\textsubscript{4})\textsubscript{2}---Al\textsubscript{32} and Cl\textsubscript{2}---Al\textsubscript{32}, where “---” denotes outer-sphere adsorption between the adsorbing ion(s) and Keggin molecule, and the double adsorption on Al\textsubscript{30} and Al\textsubscript{32} reflects the molecular inversion symmetry. An analogous scheme was used for sulfate adsorption on the surface to form (SO\textsubscript{4})\textsubscript{2}---surface, where the surface can be C3 or A3, and additional aqueous species were modeled: bare C3, bare A3, (SO\textsubscript{4})\textsubscript{2}---C3, and (SO\textsubscript{4})\textsubscript{2}---A3.
\[ \frac{1}{y} [Al_x + ySO_4^{2-} \rightarrow (SO_4)_y - Al_x] \]

\[ \frac{1}{y} [Al_x + yCl^- \rightarrow Cl_y - Al_x] \]

Scheme 4.1. Model reactions for the outer-sphere adsorption of SO\(_4^{2-}\) and Cl\(^-\), where x stands for the number of Al atoms in the nanoparticle (13, 30, or 32) and y stands for the number of SO\(_4^{2-}\)/Cl\(^-\) ions. There are 2 SO\(_4^{2-}\)/Cl\(^-\) ions for Al\(_{30}\) and Al\(_{32}\) due to the inversion symmetry of the nanocluster and one SO\(_4^{2-}\)/Cl\(^-\) ion per Al\(_{13}\).

### 4.3 Results and Discussion

Values of \(E_{rxn}\) for sulfate and chloride adsorption configurations are reported in Table 4.2, with the optimized geometries shown in Figure 4.2 (Al\(_{13}\)), Figure 4.3 (Al\(_{30}\)), Figure 4.4 (Al\(_{32}\)), and Figure 4.5 (C3/A3). The range of \(E_{rxn}\) values for each adsorbate system, \(\Delta E_{rxn}\), is also reported for convenience. The ranges of \(E_{rxn}\) for SO\(_4^{2-}\) (and Cl\(^-\) in parenthesis) on each Keggin molecule is -1.76 – -1.86 (-1.12 – -1.14) eV on Al\(_{13}\), -1.39 – -2.34 (-0.99 – -1.85) eV Al\(_{30}\) (A\(_{a30}\) and B\(_{b30}\) structures), -1.96 – -2.84 (-1.34 – -1.62) eV Al\(_{30}\) (A\(_{b30}\) and B\(_{a30}\) structures), and -1.62 – -2.89 (-1.14 – -1.95) eV for Al\(_{32}\). The range of \(E_{rxn}\) for SO\(_4^{2-}\) onto the C3 and A3 surface is -0.39 – -1.03 eV. An interesting result is that all sulfate adsorption onto the Keggin structures is stronger than sulfate adsorption onto C3/A3 by at least 0.36 eV. For simplicity, we discuss the A\(_{a30}\) and B\(_{b30}\) results to represent Al\(_{30}\), as they show the greater range in \(E_{rxn}\).
Table 4.2. Calculated values of $E_{\text{rxn}}$ (in eV) for sulfate and chloride adsorption on Al$_{13}$, Al$_{30}$, and Al$_{32}$; and sulfate adsorption onto Al surface. In the two rows for Al$_{30}$ $A$ and $B$, represents that adsorption and deprotonation are occurring in the same location while $A$ and $B$ represents that adsorption and deprotonation are occurring in mismatched locations, as described in the text.

<table>
<thead>
<tr>
<th>$E_{\text{rxn}}$ (eV)</th>
<th>A/A3</th>
<th>B/C3</th>
<th>C</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$<em>4$----Al$</em>{13}$</td>
<td>-1.76</td>
<td>-1.87</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>(SO$_4$)$<em>2$----Al$</em>{30}$($A$ and $B$)</td>
<td>-2.34</td>
<td>-1.39</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>(SO$_4$)$<em>2$----Al$</em>{30}$($A$ and $B$)</td>
<td>-2.84</td>
<td>-1.96</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>(SO$_4$)$<em>2$----Al$</em>{32}$</td>
<td>-2.89</td>
<td>-2.44</td>
<td>-1.63</td>
<td>1.27</td>
</tr>
<tr>
<td>(SO$_4$)$_2$----surface</td>
<td>-1.03</td>
<td>-0.39</td>
<td></td>
<td>0.64</td>
</tr>
<tr>
<td>Cl----Al$_{13}$</td>
<td>-1.18</td>
<td>-1.30</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>Cl$<em>2$----Al$</em>{30}$($A$ and $B$)</td>
<td>-1.85</td>
<td>0.99</td>
<td></td>
<td>0.86</td>
</tr>
<tr>
<td>Cl$<em>2$----Al$</em>{30}$($A$ and $B$)</td>
<td>-1.62</td>
<td>-1.34</td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td>Cl$<em>2$----Al$</em>{32}$</td>
<td>-1.95</td>
<td>-1.60</td>
<td>-1.14</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Figure 4.2. DFT geometry optimized structures of the SO$_4$----Al$_{13}$ and Cl----Al$_{13}$ structures. Aluminum, oxygen, hydrogen, sulfur, and chlorine are shown by blue, red, gray, orange, and greens spheres, respectively. From left to right: SO$_4$----A$_{13}$, SO$_4$----B$_{13}$, Cl----A$_{13}$, and Cl----B$_{13}$. 


Figure 4.3. DFT geometry optimized structures of the (SO$_4$)$_2$---Al$_{30}$ and Cl$_2$---Al$_{30}$ structures. Aluminum, oxygen, hydrogen, sulfur, and chlorine are shown by blue, red, gray, orange, and greens spheres, respectively. From left to right: (SO$_4$)$_2$---A$_{a30}$, (SO$_4$)$_2$---B$_{b30}$, Cl$_2$---A$_{a30}$, and Cl$_2$---B$_{b30}$. 
Figure 4.4. DFT geometry optimized structures of the (SO$_4$)$_2$---Al$_{32}$ and Cl$_2$---Al$_{32}$ structures. Aluminum, oxygen, hydrogen, sulfur, and chlorine are shown by blue, red, gray, orange, and greens spheres, respectively. From left to right and top to bottom: (SO$_4$)$_2$---A$_{32}$, (SO$_4$)$_2$---B$_{32}$, (SO$_4$)$_2$---C$_{32}$, Cl$_2$---A$_{32}$, and Cl$_2$---B$_{32}$, Cl$_2$---C$_{32}$. 
Figure 4.5. DFT geometry optimized structures of the (SO₄)₂---C₃ (left) and (SO₄)₂---A₃ (right) structures. Aluminum, oxygen, hydrogen, and sulfur are shown by blue, red, gray, and orange spheres, respectively.

The magnitude of the most favorable values of $E_{\text{rxn}}$ on the Al₃₀ and Al₃₂ molecules is greater than that for adsorption of either ion on the Al₁₃ molecule (or the Al surfaces). This begs the question if the trends are dictated by the overall formal charge on each Keggin species. As previously discussed in the literature, the total formal charge on each Al nanocluster (7+, 18 +, and 20+ respectively for Al₁₃, Al₃₀, and Al₃₂) does not represent how charge is distributed, motivating the definition of a surface specific charge, $\sigma$, that effectively normalizes the molecular charge per Al: $\sigma = (Z+\Sigma_{\text{max}})/\text{Al}_{\text{surf}}$. Here, $Z$ stands for the average number of protons lost per Al nanocluster, $\Sigma_{\text{max}}$ represents the total charge at the fully protonated state, and $\text{Al}_{\text{surf}}$ is the total number of Al atoms in each Al nanocluster. Using this definition of $\sigma$, all three of the Al polycations have $\sigma$ values in the range of 0.58 to 0.66 charge units. Here, we use the DFT results and Mulliken population analysis to investigate if there are significant variations in the local charges of Al atoms in the Al nanoclusters. The Mulliken charges on the Al atoms are on average 1.51 e, 1.52 e, and 1.53 e for Al₁₃, Al₃₀, and Al₃₂, confirming that the distribution of charge per Al atom is similar in all of the Al nanoclusters.
As no direct bonds are formed in outer-sphere adsorption, there is no single adsorbate-cluster distance to characterize the optimized configurations. We report the average distance of the sulfate (sulfur atom) and chloride on the Keggin structures to the tetrahedral Al (Al\textsubscript{tet}) center for Al\textsubscript{13}, Al\textsubscript{30}, and Al\textsubscript{32}. For sulfate adsorption the average S-Al\textsubscript{tet} bond distance is 6.070 Å, 6.479 Å, and 6.390 Å for Al\textsubscript{13}, Al\textsubscript{30}, and Al\textsubscript{32} respectively and 6.454 Å, 5.679 Å, and 6.133 Å for chloride adsorption on Al\textsubscript{13}, Al\textsubscript{30}, and Al\textsubscript{32} respectively. Since each Keggin contains its own unique shape we cannot make an equal comparison between all three Keggin structures, but note that there is no simple correlation between $E_{\text{rxn}}$ and these distances.

Charge population analysis is carried out to further characterize the adsorption configurations and is reported in Table 4.3. On Al\textsubscript{13}, the sulfate and chloride charge is unchanged between the A\textsubscript{13} and B\textsubscript{13} configurations. The largest variation in adsorbate charge between configurations is seen for SO$_4^{2-}$ on Al\textsubscript{32}. In the B\textsubscript{32} configuration, the charge on SO$_4^{2-}$ has been reduced by 0.65 e, while in the C\textsubscript{32} configuration the charge has only been reduced by 0.44 e. There are also variations in adsorbate charge in the chloride Al\textsubscript{32} configurations and the Al\textsubscript{30} SO$_4^{2-}$/Cl\textsuperscript{-} configurations. The trend can be summarized as showing that when anions adsorb in beltway configurations on Al\textsubscript{30}/Al\textsubscript{32}, there is a greater extent of charge transfer with the Al nanocluster, and this trend correlates with the larger magnitude values of $E_{\text{rxn}}$ for beltway configurations.
Table 4.3. Mulliken population analysis values for the sulfate and chloride ions in the DFT geometry optimized configurations. In the two rows for Al$_{30}$ A$_a$ and B$_b$ represents that adsorption and deprotonation are occurring in the same location while A$_b$ and B$_a$ represents that adsorption and deprotonation are occurring in mismatched locations, as described in the text.

<table>
<thead>
<tr>
<th>Mulliken Values (e)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$<em>4$---Al$</em>{13}$</td>
<td>-1.53</td>
<td>-1.53</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>(SO$_4$)$<em>2$---Al$</em>{30}$ (A$_a$ and B$_b$)</td>
<td>-1.50</td>
<td>-1.57</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>(SO$_4$)$<em>2$---Al$</em>{30}$ (A$_b$ and B$_a$)</td>
<td>-1.40</td>
<td>-1.54</td>
<td></td>
<td>0.14</td>
</tr>
<tr>
<td>(SO$_4$)$<em>2$---Al$</em>{32}$</td>
<td>-1.45</td>
<td>-1.35</td>
<td>-1.56</td>
<td>0.21</td>
</tr>
<tr>
<td>Cl---Al$_{13}$</td>
<td>-0.65</td>
<td>-0.65</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>Cl$<em>2$---Al$</em>{30}$ (A$_a$ and B$_b$)</td>
<td>-0.61</td>
<td>-0.74</td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td>Cl$<em>2$---Al$</em>{30}$ (A$_b$ and B$_a$)</td>
<td>-0.60</td>
<td>-0.67</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>Cl$<em>2$---Al$</em>{32}$</td>
<td>-0.59</td>
<td>-0.58</td>
<td>-0.66</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The comparison of $E_{rxn}$ values on Al$_{13}$, Al$_{30}$, and Al$_{32}$ nanoclusters and the charge population analysis supports that there is a shape-reactivity relationship governing adsorption behavior on the Al nanocluster surfaces: On the spherical Al$_{13}$, $E_{rxn}$ varies by at most 0.10 eV, while the variation between configurations with adsorbates at the beltway versus cap configurations on Al$_{30}$ and Al$_{32}$ is 0.28-1.27 eV. The reactivity range of the Al surfaces compared to the larger Al nanoclusters is also smaller, 0.64 eV, which further supports this shape-reactivity relationship since no matter the surface termination all surfaces are relatively flat. The Mulliken population analysis in Table 4.3 shows that the relatively strong adsorption in the beltway configurations is accompanied by a greater extent of charge transfer between the adsorbate and the Al nanocluster. In order to visualize the interactions between the anions and the Al nanoclusters, we calculate and plot the induced charge density, $\Delta \rho$, taken as $\rho_{SO_4/Al_x} - \rho_{Al_x} - \rho_{SO_4}$, where $\rho_{SO_4/Al_x}$ is the charge density from the sulfate adsorbed cluster, $\rho_{Al_x}$ is the charge density from the
Al nanocluster, and $\rho_{SO_4}$ is the charge density from just the sulfate ions in their same geometry as if there were adsorbed onto the Al nanoclusters. The resulting isosurfaces are shown in Figure 4.6. Figure 4.6 shows $\Delta \rho$ for the sulfate B configuration on $\text{Al}_{13}$ as well as the A and C configurations for $\text{Al}_{32}$. All of the $\Delta \rho$ plots use the same isosurface value. Comparing the beltway ($\text{A}_{32}$) and cap ($\text{C}_{32}$) configurations, it is qualitatively apparent that there is a larger volume bound by the isosurfaces for $\text{A}_{32}$. Again using a piece of paper as an analogy for how the functional groups are distributed on the $\text{Al}_{32}$ particle surface, the caps are like a flat page, which sterically limits how many functional groups interact with $\text{SO}_4^{2-}$ in $\text{C}_{32}$. The beltway corresponds to the inside of a rolled piece of paper, which increases $\text{Al}_{32}$-$\text{SO}_4^{2-}$ interactions in $\text{A}_{32}$. In contrast, the round shape means that $\text{Al}_{13}$-$\text{SO}_4^{2-}$ interactions are both limited relative to the $\text{Al}_{30}/\text{Al}_{32}$ beltway, and are also uniform throughout the $\text{Al}_{13}$ particle surface.

Figure 4.6. Induced charge density $\Delta \rho$ for sulfate adsorption for the $\text{B}_{13}$, $\text{A}_{32}$, and $\text{C}_{32}$ configurations. Adsorption causes electron flow from the regions bound by black isosurfaces to regions bound by yellow isosurfaces.
The shape-reactivity relationship supported by the DFT calculations can be represented by considering the $V_{el}$ as shown in Figure 4.7. The electrostatic potential for $Al_{13}$ is relatively uniform as a function of location on the particle surface while $Al_{30}$ and $Al_{32}$ show variation in $V_{el}$, with the most positive values in the beltway and the least positive values at the caps. The variations in $V_{el}$ therefore correlate with the relative values of $E_{rxn}$. We note that $V_{el}$ may be useful as a predictor of the relative strength and range of adsorption energies on differently shaped Al nanoclusters.

![Figure 4.7. Plots of $V_{el}$ mapped onto charge density isosurfaces of $Al_{13}$, $Al_{30}$, and $Al_{32}$. The electrostatic potential is positive throughout, with higher values shown in red and lower values shown in blue. For all three, the same scale is used and all three have a range of 16 eV.](image)

4.4 Conclusion

The DFT modeling of outer-sphere adsorption of $SO_4^{2-}/Cl^-$ on the surfaces of $Al_{13}$, $Al_{30}$, and $Al_{32}$ supports the existence of a shape-reactivity relationship in Al nanoclusters. Comparing the Al nanocluster reactivity to Al surfaces we see that the Al nanoclusters gives rise to unusually strong outer-sphere anion adsorption in the beltway of the larger Al Keggin nanoclusters. This demonstrates that the reactivity factors intrinsic to extended mineral-water interfaces do not translate to the molecular Keggin structures.
The shape-reactivity relationship may be of particular use in comparing adsorption trends on nanocluster sorbents of the same composition, but varying shape and size. Other aspects of the reactivity of Keggin clusters have been shown to depend on composition. The need for sustainable water remediation strategies is a driving force for ongoing efforts to fundamentally understand nanocluster reactivity and adsorption processes.

4.5 Acknowledgements

This work was supported by NSF grant CHE-1254127, and utilized computational resources provided by the University of Iowa College of Liberal Arts and Sciences.
5. ESTABLISHING TRENDS IN ION ADSORPTION ON THE AQUEOUS ALUMINUM HYDROXIDE NANOPARTICLE AL$_{30}$

From chapter 4 it is apparent that shape plays a significant role in reactivity. Even though there is a large reactivity range for Al$_{30}$ and Al$_{32}$, we choose to focus on the reactivity of Al$_{30}$ to better connect with experimental crystal structures in the following chapters. Our goals here are to better understand how the adsorbate properties govern interactions with Al$_{30}$ and to assess if generalizations can be formed. We test the reactivity of cations (Cu$^{2+}$, Pb$^{2+}$, Zn$^{2+}$) and anions (SO$_4^{2-}$, Cl$^-$) once again with aqueous Al$_{30}$ by using DFT modeling. It is determined that all the cations favor the adsorption sites on the caps of Al$_{30}$ and both anions favor outer-sphere adsorption in the beltway region. The results are once again explained using the electrostatic potential of Al$_{30}$ as well as the three-dimensional induced charge density mapping. This work is adapted with permission and was published as an invited paper for *Molecular Simulation* [Corum and Mason (2014) Establishing Trends in Ion Adsorption on the Aqueous Aluminium Hydroxide Nanoparticle Al$_{30}$, 41, 146-155]. Copyright 2014, Taylor & Francis.

5.1 Introduction

Aqueous aluminum hydroxide nanoparticles have been identified as effective sorbents of toxic heavy metals and oxyanions,$^{6,65}$ and are also regarded as ideal species for molecular geochemical models of environmental reactivity.$^7$ The aqueous aluminum hydroxide nanoparticle Al$_{30}$ (Al$_{30}$O$_8$(OH)$_{50}$(H$_2$O)$_{26}$)$^{18+}$ is known to have high reactivity due to the variety of exposed oxygen functional groups on the particle surface, and has been synthesized and characterized by many.$^{7,24,29,53,66}$ The geometry of Al$_{30}$ can be described as a Keggin-type molecular species synthesized from Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$$^{7+}$
(ε-Al_{13}) subunits (which are converted to δ-Al_{13} isomers upon aging or heating) and small Al monomer linkages. The ε-Al_{13} particles are also postulated to be the building blocks of amorphous aluminum oxyhydroxide flocculants responsible for contaminant transport in the environment. Adding to the interest in the reactivity of these aqueous aluminum nanoparticles is the fact that both Al_{13} and Al_{30} species have been shown to be effective and cost efficient sorbents for use in water remediation strategies.

The fundamental, geochemical, and applied interest in the reactivity of Al_{30} motivates molecular-level studies of its adsorption processes, though currently there are few such examples in the literature. An important question that we address here is whether the reactivity trends of Al_{30} towards cations and anions can be generalized. To this end, we model and compare inner-sphere adsorption of different aqueous cations (Pb^{2+}, Cu^{2+}, and Zn^{2+}) and, separately, the outer-sphere adsorption of different anions (SO_{4}^{2-} and Cl^{-}). The reason for studying inner-sphere adsorption for cations and outer-sphere adsorption for the anions is because the available experimentally determined structures for Al_{30} modified by contaminant cation adsorption and crystalized with anions exhibit these bonding motifs for the ions. We use DFT energetics and comparison of different adsorption geometries to determine the site preference of each ionic species on Al_{30}, and carry out electronic structure analysis to rationalize the results.

In order to form inner-sphere complexes, bonds are broken in the substrate and adsorbate, new bonds are formed between the substrate and the adsorbate, and the energy changes associated with the formation are strongly dependent on the details of the adsorption geometry. On the other hand, outer-sphere adsorption is based on electrostatic interactions and in general is described by a relatively smooth potential energy surface.
Thus, while it is straight-forward to generate models for outer-sphere adsorption in different starting geometries, designing structural models for inner-sphere adsorption involve choices in unique adsorption sites, variability in the number of bonds formed, and if or how the adsorbing functional groups deprotonate. As such, an exhaustive survey of all possible geometries is computationally prohibitive, and it is critical to constrain the modelling using experimental information. While there are only limited studies about the adsorption of ions onto Al₃₀, there is a relative wealth of information about surface complexes formed on hydrated mineral surfaces and powders. Therefore, in order to place a chemically-informed limit on the structural possibilities to be modelled in the present study, we consider literature results for how the cations included in this study bond to aluminum oxide surfaces.

Inner-sphere complexation of Pb²⁺ on aluminum oxides has been extensively studied by experiment.⁶⁸⁻⁷¹ Bargar *et al.* studied Pb²⁺ sorption onto alumina (α-Al₂O₃) powders. It was concluded that bidentate adsorption was the most plausible, with average Pb-O bond distances of 2.18-2.35 Å. When studying these powders it was found that Pb²⁺ would only bind to the AlO₆ octahedra and not the AlO₄ tetrahedra.⁶⁸ While aqueous lead has a large first coordination sphere,⁷²⁻⁷⁴ the bidentate adsorbed lead was shown to only have water molecules present at distances greater than 2.75 Å away from the surface complex. This is consistent with computational studies of Pb²⁺ adsorption onto alumina (001)⁶⁹ and (012)⁷⁵ surfaces that have been carried out, based on the experimental results of Bargar,⁶⁸ which show that the Pb²⁺ lone pair repels water ligands from bidentate inner-sphere complexes.
Cu$^{2+}$ surface complexation at alumina-water interfaces has also been characterized experimentally.\textsuperscript{76-79} Similarly to lead, copper has been found to bind in a bidentate fashion on alumina. Rudin and Motschi have shown that copper forms a pseudo square planar coordination when binding to δ-alumina.\textsuperscript{76} In this pseudo square planar configuration the equatorial Cu-O bond distances were estimated to be 2.0(1) Å while the axial Cu-O bond distances were estimated to be 2.6(1) Å.\textsuperscript{76} Some studies have found that when bound to alumina, Cu$^{2+}$ loses two of its water ligands and forms a square planar coordination only,\textsuperscript{79} so the existence of water ligands in the axial positions is up for debate. It can be concluded that Cu$^{2+}$ does retain two waters of hydration in its first coordination when bound in a bidentate fashion to octahedral Al in aluminum oxide surfaces. Similar adsorption details of Cu$^{2+}$ are demonstrated in the crystal structure of Cu$^{2+}$ bond onto Al$_3$O$_3$.

The geometry of Zn$^{2+}$ on alumina can vary based on the details of the surface and coverage. Trainor et al. have studied Zn$^{2+}$ adsorption on alumina powders comprised of α-Al$_2$O$_3$ and γ-Al$_2$O$_3$.\textsuperscript{80} For low surface coverage, Trainor et al. report a 4-fold coordination geometry, while at high Zn$^{2+}$ coverage a 6-fold coordination geometry is reported for monodentate or bidentate surface complexes,\textsuperscript{80} this means that zinc forms 1-2 bonds to the surface, while the remaining coordination is satisfied by water ligands. Six-coordinated zinc has a longer Zn-O distance of 2.08 Å compared to the 4-coordinated geometry Zn-O distance of 1.96 Å.

Based on the available information of adsorption on Al$_3$O$_3$ and experimental studies of alumina-water surface complexes, we constrain our modelling study to include bidentate adsorption of Pb$^{2+}$ and Cu$^{2+}$, and monodentate adsorption of Zn$^{2+}$ onto Al$_3$O$_3$. 
Using this knowledge of cation adsorption onto surfaces we model adsorbed Pb$^{2+}$ with no waters of hydration; Cu$^{2+}$ adsorbed with two waters of hydration, and adsorbed Zn$^{2+}$ with five waters of hydration. Later, the DFT optimized cation-oxygen bond distances on Al$_30$ are compared and discussed in terms of literature results of analogous distances in cations surface complexes on alumina.

5.2 Computational and Theoretical Methods

Structural geometry optimizations were carried out using DFT, with aqueous species embedded in the COSMO dielectric continuum model$^{27}$ as implemented in the DMOl$^3$ code developed by Delley.$^{25,26}$ Further details of the computational methods, electronic structure analyses, and benchmarking are reported in Chapter 3.$^{29}$

The aqueous forms of the three cations for which adsorption is modeled are shown in Figure 5.1. Specifically, Pb$^{2+}$(H$_2$O)$_6$, Cu$^{2+}$(H$_2$O)$_4$, and Zn$^{2+}$(H$_2$O)$_6$ hydrated cations are considered to be the cation sources, based on literature studies of these species.$^{72,81,82}$ Cation-water distances for the optimized geometries are provided in Table 5.1, and compared to literature modeling results. The optimized geometry for sulfate is also shown in Figure 5.1, and the S-O bond distances are tabulated and compared to literature results in Table 5.2.$^{83}$

Table 5.1. Average distances between cations and the oxygen atoms of the associated water ligands ($d(X - O_{H_2O})$) for geometry-optimized hydrated cations, in Å. Literature theoretical results are given in parentheses.

<table>
<thead>
<tr>
<th>Cation-Water Structure</th>
<th>$d(X - O_{H_2O})$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(H$_2$O)$_6$</td>
<td>2.659 (2.62$^{68}$)</td>
</tr>
<tr>
<td>Cu(H$_2$O)$_4$</td>
<td>1.953 (1.976$^{81}$)</td>
</tr>
<tr>
<td>Zn(H$_2$O)$_6$</td>
<td>2.150 (2.12$^{82}$)</td>
</tr>
</tbody>
</table>
Table 5.2. Calculated average sulfur-oxygen distance \((d(S-O))\) in \(\text{SO}_4^{2-}\), in Å. Literature theoretical results are reported in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>(d(S-O)) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SO}_4^{2-})</td>
<td>1.521 (1.495(^{83}))</td>
</tr>
</tbody>
</table>

Figure 5.1. The structures of four ions of interest in sorption to Al\(_{30}\). From left to right: Pb\(^{2+}\) with six bound waters, Cu\(^{2+}\) with four bound waters, Zn\(^{2+}\) with six bound waters and \(\text{SO}_4^{2-}\). Oxygen, aluminum, lead, copper, zinc, sulfur, and hydrogen are shown by red, blue, black, green, purple, orange, and gray spheres, respectively.

Experimentally, the hydrogen atoms of Al\(_{30}\) cannot be detected by X-ray characterization techniques, and therefore the protonation states of the functional groups are determined using empirical bond-valence analysis. This yields a chemical formula of \((\text{Al}_{30}\text{O}_{8}(\text{OH})_{58}(\text{H}_2\text{O})_{26})^{18+}\)). However, vibrational analysis of the geometry-optimized structure of Al\(_{30}^{18+}\) reveals instability. Guided by classical molecular dynamics simulations studying the theoretical titration of Al\(_{30}\),\(^{23}\) we consider Al\(_{30}^{16+}\) \((\text{Al}_{30}\text{O}_{8}(\text{OH})_{58}(\text{H}_2\text{O})_{24})^{16+}\)). The 16+ structures are formed by deprotonating symmetry equivalent H\(_2\)O groups. In some of the optimized Al\(_{30}^{16+}\) structures, there is a tendency to form bridging H\(_3\)O\(^-\) ligands, and this likely explains how the Al\(_{30}^{16+}\) structures can also satisfy bond-valence requirements.
The theoretical structures of Al\(_{30}\) have been compared with the Al\(_{30}\) crystal structures of Abeysinghe et al.\(^{20}\) Al\(_{30}\) has one tetrahedrally coordinated Al atom in each \(\delta\)-Al\(_{13}\) subunit. The bond distances between the tetrahedral Al and the four bound O atoms for Al\(_{30}\) are tabulated and compared to experiment in Table 5.3. As Table 5.3 shows, there is excellent structural agreement between the models used in the calculations and the precipitate from experiment.

Table 5.3. Al\(_{30}\) bond distances (in Å) from the tetrahedral Al to the four oxygen atoms compared to the experimental crystal structure. The labels of O\(_a\), O\(_b\), O\(_c\), and O\(_d\) represent the four oxygen atoms bound to the tetrahedral Al atom as defined in Ref\(^{20}\).

<table>
<thead>
<tr>
<th>Al-O(_x) O in tetrahedral Al</th>
<th>This work (Å)</th>
<th>Ref [20] (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_a)</td>
<td>1.860</td>
<td>1.837</td>
</tr>
<tr>
<td>O(_b)</td>
<td>1.811</td>
<td>1.782</td>
</tr>
<tr>
<td>O(_c)</td>
<td>1.814</td>
<td>1.774</td>
</tr>
<tr>
<td>O(_d)</td>
<td>1.810</td>
<td>1.796</td>
</tr>
</tbody>
</table>

5.2.1 Descriptions for structural models of inner-sphere and outer-sphere adsorption on Al\(_{30}\)

In order to designate distinct hypothetical adsorption sites for inner- and outer-sphere adsorption on Al\(_{30}\), the oxygen functional group categorization and labeling scheme of Rustad\(^{23}\) summarized in Figure 5.2, is used. We abbreviate the structures for inner-sphere cation adsorption-modified Al\(_{30}\) as \(X_2\)Al\(_{30}\) models, where \(X=\)Pb, Cu, or Zn, with the two cations of each structure adsorbed at symmetry-related sites on Al\(_{30}\). Likewise, we denote the structures of Al\(_{30}\) with outer-sphere anion adsorption as \(Z_2---\)Al\(_{30}\), where \(Z=\)SO\(_4^{2-}\) or Cl\(^{-}\).
Figure 5.2. Al$_{30}$O$_8$(OH)$_{56}$(H$_2$O)$_{26}^{18+}$ structure, with aluminum represented as blue polyhedra, showing the functional group categorization and labelling scheme of Rustad.$^{23}$ Copyright American Chemical Society 2013.

In order to form $X_2$Al$_{30}$, five Al$_{30}$ structures in a 16+ state were generated by deprotonating symmetry-equivalent 1, 2, 3, 4, and 5-ηH$_2$O groups in the 18+ structure, and all were optimized to yield stable structures as confirmed by vibrational analysis. First, we describe the structural models considered for the bidentate adsorption of Pb$^{2+}$ and Cu$^{2+}$, denoted as Pb$_2$Al$_{30}$ (Pb$_2$Al$_{30}$O$_8$(OH)$_{60}$(H$_2$O)$_{22}^{18+}$) and Cu$_2$Al$_{30}$ (Cu$_2$(H$_2$O)$_4$Al$_{30}$O$_8$(OH)$_{60}$(H$_2$O)$_{22}^{18+}$). Each of the four hypothetical Pb$_2$Al$_{30}$ and Cu$_2$Al$_{30}$ structures involves two inversion-symmetry related adsorption sites, and in order to accommodate bidentate adsorption modes, each adsorption site involves 2-ηH$_2$O groups. We label the four Pb$_2$Al$_{30}$ and Cu$_2$Al$_{30}$ structural models with inner-sphere (I) bidentate (B) adsorption as $A^{IB}$-$D^{IB}$, where the $A^{IB}$ model involves type 3/4-ηH$_2$O groups; the $B^{IB}$ model involves two type 1-ηH$_2$O groups; $C^{IB}$, type 2/4-ηH$_2$O groups; and $D^{IB}$, two type 5-ηH$_2$O groups. With the exception of the edge-sharing configuration in $D^{IB}$, all of the
structures have Pb$^{2+}$ and Cu$^{2+}$ attaching to Al$_{30}$ in a corner-sharing bidentate fashion. Schematics of the initial geometries for the bidentate inner-sphere adsorption models considered are shown in Figure 5.3.

![Figure 5.3](image)

Figure 5.3. Locations for inner-sphere monodentate (IM), inner-sphere bidentate (IB), and outer-sphere (O) adsorption onto Al$_{30}$ for the four geometries modelled. For all adsorption site categories, only one symmetry equivalent site is labelled in the figure.

The Zn$_2$Al$_{30}$ (Zn$_2$(H$_2$O)$_{10}$Al$_{30}$O$_8$(OH)$_{58}$(H$_2$O)$_{24}^{20+}$) structures have Zn$^{2+}$ binding in an inner-sphere (I) monodentate (M) fashion to a type 3-ηH$_2$O group (A$^{IM}$); a type 1-ηH$_2$O group (B$^{IM}$); a type 2-ηH$_2$O group (C$^{IM}$); and a type 5-ηH$_2$O group (D$^{IM}$). Schematics of the inner-sphere monodentate adsorption models are shown in Figure 5.3.

Four hypothetical (SO$_4$)$_2$---Al$_{30}$ ((SO$_4$)$_2$---Al$_{30}$O$_8$(OH)$_{58}$(H$_2$O)$_{24}^{12+}$) and Cl$_2$---Al$_{30}$ (Cl$_2$---Al$_{30}$O$_8$(OH)$_{58}$(H$_2$O)$_{24}^{14+}$) configurations with outer-sphere (O) anion adsorption were also designed, labeled as A$^O$ for A$^O$-D$^O$ and as shown schematically in Figure 5.3. Z$_2$—Al$_{30}$ model A$^O$ has the anion between the type 3/4-ηH$_2$O groups. The other hypothetical structures are defined as follows: B$^O$, anion between two type 1-ηH$_2$O
groups; C\textsuperscript{O}, anion between type 2/4-\eta\textsubscript{H}_2\textsuperscript{O} groups; and D\textsuperscript{O}, anion between two type 5-\eta\textsubscript{H}_2\textsuperscript{O} groups.

5.2.2 Reaction energy analysis approach for inner-sphere and outer-sphere adsorption on Al\textsubscript{30}

In order to determine the site preference for each adsorption system (inner-sphere cation adsorption and outer-sphere anion adsorption on Al\textsubscript{30}), we represent the formation of the final product using multi-step, stoichiometrically balanced chemical reaction schemes. DFT reaction energies, $E_{\text{rxn}}$, are then calculated for overall and mechanistic steps by using the total energy information for each reactant and product species, weighted by the appropriate stoichiometric coefficients.

The modeled formation of $X_2$Al\textsubscript{30} with bidentate cation adsorption is summarized in Scheme 5.1 using a three-step mechanism, while the formation of monodentate Zn\textsubscript{2}Al\textsubscript{30} is summarized in Scheme 5.2 using a two-step mechanism. In order to calculate values of $E_{\text{rxn}}$ for Schemes 5.1 and 5.2, the following molecular aqueous species were modeled: Al\textsubscript{30}$^{16+}$, Al\textsubscript{30}$^{14+}$ (Al\textsubscript{30}O\textsubscript{8}(OH)\textsubscript{60}(H\textsubscript{2}O)\textsubscript{22}$^{14+}$), Pb\textsuperscript{2+}(H\textsubscript{2}O)\textsubscript{2}, Cu\textsuperscript{2+}(H\textsubscript{2}O)\textsubscript{4}, Zn\textsuperscript{2+}(H\textsubscript{2}O)\textsubscript{6}, Pb\textsubscript{2}Al\textsubscript{30}, Cu\textsubscript{2}Al\textsubscript{30}, and Zn\textsubscript{2}Al\textsubscript{30}.

$$\text{Al}_{30}^{16+} + 2 \text{H}_2\text{O} \rightarrow \text{Al}_{30}^{14+} + 2 \text{H}_3\text{O}^+$$
$$2X^{2+}(\text{H}_2\text{O})_Y \rightarrow 2X^{2+}(\text{H}_2\text{O})_Y + W \text{H}_2\text{O}$$
$$\text{Al}_{30}^{14+} + 2X^{2+}(\text{H}_2\text{O})_Y \rightarrow X_2\text{Al}_{30}$$

Scheme 5.1. Three-step mechanism to form Pb\textsubscript{2}Al\textsubscript{30} or Cu\textsubscript{2}Al\textsubscript{30}. X refers to Pb or Cu and Y refers to the number of water molecules bound to the cation, six for Pb and four for Cu. V refers to the number of waters left bound to the cation, zero for Pb and two for Cu. W represents the number of water molecules broken off of the two cations, twelve for Pb and four for Cu.
\[2 \text{Zn}^{2+}(\text{H}_2\text{O})_6 \rightarrow 2 \text{Zn}^{2+}(\text{H}_2\text{O})_5 + 2 \text{H}_2\text{O}\]
\[\text{Al}_{30}^{16+} + 2 \text{Zn}^{2+}(\text{H}_2\text{O})_5 \rightarrow \text{Zn}_2\text{Al}_{30}\]

Scheme 5.2. Two-step mechanism to form \(\text{Zn}_2\text{Al}_{30}\).

A one-step mechanism is used to model the outer-sphere anion adsorption on \(\text{Al}_{30}\). In forming \((\text{SO}_4)_2\text{---Al}_{30}\) and \(\text{Cl}_2\text{---Al}_{30}\), \(\text{Al}_{30}\) interacts electrostatically with the anion species, as is summarized in Scheme 5.3. In order to simulate Scheme 5.3 the following molecular aqueous species were modeled: \(\text{Al}_{30}^{16+}, \text{SO}_4^{2-}, \text{Cl}^-, (\text{SO}_4)_2\text{---Al}_{30}\) and \(\text{Cl}_2\text{---Al}_{30}\).

\[\text{Al}_{30}^{16+} + 2 \text{anion} \rightarrow \text{anion}_2 \cdots \text{Al}_{30}\]

Scheme 5.3. One-step mechanism to form \((\text{SO}_4)_2\text{---Al}_{30}\) and \(\text{Cl}_2\text{---Al}_{30}\).

5.2.3 Electronic structure analysis

The electronic structure of the \(\text{Al}_{30}\)-based models was analyzed in terms of the adsorption-induced change rearrangements, or induced charge density \(\Delta \rho_Z\). \(\Delta \rho_Z\) was calculated for the fragmentation of \((\text{SO}_4)_2\text{---Al}_{30}\), and \(\text{Cl}_2\text{---Al}_{30}\) into constituent species to isolate specific bonding interactions and \(\Delta \rho_Z\) was calculated as \(\rho_{Z\cdots\text{Al}_{30}} - \rho_{\text{Al}_{30}} - \rho_Z\), where \(\rho_{Z\cdots\text{Al}_{30}}\) is the ground state charge density of the geometry optimized \(Z\cdots\text{Al}_{30}\) and \(\rho_{\text{Al}_{30}}\) is the ground state charge density of the geometry optimized \(\text{Al}_{30}\). Additionally, visualization of the electrostatic potential, \(V_{el}\), of \(\text{Al}_{30}\) was used to explain trends in DFT reactivity in terms of a governing physical property of the nanoparticle.
5.3 Results and Discussion

5.3.1 Pb$_2$Al$_{30}$ and Cu$_2$Al$_{30}$

We first discuss the geometry of bidentate cation adsorption to form Pb$_2$Al$_{30}$ or Cu$_2$Al$_{30}$. The most favorable optimized geometries for each correspond to the B$^{IB}$ model and are shown in Figure 5.4, while key bond distances are reported in Table 5.4. Comparing the cation-oxygen distances for our DFT calculations of X$_2$Al$_{30}$ to the above reviewed surface adsorption studies, we see that our Pb − O$_{Al_{30}}$ distances are within 0.12 Å with Pb − O$_{surface}$ distances.$^{68}$ For Cu our results are within 0.03 Å and 0.05 Å for the distance between Cu − O$_{Al_{30}}$ compared to reported results for Cu − O$_{surface}$ distances$^{76}$ and the experimental crystal structure of Cu$_2$Al$_{30}$.$^{29}$ Our results are within 0.01 Å and 0.03 Å for the distance between Cu − O$_{H_2O}$ compared with the same two studies.

Figure 5.4. Optimized structures of Pb$_2$Al$_{30}$ at the B$^{IB}$ site (left) and Cu$_2$Al$_{30}$ at the B$^{IB}$ site (right). Oxygen, aluminum, lead, copper, and hydrogen are shown by red, blue, black, green, and gray spheres, respectively.
Table 5.4. Bond distances (in Å) between experimental surface adsorption and DFT modelled nanoparticles. X(II)/Al$_2$O$_3$ labels results for the experimentally studied surface complexes as in References$^{68,76}$ while X$_2$Al$_{30}$ labels results for Pb$^{2+}$ or Cu$^{2+}$ adsorption on the Al$_{30}$ nanoparticle. The three distances in the table represent the average distance between the cations and adsorbing oxygen atoms on Al$_{30}$ ($d(X - O_{Al_{30}})$), the average distance between the cation and surface oxygen ($d(X - O_{surface})$), and the average distance between the cation and the oxygen atom of the adsorbed cation water ligands ($d(X - O_{H_2O})$).

<table>
<thead>
<tr>
<th>Average distances, (Å)</th>
<th>$d(X - O_{Al_{30}})$</th>
<th>$d(X - O_{surface})$</th>
<th>$d(X - O_{H_2O})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)/Al$_2$O$_3$$^{68}$</td>
<td>-----</td>
<td>2.18-2.35</td>
<td>-----</td>
</tr>
<tr>
<td>Pb$<em>2$Al$</em>{30}$ B$^{IB}$</td>
<td>2.301</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Cu(II)/Al$_2$O$_3$$^{76}$</td>
<td>-----</td>
<td>2.0(1)</td>
<td>2.0(1)</td>
</tr>
<tr>
<td>Cu$<em>2$Al$</em>{30}$-S$^{29}$</td>
<td>1.935</td>
<td>-----</td>
<td>1.988</td>
</tr>
<tr>
<td>Cu$<em>2$Al$</em>{30}$ B$^{IB}$</td>
<td>1.983</td>
<td>-----</td>
<td>2.022</td>
</tr>
</tbody>
</table>

Next we discuss the energetic results for the bidentate cation adsorption to form Pb$_2$Al$_{30}$ or Cu$_2$Al$_{30}$. The DFT step-wise and overall values for $E_{rxn}$ for the adsorption mechanism described in Scheme 5.1 are given in Table 5.5. Steps 1 and 2 of Scheme 5.1 are both bond breaking steps, with the first step involving deprotonation of the reactive functional groups of Al$_{30}$ and the second step involving waters of hydration breaking away from the cation. It is only Step 3 Scheme 5.1 that involves bond formation, and thus the values of $E_{rxn}$ are only negative for that step. While the overall values of $E_{rxn}$ for Scheme 5.1 are all positive, we note that the protonation state of Al$_{30}$ is pH dependent (thus under more basic conditions, Step 1 Scheme 5.1 may be unnecessary), and other aqueous sources of the cations may adsorb more readily than the fully hydrated species referenced by our schemes. Our main objective of determining the general trends in cation site preference on Al$_{30}$ is best explored through Step 3 Scheme 5.1, which shows that the B$^{IB}$ model for both X$_2$Al$_{30}$ species is preferred relative to the A$^{IB}$ model by 2.27 and 2.09 eV for Pb$^{2+}$ and Cu$^{2+}$, respectively. There are no energetics reported for the D$^{IB}$
structure since the intermediates to form $X_2Al_{30}$-$D^{IB}$ were found to be not stable. Overall, the results support the generalization of the fact that cation adsorption alone is preferred at sites away from the beltway, which conforms to the interpretation that $V_{el}$ is the most positive (and thus the most repulsive to cations) in the beltway.

Table 5.5. The stepwise and total DFT reaction energies $E_{rxn}$ for the formation of Pb$_2$Al$_{30}$ and Cu$_2$Al$_{30}$ as modelled using Scheme 5.1, reported in eV. Step 1 is the deprotonation of Al$_{30}^{16+}$ to Al$_{30}^{14+}$. Step 2 is the cation breaking bonds with its waters. Step 3 is the formation of $X_2Al_{30}$.

<table>
<thead>
<tr>
<th></th>
<th>Lead</th>
<th></th>
<th>Copper</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A$^{IB}$</td>
<td>B$^{IB}$</td>
<td>C$^{IB}$</td>
<td>A$^{IB}$</td>
</tr>
<tr>
<td>Step 1</td>
<td>1.37</td>
<td>3.03</td>
<td>2.19</td>
<td>Step 1</td>
</tr>
<tr>
<td>Step 2</td>
<td>7.20</td>
<td>7.20</td>
<td>7.20</td>
<td>Step 2</td>
</tr>
<tr>
<td>Step 3</td>
<td>-4.51</td>
<td>-6.78</td>
<td>-4.40</td>
<td>Step 3</td>
</tr>
<tr>
<td>Total</td>
<td>4.06</td>
<td>3.45</td>
<td>4.99</td>
<td>Total</td>
</tr>
</tbody>
</table>

Another trend that comes out of the values for $E_{rxn}$ in Scheme 5.1 to form Pb$_2$Al$_{30}$ and Cu$_2$Al$_{30}$ is that, for the cation adsorption step (Step 3 Scheme 5.1), Cu$^{2+}$ adsorption is much stronger than Pb$^{2+}$ adsorption at all modeled sites on Al$_{30}$ by at least 0.81 eV. While both Cu$^{2+}$ and Pb$^{2+}$ are modeled through the same mechanism and both form bidentate inner-sphere complexes to Al$_{30}$, a key difference is the number of water ligands in the adsorbed complex. While adsorbed Cu$^{2+}$ maintains two waters of hydration (as observed in the experimental crystal structure),$^{29}$ Pb$^{2+}$ satisfies its valence through the two bonds formed to Al$_{30}$. We tested the effect of adding molecular H$_2$O to the optimized Pb$_2$Al$_{30}$ structures, and the resulting Pb – O$_{H_2O}$ distances were at least 2.51 Å for three H$_2$O, compared to the average Cu – O$_{H_2O}$ distance of 2.02 Å. Also, while the valence configuration of Pb$^{2+}$ is $4f^{14}5d^{10}6s^2$, that of Cu$^{2+}$ is $3d^{9}$. Thus, while the adsorption mode and mechanism share similarities, the values of $E_{rxn}$ for Step 3 Scheme 5.1 do not offer a
direct comparison of cation reactivity. The significant difference in the magnitude of $E_{\text{rxn}}$ values for Pb$^{2+}$ and Cu$^{2+}$ in Step 3 Scheme 5.1 is explored using a Mulliken population analysis.\textsuperscript{47} We determine that the charge on the Pb atoms in Pb$_2$Al$_{30}$ has decreased to 1.385 charge units while the charge for Cu in Cu$_2$Al$_{30}$ has decreased to 0.734 charge units. Thus, we attribute the relative values of $E_{\text{rxn}}$ to the lower charge on copper due to the retention of water ligands.

\subsection*{5.3.2 Zn$_2$Al$_{30}$}

Like the other cations the most favorable Zn$_2$Al$_{30}$ structure was when Zn$^{2+}$ adsorbed in a monodentate fashion to the caps of Al$_{30}$ in model B$^{\text{IB}}$, as shown in Figure 5.5. The local adsorption geometry of Zn$_2$Al$_{30}$ was found to be in agreement with Zn$^{2+}$ alumina surface complex characterization experiments, with the reported average Zn$-$O$_{\text{Al}_{30}}$ and Zn$-$O$_{\text{H}_2\text{O}}$ distances both varying by 0.06 Å with the DFT structure of Zn$_2$Al$_{30}$.\textsuperscript{80,82}

![Figure 5.5. Optimized structure of Zn$_2$Al$_{30}$ at the B$^{\text{IB}}$ site. Oxygen, aluminum, zinc, and hydrogen are shown by red, blue, purple, and gray spheres, respectively.](image)
The adsorption of Zn$^{2+}$ is modeled through Scheme 5.2, a two-step mechanism. Step 1 Scheme 5.2 represents the bond breaking between the zinc and a water ligand. Step 2 Scheme 5.2 represents the cation adsorption onto Al$_{30}$. Step 2 Scheme 5.2 is only exothermic for structures B$^\text{IM}$ and D$^\text{IM}$, with B$^\text{IM}$ being the most exothermic. Again, cation adsorption at the caps (as in structure B$^\text{IM}$) is found to be preferred relative to adsorption in the beltway (structure A$^\text{IM}$), 1.06 eV. Table 5.6 contains the results for $E_{\text{rxn}}$ for all four structures.

Table 5.6. The stepwise and total DFT reaction energies $E_{\text{rxn}}$ for the formation of Zn$_2$Al$_{30}$, based on Scheme 5.2, in eV. Step 1 is the Zn breaking a bond with one water ligand and Step 2 is the formation of Zn$_2$Al$_{30}$.

<table>
<thead>
<tr>
<th>$E_{\text{rxn}}$ (eV)</th>
<th>A$^\text{IM}$</th>
<th>B$^\text{IM}$</th>
<th>C$^\text{IM}$</th>
<th>D$^\text{IM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>0.76</td>
<td>0.76</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>Step 2</td>
<td>0.18</td>
<td>-0.88</td>
<td>0.70</td>
<td>0.65</td>
</tr>
<tr>
<td>Total</td>
<td>0.94</td>
<td>-0.12</td>
<td>1.46</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Summarizing the results for all three cations bound to Al$_{30}$, a universal trend emerges: The caps are more favorable for cation adsorption, as rationalized by $V_{cl}$. When the cation adsorption steps of Scheme 5.1 and Scheme 5.2 are compared, the order of reactivity is ranked as Cu$^{2+}$ > Pb$^{2+}$ > Zn$^{2+}$. However, this trend is likely governed by differences in adsorption modes (bidentate for Cu$^{2+}$ and Pb$^{2+}$) and the number of cation-water bonds broken and maintained in forming the final surface complex as opposed to intrinsic cation properties.

5.3.3 (SO$_4$)$_2$---Al$_{30}$ and Cl$_2$---Al$_{30}$

As shown in Table 5.7, the Scheme 5.3 values for $E_{\text{rxn}}$ that model an outer-sphere anion adsorption onto Al$_{30}$ are exothermic in all cases, with site preference in the beltway.
region as shown for geometry optimized (SO₄)₂⁻ₐl₃₀ and for Cl₂₋ₐl₃₀ in Figure 5.6. In the most favorable optimized (SO₄)₂₋ₐl₃₀ structure the sulfate is 3.900 Å from Al₃₀ while Cl⁻ is 2.989 Å from Al₃₀. Details of the preferred adsorption sites differ between the two anions. The A⁰ and C⁰ structures are both in the beltway region, and from Table 5.7, sulfate adsorption is preferred in the C⁰ structure, while chloride adsorption is preferred in the A⁰ structure. The energetic preference of the C⁰ structure per adsorbed sulfate is 0.13 eV relative to the A⁰ structure, while preference per chloride in the A⁰ structure is 0.16 eV relative to the C⁰ structure. Thus, the preference for one beltway site over the other is relatively small for both anions. It is worth noting that the C⁰ structure for Cl₂₋ₐl₃₀ started with an initial geometry of the Cl⁻ ions between the type 2/4-ηH₂O but optimized in a final geometry between the type 3/4-ηH₂O which is similar to the A⁰ structure. On the other hand the difference between reactivity at the caps compared to the beltway is relatively large for both anions. For sulfate adsorption the difference between adsorption in beltway geometry A⁰ configuration is preferred by 2.18 eV over adsorption in the cap geometry the B⁰. For chloride, the preference of the A⁰ structure over the B⁰ structure is 2.53 eV.

Table 5.7. The reaction energies $E_{rxn}$ for the formation of Z₂₋ₐl₃₀, derived from Scheme 5.3, in eV.

<table>
<thead>
<tr>
<th>$E_{rxn}$ (eV)</th>
<th>A⁰</th>
<th>B⁰</th>
<th>C⁰</th>
<th>D⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>-3.93</td>
<td>-1.75</td>
<td>-4.19</td>
<td>-3.78</td>
</tr>
<tr>
<td>Cl</td>
<td>-3.78</td>
<td>-1.25</td>
<td>-3.46</td>
<td>-2.46</td>
</tr>
</tbody>
</table>
Figure 5.6. Optimized structure of \((\text{SO}_4)_2\text{---Al}_{30}\) at the \(\text{C}^0\) site (left) and \(\text{Cl}_2\text{---Al}_{30}\) at the \(\text{A}^0\) site (right). Oxygen, aluminum, sulfur, chlorine and hydrogen are shown by red, blue, orange, bright green, and gray spheres, respectively.

A deeper understanding of why anion adsorption is preferred in the beltway is obtained by studying the anion adsorption-induced charge density \(\Delta \rho_Z\), shown for the \(\text{A}^0\) and \(\text{B}^0\) models of \((\text{SO}_4)_2\text{---Al}_{30}\) and \(\text{Cl}_2\text{---Al}_{30}\) in Figure 5.7. A clear contrast in \(\Delta \rho\) between the \(\text{A}^0\) and \(\text{B}^0\) structures for each anion is that in the \(\text{A}^0\) structures there are more numerous and larger isosurfaces than in the \(\text{B}^0\) structures. We qualitatively interpret the larger and more numerous \(\Delta \rho\) surfaces when anions adsorb in the beltway as being due to a greater extent of electrostatic interactions between the anion and the functional groups of \(\text{Al}_{30}\) in this geometry. Chemically speaking, the exposed functional groups in the semi-pore of the \(\text{Al}_{30}\) beltway exhibit a collective electrostatic interaction with anions in this region of the molecule, while the lack of concavity at the caps limits the extent of anion-\(\text{Al}_{30}\) interaction.
Figure 5.7. Induced charge densities of the most (C$^O$ for sulfate and A$^O$ for chloride) and least favorable (B$^O$ for both) anion adsorption geometries onto Al$_{30}$ structure. Yellow isosurfaces show where charge gained and black isosurfaces show where charge lost. To better show the isosurfaces, bonds and H atoms are not shown. Oxygen, aluminum, sulfur, and chlorine are shown by red, blue, orange, and bright green spheres, respectively.

5.4 Conclusion

After analysis of the various $X_2$Al$_{30}$ and $Z_2$---Al$_{30}$ structures there is consistent evidence for the preference of inner-sphere cation adsorption onto the caps and outer-sphere anion adsorption to the beltway of Al$_{30}$. The electronic structure results explain the distinct structure-reactivity relationships for the cation and anion adsorption sites of Al$_{30}$. Given that the explanation for the topology-dependent site preference trends of cations and anions depend on the existence of semi-pore regions in the Al$_{30}$ beltway, we predict that other aluminum hydroxide nanoparticles, such as Al$_{13}$ (which has no semi-pore) and Al$_{32}$ ((Al(IDA)H$_2$O)$_2$(Al$_{30}$O$_8$(OH)$_{60}$(H$_2$O)$_{22}$)$^{16+}$) (where IDA stands for iminodiacetic acid), in which the semi-pore is partially filled in with additional Al will not exhibit the same trends.
An important continuation of this work would be to model inner-sphere anion adsorption. In this study and our previous study anion adsorption has solely been outer-sphere adsorption, which is thought to be important to the crystallization process of Al$_{30}$. However, inner-sphere anion adsorption is reported for some Keggin-based aluminum polycations. While outer-sphere adsorption is strongly influenced by the collective electrostatics of functional groups in the semi-pore of Al$_{30}$, inner-sphere anion adsorption may be influenced by other properties of the molecule. We also see an opportunity to better understand how adsorption mechanisms vary between true nanoparticles such as Al$_{30}$ and other geochemical surface models such as mineral-water interfaces. Computational studies may be an ideal means for comparing these reactivities, and may lead to more cohesive theories of ion adsorption to environmental interfaces.

5.5 Acknowledgements

KWC acknowledges the University of Iowa Center for Global and Regional Environmental Research for financial support. SEM acknowledges the University of Iowa College of Liberal Arts and Sciences for partial funding of this work. Both authors thank Prof. Tori Z. Forbes and the Forbes Research Group at the University of Iowa for collaborations and insightful research discussions.
6. CONTAMINANT ADSORPTION ON NANOSCALE PARTICLES: STRUCTURAL AND THEORETICAL CHARACTERIZATION OF CU$^{2+}$ BONDING ON THE SURFACE OF KEGGIN TYPE POLYALUMINUM (AL$_{30}$) MOLECULAR SPECIES

An Al$_{30}$ Keggin-type species with two surface-bound Cu$^{2+}$ cations (Cu$_2$Al$_{30}$-S) has been crystallized in the presence of disulfonate anions and structurally characterized by single-crystal X-ray diffraction. DFT calculations of aqueous molecular analogs for Cu$_2$Al$_{30}$-S suggest that the reactivity of Al$_{30}$ towards Cu$^{2+}$ and SO$_4^{2-}$ follows the opposite reaction trends as discussed in Chapter 5 but the associated DFT energetics and charge density analyses suggest that strong electrostatic interactions between SO$_4^{2-}$ and the beltway of Al$_{30}$ play a vital role in governing where Cu$^{2+}$ binds in the presence of sulfate ions. This collaboration with Prof. Tori Z. Forbes group is adapted with permission from "Langmuir" [Abeysinghe, Corum, Neff, Mason, and Forbes (2013) Contaminant Adsorption on Nanoscale Particles: Structural and Theoretical Characterization of Cu$^{2+}$ Bonding on the Surface of Keggin-Type Polyaluminum (Al$_{30}$) Molecular Species. 29, 14124-14134]. Copyright 2013, American Chemical Society.

6.1 Introduction

Poorly-crystalline iron and aluminum oxyhydroxide nanoparticles with Keggin-type structural features are considered some of the most effective materials for adsorption of toxic heavy metals, radionuclides, and oxyanions. Ferrihydrite is a nanomineral that is ubiquitous in environmental systems and an effective scavenger for a wide range of contaminants. The structure of ferrihydrite has recently been the subject of debate within the literature, but a majority of the current evidence points to a topology with similarities
to the mineral akdalaite (Al$_{10}$O$_{14}$(OH)$_2$). This proposed core structure contains 20% tetrahedrally and 80% octahedrally coordinated iron with topological similarities to Keggin-type molecular species. Polyaluminum Keggin-type clusters, such as the ε-Al$_{13}$, have also been identified as the building blocks of amorphous aluminum oxyhydroxide flocculants that precipitate from streams impacted acid mine drainage and are widely used as adsorbent in water treatment applications. Several previous studies have demonstrated that the one nm ε-Al$_{13}$ clusters perform better than alum (KAl(SO$_4$)$_2$•nH$_2$O) in clarifying potable water sources, but chemical agents containing the two nm Keggin-type Al$_{30}$ species improves the removal efficiency of contaminants over a broader dosage and pH range.

While the adsorptive capabilities of Keggin-type metal oxyhydroxides have been established, identification of specific reactivity factors and mechanistic understanding of the process is lacking. The surface features of poorly-crystalline nanominerals, such as 2-line ferrihydrite, are difficult to study by traditional X-ray and spectroscopic techniques due to lack of long range ordering within the material. However, the use of geochemical model compounds provides a unique means to investigate adsorption at the molecular level. Polyaluminum Keggin-type species are an ideal experimental system because they form well-defined species that are between 1-2 nm in diameter that have been extensively characterized over the past 50 years. These species can be ordered into three-dimensional crystalline arrays that can be characterized using X-ray diffraction, providing concrete structural information regarding binding modes of the contaminant. The resulting experimental structures comprise a basis for atomistic simulations,
providing an opportunity to investigate mechanistic details of contaminant adsorption onto nanoparticulate surfaces.

We have recently begun a combined experimental and theoretical investigation on nanoscale Keggin-type clusters as a starting point for developing a molecular-level understanding of contaminant adsorption on small metal oxyhydroxide nanoparticles. Our initial study focuses on the adsorption of Cu$^{2+}$ on the surface of Keggin-type polyaluminum species. Of the various heavy metal contaminants, Cu$^{2+}$ is of particular interest as it is a constituent of widely used fungicides, pesticides, and algacides.$^{89,90}$ Herein, we have provided the synthesis and structural characterization of a Keggin-type Al$_{30}$ molecule with two surface-bound Cu$^{2+}$ atoms (Cu$_2$Al$_{30}$-S) and explored the adsorption process through of density functional theory (DFT) studies.

6.2 Experimental Methods

6.2.1 Synthesis of Cu$_2$Al$_{30}$

A stock solution of the partially hydrolyzed aluminum solution was prepared by heating a 25 mL of 0.25 M AlCl$_3$ (6.25 mmol) solution to 80 °C in a water bath, followed by dropwise addition of 60 mL of 0.25 M NaOH (6.25 mmol) to a hydrolysis ratio (OH$^-$/Al$^{3+}$) of 2.4. Seven mL of the cooled Al$_{13}$ stock solution was mixed with 0.0349 g of Trizma base buffer and 0.0382 g of CuCl$_2$. The resulting dark blue solution was stirred for 20 minutes to allow for complete dissolution of the starting materials and loaded into a 23-mL Teflon-lined Parr reaction vessel. This solution was heated to 80 °C in a gravimetric oven for 24 hours, cooled slowly to room temperature, and transferred to a glass scintillation vial. Three mL of a 0.1 M 2,6-napthalene disulfonate (2,6-NDS)
solution was added as a crystallization agent and after 14 days of slow evaporation at room temperature, light-blue crystalline blades formed on the bottom of the reaction vial.

6.2.2 Structural characterization

Suitable crystals were separated from the mother liquor, coated in Infinium oil, and mounted on a Nonius Kappa CCD single crystal X-ray diffractometer equipped with Mo Kα radiation (λ = 0.7107 Å) and a low temperature cryostat. Data collection, cell refinement, data reduction and absorption corrections were performed using Collect\textsuperscript{91} and APEX II\textsuperscript{92} software. The structure was solved using direct methods and refined on the basis of F\textsuperscript{2} for all unique data using the Bruker SHELXTL version 6.10 programs.\textsuperscript{93} Al, S, and Cu atoms were located in the direct methods solution and the O and C atoms were identified in the difference Fourier maps calculated following refinement of the partial-structure models. Selected data collection parameters are given in Table 6.1.

Table 6.1. Selected Crystallographic information for Cu\textsubscript{2}Al\textsubscript{30}-S.

| a (Å) | 18.323(5) | μ (mm\textsuperscript{-1}) | 0.471 |
| b (Å) | 18.469(5) | F(000) | 2798 |
| c (Å) | 24.985(8) | Crystal Size (mm) | 0.192 x 0.18 x 0.095 |
| α (°) | 73.966(10) | Theta range | 1.48 to 25.06° |
| β (°) | 80.078(10) | Data collected | -21<h<21, -21<k<21, -29<l<29 |
| γ (°) | 62.392(9) | Completeness to theta = 26.07° | 99.2% |
| V (Å\textsuperscript{3}) | 7191(4) | Reflections collected/unique | 135761 / 25292 |
| Z | 1 | GOF on F\textsuperscript{2} | 1.082 |
| FW(gmol\textsuperscript{-1}) | 6218.5 | Final R indices [I> 2σ(I)] | R\textsubscript{1} = 0.0818, wR\textsubscript{2} = 0.2456 |
| Space Group | P-1 | R indices (all data) | R\textsubscript{1} = 0.1025, wR\textsubscript{2} = 0.2634 |
| \(ρ\textsubscript{calc} \text{ (g/cm}^3\text{)}\) | 1.291 | Largest peak and hole (Å\textsuperscript{3}) | 2.141 and -1.077 |
Cu$_2$Al$_{30}$-S crystallized in the triclinic space group $P-1$ with $a = 18.323(5)$ Å, $b = 18.469(5)$ Å, $c = 24.985(8)$ Å, $\alpha = 73.966(10)^\circ$, $\beta = 80.078(10)^\circ$, and $\gamma = 62.392(9)^\circ$. H atoms associated with the naphthalene rings of the disulfonate anion were constrained using a riding model. Disorder was present for several of the 2,6-NDS anions due to free rotation about the S-C bond; therefore, O atoms associated with the sulfonate functional group (O52, O53, O55, and O74) were modeled as split sites with 50% occupancy. The presence of large void space (2113 Å$^3$) within the crystalline lattice also resulted in the presence of disordered solvent (water) molecules. This diffuse electron density was modeled using the SQUEEZE command in the PLATON software,$^{94}$ reducing the $R_1$ value from 11.89% to 8.8% and accounting for 1090 electrons within the cavity.

6.2.3 Computational methodology

To better understand how the observed Cu$_2$Al$_{30}$ solid structure is formed, aqueous Al$_{30}$ and several Cu$_2$Al$_{30}$ models were simulated using DFT and the COSMO dielectric continuum model$^{27}$ as implemented in the DMol$^3$ code developed by Delley.$^{25,26}$ An aperiodic structural model for Al$_{30}$O$_8$(OH)$_{56}$(H$_2$O)$_{26}$$^{18+}$ based on the periodic geometry was generated using a simple bond-valence analysis relying on literature parameters$^{95}$ to determine the protonation states of the oxygen functional groups. The bond-valence analysis was compared to, and matched, the Al$_{30}$ description of Casey et al.,$^{95}$ which details the functional groups present in Al$_{30}$ as 26 bound water groups (ηH$_2$O) and 56 bridging hydroxyl groups ($\mu_i$OH, where i can be 2 or 3 for double or triple O-Al coordination). Aperiodic all-electron spin-polarized DFT calculations were performed using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)$^{42}$ with a double-numeric-plus polarization atom-centered basis set. A real-space basis set
cutoff of 3.5 Å was used for efficiency, and did not have a significant effect on total energies, reaction energies, or the magnitude of forces. For geometry optimizations, each system was embedded in the COSMO model such that the calculated gradients include forces between the solute and screening charges. All structures were fully optimized until an energy tolerance of 0.003 eV was obtained, which resulted in an average residual force magnitude of 0.0020 eV/Å on aluminum and oxygen atoms or 0.0005 eV/Å on hydrogen atoms.

The oxygen functional group categorization and labeling scheme of Rustad, summarized in Figure 6.1, is used to describe our Al₃₀ and Cu₂Al₃₀ models. A vibrational analysis of the final 18+ structure revealed a negative frequency >1000 cm⁻¹, and inducing the associated normal mode produced atomic displacements which effectively separated the Al₃₀ into two pieces. As it is reported that acidic ηH₂O sites can deprotonate to form Al₃₀ in the 16+ state at modeled circum-neutral conditions, the stability of different 16+ configurations of Al₃₀ was considered. Five Al₃₀ structures in a 16+ state, denoted Al₃₀¹⁶⁺, were generated by deprotonating symmetry-equivalent 1, 2, 3, 4, and 5-ηH₂O groups in the 18+ structure, and all optimized to yield stable structures as confirmed by vibrational analysis. Similar to what is reported for classical molecular dynamics simulations of Al₃₀, deprotonation of 2-ηH₂O or 3-ηH₂O sites the resulting in OH groups pairing with a neighboring 4-ηH₂O groups to form bridged H₃O⁻ ligands as shown in Figure 6.2.
Figure 6.1. $\text{Al}_{30}\text{O}_{8}(\text{OH})_{56}(\text{H}_{2}\text{O})_{26}^{18+}$ ($\text{Al}_{30}$) structure (left), with aluminum represented as blue polyhedral, showing functional group categorization and labeling scheme of Rustad. $\text{Al}_{30}$ structure showing the tetrahedral aluminum in dark blue bound to four (a, b, c, and d) oxygen atoms (right).

Figure 6.2. Optimized geometries of different configurations for $\text{Al}_{30}$ in the 16+ state. From left to right structure correspond to the deprotonation of 1-\text{H}_2\text{O} through 5-\text{H}_2\text{O}. In the deprotonation of 2-\text{H}_2\text{O} and 3-\text{H}_2\text{O}, the resulting OH group a hydrogen bond from a nearby 4-\text{H}_2\text{O} group, labeled, to form $\text{H}_3\text{O}_2^+$ bridges, indicated with dashed lines. The color scheme for the Al, O, and H atoms are blue, red, and gray, respectively. Atom labeling scheme is consistent throughout.

Details of the optimized geometries of the five $\text{Al}_{30}^{16+}$ models are presented in Table 6.2, and the structures are shown in Figure 6.2. Following in the style of Yang et
Table 6.2 reports the distances between the tetrahedral aluminum and the four oxygen atoms to which it is bound, using a labeling scheme defined in Figure 6.1. Excellent agreement between Al$_{30}^{16+}$ structures modeled with the two computational methods discussed in Chapter 3 is achieved.

Table 6.2. Details of experimental and theoretical Al$_{30}$ geometries in terms of the tetrahedral Al-O distances. The oxygen labeling scheme is shown in Figure 6.1.

<table>
<thead>
<tr>
<th>Al-O$_x$ O on tetrahedral Al (Å)</th>
<th>O$_a$</th>
<th>O$_b$</th>
<th>O$_c$</th>
<th>O$_d$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitated out of solution (Expt.)</td>
<td>1.837</td>
<td>1.782</td>
<td>1.774</td>
<td>1.796</td>
<td>1.797</td>
</tr>
<tr>
<td>1</td>
<td>1.885</td>
<td>1.804</td>
<td>1.809</td>
<td>1.801</td>
<td>1.823</td>
</tr>
<tr>
<td>2</td>
<td>1.867</td>
<td>1.811</td>
<td>1.810</td>
<td>1.817</td>
<td>1.826</td>
</tr>
<tr>
<td>3</td>
<td>1.857</td>
<td>1.812</td>
<td>1.809</td>
<td>1.813</td>
<td>1.823</td>
</tr>
<tr>
<td>4</td>
<td>1.860</td>
<td>1.811</td>
<td>1.814</td>
<td>1.810</td>
<td>1.824</td>
</tr>
<tr>
<td>5</td>
<td>1.870</td>
<td>1.805</td>
<td>1.814</td>
<td>1.810</td>
<td>1.825</td>
</tr>
</tbody>
</table>

As the synthesis of Cu$_2$Al$_{30}$-S involves charge balancing with a complexing agent, bonding competition between aqueous cations and anions was considered in the adsorption modeling. Different pathways from common starting reactants to end products were proposed, as summarized in Schemes 6.1 and 6.2. DFT reaction energies for theoretical mechanistic steps, $E_{\text{rxn}}$, were calculated by using total energy information for each reactant and product species, weighted by the appropriate stoichiometric coefficients.

$$\text{Al}_{30}^{16+} + 2 \text{H}_2\text{O} \rightarrow \text{Al}_{30}^{14+} + 2 \text{H}_3\text{O}^+$$
$$\text{Al}_{30}^{14+} + 2 \text{Cu}^{+2}(\text{H}_2\text{O})_4 \rightarrow \text{Cu}_2\text{Al}_{30} + 4\text{H}_2\text{O}$$
$$\text{Cu}_2\text{Al}_{30} + 2 (\text{SO}_4)^{2-} \rightarrow \text{Cu}_2(\text{SO}_4)_2\text{Al}_{30}$$

Scheme 6.1. Formation of Cu$_2$(SO$_4$)$_2$Al$_{30}$ by Al$_{30}^{16+}$ activation (step 1), inner-sphere adsorption of Cu(II) (step 2), followed by outer-sphere adsorption of sulfate (step 3).
\[ \text{Al}_{30}^{16+} + 2 \left( \text{SO}_4^{2-} \right) \rightarrow \left( \text{SO}_4 \right)_2\text{Al}_{30}^{12+} \]
\[ \left( \text{SO}_4 \right)_2\text{Al}_{30}^{12+} + 2 \text{H}_2\text{O} \rightarrow \left( \text{SO}_4 \right)_2\text{Al}_{30}^{10+} + 2 \text{H}_3\text{O}^+ \]
\[ \left( \text{SO}_4 \right)_2\text{Al}_{30}^{10+} + 2 \text{Cu}^{2+} \left( \text{H}_2\text{O} \right)_4 \rightarrow \text{Cu}_2\left( \text{SO}_4 \right)_2\text{Al}_{30} + 4\text{H}_2\text{O} \]

Scheme 6.2. Formation of \( \text{Cu}_2\left( \text{SO}_4 \right)_2\text{Al}_{30} \) proceeding by outer-sphere adsorption of 2 \( \text{SO}_4^{2-} \) anions by \( \text{Al}_{30} \) \( 16^+ \) (step 1), followed by activation of \( \left( \text{SO}_4 \right)_2\text{Al}_{30} \) (step 2), and ending with inner-sphere adsorption of \( \text{Cu}(II) \).

In order to simulate Schemes 6.1 and 6.2, the following \( \text{Al}_{30} \)-based molecular aqueous species were modeled: \( \text{Al}_{30}^{16+}, \text{Al}_{30}^{14+}, \left( \text{SO}_4 \right)_2\text{Al}_{30} \) (with a net charge 12+ or 10+), \( \text{Cu}_2\text{Al}_{30} \) (net charge 18+), and \( \text{Cu}_2\left( \text{SO}_4 \right)_2\text{Al}_{30} \) (net charge 14+). A key difference between the modeled species and the experimental structure is the identity of the anion, which serves to charge-balance and aid in the crystallization of the synthesis product. The rationale for including two \( \text{SO}_4^{2-} \) anions in the simulations as opposed to fully modeling all nine of the 2,6-NDS anions of the crystal structure was based on a compromise between model tractability and a physically sufficient representation of the synthesis experiment. Due to the possibility of conjugated ring-\( \text{Al}_{30} \) interactions, plus the higher computational cost of the greater number of atoms involved, simulations with 2,6-NDS were deemed prohibitive. The approximate aqueous analog to the crystal structure was instead built by considering that in the solid hydrate, each adsorbed \( \text{Cu}^{2+} \) is associated with one sulfonate functional group. The model developed for the final product, denoted \( \text{Cu}_2\left( \text{SO}_4 \right)_2\text{Al}_{30} \), has one explicit \( \text{SO}_4^{2-} \) group for each bound \( \text{Cu}^{2+} \). Mechanistically, sulfate addition was modeled as occurring after (Scheme 6.1) or before (Scheme 6.2) \( \text{Cu}^{2+} \) adsorption. Based on the crystal structure, \( \text{SO}_4^{2-} \) is assumed to have an outer-sphere relationship to the \( \text{Al}_{30} \), with one oxygen atom in an axial position relative to adsorbed \( \text{Cu}^{2+} \), and these details are reproduced in the theoretical structures.
To form a basis of comparison, several hypothetical Cu$_2$Al$_{30}$ and (SO$_4$)$_2$Al$_{30}$ configurations were designed, starting from each of the five Al$_{30}^{16+}$ structures. The model (SO$_4$)$_2$Al$_{30}$, Cu$_2$Al$_{30}$, and Cu$_2$(SO$_4$)$_2$Al$_{30}$ configurations are labeled in terms of the functional groups that form inner-sphere bonds to copper. Bidentate adsorption of Cu$^{2+}$ groups at inversion symmetry-related sites was modeled in configurations involving distinct pairs of Al$_{30}$ functional groups. The model that reflects the experimental structure, labeled as A, has Cu$^{2+}$ reacting with type 3- and 4-$\eta$H$_2$O groups. The remaining hypothetical structures are defined as follows: B, two type 1-$\eta$H$_2$O groups; C, type 2- and 4-$\eta$H$_2$O groups; and D, two type 5-$\eta$H$_2$O groups. While considered unlikely due to the need to activate the Al$_{30}$ through deprotonation, for completeness two Cu$_2$Al$_{30}$ structures that bind copper through $\eta_2$OH groups (as opposed to $\eta$H$_2$O groups) were also modeled but the resulting total energies of the optimized Cu$_2$Al$_{30}$ structures were over one eV higher than the experimental crystal structure and will not be further discussed. With the exception of the edge-sharing configuration in D, all of the structures have Cu(II) attaching to Al$_{30}$ in a corner-sharing bidentate fashion. The A and C configurations bind copper through two types of $\eta$H$_2$O groups, which could result from either of two starting 16+ structures, and only the lowest energy results are reported.

The electronic structure of the Al$_{30}$-based models was analyzed in terms of the adsorption-induced change rearrangements, or induced charge density $\Delta \rho$. $\Delta \rho$ was calculated for different fragmentations of Cu$_2$Al$_{30}$ or Cu$_2$(SO$_4$)$_2$Al$_{30}$ to isolate specific bonding interactions. Additionally, visualization of the electrostatic potential, $V_{el}$, of Al$_{30}$ was used to explain trends in DFT reactivity in terms of a governing physical property of
the nanoparticle. Mulliken population analysis\textsuperscript{47} was also used in explaining reactivity trends in terms of charge transfer.

\textbf{6.3 Results and Discussion}

\textbf{6.3.1 Structural description}

The core feature of the Cu\textsubscript{2}Al\textsubscript{30}-S compound is the Al\textsubscript{30} polynuclear species, which is built upon two smaller Keggin-type \(\delta\)-Al\textsubscript{13} moieties (Figure 6.3). Polyaluminum Al\textsubscript{13} clusters possessing Keggin topologies are composed of a central tetrahedrally coordinated Al\textsuperscript{3+} cation surrounded by twelve octahedrally coordinated Al atoms. These twelve aluminum polyhedra are arranged into four planar \([\text{Al}_3(\mu_2\text{-OH})_6(\text{H}_2\text{O})_3]\) trimers through edge sharing of hydroxyl groups and link to the tetrahedrally coordinated Al\textsuperscript{3+} cation through four \(\mu_4\)-O atoms. Bond lengths for the Al(O)\textsubscript{4} tetrahedron range from 1.775(3) to 1.837(3) Å and slightly longer distances (1.811(3) to 2.073(3) Å) are observed for the octahedrally coordinated Al\textsuperscript{3+} cations. From these components, five Al\textsubscript{13} isomers can be constructed and are delineated by the number of hydroxyl edges shared between the trimeric units. The \(\varepsilon\)-Al\textsubscript{13} isomer dominates in the initial partially-hydrolyzed aluminum solution used in the synthesis of Cu\textsubscript{2}Al\textsubscript{30}-S and contains edge-sharing between all four of the \([\text{Al}_3(\mu_2\text{-OH})_6(\text{H}_2\text{O})_3]\) trimers. Upon heating, the \(\delta\)-Al\textsubscript{13} isomer is created when one trimer rotates by 60°, resulting in the transformation of the hydroxyl edges into six shared vertices. The larger Al\textsubscript{30} species is then formed when two meta-stable \(\delta\)-Al\textsubscript{13} moieties are linked by four additional octahedrally coordinated Al\textsuperscript{3+} cations.
Figure 6.3. Structural characterization of the Cu$_2$Al$_{30}$-S compound reveals two Cu$^{2+}$ cations in a square planar configuration bonded to the Keggin-type Al$_{30}$ cation on either side of the central beltway. An additional water molecule and the sulfonate group of the 2,6-NDS anion are positioned approximately 2.6 Å away from the metal center. The color scheme for the Cu, Al, S, O, C, and H atoms are green, blue, orange, red, black and gray, respectively. Atom labeling scheme is consistent throughout.

Two Cu$^{2+}$ cations are also bonded to the Al$_{30}$ species in a bridging bidentate configuration to create the Cu$_2$Al$_{30}$-S polynuclear species. The Cu$^{2+}$ atoms are located on opposite sides of the central beltway region of the cluster and share two hydroxyl groups with two neighboring octahedrally coordinated Al$^{3+}$ cations. Bond lengths for the Cu$^{2+}$-$\mu_2$-OH bridges are 1.921(3) and 1.948(3) Å and two additional water molecules form bonds at 1.969(4) and 2.007(4) Å, resulting in a square planar geometry about the metal center. An additional water molecule and an O atom associated with a sulfonate functional group of the 2,6-NDS molecule are positioned 2.571 and 2.589 Å above and below Cu$^{2+}$ cation, suggesting the formation of a distorted octahedron. These bond lengths imply the presence of Jahn-Teller distortions, which are commonly observed in Cu$^{2+}$ species owing to the $d^9$ configuration of the metal. Compounds with elongated axial Cu-O bonds have previously been reported in the literature with distances ranging
between 2.1 to 2.7 Å, but the presence of orbital interactions between the metal center and ligand have not been confirmed computationally.\textsuperscript{32-37} The overall Cu\textsubscript{2}Al\textsubscript{30}-S polynuclear species is approximately two nanometers in diameter and possesses an 18+ formal charge based upon structural characterization of the compound.

Crystallization of the Cu\textsubscript{2}Al\textsubscript{30}-S species occurs through charge balancing with nine 2,6-NDS anions and hydrogen bonding between the deprotonated oxygen on disulfonate anions and the hydrogen atoms of the OH and H\textsubscript{2}O molecules of the aluminum polycations. The O-H…O distances associated with hydrogen bonding range between 2.66-2.87 Å and additional π-π interactions may also aid in crystallization, as the naphthalene rings of the 2,6-NDS molecules are separated by approximately 3.5 Å. Solvent water molecules are also present in the void spaces, forming additional hydrogen bonds with the aluminum polycations and 2,6-NDS anions. The exact amount of water present in the structure was verified by thermogravimetric analysis, resulting in a final composition of [Cu(H\textsubscript{2}O)\textsubscript{2}Al\textsubscript{2}O\textsubscript{8}Al\textsubscript{28}(OH)\textsubscript{60}(H\textsubscript{2}O)\textsubscript{22}](2,6-NDS)\textsubscript{9}(H\textsubscript{2}O)\textsubscript{52}.

Both Al\textsubscript{13} isomers and Al\textsubscript{30} molecule, along with related Al\textsubscript{26} and Al\textsubscript{32} species, have been previously isolated and characterized by a variety of solid-state techniques, usually with the addition of sulfate and selenate anions.\textsuperscript{7,20,24,53,67} Armstrong et al.\textsuperscript{98} reported the ΔH\textsubscript{rel} for ε-Al\textsubscript{13} clusters were exothermic based upon the initial oxide-based components, indicating that the formation of these clusters are stable in the presence of the SO\textsubscript{4}\textsuperscript{2-} and SeO\textsubscript{4}\textsuperscript{2-} crystallizing agents. We have recently utilized a supramolecular approach with the larger 2,6-NDS molecule that has resulted in more control over the crystallization of the δ- Al\textsubscript{13} and Al\textsubscript{30} molecules and the identification of the novel Al\textsubscript{26} species.\textsuperscript{20}
Bulk aluminum oxide materials are known to possess an affinity for Cu$^{2+}$ cations and generally form an inner-sphere complex with the mineral surface.\textsuperscript{77} McBride et al. performed electron spin resonance (ESR) spectroscopy to provide insight into the adsorption of Cu$^{2+}$ on the surface of gibbsite and observed square planar coordination geometry about the metal center.\textsuperscript{79} The $C_4$ rotation axis of the square planar Cu$^{2+}$ species is modeled as perpendicular to the gibbsite surface and complexation is expected to occur through adjacent hydroxyl groups, or in a bridging bidentate manner. Similar results have been reported for amorphous aluminum hydroxide, Al$_2$O$_3$, boehmite, and clays, such as hydroxyl-Al$^{3+}$-monotmorilonite and hectorite.\textsuperscript{76,100-104}

Structural characterization of the polyaluminum species suggests that the central beltway of Al$_{30}$ is the most reactive area of the cluster, as evidence by Cu$^{2+}$ adsorption to symmetric sites within that region. This idea is substantiated with other structural models including Al$_{32}$ clusters that contain two additional Al$^{3+}$ cations bonding in an identical fashion to the same adsorption site.\textsuperscript{20,24} In both cases, the additional Al$^{3+}$ cations form a ternary complex with either a sulfate anion or iminodiacetate ligand, decreasing the overall charge of the cluster. In addition, the Zn$_2$Al$_{32}$-NTA cluster has also been identified, which contains the Al$_{32}$ polyaluminum cluster with two Zn$^{2+}$ cations complexed by nitrilotriacetate (NTA) bonded in a monodentate manner within the reactive central beltway region.\textsuperscript{21}

6.3.2 Computational analysis

Key bond distances and angles for all of the Cu$_2$Al$_{30}$ and Cu$_2$(SO$_4$)$_2$Al$_{30}$ structures are given in Table 6.3, and the structures are shown in Figure 6.4. Specifically we report on the distance between the copper and oxygen functional groups of Al$_{30}$ $d$(Cu $-$ O$_{Al_{30}}$).
$d(Cu - O_{H_2O})$, as well as the angle of the copper and the two oxygen functional groups of $Al_{30}$ $a(O_{Al_{30}} - Cu - O_{Al_{30}})$, and the angle of the copper and the two oxygen atoms of water ligands $a(O_{H_2O} - Cu - O_{H_2O})$. For $Cu_2(SO_4)_2Al_{30}$, the distance between the adsorbed copper and the axial sulfate oxygen atom, $d(Cu \cdots O_{SO_4^{2-}})$, is also given and is in great agreement. In the $Cu_2(SO_4)_2Al_{30}$ optimized geometries, $d(Cu \cdots O_{SO_4^{2-}})$ is 2.238 Å for the A structure, while the corresponding distance in the experimental structure is 2.589 Å. As all other Cu-O distances are in good agreement between theory and experiment, this difference in $d(Cu \cdots O_{SO_4^{2-}})$ distance is attributed to not simulating the full 2,6-NDS counter ion.

Table 6.3. Key bond distances in the experimental $Cu_2Al_{30}$-S and theoretical $Cu_2Al_{30}$/Cu$_2$(SO$_4$)$_2$Al$_{30}$ models.

<table>
<thead>
<tr>
<th>Average distances (Å) and angle comparisons ($^{\circ}$)</th>
<th>$d(Cu - O_{Al_{30}})$</th>
<th>$d(Cu - O_{H_2O})$</th>
<th>$a(O_{Al_{30}} - Cu - O_{Al_{30}})$</th>
<th>$a(O_{H_2O} - Cu - O_{H_2O})$</th>
<th>$d(Cu \cdots O_{SO_4^{2-}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cu_2Al_{30}$-S</td>
<td>1.935</td>
<td>1.988</td>
<td>93.430</td>
<td>90.112</td>
<td>2.589</td>
</tr>
<tr>
<td>$Cu_2Al_{30}$ A</td>
<td>1.960</td>
<td>2.006</td>
<td>95.856</td>
<td>92.488</td>
<td>--------</td>
</tr>
<tr>
<td>$Cu_2(SO_4)<em>2Al</em>{30}$ A</td>
<td>1.981</td>
<td>2.067</td>
<td>97.064</td>
<td>89.423</td>
<td>2.238</td>
</tr>
<tr>
<td>$Cu_2Al_{30}$ B</td>
<td>2.112</td>
<td>2.029</td>
<td>82.801</td>
<td>94.986</td>
<td>--------</td>
</tr>
<tr>
<td>$Cu_2(SO_4)<em>2Al</em>{30}$ B</td>
<td>1.997</td>
<td>2.063</td>
<td>95.882</td>
<td>90.269</td>
<td>2.333</td>
</tr>
<tr>
<td>$Cu_2Al_{30}$ C</td>
<td>1.983</td>
<td>2.009</td>
<td>99.315</td>
<td>86.652</td>
<td>--------</td>
</tr>
<tr>
<td>$Cu_2(SO_4)<em>2Al</em>{30}$ C</td>
<td>2.023</td>
<td>2.042</td>
<td>105.243</td>
<td>86.254</td>
<td>2.292</td>
</tr>
</tbody>
</table>
Overall, the DFT energetics provide theoretical evidence for preferential formation of an aqueous Cu$_2$(SO$_4$)$_2$Al$_{30}$ species with copper adsorbed in the same fashion as in the crystal structure, shown in Figure 6.5. The total energy information of the Cu$_2$Al$_{30}$ structures shows that the A and D models are nearly degenerate, with B and C higher in energy by 0.43 eV and 0.81 eV, respectively. The DFT values for $E_{\text{rxn}}$ are reported in Table 6.4 and Table 6.5, including the overall and stepwise values for $E_{\text{rxn}}$. No stable Al$_{30}^{14+}$ geometry leading to the final D structure could be found, which further confirms the relative stability of the A model. $E_{\text{rxn}}$ values depending on the total energy of the Al$_{30}^{14+}$ D structure are unavailable and are left blank in Tables 6.4 and 6.5.
Figure 6.5. Optimized geometry of the $\text{Cu}_2(\text{SO}_4)_2\text{Al}_{30}$-A structure.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Equation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td>1.37</td>
<td>-0.43</td>
<td>-5.23</td>
<td>-4.29</td>
</tr>
<tr>
<td>B</td>
<td>3.03</td>
<td>-2.52</td>
<td>-2.60</td>
<td>-2.09</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.19</td>
<td>-0.44</td>
<td>-5.36</td>
<td>-3.61</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>-------</td>
<td>-------</td>
<td>-4.88</td>
<td>-4.56</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4. DFT reaction energies, in eV, for the Scheme 6.1 formation of $\text{Cu}_2(\text{SO}_4)_2\text{Al}_{30}$.

To summarize the two model pathways from starting $\text{Al}_{30}^{16+}$ to final $\text{Cu}_2(\text{SO}_4)_2\text{Al}_{30}$, the Scheme 6.1 mechanism begins with deprotonation of 2 $\eta$-H2O groups at each pair of symmetry-related sites to form $\text{Al}_{30}^{14+}$, followed by reaction with $\text{Cu(H}_2\text{O})_4$ to form $\text{Cu}_2\text{Al}_{30}$ (an inner-sphere complex) and subsequent outer-sphere $\text{SO}_4^{2-}$. 

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Equation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Total</th>
</tr>
</thead>
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<td>-3.10</td>
<td>-4.29</td>
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<td>B</td>
<td>-1.75</td>
<td>1.28</td>
<td>-1.62</td>
<td>-2.09</td>
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<tr>
<td>C</td>
<td>-4.19</td>
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<td>-1.76</td>
<td>-3.61</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>-3.78</td>
<td>-------</td>
<td>-------</td>
<td>-4.56</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.5. DFT reaction energies, in eV, for the Scheme 6.2 formation of $\text{Cu}_2(\text{SO}_4)_2\text{Al}_{30}$. 

80
adsorption to yield Cu$_2$(SO$_4$)$_2$Al$_{30}$. Alternatively, in Scheme 6.2 starts with SO$_4^{2-}$ and Al$_{30}^{16+}$ reacting to form outer-sphere (SO$_4$)$_2$Al$_{30}$, followed by deprotonation of the respective reacting oxygen functional groups and ending with the inner-sphere adsorption of Cu(H$_2$O)$_4$ to produce Cu$_2$(SO$_4$)$_2$Al$_{30}$. Chemically speaking, the two Schemes describe the same net reaction, but are broken down into different elementary steps that allow us to consider how cation and anion adsorption compete or cooperate in the formation of Cu$_2$(SO$_4$)$_2$Al$_{30}$.

Going through the results for Scheme 6.1, the DFT values of $E_{\text{rxn}}$ step 1 Scheme 6.1 show that the reacting oxygen functional groups of the A site have a lower barrier to activation through deprotonation, suggesting that the 4-$\eta$H$_2$O groups are the most acidic. However, in step 2 Scheme 6.1, the A model subsequently shows the least favorable uptake of Cu$^{2+}$. The same qualitative behavior is seen in the energetics of the C model. In contrast, the B model exhibits a relatively high endothermic activation (step 1 Scheme 6.1) compared to A/C, while copper addition (step 2 Scheme 6.2) is predicted to be significantly more exothermic at B than in the A/C structures. For step 3 Scheme 6.1, grouping of like trends between A/C compared to B persists, with the former showing more favorable reactivity towards SO$_4^{2-}$ than the latter.

The trends in $E_{\text{rxn}}$ for Scheme 6.2 pose contrast to those reported for Scheme 6.1. $E_{\text{rxn}}$ values for step 1 Scheme 6.2 span a range of 2.44 eV, with the B model Al$_{30}^{16+}$ showing the lowest reactivity towards sulfate. Subsequently in step 2 Scheme 6.2, the B site exhibits the lowest energetic cost to deprotonate (as opposed to the A site in step 1 Scheme 6.1). In step 3 Scheme 6.2, Cu$^{2+}$ adsorption is the most favorable at the A site, which again counters the analogous step in Scheme 6.1 for which the A site was the least
reactive towards Cu$^{2+}$. Another noteworthy comparison of the DFT $E_{\text{rxn}}$ values is the fact that the outer-sphere adsorption energy of SO$_4^{2-}$ (step 3 Scheme 6.1, step 1 Scheme 6.2) is greater in magnitude than the inner-sphere adsorption energies of Cu$^{2+}$ (step 2 Scheme 6.1, step 3 Scheme 6.2). This goes against the chemically intuitive prediction that chemisorption is stronger than physisorption, and will be later discussed by relating the local Al$_{30}$ geometry of beltway sites to electrostatic arguments.

A fundamental question posed by the experimental structure is whether the interaction between adsorbed Cu$^{2+}$ and SO$_4^{2-}$ is covalent or electrostatic in nature. The position of one of the SO$_4^{2-}$ oxygen atoms appears to be axial to Cu$^{2+}$, intuitively suggesting a covalent relationship. However, the isosurface of $\Delta \rho_{\text{CuSO}_4}$ (calculated as the difference of $\rho_{\text{Al}_{30}/\text{Cu}/\text{SO}_4} - \rho_{\text{Al}_{30}/\text{Cu}} - \rho_{\text{SO}_4}$), shown in Figure 6.6, exhibits a void in between the Cu and “axial” sulfate oxygen in the B model. In the A model, the isosurface between the Cu and “axial” sulfate oxygen is indicative of charge loss, as opposed to the buildup of charge that would characterize covalent interaction. On the other hand, oxygen atoms of sulfate not in the Cu axial site exhibit electrostatic interactions with the water ligands of bound Cu$^{2+}$ and/or with functional groups of Al$_{30}$. Thus the occupation of the Cu$^{2+}$ axial site by a sulfate oxygen atom seems coincidental, with sulfate interacting predominantly through electrostatic interactions.
Figure 6.6. Induced density $\Delta \rho$ (defined in the text) for Cu$_2$(SO$_4$)$_2$Al$_{30}$ structures. From left to right A, B, C, and D. Charge loss is shown in purple and charge gain is shown in gray. To better show the isosurfaces, bonds and H atoms are not shown.

While the net reaction to form Cu$_2$(SO$_4$)$_2$Al$_{30}$ is the same for both Schemes, reversing the order of anion/cation adsorption steps reveals opposing trends in DFT reaction energies. The various trends in $E_{\text{rxn}}$ initially seem to be opposing, but can go on to be explained consistently through the single physical property of electrostatic potential. Visualization of $V_{\text{el}}$ of Al$_{30}$ mapped onto an electron density isosurface is presented in Figure 6.7. Owing to the 16+ charge of the molecule, $V_{\text{el}} > 0$ throughout, and qualitatively the red surfaces represent regions with higher values of $V_{\text{el}}$ while the blue surfaces represent regions with lower values. The highest values are found in the beltway, while the caps of Al$_{30}$ exhibit the lowest. The driving force for $V_{\text{el}}$ variation on the Al$_{30}$ exterior is likely due to the cooperative contributions of inwardly folded oxygen functional groups, or “pockets,” in the beltway, while the distribution of functional groups on the caps of Al$_{30}$ are more consistent with what is seen in extended surfaces.
Similar “pockets” in zeolites have been linked to highly reactive surface sites in EU-1 and may contribute to enhanced catalytic processes, such as the hydroisomerization of \( n \)-hexane contained within Mordenite\textsuperscript{105,106}. Concave curvature has also been implicated in the enhanced interactions with gaseous molecules on the surface of TiO\(_2\) nanotubes and may play a minor role on the adsorption of water vapor within these materials\textsuperscript{107,108}.

Figure 6.7. Electrostatic potential of Al\(_{30}\)\(^{16+}\) mapped onto a charge density isosurface. The electrostatic potential is positive throughout, with higher values shown in red and lower values shown in blue. The structure shown is the configuration that is the initial structure for the A and C sites.

The outer-sphere adsorption of SO\(_4^{2-}\) onto Al\(_{30}\) (as in step 1 of Scheme 6.2) is expected to be electrostatic in nature. This was confirmed by visualizing the sulfate adsorption-induced charge density \( \Delta \rho_{SO_4} \) taken as \( \rho_{Al_{30}/SO_4} - \rho_{Al_{30}} - \rho_{SO_4} \), shown for (SO\(_4\))\(_2\)Al\(_{30}\) A-D in Figure 6.8. The large volume enclosed by the negative \( \Delta \rho_{SO_4} \) isosurface surrounding the sulfate group indicates that electron density goes from the anion into the Al\(_{30}\) core, and the alternating positive/negative \( \Delta \rho_{SO_4} \) isosurface volumes
between the sulfate and functional groups of Al$_{30}$ is characteristic of Coulombic interactions between oppositely charged groups. Furthermore, there is an obvious correlation between the plots of $\Delta \rho_{SO_4}$ and $E_{rxn}$ for step 1, Scheme 6.2: Adsorption of SO$_4^{2-}$ in the B model results in the least favorable value of $E_{rxn}$ (-1.75 eV), and $\Delta \rho_{SO_4}$ in Figure 6.8 visualizes the relatively weak sulfate-Al$_{30}$ interaction through the smaller $\Delta \rho_{SO_4}$ volumes enclosed by the isosurfaces. A physical interpretation is that the flat, surface-like topology at the B site prevents more extensive SO$_4$-Al$_{30}$ interaction. For the beltway sights A, C, and D, for which the corresponding values of $E_{rxn}$ are -3.93, -4.19, and -3.78 eV, greater $\Delta \rho_{SO_4}$ isosurface volumes reflect the greater extent of SO$_4$-Al$_{30}$ interaction. The contrast in the extent of Al$_{30}$-SO$_4^{2-}$ interaction is also studied by calculating the sum of Mulliken charges in the (SO$_4$)$_2$Al$_{30}$ configurations, reported in Table 6.6. While the summed charges for the configurations with sulfate in the beltway range from 14.96-15.02 $e$, the value for the B configuration is 15.29 $e$, which again supports weaker outer-sphere bonding at the cap site B and also aids in quantifying the above interpretation of $\Delta \rho_{SO_4}$. The limitation of Coulombic Al$_{30}$-SO$_4^{2-}$ interaction sterically imposed by the B site functional group topology also manifests in step 3 Scheme 6.1, in which sulfate adsorption is modeled after Cu$^{2+}$adsorption. As in Scheme 6.2, the sulfate adsorption in Scheme 6.1 is the least favorable at the B site, and the associated plots of $\Delta \rho_{CuSO_4}$ (Figure 6.6) visualize the lesser extent of SO$_4$-Cu$_2$Al$_{30}$ interaction in that structure.
Figure 6.8. Induced density $\Delta \rho$ for $(SO_4)_{2}Al_{30}$ configurations. From left to right A, B, C, and D. Charge loss is shown in purple and charge gain is shown in gray. To better show the isosurfaces, bonds and H atoms are not shown.

Table 6.6. Results of Mulliken population analysis for the total charge in different $(SO_4)_{2}Al_{30}$ structures, given in units of fundamental charge.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.97</td>
</tr>
<tr>
<td>B</td>
<td>15.29</td>
</tr>
<tr>
<td>C</td>
<td>14.96</td>
</tr>
<tr>
<td>D</td>
<td>15.02</td>
</tr>
</tbody>
</table>

The question of how inner-sphere cation adsorption depends on the $Al_{30}$ adsorption site in the absence of $SO_4^{2-}$ is addressed by comparing the values of $E_{\text{rxn}}$ for step 2, Scheme 6.1. As summarized above, $E_{\text{rxn}}$ for the specific adsorption of $Cu^{2+}$ is the least favorable at the A site (-0.43 eV). On the other hand, $E_{\text{rxn}}$ is the most favorable for the B site (-2.52 eV). This demonstrates a reversal in site-wise reactivity trends of $Al_{30}$ towards $SO_4^{2-}$ vs. $Cu^{2+}$. The adsorption of $Cu^{2+}$ was further probed by Mulliken charge analysis. The sum of charge on the bound $Cu^{2+}$ and its ligands (including the bridging
hydroxyl groups binding it to the Al$_{30}$) was calculated and is reported in Table 6.7. The results show that the adsorbed Cu$^{2+}$ fragments retain the most positive charge at the A and C sites (1.24 and 1.12 e, respectively), while the Cu charge is more passivated at the B and D sites (both 1.08 e). As the D configuration has the unique trait of edge-sharing Cu$^{2+}$, and also produced unstable intermediate structures which prevented reliable calculations of $E_{\text{rxn}}$ for several steps, we form an interpretation based on comparison of the A, B, and C sites. The charge analysis correlates with $E_{\text{rxn}}$ such that stronger Cu$^{2+}$ adsorption is associated with more electron density transfer to the adsorbing Cu$^{2+}$ fragments. The larger positive charge on Cu fragments in A/C can go on to be associated with the favorable values of $E_{\text{rxn}}$ for step 3 Scheme 6.1 (outer-sphere adsorption of SO$_4^{2-}$ onto Cu$_2$Al$_{30}$), as the negative sulfate ion is more strongly attracted to the larger positive charges on the Cu fragment of A and C.

Table 6.7. Results of Mulliken population analysis for the Cu fragments in Cu$_2$Al$_{30}$, given in units of fundamental charge.

<table>
<thead>
<tr>
<th>Mulliken Analysis of cluster bound Cu$^{2+}$ + four ligands</th>
<th>Charge on Cu$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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</tr>
<tr>
<td>B</td>
<td>1.08</td>
</tr>
<tr>
<td>C</td>
<td>1.12</td>
</tr>
<tr>
<td>D</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Common to both proposed Schemes is the need to activate the Al$_{30}$ through deprotonation of $\eta$H$_2$O groups as depicted in step 1 Scheme 6.1 and step 2 Scheme 6.2. In both schemes, the activation step is endothermic. For Scheme 6.1, deprotonation is the most favorable at the beltway A site, while in Scheme 6.2, the cap site B has the lowest energetic cost to deprotonation. Though opposing, the trends in the deprotonation step of each Scheme conform to the emerging overall description of Al$_{30}$ reactivity: The above
comparisons of Cu$^{2+}$ and SO$_4^{2-}$ adsorption show that the functional groups of the Al$_{30}$ cap show greater affinity for cations, while those of the beltway show greater affinity for anions. An alternative but consistent statement is that the strong SO$_4$-Al$_{30}$ interaction at the A site impedes subsequent deprotonation of (SO$_4$)$_2$Al$_{30}$ in step 2 Scheme 6.2 relative to the deprotonation of Al$_{30}$ in step 1 Scheme 6.1.

The electronic structure analysis suggests that, regardless of the order of cation and anion adsorption, the formation of Cu$_2$Al$_{30}$-S is influenced by cooperative effects between the adsorption processes, as well as the shape and electrostatic properties of Al$_{30}$. Experimental data regarding the impact of counter ions on bulk Al- and Fe-oxides suggests similar enhancement of adsorption of a variety of metals (Cd, Cu, Pb, Cd, and Zn), particularly in the presence of sulfate and phosphate anions. Sulfate itself is expected to form outer-sphere complexes with the mineral surface, although inner-sphere interactions may occur with decreasing pH and increasing sulfate concentrations in solution.$^{109-111}$ The enhanced metal adsorption on the surface of Al- and Fe-oxides in the presence of anions, such as sulfate, has been described in three ways$^{112}$:

1) Electrostatic Enhancement – reduction of the positive surface charge by initial adsorption of the anion, resulting in a more attractive surface for the metal cation.
2) Formation of ternary cation-anion-surface complex - a cation-anion complex bind to the surface by inner or outer-sphere interactions.
3) Surface precipitation – addition of the crystalline lattice that contains the metal species.

Surface precipitation can be ruled out in the Cu$_2$Al$_{30}$ complex, but the interaction between the Cu$^{2+}$ and SO$_4^{2-}$ could be modeled by either electrostatic enhancement or
formation of ternary complex. Elongation of the Cu-O-SO$_3$ bond in Cu$_2$Al$_{30}$-S and limited covalent interactions between Cu$^{2+}$ and sulfate as revealed in the analysis of $\Delta \rho_{SO_4}$ suggests electrostatic enhancement to be the major mechanism for the synergetic metal-anion adsorption. The electronic structure analysis elucidates not only that the SO$_4$-Al$_{30}$ and the SO$_4$-Cu$_2$Al$_{30}$ interactions are dominated by electrostatics, but also shows how the concavity of the Al$_{30}$ beltway allows for enhanced anion-Al$_{30}$ interactions with the inwardly-folded oxygen functional groups.

Collecting our interpretations of the individual trends in $E_{\text{rxn}}$ in terms of adsorption site, a universal interpretation emerges: In Al$_{30}$, $V_{\text{el}}$ is less positive at the caps and more positive in the beltway, which consistently explains the relative ease of deprotonating the A site in step 1 Scheme 6.1 or the B site in step 2 Scheme 6.2, the less favorable SO$_4$ adsorption at the B site in step 3 Scheme 6.1 and step 1 Scheme 6.2, and the less favorable Cu$^{2+}$ adsorption at the A site relative to the B site in step 2 Scheme 6.1, etc. Thus, a concise way to summarize the trends in $E_{\text{rxn}}$ is that the variation in $V_{\text{el}}$ between the cap and beltway regions is sufficient to result in opposite trends in cation/anion affinity at adsorption sites in the two topologically distinct regions of Al$_{30}$.

**6.4 Conclusions**

The combined structural characterization and computational study of the Cu$_2$Al$_{30}$-S polyaluminum species provides consistent evidence for the preferred Cu$^{2+}$ adsorption site on the Al$_{30}$ cluster. The net formation of Cu$_2$(SO$_4$)$_2$Al$_{30}$ was studied via two theoretical step-wise mechanisms differing in the order of anion outer-sphere and cation inner-sphere adsorption steps, and revealed opposing trends in anion/cation affinity as a function of adsorption site on Al$_{30}$. We conclude that the coupling of Al$_{30}$ geometry and
electronic structure results in distinct structure-reactivity relationships for adsorption sites in the beltway versus the caps of Al\textsubscript{30}, with the former exhibiting greater reactivity towards outer-sphere adsorption of SO\textsubscript{4}\textsuperscript{2−} and the latter showing greater reactivity towards specific adsorption of Cu\textsuperscript{2+}. The inwardly-folded oxygen functional groups present in the beltway contrast to the more surface-like functional group topology on the caps, and we note that the reversal of anion/cation affinity in Al\textsubscript{30} may be conceptually extendable to understand fundamental differences between extended surface and nanoparticle aluminum hydroxide reactivity.

6.5 Acknowledgements

T.Z.F. would like to acknowledge the University of Iowa Vice President of Research Mathematical and Physical Science Funding program for partial support of this work. T.Z.F. and S.E.M. thanks the College of Liberal Arts and Sciences for additional funding. We thank the UI Central Microscopy Facility for training and use of the SEM and Paul Mueller and Dr. Sarah Larsen, UI Department of Chemistry, for providing the ICP-OES data. We also thank Randall T. Holmes, an undergraduate summer intern, for assisting in the analysis and discussion of computational results. R.T.H. was supported by the Center for Global and Regional Environmental Research at the University of Iowa. Many of the simulations contributing to this work were carried out through the Arctic Region Supercomputing Center at the University of Alaska Fairbanks.
7. CHARACTERIZATION OF PHOSPHATE AND ARSENATE ADSORPTION ONTO KEGGIN-TYPE Al\textsubscript{30} CATIONS BY EXPERIMENTAL AND THEORETICAL METHODS

Inner-sphere cation reactivity and outer-sphere anion reactivity as well as co-adsorption on Al\textsubscript{30} have been the focus of previous chapters, now inner-sphere anion adsorption is modeled in collaboration with experiment. Keggin-type aluminum oxyhydroxide species such as the Al\textsubscript{30} polycation can readily sequester inorganic and organic forms of P(V) and As(V), but there is a limited chemical understanding of the adsorption process. Herein, experimental and theoretical structural and chemical characterization of (TBP)$_2$[Al$_2$(μ$_4$-O)$_8$(Al$_{28}$(μ$_2$-OH)$_{56}$(H$_2$O)$_{26}$)]$^{14+}$ (TBP = t-butylphosphonate) is presented. Furthermore, DFT calculations of R-substituted phosphates and their arsenate analogues is modeled to determine if the reactivity trends ever change site preference. This chapter is another collaboration with Prof. Tori Z. Forbes research group and the published work is reproduced with permission from Inorganic Chemistry [Corum, Fairley, Unruh, Payne, Forbes, and Mason (2015) Characterization of Phosphate and Arsenate Adsorption onto Keggin-Type Al$_{30}$ Cations by Experimental and Theoretical Methods, 54, 8367-8374]. Copyright 2015, American Chemical Society.

7.1 Introduction

Aluminum is an amphoteric element that readily hydrolyzes in aqueous solution to form polynuclear species that are the building blocks of poorly crystalline and/or amorphous oxyhydroxide phases.\cite{113,114} Initial condensation products have been identified by NMR and potentiometric measurements as soluble monomeric (AlOH)$_{2+}$, ...
(Al(OH)$_2$)$^+$, (Al(OH)$_4$)$^-$, dimeric (Al$_2$(OH)$_2$)$_2$$^{4+}$, and trimeric (Al$_3$(OH)$_4$)$_5$$^{5+}$ complexes.\textsuperscript{113,115-118} Larger polynuclear species can be formed upon additional titration with a hard base, forming a range of molecules that contain the Baker-Figgis-Keggin or Keggin-type structural arrangement.\textsuperscript{7,54,119} The core feature of the Keggin-type topography is the Al$_{13}$ tridecamer ((Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$)$^{7+}$), which can be linked with additional monomers, dimers, and other oligomers to form soluble aqueous species containing 26, 30, and 32 Al$^{3+}$ cations.\textsuperscript{20,24,53,66} These nanoscale molecular species have been identified as the primary building unit in amorphous hydroxide solids and gels used as precursor phases in the synthesis of crystalline alumina materials and serve as a coagulant and adsorbent for contaminants in water treatment facilities.\textsuperscript{3,4,53,65,120-123}

Phosphate and arsenate polyoxoanions are two problematic contaminants targeted during water purification processes.\textsuperscript{1,2} Phosphorus and arsenic are both Group 15 elements that display similar chemical reactivity, but their impact on human health and the environment differ significantly. In natural systems, P(V) is an abundant and essential nutrient for humans, animals, plants, and aquatic life. Phosphorus enrichment has come under increased scrutiny due to enhanced loading in soils caused by over fertilization of agricultural lands and its role in eutrophication of freshwater systems, plant and animal deaths, and growth of toxic algae.\textsuperscript{124} Due to its toxicity, As is considered a significant public health concern in areas worldwide, including Bangladesh, Hungary, Romania, Thailand, Mongolia and parts of the Western United States. Human exposure occurs mostly through contaminated drinking water\textsuperscript{125-127} and As is classified as a known human carcinogen by the U.S. Agency for Toxic Substances and Disease Registry, as well as being on the USEPA priority pollutant list.\textsuperscript{127,128}
The exact chemical speciation of P and As is an important consideration for developing an enhanced understanding of the adsorption process and removal of these species from aqueous solutions. According to Read et al., a variety of organic and inorganic P species exist in natural water including orthophosphates, pyrophosphates, polyphosphates, and phosphonates. Both P(V) and As(V) form the $\text{H}_3\text{XO}_4$ ($\text{X}=\text{P}, \text{As}$) acid in solution, deprotonating upon increasing pH to form the anionic forms. In the case of arsenic, reduction to the $\text{H}_3\text{AsO}_3$ and derivatization to methylarsonic acid (CH$_3$AsO(OH)$_2$) are quite common in natural systems. According to the U.S. Environmental Protection Agency (EPA) inorganic H$_3$As(III)O$_4$ is more toxic than H$_3$As(V)O$_4$ and organic forms, but oxidation of the reduced form is the first step in removal strategies. After formation of As(V), co-precipitation and adsorption reactions with aluminum and iron hydroxide phases are the primary means of removing inorganic forms from water.

While there is widespread use of amorphous aluminum oxides as a coagulant and adsorbent, much less is known about the exact binding mechanisms of adsorbates onto the exposed surfaces. $^{31}$P solid-state NMR experiments have shown that phosphate forms predominantly inner-sphere bidentate complexes on alumina, with only a few monodentate complexes observed. Amorphous aluminum oxyhydroxide phases have been reported to have the highest adsorption rate and most rapid uptake for organic and inorganic phosphates compared to more crystalline forms. A study by Yan et al. indicated that the identity of the adsorbed species does impact uptake and that the densities of organic phosphate on the surface of amorphous and crystalline forms of aluminum hydroxide increases with decreasing molecular weight. Similar to phosphate,
arsenate also forms inner-sphere bidentate and monodentate complexes on metal oxides, with bidentate complexes being predominant as shown by EXAFS,$^{139}$ FTIR, and XPS.$^{134}$ In terms of arsenate reactivity towards non-crystalline aluminum hydroxides, Mertens et al., investigated the removal of arsenate from contaminated water samples by Al$_{13}$ and Al$_{30}$ polycations and observed that 98.5-99.4% of the As(V) was removed when total aluminum concentrations were between 1 and 6 mM.$^{1,2,8}$ This study also revealed that the Al$_{30}$ nanoclusters were the most efficient for the removal of As(V) from aqueous solutions with a near neutral pH, making it an excellent candidate for the purification of natural waters.

In the present study, we utilize the Al$_{30}$ polycation (Al$_{30}$O$_8$(OH)$_{56}$(H$_2$O)$_{26}^{18+}$) as a model compound for phosphate and arsenate adsorption. The experimental crystal structure of (TBP)$_2$[Al$_2$(μ$_4$-O)$_8$(Al$_{28}$(μ$_2$-OH)$_{56}$(H$_2$O)$_{26}$)]$^{14+}$ (where TBP = t-butylphosphonate (CH$_3$)$_3$CPO$_3$ and with the solid structure denoted as (TBP)$_2$Al$_{30}$-S) is reported and is used as a basis for density functional theory (DFT) calculations. Experimental data, particularly for crystallization studies, is somewhat limited to successful synthesis procedures. For example, TBP was chosen to provide steric hindrances and prevent polymerization/aggregation by the phosphate ligand so highly crystalline material could be obtained for structural characterization. Other ligands, such as methoxyphosphonate have not successfully produced material for X-ray diffraction analysis. Similarly, arsenate and organoarsenate compounds are quite toxic and can be hazardous in material synthesis. To extend the experimental studies, DFT calculations can provide energetic and mechanistic information regarding the adsorption process. In
addition, it can overcome experimental limitations and provide insight into As(V) adsorption and the importance of the ligand functional groups.

In our modeling approach, we model the molecular analogue of the \((TBP)_2Al_{30}-S\) crystal structure, and compare the DFT energetics of TBP forming attachments through different exposed functional groups on Al\(_{30}\). In order to probe whether chemically similar arsenate exhibits similar reactivity as phosphate to Al\(_{30}\), the computational studies go on to compare the adsorption of TBP to TBA (t-butylarsenate, \((CH_3)_3CASO_3\)). Furthermore, as both arsenate and phosphate exhibit vast speciation in natural waters, DFT calculations modeling the adsorption of other phosphates, organophosphates, and their As(V) analogues are also carried out. In doing so, we are able to identify the sites on Al\(_{30}\) that are most reactive towards oxyanion species, and demonstrate generality in adsorption trends across a range of P(V) and As(V) speciation. This study builds off of our previous combined experimental and theoretical investigation of Cu\(^{2+}/SO_4^{2-}\) co-adsorption to the surface of Al\(_{30}\). There in, we demonstrated that the semipores in the so-called beltway region of Al\(_{30}\) enable enhanced electrostatic interactions between surface functional groups and outer-sphere sulfate ions. The strength of the Al\(_{30}-SO_4^{2-}\) interaction was shown to correlate with topographical variation in the Al\(_{30}\) electrostatic potential.\(^{28,29}\) Here, we focus on the reactivity of Al\(_{30}\) towards polyoxoanion adsorbates, comparisons of phosphate and arsenate analogues, and ligand substitutions of the oxyanions.
7.2 Experimental

7.2.1 Synthesis of (TBP)$_2$Al$_{30}$-S

A partially hydrolyzed aluminum stock solution was prepared by adding 60 mL of a 0.25 NaOH (6.25 mmol) solution dropwise to 25 mL of 0.25 M AlCl$_3$ (6.25 mmol) at 80 °C. This solution was cooled to room-temperature and a 7 ml aliquot was loaded into a 23-ml Teflon-lined Parr reaction vessel. The vessel was placed in a gravimetric oven at 80 °C to promote additional hydrolysis and formation of the Al$_{30}$ species. After 24 hours, the sample was cooled slowly to room temperature, transferred to a glass scintillation vial, and 0.0575 g (0.42 mmol) of TBP was added to the solution. After stirring the resulting solution for ten minutes, a 3mL aliquot of a 0.1 M 2,6 napthalene disulfonate (2,6-NDS) solution was added as a crystallization agent. A small amount of amorphous flocculants formed upon addition of the 2,6-NDS and additional stirring was necessary to form a transparent solution. The pH of the final solution was measured at 5.7. After two weeks of slow evaporation, plate-like, clear crystals of (TBP)$_2$Al$_{30}$-S formed on the bottom of the glass vial with yields of 51% based upon Al.

7.2.2 Structural characterization

Single crystals of (TBP)$_2$Al$_{30}$-S were separated from the mother liquor, coated in Infinium oil and mounted on a Nonius Kappa CCD single crystal X-ray diffractometer equipped with Mo Kα radiation (λ = 0.7107 Å) and a low temperature cryostat. Data collection, cell refinement, data reduction, and absorption corrections were performed using Collect and APEX II software. The structure was solved using direct methods and refined on the basis of $F^2$ for all unique data using the Bruker SHELXTL version 6.10 programs. Al, S, and P atoms were located in the direct methods solution and the O and C
atoms were identified in the difference Fourier maps calculated following refinement of the partial-structure models. Selected data collection parameters are given in Table 7.1.

Table 7.1. Selected crystallographic information for the (TBP)$_2$Al$_{30}$-S compound.

<table>
<thead>
<tr>
<th>FW (g/mol)</th>
<th>5420.13</th>
<th>F(000)</th>
<th>2132</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>16.249(3)</td>
<td>Theta range</td>
<td>1.36 to 26.03°</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>20.213(3)</td>
<td>Limiting indices</td>
<td>-19&lt;h&lt;19</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>20.859(3)</td>
<td>-24&lt;k&lt;24</td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>87.323(4)</td>
<td>-25&lt;l&lt;25</td>
<td></td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>73.148(3)</td>
<td>Ref. collected / unique</td>
<td>104408 / 24607</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>73.918(3)</td>
<td>GOF</td>
<td>1.106</td>
</tr>
<tr>
<td>V(Å$^3$)</td>
<td>6295.8(16)</td>
<td>Final R indices</td>
<td>$R_1 = 0.0724$</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>[$I&gt;2\sigma(I)$]</td>
<td>$wR_2 = 0.2123$</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g/cm$^3$)</td>
<td>1.120</td>
<td>R indices (all data)</td>
<td>$R_1 = 0.0886$</td>
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<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>0.324</td>
<td></td>
<td>$wR_2 = 0.2258$</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.2 x 0.14 x 0.12</td>
<td>Larges diff. (e.A$^{-3}$)</td>
<td>1.716 and -1.422</td>
</tr>
</tbody>
</table>

(TBP)$_2$Al$_{30}$-S crystallized in the triclinic space group $P-1$ with $a = 16.249(3)$ Å, $b = 20.213(3)$ Å, $c = 20.859(3)$ Å, $\alpha = 87.323(4)$°, $\beta = 73.148(3)$°, and $\gamma = 73.918(3)$°. H atoms associated with the naphthalene rings of the disulfonate anion were constrained using a riding model. Disorder was present for several of the 2,6-NDS anions due to free rotation about the S-C bond; therefore, O atoms associated with the sulfonate functional group were modeled as split sites with 50% occupancy. The presence of large void space (2725 Å$^3$) within the crystalline lattice also resulted in the presence of disordered solvent (water) molecules. This diffuse electron density was modeled using the SQUEEZE command in the PLATON software, reduc$^{94}$ reducing the $R_I$ value from 21% to 7% and accounting for 1060 electrons within the cavity.
7.2.3 Computational Methodology

Computational modeling was carried out to compare the experimental \((TBP)_{2}Al_{30-}\)S structure to other adsorption geometries of TBP on Al\(_{30}\). The approach used to solve this problem was to generate a series of isolated aqueous molecular structures with TBP bound through varying Al\(_{30}\) surface functional groups. The adsorption geometries were then subjected to geometry optimizations and total energy comparisons. Geometry optimization calculations were carried out at the DFT-GGA level,\(^{42}\) with aqueous effects accounted for by the Conductor-like Screening Model (COSMO) with the dielectric constant chosen to model water in order to simulate environmental conditions.\(^{27}\) When using COSMO, the cluster is placed into a cavity within the implicit water as described by the dielectric constant. The charge distribution of the cluster polarizes the dielectric continuum, and the response to the medium is described by screening charges on the cavity’s surface. The structural optimizations used a convergence criterion of 0.03 eV/Å. A DNP numerical atom-centered basis set (with a cutoff radius of 3.5 Å) was employed, as implemented in DMol\(^{3}\).\(^{25,26}\) Further details of the computational methods (including benchmarking and convergence studies for Al\(_{30}\)) are reported in our previous work.\(^{28,29}\)

The initial isolated molecular structure for Al\(_{30}\) was based on the experimental crystal structure, which has been reported previously.\(^{20,53,66}\) Based on bond valence analysis,\(^{95}\) the molecular formula of Al\(_{30}\) is expected to be \((Al_{30}O_{8}(OH)_{58}(H_{2}O)_{26})^{18+}\), and the molecule has inversion symmetry. However, as previously reported, DFT vibrational calculations imply that the 18\(^+\) form of Al\(_{30}\) is unstable. Instead, Al\(_{30}\)^{16+} \((Al_{30}O_{8}(OH)_{58}(H_{2}O)_{24})^{16+}\) was used as the starting molecular form in the adsorption modeling. In order to systematically define the adsorption geometries, the functional group naming scheme of Rustad is used, as discussed in earlier chapters.\(^{23}\) There are five
different water functional groups ($\eta$H$_2$O) of varying distance from the tetrahedral Al in each end of Al$_{30}$. A total of three Al$_{30}^{16+}$ species were generated by deprotonating symmetry-equivalent 1, 4, and 5-$\eta$H$_2$O groups in the 18+ structure, and all were optimized to yield stable structures as confirmed by vibrational analysis. The 16+ form of Al$_{30}$ is also supported by classical molecular dynamics simulations$^{23}$ that show the formation of bridged H$_3$O$_2^-$ groups, also seen in the DFT 16+ molecules resulting from deprotonation of 3/4-$\eta$H$_2$O groups.

The salient features of the crystal structure were used to guide and constrain the model adsorption geometries considered. As discussed in detail in the results, the experimental (TBP)$_2$Al$_{30}$-S structure has each TBP bound covalently to Al$_{30}$ through two $\eta$H$_2$O functional groups in an inner-sphere bidentate mode. Bond valence analysis of the experimental structure shows that the oxygen atoms of the $\eta$H$_2$O groups in the adsorbed structure are no longer protonated and instead satisfy their valence through the new bonds formed to the phosphorus atom of TBP. Four models for bidentate adsorption were generated and labeled as (TBP)$_2$Al$_{30}$ A-D, defined by the identity of the functional groups binding P, as follows: A 3/4-$\eta$H$_2$O, B 1-$\eta$H$_2$O, C 2/4-$\eta$H$_2$O and D 5-$\eta$H$_2$O. With the exception of the edge-sharing configuration in D, all of the structural models form corner-sharing, bidentate complexes (as seen in the crystal structure), with the A structure corresponding to the experimental (TBP)$_2$Al$_{30}$-S geometry. In terms of Al$_{30}$ topography, the A and C structures involve functional groups in the beltway, while the B structure involves functional groups on the caps of the molecule. Arsenate analogs to the four theoretical (TBP)$_2$Al$_{30}$ A-D structures are also modeled and subjected to full geometry optimization, and are referred to as (TBA)$_2$Al$_{30}$ A-D.
The adsorption of four other organophosphate species, methylphosphonate, phenylphosphonate, hydroxyphosphonate, and methoxyphosphonate was also modeled in the same A-D configurations as used for TBP adsorption. All adsorption geometries were subjected to DFT geometry optimization, and the total energy information was analyzed. The DFT optimized geometries of the four acids are shown in Figure 7.1. Throughout, methylphosphonate is referred to as M, phenylphosphonate as Ph, hydroxyphosphonate as OH, and methoxyphosphonate as OCH₃. The different R groups were chosen to include a range of inductive effects. Based on the large positive charge on Al₃₀, it is expected that substituting the ligand with electron donating R-groups will enhance the reactivity. Comparing the five ligands, the values of $E_{\text{rxn}}$ for the five $(RP)_2Al_{30}$ structures are expected to follow the order of $(TBP)_2Al_{30} < (MP)_2Al_{30} < (PhP)_2Al_{30} < (POH)_2Al_{30} < (POCH_3)_2Al_{30}$. The arsenate analogs, $(MAs)_2Al_{30}$, $(PhAs)_2Al_{30}$, $(AsOH)_2Al_{30}$, and $(AsOCH_3)_2Al_{30}$, are also modeled, with the same four adsorption sites A-D considered for each.

Figure 7.1. DFT optimized geometries of the various phosphate species binding to Al₃₀ with varying R groups. From left to right the R groups are tert-butyl (TB), methyl (M), benzene (Ph), hydroxyl (OH), and methoxy (OCH₃). The color scheme for the P, O, C, and H atoms are orange, red, black and gray, respectively.
7.3 Results and Discussion

7.3.1 Structural characterization by single crystal X-ray diffraction

The core feature of the \((TBP)_{2}Al_{30}S\) molecule is the Keggin-type aluminum polycation (Figure 7.2). All Keggin-type species contain the tridecamer \((Al_{13})\) species with a central AlO$_4$ tetrahedron surrounded by twelve octahedrally coordinated Al atoms. Al-O bond lengths for the tetrahedrally coordinated Al$^{3+}$ atoms in \((TBP)_{2}Al_{30}S\) range from 1.776(2) to 1.819(2) Å, whereas the distances for the octahedra are between 1.826(2) and 2.042(3) Å. The exterior Al$^{3+}$ cations are arranged into four \([Al_{3}(\mu_{2}-OH)_{6}(H_{2}O)_{3}]\) units, with each of the trimers connected through bridging hydroxyl groups. Five possible isomers have been identified for Al$_{13}$ Keggin molecules that are based on the orientation and number of shared edges existing between the trimeric units. The \(\epsilon\)-Al$_{13}$ isomer is the dominant form present in the partially hydrolyzed aluminum stock solution and can be identified by the formation of edge-sharing hydroxyl groups between the four \([Al_{3}(\mu_{2}-OH)_{6}(H_{2}O)_{3}]\) units. Rotation of one trimer by 60° results in the formation of shared vertices to the neighboring \([Al_{3}(\mu_{2}-OH)_{6}(H_{2}O)_{3}]\) groups and constitutes the \(\delta\)-Al$_{13}$ isomer. The \(\delta\)-Al$_{13}$ is prone to additional hydrolysis with soluble monomers, dimers, and neighboring Al$_{13}$ molecules to form larger Al$_{30}$ polynuclear species with the molecular formula \([Al_{2}(\mu_{4}-O)_{8})(Al_{28}(\mu_{2}-OH)_{56}(H_{2}O)_{26})]^{18+}\). This polycation possesses an hourglass shape, with each of the Al$_{13}$ units forming the exterior caps that narrow through the central beltway region.
Figure 7.2. Structural characterization of the experimental (TBP)$_2$Al$_{30}$-S molecule. Al$^{3+}$ cations are represented by the blue ellipsoids whereas O, P, and C atoms are indicated by the red, orange, and gray spheres, respectively.

Two TBP ligands are bonded to the surface of the Al$_{30}$ molecule through the O atoms of the phosphate functional group, resulting in the formation of a (TBP)$_2$[Al$_2$(μ$_4$-O$_8$)(Al$_{28}$(μ$_2$-OH)$_{56}$(H$_2$O)$_{26}$)]$^{14+}$ cation. The phosphate ligands coordinate in the central beltway region and form a bridging bidentate configuration with tert-butyl functional group pointed away from the Al$_{30}$ molecule. P-O bond distances within the phosphate group are 1.610(7) Å for the free O atom (O46), while bond lengths for the bridging O atoms are 1.510(3) and 1.519(30) Å for O29 and O45, respectively. Complexation of the TBP molecule on the surface of the Al$_{30}$ polycation also results in contraction of the Al-O bond distance (1.826(3) and 1.853(3) Å for O29 and O45) compared to the ηH$_2$O groups that are generally observed at approximately 2.0 Å.
Arrangement of the \((TBP)_{2}Al_{30}-S\) structure into an ordered 3D lattice occurs with the addition of 2,6 Naphthalene disulfonate as the charge balancing crystallization agent. The sulfonate functional groups participate in H-bonding with the aluminum polycation and additional \(\pi-\pi\) stacking of the naphthalene rings provides a supramolecular interaction that result in the crystallization of the material. Two Cl\(^{-}\) anions and 60 water molecules are also present in the interstitial void spaces, but the solvent molecules are relatively disordered in the crystalline lattice. The resulting \((TBP)_{2}Al_{30}-S\) solid phase has an overall formula of \((TBP)_{2}[Al_{2}(\mu_{4}-O)(Al_{28}(\mu_{2}-OH)_{56}(H_{2}O)_{26})](2,6\text{-NDS})_{6}Cl_{2}(H_{2}O)_{60}\).

Structural and mechanistic details between previously reported studies investigating phosphate adsorption on aluminum hydroxide surfaces and the \((TBP)_{2}Al_{30}-S\) molecule are similar. Bridging bidentate coordination of the TBP ligand to the surface of the Al\(_{30}\) polycation is identical to the predicted coordination for aluminum oxide and hydroxide surfaces based upon NMR and EXAFS spectroscopy. Li et al., observed from \(^{31}\)P NMR data that a peak at 0 ppm corresponds to a deprotonated bridging bidentate configuration and is found to be favored over the monodentate mode on a variety of aluminum oxide and hydroxide surfaces.\(^{140}\) Rajan also predicted that the adsorption occurs through a terminal water site on the surface of hydrous alumina that would result in lower surface charge.\(^{135}\) The same result occurs for the adsorption of the TBP molecules to the Al\(_{30}\) surface because the binding results from the displacement of a water molecule, lowering the overall charge on the molecule to 14+.

Additional information can be gained from the structural characterization of the \((TBP)_{2}Al_{30}-S\) molecule. First, diffraction data can provide the exact binding site for the phosphate ligand. In this case, the bridging bidentate coordination does not occur at the
end members of the Al$_{30}$ molecule, but within the beltway region. This site is identical to the position of the bridging bidentate Cu$^{2+}$ adsorption$^{29}$ and is also where the greatest solvent and (outer-sphere) anion densities were reported in classical molecular dynamics simulations of Al$_{30}$ by Rustad.$^{23}$ Second, structural models have previously reported atomic distances for bidentate phosphate surface complexes, predicting that Al-P distances should be 3.1 Å, which is slightly longer than the values observed by X-ray diffraction of 3.01 and 3.06 Å.$^{35}$ The discrepancy may arise from the presence of the tert-butyl functional group, but Differential Pair Distribution Function analysis of high energy X-ray scattering data on arsenate adsorbed to gamma alumina found As-O and As-Al atomic pair correlations of 1.66 and 3.09 Å.$^{35}$ Additional DFT calculations theorize that these atomic distances corresponded to a bridging bidentate coordination. As the As(V) atom (r=0.34 Å) is larger than the P(V) (r=0.29 Å) atom, the value observed by X-ray diffraction for the Al-P distance is likely more accurate.$^{35}$

### 7.3.2 Computational analysis

The (TBP)$_2$Al$_{30}$ molecule can be described as a contact ion pair between the cationic Al$_{30}$ and anionic TBP. Following the discussion of Casey and Rustad$^{22}$ on the formation of analogous ion pairs between fluoride and the Al$_{13}$ polycation, we consider the Eigen-Wilkens (EW) mechanism$^{141-143}$ that proceeds by the initial formation of an outer-sphere ion pair followed by ligand exchange to form the final product as shown in Scheme 7.1. DFT reaction energies, $E_{\text{rxn}}$, are then calculated from the net reaction in Scheme 7.1 and using the total energy information for each reactant and product species, weighted by the appropriate stoichiometric coefficients. The minimum value of $E_{\text{rxn}}$ is used to predict which (TBP)$_2$Al$_{30}$ structure is energetically preferred. For the modeled
addition of different organophosphate, values of $E_{rxn}$ were calculated based on the net reaction of Scheme 7.1 (and graphically depicted in Figure 7.3) modified to include the appropriate singly deprotonated phosphonic acid (methylphosphonic acid ($\text{CH}_3\text{CPO}_2\text{OH}^{1-}$), phenylphosphonic acid ((C$_6$H$_5$)CPO$_2\text{OH}^{1-}$), hydroxyphosphonic acid (OHCP$_2\text{O}^{1-}$), and methoxyphosphonic acid (OCH$_3$CPO$_2\text{OH}^{1-}$)). Values of $E_{rxn}$ for the addition of different organoarsenates were similarly calculated.

Step 1: Ion-Pair Formation

$$\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{22} - (\text{OH})_2(\text{H}_2\text{O})_2^{16+} + 2 \text{RXO}_2\text{OH}^{1-} \rightarrow$$

$$[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{22} - (\text{OH})_2(\text{H}_2\text{O})_2^{16+}, 2 \text{RXO}_2\text{OH}^{1-}]^{14+}$$

Outer-sphere ion pair

Step 2: Ligand-Exchange

$$[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{22} - (\text{OH})_2(\text{H}_2\text{O})_2^{16+}, 2 \text{RXO}_2\text{OH}^{1-}]^{14+} \rightarrow$$

$$\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{22} - (\text{RXO}_2\text{O})_2^{14+} + 4 \text{H}_2\text{O}$$

Net Reaction

$$\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{22} - (\text{OH})_2(\text{H}_2\text{O})_2^{16+} + 2 \text{RXO}_2\text{OH}^{1-} \rightarrow$$

$$\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{22} - (\text{RXO}_2\text{O})_2^{14+} + 4 \text{H}_2\text{O}$$

Scheme 7.1. The Eigen-Wilkens (EW) mechanism that proceeds by the initial formation of an outer-sphere ion pair followed by ligand exchange to form the final product.
Figure 7.3. A graphical depiction of the adsorption reaction of phosphate and arsenate species to Al₃₀ to form (RX)₂Al₃₀ following the net reaction shown in Scheme 7.1. R represents the ligand bound to P/As. The Al₃₀ polycation is shown in a polyhedral representation with the reactive functional groups shown in a ball and stick representation. AlO₆/AlO₄ octahedra/tetrahedra are shown in blue while P, O, and H atoms are represented by orange, red, and gray spheres, respectively. The R groups examined include tert-butyl (TB), methyl (M), benzene (Ph), hydroxyl (OH), and methoxy (OCH₃).

Calculated values of $E_{\text{rxn}}$ are used to probe the relative reactivity of the modeled adsorption sites on Al₃₀. The results (Table 7.2, calculated based on the net reaction shown in Scheme 7.1 then divided by two to represent the energy per adsorbate) show that the theoretically preferred adsorption geometry for all species is C. However, the difference between the values of $E_{\text{rxn}}$ for the A and C structures (both with adsorption in the beltway region) is less than 0.20 eV (4.6 kcal/mol) in all cases, and thus the two sites are essentially degenerate within the accuracy of the DFT methods employed. On the other hand, the differences in values of $E_{\text{rxn}}$ for the A structures (beltway adsorption) compared to the B structures (cap adsorption) is relatively large for all adsorbing species, with the A structure preferred by 0.27 − 0.36 eV and 0.32 − 0.51 eV for the various
phosphate and arsenate adsorbates, respectively. This highlights the distinction of adsorption sites in terms of Al$_{30}$ topography and the exceptional reactivity of the Al$_{30}$ beltway. The D site, as noted, is an edge sharing configuration, and has $E_{\text{rxn}}$ values that are unfavorable by 0.35-0.62 eV and 0.44-0.47 eV compared to the A structure for the various phosphate and arsenate adsorbates, respectively. We therefore focus on the distinction between the beltway adsorption geometries (A and C) compared to the B structure which has adsorption occurring on the caps of Al$_{30}$.

Table 7.2. Calculated values of $E_{\text{rxn}}$ of various phosphate and arsenate species as defined in the text.

<table>
<thead>
<tr>
<th>$E_{\text{rxn}}$ (eV)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TBP)$<em>2$Al$</em>{30}$</td>
<td>-1.05</td>
<td>-0.73</td>
<td>-1.25</td>
<td>-0.43</td>
</tr>
<tr>
<td>(MP)$<em>2$Al$</em>{30}$</td>
<td>-1.03</td>
<td>-0.67</td>
<td>-1.20</td>
<td>-0.41</td>
</tr>
<tr>
<td>(PhP)$<em>2$Al$</em>{30}$</td>
<td>-0.92</td>
<td>-0.58</td>
<td>-1.04</td>
<td>-0.30</td>
</tr>
<tr>
<td>(POH)$<em>2$Al$</em>{30}$</td>
<td>-0.87</td>
<td>-0.57</td>
<td>-1.05</td>
<td>-0.52</td>
</tr>
<tr>
<td>(POCH$_3$)$<em>2$Al$</em>{30}$</td>
<td>-0.80</td>
<td>-0.53</td>
<td>-1.00</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

While it was anticipated that the inductive effects of varying R-groups on the ligands would tune reactivity, only a subtle effect is reflected in the values of $E_{\text{rxn}}$. Comparing the TB and OCH$_3$ ligand for the A site structures, the values of $E_{\text{rxn}}$ for P vary by 0.25 eV, while for As the variation is 0.49 eV. The similarities in values of $E_{\text{rxn}}$ between the R-substituted anions can be viewed as evidence that the preference to adsorb in the beltway region persists over a range of P or As speciation.
Optimized geometries for all four configurations of \((TBP)_{2}Al_{30}\) are shown in Figure 7.4 and key bond distances are compared to the experimental values in Table 7.3. Specifically, we report on the distance between the P and bridging oxo groups of Al\(_{30}\) as well as the distance between the P and the unshared O atom of the phosphate group \(d(P-O)\). The experimental structure and the theoretical structures are in reasonable agreement. For example the distance between phosphorous and the bridging oxo groups of Al\(_{30}\), \(d(P-O_{Al_{30}})\), differs by 0.073 Å for the A site and 0.081 Å for the C site when compared to the experimental crystal structure. Geometry analysis also provides a possible explanation for the unfavorable value of \(E_{\text{rxn}}\) at the D site, in which the oxyanions adsorb in an edge-sharing configuration. The angle between the adsorption sites and the P shows that the angle in the \((TBP)_{2}Al_{30}\)-D structure is 14.7% smaller compared to the experimental structure, shown in Table 7.4, which implies that the edge-sharing configuration is sterically unfavorable. Key bond distances and bond angels for the arsenic analogue \((TBA_{s})_{2}Al_{30}\) structures A-D are also reported in Table 7.3 and Table 7.4 while the \((TBP)_{2}Al_{30}\)-A structure is shown in Figure 7.5. The distance between the arsenic and bridging oxo groups of Al\(_{30}\) as well as the distance between the arsenic and the unshared O atom of the arsenate group of the \((TBP)_{2}Al_{30}\)-A configuration are longer than its crystal structure P analogue by 0.172 Å. In addition, the distance between arsenic and the bridging oxo groups of Al\(_{30}\) differs by 0.245 Å for the A site when compared to the \((TBP)_{2}Al_{30}\)-S crystal structure. Elongation of the bond lengths are expected because the radius of As (0.34 Å) is larger than that of P (0.29 Å). Once again the <O-As-O is much smaller for the D structure (91.02°) compared to the corner-sharing structures.
Figure 7.4. DFT optimized geometries of the modelled (TBP)$_2$Al$_{30}$ structures. From left to right A, B, C, and D structures (defined in the text) are shown. AlO$_6$/AlO$_4$ octahedra/tetrahedra are shown in blue while P, O, C, and H atoms are represented by orange, red, black, and gray spheres, respectively.

Table 7.3. Key bond distances as defined in the text for the experimental (TBP)$_2$Al$_{30}$-S structure and the computational (TBP)$_2$Al$_{30}$ and (TBAs)$_2$Al$_{30}$ structures.

<table>
<thead>
<tr>
<th>P/As distances (Å)</th>
<th>Expt.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d(P - O))</td>
<td>1.610</td>
<td>1.558</td>
<td>1.527</td>
<td>1.540</td>
<td>1.525</td>
</tr>
<tr>
<td>(d(P - O_{Al_{30}}))</td>
<td>1.515</td>
<td>1.588</td>
<td>1.595</td>
<td>1.596</td>
<td>1.600</td>
</tr>
<tr>
<td>(d(As - O))</td>
<td>1.751</td>
<td>1.701</td>
<td>1.741</td>
<td>1.724</td>
<td></td>
</tr>
<tr>
<td>(d(As - O_{Al_{30}}))</td>
<td>1.760</td>
<td>1.773</td>
<td>1.753</td>
<td>1.775</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.4. Key bond angles as defined in the text for the experimental (TBP)$_2$Al$_{30}$-S structure and the computational (TBP)$_2$Al$_{30}$ and (TBAs)$_2$Al$_{30}$ structures.

<table>
<thead>
<tr>
<th>Angles (°)</th>
<th>Expt.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;(O_{Al_{30}} - P - O_{Al_{30}}))</td>
<td>113.75</td>
<td>107.15</td>
<td>108.12</td>
<td>109.87</td>
<td>97.00</td>
</tr>
<tr>
<td>(&lt;(O_{Al_{30}} - As - O_{Al_{30}}))</td>
<td>104.82</td>
<td>106.10</td>
<td>109.56</td>
<td>91.02</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.5. DFT optimized geometry of the (TBAs)$_2$Al$_{30}$ –A configuration. The representation of species is the same as in Figure 7.4 with As shown in purple spheres.

The trends in $E_{\text{rxn}}$ and the structural details presented suggest similar adsorption behavior between phosphates and arsenates. To further compare P and As adsorption, we visualize the P/As adsorption induced charged density. The induced charge density is denoted as $\Delta \rho_{P/As}$ and taken as $\rho_{(TBX)_2Al_{30}} - \rho_{Al_{30}} - \rho_{TBX}$, $\Delta \rho_{P/As}$. Plots of $\Delta \rho_{P/As}$ are shown for (TBP)$_2$Al$_{30}$-A and (TBAs)$_2$Al$_{30}$-A in Figure 7.6. The qualitative agreement in $\Delta \rho_{P/As}$ for both polyoxoanions further supports that experimental results for phosphates may be extrapolated to arsenate. We also note that the tert-butyl ligand is not covered by the $\Delta \rho_{P/As}$ isosurface. This supports that the identity of the functional group does not play a major role in P/As reactivity with Al$_{30}$. Details of the optimized geometries for the A structures of the various organophosphate adsorption structures and arsenate analogue species are reported in Table 7.5. The A structures for phosphate adsorption are shown in Figure 7.7 and appear similar to the arsenate analogues. The distance between the P/As and the R group (connecting C in the R group for TB, M, and Ph and connecting O in the
R group for OH and OCH$_3$) is denoted as $d(\text{P}/\text{As} - R)$ while the distance between the P/As and the bridging oxo groups of Al$_{30}$ is denoted as $d(\text{P}/\text{As} - O_{\text{Al}_{30}})$. Variation of the P/As-R bond is observed over the range of R groups. Larger R groups have longer P/As-R bond distances while the smaller R groups have slightly shorter P/As-R distances. The greatest difference in $d(\text{P}/\text{As} - R)$ for either P or As is between TB and OCH$_3$ with the former being at least 0.2 Å longer.

Figure 7.6. Induced density $\Delta \rho_{\text{P}/\text{As}}$ for the (TBP)$_2$Al$_{30}$–A and (TBAs)$_2$Al$_{30}$–A structures. Charge loss is shown in blue and charge gain is shown in yellow. The color scheme for the P, As, Al, O, C, and H atoms are orange, purple, blue, red, black, and gray, respectively.

Table 7.5. Key bond distances as defined in the text for the computational (RP)$_2$Al$_{30}$ and (RAs)$_2$Al$_{30}$ structures for each R group for the A site.

<table>
<thead>
<tr>
<th>P/As distances (Å)</th>
<th>TB</th>
<th>M</th>
<th>Ph</th>
<th>OH</th>
<th>OCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d(\text{P} - R)$</td>
<td>1.828</td>
<td>1.787</td>
<td>1.793</td>
<td>1.603</td>
<td>1.600</td>
</tr>
<tr>
<td>$d(\text{P} - O_{\text{Al}_{30}})$</td>
<td>1.588</td>
<td>1.587</td>
<td>1.587</td>
<td>1.577</td>
<td>1.576</td>
</tr>
<tr>
<td>$d(\text{As} - R)$</td>
<td>1.989</td>
<td>1.921</td>
<td>1.917</td>
<td>1.767</td>
<td>1.769</td>
</tr>
<tr>
<td>$d(\text{As} - O_{\text{Al}_{30}})$</td>
<td>1.760</td>
<td>1.758</td>
<td>1.759</td>
<td>1.745</td>
<td>1.745</td>
</tr>
</tbody>
</table>
Figure 7.7. The A configurations of the \((RP)_2\text{Al}_{30}\) structures computationally modeled. From left to right \((MP)_2\text{Al}_{30}\), \((\text{PhP})_2\text{Al}_{30}\), \((\text{POH})_2\text{Al}_{30}\), and \((\text{POCH}_3)_2\text{Al}_{30}\).

To further rationalize the subtle variations in \(E_{\text{rxn}}\) as a function of \(R\) group substitution of the oxyanions, we analyze the Mulliken charge population values.\textsuperscript{47} In particular, we monitor \(\Delta(RX)_2\text{Al}_{30}-R\), the difference between the Mulliken charge on P/As in the \((RX)_2\text{Al}_{30}\) structures and the value in the corresponding isolated polyoxoanion form. Table 7.6 shows that the \(\Delta(RX)_2\text{Al}_{30}\) values differ by only 0.03 charge units for all of the phosphates and 0.04 charge units for all of the arsenates. This further supports that adsorption behavior is not strongly dependent on speciation and that phosphate and arsenate interact with \(\text{Al}_{30}\) similarly.

Table 7.6. Values of \(\Delta(RX)_2\text{Al}_{30}\), the difference between the Mulliken charge on P/As in the \((RX)_2\text{Al}_{30}\) structures and the value in the corresponding isolated polyoxoanion form. Values are reported in units of fundamental charge.

<table>
<thead>
<tr>
<th>(\Delta(RX)<em>2\text{Al}</em>{30}) (charge units)</th>
<th>TB</th>
<th>M</th>
<th>Ph</th>
<th>OH</th>
<th>OCH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.18</td>
<td>0.15</td>
<td>0.17</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>As</td>
<td>0.13</td>
<td>0.14</td>
<td>0.16</td>
<td>0.12</td>
<td>0.10</td>
</tr>
</tbody>
</table>
7.4 Conclusions

The experimental structural characterization of \((TBP)_{2}Al_{30}-S\) shows that an inner-sphere ion pair between TBP and \(Al_{30}\) forms via adsorption in the beltway region of the polycation. Complementary computational studies of \(R\)-substituted phosphate and arsenate species adsorbing to \(Al_{30}\) provide evidence for a shape-reactivity relationship in the \(Al_{30}\) polycation. Specifically, the distinction of adsorption sites in terms of the molecular topography (i.e., “beltway” \textit{versus} “cap” sites on \(Al_{30}\)) and electrostatic properties of the polycation are shown to be reliable predictors of adsorption trends on the polycation surface. Our previous studies have revealed strong outer-sphere ion pair formation for ions in the beltway.\textsuperscript{28} Extending this knowledge to the \((TBP)_{2}Al_{30}-S\) structure, we intuit that Step 1 of the EW mechanism (Scheme 7.1) drives the beltway site preference, and subsequent ligand exchange then results in the final inner-sphere ion pair. It is noteworthy that oxygen functional group type and coordination alone cannot explain the greater reactivity of adsorption sites in the \(Al_{30}\) beltway region, even though such arguments have been successfully applied to a variety of mineral surface reactivities. This result motivates ongoing research to converge the well-described structure reactivity relationships of mineral surfaces with the apparent shape-reactivity relationship in Keggin-based molecular geochemical models.

7.5 Acknowledgements

S.E.M. acknowledges support from NSF grant CHE-1254127 and both S.E.M and T.Z.F thank the University of Iowa College of Liberal Arts and Sciences for initial funding. We would like to thank the UI NMR Facility and Fu Chen for his help collecting the Al-27 and P-31 NMR spectra.
8. DENSITY FUNCTIONAL THEORY STUDY OF ARSENATE ADSORPTION ONTO ALUMINA SURFACES

The main focus of this dissertation has been to determine and explain the unique reactivity of Al Keggin clusters; in this chapter the focus shifts from Al Keggin based compounds to Al surface reactivity. Experimentally arsenate has been shown to bind to alumina surfaces in a bidentate binuclear configuration but there has not been an extensive computational study to explain why arsenate binds in a bidentate binuclear configuration to alumina. In this chapter we set out to model a variety of configurations to better understand arsenate adsorption. Instead of modeling the time consuming alumina surface some studies prefer to model small Al octahedral clusters and in this chapter we also test the validity of this alternative method. The small Al clusters are composed of two Al octahedrally bound to water and hydroxyl groups in order for the small Al cluster to be charge neutral. A variety of adsorption sites including edge sharing and corner sharing Al are modeled and it is concluded that the energy magnitude and ranges greatly differ between the two systems. This work has been drafted with the goal to submit April 2016.

8.1 Introduction

Arsenic (As) contamination of ground water is a global problem of high profile thought to affect more than 137 million people in 70 countries and is one of the most toxic ions found in drinking water.\textsuperscript{144,145} Arsenic has been found in water all over the world but arsenic poisoning is most common in countries from southeast Asia, such as Bangladesh, Vietnam, and India.\textsuperscript{133,146-148} Negative health impacts caused by As include respiratory problems, cardiovascular disease, diabetes, and cancers of the skin and lungs;
ultimately, As poisoning can be fatal. As can exist in a range of oxidation states depending on the environmental systems but is most commonly a +3 or +5 cation, with the +3 cation being more toxic than the +5 cation. Water in nature tends to be between a pH of 4-9 and in water As (V) is more stable than As (III). Wilson et al. have determined that from pH ~2-7 H$_2$AsO$_4^-$ is the most stable form of As (V) and at a pH above 7 HAsO$_4^{2-}$ is the most stable.

Mineral surfaces can form chemical bonds to aqueous As, therefore, interactions of As with solid phases are critical to understanding the mobility, transport, and fate of As in the environment. Surface studies are a common focus of geochemical research and there is no shortage of arsenate adsorption studies currently published using aluminum and iron oxide surfaces, however the bulk of Al or Fe surface studies are mainly experimental. There is a consensus in the literature as to how arsenate binds to aluminum or iron surfaces based off of Extended X-Ray Absorption Fine Structure (EXAFS) data. When arsenate binds to α-alumina, γ-alumina, and gibbsite these studies find that arsenate prefers to bind in a bidentate fashion to the aluminum surface. The As also binds in a binuclear fashion to the surface (also called a corner-sharing configuration) which means that the As binds to two oxygen atoms which are bound to two separate Al atoms, this type of configuration we will reference as bidentate binuclear (BB) throughout this paper. Aluminum and iron are isostructural and arsenate adsorption onto iron surfaces is also found to be more favorable in a bidentate binuclear configuration.

Recently Blanchard et al, did a detailed structural analysis to explain arsenate adsorption to the surface of hematite. EXAFS studies show that arsenate binds to
hematite mostly in a BB fashion and Blanchard et al. uses geometry comparisons in order to show that the modeled BB configuration best matches the EXAFS-derived data. Until now there has not been a computational study that has thoroughly modeled a variety of arsenate configurations onto alumina. EXAFS studies show that the As(V)-O$_{\text{surface}}$ bond distance on α-alumina is 1.69 +/- 0.005 Å, gibbsite is 1.68 +/- 0.02 Å, and 1.69 +/- 0.01 Å for γ-alumina and for both surfaces the coordination number of As is ~4.31,35,37 By using bond geometry analysis we model a variety of configurations for As adsorption in order to compare EXAFS bond distances with our computational studies.

We also take this opportunity to compare Al cluster models to full alumina surface models. A properly modeled metal oxide surface can contain many M and O layers and can be computational expensive while small M clusters contain many less atoms and thus the computational speed will dramatically increase. In order to speed up adsorption studies of arsenate (or another similar ion) some studies choose to model small octahedral clusters, these clusters usually contain on average 2 metal atoms with about 10-14 oxygen atoms and a handful of hydrogen atoms. Paul et al. has modeled sulfate adsorption onto Fe clusters; they used Fe clusters that contained two Fe atoms, ten O atoms, and a varying amount of hydrogen atoms.33 They concluded that both the cluster models and the surface had good bond agreement with EXAFS data however the long range interactions are not and cannot be present in the Fe cluster models due to the small size of the cluster. Baltrusaitis et al. have used iron and aluminum clusters to study bicarbonate adsorption.155 In their study two tetrahedral metal atoms were linked by one bridging oxygen atom and different configurations of bicarbonate were modelled. Another study by Watts et al. used a three Fe cluster structure to model As adsorption.36
In this Fe structure two Fe atoms are octahedrally coordinated while one Fe atom only has five bonds. These authors compared the extended Fe structure as well as a Fe surface to EXAFS studies and concluded that while both systems matched bonding patterns to the EXAFS data the surface showed precise bond distance agreement over the cluster. The cluster model underestimated the As-Fe bond distance so they concluded that while both systems showed that BB configuration is the most favorable for As adsorption the surface better matched with experiment. Another study that second guesses these cluster models is by Pierre-Louis et al. These authors used Al, Fe and Al/Fe structures to model CO$_2$ adsorption.\textsuperscript{156} This study modeled monodentate and bidentate CO$_2$ adsorption on what they call Al$_2$ clusters, Fe$_2$ clusters, and Al/Fe clusters (one Al atom and one Fe atom) in order to compare these computational models with EXAFS data. The authors recognize that these small metal clusters do not correctly model Al/Fe surface adsorption studies but are sufficient in determining the bonding interactions of adsorbents.

Our goal as modelers is to develop a molecular-level understanding of how As bonds to minerals such as alumina, Al$_2$O$_3$. Even though many EXAFS studies show that inner-sphere arsenate binds in a BB fashion we model a variety of configurations on three different Al surface terminations (A3, C3, and C4) in order to explain why arsenic binds in a BB fashion onto alumina. We also set out to test how clusters and surfaces compare by modeling an Al cluster. Our small aluminum cluster contains two Al atoms, ten O atoms and enough H atoms to make these clusters charge neutral. We hypothesize that the adsorption energy cannot be the same on the surface and the clusters due to their inherent differences in structure. Lastly, we explore different protonation states of As adsorption to simulate a variety of environmental conditions and possibly help make
connections with future experimental studies. As Wilson et al. showed, in water arsenate generally exists as H$_2$AsO$_4^-$, when arsenate binds to the alumina surface it can lose 0, 1, or 2 H atoms. Our focus is singly protonated arsenate but we also explore deprotonated and doubly protonated arsenate to determine if reactivity differs.

8.2 Methods

Structural calculations of $\alpha$-Al$_2$O$_3$ (001) and small Al clusters were carried out using density functional theory (DFT) as implemented in the DMol$^3$ code developed by Delley.$^{25,26}$ Aperiodic all-electron spin-polarized DFT calculations were performed using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)$^{42}$ with a double-numeric-plus polarization atom-centered basis set. A real-space basis set cutoff of 4.50 Å was used. Before the surfaces were cleaved, lattice optimizations for the bulk $\alpha$-Al$_2$O$_3$ (001) surface were converged with respect to $k$-points using a Monkhorst-Pack (MP) grid of 2x2x1 to sample the Brillouin zone. The optimized lattice constants are 4.821 Å (+1.3%) and 13.111 Å (+0.9%) for alumina and are in excellent agreement with experiment (as indicated by parentheses)$^{157}$ and other DFT-GGA results.$^{158-162}$

Geometry optimization calculations were carried out with aqueous effects accounted for by the Conductor-like Screening Model (COSMO) with the dielectric constant chosen to model water in order to simulate environmental conditions.$^{27}$ When using COSMO, the cluster is placed into a cavity within the implicit water as described by the dielectric constant. The charge distribution of the cluster polarizes the dielectric continuum, and the response to the medium is described by screening charges on the cavity’s surface. The structural optimizations used a convergence criterion of 0.03 eV/Å.
In this study we focus on arsenate adsorption binding to three different types of alumina surfaces and small Al clusters in multiple configurations. Using the alpha-numeric surface stoichiometry naming scheme of Lo et al., we model arsenate on the C3, C4, and A3 \(1 \overline{1}02\) surface. These three structures are shown in Figure 8.1. These surfaces all differ in their topmost layer. The C4 and C3 surfaces have a missing layer of Al cations compared to the A3 surface. The A3 and C3 surfaces are capped with hydroxyls while the C4 surface contains water groups on the top and bottom of the surface. With these differences, the C3, C4, and A3 slabs consist of 12, 12, and 14 O layers and 6, 6, and 8 Al layers, respectively. All three surfaces have 25 Å of vacuum space separating the periodic images along the z direction. We model arsenate adsorption in three different configurations on each type of surface. Each surface contains inversion symmetry so there is one arsenate ion bound to each side of the surface.

![Figure 8.1. C3 (top left), A3 (top right), and C4 (bottom left) alumina surface and the Al cluster (bottom right) model. Aluminum, oxygen, and hydrogen are represented by the colors turquoise, red, and gray respectively.](image)

The small aluminum cluster models are composed of two Al octahedral that contain bound hydroxyl and bound water groups in order for the small Al clusters to be neutral. This structure was based off of cluster model figures in previously reported
literature and is also shown in Figure 8.1.\textsuperscript{33,156,163} We model arsenate adsorption in multiple configurations to compare with the surface models.

The different configurations modeled for each surface were based off of which oxygen atoms arsenic is bound to. Following the language in current literature arsenate can bind in a bidentate mononuclear (BM) fashion or a bidentate binuclear (BB) fashion.\textsuperscript{31,35,37} A BM adsorption occurs when the two oxygen atoms bound to the arsenate are bound to the same Al atom, this configuration can also be labeled as edge sharing. A BB adsorption occurs when the two oxygen atoms bound to the arsenate are bound to two different Al atoms, this configuration can also be called corner sharing. For the cluster models we test three different BM configures and one BB configuration. For all three surface models we test two different BB configurations and one BM configuration. The two BB configurations differ in which surface O atoms the arsenate binds too.

The three different protonation states modeled all start from the same surfaces, cluster, and arsenate structures and differ in the number of H on the arsenate in the product. The number of water and H\textsubscript{3}O\textsuperscript{+} molecules differ for each protonation state. We model reaction energies using the total energy of the surface/cluster/molecule multiplied by the appropriate stoichiometric coefficient in order to form a balanced reaction. For the single protonation surfaces and cluster we use equations 8.1a and 8.1b, respectively. The deprotonated equation for the adsorption of arsenate on the surface and cluster is calculated using equation 8.2a and 8.2b, respectively, and the doubly protonation equation for arsenate adsorption on the surfaces and cluster is calculated using equation 8.3a and 8.3b.
\[
\text{Al}_2\text{O}_3 + 2 \text{AsO}_2(\text{OH})_2^- + 2 \text{H}_3\text{O}^+ \rightarrow (\text{AsO(OH)})_2\text{Al}_2\text{O}_3 + 6 \text{H}_2\text{O} \quad \text{Equation 8.1a}
\]

\[
\text{Cluster} + \text{AsO}_2(\text{OH})_2^- + \text{H}_3\text{O}^+ \rightarrow \text{AsO(OH)Cluster} + 3 \text{H}_2\text{O} \quad \text{Equation 8.1b}
\]

Scheme 8.1. Singly protonated arsenate adsorption onto alumina (8.1a) and the small Al clusters (8.1b).

\[
\text{Al}_2\text{O}_3 + 2 \text{AsO}_2(\text{OH})_2^- \rightarrow (\text{AsO}_2)_2\text{Al}_2\text{O}_3 + 4 \text{H}_2\text{O} \quad \text{Equation 8.2a}
\]

\[
\text{Cluster} + \text{AsO}_2(\text{OH})_2^- \rightarrow \text{AsO}_2\text{Cluster} + 2 \text{H}_2\text{O} \quad \text{Equation 8.2b}
\]

Scheme 8.2. Deprotonated arsenate adsorption onto alumina (8.2a) and the small Al clusters (8.2b).

\[
\text{Al}_2\text{O}_3 + 2 \text{AsO}_2(\text{OH})_2^- + 4 \text{H}_3\text{O}^+ \rightarrow (\text{As(OH)})_2\text{Al}_2\text{O}_3 + 8 \text{H}_2\text{O} \quad \text{Equation 8.3a}
\]

\[
\text{Cluster} + \text{AsO}_2(\text{OH})_2^- + 2 \text{H}_3\text{O}^+ \rightarrow \text{As(OH)}_2\text{Cluster} + 4 \text{H}_2\text{O} \quad \text{Equation 8.3b}
\]

Scheme 8.3. Doubly protonated arsenate adsorption onto alumina (8.3a) and the small Al clusters (8.3b).

### 8.3 Results

In this study we model arsenate \((\text{AsO}_2(\text{OH})_2^-)\) adsorption on three different alumina surfaces – A3, C3, and C4. Truncated optimized structures are shown in Figure 8.2 for the A3 surface, Figure 8.3 for the C3 surface, and Figure 8.4 for the C4 surface. In Table 8.1 we report the adsorption energies for all modeled surfaces using equations 8.1a and 1b. We use a naming scheme for all of our structures that will now be described. For the three A3 structures we use the names HHBB, HVBB, HVBM that represents a hill-hill bidentate binuclear structure, a hill-valley bidentate binuclear structure, and a hill-valley bidentate mononuclear structure where a hill signifies an O atom from the top surface O layer and valley signifies an O atom from the second O surface layer.
Figure 8.2. The A3 optimized structures. From left to right: HHBB, HVBB, and HVBM. Aluminum, oxygen, hydrogen, and arsenic are represented by the colors turquoise, red, gray, and purple respectively.

Figure 8.3. The C3 optimized structures. From left to right: HHBB, HVBM(HHBB), and HHBB-H. Aluminum, oxygen, hydrogen, and arsenic are represented by the colors turquoise, red, gray, and purple respectively.

Figure 8.4. The C4 optimized structures. From left to right: HHBB, HHVTB, and HVBM. Aluminum, oxygen, hydrogen, and arsenic are represented by the colors turquoise, red, gray, and purple respectively.
Table 8.1. Arsenic adsorption energies for all structures calculated using equations 8.1a for the surfaces and 8.1b for the cluster model.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3 HHBB</td>
<td>-1.15</td>
</tr>
<tr>
<td>A3 HVBB</td>
<td>-0.57</td>
</tr>
<tr>
<td>A3 HVBM</td>
<td>-0.10</td>
</tr>
<tr>
<td>C3 HHBB</td>
<td>-1.35</td>
</tr>
<tr>
<td>C3 HVBM (HHBB)</td>
<td>-2.30</td>
</tr>
<tr>
<td>C3 HHBB-H</td>
<td>-2.26</td>
</tr>
<tr>
<td>C4 HHBB</td>
<td>-0.88</td>
</tr>
<tr>
<td>C4 HVBM</td>
<td>-1.29</td>
</tr>
<tr>
<td>Al – BB</td>
<td>-2.52</td>
</tr>
<tr>
<td>Al – BM1</td>
<td>-2.17</td>
</tr>
<tr>
<td>Al – BM2</td>
<td>-2.25</td>
</tr>
<tr>
<td>Al – BM3</td>
<td>-2.09</td>
</tr>
</tbody>
</table>

For C3 we model a HHBB and HVBM structure which represents a hill-hill bidentate binuclear structure and a hill-valley bidentate mononuclear structure. The HVBM structure optimizes to a HHBB (hill-hill bidentate binuclear) configuration so we call the HVBM structure HVBM (HHBB). After optimization the major difference between C3 HHBB and C3 HVBM (HHBB) is the location of some H atoms. When the HVBM (HHBB) structure optimizes proton rearrangement occurs and ultimately makes the C3 HVBM (HHBB) structure more favorable than C3 HHBB. We rearrange the protons on the C3 HHBB surface to better resemble the C3 HVBM (HHBB) surface and we call this surface C3 HHBB-H for a hill-hill bidentate binuclear structure with a proton rearrangement.

Initially we chose to model two C4 surfaces, HHBB and HVBM which represents hill-hill bidentate binuclear and hill-valley bidentate mononuclear configurations. We
realized that how the arsenate is situated on top of two surface waters for the HHBB configuration will result in a bidentate or tridentate bonding to the surface so we ended up modeling an additional HHBB structure. We call the HHBB structure that resulted in a tridentate configuration on the C4 surface HHVTB which represents a hill-hill-valley tridentate binuclear configuration.

One BB configuration and three BM configurations for the Al clusters are modeled to ensure that multiple configurations are tested and are shown in Figure 8.5. Two BM configurations differ in which H$_2$O/OH groups the arsenate is bound to and two BM configurations differ in the placement of the protons. All cluster models are initially protonated to be a neutral cluster which was the only way the cluster would remain intact and not break apart.

![Figure 8.5. Optimized cluster structures. From left to right: Al-BB, Al-BM1, Al-BM2, and Al-BM3. Aluminum, oxygen, hydrogen, and arsenic are represented by the colors turquoise, red, gray, and purple respectively.](image)

Based off all our structures we observe reactivity trends between all four systems. The reaction energies are reported in Table 8.1 and for all systems a BB configuration is more favorable then a BM configuration. For the A3 surface the two BB configurations are 0.47 eV and 1.05 eV lower in energy than the HVBM structure. For the C3 surface the BM configuration optimized to a BB configuration thus resulting in a BM
configuration not being stable for the C3 surface. For the C4 surface the two BB configurations are 0.71 eV and 1.12 eV lower in energy than the BM configuration. While all BB surface configurations are significantly lower in energy than the BM configurations, the BB configuration on the small Al cluster is only more favorable by 0.27-0.43 eV compared to the three BM configurations.

We also see a trend between the HH and the HV configurations with the HH configurations being more favorable than the HV configurations. For the A3 structure the HHBB structure was the most favorable by at least 0.58 eV compared to the HV structures. For the C3 surface once again a HV configuration could not be optimized. The HV configuration optimized to a HH configuration. For the C4 surface the HH configuration is more favorable than the HV configuration by 0.71 eV. However the most favorable C4 surface was when the arsename forms a tridentate configuration and bonds to two hill oxygen atoms and one valley oxygen.

Even though, as we see in Table 8.1, there is a significant energy difference between the BB and BM configurations and the HH and HV configurations we do not see a significant difference in the bond lengths between the surface/cluster O atom and the As, we label this as O_{surf/cluster}-As. We report our findings in Table 8.2. For A3 we find that the most favorable structure (HHBB) has the shortest O_{surf}-As bond length by 0.071 Å. For the most favorable C3 structure the O_{surf}-As bond length is longer by only 0.021 Å. The bonding in the C4 structure is hard to compare since bidentate and tridentate adsorption both occurs. The structure that binds in a tridentate fashion has longer bond lengths than the bidentate configurations. For the Al clusters the BB configuration has the shortest O_{cluster}-As bond length by at most 0.022 Å.
Table 8.2. Average $O_{\text{surf/cluster}}$-As bond distances. T represents the arsenate forming three bonds to the surface.

<table>
<thead>
<tr>
<th></th>
<th>Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3 HHBB</td>
<td>1.742</td>
</tr>
<tr>
<td>A3 HVBB</td>
<td>1.813</td>
</tr>
<tr>
<td>A3 HVBM</td>
<td>1.811</td>
</tr>
<tr>
<td>C3 HHBB</td>
<td>1.742</td>
</tr>
<tr>
<td>C3 HVBM (HHBB)</td>
<td>1.763</td>
</tr>
<tr>
<td>C3 HHBB-H</td>
<td>1.754</td>
</tr>
<tr>
<td>C4 HHBB</td>
<td>1.783</td>
</tr>
<tr>
<td>C4 HHVTB</td>
<td>1.850</td>
</tr>
<tr>
<td>C4 HVBM</td>
<td>1.779</td>
</tr>
<tr>
<td>Al – BB</td>
<td>1.747</td>
</tr>
<tr>
<td>Al – BM1</td>
<td>1.769</td>
</tr>
<tr>
<td>Al – BM2</td>
<td>1.758</td>
</tr>
<tr>
<td>Al – BM3</td>
<td>1.758</td>
</tr>
</tbody>
</table>

The equations to calculate the total reaction energy for each protonation state of As differs, and therefore the reaction energies of the different protonation states cannot be compared. Figure 8.6 shows the most favorable deprotonated structures for each surface/cluster and Figure 8.7 shows the most favorable doubly protonated structures for each surface and cluster. The rest of the figures are not shown due to the fact that the structures mainly differ in their number of H atoms and do not have major structural differences. Table 8.3 shows the reaction energies for the all the structures modeled. Some structures are not stable in different protonated forms and will be discussed later, that is why there are some numbers absent from Table 8.3.
Figure 8.6. Optimized deprotonated surface structures. From left to right: A3 HHBB, C3 HVBM (HHBB), C4 HHVTB, and Al-BB. Aluminum, oxygen, hydrogen, and arsenic are represented by the colors turquoise, red, gray, and purple respectively.

Figure 8.7. Optimized doubly protonated surface structures. From left to right: A3 HHBB, C3 HVBM (HHBB), C4 HHVTB, and Al-BB. Aluminum, oxygen, hydrogen, and arsenic are represented by the colors turquoise, red, gray, and purple respectively.

Table 8.3. Arsenic adsorption energies for all structures calculated using equations 8.2a and 8.3a for the deprotonated and doubly protonated surfaces and 8.2b and 8.3b for the deprotonated and doubly protonated cluster model. No numbers represent a structure that did not correctly optimize.

<table>
<thead>
<tr>
<th>$E_{ads}$ (eV)</th>
<th>Deprotonated</th>
<th>Doubly Protonated</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3 HHBB</td>
<td>-0.63</td>
<td>-2.04</td>
</tr>
<tr>
<td>A3 HVBB</td>
<td>0.41</td>
<td>-1.63</td>
</tr>
<tr>
<td>A3 HVBM</td>
<td>0.48</td>
<td>-0.67</td>
</tr>
<tr>
<td>C3 HHBB</td>
<td>-1.00</td>
<td>-1.77</td>
</tr>
<tr>
<td>C3 HVBM (HHBB)</td>
<td>-1.15</td>
<td>-3.12</td>
</tr>
<tr>
<td>C3 HHBB-H</td>
<td>-0.94</td>
<td>-2.96</td>
</tr>
<tr>
<td>C4 HHBB</td>
<td>0.04</td>
<td>-3.14</td>
</tr>
<tr>
<td>C4 HHVTB</td>
<td>0.44</td>
<td>-2.01</td>
</tr>
<tr>
<td>C4 HVBM</td>
<td>-----</td>
<td>-1.81</td>
</tr>
<tr>
<td>Al – BB</td>
<td>-0.61</td>
<td>-3.51</td>
</tr>
<tr>
<td>Al – BM1</td>
<td>-----</td>
<td>-2.91</td>
</tr>
<tr>
<td>Al – BM2</td>
<td>-0.46</td>
<td>-3.18</td>
</tr>
<tr>
<td>Al – BM3</td>
<td>-0.43</td>
<td>-2.92</td>
</tr>
</tbody>
</table>
We can conclude that in all of our results the HH configurations are more favorable than HV configurations and BB bonding is more favorable than BM bonding. We also see a large energy difference between the surface structures and a small energy range for the Al clusters.

8.4 Discussion

We do not observe a significant energy difference in the multiple structural configurations for the Al cluster, but we do see a much larger energy range for all three surfaces. We model three different configurations for arsenate adsorption on the A3 surface – HHBB, HVBB, and HVBM. The most favorable arsenate configuration on the A3 surface is the HHBB configuration and the least favorable arsenate configuration is the HVBM configuration. These two structures differ by 1.05 eV and the O_{surf}-As bond distance varies by 0.069 Å. In order to explain why the HHBB configuration was much more favorable than a HVBM configuration we turn to the $\angle$O_{surf}-As-O_{surf} angle. The arsenic in arsenate has a tetrahedral configuration so we would expect the $\angle$O_{surf}-As-O_{surf} angle to be close to the ideal tetrahedral bond angle of 109.5°. We see that the most favorable HHBB structure has a $\angle$O_{surf}-As-O_{surf} angle of 105.25° and the least favorable structure, HVBM, has a $\angle$O_{surf}-As-O_{surf} angle of 88.55°. The smaller angle puts a strain on the arsenic which can explain why the HVBM structure is the least favorable for the A3 surface.

For the C3 surface we were not able to adsorb arsenate in as many configurations. We tried HV vs. HH and BM vs. BB but only the HHBB configuration optimized. The major difference between the HHBB and HVBM(HHBB) structures is the proton arrangement. The initial geometry of the HVBM(HHBB) configuration was HVBM but
as the structure optimized one of the $O_{\text{surf}}$-As bonds broke and another $O_{\text{surf}}$-As bond formed. When the As bound to a new surface O atom, the proton on this O atom needed to adjust and migrate since the O atom only wants two bonds. Therefore there is proton rearrangement occurring in the HVBM(HHBB) structure. After optimization, the HVBM(HHBB) and HHBB structures both have the arsenate in a hill-hill bidentate binuclear configuration but have a slightly different proton arrangement, these two structures have a large energy difference of 0.95 eV for the same type of arsenate adsorption. We rotate the rearranged protons on the HVBM(HHBB) structure to better match the HHBB structure and we find that we get a reaction energy almost identical to the HVBM(HHBB) structure, a difference of only 0.04 eV. For all three C3 structures a similar $O_{\text{surf}}$-As bond distance was formed, the HVBM(HHBB) structure has the longest $O_{\text{surf}}$-As bond distance of 1.763 Å while the HHBB structure has the shortest $O_{\text{surf}}$-As bond distance of 1.742 Å, this is only a 0.021 Å difference. For the C3 surface we can conclude that even though the arsenate is adsorbed in the same way on two different structures the significant energy difference is due to the proton arrangement. The different protonation states will be discussed later, but an interesting result is that we see only a 0.21 eV difference in reaction energies for the three different C3 deprotonated structures, and this supports our conclusion that the H on the arsenate affects the reaction energies.

C4 is the only surface that prefers a tridentate adsorption to the arsenic ions. For the C4 surface a HHBB and HVBM configuration was modeled and the HHBB structure was 0.71 eV more favorable than a HVBM structure but the $O_{\text{surf}}$-As bond distances only differ by 0.004 Å. However, depending on how the arsenic is initially placed on the C4
surface the arsenic can doubly or triply bond to the surface (when arsenate is doubly deprotonated it always forms five bonds, this is discussed later). When the arsenic bonds to the surface in a tridentate fashion this configuration is actually the most favorable. The tridentate configuration is 0.41 eV lower than the HHBB structure and 1.12 eV lower than the HVBM structure. The $O_{\text{surf}}$-As bond distance is about 0.07 Å longer than both bidentate configurations. The C4 surface is also capped with water instead of OH groups and this could contribute to the different bonding preferences between C4 and the other surfaces.

We can clearly see that the surface calculations differ from the small Al cluster calculations. The cluster calculations are done by modeling two octahedral Al. In this structure there is only one location for a reasonable arsenate BB adsorption, but there are a couple locations for a BM adsorption. We choose to model two different adsorption sites for the BM configurations (structures Al-BM1 and Al-BM2) and we also model different proton rearrangements (structures Al-BM2 and Al-BM3). Since these structures are highly unstable must keep the charge of all Al clusters neutral and in order to do this the protons can be arranged in a variety of different ways. We noticed that for all the cluster models there is significant hydrogen bonding occurring in order to stabilize the cluster. Even though we see the BB configuration being the most favorable, the energy range between Al-BB and Al-BM3 is only 0.43 eV. Just comparing the three BM structures there is an energy range of 0.16 eV, which is within our DFT error of about 0.2 eV.

Comparing the energies of the surfaces to the cluster we see a much larger energy difference on the surfaces than the clusters. The energy range for the A3, C3, and C4
surfaces are 1.05 eV, 0.95 eV, and 1.12 eV, respectively, but only a range of 0.43 eV for the cluster models. The surface range is almost three times larger than the energy range for the cluster models. The energy magnitude for the clusters is larger compared to the surface calculations. The most favorable cluster configuration is 0.36 eV more favorable than the most favorable structure for the C3 surface, but over a 1 eV difference compared to the most favorable structures for the A3 and C4 surface. These differences support that cluster models cannot be substituted for periodic slab models.

We see similar results for when the arsenate is deprotonated and doubly deprotonated. For the A3 surface the HHBB structure is the most favorable for all three (de)protonated forms. However, the deprotonated HHBB structure takes a H from a nearby O atom and becomes singly deprotonated. This proton rearrangement makes the reaction energy exothermic while the other two A3 structures, which do not result in proton rearrangement, are endothermic. For the doubly deprotonated HHBB structure proton rearrangement occurs once again but this time the doubly deprotonated arsenate becomes singly deprotonated.

Proton rearrangement also occurred in the C3 HHBB deprotonated structure in order to become singly deprotonated. Even though the deprotonated C3 HHBB structure became singly protonated upon adsorption, the C3 HVBM(HHBB) configuration was always the most favorable.

Not all protonated states properly optimized for the C4 structure. Deprotonated arsenate would not optimize in a bidentate configuration for the HVBM structure. The HHVTB configuration always resulted in a tridentate configuration no matter which protonation state was being modeled. Also proton rearrangement occurred in the
deprotonated HHVTB structure making the arsenate once again singly deprotonated. For all doubly deprotonated configurations the arsenate optimized to bond in a tridentate fashion onto the C4 surface. When all arsenate binds in a tridentate fashion the HHBB structure is more favorable than the HHVTB. No matter the protonation state a HH configuration is more favorable than a HV configuration and a BB or TB binding is more favorable than a MB (monodentate binuclear).

For the cluster models all structures correctly optimized except the deprotonated Al-BM1. However, for all protonation states of the arsenate the BB configuration is always the most favorable and the energy range for all protonated forms is much smaller than the energy ranges for the surfaces. The energy range for the deprotonated structures is only 0.18 eV and the range for the doubly protonated structures is 0.59 eV. No matter the protonation state of the arsenate cluster models cannot be substituted for the full periodic slab models.

8.5 Conclusion

Before this study we knew from many experimental research studies that inner-sphere arsenate adsorption preferred a BB configuration, but this study is the first to look at a variety of arsenate configurations in order to explain why the BB configuration is the most favorable. Hydrogen bonding interactions were shown to play an important role in the reactivity. Hydrogen bonding is a struggle to observe experimentally so experimentalists could not have predicted this outcome. Another new result from this study is the comparison between cluster models and full alumina surface models. Cluster models are approximations of surfaces and therefore the small models cannot represent a full surface, only surface models give an accurate energy range for a variety of different
arsenate configurations and cluster models should not take place of modeling a full surface. Hopefully this result motivates ongoing research to model accurate systems that may be computationally more expensive in order to obtain more realistic structures that agree with experimental data, and we hope our protonation study gives insights to studying arsenate adsorption in a variety of environmental conditions.

8.6 Acknowledgements

This work was supported by NSF grant CHE-1254127, and utilized computational resources provided by the University of Iowa College of Liberal Arts and Sciences.
9. CONCLUSION AND FUTURE WORK

The results presented in this dissertation demonstrate that aluminium nanoclusters exhibit unique reactivity patterns, which can be explained based on their shape, and are successful molecules to use in adsorption based water remediation methods. A better understanding of how adsorption mechanisms vary between true nanoparticles and other geochemical surface models such as mineral-water interfaces is also explored and explained. Using a collaborative approach we were able to connect with experimental crystal structures in order to help bridge the knowledge gap between experiment and theory in order to model and explain the reactivity of Keggin based compounds. Computational studies are an ideal means for comparing Al nanocluster reactivities, and may lead to more cohesive theories of ion adsorption to environmental interfaces.

In Chapter 4 it was demonstrated that the reactivity factors intrinsic to extended mineral-water interfaces do not translate to the molecular Keggin structures. Our new idea of shape-reactivity relationship was found to govern the reactivity of outer-sphere adsorption of SO$_4^{2-}$/Cl$^-$ on the surfaces of Al$_{13}$, Al$_{30}$, and Al$_{32}$. The shape-reactivity relationship was able to be visualized by plotting the electrostatic potential. An interesting result was that the outer-sphere anion adsorption in the beltway of the larger Al Keggin nanoclusters was unusually strong. The shape-reactivity relationship may be of particular use in comparing adsorption trends on nanocluster sorbents of the same composition.

After analyzing various $X_2$Al$_{30}$ and $Z_2$–Al$_{30}$ structures in Chapter 5, we established consistent evidence for the preference of inner-sphere cation adsorption onto the caps and outer-sphere anion adsorption to the beltway of Al$_{30}$. Once again using the
electronic potential we were able to explain the distinct structure-reactivity relationships for the cation and anion adsorption sites of Al$_{30}$. A major unexpected result was that outer-sphere anion adsorption was stronger than inner-sphere cation adsorption, which could not have been predicted based on surface studies. Given that the explanation for the topology-dependent site preference trends of cations and anions depend on the existence of semi-pore regions in the Al$_{30}$ beltway, we next were able to extend our calculations to study co-adsorption.

In Chapter 6, a combined structural characterization and computational study of the Cu$_2$Al$_{30}$-S polyaluminum species was achieved. The net formation of Cu$_2$(SO$_4$)$_2$Al$_{30}$ was studied via a theoretical step-wise mechanisms differing in the order of anion outer-sphere and cation inner-sphere adsorption steps but it was determined that adsorption order did not matter. The strong outer-sphere sulfate adsorption governed the inner-sphere Cu$^{2+}$ to adsorb to the beltway region, which provided consistent evidence for the preferred Cu$^{2+}$ adsorption site on the Al$_{30}$ cluster compared to the experimental crystal structure.

In Chapter 7 inner-sphere anion adsorption was studied in another collaborative approach. A combined structural characterization and computational study of (TBP)$_2$Al$_{30}$-S shows that an inner-sphere ion pair between TBP and Al$_{30}$ forms via adsorption in the beltway region of the polycation. R-substituted phosphate and arsenate species adsorbing to Al$_{30}$ were also studied but no matter the R-group the anion always preferred to adsorb to the beltway region of Al$_{30}$. A common theme in this dissertation is that the adsorption sites can be explained in terms of the molecular topography. We showed that oxygen functional group type and coordination alone cannot explain the greater reactivity of
adsorption sites in the Al$_{30}$ beltway region, even though such arguments have been successfully applied to a variety of mineral surface reactivities.

Lastly in Chapter 8, mineral surface reactivity was studied. We took the opportunity to systematically compare As(V) adsorption on periodic slab models and small fictitious Al cluster models; this slab/cluster debate already exists in current literature but up to now had not been thoroughly examined. The reactivity of fictitious Al cluster models was compared to alumina surface models, and we determined that Al cluster models cannot be substituted for large alumina surfaces. Only surface models give an accurate energy range for a variety of different arsenate configurations and cluster models should not (and cannot) take the place of modelling a proper surface. We hope that our results motivate ongoing research to model more accurate systems in order to obtain more environmentally realistic structures. In the future, the results obtained from this study can be used as the starting point to study water ordering on Al surfaces. When adsorbents, such as As(V), bind to Al surfaces in the environment there is water surrounding the system and this has not yet been taken into consideration in the computational studies. By modeling 10-20 water molecules around the surface the ordering of the water molecules could be studied and therefore be a better representation of the environment.

The work presented here can also help guide future Keggin research. The research in this dissertation provides an important contribution in our understanding of Keggin based Al compounds. Keggin based compounds are very sparsely studied computationally and this work fills a knowledge gap. Now that we have studied Al Keggins and are confident in our structural agreement with experiment, this work can
lead to studying heteroatom substitution in the Al$_{13}$ Keggin. In the Keggin structure there is one tetrahedrally coordinated Al atom, and previous studies by Rustad and Casey have determined that heteroatom substitution can impact the kinetics of ligand exchange reactions.$^{67,164,165}$ By studying heteroatom substitution structural similarities and differences might be observed that can explain why the kinetics are impacted from substituting the tetrahedral metal.

Another area that can be explored is Fe based Keggin structures. Al and Fe have been shown to be isostructural in surface calculations but experimentally Fe Keggins are much harder to synthesize compared to Al Keggins. Recently, the α-Keggin has been synthesized for only Fe and not Al and we could use theory to try to determine why the Fe α-Keggin can be synthesized and not the Al α-Keggin.$^{58}$ Another Fe material of future interest is ferrihydrite; ferrihydrite is a nanomineral that is ubiquitous in environmental systems and has said to be formed from the Fe δ-Keggin, however, the Fe δ-Keggin has not yet been synthesized. Using computationally chemistry one can set out to determine how ferrihydrite might form or why the Fe δ-Keggin has not yet been crystalized. In time, computational chemistry can guide experimentalists by understanding interactions that cannot be seen experimentally in order to obtain innovative results.
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APPENDIX A. DMOL³ INPUT FILES

# Input for DMol3
# Title: Al surface optimization

Calculate      optimize   550
Functional     pbe
Pseudopotential  none
Basis_Version  default
Basis          dnp
Cutoff_global  3.5000 angstrom

# Electronic parameters
Spin_polarization  restricted
Occupation          Thermal 0.004
COSMO               iibs
COSMO_Dielectric    78.5400
Integration_Grid    fine
Aux_Density         octupole
Charge              0.0

# Properties Keywords
Mulliken_Analysis  charge
Hirshfeld_Analysis charge
Convergence_density 1.00E-07
Charge_Mixing      0.10000000  10.00000000
Spin_Mixing        0.05
Number_bad_Steps   90
Direct_scf         off
use_old_density
Kpoints monk       2 2 1
OPT_Energy_Convergence     0.00001000
OPT_Gradient_Convergence   0.00200000
OPT_Displacement_Convergence 0.00100000
OPT_Iterations       10
OPT_Coordinate_System internal_cartesian
OPT_Restart          off
OPT_Max_Displacement 0.30000000
OPT_Hessian_Project on
Partial_dos        on
plot_dos
Print               SCF Brief
Print               OPT Normal
Print               Eigval_Last_It
# Input for DMol3
# Title: Al13 nanoparticle optimization

# Task parameters
Calculate optimize 550
Functional pbe
Pseudopotential none
Basis dnp
Cutoff_global 3.5000 angstrom
Charge 7
Symmetry C1

# Electronic parameters
Spin_polarization restricted
COSMO on
Occupation Thermal 0.004
Integration_grid fine
Aux_density octupole
Opt_energy_convergence 1.0000E-004
Opt_gradient_convergence 3.5000E-003 Å
Opt_displacement_convergence 1.0000E-003 Å
Opt_iterations 20
Opt_max_displacement 0.3000 Å

# Internal constraints

# Calculated properties
Mulliken_analysis charge
Hirshfeld_analysis charge
Convergence_density 1.0000E-007
Charge_Mixing 0.1000
Spin_Mixing 0.200
D_diis_history 20
Number_bad_Steps 90
Direct_scf off

# Print options
Print eigval_last_it
Partial_dos on
plot_dos
Print SCF Brief
Print OPT Normal