Using First-Principles DFT to Study the Reactivity of Hydrated Oxide Surfaces

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Abstract

Geochemical reactions occurring at the interface between oxide surfaces and aqueous solution exert control on the transport and fate of contaminants. Molecular-level understanding of how metal ions adsorb to these surfaces is needed to understand contaminant speciation and bioavailability. Complexity arising from multiple surface stoichiometries, hydrogen bonding patterns, and varying oxygen functional group reactivities must be carefully considered. We use the interaction of lead with alumina and hematite as model systems to probe for essential factors governing the reactivity of hydrated surfaces towards contaminant ions. While geometrically isostructural, these two oxides have sharp contrasts in reactivity and electronic structure. We use this fact to make comparisons between the preferred adsorption modes of Pb(II) and discuss the relationships between surface structure, reactivity, and electronic structure.

Introduction

Lead (Pb) contamination in topsoil is one of the most serious environmental issues in the U.S. and other countries. Pb is toxic to almost all organs in the body, posing notable problems to neurological development, the hematological and cardiovascular systems, and the kidney. Despite its prevalence in the environment, molecular-level understanding of Pb adsorption is poorly understood.

The interfaces between natural soils and aqueous solutions make up a geochemically important part of the earth's surface where Pb ions adsorb and desorb, affecting the transport and ultimate fate of this contaminant.

In this work we present a detailed *ab initio* study aimed at understanding fundamental structure-reactivity relationships of Pb adsorption on model mineral-water interface systems. Fe- and Al-(oxyhyr)oxides comprise important examples of reactive mineral surfaces. Our study focuses on Pb(II) adsorbed to the hydroxylated (0001) surface termination of alumina and hematite. The fully hydroxylated, oxygen-terminated (0001) surface, denoted $(HO)_3$-M-M-*R* (where Fe or Al is indicated by M and *R* represents the continuing bulk atomic stacking sequence), is the dominant structure for hematite and the only one observed for alumina under geologically relevant conditions. By modeling Pb adsorption on the isostructural $(HO)_3$-M-M-*R* surface, we are able to isolate and study the reactivity-composition relationship.

Methodology

Periodic spin-polarized Density Functional Theory (DFT) calculations are carried out, using a double zeta, polarized atom-centered numerical basis set, as implemented in the Dmol3 code. Benchmarking and testing of our methods are carried out and compared to gas phase spectroscopy of the PbO molecular dimer and X-ray diffraction structures of crystalline PbO and PbO_2 oxides. We carry out additional benchmarking for other Pb compounds studied my various theoretical methods.

The results of our extensive benchmarking support the ability of our employed electronic structure methods to perform consistently and accurately across a range of possible Pb oxidation states and coordination environments.

The alumina and hematite surfaces are modeled by periodic slabs consisting of six O layers and 10 M layers. Periodic slab images are separated by no less than 25 Angstroms of vacuum. The two exposed surfaces are treated equivalently and related by inversion. We carry out a careful investigation of surface hydroxyl group orientation on both the hematite and alumina surfaces, and study this reactivity consideration. Full geometry optimizations are carried out with a structural convergence set to a force tolerance of 0.01 eV/Angstrom. To model Pb adsorption at geochemically feasible concentrations, large (2x2) surface supercells are used.

Initial Pb(II) adsorption sites are determined through consideration of Pb chemistry and the oxide surface geometry. In inorganic compounds, Pb is rarely in the elemental form and is generally present in the +2 oxidation state. Furthermore, it is resistant to redox reactions under geochemically relevant ranges in pH. The outermost O layer of the $(HO)_3$-M-M-*R* surface forms a triangular lattice. The centers of these O-triangles are inherently reasonable binding sites for Pb based on the experimentally observed trigonal pyramidal structure of Pb adsorption. The adsorbed structures are always charge-balanced such that Pb is in the naturally dominant +2 oxidation state. This requires displacement of 2 of the 3 H^+ at each adsorption site.

Applying electronic structure methods to environmental molecule science is an exciting and new area of research. The charge density, the essential quantity of DFT, can be analyzed in a number of ways to uncover important bonding interactions at reactive surfaces before and after adsorption. The electronic origins of Pb adsorption are studied using atom-projected density of states (PDOS) analysis. This semi-quantitative tool allows us to determine the atomic orbital character of the charge density. Covalent interactions are indicated in the PDOS by overlapping intensity between bonding atoms below the Fermi level, while ionic interactions are expressed by neighboring filled and empty valence states. Through PDOS analysis, we can identify the electronic interactions governing alumina and hematite surface reactivity and Pb binding.

Discussion

Our DFT comparative study of Pb(II) binding on isostructural hydrated alumina and hematite surfaces produces several trends that we study and explain through structural and electronic analysis. We construct a theoretical framework for Pb/water/oxide interactions with possible extension to other geochemically important interfaces.

Our periodic calculations model the surface H-bond arrangements as extended networks. We report two qualitatively different, but energetically similar, H-bonding patterns on both the alumina and hematite hydrated surfaces. The local geometry at the different Pb adsorption sites varies between the two reported energetically similar H-bond patterns. These two patterns therefore provide the opportunity to study the influence of hydroxyl group orientation on surface reactivity on both alumina and hematite. This is the first study addressing the impact of surface hydroxyl group orientation on hydrated surface reactivity.

We compute Pb adsorption energies that reproduce the experimentally established trend that hematite is more reactive towards Pb than alumina. What is unique to our result is that we determine the hematite surface to be more reactive based only on composition. The underlying origins of the varying surface reactivity can be traced to the partially occupied Fe *d*-band. Our analysis of the PDOS reveals two mechanisms through which the *d*-electrons influence the Pb binding. The two mechanisms are distinct in that one arises from the inherent hematite surface electronic structure, while the other is a localized interaction that depends strongly on the Pb binding geometry.

In the hematite surface, the Fe atoms are in a near octahedral environment. This coordination with surface oxygen atoms leads to a crystal field splitting in the Fe *d*-band. The spitting of the d-bands is very sensitive to the surface geometry. In the bulk, the Fe spins in hematite are in an anti-ferromagnetic configuration, alternating in sign between each Fe bilayer. Exposing the surface to either vacuum or water results in surface relaxations which result in varied Fe-O bond distances and therefore different Fe *d*-band energy splittings. We report how the hematite *d*-band is influenced by surface structure, and how this in turn influences electronic interactions with the Pb ion.

We also investigate the shape of the charge density for adsorbed Pb. We identify that the Pb lone pair is directed away from the oxide surface. By modeling additional molecular water, we demonstrate that the Pb lone pair is significantly hydrophobic. This result is likely general to Pb adsorbed on different (in both structure and composition) oxide surfaces. This result is key to assessing our methods in that it shows inappreciable stabilization provided by the addition of water molecules to the modeled systems.

Our results demonstrate the utility of DFT modeling to study and extract fundamental molecular-level understanding of geometrical interfaces. Our results span the steric effects imposed by hydroxyl group orientations, directionality of Pb charge, inherent alumina and hematite surface reactivity, hematite d-band splitting and it's sensitivity to surface structure, and Pb-surface electronic interactions.

Acknowledgments

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