Surface Complexation of $As(OH)_3$ and $AsO(OH)_3$ on Nanocrystalline Iron Oxide (Ferrihydrite): A First-principles DFT-D3 Investigation

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Reactive iron oxide nanoparticles exert control on the bioavailability of contaminant arsenic species in natural aqueous systems. The ability to accurately predict arsenic surface complexation and gain detailed insight into the adsorption mechanisms is, however, limited by the lack of molecular-level understanding of arsenic−water−nanoparticle interactions. In this work, the adsorption structures and properties of arsenous acid ($As(OH)_3$) and arsenic acid ($AsO(OH)_3$) on the hydrated ferrihydrite (110) surface were investigated by Density Functional Theory (DFT) calculations. Dissociative adsorption is observed to dominate over molecular adsorption for both arsenic species on the hydrated ferrihydrite (110) surface. The lowest-energy stable configuration for $As(OH)_3$ on the surface is a dissociated monodentate structure, Fe−O−D1, with an adsorption energy of −1.54 eV. For $AsO(OH)_3$, the most stable configuration is a dissociated bidentate structure, Fe−OOH−Fe−D2, with an adsorption energy of −2.85 eV. Analysis of the bonding mechanism of the arsenic species onto the hydrated ferrihydrite (110) surface reveals that the adsorption process is characterized by hybridization of the adsorbates S- and O-p states with the surface Fe-d states. Vibrational frequency assignments of the adsorbed arsenic species are also presented and discussed. We consider that the analysis of surface reactivity and the insights into the structure–property relationships of the ferrihydrite–water−arsenic interface presented here will be useful in the interpretation of future experimental investigations or applications of iron oxide nanomaterials for the treatment of arsenic-contaminated water.