

Paul K.W., Borda M.J., Kubicki J.D., Sparks D.L. How Dehydration Affects SO_4^{2-} Adsorption at the Fe-(Hydr)oxide- H_2O Interface. IUSS Symposium Advances of Molecular Modeling – Perspectives for Soil Research. October 21-22, 2005. University of Natural Resources and Applied Life Sciences, Vienna, Austria.

Abstract

The effect of dehydration on the coordination and speciation of sulfate at the Fe-(hydr)oxide- H_2O interface was investigated using molecular orbital/density functional theory (MO/DFT) and Fourier transform infrared (FTIR) spectroscopy. IR frequency calculations were performed at the UB3LYP/6-31+G(d) level of theory for potential sulfate (bidentate bridging, monodentate, and H-bonded) and bisulfate (bidentate bridging and monodentate) surface complexes. MO/DFT calculated IR frequencies were compared to available IR literature results and attenuated total reflectance (ATR) FTIR spectra collected in our laboratory of sulfate adsorbed at the hematite- H_2O interface. IR frequency calculations performed using the larger 6-311+G(d,p) basis set resulted in minor frequency shifts that did not dramatically alter the agreement with experiment. This investigation proposes that sulfate undergoes a speciation change as a function of surface dehydration. A generalized model for the speciation change is proposed as follows:

1. At the Fe-(hydr)oxide- H_2O interface sulfate adsorbs as a bidentate bridging or monodentate surface complex under most experimental conditions.
2. Upon surface dehydration, sulfate changes speciation to form bidentate bridging and/or monodentate bisulfate. However, surface dehydration does not yield 100% speciation change, but leads to a mixture of sulfate and bisulfate.
3. The speciation change is reversible as a function of rehydration.

The reversibility of the sulfate-bisulfate speciation change is chiefly determined by the local hydration environment of the O-H bond in bisulfate. Under dehydrated conditions, the O-H bond length is approximately 0.98 Å. The bond length substantially increases (bond strength decreases) to approximately 1.03 Å when the initial H-bond network is reestablished through hydration, likely leading to deprotonation upon full mineral surface hydration.