

## Structures of carboxylates on iron(hydr)oxide surfaces studied with FTIR and DFT calculations

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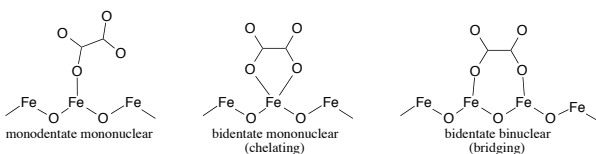
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Ligand-controlled and reductive dissolution of iron(hydr)oxides are key processes in biological iron acquisition and in the cycling of iron and trace elements. Rates of dissolution which are thermodynamically driven and accelerated by e.g., siderophores have been shown to further increase in the presence of small organic ligands, particularly for strongly adsorbing dicarboxylates such as oxalate [1]. Although the adsorption of oxalate on iron(hydr)oxides has been studied previously [2], the bonding structures and the labilization of the lattice surrounding the adsorption site remain poorly understood. Aided by computational methods, analysis of vibrational spectra of oxalate adsorbed on lepidocrocite and goethite can yield detailed information about structural changes and mechanisms promoting dissolution.

In this study, molecular cluster and periodic calculations were used to obtain energy-minimized surface complex structures and vibrational frequencies of possible surface structures, which were then compared to FTIR spectra measured under a range of conditions. Monodentate mononuclear, bidentate mononuclear (chelating), and bidentate dinuclear (bridging) structures were considered for both dry and wet surfaces. Changes in lattice bond strengths and expected effects on dissolution rates will be discussed.



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