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# Interfacial structures and acidity constants of goethite from first-principles Molecular Dynamics simulations

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## Abstract

In this paper, we report a first-principles Molecular Dynamics (FPMD) study of interfacial structures and acidity constants of goethite. The p*K*a values of the groups on (010), (110), and (021) surfaces (space group *Pbnm*) are derived with the FPMD based vertical energy gap technique. The results indicate that major reactive groups include $\equiv Fe_2OH_2$ and $\equiv FeOH_2$ on (010), $\equiv FeOH_2$, $\equiv Fe_3O_LH$, and $\equiv Fe_3O_UH$ on (110), and $\equiv FeO_hH_2$ and $\equiv Fe_2OH$ on (021). The interfacial structures were characterized in detail with a focus on the hydrogen bonding environment. With the calculated p*K*a values, the point of zero charges (PZCs) of the three surfaces are derived and the overall PZC range of goethite is found to be consistent with the experiment. We further discuss the potential applications of these results in future studies toward understanding the environmental processes of goethite.

**Keywords:** Goethite, acidity constant, interfacial structure, first-principles Molecular Dynamics