

Hydrogen Bonding at Corundum–Water Interfaces from First-Principle Molecular Dynamics

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The interface between water and mineral surfaces plays a critical role in wide-ranging biogeochemical and technological processes. Key surface processes such as adsorption, dissolution, corrosion, and catalysis all depend on the atomic structure within the interfacial domain. The structure of interfacial water, which may be quite distinct from bulk liquid water, arises from interactions between water molecules and surface functional groups. The specific types and arrangements of surface functional groups are distinct for each mineral surface. The interplay between the relatively static mineral surface atoms and more dynamic water molecules determines the structural and dynamic properties of mineral-water interfaces. At the interface, the surface may be hydrophilic or hydrophobic, and water molecules may adsorb associatively or dissociate, resulting in interfacial properties strongly coupled to the prevailing hydrogen bonding network. At interfaces both inter- and intramolecular H-bonding exists, depending on surface structure. First-principle molecular dynamics simulations (FPMD) can provide a detailed picture of the structure and H-bonding networks within mineral–water interfacial domains.

In this presentation, we present our results of FPMD simulations examining the hydrogen bonding networks at alumina (corundum, α -Al₂O₃) interfaces. We compare the (001), (012), (113) and (110) corundum–water interfaces, which have distinct surface functional groups (–OH, μ -OH, and μ_3 -OH) and topographies. There were distinct differences between the four surfaces and relative to bulk water. In bulk water, the average number of H-bonds per water molecule is ~ 3.6 . On the (001) and (012) surfaces there are ~ 3.1 and 3.2 H-bonds per water molecule, respectively, whereas there are only ~ 2.8 H-bonds per water molecule on the (113) and (110) surfaces. Looking at the H-bond profile from the surface into bulk water, there is a maximum of hydrogen bonds immediately adjacent to the surface for the (001) and (012) surfaces. In contrast at the (113) and (110) surface the number of H-bonds is level. We consider the (001) and (012) surfaces hydrophilic while the (113) and (110) surfaces have a more hydrophobic character.