

# Water-calcite (104) surface interactions using first-principles simulations

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**Abstract:** An in-depth understanding of the water and mineral interaction is indispensable for many fields including enhanced oil recovery, global carbon cycle, and environment sustainability. In this work, using first-principles calculations based on density functional theory supplemented with semiempirical DFT-D2 dispersion corrections, we study the structural, energetic, electronic, and optical properties of hydrated calcite (104) surfaces via an exhaustive sampling of all the adsorption sites with up to full (monolayer) water coverage. Our results suggest that on-top Ca surface sites are the most energetically favorable sites for water adsorption. Also, we found sizable differences in the binding energies among the configurations having the same number of adsorbed water molecules, highly likely due to the differences in the organization and tilting of  $\text{Ca}_s\text{-O}_s$  octahedra along with the differences in the  $\text{Ca}_s\text{-O}_w$  bond distance and  $\text{Ca}_s\text{-O}_w\text{-H}$  bond angles. We also report intriguing variations in the optical absorption spectra of hydrated calcite (104) surfaces with respect to pristine (anhydrous) calcite (104) surface. Interestingly, we find significant variations in the optical absorption spectra among the hydrated calcite (104) surfaces having the same of adsorbed water molecules. The findings in this theoretical study would help in improving our fundamental understanding of hydrated calcite (104) surface that has impact on many processes in nature.