WATER ON CALCITE: SELF-ASSEMBLY AND DESORPTION AT LOW COVERAGE

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Calcite, the dominating polymorph of calcium carbonate ($CaCO_3$), is among the most abundant minerals on planet Earth. Understanding its interactions with the environment thus bears some significance, especially towards biomineralization. For example, the interplay between calcite, water and carbon dioxide might provide a very effective and safe carbon capture mechanism [1]. However, the future technological applications require a robust understanding of calcite interactions at all scales.

Here, we present a multimethod investigation probing water-calcite interactions up to monolayer water coverage. Using atomic force microscopy in ultra-high vacuum, a striking water self-assembly pattern at half monolayer coverage is observed. With density functional theory (DFT) calculations and first-principles molecular dynamics (FPMD) simulations, we explore the energetics and the molecular-level details of the formed pattern. Temperature programmed desorption experiments are then used to yield more insight into the water-calcite bonding strength. During the monolayer desorption, an interesting double-peak is observed. Again, DFT calculations and FPMD simulations are utilised to construct a consistent and detailed molecular-level desorption mechanism.

Our work, thus, constitutes a major step towards a molecular-level understanding of water-calcite interaction.

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