Water adsorption on the calcite(104)-(2×1) surface

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The interaction between water and mineral surfaces is of broad importance from the planetary down to the atomic level. The mineral calcite, the most stable polymorph of calcium carbonate ($CaCO_3$), is in this context of key relevance due to its involvement in many natural and biological processes [1].

Very recently, the calcite(104) surface, the most stable cleavage plane that supports virtually all reactions, has been investigated by high-resolution non-contact atomic force microscopy (NC-AFM) and density functional theory (DFT) [2]. It was established that the pristine surface is (2×1) reconstructed, belongs to the planar space group *pg*, and that the reconstruction generates two adsorption sites for carbon monoxide molecules.

Here, we introduce the structure of the (2×1) reconstructed surface [2] and revisit the adsorption of water on calcite(104) in light of the (2×1) reconstruction by NC-AFM experiments combined with DFT calculations. We find that water exclusively occupies only one half of each (2×1) unit cell up to a coverage of 0.5 ML and at a temperature of 140 K (see Fig. 1a) [3]. This finding can be explained by a difference in the adsorption energy at the two different adsorption sites within the (2×1) unit cell (optimum adsorption geometry of a single water molecule is shown in Fig. 1b). The optimum adsorption geometry is confirmed [4] by high-resolution NC-AFM data acquired at 5K with CO-functionalised tips (see Fig. 1c). In contrast, a (1×1) structure is observed at coverage of a full monolayer [3]. The transition between these structures is explained by water-induced lifting of the (2×1) surface reconstruction and unravels an unexpected mechanism that influences molecular adsorption on this important mineral surface.

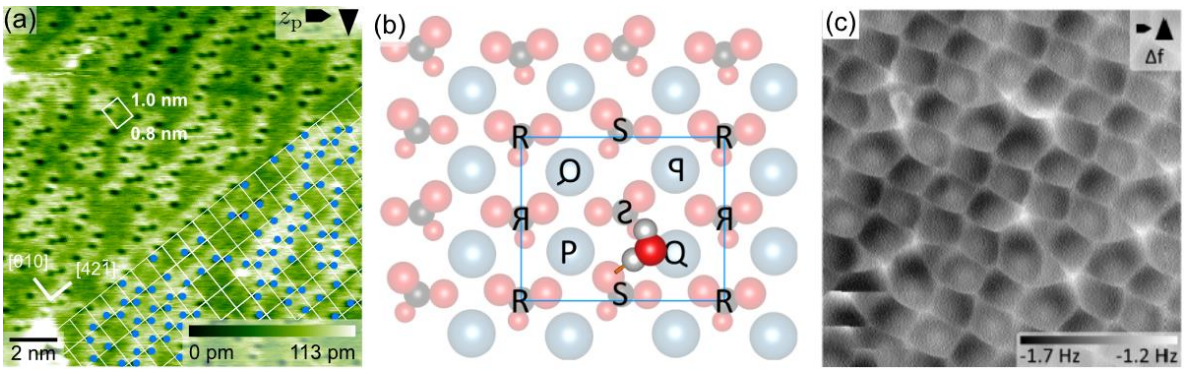

Fig. 1. (a) Water/calcite(104) (coverage of 0.26 ML) imaged at 140K [3]. (b) Optimum DFT geometry for a single water molecule adsorbed on the calcite(104)-(2×1) reconstructed surface [3]. (c) High-resolution imaging of single water molecules on calcite(104)-(2×1) with a CO-functionalised tip at 5K [4].

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