Electronic Supplementary Information

Water adsorption lifts the (2×1) reconstruction of calcite(104)

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Materials and Methods

Sample preparation

Sample preparation, water dosing, and NC-AFM experiments were all performed under ultra-high vacuum conditions (p < 2×10^{-11} mbar). Calcite crystals (Korth Kristalle, Altenholz, Germany) were cleaved [1] *in-situ* parallel to a (104) surface, followed by heating the crystal for 1 h at about 326°C to remove residual charges [2]. The crystals were optically transparent. The orientation of the [421] direction was determined by an optical procedure *ex-situ* after the NC-AFM experiments [3]: The split between the ordinary and extraordinary ray is pointing along the [421] direction. Deionized water (from a Merck Millipore purification setup) was deposited by dosing through a variable leak valve at a pressure of 1×10^{-9} mbar. Water was purified by freeze-pump-thaw cycles before dosing.

NC-AFM experiments

NC-AFM experiments were performed using a VT AFM/STM instrument (ScientaOmicron, Taunusstein, Germany) operated by a MATRIX controller. N-doped silicon cantilevers (Nanosensors) with a nominal force constant of 40 N/m and an eigenfrequency of 300 kHz were used and cleaned before NC-AFM experiments by bombardment with Argon ions. NC-AFM was performed in the frequency-modulation constant-amplitude mode [4]. Oscillation amplitudes (zero-peak) in the range of 5 nm to 10 nm were used. The fast and slow scan directions are indicated by an arrow and a triangle, respectively, in the experimental topography images that represent a map of the piezo position z_p . During the measurements on calcite(104), a bias voltage

in the range of $U_{\text{bias}} = -2.4 \text{ V}$ to $U_{\text{bias}} = 4 \text{ V}$ was applied between tip and sample holder to reduce electrostatic background forces. The microscope was cooled with liquid He or N₂ via a flow cryostat. Residual drift was corrected by comparing pairs of up and down images [5, 6] and accordingly shearing the image data.

DFT calculations

All first-principles calculations in this work were performed using a similar methodology as in a previous study [7]. In particular, the periodic plane-wave basis VASP code [8, 9] implementing the spin-polarized Density Functional Theory (DFT) was used. To accurately include van der Waals interactions for this system, we further used the Tkatchenko-Scheffler method with iterative Hirshfeld partitioning [10], shown to be best suited for ionic systems [11, 12]. Projected augmented wave potentials were used to describe the core electrons [13] with a kinetic energy cutoff of 500 eV (with PREC = accurate). Systematic *k*-point convergence was checked for all systems with sampling chosen according to the system size. This approach converged the total energy of all the systems to the order of 1 meV. For calculations of the calcite surface, we used a $4 \times 4 \times 4$ supercell (320 atoms total), a vacuum gap of at least 1.5 nm and a $5 \times 5 \times 1$ *k*-point grid. The upper two layers of calcite were allowed to relax to a force of less than 0.001 eV/Å. Barrier calculations were performed initially using the standard Nudged Elastic Band (NEB) method with increasing image density [14], before implementing the Climbing NEB approach [15] to find the final barrier. For these calculations, only the *gamma* point was used.

Atomic shifts between geometric models of different coverage are calculated from the Euclidean norm of the displacement vector between identical atoms in the two models.

Structure files

CIF data files are provide	d as part of the E	SI for the different	models as listed	in the table below.
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File name	Description		
2x1_final.cif	(2×1) reconstructed calcite(104) surface		
	[Reference [7]]		
n8.cif	Surface with N=8 water molecules (0.5 ML)		
	[Figure 1(b) and S1(b)]		
n9.cif	Surface with N=9 water molecules		
	[Figure 3(a) and S3(a)]		
n10.cif	Surface with N=10 water molecules		
	[Figure 3(b) and S3(b)]		
n11.cif	Surface with N=11 water molecules		
	[Figure 3(c) and S3(c)]		
n12.cif	Surface with N=12 water molecules		
	[Figure 3(d) and S3(d)]		
full.cif	Surface with N=16 water molecules (1 ML)		
	[Figure S4(d)]		



Figure S1: Atomic shifts (in pm) within the calcite(104) surface geometry after adsorption of (a) a single QS water molecule and (b) a {QS} water row. Numbers denote the total atomic shift (in pm) with respect to the (2×1) reconstruction of a pristine calcite(104) surface of more than (a) 5pm and (b) 10pm. Black lines highlight the XY-projected shift trajectories.



Figure S2: *DFT* geometries for potential water row structures (N=8), both lying higher in energy than the {QS} row structure in Figure 1(b). Adsorption energy per water molecule: (a) -0.81 eV and (b) -0.64 eV.



Figure S3: Atomic shifts (in pm) upon filling water along the reconstructed carbonate group row. Small black numbers denote the absolute atom shifts (in pm) relative to (a) Figure 1b, (b) Figure S3a, (c) Figure S3b (shifts below 10 pm not shown), and (d) Figure S3c (shifts below 5 pm not shown).



Figure S4: (a) Geometry for N=10 with two water molecules adsorbed at PR positions $(E_{PR,10} = -0.77eV)$. (b) Geometry for N=10 with two PR water molecules at two positions along a [010] surface row $(E_{PR,10,b} = -0.72eV)$. (c) Geometry for N=12 with four PR water molecules at positions along two separated [010] surface row $(E_{PR,12} = -0.79eV)$ (d) Structure of a full water monolayer $(E_{IPR,16} = -0.87eV)$.



Figure S5: *NEB calculations for a single PR water molecule diffusing along the* $[42\overline{1}]$ *direction* (*a*) *without* (*N*=9) *and* (*b*) *with* (*N*=10) *one adjacent PR water molecule.* (*c*) *Energy profile, each energy calculated from Eq. 4, relative to* $E_{\{PR\},10}$. *The lowest energy configuration is given for a PR dimer geometry. Additionally, a higher barrier is found for a water molecule diffusing next to a PR water.*

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