

Supporting Information

Resolving the Structure of a Well-Ordered Hydroxyl Overlayer on $\text{In}_2\text{O}_3(111)$: Nanomanipulation and Theory

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Additional Experimental Data

1) XPS: O 1s data

The XPS spectra presented in the main text were measured in normal incidence, i.e, grazing emission (60° with respect to the surface normal), using a non-monochromatic Mg $K\alpha$ source. The contributions in the O 1s core level related to the water exposure are investigated in the difference spectra shown in Figure S1. At room temperature, where the surface saturates at ~ 0.3 L, the shoulder seen in the spectra of Figure 2 of the main text belongs to a peak at ~ 532 eV, see Figure S1(a). At 100 K, both dissociative and molecular adsorption seem to coexist, visible as two additional peaks at ~ 532 and ~ 533 eV in Figure S1(b).

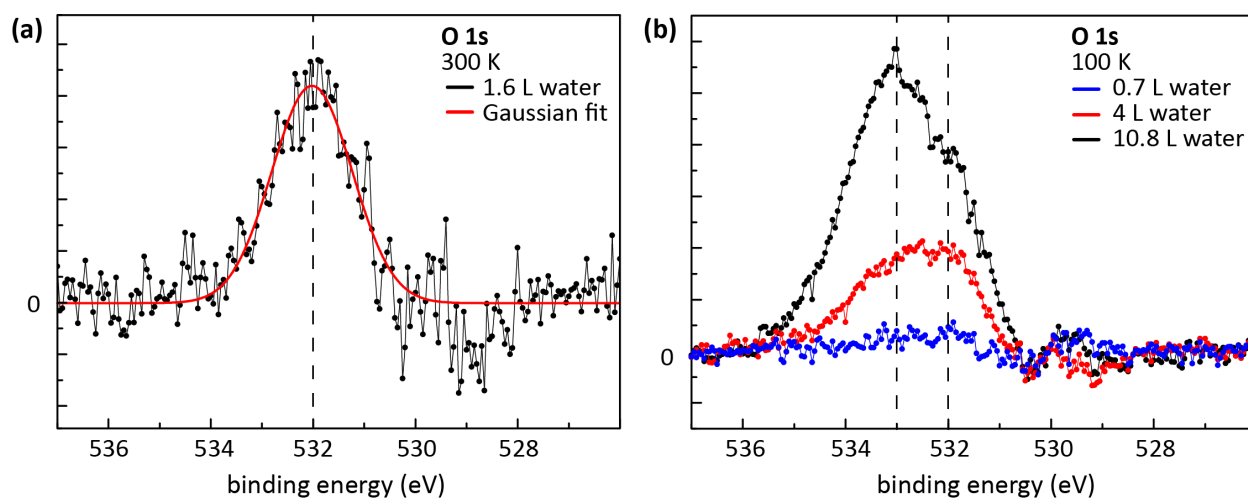


Figure S1: Difference spectra of the O 1s core level after exposure to water with respect to the clean surface. Prior to the subtraction, the spectra have been shifted to compensate for the band bending and the substrate O peak located at ~ 530 eV has been used for normalization. The sample temperature during water exposure and the XPS measurements is (a) 300 K and (b) 100 K.

2) STM: Water multilayer

A water multilayer was prepared by dosing 2 L at 100 K and investigated with STM as prepared and also after warming up for 5 min on the wobble stick. Figure S2 shows images of the initial preparation; the whole surface appears fuzzy as the STM tip interacts strongly with the water multilayer while scanning. Stripes in $[\bar{1}01]$ direction indicate weak ordering or water species being continuously pushed by the tip along the azimuthal direction closest to the slow scanning direction.

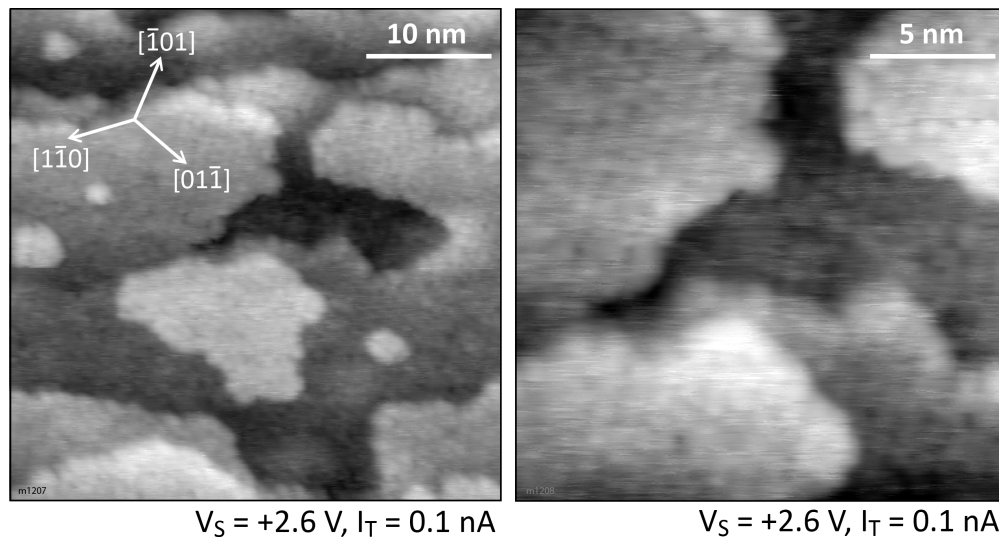


Figure S2: STM images showing 2 L of water dosed at 100 K and measured at 79 K.

3) STM: Scanning with high bias voltage

The curved and oval features observed in the STM images after water exposure are both immobile at 79 K and stable during scanning up to (sample) bias voltages of +3.0 V. At higher voltages the tip starts to interact with them and scanning with +4.0 V removes the adsorbate from the scanned area, as demonstrated in Figures S3(a-c). Panel (a) shows the initial surface with a low coverage of curves (black lines) and ovals (white circles). The same area is shown in panel (b) after removal of most of the adsorbed species by scanning with +4.0 V. Figure S3(c) shows a zoomed-out image of the terrace where the manipulation had taken place; the ‘cleaned’ area is clearly visible.

Moreover, also the transformation of the saturated ‘bright triangle’ into a curved feature and a dot does not only work with single voltage pulses, it is also induced by scanning a larger area at high bias voltage, although a slightly higher value is necessary to transform the entire scan area at once. An example is given in Figures S3(d-f), where a $10 \times 10 \text{ nm}^2$ area is completely transformed by scanning with +3.6 V. Panel (d) shows the initial hydroxylated surface region. After scanning with +3.6 V the manipulated area is again imaged, see panel

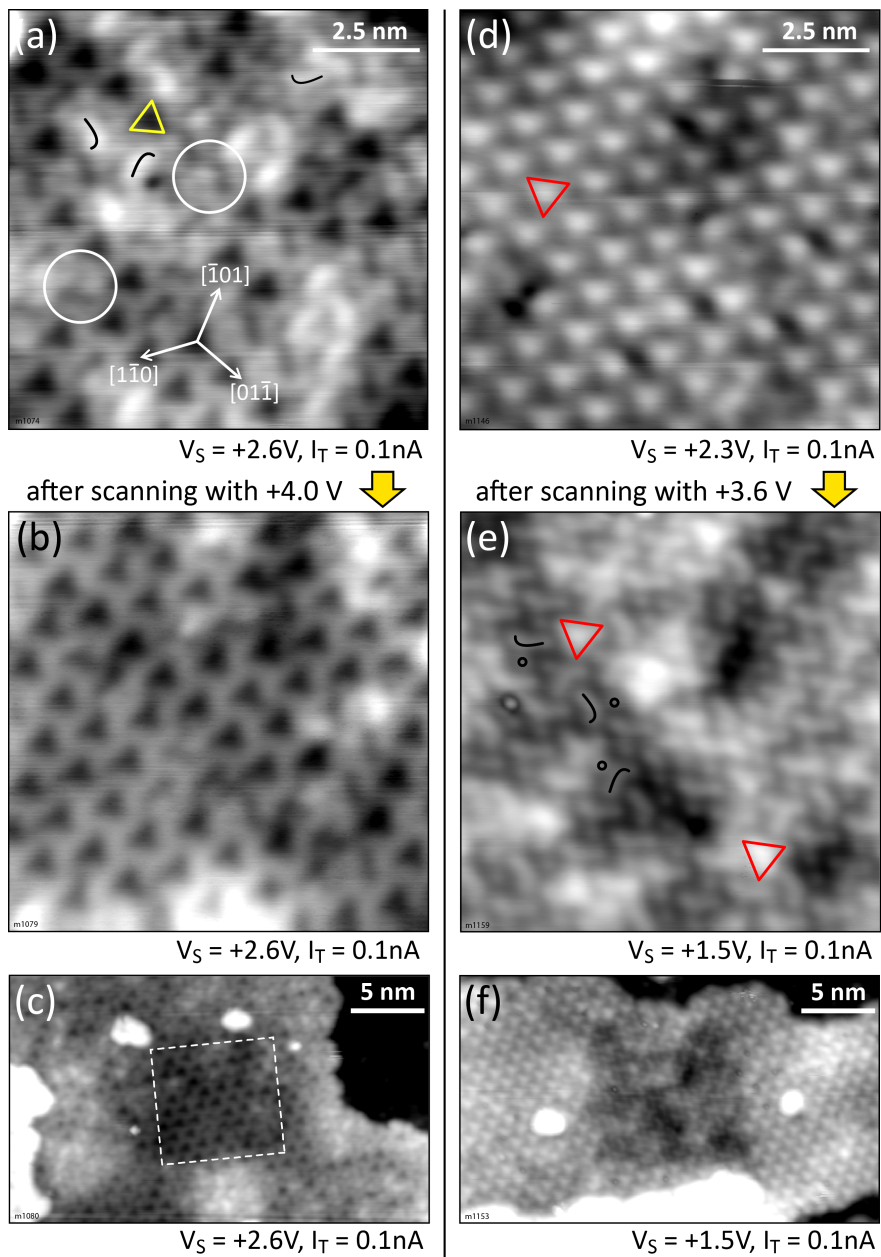


Figure S3: Removing OH groups from $\text{In}_2\text{O}_3(111)$ by scanning with high bias voltage. (a) Sub-monolayer coverage of dissociated water. (b) The same surface area after scanning with +4.0 V. Most of the OH groups have desorbed. (c) Overview of the terrace and the manipulated area. (d) Fully hydroxylated surface. (e) The same surface area after scanning with +3.6 V to remove some OH groups. The area exhibits curved features and dots. (f) Overview on the terrace where the modified area is clearly visible. T_{STM} : 79 K.

(e). Almost all (except for 5) bright triangles are transformed into the curved species with a dot next to the convex side of the curve. The manipulated area is also clearly visible in the large-scale image of panel (f).

Further evidence for the curved species consisting of two dissociated water molecules is presented in Figure S4, after performing the same high voltage scan as described above. Figure S4(a) shows the surface after removing one OH per unit cell, leaving the curved

features and the dots on the surface (one curve + one dot per surface unit cell). Close-ups on the features are provided in panels (b,c), where four protrusions per curved feature are discernible. We postulate that these four protrusions correspond to four OH groups, i.e., two dissociated water molecules. The dot next to the convex side of the curve corresponds (in terms of position) to the O_wH group, suggesting that the proton is removed by the high bias voltage treatment.

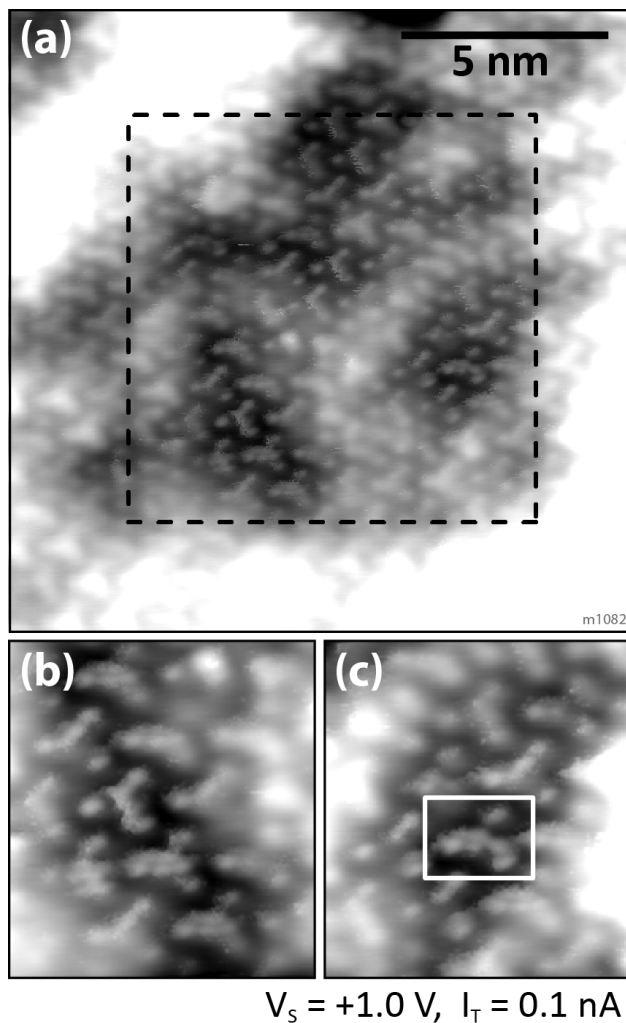


Figure S4: Imaging individual OH groups. (a) Overview on the surface area after a high voltage scan with +3.6 V (dashed frame), showing curved features and dots. (b,c) Close-ups on the modified area where four protrusions are discernible in each curved feature plus the dot next to its convex side (white frame). T_{STM} : 79 K.

Additional DFT Calculations

1) Atomic structure of the adsorbate-free surface

The primitive (1×1) unit cell of the bulk-terminated $\text{In}_2\text{O}_3(111)$ surface contains an O–In–O trilayer consisting of 16 In and 24 O atoms (see Figure S5). Four of the 16 In atoms are 6-fold coordinated In(6c) in two symmetry-inequivalent positions (labeled ‘b’ and ‘d’), and 12 atoms are 5-fold coordinated In(5c) in four symmetry-inequivalent positions (labeled ‘a’, ‘c’, ‘e’ and ‘f’). Half of the 24 O atoms sit above the In layer and are 3-fold coordinated O(3c), and the other half are 4-fold coordinated O(4c) with a position below the In layer. The 12 O(3c) atoms occupy four symmetry-inequivalent sites, labeled ‘ α ’, ‘ β ’, ‘ γ ’, and ‘ δ ’ in Figure S5.

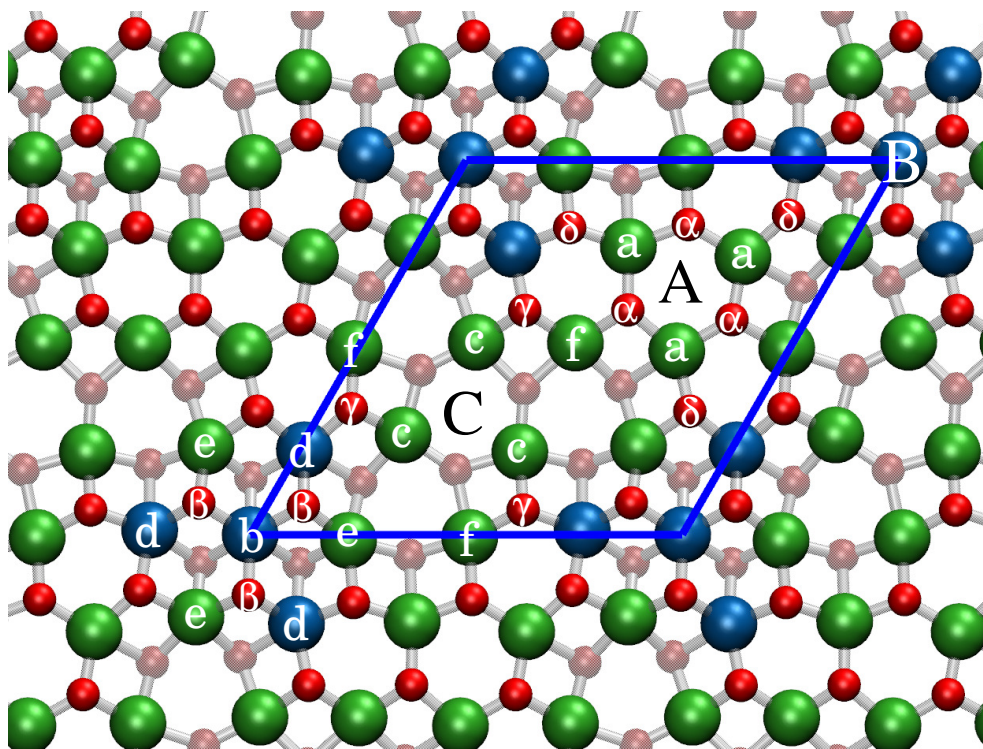


Figure S5: Structure of the bulk-terminated $\text{In}_2\text{O}_3(111)$ surface. In(6c) is shown in blue, In(5c) in green, O(3c) in bright red and O(4c) in shaded red. The surface unit cell is indicated by blue solid lines. The 3 high-symmetry positions of the surface with a 3-fold rotational symmetry axis, i.e., the center of the In(5c)–O(3c) rings, the central In(6c) atom and the center of the In(5c)–O(4c) rings, are labeled by A, B and C, respectively. Labels a–f and α – δ indicate symmetry-equivalent positions of the 16 surface In and the 12 O(3c) atoms (see text).

After cleavage, the $\text{In}_2\text{O}_3(111)$ surface shows some pronounced relaxations (see Figure S6). The largest atomic movement with an inward relaxation of 0.23 \AA is found for the central In(6c) atom at site B. The three neighboring O(3c) atoms also move inwards by 0.15 \AA . These relaxations will become important for the water adsorption (see below). Surprisingly, the second-largest relaxations are found for the three O(4c) atoms next to symmetry site C. These O atoms strengthen their bond to the neighboring, now 5-fold coordinated In atoms within the surface layer, but weaken their bond to the neighboring In atom below in the sub-surface layer. Thus, an outward relaxation of 0.22 \AA is observed.

For the unrelaxed surface energy we obtain a value of 1.06 J/m^2 . The surface relaxations lower the surface energy by 0.28 J/m^2 (3.22 eV per (1×1) surface unit cell), thus resulting in a final relaxed surface energy of 0.78 J/m^2 .

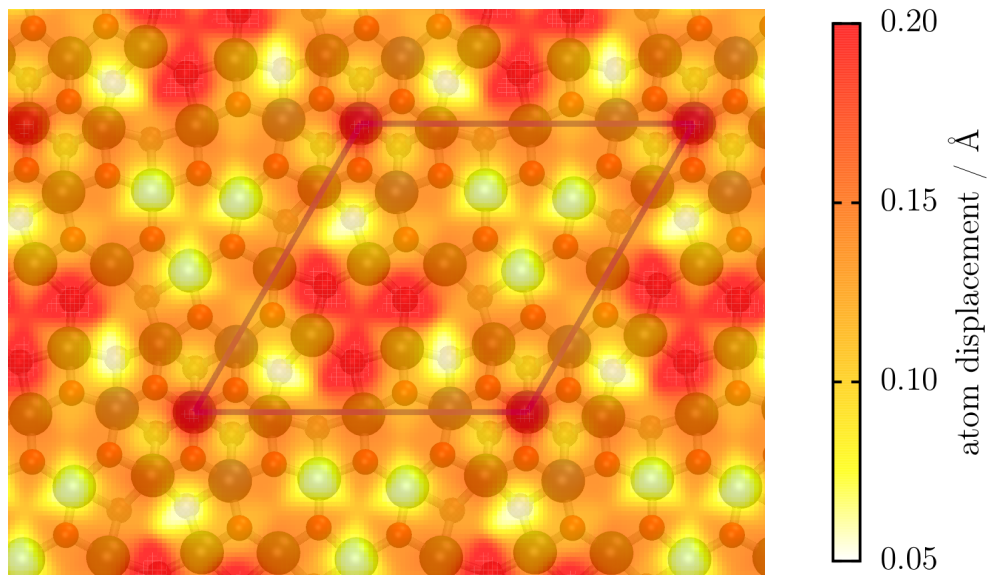


Figure S6: Schematic representation of the atomic relaxations at the $\text{In}_2\text{O}_3(111)$ surface after cleavage. The magnitude of the atomic displacement vectors is shown by color code.

2) Surface electronic structure

To get first ideas about site-specific differences in the reactivity of the $\text{In}_2\text{O}_3(111)$ surface atoms, we calculated the atom-resolved density-of-states (DOS). The DOS calculations were done using a (12,12,1) Monkhorst-Pack k -point grid and a Gaussian smearing of 0.1 eV. As typical for an oxide, the valence band mainly consists of O-2*p* states, whereas the conduction band is mainly formed by the 4*s* and 4*p* states of the indium atoms. We therefore only focus on the O states in the valence band region and the In states in the conduction band range.

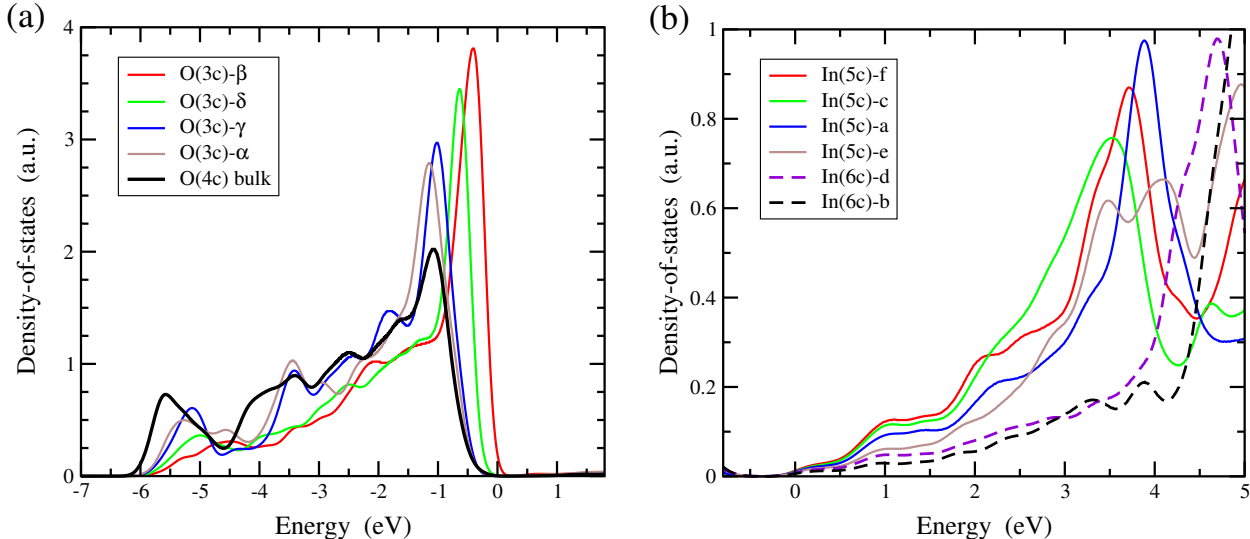


Figure S7: Atom-resolved density-of-states (DOS) for the $\text{In}_2\text{O}_3(111)$ surface. (a) Valence band DOS of the four symmetry-inequivalent 3-fold coordinated surface oxygen atoms. The valence band maximum is at 0 eV. (b) Conduction band DOS of the six symmetry-inequivalent 5- and 6-fold coordinated surface indium atoms. The conduction band minimum is at 0 eV. Atom labels are introduced in Figure S5.

Since the topmost surface oxygen atoms are all 3-fold coordinated and are rather regularly distributed on the $\text{In}_2\text{O}_3(111)$ surface, one might expect that they all exhibit a similar reactivity. However, the atom-resolved DOS in Figure S7(a) shows very characteristic differences between the four symmetry-inequivalent O(3c) sites. The DOS of the O(3c) atoms ‘ β ’ next to the central In(6c) atom ‘b’ at site B have a pronounced maximum right at the top of the valence band. The maximum gradually becomes smaller and shifts to lower energy when going to sites ‘ δ ’, ‘ γ ’ and ‘ α ’. We therefore expect ‘ β ’ to be the most reactive and ‘ α ’ to be the least reactive O(3c) sites. This order in reactivity is indeed found for the dissociative adsorption of water and the preferred site of the dissociated proton (see below). The highest reactivity of the ‘ β ’ sites was also found previously for In adatoms, which preferentially occupy site B on the $\text{In}_2\text{O}_3(111)$ surface where they are bound simultaneously to three ‘ β ’ O(3c) atoms. The order in reactivity of the surface O(3c) atoms correlates with the coordination of the neighboring In atoms: ‘ α ’ sites have three In(5c), ‘ γ ’ and ‘ δ ’ sites have two In(5c) and one In(6c), and ‘ β ’ sites have one In(5c) and two In(6c) neighbors. Thus, the difference in reactivity can be explained by the degree of local autocompensation (i.e.,

reciprocal compensation of broken bonds) of the O(3c) and In(5c) atoms: while the oxygen atoms at site ' α ' are fully autocompensated by the three In(5c) neighbors, autocompensation is least fulfilled for the O(3c) atoms at site ' β ' with only one In(5c) and two In(6c) neighbors.

The atom-resolved DOS for the surface indium atoms in Figure S7(b) shows a significant difference between the In(5c) and In(6c) sites. The DOS of the In(6c) already closely resembles the DOS of indium bulk atoms (not shown). In the energy region between 0 and 4 eV the In(6c) DOS is much lower than for the In(5c) atoms. This is the reason why the In(6c) atoms are imaged as dark triangles in STM at positive bias voltage (empty state images). The difference in the atom-resolved DOS between the symmetry-inequivalent In(5c) atoms is much less pronounced than between the O(3c) sites in Figure S7(a) (note that the scale of the y -axis is a factor 4 smaller). We therefore do not expect a significant difference in reactivity between the In(5c) atoms. One might expect that the O_wH groups of dissociated water molecules are slightly more attracted to sites 'f' and 'c' than to sites 'a' and 'e', however, as shown below, the proximity to the preferred adsorption site ' β ' of the proton will be the more decisive factor.

3) Adsorption of single water molecules

For an unambiguous notation of all probed configurations of water molecules in the (1×1) unit cell of the $\text{In}_2\text{O}_3(111)$ surface we have introduced labels to a few more surface atoms, see Figure S8.

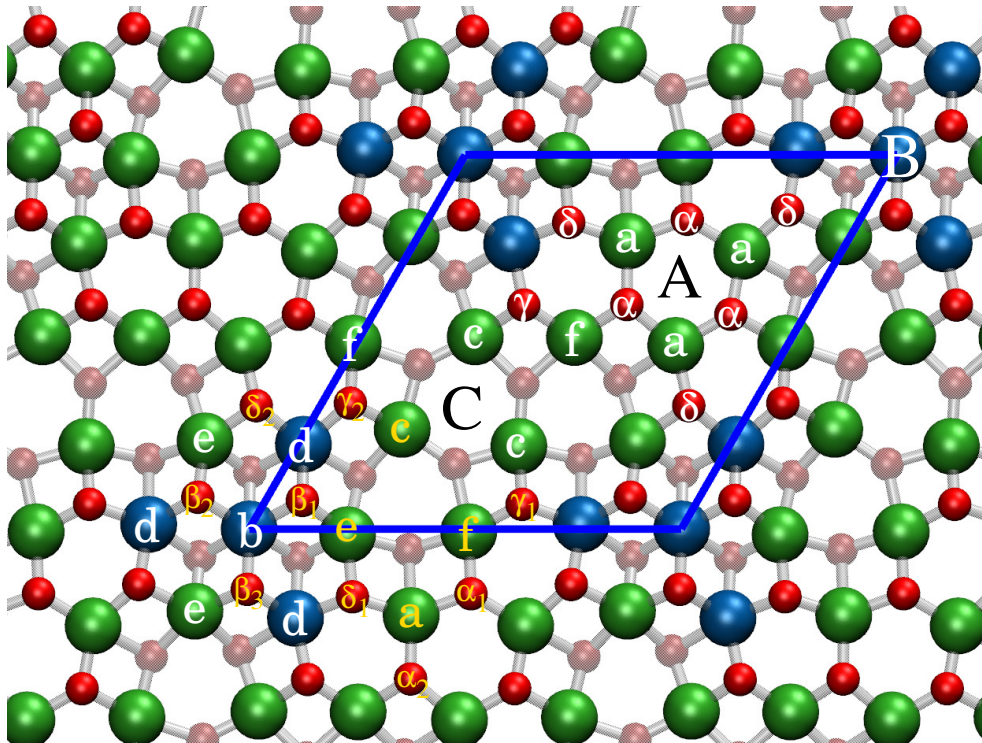


Figure S8: Same as Figure S5. Additional labels have been introduced for describing all water adsorption sites considered in the DFT calculations. The atomic positions listed in the forthcoming tables are highlighted in yellow.

Molecular adsorption: On oxides, water molecules coordinate in their most stable configuration with their oxygen O_w atom to an undercoordinated surface cation via one of their electron lone pairs. In our systematic search for the most favorable adsorption site for undissociated water molecules on the $\text{In}_2\text{O}_3(111)$ surface we placed a single water molecule in various orientations with its O_w atom on top of all inequivalent $\text{In}(5c)$ sites in the (1×1) unit cell and started a geometry optimization, see Table S1. After relaxation, the water molecule lies more or less flat on the surface and one or both H_w atoms are oriented toward a 3-fold coordinated surface $\text{O}(3c)$ atom. In Table S1, the final orientation of the adsorbed water molecule is given by the labels of the surface $\text{O}(3c)$ to which the H_w are pointing, or, in case that only one H_w is directed towards an $\text{O}(3c)$, the position of the second H_w will be described either to be in clockwise ('CW') or counterclockwise ('CCW') orientation with respect to the first H_w .

adsorption site of O _w (surface In atom)	orientation of H _w (surface O atoms)	E_b (eV)
ontop-a	δ_1, α_2	0.57
ontop-a	α_1, α_2	0.50
ontop-c	γ_2, CCW	0.62
ontop-c	γ_2, CW	0.59
ontop-e	β_1, δ_1	0.73
ontop-f	α_1, γ_1	0.68

Table S1: Binding energy E_b and structure for molecular adsorption of a single water molecule in the primitive (1×1) unit cell of the In₂O₃(111) surface.

position of O _w H (surface In atoms)	position of H _w (surface O atom)	E_b (eV)
ontop-a	δ_1	0.51
ontop-a	α_1	0.44
ontop-a	β_1	0.27
ontop-c	γ_1	0.58
ontop-c	β_1 or δ_1	unstable ⁽¹⁾
ontop-e	δ_1	0.71
ontop-e	β_1	unstable ⁽²⁾
ontop-f	α_1	0.77
ontop-f	γ_1	0.52
bridge-ce	β_1	1.22
bridge-ce	δ_1	0.92
bridge-ce	γ_2	0.42
bridge-cf		unstable ⁽²⁾
bridge-ef	β_1	1.28
bridge-ef	δ_1	1.04
bridge-ef	α_1	0.68
bridge-ef	γ_1	0.61
hollow-C	β_1	0.96
hollow-C	δ_2	0.67
hollow-C	γ_2	0.31
hollow-C	α_1	0.23

⁽¹⁾ O_wH group relaxes into bridge-ce position

⁽²⁾ O_wH group relaxes into bridge-cf position

Table S2: Binding energy E_b and structure for dissociative adsorption of a single water molecule in the primitive (1×1) unit cell of the In₂O₃(111) surface.

Dissociative adsorption: For the O_wH group we considered all symmetry-inequivalent ontop positions above single $\text{In}(5c)$ atoms and all possible bridging sites between two neighboring $\text{In}(5c)$, see Table S2. The proton H_w from water dissociation was placed ontop of all possible 3-fold coordinated $\text{O}(3c)$ atoms. In all cases, the highest binding energy was found if the H_w occupies an $\text{O}(3c)$ site that shares an $\text{In}(5c)$ with the O_wH group. Therefore, all configurations, in which the H_w is farther away, have been omitted in Table S2 (see also Table S3).

Tables S1+S2 show that for single water molecules dissociation is much more favorable than molecular adsorption. The $\text{In}(5c)$ site ‘a’ is clearly less stable than positions ‘c’, ‘e’ and ‘f’, for molecular as well as dissociative adsorption. Therefore, site ‘a’ will be no longer considered in the forthcoming calculations. The highest binding energy is found for the configuration in which the proton adsorbs on a ‘ β ’ site and the O_wH group occupies the neighboring ‘bridge-ef’ position. Since there are three ‘bridge-ef’ and three ‘ β ’ sites in the primitive (1×1) unit cell, up to three water molecules can be adsorbed in this configuration.

The binding energies when one, two or three water molecules occupy the ‘bridge-ef’ and the ‘ β ’ sites in a (1×1) unit cell are given in Table S3. The results show that the dissociated proton clearly prefers to be on a neighboring $\text{O}(3c)$ site to the O_wH group. The binding energy decreases even if the H_w still occupies a ‘ β ’ site but not the one that shares an $\text{In}(5c)$ with the O_wH .

number of water molecules	position of O_wH (surface In atoms)	position of H_w (surface O atom)	E_b (eV)
1	bridge-ef	β_1	1.28
		β_2	1.19
		β_3	1.15
2	bridge-ef	β_1, β_2	1.24
		β_1, β_3	1.17
3	bridge-ef	$\beta_1, \beta_2, \beta_3$	1.18

Table S3: Binding energies E_b per molecule for occupying the three symmetry-equivalent adsorption sites ‘bridge-ef’ and ‘ β ’ in the primitive (1×1) unit cell of the $\text{In}_2\text{O}_3(111)$ surface by one, two or three water molecules.

Interestingly, the binding energy per molecule decreases with increasing water coverage. The reason is that the dissociative adsorption of the water molecules induces a significant re-relaxation of the surface. Recall, upon cleavage, the surface lowers its energy by 3.22 eV per unit cell by relaxation. Thus, adsorption-induced re-relaxations of the surface will contribute significantly to the overall binding energy.

The structural changes upon the adsorption of the first water molecule are shown in Figure S9. The lifting of surface relaxations does not only involve the atoms at the adsorption site, but also atoms in the neighborhood. We term this region the ‘adsorption footprint’.

The footprint region also extends to the neighboring ‘bridge-ef’ and ‘ β ’ sites. Therefore, the full energy gain by the re-relaxation of the surface is only available for the first water molecule. The re-relaxations, and thus their contributions to the binding energy, are smaller for the second and third water molecule, as schematically indicated in Figure S9.

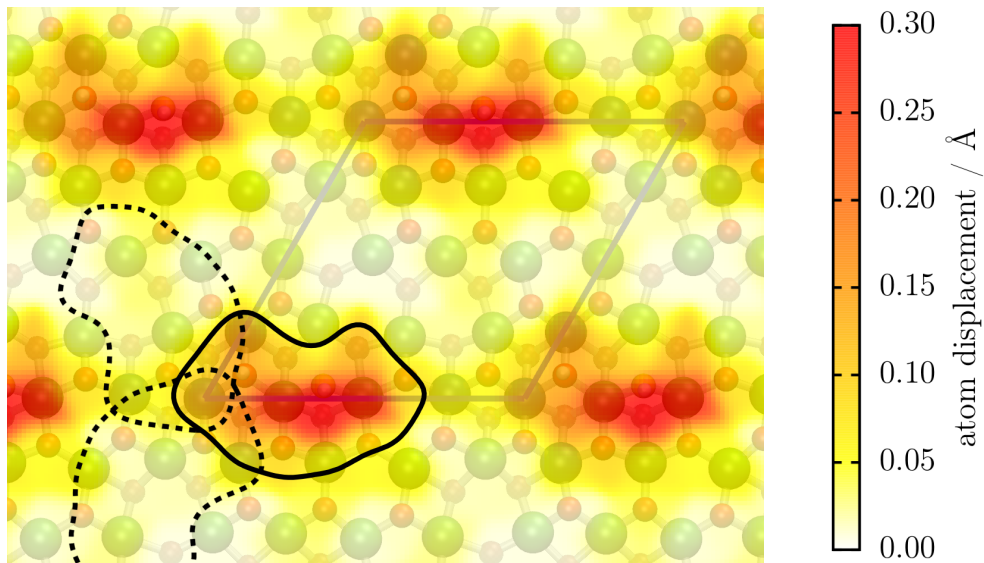


Figure S9: Schematic representation of the atomic relaxations at the $\text{In}_2\text{O}_3(111)$ surface induced by the dissociative adsorption of one water molecule. The absolute magnitude of the atomic displacements with respect to the relaxed, clean surface are shown by color code. The black solid line indicates the adsorption footprint of the water molecule. The dashed lines demonstrate that the second and third water molecule will see a partially re-relaxed surface which results in a reduction of the binding energy.

4) Alternative configurations for two adsorbed water molecules

The structures listed in Table S3 are likely to be the most favorable configurations for two and three water molecules in the primitive (1×1) surface unit cell. However, when water molecules form pairs, the formation of H-bonds can significantly stabilize alternative structures. Therefore, to make sure that we are not missing such a new motif in our systematic search, we probed all possible configurations in which the second water molecule does not occupy the second ‘bridge-ef/ β ’ site. Only water pairs on nearest-neighbor positions were considered to capture the stabilizing effect of H-bond formation. We start our structure search with the first water molecule in the ‘bridge-ef/ β ’ position. However, we allow that the second molecule displaces the O_wH group from its bridge site. For this second water molecule, disociative (see Table S4) as well as molecular (see Table S5) adsorption are considered.

first O_wH	first H_w	second O_wH	second H_w	E_b (eV)
bridge-ce	β_1	ontop-f	α_1	1.00
bridge-ce	β_1	ontop-f	δ_1	0.91
bridge-ce	β_1	ontop-f	γ_1	0.89
bridge-ce	β_1	ontop-f	δ_2	0.75
bridge-ef	β_1	ontop-c	δ_1	1.05
bridge-ef	β_1	ontop-c	γ_2	0.90
bridge-ef	β_1	ontop-c	γ_1	unstable ⁽¹⁾
bridge-ef	β_1	hollow-C	δ_1	0.96
bridge-ef	β_1	hollow-C	γ_1	0.87
bridge-ef	β_1	hollow-C	δ_2	0.84
bridge-ef	β_1	hollow-C	γ_2	0.69

⁽¹⁾ second O_wH group relaxes into hollow-C position

Table S4: Binding energy E_b per molecule and structure for two dissociated water molecules in the primitive (1×1) unit cell of the $In_2O_3(111)$ surface.

The results of Tables S4+S5 show that the configuration of Table S3 remains the most favorable structure for two water molecules in the primitive unit cell. However, when not occupying simultaneously two ‘bridge-ef’ and two ‘ β ’ sites, two dissociated molecules now become less favorable than mixed dissociated/molecular structures. The most favorable alternative structural motif (a dissociated molecule at site ‘bridge-ef/ β ’ and an intact molecule at site ‘ontop-c’ with CW orientation) can be placed three times in the primitive (1×1) surface unit cell. This gives the structure with the highest binding energy for 6 water molecules in the primitive unit cell that we found in our DFT calculations, see Figure S10.

diss: O _w H	mol: O _w	mol: orient	E_b (eV)
bridge-ef	ontop-c	CW	1.12
bridge-ef	ontop-c	CCW	unstable ⁽¹⁾
ontop-e	ontop-c	CCW	1.04
ontop-e	ontop-c	CW	unstable ⁽²⁾
ontop-e	ontop-f	CCW	1.06
ontop-e	ontop-f	CW	1.04
bridge-ce	ontop-f	CCW	unstable ⁽¹⁾
bridge-ce	ontop-f	CW	unstable ⁽³⁾
ontop-c	ontop-f	CW	1.12
ontop-c	ontop-f	CCW	unstable ⁽⁴⁾
ontop-c	ontop-e	CW	unstable ⁽⁴⁾
ontop-f	ontop-c	CW	1.12
ontop-f	ontop-c	CCW	unstable ⁽⁴⁾
ontop-f	ontop-e	CW	unstable ⁽⁴⁾

⁽¹⁾ diss O_wH group relaxes into ontop-e position

⁽²⁾ diss O_wH group relaxes into bridge-ef position

⁽³⁾ diss O_wH group relaxes into ontop-c position

⁽⁴⁾ mol dissociates and transfers proton to diss O_wH

Table S5: Binding energy E_b per molecule and structure for two water molecules with mixed adsorption mode in the primitive (1×1) unit cell of the In₂O₃(111) surface. The first molecule is dissociated. The proton H_w always occupies site ‘ β_1 ’. The second water molecule remains intact and always forms an H-bond with one of its H_w atoms to the O_wH group. The position of the second H_w is either in clockwise (‘CW’) or counterclockwise (‘CCW’) orientation with respect to the first H_w.

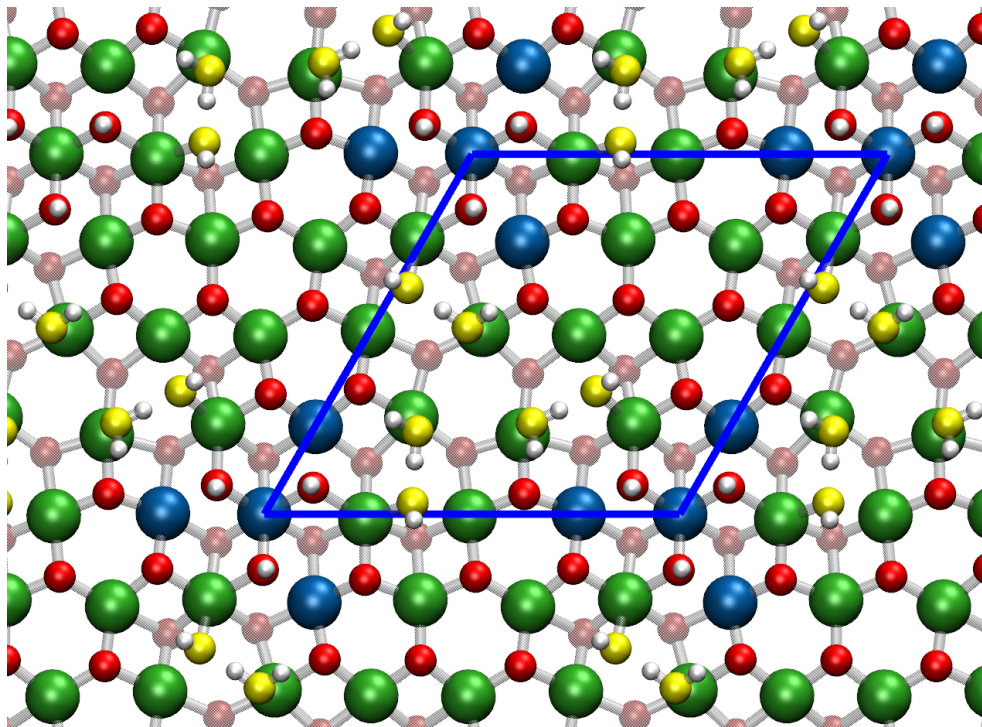


Figure S10: Most favorable structure for 6 water molecules in the (1×1) unit cell of the $\text{In}_2\text{O}_3(111)$ surface. Three molecules are dissociated and occupy the ‘bridge-ef’ and ‘ β ’ sites, the other three molecules remain intact and sit ontop of ‘c’ atoms (the structure is obtained by tripling the first configurations of Table S5).

5) Alternative configurations for three adsorbed water molecules

Finally, we explore all possibilities in which three water molecules occupy three neighboring inequivalent In(5c) sites ‘c’, ‘e’ and ‘f’. Since on these sites mixed molecular/dissociated structures are already more stable for two molecules than full dissociation, we considered only configurations with one dissociated and two intact water molecules. Since now only three adsorption sites are available for the three molecules, the O_wH group of the dissociated water molecule has to be displaced from its bridging position, see Table S6.

Surprisingly, in the most favorable configuration the O_wH group has moved to the ‘ontop-f’ site but not to ‘ontop-e’, which would be the neighboring position to its dissociated proton at ‘β’. Nevertheless, the three dissociated water molecules at the three ‘bridge-ef/β’ sites of Table S3 remains the most stable configuration for three water molecules in the primitive (1×1) surface unit cell. However, tripling the most favorable alternative configuration (a dissociated molecule at site ‘ontop-f/β’ and two intact molecule at sites ‘ontop-c’ and ‘ontop-e’ with CW orientation) gives the best structure for 9 water molecules in the primitive unit cell that we found in our DFT calculations, see Figure S11.

diss: O _w H	mol1: O _w	mol1: orient	mol2: O _w	mol2: orient	E_b (eV)
ontop-f	ontop-c	f, CW	ontop-e	f, CW	1.05
ontop-f	ontop-c	f, CW	ontop-e	f, CCW	0.97
ontop-f	ontop-c	f, CCW	ontop-e	f, CW	unstable ⁽¹⁾
ontop-e	ontop-c	e, CW	ontop-f	e, CCW	1.00
ontop-e	ontop-c	e, CW	ontop-f	e, CW	0.99
ontop-e	ontop-c	f, CW	ontop-f	e, CCW	unstable ⁽²⁾
ontop-c	ontop-e	c, CW	ontop-f	c, CW	1.00
ontop-c	ontop-e	c, CCW	ontop-f	c, CW	unstable ⁽¹⁾
ontop-c	ontop-e	f, CW	ontop-f	c, CW	unstable ⁽²⁾

⁽¹⁾ mol1 rotates to CW orientation

⁽²⁾ mol2 dissociates and proton is transferred to O_wH

Table S6: Binding energy E_b per molecule and structure for three water molecules with mixed adsorption mode in the primitive (1×1) unit cell of the In₂O₃(111) surface. The first molecule is dissociated. The proton H_w always occupies site ‘β₁’. The second and third water molecule remain intact and always form an H-bond to the O_w atom of a neighboring dissociated or undissociated water molecule. The orientation of the intact water molecules is given by the position of the O_w atom to which the first H_w forms the H-bond. The position of the second H_w is either in clockwise (‘CW’) or counterclockwise (‘CCW’) orientation with respect to the first H_w.

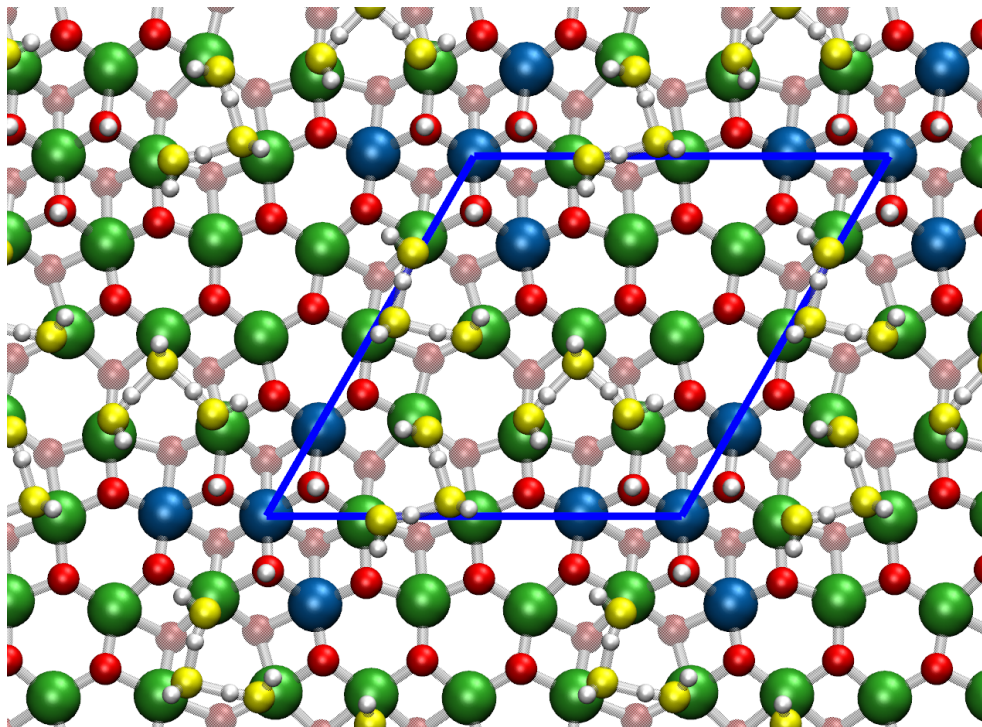


Figure S11: Most favorable structure for 9 water molecules in the (1×1) unit cell of the $\text{In}_2\text{O}_3(111)$ surface. Three molecules are dissociated and occupy the ‘ontop-f’ and ‘ β ’ sites, the other six molecules remain intact and sit ontop of ‘c’ and ‘e’ atoms (the structure is obtained by tripling the first configuration of Table S6).