

Water Dissociation and Hydroxyl Ordering on Anatase $\text{TiO}_2(001)-(1 \times 4)$

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We studied the interaction of water with the anatase $\text{TiO}_2(001)$ surface by means of scanning tunneling microscopy, x-ray photoelectron spectroscopy, and density functional theory calculations. Water adsorbs dissociatively on the ridges of a (1×4) reconstructed surface, resulting in a (3×4) periodic structure of hydroxyl pairs. We observed this process at 120 K, and the created hydroxyls desorb from the surface by recombination to water, which occurs below 300 K. Our calculations reveal the water dissociation mechanism and uncover a very pronounced dependence on the coverage. This strong coverage dependence is explained through water-induced reconstruction on anatase $\text{TiO}_2(001)-(1 \times 4)$. The high intrinsic reactivity of the anatase $\text{TiO}_2(001)$ surface towards water observed here is fundamentally different from that seen on other surfaces of titania and may explain its high catalytic activity in heterogeneous catalysis and photocatalysis.

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Owing to its wide applications in heterogeneous catalysis, photovoltaic cells, gas sensors, hydrophilic films, and its properties as a photocatalyst, titanium dioxide (TiO_2) is an intensely studied oxide material [1,2]. Particularly, the water- TiO_2 interaction has been studied intensively [2–18] because the presence of water cannot be avoided in these applications. Thus far, most studies focused on the rutile polymorph [2–8,11,14,16], but in the nanocrystalline form, anatase is more stable than rutile [19], which makes it technologically more relevant.

Anatase nanocrystals expose a high fraction of low surface energy (101) facets and a smaller fraction of high-energy, but supposedly more reactive, (001) facets [20–22]. Because of its high surface energy, the (001) surface may be self-compensated by forming reconstructed terraces. In the reconstruction, rows of bridging O atoms in [100] and [010] directions are replaced by TiO_3 units [23] with a (1×4) periodicity, as shown in Fig. 1(a). This substitution results in the appearance of ridges that protrude above the regular terrace sites and consist of twofold coordinated $\text{O}(\text{O}_{2c})$ and fourfold coordinated Ti atoms (Ti_{4c}). Such (1×4) reconstruction is commonly found on the (001) surfaces of anatase single crystals and thin films [24,25] that were subjected to high-temperature annealing in ultrahigh vacuum (UHV). Recently, this reconstruction was also found on the facets of anatase nanoparticles in catalyst powders [26,27], emphasizing the validity of the admolecule (ADM) model [23] [shown in Fig. 1(a)].

Various models have been put forward regarding the interaction of water with the anatase (A)- $\text{TiO}_2(001)-(1 \times 4)$ surface. On the one hand, an x-ray photoelectron spectroscopy (XPS) study by Blomquist suggested that water dissociates on the A- $\text{TiO}_2(001)-(1 \times 4)$ surface at

120 K, forming a mixed layer that contains both molecular water and hydroxyls [9]. It was proposed that the (1×4) ridges are reactive, in agreement with density functional theory (DFT)-based models by Gong [28]. On the other hand, recent scanning tunneling microscopy (STM) studies on thin (001)-terminated anatase films reported on a limited reactivity towards water that may be traced back to reactions at surface point defects [25]. Whereas the earlier studies suggest intrinsic water dissociation (no point defects are required) [9,28], the latter study points to defect-controlled water dissociation processes, similar to what is known for the well-studied rutile $\text{TiO}_2(110)$ surface [3–8,14].

Here, we used a combination of STM, synchrotron-based XPS, and DFT calculations and show that the A- $\text{TiO}_2(001)-(1 \times 4)$ surface is, indeed, very reactive towards water. We identified the Ti_{4c} atoms within the ridges as dissociation sites, in agreement with previous studies [9,28]. At saturation, high-resolution STM images and DFT modeling reveal a novel periodic structure of Ti_{4c} -bonded OH groups. We explain this particular ordering as the optimal combination of contributions from stabilizing adsorbate-induced reconstructions (more significant at lower coverage) and adsorbate-substrate bond formation (more significant at higher coverage). Finally, we discuss why the water chemistry on A- $\text{TiO}_2(001)-(1 \times 4)$ is distinctly different from that on the rutile $\text{TiO}_2(110)$ surface.

In our experiments [29], we used natural anatase single crystals that were prepared by several Ar⁺ sputtering and annealing cycles in UHV. This preparation led to bulk-reduced samples with sufficient conductivity for the conduction of STM and XPS experiments. As shown in Fig. 1(b), the freshly prepared surface is characterized by

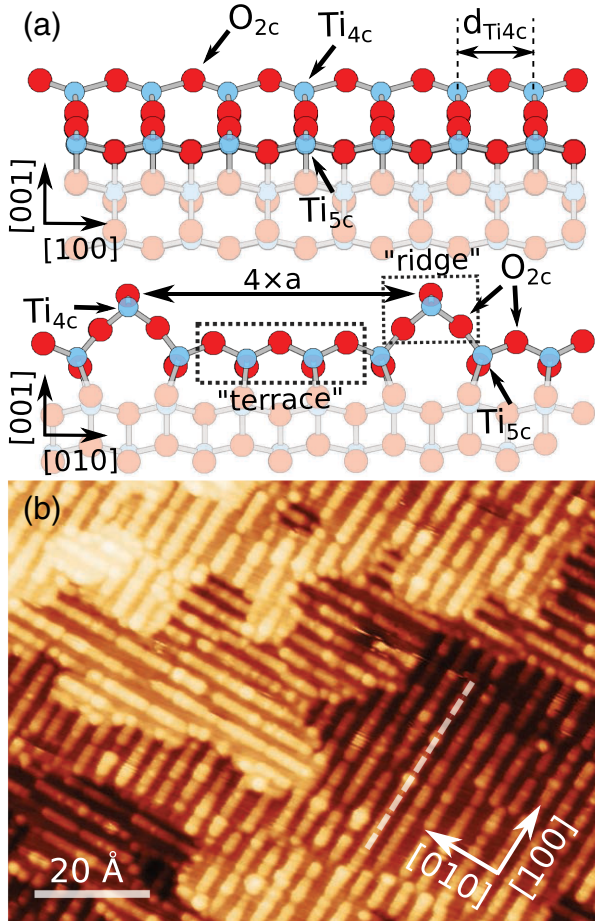


FIG. 1. (a) Ball model of the bare anatase (001)-(1 × 4) reconstructed surface according to the ADM model proposed by Lazzeri and Selloni [23]. (b) STM image of the bare anatase (001)-(1 × 4) reconstructed surface recorded at RT.

30 Å wide terraces and the entire surface adopts the (1 × 4) reconstruction. Various pointlike defects (<0.01 ML) are also seen. They appear along the ridges of the (1 × 4) reconstruction either as bright protrusions or as depressions. The nature of such defects is not fully settled, [24,25,37,38], but their presence was found to be irrelevant for our water adsorption experiments, since no correlation was seen between water dissociation and the density of such pointlike defects.

An O 1s XP spectrum of the freshly prepared, clean A-TiO₂(001)-(1 × 4) surface is shown in Fig. 2(a), uppermost curve. It was recorded at 610 eV photon energy, so that the surface sensitivity is at the maximum. The O 1s peak is centered at ~530.7 eV binding energy (BE) and has a width of 1.44 eV at the half-maximum intensity. Fitting of the O 1s XP spectrum of the clean A-TiO₂(001) surface [29] did not result in additional peaks at higher BE, indicating that there are no traces of molecular water or hydroxyls adsorbed on the clean surface.

The corresponding resonant valence band (VB) spectrum [Fig. 2(b), black, continuous curve] confirms this

conclusion. Previous XPS studies revealed that the presence of water on TiO₂ surfaces leads to the appearance of several characteristic states below the TiO₂ VB [3,6,7,17]. The VB spectrum of the clean A-TiO₂(001)-(1 × 4) surface shows zero intensities of the 3a₁ and 1b₂ electronic states (in our case, centered at ~10.7 and ~13.6 eV BE, respectively) that are, otherwise, attributed to molecular water as well as zero intensity of the 3σ state of OH groups (centered at ~10.6 eV BE).

In a first experiment, we exposed the clean A-TiO₂(001)-(1 × 4) surface to ~2 L of water at room temperature (RT). As judged from the O 1s and VB spectra (not shown), this did not lead to the adsorption of water or any other modification of the surface. Likewise, STM measurements did not reveal any noticeable changes of the surface. We attribute this result to a very low sticking probability of water on the surface at RT.

In contrast, ~1 L water exposure at 120 K leads to clear changes in the O 1s spectrum [Fig. 2(a)]. Surprisingly, the O 1s spectrum is composed of three components, reflecting lattice O atoms and two smaller peaks at higher BE that derive from OH groups (+1.4 eV higher BE compared to lattice O atoms) and molecularly adsorbed water (+3.4 eV higher BE), respectively. The corresponding VB spectrum [Fig. 2(b), blue dashed line, area shaded in blue] reveals the appearance of at least two new states below the VB that are assigned with certainty to 3a₁ and 1b₂ water states, respectively. The 3σ hydroxyl feature cannot be unambiguously distinguished due to a significant overlap with the 3a₁ water feature. These spectra reveal that water adsorbs dissociatively on the surface at 120 K, in agreement with the study by Blomquist [9]. Thus, exposure of A-TiO₂(001)-(1 × 4) to water at 120 K leads to a mix of unreacted molecular water and OH groups that originate from water dissociation.

We estimated the amounts of molecularly adsorbed water and hydroxyls on the surface at 120 K [Fig. 2(a)] to be 0.33 ± 0.05 and 0.15 ± 0.05 ML, respectively, where 1 ML corresponds to the number of O_{2c} sites on the reconstructed (1 × 4) surface (10 atoms per surface unit cell). Note that there is no gap state (also frequently referred to as the 3d-derived gap state) [3,39–42] on the clean and the water exposed A-TiO₂(001)-1 × 4 surface [Fig. 2(b)]. This indicates that the clean A-TiO₂(001)-(1 × 4) surface is fully oxidized, and that the adsorption and dissociation of water does not lead to the reduction of surface Ti atoms, which remain in the 4+ state. Following water exposure at 120 K, we also performed STM measurements (not shown). The obtained STM images were very fuzzy, indicating the presence of highly mobile adsorbates. This result is in line with our spectroscopic results presented in Figs. 2(a) and 2(b).

Upon temperature rise to 230 K, water desorbs, whereas hydroxyls remain on the surface [Fig. 2(a), bottom panel] and the VB spectrum [Fig. 2(b), long dashed line,

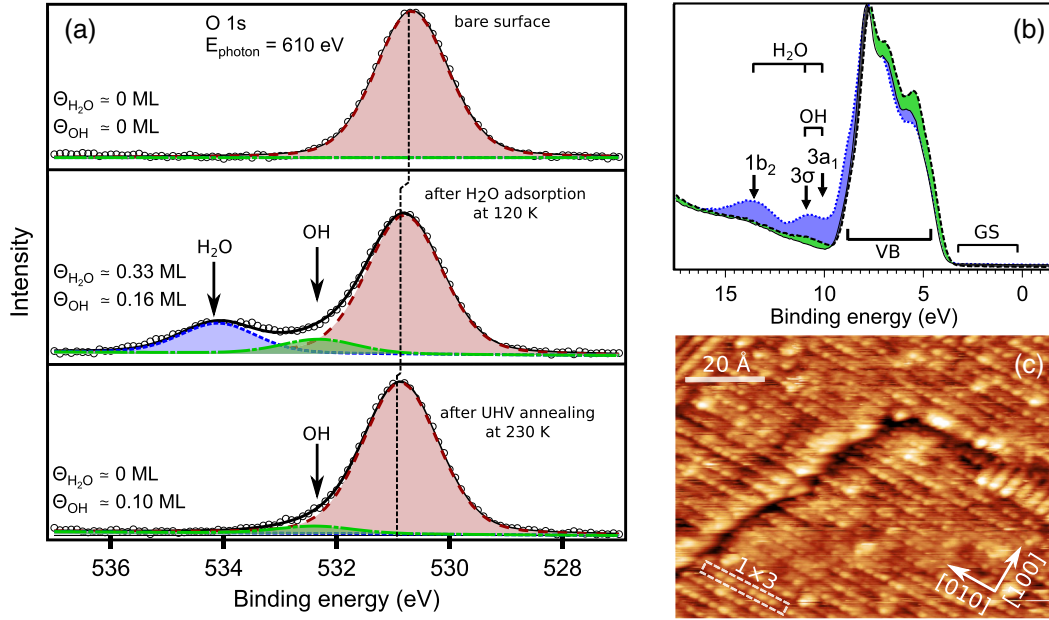


FIG. 2. (a) O 1s spectra of A-TiO₂(001)-(1 × 4) reconstructed surface before and after water exposure at 120 K followed by annealing at 230 K for five minutes. The blue and red shaded components appear as a result of O 1s chemical shift in water and hydroxyls, respectively. (b) Corresponding VB photoelectron spectra recorded with 47.5 eV photon energy. (c) STM image of a surface that was exposed to ~1 L of H₂O at 120 K, followed by annealing at 230 K for five minutes. The STM image was recorded at 190 K using +1.2 V sample bias and ~120 pA tunneling current.

area shaded in green]. A series of separate annealing experiments revealed that molecular water desorbs from the surface above ~190 K. In the present experiment, we estimated the coverage of hydroxyls and water on the basis of the O 1s spectra. After 1 L water exposure at 120 K followed by brief annealing at 230 K, the OH coverage was $\sim 0.1 \pm 0.05$ ML, and no molecular water remained on the surface. The presence of the 3σ state in the VB spectrum [Fig. 2(b), long dashed line, area shaded in green] and the absence of the $1b_2$ state confirm that there are OH groups but no molecular water adsorbed on the surface.

In our STM studies, we exposed a freshly prepared A-TiO₂(001)-(1 × 4) sample to ~1 L water at 120 K and then annealed it at 230 K for five minutes to reach the hydroxylated state corresponding to Fig. 2(a), bottom panel. Subsequently, we recorded STM images at 190 K (instead of at 110 K) to avoid readsorption of water onto the surface. A typical STM image of the hydroxylated A-TiO₂(001) surface is shown in Fig. 2(c). It can be seen that the ridges of the (1 × 4) reconstruction are decorated by periodically ordered protrusions that are, on average, separated from each other by ~11.4 Å. This corresponds to a threefold periodicity along the ridges (i.e., an overall (3 × 4)-OH overlayer). In some areas on the sample, the (3 × 4) periodicity is broken up and the protrusions are separated by larger distances. However, protrusions located closer to each other than in the (3 × 4) periodic structure were observed very rarely. We interpret the periodically

arranged protrusions as OH groups that originate from the dissociation of water molecules. According to the coverage estimated on the basis of the XPS data in Fig. 2(a), we propose that each protrusion in the (3 × 4) periodic structure represents a pair of OH groups, a configuration which becomes clear in what follows.

To understand the water dissociation process and the resulting (3 × 4) periodic structure, we have modeled possible water dissociation pathways and various water coverages along the ridges by means of DFT calculations. We considered six different water coverages, namely $\Theta = 1/n$ for n ranging from 1 to 6, by adsorbing a single water molecule at A-TiO₂-($n \times 4$) supercells. This leads to periodicities longer and shorter than the experimentally observed (3 × 4) periodicity. In this way, we can evaluate incremental steps of increasing the water coverage along the ridges from zero up to a fully covered ridge. Here, the water coverage Θ is defined with respect to the number of topmost ridge sites only and does not account for terrace sites, which were kept unoccupied, as observed experimentally. Upon geometry optimization, water molecules dissociate for all coverages except for $\Theta = 1$. Therefore, the dissociation of a H₂O molecule at the ridge leads to the formation of two neighboring OH groups, occurring alongside with a rather severe reconstruction of the ridge. Reconstruction of the ridge occurs because O_{2c}-Ti_{4c} bonds are cleaved upon water dissociation on Ti_{4c} sites and H transfers to adjacent bridging O_{2c} atoms, see Fig. 3(a). When a water molecule dissociates on the ridge at low

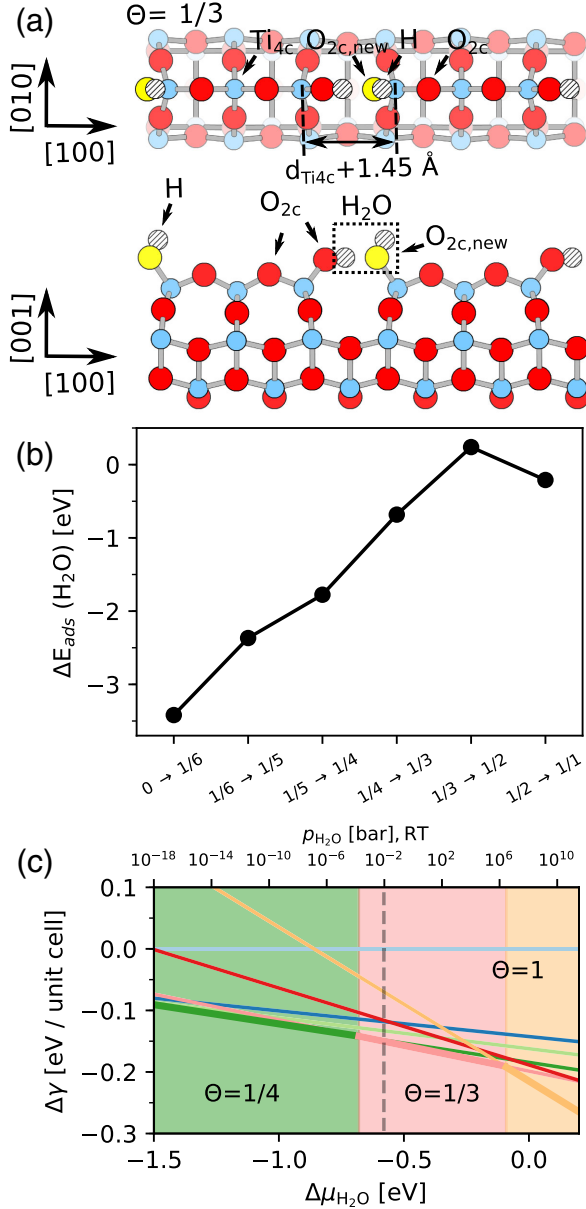


FIG. 3. (a) Top and side view on the optimized structure of dissociatively adsorbed water on A-TiO₂(001)-(1×4) with a water coverage of $\Theta = 1/3$ along the ridge. (b) Differential adsorption energy (ΔE_{ads}) for subsequent increases in coverage. (c) Variation in surface free energy with respect to bare TiO₂(001)-(1×4) evaluated as a function of the chemical potential of H₂O. Different regions are colored according to the most stable H₂O coverage (indicated for each region).

coverage, one Ti-O bond is broken and the other Ti-O bonds of the ridge acquire more favorable distances. Thus, the high binding energy of dissociated H₂O results both from a slight instability of the Ti-O bonds at the ridge and the ability of the ridge to reconstruct.

The two Ti_{4c} atoms holding the resulting OH groups are displaced from each other by up to 1.45 Å with respect to the equilibrium distance in the bare ridge. The two adjacent

OH groups have different structure and interact with each other via a hydrogen bond. The separation between the OH groups and the displaced Ti_{4c} atoms is larger the smaller the water coverage due to the larger displacement of the underlying Ti atoms. At low water coverages, there is more space along the ridge direction between dissociatively adsorbed water molecules, allowing a more pronounced adsorbate-induced substrate relaxation.

The differences in structural relaxation have a dramatic effect on the H₂O adsorption energies, that vary from -3.42 eV for $\Theta = 1/6$ up to -1.51 eV for $\Theta = 1/2$ (see Fig. S1 [29]). Despite these large adsorption energy differences, it remains energetically favorable to further increase the H₂O coverage up to $\Theta = 1/3$, reflecting the (1×3) periodicity along the ridges. To show this clearly, we consider the differential adsorption energy (ΔE_{ads}), corresponding to each coverage increase from $1/n$ to $1/(n-1)$ [Fig. 3(b)]. ΔE_{ads} was calculated by the expression $\Delta E_{\text{ads}}(\Theta_i \rightarrow \Theta_j) = [\Theta_j/(\Theta_j - \Theta_i)]E_{\text{ads}}(\Theta_j) - [\Theta_i/(\Theta_j - \Theta_i)]E_{\text{ads}}(\Theta_i)$.

Thus, ΔE_{ads} is the gained energy (per added H₂O molecule) when the H₂O coverage increases from Θ_i to Θ_j . Upon increase of the H₂O coverage, starting from $\Theta = 1/6$, the differential adsorption energies of each of the added water molecules becomes smaller (in magnitude). For the step from $\Theta = 1/3$ to $\Theta = 1/2$, ΔE_{ads} becomes positive, indicating that this coverage increase is endothermic. We note that H₂O molecules may be adsorbed exothermically at other sites, but a ridge structure where every other site is occupied by dissociatively adsorbed water is not stable. This is also clear from Fig. 3(c), where we have plotted, for each H₂O coverage, how the Gibbs surface free energy evolves as a function of the chemical potential of H₂O, $\Delta \mu_{\text{H}_2\text{O}}$. The diagram shows that $\Theta = 1/3$ and $\Theta = 1/4$ are the H₂O coverages that stabilize the surface most strongly for relevant $\Delta \mu_{\text{H}_2\text{O}}$ values. These DFT results show that the equilibrium OH structures at various conditions and the reactivity of the ridges strongly depend on the H₂O coverage.

Taken our XPS, STM data, and DFT calculations together, we can state that the ridges of the A-TiO₂-(1×4) surface are intrinsically reactive towards water. The dissociation barrier must be low, because we find evidence for partially dissociated water already at 120 K. The water dissociation reactions lead to ordered pairs of OH groups with threefold periodicity along the ridges. By contrast, we do not observe any evidence for water dissociation on the surface sites between the ridges. Splitting of the OH pairs within the ridges was not observed either. Our XP-O 1s and VB data show that the OH groups are stable on the surface up to ~260 K, where their concentration starts to decrease significantly. We interpret this decline as a reversible desorption process in which the OH pairs recombine and form water molecules. The low desorption temperature may reflect that the OH pairs do not separate, in contrast to the situation on rutile TiO₂(110), where H adatoms diffuse on

the surface and water desorption due to hydroxyl recombination occurs at a much higher temperature [4,5].

Further, comparing the situation described here for $\text{H}_2\text{O}/\text{A-TiO}_2(001)-(1 \times 4)$ with the $\text{H}_2\text{O}/\text{rutile TiO}_2(110)-(1 \times 1)$ system, we find striking differences. On rutile $\text{TiO}_2(110)$, H_2O dissociates at point defects [3–5,7,8,14], and dissociation at regular Ti surface sites is not preferred [11,16]. On rutile $\text{TiO}_2(110)$, hydroxylation is facile at RT, but at 120 K only very small amounts of hydroxyls can be detected [6,7]. On $\text{A-TiO}_2(001)-(1 \times 4)$, the situation is opposite. Water dissociation is strongly preferred at regular Ti_{4c} surface sites along the ridges, particularly for low coverages, and dissociation at point defects seems not to occur or is negligible. Following 1–3 L H_2O exposure at RT, we did not find evidence for H_2O dissociation on $\text{A-TiO}_2(001)-(1 \times 4)$. However, 1–3 L H_2O exposure at 120 K clearly leads to hydroxylation, as shown in Fig. 2. On this basis, we conclude that the water interaction with $\text{A-TiO}_2(001)-(1 \times 4)$ is fundamentally different from those observed for other surfaces of titania, such as the rutile $\text{TiO}_2(110)$ surface.

Elucidating the water dissociation process along the ridges, we find, by DFT modeling, a pronounced dependence on the water coverage. The computed coverage dependent adsorption energies go beyond typical lateral interactions of adsorbates, because the hydroxylation process leads to reconstructions of the ridges, see Fig. 3(a). Most importantly, the $\text{O}_{2c}\text{-Ti}_{4c}$ bonds are cleaved upon water dissociation, and the number of such cleavages depends on the water coverage. This is a very peculiar behavior, which has not been observed on any other TiO_2 surface. It is the high reactivity towards water at low coverages that makes the $\text{A-TiO}_2(001)-(1 \times 4)$ special, and we anticipate that the reported high catalytic activity of the (001) facets in catalysis studies [20–22] can be largely explained by this peculiar property.

In conclusion, by means of STM, XPS, and DFT calculations, we find that water adsorbs dissociatively on the ridges of a (1×4) reconstructed $\text{A-TiO}_2(001)$ surface. Thus, dissociation of water on this surface is an intrinsic property, and surface point defects are not needed. Water dissociation results in ordered pairs of terminal hydroxyls along the ridges, leading to a (3×4) periodic structure. This water-induced reconstruction of the ridges occurs at 120 K already. Our DFT calculations revealed the underlying dissociation mechanism and uncovered a very pronounced dependence on the coverage. This strong dependence on the water coverage differs from typical and much weaker lateral interactions between adsorbed species observed on other surfaces.

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