Hydroxylation Structure and Proton Transfer Reactivity at the Zinc Oxide—Water Interface

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ABSTRACT: The hydroxylation structural features of the first adsorption layer and its connection to proton transfer reactivity have been studied for the ZnO—liquid water interface at room temperature. Molecular dynamics simulations employing the ReaxFF forcefield were performed for water on seven ZnO surfaces with varying step concentrations. At higher water coverage a higher level of hydroxylation was found, in agreement with previous experimental results. We have also calculated the free energy barrier for transferring a proton to the surface, showing that stepped surfaces stabilize the hydroxylated state and decrease the water dissociation barrier. On highly stepped surfaces the barrier is only 2 kJ/mol or smaller. Outside the first adsorption layer no dissociation events were found during almost 100 ns of simulation time; this indicates that these reactions are much more likely if catalyzed by the metal oxide surface. Also, when exposed to a vacuum, the less stepped surfaces stabilize adsorption beyond monolayer coverage.

1. INTRODUCTION

Zinc oxide is used in nanoparticle applications, for instance in mesoporous metal oxide electrodes and as a component in dye-sensitized solar cells. It has shown great potential in the production of self-assembled nanostructures for use in functional nano devices, e.g. gas sensors.1,2 ZnO or ZnO-containing compounds catalyze a number of chemical reactions, including methanol formation from CO and H2 and the water—gas shift reaction (H2O + CO → H2 + CO2). The catalytic particles used are typically synthesized by coprecipitation from an aqueous solution.3 Water is present as a product, an intermediate product, or a byproduct in many of the technically important reactions on ZnO.

The metal oxide—water interface region differs strongly from the aqueous and solid bulk phases, leading to many interesting properties. These properties are mainly determined by surface-specific chemistry.4,5 For the reasons presented above it is important to understand how the first few layers of water in the interface region combine to interact with the ZnO surface.5 Specifically, determining whether the water is adsorbed molecularly or dissociatively is an important step in the characterization of the interface. The dissociation products (OH, H, and O) are chemically very different from water. They may also promote or suppress the desired catalytic effect. The similarity in the vibrational properties of H2O and OH bound to the surface makes the characterization difficult using experimental techniques.6 Therefore, theoretical investigations can provide valuable insight.

The interface between liquid water and ZnO has been studied experimentally. Using potentiometric titration, Blok and de Bruyn7 proposed that the ZnO surface in contact with water may be regarded as zinc hydroxide ordered into an ionic double layer. This assumption about the structure was based on the fact that the exchange between surface hydroxyls and anions in solution is accompanied by a consumption or a release of OH−, which in turn explained the slow pH variation they observed. It also helped to explain, at least qualitatively, the observed dependence of the point of zero charge (pzc) on the method of preparation of the various zinc oxide precipitates.8 Other experimental results include infrared, thermogravimetric, volumetric and conductivity measurements; these were summarized by Hirschwald in 1981.9 Hirschwald concluded that water dissociates in the first adsorption layer and additional water molecules are adsorbed onto these hydroxyls through hydrogen bonding.

The interaction between water and ZnO (1010) at monolayer coverage has been studied both experimentally and theoretically. Meyer et al.10 reported that the monolayer consists of alternating dissociated and molecular water, resulting in a (2 × 1) pattern with respect to the surface cell. This phenomenon was explained by the fact that the ZnO (1010) surface acts as a template...
ordering the water molecules into a favorable configuration. Within such a monolayer every other water donates a hydrogen bond to its neighboring molecule, thus activating it for dissociation. The existence of a half dissociated \((2 \times 1)\) pattern was supported by both experiment (STM) and quantum mechanical calculations (DFT).\(^{10-12}\) Raymond et al.\(^{13}\) used MD simulations to study how water is adsorbed, molecularly or dissociatively, at monolayer coverage on flat and stepped ZnO surfaces and found that an equilibrium between dissociated and molecular water is reached quickly (<10 ps), and persists even during desorption at elevated temperature (600 K) preserving the 1:1 water:hydroxyl ratio on ZnO (10\(\overline{1}0\)) surface terraces. The presence of steps was found to promote hydroxylation. Moreover, Raymond et al. also simulated the ZnO (10\(\overline{1}0\)) surface at higher water coverage than one monolayer and found a hydrogen bond pattern, mediated via the water molecules in the second adsorption layer, cf. ref 14. The main conclusions were that structures promoting hydrogen bonding are favored. The theoretical literature regarding the ZnO—liquid water interface is limited. For other metal oxides, theoretical studies exist, and they can be divided into two main categories: first, larger systems simulated for extended periods using classical force fields (see for instance refs 15—19) and, second, smaller systems limited in time and number of atoms, using first-principles simulation techniques, i.e. they were modeled using molecular dynamics using DFT to describe the interactions between the ions, using the B-LYP or PBE functionals, either with Born–Oppenheimer dynamics or employing a Car–Parrinello Lagrangian (see for instance refs 20—22). Most of the first-principles studies are focused on systems of up to one water monolayer of coverage. However, it is clear that for most metal oxides hydrogen bonding between adsorbed water molecules greatly affects the structure of the interface. In this paper, we present a study of the structure of the liquid water—ZnO interface and address the following questions: (1) Does the mixed molecular-dissociative adsorption mechanism reported for the monolayer remain at higher coverage? (2) How is the adsorption influenced by steps on the surface? (3) How dynamic is the dissociation—reassociation reaction? (4) How does the type of adsorption in the first adsorption layer affect water desorption? To answer the questions we have performed molecular dynamics simulation (MD) using the ReaxFF reactive force field\(^{23,24}\) to model the interface between the ZnO surface and water. The ReaxFF force field is designed to accurately model the formation and breaking of bonds during dynamics. The layout of this article is as follows: section 2 describes the methods used, in particular, details about the ReaxFF model; in section 3, this model is applied in MD simulations to study the structural and dynamic properties of water at or near ZnO surfaces; section 4 presents the conclusions.

2. METHODS

2.1. The ReaxFF Reactive Force Field. The ReaxFF force field makes no distinction between intramolecular and intermolecular interactions. The potential energy expression for the ReaxFF force field is given by

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{vdW}} + E_{\text{el}} + E_{\text{ion}} + E_{\text{vdW}\text{salt}} + E_{\text{Coulomb}}
\]

One distinctive feature of ReaxFF is that many-body effects are included through the bond-order variable. For each atom, the bond-order variable is calculated at each step, from the interatomic distances between it and its neighbors using a fitted function. For example, the bond energy term \((E_{\text{bond}})\) is not only a function of the pairwise distances but also the local density around each atom (the sum of the bond orders). Also, the terms for bond energies \((E_{\text{bond}})\), overcoordination and undercoordination energies \((E_{\text{over}}\) and \(E_{\text{under}}\)), lone-pair energies \((E_{\text{lp}})\), valence angle energies \((E_{\text{val}})\), and torsion angle energies \((E_{\text{tors}})\) depend on the bond order. ReaxFF also includes environment-dependent Coulombic interactions \((E_{\text{Coulomb}})\) using the electronegativity equalization method (EEM),\(^{25}\) in which individual atomic charges vary as the system geometry varies. This feature allows ReaxFF to describe charge transfer in chemical reactions. Short-range repulsion and long-range dispersion is included through a nonbond order-dependent Morse function \((E_{\text{vdW}\text{salt}})\). The nonbond order-dependent terms \((E_{\text{Coulomb}}\) and \(E_{\text{vdW}\text{salt}})\) are screened by a taper function at long distances and shielded to avoid excessive repulsion at short distances. A detailed description of the meaning of the individual terms can be found in refs 23 and 24. The force field parameters used here were fitted in previous studies to data sets comprising energies and charges from quantum-mechanical B3LYP calculations for various configurations. For the ZnO—water interactions, the data set included several ZnO and Zn bulk and surface configurations and several water adsorption geometries for isolated water molecules and monolayers on ZnO. For the water—water interactions, the force field was fitted to a data set that included, for example, a large number of water clusters and hydrogen transfer barriers. The parameters are summarized in ref 13.

2.2. System Descriptions. At ambient conditions ZnO crystallizes in the wurtzite-type structure (space group \(\text{P6}_{3}mc\); number 186 in The International Tables for Crystallography\(^{26}\)) with lattice constants \(a = 3.25\ \text{Å}\) and \(c = 5.21\ \text{Å}\).\(^{27}\) The surface of ZnO is dominated by four faces, two nonpolar ones, (10\(\overline{1}0\)) and (11\(\overline{2}0\)), parallel to the \(c\)-axis, and two polar ones, (00\(\overline{1}0\)) and (00\(\overline{0}1\)), perpendicular to the \(c\)-axis. It has been determined experimentally that in ZnO powders the nonpolar faces make up \(\sim 80\%\) of the surface.\(^{28}\) In the present study, water adsorption on seven terraced ZnO—wurtzite surface systems were studied, all having (10\(\overline{1}0\)) terraces and all (except for (10\(\overline{1}0\))) having steps parallel to the (00\(\overline{0}1\)) direction. The surfaces are in order of decreasing step concentration: (11\(\overline{2}0\)), (21\(\overline{3}0\)), (3\(\overline{1}4\)0), (41\(\overline{5}0\)), (51\(\overline{6}0\)), and (61\(\overline{7}0\)), and (10\(\overline{1}0\)). The ZnO—water systems were represented by lamellar systems periodic in three dimensions, in which the ZnO surfaces were represented by slabs separated in the \(z\)-direction. In all cases supercells were used to describe the periodicity in the \(xy\)-plane. The top layer of each slab is shown in Figure 1, viewed along the (00\(\overline{0}1\)) direction. In the (00\(\overline{0}1\)) direction the supercell consisted of 4 times the minimum repeat unit (surface cell). In the direction perpendicular to the (00\(\overline{0}1\)) direction and the normal of the surface, the following number of surface cells were used: four for (11\(\overline{2}0\)), two for (21\(\overline{3}0\)) and (31\(\overline{4}0\)), one for (41\(\overline{5}0\)), (51\(\overline{6}0\)), and (61\(\overline{7}0\)), and finally six for (10\(\overline{1}0\)). The supercell sizes were chosen to give similar surface areas for all surfaces while remaining within the computational constraint of creating model systems of less than 1500 atoms. For a detailed description of the ZnO slabs, see Table 1. An explanation of the definition of a step and a terrace is shown in Figure 3a.

2.2.1. Monolayer Water—ZnO Interface. The surfaces were covered with one water molecule per surface Zn ion to simulate ZnO covered with a monolayer of molecular water. The \(z\)-axis of
the simulation box was elongated to 100 Å to make the slabs noninteracting perpendicular to the surfaces; see Table 1 for details.

2.2.2. Liquid Water–ZnO Interface. To simulate ZnO in contact with liquid water, the gap in the z-direction between the slabs was filled with water molecules, cf. Figure 2. Each system contained 256 water molecules. Since the different model systems have different surface areas the thickness of the water layers vary, but are always larger than 16 Å; see Table 1 for details.

2.2.3. Water Evaporation. The final structure of each model system from the liquid water–ZnO simulation was used as starting geometry for simulation of water evaporation from the ZnO surface. However, first the z-axis of each simulation box was elongated by ~150 Å to create a vacuum gap in the middle of the water region. This resulted in a ZnO slab with each of its two opposite surfaces covered by a water layer consisting of 128 water molecules (half of the total number of water molecules).

Figure 1. Top layer of each ZnO wurtzite slab used in the MD simulations. Here and in the following figures oxygen ions are represented by large red spheres and zinc ions by smaller gray ones. The periodic images of the surface layers have been shaded. The direction of the z-axis of the simulation box is indicated, parallel to the surface normal.

Table 1. Slab Models Used with ReaxFF; Values Are Given per Repeating Unit (Simulation Box) after Equilibration

<table>
<thead>
<tr>
<th>surface</th>
<th>no. of ZnO surface sites</th>
<th>no. of water molecules in monolayer simulation</th>
<th>surface areaa (Å²)</th>
<th>steps</th>
<th>width of (10T0) terrace (rows)</th>
<th>step concentration (steps/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10T0)</td>
<td>48</td>
<td>48</td>
<td>19.9 × 21.6</td>
<td>0</td>
<td>6</td>
<td>0.000</td>
</tr>
<tr>
<td>(61T0)</td>
<td>56</td>
<td>56</td>
<td>21.6 × 21.6</td>
<td>1</td>
<td>5</td>
<td>0.046</td>
</tr>
<tr>
<td>(51T0)</td>
<td>48</td>
<td>48</td>
<td>21.6 × 18.4</td>
<td>1</td>
<td>4</td>
<td>0.054</td>
</tr>
<tr>
<td>(41T0)</td>
<td>40</td>
<td>40</td>
<td>21.5 × 15.1</td>
<td>1</td>
<td>3</td>
<td>0.066</td>
</tr>
<tr>
<td>(31T0)</td>
<td>64</td>
<td>64</td>
<td>21.6 × 23.8</td>
<td>2</td>
<td>2</td>
<td>0.083</td>
</tr>
<tr>
<td>(21T0)</td>
<td>48</td>
<td>48</td>
<td>21.5 × 17.5</td>
<td>2</td>
<td>1</td>
<td>0.114</td>
</tr>
<tr>
<td>(11T0)</td>
<td>64</td>
<td>64</td>
<td>21.6 × 22.8</td>
<td>4</td>
<td>0</td>
<td>0.174</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>surface</th>
<th>no. of ZnO formula units</th>
<th>no. of atoms for liquid water simulation</th>
<th>thicknessb (Å)</th>
<th>thickness of water layer (Å)</th>
<th>equilibration time for liquid water simulation (ns)</th>
<th>total simulation time for evaporation simulation (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10T0)</td>
<td>288</td>
<td>1344</td>
<td>14.9</td>
<td>22.4</td>
<td>9.1</td>
<td>9.5</td>
</tr>
<tr>
<td>(61T0)</td>
<td>312</td>
<td>1392</td>
<td>15.3</td>
<td>18.9</td>
<td>9.4</td>
<td>9.2</td>
</tr>
<tr>
<td>(51T0)</td>
<td>280</td>
<td>1328</td>
<td>15.2</td>
<td>23.0</td>
<td>11.8</td>
<td>9.5</td>
</tr>
<tr>
<td>(41T0)</td>
<td>240</td>
<td>1248</td>
<td>17.7</td>
<td>26.0</td>
<td>12.6</td>
<td>9.9</td>
</tr>
<tr>
<td>(31T0)</td>
<td>320</td>
<td>1408</td>
<td>11.6</td>
<td>18.9</td>
<td>9.4</td>
<td>9.0</td>
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<td>1408</td>
<td>19.6</td>
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<td>1408</td>
<td>14.6</td>
<td>16.2</td>
<td>11.6</td>
<td>9.0</td>
</tr>
</tbody>
</table>

*Value after equilibration. **Difference in z-coordinate between topmost and bottommost Zn- and O ions.

2.3. Molecular Dynamics Simulations. The molecular dynamics simulations were performed with the GRASP software package.29 In all simulations, the equations of motion were solved with the velocity-Verlet algorithm,30 using a time-step of 0.25 fs. The NVT ensemble was used where the temperature was kept constant at 300 K using a Nosé–Hoover thermostat31,32 with a time constant of 2.5 fs, integrating the equations of motion using the velocity-Verlet implementation by Tuckerman et al.33

2.3.1. Monolayer Water–ZnO Interface. The simulations were performed with a constant box volume and the temperature was kept constant using a thermostat as detailed above, i.e. the NVT ensemble was used. Prior to the production simulations the systems were equilibrated until the level of hydroxylation had stabilized; see Figure 4a for the total level of hydroxylation during the production simulation. For the least stepped surface, (10T0), the degree of hydroxylation is close to 50%, while for the most stepped surface (11T0), it approaches 80%, with intermediate degrees of hydroxylation for the other surfaces. In all cases no large drift in hydroxylation with respect to time is found. The level of hydroxylation is defined as the number of dissociated water molecules divided by the number of surface zinc and oxygen pairs. For each of the seven systems the time required for equilibration with respect to the level of hydroxylation was 1 ns followed by a 4 ns production simulation.

2.3.2. Liquid Water–ZnO Interface. The simulations were performed within the NPT ensemble, i.e., constant pressure and constant temperature. The temperature was kept constant using the same method as for the water monolayer simulations, while the pressure was kept constant at 1 atm using Hoover’s method,34 as implemented in GRASP. Prior to the production simulations the systems were equilibrated until the level of hydroxylation had stabilized. Figure 4b shows the total level of hydroxylation during the production simulation. For the least stepped surface, (10T0), the degree of hydroxylation is 80–85%, while for the most stepped surface, (11T0), is fully hydroxylated. The other surfaces are hydroxylated to 90% or more. In all cases no large drift in hydroxylation with respect to time is found. The
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3. RESULTS AND DISCUSSION

3.1. Adsorption Structures from Monolayer and Liquid Water Interfaces. To facilitate the discussion of the results a few definitions are introduced here. If we consider the dissociation of a water molecule on the ZnO surface as the transfer of a proton to a surface oxygen complemented by a formation of a hydroxyl bound to a Zn surface ion, we can distinguish five different types of hydroxyls: “Terrace”, “Top edge”, “Low edge”, “Terrace bridge”, and “Step”, as illustrated in Figure 3b. The different kind of hydroxyls mainly differ in that the former three bind to one surface Zn ion while the latter two bind to two (using a 2.7 Å distance criterion for a O–Zn bond).

In the monolayer simulations, we only find the formation of hydroxyls binding to one surface Zn ion (i.e., “Terrace”, “Top edge”, “Low edge” hydroxyls). As seen in Figure 4a, the levels of hydroxylation ranges between 50 and 80%. No instance of desorption was found and total coverage remained at 100%, meaning that the undisturbed monolayer is stable with respect to desorption on this time scale. As previously reported the half dissociated (2 × 1) pattern is present on the terraces.

For the liquid water interface, the level of hydroxylation is in all cases more than 80% and a corresponding fraction of the Zn surface sites are bound to an OH group, as seen in Figure 4b. This means that the equilibrium between dissociatively adsorbed and molecularly adsorbed water is shifted toward dissociated compared to the monolayer case. This result supports previous experimental conclusions that water dissociates in the first adsorption layer.

In the liquid interface, all five different types of hydroxyls listed in Figure 3b are present. In addition, the terrace hydroxyls appear in a range of hydrogen bond patterns, summarized in Figure 5. We distinguish between adsorption structures of reactive water molecules of type a and b, corresponding to dissociated (OH + H) water and molecular (H2O), respectively, and nonreactive adsorption structures types c and d, corresponding to adsorbed isolated OH groups and water molecules with a proton blocking the reaction path, respectively. We also find four structures e–h where an additional water molecule is included into the adsorption structure compared to types a–d. All these were found to varying degrees in our simulations. Structures a and b make up the alternating rows in the (2 × 1)-pattern found in the monolayer. In a the formed hydroxyl is stabilized by a hydrogen bond donated from the transferred proton, and in b the water molecule donates a hydrogen bond to the surface. Structures c and d are products of hydrogen transfer within the adsorption layer and are not hydrogen-bonded. The final four patterns are variations of the former four patterns, albeit mediated via the water molecules in the second layer above the surface. The H–bond pattern highlighted in Figure 5 of ref 14 is likely a combination of these (e–h).

3.2. Proton Transfer to the Metal Oxide Surface in the Liquid Water Interface. During the simulations no instance of water dissociation outside the first adsorption layer was found for any of the surfaces, which indicates that the dissociation reaction can only proceed in the simulation time scale if catalyzed by the ZnO surface. Also, no proton transfer from the first adsorption layer into the water region outside was found. We do find proton transfer reactions between water molecules and hydroxyls within the first adsorption layer via a “Grotthus”-like mechanism, but these reactions do not contribute to the hydroxylation of the surface. However, they do affect the probability of the occurrence of...
of the necessary configurations for hydrogen transfer to the surface; this is not described here and is left for future studies.

In order to distinguish the reactive water molecules and hydroxyls we make use of spatial distribution functions. We begin by locating all water/hydroxyl oxygens which bind to a single Zn ion (criterion (i) below), i.e. we exclude the ”terrace bridge” and “step” hydroxyls of Figure 3b. We do this since we did not find a single case where these hydroxyls participate in a proton transfer reaction. We then collect all hydrogens closer than 1.9 Å to the water/hydroxyl oxygen in a spatial distribution function and visualize it, by drawing an isosurface in the distribution, showing the most likely locations of the hydrogen atoms. This isosurface is shown as both gray and green surfaces in Figure 6. Close to the ZnO surface there is a double meniscus, representing the proton transfers to the surface. Capturing these events requires two additional criteria, listed as (ii) and (iii)

![Figure 4](image)

**Figure 4.** Time dependence of the OH-coverage at the ZnO/water—interface for the different ZnO surfaces, (a) the monolayer water—ZnO interface. (b) Liquid water—ZnO interface.

![Figure 5](image)

**Figure 5.** Illustrations (from above and side) and classification (a, b, c, d, e, f, g, h) of the different types of adsorption structures (for water molecules and hydroxyls bound to one surface Zn ion) that we have found on the (1010) terraces. The structures shown were taken from snapshots of the production MD simulation. Hydrogen bonds are represented by blue lines, All other water molecules have been removed so as not to block the structure pictured. The side view is rotated 90° compared to that in previous figures. The notation OH + H2O (e), for example, means that two adsorbed water molecules give rise to a H2O•••OH structure, while the ”missing” H atoms have migrated somewhere else.
In total we find that the following criteria must be fulfilled in order for a water molecule to transfer a proton to the surface or vice versa:

(i) The water/hydroxyl oxygen binds to a single surface Zn ion.

(ii) The reactive H of the water molecule points toward a naked surface O\(^{2-}\). In the case of reassociation, the transferred proton points toward a hydroxyl group.

(iii) The reaction path is not blocked by another water molecule.

In Figure 6, the isosurface in all the spatial distribution function of the hydrogen atoms fulfilling all the three criteria is green, while all the remaining hydrogen atoms have their isosurface colored gray. The same criteria (i−iii) were used to calculate a probability distribution function pdf\((r_{O-H})\) as a function of the distance between the oxygen in the water molecule (turning hydroxide) and the hydrogen that is transferred to the surface. From the probability distribution function the potential of mean force (PMF) is obtained according to eq 2.

\[
\text{PMF}(r_{O-H}) = -k_B T \ln(pdf(r_{O-H}))
\]

3.3. Water Evaporation. Rapid evaporation is found for surfaces exposed to a vacuum. Initially, very fast evaporation is calculated \((40000−80000 \text{ mol m}^{-2} \text{ s}^{-1})\). For most of the surfaces, apart from the most stepped surfaces, \((2130)\) and \((11\overline{2}0)\), the rate of evaporation drops substantially \((\approx 1000−1500 \text{ mol m}^{-2} \text{ s}^{-1})\), when the coverage falls below two water molecules per surface Zn ion which corresponds to twice the monolayer coverage; cf. Figure 8. The reason for the change in desorption rate is probably that extra water molecules are bound to the surface through adsorption structures like e−h in Figure 5 and are therefore less prone to evaporate. For the \((2130)\) and \((11\overline{2}0)\) surfaces, the rate of evaporation is seen to be steady until the coverage falls to close to 1 monolayer, where the rate drops significantly. We assign the difference in behavior

\[
\text{PMF}(r_{O-H}) = -k_B T \ln(pdf(r_{O-H}))
\]
4. CONCLUSIONS

In this contribution, the ZnO—liquid water interface has been studied with respect to the structural features and their connection to proton transfer reactivity. Compared to monolayer coverage, a higher level of hydroxidation was found, supporting previous descriptions in the literature that water dissociates in the first adsorption layer. We find that this is due to the increased possibility of hydrogen bonding with the water phase outside the first monolayer. The mixed molecular—dissociative adsorption mechanism of the monolayer is still present but of lower importance due to new types of water-mediated adsorption structures blocking this reaction path. The presence of water-mediated structures is qualitatively in agreement with previous experimental assessments in the literature that ZnO surfaces are hydroxylated, with molecular water adsorbed onto these hydroxyls. We find that the presence of a step both stabilizes the hydroxylated state and decreases the barrier for dissociation, leading to a higher level of hydroxidation. On highly stepped surfaces, the favorable half dissociated (2 × 1) structure found for monolayers on flat surfaces is not possible, and the barrier for dissociation is only 2 kJ/mol or smaller. In the simulations no dissociation or proton transfer reaction is found outside the first adsorption layer, indicating that these reactions can only proceed in the simulation time scale if catalyzed by the metal oxide surface.

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Figure 8. Evaporation curves for the seven surface models. Water on the (1120) and (2130) surfaces decay faster to monolayer coverage compared to the others. For the other surfaces there is a change the desorption rate at a coverage of ~2 water molecules per surface Zn atom, corresponding to two monolayers. The black horizontal line corresponds to monolayer coverage.

of the former, less stepped, surfaces and, the latter highly stepped, surfaces to the same structural feature as in section 3.2: two parallel terrace rows.