

# Dissociative and molecular adsorption of water on $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001)

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A systematic analysis of the adsorption of water monomers, small water clusters and water thin films on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surfaces on the basis of density functional theory calculations is performed. In agreement with most existing studies, our calculations favor the dissociative adsorption for low coverages.

For water-rich conditions, however, the formation of hexagons of alternating dissociatively and molecularly adsorbed water monomers is predicted. Accordingly, the adsorption energy per water molecule decreases from about 1.5 eV for single adsorbed molecules to about 1.2 eV for thin films.

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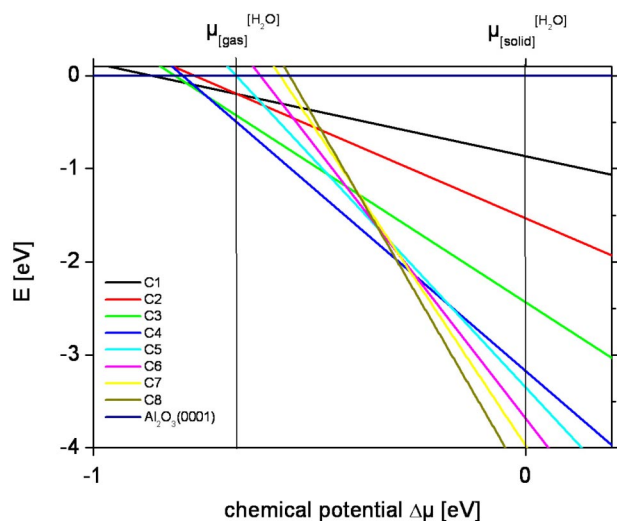
The interaction of water with solid surfaces is fundamental to research in various fields ranging from atmospheric chemistry to corrosion and heterogeneous catalysis. Despite substantial research efforts, however, precise information on the water geometry at the atomic level often seems elusive, for the ubiquitous liquid phase [1, 2] as well as for many cases of substrate-supported thin water films and clusters prepared in the laboratory [3–9].

The interaction of water with aluminum oxide has found interest because of the extensive use of this material, e.g., as a catalyst as well as a catalyst support, and by its role in environmental chemistry. Moreover, the well defined Al-terminated Al<sub>2</sub>O<sub>3</sub>(0001) surface is a widely studied model system for water interaction with metal oxide surfaces. Experimentally, most studies suggest water dissociation on the Al-terminated Al<sub>2</sub>O<sub>3</sub>(0001) surface. This was concluded from high-resolution electron-energy-loss spectroscopy (HREELS) studies [10] as well as thermal desorption experiments (TDS) [11, 12]. X-ray photoemission experiments [13] were interpreted to indicate water dissociation in particular at surface defect sites. Early ultraviolet photoelectron spectra, on the other hand, seem to indicate molecular adsorption of water at room temperature [14]. Theoretically, most *ab initio* studies agree on

the stability of the dissociative vs the molecular adsorption [16–18] while one cluster study [19] found little difference between the energies of molecular and dissociative adsorption of water. A recent density functional theory (DFT) study compares the energetics of a wide range of adsorption geometries for various coverages [20]. However, this comparison does not include the possibility of a dissociative adsorption as concluded from many experimental studies.

Here we present a comparison of the adsorption energetics of both molecularly and dissociatively adsorbed water for various coverages based on density functional theory.

The calculations are performed using density functional theory (DFT) within the generalized gradient approach (GGA) as implemented in the Vienna *Ab initio* Simulation Package (VASP) [21]. The electron-ion interaction is described by the projector-augmented wave scheme [22]. The electronic wave functions are expanded into plane waves up to a kinetic energy of 360 eV. The surface is modeled by periodically repeated slabs. Each supercell consists of 18 atomic layers within (2×2) periodicity plus the adsorbed water and a vacuum region equivalent to 18 Å. The 15 uppermost layers as well as the



**Figure 1** Calculated phase diagram of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface in dependence on the water chemical potential  $\Delta\mu$  given with respect to hexagonal ice  $I_h$ . The enumeration  $C_n$  corresponds to the number of H<sub>2</sub>O monomers per unit cell

adsorbate degrees of freedom are allowed to relax until the forces on the atoms are below 20 meV/Å. The Brillouin zone integration is performed using  $2 \times 2 \times 1$  Monkhorst-Pack meshes. We use the PW91 functional [23] to describe the electron exchange and correlation energy within the GGA. It describes the hydrogen bonds in solid water (ice Ih) in good agreement with experiment [24,25].

We begin the adsorption study by determining the potential energy surfaces for single water monomers, hydrogen atoms in presence of a surface adsorbed OH group and hydroxyl groups in the presence of a surface adsorbed hydrogen atom on the clean  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface, respectively. The calculated data show that the lowest energy adsorption configuration corresponds to dissociated H<sub>2</sub>O monomers located at the 1-2 position (following the notation in Ref. [16]). Starting from this adsorption configuration in the  $(2 \times 2)$  unit cell, the water coverage was systematically increased to eight molecules, representing a single complete H<sub>2</sub>O bilayer. The corresponding lowest-energy structures for the respective coverage are denoted by  $C_n$  in the following, where  $n$  corresponds to the number of molecules per  $(2 \times 2)$  surface unit cell. Among others, the adsorption configurations from Ref. [20] as well as (partially) dissociated adsorption models were probed. In order to compare adsorption models with different water coverages, the thermodynamic grandcanonical potential

$$\Omega(\mu_i) = F_{surf}(n_i) - \sum_i n_i \mu_i \approx E_{surf}(n_i) - \sum_i n_i \mu_i \quad (1)$$

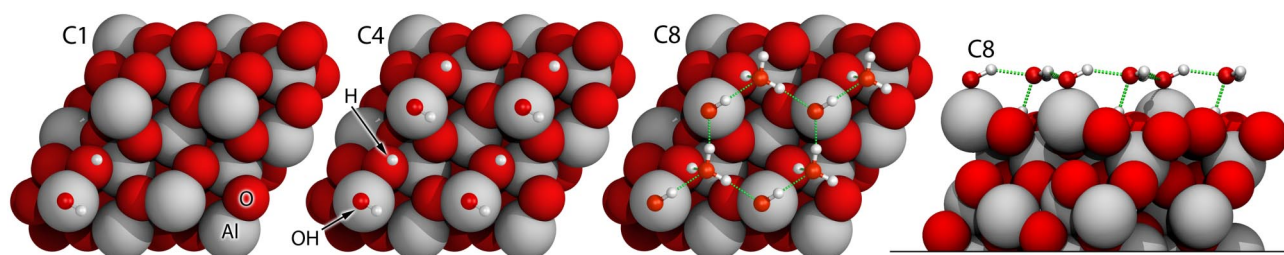
needs to be calculated [26], where  $F_{surf}(n_i)$  is the surface free energy which we approximate by the total sur-

face energy  $E_{surf}(n_i)$  at zero temperature, assuming similar entropy contributions for different adsorption configurations. The number of adsorbate molecules is represented by  $n_i$ . Figure 1 shows the resulting phase diagram in the dependence of the water chemical potential. Two important values of the water chemical potential are indicated. Extreme water-rich conditions are marked by the vertical line at  $\Delta\mu = 0$ . This value corresponds to a Al<sub>2</sub>O<sub>3</sub> surface in equilibrium with bulk water, approximated here by calculations for ice Ih [25]. Lower values of  $\Delta\mu$  indicate an increasingly less water-rich environment. The zero temperature calculation for gas-phase water molecules is indicated. At finite temperatures, entropy corrections will lower the respective value of  $\mu$  for the surface in equilibrium with a reservoir of water vapor [27].

As expected, for low values of the water chemical potential the clean Al<sub>2</sub>O<sub>3</sub> surface is stable and effectively no wetting occurs. As the environment gets more and more humid, a variety of water-adsorbed surface structures should be observed. While the adsorption models C1 and C3 are stable for a very small window of preparation conditions, we find the full monolayer (C4) and the bilayer (C8) to be stable for a relatively wide range of water-rich and extreme water-rich conditions. Of course, in the extreme limit even higher coverages not considered here will form.

Low coordination of surface aluminium ions on clean  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) makes these sites strong Lewis acids, i.e. electron acceptors, which readily adsorb molecules like H<sub>2</sub>O, that can add electron-density. The dissociative adsorption is primarily heterolytic in nature. Adsorbed H<sub>2</sub>O dissociating can be viewed as splitting into H<sup>+</sup> and OH<sup>-</sup>, with the proton transferred to a nearby surface site in a 1-4 mechanism [16]. For all coverages, adsorption of H<sub>2</sub>O significantly disrupts the clean  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface geometry. The adsorption pulls the surface aluminium ion out of its relaxed surface position and elongates its three bonds to neighboring oxygen ions. Bonds between this aluminium and second-layer oxygen ions are significantly longer, and they are elongated even beyond the bulk values. That a relatively isolated H<sub>2</sub>O molecule prefers to adsorb dissociatively on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001), even in the absence of defects, differs from the behavior predicted in an earlier study of H<sub>2</sub>O on MgO(100) [28]. In that case, dissociative adsorption was favored in the vicinity of a step, but molecular adsorption was more stable on the ideal surface.

The most stable structures from the surface phase diagram are shown in Fig. 2. For low coverages, single dissociated molecules (C1) are stable. The ground-state geometry calculated here corresponds to the 1-2 geometry discussed in Ref. [16]. It is energetically nearly degenerate with the 1-4 structure. The latter structure, however, requires a substantially lower activation energy [16]. Interestingly, if all surface Al atoms are occupied by hydroxyl groups, additional water molecules do not dissociate but form hydrogen bonds with the pre-adsorbed H and OH



**Figure 2** Schematic top and side views of the thermodynamically stable adsorption structures C1, C4 and C8. The C3 structure is not shown, but is constructed by removing a single dissociated  $\text{H}_2\text{O}$  monomer from the C4 structure.  $\text{Al}_2\text{O}_3$  bulk-incorporated O atoms are indicated by a larger diameter than for OH/ $\text{H}_2\text{O}$ , respectively.

groups, see Fig. 2. Hexagons form (C8) that are somewhat reminiscent of the water hexagons formed on many metal surfaces [6,9]. In contrast to the latter, however, the hexagon structures formed on  $\alpha\text{-Al}_2\text{O}_3(0001)$  consist of alternating dissociated and intact molecules, which might explain some of the experimental ambiguities discussed above. It is interesting to note that a recent theoretical study by Scheffler and co-workers found similarly a crossover to a mixed molecular and dissociative adsorption mode with increasing water chemical potential for water adsorption on  $\text{Fe}_3\text{O}_4(0001)$  [29].

Figure 3 shows the adsorption energy per molecule for the adsorption structures C1 - C8. We find the relative adsorption energy to vary only moderately between the different adsorption geometries. This indicates that the surface-molecule interaction is dominant over the molecule-molecule interaction. A closer look at the adsorption energies shows two additional trends: A slight decrease of the adsorption energy with increasing coverage of dissociated molecules is followed by a somewhat more pronounced decrease as soon as the molecular adsorption starts for coverages above one water molecule per primitive surface unit cell (C4). Overall we find a vari-

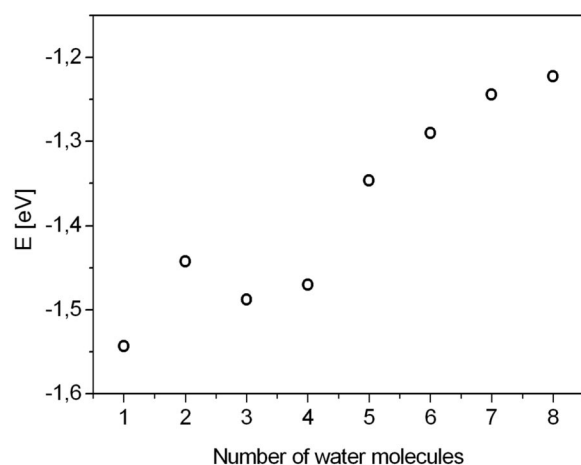
ation between about 1.5 and 1.2 eV for the adsorption energy. The lower limit agrees well with the calculations of Ranea *et al.* [20], who considered exclusively molecularly adsorbed water. Also the energy difference between molecularly and dissociatively adsorbed water is close to the earlier calculations which state about 0.43 eV for the low-coverage regime [16].

To summarize, DFT-GGA calculations for water adsorbed on the clean  $\alpha\text{-Al}_2\text{O}_3(0001)$  surface were performed. For low water coverages dissociated single water molecules are energetically most favored. Increasing the water coverage, however, favors complex structures consisting of both dissociated and intact water monomers by forming hydrogen bonds between preadsorbed H/OH groups and intact  $\text{H}_2\text{O}$  monomers. The relative adsorption energies suggest that the molecule-surface interaction is dominant over the molecule-molecule interaction.

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**Figure 3** Calculated adsorption energy per  $\text{H}_2\text{O}$  molecule for the adsorption geometries C1 - C8.

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