

Structure and dynamics of liquid water on rutile $\text{TiO}_2(110)$

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Water on $\text{TiO}_2(110)$ is the most widely studied water-oxide interface, yet questions about water dissociation and hydrogen bonding are controversial. Here we report density-functional theory simulations which show that water does not dissociate at the coverages examined. The aqueous film is layered, with slow moving molecules in the contact layer and fast moving molecules in a second layer, revealing strongly inhomogeneous dynamics of the interfacial water. Hydrogen bonding between the first and second layers is observed as is the exchange of water molecules. These results help to resolve a number of controversies pertaining to the molecular scale behavior of water on TiO_2 and provide insight in to the structure and dynamics of water-solid interfaces by, e.g., demonstrating that water dynamics can vary on the Angström length scale and that the presence of second layer water molecules can cause those in the first layer to reorient.

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Under ambient conditions most solid surfaces are covered by a thin film of water. Of all the many water-solid interfaces, there are few (if any) of more contemporary scientific and technological importance than those between water and titanium dioxide (TiO_2). Water- TiO_2 interfaces are relevant to photocatalysis, gas sensors, and biocompatible devices not to mention the varied applications of TiO_2 in pigments and coatings. Motivated by the desire to better understand and ultimately control processes at wet TiO_2 surfaces as well as to answer fundamental questions of wetting and the properties of interfacial water, these systems have been intensively investigated. The rutile $\text{TiO}_2(110)$ -water interface is the most widely studied model system and to it almost every surface-sensitive probe has been employed in pursuit of a clear molecular-level description (e.g., Refs. 1–18).

Despite the enormous body of work on water- $\text{TiO}_2(110)$ interfaces, a number of crucial issues remain controversial. First, there is the long-standing debate on which adsorption state the water molecules are in at the interface: dissociated or molecular? Many experimental studies have indicated that oxygen defect sites are required for dissociation.^{3,4,6,7} However, density-functional theory (DFT) studies predict either molecular or dissociative adsorption on the perfect defect-free surface with results being sensitive to slab thickness, coverage, and exchange-correlation (xc) functional.^{9–14,16–18} Second, there is the question of the hydrogen bond (HB) network at the interface at coverages in excess of 1 monolayer (ML, where 1 ML is defined as one water per fivefold coordinated Ti site). Specifically, the seemingly simple question of whether there are HBs between the first and second interfacial water “layers” is under debate. Campbell and co-workers³ interpreted work-function measurements as an indication of interlayer HBs, a view supported by recent electron-stimulated desorption (ESD) measurements.¹⁹ However, spectroscopic measurements [high-resolution electron-energy-loss spectroscopy (HREELS)] (Ref. 4) did not show any redshift in the O-H stretching region upon going from 1 ML to multilayer adsorption, an observation that was interpreted as evidence against interlayer HBs. Answering these particular questions is not only essential for understanding water on TiO_2 but it also has potential to reveal general insight into the behavior of interfacial water through detailed

examination of a well-defined model system. These are questions that can ideally be tackled with *ab initio* molecular dynamics (AIMD). In AIMD the interatomic interactions are determined from the electronic-structure (generally DFT), and real-time dynamics and thermal fluctuations at finite temperature can be explored. However, AIMD simulations of liquid water-solid interfaces are computationally very demanding^{12–14,16,20} and only in the last few years have meaningful simulations of liquid water-solid interfaces been possible.

Here, we report on extensive DFT simulations aimed at clarifying several fundamental yet unresolved aspects of the structure and dynamics of water on the perfect defect-free $\text{TiO}_2(110)$ surface. Our calculations with various semilocal and hybrid xc functionals indicate that water does not dissociate in the coverage regime examined (0.5 ML to multilayer). The molecules within the liquid film adsorb in at least two distinct layers: those in the first layer diffuse slowly and bond strongly to fivefold coordinated Ti sites; those in the second layer interact weakly with the substrate and diffuse rapidly. This reveals that the dynamics of interfacial water can be strongly inhomogeneous, varying on the Angström length scale. Hydrogen bonding between the first and second layers is observed as is the exchange of molecules between the layers. The presence of second layer water molecules causes those in the first layer to reorient, indicating that the monolayer is a model of at best limited applicability to understanding the aqueous water- TiO_2 interface. These findings help to resolve a number of longstanding debates in the literature and underscore the complex nature of the structure and dynamics of aqueous water films on flat hydrophilic surfaces.

The calculations reported here have been performed with two codes. The plane-wave basis set code VASP (Refs. 21 and 22) has been used to explore the sensitivity of the results to xc functional and slab thickness. The mixed Gaussian and plane-wave basis set code CP2K/QUICKSTEP (Ref. 23) has been used mostly for the AIMD simulations. In the AIMD simulations the canonical ensemble was employed with a target temperature of 360 K, maintained with a Nose-Hoover chain thermostat. Further computational details are given in the supplementary information²⁴ and the good agreement be-

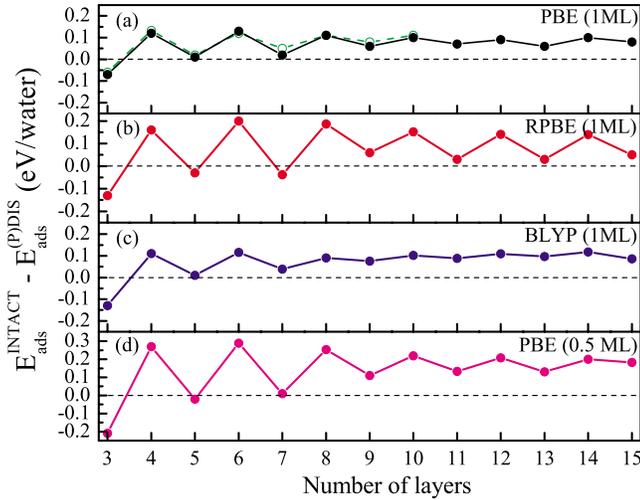


FIG. 1. (Color online) Energy differences, $E_{\text{ads}}^{\text{INTACT}} - E_{\text{ads}}^{(\text{P})\text{DIS}}$, between intact and partially (1 ML) or fully (0.5 ML) dissociated states versus number of TiO_2 layers in the slab. A layer of TiO_2 is defined as one O-Ti-O trilayer. (a) PBE at 1 ML. (b) RPBE at 1 ML. (c) BLYP at 1 ML. (d) PBE at 0.5 ML. Results are from VASP except for the open circles which are from CP2K.

tween the two codes can be seen from Fig. 1.

To begin, we examine how slab thickness and xc functional affect the picture that emerges for a water monolayer at 0 K. At this stage the focus is on three common generalized gradient approximation functionals [PBE,²⁵ RPBE,²⁶ and BLYP (Refs. 27 and 28)]. At 1 ML the two states of interest are a pure molecular (INTACT) state in which water molecules adsorb at fivefold coordinated Ti sites (Ti_{5c}) and a partially dissociated (PDIS) state in which every second water molecule at the Ti_{5c} sites has dissociated. In Figs. 1(a)–1(c), the relative energies of these states is plotted as a function of slab thickness. Clearly the relative energies of the two states oscillate strongly, as discussed before (e.g., Refs. 9 and 17). However the key point, which has hitherto been a matter of debate,^{9–12,14,16–18,20,29} is that for the thickest slabs all three functionals give essentially the same result, namely, that the INTACT state is more stable than the PDIS state by about ~ 0.05 eV/water to ~ 0.1 eV/water. The conclusion that the INTACT state is more stable than the PDIS state is

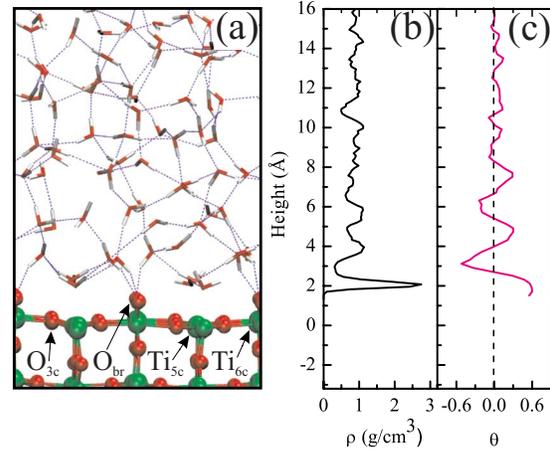


FIG. 2. (Color online) (a) Part of the simulation cell for the AIMD simulations of the liquid water/ TiO_2 interface. Red/gray, green, and white spheres represent O, Ti, and H atoms, respectively. Red/gray and white sticks represent O and H atoms of water molecules, respectively; (b) mass density (ρ) versus height for the water film on a four-layer TiO_2 slab. (c) Water dipole orientational order parameter (θ) along the z axis. In (b) and (c) the average position of the TiO_2 surface layer [the layer containing the Ti_{5c} , the sixfold coordinated Ti (Ti_{6c}), and threefold coordinated oxygen (O_{3c}) atoms] is defined as zero.

not altered if hybrid xc functionals such as PBE0,³⁰ HSE06,³¹ and B3LYP (Refs. 28 and 32) are used (Table I) or if van der Waals forces are accounted for.³³ Finally, we note that at a lower coverage of 0.5 ML, the intact water state is again preferred over the dissociated (DIS) state when a sufficiently thick slab is used [Fig. 1(d) and Table I].

To establish if finite-temperature or kinetic²⁹ effects are relevant to the question of water dissociation, AIMD simulations were carried out for water films on TiO_2 at 360 K with PBE. AIMD simulations were performed at 1 ML and for a multilayer film [Fig. 2(a)] on three, four, and six-layer TiO_2 slabs. The picture that emerges from AIMD is consistent with the total-energy calculations: on the four- and six-layer slabs water does not dissociate but on the three-layer slab some water molecules do (half the molecules in the first layer). Since the previous AIMD studies of this system were performed on a three-layer slab,^{12,16} we suggest that the dis-

TABLE I. Adsorption energies, E_{ads} (eV/water), from VASP at 1 and 0.5 ML for four-layer and nine-layer slabs with several xc functionals. $E_{\text{ads}} = E_{\text{TiO}_2(110)} + E_{\text{water}} - E_{\text{water/TiO}_2(110)}$, where $E_{\text{water/TiO}_2(110)}$, $E_{\text{TiO}_2(110)}$, and E_{water} are the total energies of the adsorption system, the clean $\text{TiO}_2(110)$ surface, and the appropriate number of isolated gas phase water molecules, respectively. The most stable state is indicated in bold.

| Layers | Functional | 1 ML | | 0.5 ML | |
|--------|------------|-------------|------|-------------|------|
| | | INTACT | PDIS | INTACT | DIS |
| 4 | PBE | 0.77 | 0.65 | 0.66 | 0.39 |
| | HSE06 | 0.83 | 0.74 | 0.74 | 0.54 |
| | PBE0 | 0.85 | 0.75 | 0.76 | 0.57 |
| | B3LYP | 0.69 | 0.57 | 0.68 | 0.40 |
| 9 | PBE | 0.79 | 0.73 | 0.68 | 0.57 |
| | HSE06 | 0.91 | 0.85 | 0.84 | 0.74 |

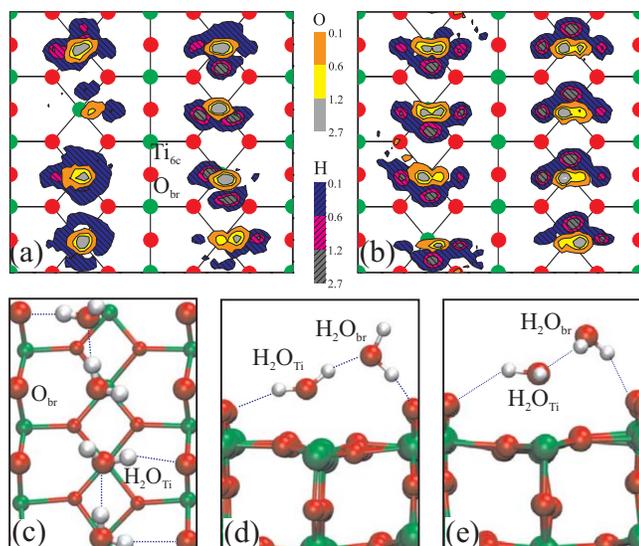


FIG. 3. (Color online) Spatial probability distribution functions of the O and H atoms within (a) the first layer of the water film and (b) for a single monolayer projected onto $\text{TiO}_2(110)$. (c) Top view illustrating HBs between neighboring $\text{H}_2\text{O}_{\text{Ti}}$ molecules. [(d) and (e)] Side views of HBs between $\text{H}_2\text{O}_{\text{Ti}}$ and O_{br} sites and between $\text{H}_2\text{O}_{\text{Ti}}$ and $\text{H}_2\text{O}_{\text{br}}$.

sociation observed in these studies is a consequence of the surface model employed. Overall, the fact that a consistent picture emerges from the range of simulations reported here (at both 0 K and finite temperature with functionals that have quite different treatments of exchange and correlation and yield, e.g., different TiO_2 band gaps, covalent, and hydrogen bond strengths) provides strong evidence against dissociation.

Having established that water does not dissociate on $\text{TiO}_2(110)$ and that this is adequately reflected with a four-layer slab, we now examine certain properties of the water film. An overview is provided by the planar-averaged density along the surface normal [Fig. 2(b)]. This is characterized by a large peak in the density of $\sim 3 \text{ g/cm}^3$ at $\sim 2.1 \text{ \AA}$ from the surface. The high-density maximum indicates that molecules in this layer are adsorbed at well-defined surface sites; as we show below these are the molecules at the Ti_{5c} sites (referred to as “ $\text{H}_2\text{O}_{\text{Ti}}$ ” molecules). Beyond the first layer are two other, less-well-defined layers. The second layer is centered at a height of $\sim 3.8 \text{ \AA}$ and corresponds to water at the O_{br} sites (“ $\text{H}_2\text{O}_{\text{br}}$ ” molecules). The weak third layer is just about discernible and is associated with molecules that act as HB bridges between adjacent $\text{H}_2\text{O}_{\text{br}}$ molecules. Outside the third layer, from $\sim 6 \text{ \AA}$, the oscillations are less pronounced and the bulk density of $\sim 1 \text{ g/cm}^3$ is obtained. While the layering and density oscillations observed here are a general feature of solid-liquid interfaces, the detailed nature of the oscillations are specific to water on $\text{TiO}_2(110)$. Indeed it is encouraging that the first hydration peak appears to be in excellent agreement with the peak in the oxygen density profile observed at $2.12 \pm 0.02 \text{ \AA}$ with x-ray diffraction.⁵

Let us focus on the molecules in the contact layer. Figure 3(a) displays spatial probability distribution functions projected on to the TiO_2 surface for the O and H atoms within

the contact layer. Consistent with the high peak in the density profile there is indeed a high degree of order within the first layer, wherein the molecules are adsorbed above Ti_{5c} sites. Most Ti_{5c} sites are occupied during the course of the AIMD simulation with the effect that the time-averaged coverage in this layer is close to 1 ML (0.84 ML). The $\text{H}_2\text{O}_{\text{Ti}}$ molecules are generally adsorbed with their dipoles inclined slightly away from the surface. This is shown by the snapshot in Fig. 2(a) and quantified by the orientational order parameter, θ , reported in Fig. 2(c). θ is defined as the average of the cosine of the angle between the water dipole and the surface normal. The large positive value of $\theta \sim 0.6$ implies an anisotropic water distribution with the dipole moments inclined by about 35° from the surface. The $\text{H}_2\text{O}_{\text{Ti}}$ molecules form several distinct types of HBs. Specifically, they can donate and accept HBs to water molecules at adjacent Ti_{5c} sites [Fig. 3(c)], they can donate HBs to the O bridge sites [Figs. 3(c) and 3(d)], and they can donate and accept HBs to and from water molecules in the second layer [Figs. 3(d) and 3(e)]. Using a geometric definition of hydrogen bonding,³⁴ the average number of HBs each $\text{H}_2\text{O}_{\text{Ti}}$ is involved in is 2.2.

Although our simulations reveal HBs between the first and second layers, the existence of interlayer HBs is under debate. This debate originates in HREELS experiments which did not show a redshift in the O-H stretching region upon going from monolayer to multilayer.⁴ To address this we used AIMD to calculate vibrational frequency spectra for the monolayer and multilayer films (Fig. S2). The key finding is that for the monolayer the molecules rearrange and compensate for the missing HBs to the second layer by “tightening up” the HBs in the plane parallel to the surface. This can be seen by comparing the spatial probability distributions for the monolayer simulation [Fig. 3(b)] with the results from the first layer beneath the water film [Fig. 3(a)]. Indeed the average number of HBs per $\text{H}_2\text{O}_{\text{Ti}}$ in the case of a monolayer remains at 2.2, identical to the value obtained for the first wetting layer in the multilayer. Likewise the relevant HB peak in the O-H (O-D) stretching region is unchanged upon going from the monolayer to the multilayer [Fig. S2(a)]. The rearrangement of the HBs at water film coverages and the resultant similar number of HBs in the first layer for the monolayer and the multilayer helps to explain the longstanding puzzle on the existence of interlayer HBs.^{34,19} Note that an equivalent set of simulations on a three-layer slab upon which water dissociates does not yield spectra that can explain the HREELS experiments [Fig. S2(b)], thus providing further evidence against dissociation. Not only do the 1 ML simulations allow the issue of interlayer HBs to be addressed but they show that the structure of the first layer is perturbed by the presence of the water film [cf. Figs. 3(a) and 3(b)]. A general implication of this is that the monolayer is a model of at best limited applicability to understanding the liquid water- TiO_2 interface.

Finally, we discuss the diffusive properties of the molecules within the first two layers. From a force-field study³⁵ it was concluded that the molecules in the first layer were immobile. Here, we find that while these molecules are sluggish (with a diffusion coefficient of $0.02 \text{ \AA}^2/\text{ps}$), they are mobile and the exchange of molecules between the first and second layers is observed; such exchange is consistent with

recent ESD measurements.¹⁹ Immediately beyond the first layer, the $\text{H}_2\text{O}_{\text{br}}$ molecules exhibit a diffusion coefficient of $0.07 \text{ \AA}^2/\text{ps}$, which is characteristic of PBE bulk water.³⁶ Thus our calculations predict a large discontinuity in diffusion coefficients upon moving away from the surface rather than the gradual change predicted previously.³⁵ To understand why the water dynamics can vary on the Angström length scale, HB lifetimes were computed.³⁴ Whereas the calculated HB lifetime for PBE bulk water is about 7 ps, the lifetime for the interlayer HBs is only 0.9 ps, and for the HBs between the $\text{H}_2\text{O}_{\text{br}}$ molecules and the O_{br} sites it is also short at 3.8 ps. Thus, although $\text{H}_2\text{O}_{\text{br}}$ molecules form HBs to both the $\text{H}_2\text{O}_{\text{Ti}}$ molecules and the O_{br} bridge sites, these HBs are short lived and it is this that enables relatively rapid diffusion of the molecules in the second layer. This establishes for this system a clear connection between local bonding and dynamics.

In conclusion, an extensive series of first-principles simulations for water on $\text{TiO}_2(110)$ have been performed. By carefully evaluating the sensitivity of the results to slab thickness and xc functional (including the first periodic hybrid functional calculations for water on TiO_2) we have arrived at a consistent picture with regard to water dissociation: water does not dissociate in the entire coverage regime examined. This clear understanding has then allowed us to address other long-standing questions of general importance

relating to the structure and dynamics of the wet TiO_2 interface. We find that molecules within the liquid film adsorb in at least two distinct layers: those in the first layer are sluggish and bond strongly to fivefold coordinated Ti sites; those in the second layer interact weakly with the substrate and diffuse rapidly. This reveals strongly inhomogeneous dynamics of the interfacial water and shows that in the immediate vicinity of the interface the dynamical properties of the water can vary on the Angström length scale. Hydrogen bonding between the first and second layers is observed as well as the exchange of molecules. In addition, the presence of second layer molecules causes those in the first layer to reorient, indicating that the monolayer is a model of at best limited applicability to understanding the aqueous water- TiO_2 interface. Not only does this study help to resolve a number of important debates relating to the molecular level details of water on TiO_2 but it also demonstrates the complex nature of wetting at a seemingly simple defect-free hydrophilic surface.

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