

Acidity of the Aqueous Rutile $\text{TiO}_2(110)$ Surface from Density Functional Theory Based Molecular Dynamics

Jun Cheng and Michiel Sprik*

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

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Abstract: The thermodynamics of protonation and deprotonation of the rutile $\text{TiO}_2(110)$ water interface is studied using a combination of density functional theory based molecular dynamics (DFTMD) and free energy perturbation methods. Acidity constants are computed from the free energy for chaperone assisted insertion/removal of protons in fully atomistic periodic model systems treating the solid and solvent at the same level of theory. The $\text{p}K_{\text{a}}$ values we find for the two active surface hydroxyl groups on $\text{TiO}_2(110)$, the bridge OH (Ti_2OH^+), and terminal H_2O adsorbed on a 5-fold Ti site (TiOH_2) are -1 and 9 , leading to a point of zero proton charge of 4 , well within the computational error margin ($2 \text{ p}K_{\text{a}}$ units) from the experimental value ($4.5\text{--}5.5$). The computed intrinsic surface acidities have also been used to estimate the dissociation free energy of adsorbed water giving 0.6 eV , suggesting that water dissociation is unlikely on a perfect aqueous $\text{TiO}_2(110)$ surface. For further analysis, we compare to the predictions of the MULTiSite Complexation (MUSIC) and Solvation, Bond strength, and Electrostatic (SBE) models. The conclusion regarding the MUSIC model is that, while there is good agreement for the acidity of an adsorbed water molecule, the proton affinity of the bridging oxygen obtained in the DFTMD calculation is significantly lower (more than $5 \text{ p}K_{\text{a}}$ units) than the MUSIC model value. Structural analysis shows that there are significant differences in hydrogen bonding, in particular to a bridging oxygen which is assumed to be stronger in the MUSIC model compared to what we find using DFTMD. Using DFTMD coordination numbers as input for the MUSIC model, however, led to a $\text{p}K_{\text{a}}$ prediction which is inconsistent with the estimates obtained from the DFTMD free energy calculation.

1. Introduction

Metal oxides develop a sizable positive surface charge when immersed in water of sufficiently low pH. The origin of the excess charge is protonation of basic surface oxygens. Similarly, at high pH, deprotonation of adsorbed water molecules or hydroxyl groups builds up a negative surface charge. This charging process controls the sorption of ions and surface speciation and, hence, affects the chemical reactivity of the metal oxide surface.¹ The surface charge density at given pH is however not only determined by the proton affinity or acidity of surface groups. It also depends on surface composition and the electrostatic potential difference across electrical double layers and therefore on the

structure of the electrical double layer. It is notoriously difficult to disentangle these three factors using only experimental data such as potentiometric titration curves and electrokinetic measurements. Modeling and prediction of “intrinsic” surface proton affinities has therefore played a crucial role in the understanding of surface protonation.^{2–8}

This complexity also leaves surface protonation models a large degree of freedom. Indeed, two of the most developed and successful models used in the literature, the MULTiSite Complexation (MUSIC) model^{2,3,5} and the Solvation, Bond strength, and Electrostatic (SBE) model,^{4,6} are capable of representing a large set of experimental data. Both models use bond valence as the key parameter determining proton affinity. Bond valence was introduced by Pauling to rationalize the structure of ionic crystals. To predict intrinsic $\text{p}K_{\text{a}}$, a

* To whom correspondence should be sent. E-mail: ms284@cam.ac.uk.

bond length dependent generalization due to Brown and Altermatt is used.⁹ The precise form of the correlation between pK_a and bond valence is however different in the MUSIC and SBE models^{3,6} (the more recent model of Bickmore et al.^{7,8} employs yet another relation). Also, the type of experimental data used for the parametrization is not the same. Equilibrium constants for surface protonation in the MUSIC model are based on a linear correlation of bond valence with experimental acidities of (hydr)oxyacids in homogeneous solution,³ while the SBE model fits directly to experimental surface acidities.⁴ A further important distinction is the treatment of solvation, hydrogen bonding, and local structure of the surface. The SBE model maintains the classical single site-two pK_a concept considering only a single generic surface hydroxyl group.¹ Long range interactions with the solvent (and the oxide) are described by the coupling to a dielectric continuum.⁴ The MUSIC model differentiates between surface sites, recognizing that the number of metal ions coordinating with surface oxygens is a key factor in the differences in their chemical behavior.^{2,3} Short range specific hydrogen bonding is also accounted for by assigning a bond valence to hydrogen bonds to basic oxygens.³ It is however this feature special to the MUSIC model that has been called recently into question^{6–8} and will also be investigated in the present contribution.

In view of the variety in assumptions made in these models, a less empirical approach could be instructive even if only applied to a subset of typical systems. A significant step toward this goal was made by Rustad and co-workers in their studies of iron (hydr)oxide^{10,11} and silica.¹² While their model is also parametrized using the pK_a of solution complexes, the molecular quantity correlated with these data is the proton binding energy of the corresponding gas-phase complex computed by molecular mechanics (MM) methods. Surface acidity constants are obtained by applying the MM Hamiltonian to an atomistic model of the gas-phase surface and substituting the calculated proton affinity in expression for pK_a . The advantage over the MUSIC and SBE approach is that the effect of the structural relaxation of surfaces and coupling between protonated sites can be studied in microscopic detail.¹¹ The importance of a realistic description of metal oxygen surface bonds is also stressed by Bickmore and co-workers.⁷ The valence of surface bonds in their approach is calculated from detailed information on bond lengths as determined by full Density Functional Theory (DFT) modeling of periodic oxide vacuum interfaces. This method was applied in an investigation of the protonation of aluminum hydroxide(gibbsite) and silica.⁷ A similar strategy was used by Machesky and co-workers to obtain the structural input for a MUSIC model estimation of surface protonation constants of TiO₂ (rutile).¹³ The Ti–O bond lengths were estimated from a density functional theory based molecular dynamics (DFTMD) simulation of multilayer adsorption of water on TiO₂ surfaces. pK_a in a MUSIC model, however, also depends on coordination numbers (number of hydrogen bonds) which were computed using a classical MD simulation of solid–water interfaces. The force field model in the classical MD was optimized using DFT,^{14,15} ensuring consistency between the two calculations.

A feature common to all methods mentioned above is reliance on an empirical linear free energy relationship of some kind for the description of the solvent effects on pK_a . Eliminating such a phenomenological relation requires either monitoring the surface protonation as it evolves in a MD simulation allowing for proton dissociation or the application of free energy sampling methods. Examples of the first approach are the classical MD studies of the charging of magnetite¹⁶ and goethite¹⁷ by Rustad and co-workers using dissociative water potentials. The present DFTMD investigation of the protonation of the rutile TiO₂(110) surface uses free energy perturbation methods. Proton affinities are computed directly as finite temperature free energy changes using our recently developed DFTMD method of reversible proton insertion.^{18,19} The motivation for choosing the TiO₂/H₂O interface is because this system is well characterized by experiment^{20–23} and has become a benchmark for the modeling of surface protonation and complexation.^{2–5,13,21,24}

A related issue, which has caused considerable controversy in the computational surface science community, is whether water dissociates on the rutile TiO₂(110) surface.^{25–35} Experiments of TiO₂ surfaces exposed to a low density water vapor seem to indicate that water cannot dissociate on the perfect surface except at defect sites (i.e., O vacancies).^{36–38} The first DFT calculations came to the opposite conclusion (see ref 35 for a recent review). An important step was made by Lindan and co-workers,²⁶ who showed the importance of inter-adsorbate hydrogen bonding at higher coverages, thus distinguishing mono- and multilayer coverage from sub-monolayer systems for which the disagreement between theory and experiment is most pronounced. However, a clear agreement on the structure of a H₂O monolayer adsorbed on TiO₂ rutile (110) is also still lacking. DFT calculations on this system vacillate between molecular (associative)^{25,29,30,33–35} or mixed associative and dissociative adsorption.^{26–28,31,32} These conclusions are based on a comparison of adsorption energies computed from total energies of systems placed in vacuum. The differences per H₂O molecule are however often small and dependent on a variety of conditions (see section 3.2). In contrast, in the present approach, the free energy for water dissociation at the TiO₂/H₂O interface is computed by combining the acidities of surface groups taking into account the solvation of surface (hydr)oxide groups.

2. Theory and Methods

2.1. Surface Protonation Model and Point of Zero Charge. On rutile TiO₂(110) there are two types of surface sites capable of binding additional protons under normal pH conditions (see Figure 1): the hydroxylated 5-fold coordinated Ti (“titanol”) groups



and bridging oxygens



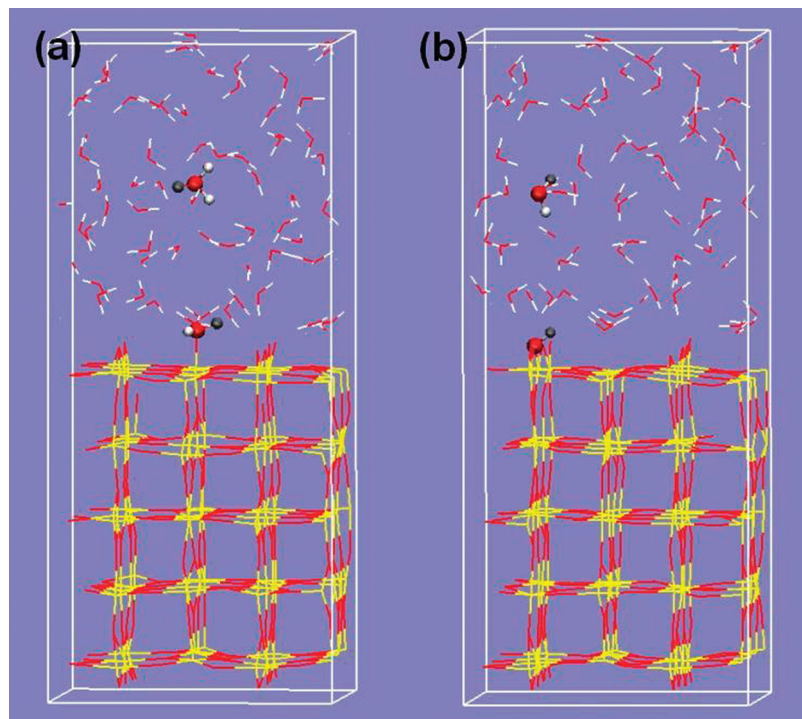


Figure 1. Molecular dynamics model system and schematic representation of the method for the computation of acidity constants of surface (hydr)oxide groups at the rutile $\text{TiO}_2(110)/\text{H}_2\text{O}$ interface. The pictures show the full MD supercell in the (a) $\text{TiOH}_2^-/\text{TiOH}^-$ and (b) $\text{Ti}_2\text{OH}^+/\text{Ti}_2\text{O}$ conformations. These systems have been set up as 5 O–Ti–O trilayers and 71 water molecules. 3D periodic boundary conditions are applied leading to an alternation of TiO_2 slabs and water layers. Ti, O, and H atoms are distinguished in yellow, red, and white, respectively. The molecules involving protonation/deprotonation reactions are highlighted by a ball and stick representation. The gray balls denote the inserted/annihilated protons. Switching one proton on and the other off in a and b simulates eqs 9 and 11, respectively.

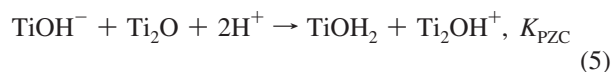
where K_{H1} and K_{H2} are the corresponding protonation equilibrium constants. Following the notation of ref 2, the subscripts 1 and 2 to the equilibrium constants refer to the metal coordination of the active oxygen.

Charges in schemes 1 and 2 have been assigned according to the formal charge of an adsorbed OH_n group ($n = 0, 1, 2$) assuming that the OH_2 species (a water molecule) is neutral. The TiO_2 solid, represented in the DFTMD model by a finite slab, is therefore viewed as a large molecular unit (cluster) which is neutral when associatively hydrated by water molecules. This simple ionic picture, based on integer proton charge only, ignores contributions from the coordinated Ti ions to the surface charge. This effect is taken into account in the MUSIC model by adding in the fractional Pauling bond valence (+2/3) of the TiO bond. Reactions 1 and 2 are then written as^{3,24}



While this may be a more realistic model of surface charge, such a model is not needed in a DFTMD calculation of the corresponding protonation free energy. The simple “pseudo” molecular representation of eqs 1 and 2 therefore seems more appropriate in this context. Note that the charges in scheme 1 also differ from the charges in the single-site two- $\text{p}K_a$ model of ref 4 in which the TiOH group is formally neutral with a positive conjugate acid TiOH_2^+ . The argument for

relating the point of zero net proton charge (PZC) to the acidities of the surface groups used in ref 4 however still applies in our two-site model. The PZC is derived by combining two successive protonation reactions to a reaction reversing the sign of the surface charge. In our case, these are reactions 1 and 2, which leads to



At the PZC equilibrium, surface concentrations of TiOH^- and Ti_2OH^+ are equal. Moreover, the ratio of 5-fold coordinated Ti^{4+} ions to bridging oxygens on a 110 face is 1:1. Substituting in the chemical equilibrium equation of reaction 5, we find $[\text{H}^+]_{\text{PZC}} = (K_{\text{PZC}})^{-1/2} = (K_{\text{H1}}K_{\text{H2}})^{-1/2}$ or in terms of pH and $\text{p}K_a$ units using $\text{p}K_{\text{an}} = \log K_{\text{Hn}}$

$$\text{PZC} = \frac{1}{2}(\text{p}K_{\text{a1}} + \text{p}K_{\text{a2}}) \quad (6)$$

Reaction 2 can also be coupled with the reverse of reaction 1, giving



This process can be interpreted as the dissociation of an adsorbed water molecule (leaving the total surface charge the same). Since $K_d = K_{\text{H2}}/K_{\text{H1}}$, the corresponding free energy change $\Delta A_{\text{diss}} = -k_B T \ln K_d$ is the difference in acidities of the two conjugate acids:

$$\Delta A_{\text{diss}} = 2.30k_{\text{B}}T(\text{p}K_{\text{a1}} - \text{p}K_{\text{a2}}) \quad (8)$$

2.2. Calculation of Acidities. The proton affinities of the surface (hydr)oxide groups were computed using a combination of DFTMD simulation and free energy perturbation (FEP) methods.¹⁸ The role of the MD is to sample a mapping potential consisting of a linear mixing of the Born–Oppenheimer energy surfaces of reactant and product states. Free energy changes are obtained by integrating ensemble averages of vertical energy gaps along the alchemical transformation path from reactant to product. This method effectively inserts acid protons or deletes them. A similar FEP approach has been used by our group for the DFTMD estimation of redox free energies of inorganic^{39–42} and organic^{19,43,44} ions or molecules in solution. The method for the computation of acidities is more involved as it is more difficult to add or remove protons from a condensed phase system than adding or removing electrons. Rather than eliminating the proton entirely from the system, its charge is switched off with a harmonic restraining potential holding it in place. This method can be regarded as a DFTMD implementation of the chaperone assisted methods for reversible insertion of protons which have been applied, for example, for computation of tautomerization free energies of organic molecules.⁴⁵ For a detailed description, we refer to our previous publications.^{18,19} A brief summary is given in the Supporting Information.

The insertion of a single proton can be regarded as a half reaction.¹⁹ The DFTMD model systems to which the protons are added are the usual periodically repeated supercells of molecular dynamics simulation. The reference (zero) of the electrostatic potential in such a setup is artificial and has no physical meaning.^{19,46,47} Addition or removal of a single ion changes the net charge of the cell and the corresponding free energy can therefore not be identified with the absolute solvation free energy (even in the limit of large cell size). The discrepancies for a typical DFTMD model system are significant (3 eV or more).^{19,42} This bias cancels when deprotonation of a species or group is carried out in conjunction with protonation of another species in the same cell, thus avoiding a change of net charge. However, the drawback of such a full reaction scheme compared to a half reaction scheme is that model systems must be considerably larger in order to minimize the interaction between charged acid or base species (recall that in order to reproduce standard conditions these interactions must be eliminated). Furthermore, because of the powerful screening properties of water, the effective interactions of ions with their periodic images and compensating background charge in MD models of homogeneous solution are surprisingly small⁴⁸ (see also ref 19). This is the reason why we preferred a half reaction scheme based on the insertion of single protons in our previous calculations of the acidity of aqueous species in homogeneous solution.^{18,19} Provided the model systems have an excess of solvent, the sum of the free energies of a protonation and deprotonation half reaction is equally unaffected by a shift in the reference of the electrostatic potential because the reference of the electrostatic potential in a low concentration solution is determined by the solvent and is therefore the same in the two half reactions.

A solid liquid interface is a highly inhomogeneous system. Periodic boundary effects are likely to be different from homogeneous solutions, which is why we decided to use the more direct full reaction scheme in our first study of the TiO₂–water interface. This scheme is illustrated in Figure 1a. Deprotonation of TiOH₂ to TiOH[−] is coupled to a simultaneous protonation of H₂O in the liquid water part of the same inhomogeneous model system. The reverse of this reaction amounts to a proton transfer from a hydronium in solution to a TiOH[−] surface group:



and is equivalent to the surface protonation reaction eq 1. The free energy change of reaction 9, which will be indicated by ΔA_1 , is obtained from a coupling parameter integral of the corresponding vertical energy gap. Referring ΔA_1 to the $\text{p}K_{\text{a}}$ of H₃O⁺ (= −1.74) gives an estimate of the $\text{p}K_{\text{a}}$ of TiOH₂:

$$\text{p}K_{\text{a1}} = \text{p}K_{\text{a,H}_3\text{O}^+} - \frac{1}{2.30k_{\text{B}}T}\Delta A_1 \quad (10)$$

Similarly, the protonation of a Ti₂O group (reaction eq 2) must also be balanced by a reference deprotonation (Figure 1b):



The free energy change of reaction 11 will be indicated by ΔA_2 . The argument for deprotonating a H₂O molecule rather than a H₃O⁺ is that the computation of the PZC and water dissociation constant requires that the reactant state be the same as the product state in reaction 9 (note that this also ensures that the molecular dynamics keep a zero net charge at all times). The $\text{p}K_{\text{a}}$ of Ti₂OH⁺ is found from the $\text{p}K_{\text{b}}$ of Ti₂O. Adding the $\text{p}K_{\text{a}}$ of H₂O (= 15.74) to (minus) the free energy change ΔA_2 of reaction 11 yields the expression

$$\text{p}K_{\text{a2}} = \text{p}K_{\text{a,H}_2\text{O}} - \frac{1}{2.30k_{\text{B}}T}\Delta A_2 \quad (12)$$

The values used for $\text{p}K_{\text{a,H}_3\text{O}^+}$ and $\text{p}K_{\text{a,H}_2\text{O}}$ need some clarification. $\text{p}K_{\text{a,H}_3\text{O}^+}$ is a constant and by definition equal to $-\log[\rho_{\text{H}_2\text{O}}/c^\circ] = -1.74$ where $\rho_{\text{H}_2\text{O}} = 55.5 \text{ mol dm}^{-3}$ is the ambient density of liquid water and $c^\circ = 1 \text{ mol dm}^{-3}$ is the standard concentration of solution chemistry. The reason why the reaction free energy ΔA_1 must be corrected by this term when converted to an acidity on the $\text{p}K_{\text{a}}$ scale is that our method is based on the Brønsted picture of acidity in which acid dissociation is treated as a proton transfer to the solvent.¹⁹ Accordingly, in the present application, reaction 1 is replaced by reaction 9. Similarly, the reference term in eq 12 is not $\text{p}K_{\text{w}}$, the dissociation constant of water, but $\text{p}K_{\text{a,H}_2\text{O}} = \text{p}K_{\text{w}} - \text{p}K_{\text{a,H}_3\text{O}^+} = 14.0 + 1.74$. To be strictly consistent, a DFTMD computed value for $\text{p}K_{\text{w}}$ should be used. This calculation is under way in our group. In default of this result, the experimental value is used instead.

A further comment concerns the bias introduced by the restraining potentials. Let us first reiterate that these restraining potentials play an absolutely crucial role. There is first

of all the rather practical consideration that the dummy proton is invisible to its environment and, when not restrained, can wander off anywhere in the system. The restraining potentials keep the dummy close to where it was, avoiding the highly unstable configurations that might otherwise arise when the charge is switched back on.¹⁸ However, there is also a more fundamental side to the application of restraints. We are interested in the acidity of a specific functional group. The proton is therefore removed from a group of this kind and must also be reattached to this group. This species specific insertion is directed by the restraining potentials. These potentials will however inevitably introduce a bias in the free energy for which we must correct. In ref 19, this question is approached by resolving the transfer of a proton from an acid AH to a H₂O molecule into a Born–Haber cycle involving the acid proton. The acid proton is transferred to the gas phase and then reinserted in solution attached to a water molecule. This fictitious process makes it easier to keep track of the various entropy and zero point motion contributions. The result is a thermochemical correction which is specified for the present system in the Supporting Information. This thermochemical correction for a half reaction can be substantial (amounting for a H₂O molecule to about 0.5 eV).¹⁹ For full reactions (proton transfers), these corrections cancel to a large extent but not completely (see below).

2.3. Computational Implementation. The rutile TiO₂–(110) surface was modeled by periodic slabs of five O–Ti–O trilayers with lateral dimensions of a 4 × 2 surface cell. The slabs are separated by a space of 15 Å leading to an orthorhombic supercell cell of 11.9 × 13.2 × 30.8 Å³. Full 3D periodic boundary conditions are applied. To model the TiO₂/H₂O interface, the space between the TiO₂ slabs is fully filled with 71 water molecules so that there are two symmetric interfacial planes in each unit cell. The number of water molecules has been chosen to adjust the effective density of the water layer to the ambient density of water. A further consideration was to make the volume of water in a supercell approximately cubic in order to minimize confinement effects.

The gradient-corrected Perdew–Burke–Ernzerhof (GGA-PBE) functional⁴⁹ was used for all calculations. The DFTMD simulations use the Born–Oppenheimer method and have been carried out using the freely available program package CP2K/Quickstep.^{50,51} The density functional implementation in Quickstep is based on a hybrid Gaussian plane wave (GPW) scheme. Orbitals are described by an atom-centered Gaussian-type basis set, while an auxiliary plane wave basis is used to re-expand the electron density.⁵² The wave function optimization is performed using an orbital transformation minimizer, which avoids the traditional matrix diagonalization method and gives optimal convergence control.⁵³ Analytic Goedecker–Teter–Hutter (GTH) pseudopotentials^{54,55} have been employed to represent the core electrons. The basis sets for the valence electrons (2s²2p⁴ for O and 3s²3p⁶3d²4s² for Ti) consist of short-ranged (less diffuse) double- ζ basis functions with one set of polarization functions (DZVP).⁵⁶ The plane wave basis for the electron density is cut off at 280 Ry. All our simulations only use the Γ point of the supercell for expansion of the orbitals. The convergence

criterion for wave function optimization is set by a maximum electronic gradient of 3×10^{-7} and an energy difference tolerance between self-consistent field (SCF) cycles of 10^{-13} . We should admit that because of the very large system required to model a TiO₂/H₂O interface the present study uses smaller basis sets than our previous work (TZV2P).^{18,19} This may be justified by two facts: (i) the currently used basis sets reproduce other DFT calculations of water adsorption energies with various configurations and coverages on TiO₂(110) with good accuracy^{26,29} (see section 3.2), and (ii) dynamical effects in water are not very sensitive to the basis sets used.⁵⁷

The time step for the MD simulation was 0.5 fs. NVT conditions were imposed by a Nose-Hoover thermostat with a target temperature of 330 K. All settings have been tested in previous work of our and other groups and have been proven to be sufficient to give a reasonable representation of structural and dynamical properties of liquid water at room temperature.⁵⁷ It should be noted that the elevated temperature of 330 K is chosen to avoid the glassy behavior of PBE liquid water on the 20 ps time scale observed for trajectories at lower temperatures.⁵⁷ In MD runs, 1–2 ps of equilibration period is followed by ~ 5 ps of production period. This duration is adequate to obtain sufficiently accurate estimates of the vertical energy gap ΔE of reactions 9 and 11. The corresponding free energies ΔA_1 and ΔA_2 were determined using a three point quadrature of the thermodynamic integral (Simpson's rule). Further details on method and error estimation can be found in the Supporting Information.

In order to investigate the dependence of water adsorption energies on the number of TiO₂ layers, some static calculations were also performed. The same settings stated above were adopted, and ion configurations were optimized by using the BFGS minimizer. Water adsorption was applied to both surfaces of the slab symmetrically, resulting in the cancellation of surface dipoles.

3. Results and Discussion

3.1. Acidity of Surface Groups. The method of simultaneous deletion and insertion of protons was applied to the DFTMD model system depicted in Figure 1. We find an intrinsic pK_a of 7.8 for TiOH₂ and -1.9 for Ti₂OH⁺. The statistical uncertainty in these estimates is approximately 2 pK_a units (see the Supporting Information). The pK_a 's as entered in Table 1 have therefore been rounded off to $pK_a = 8$ for TiOH₂ and $pK_a = -2$ for Ti₂OH⁺. Substitution in eq 6 yields a PZC of 3. If the thermochemical corrections for restraining potentials are applied (see the Supporting Information), these numbers increase by 1 pK_a unit to 9, -1 , and 4, respectively.

Experimental data on the PZC of TiO₂ available from the literature are mostly based on measurements performed with rutile powder or polycrystalline samples. The results vary between 3 and 7 depending on sample preparation (synthesis) and electrolytes used. The consensus according to the compilation of ref 20 is a value of about 6. More recently, Bullard and Cima investigated the surface orientation

Table 1. Results for the Free Energies ΔA of Reactions 9 and 11 (referred to in the text as ΔA_1 respectively ΔA_2), the pK_a of TiOH₂ and Ti₂OH⁺ Computed According to eqs 10 and 12, the Corresponding PZC (eq 6), ΔpK_a , and ΔA_{diss} [the dissociation free energy of adsorbed water] (numbers in parentheses are corrected for restraining potentials, see Supporting Information) for This Work (DFTMD), Using the MUSIC Model Taken from refs 3 and 13, and the SBE Model Taken from ref 4^a

	DFTMD (this work)		MUSIC (refs 3, 13)		SBE (ref 4)	
	TiOH ₂	Ti ₂ OH ⁺	TiOH ₂	Ti ₂ OH ⁺	TiOH ₂	Ti ₂ OH ⁺
ΔA (eV)	−0.6	1.0				
pK_a	8 (9)	−2 (−1)	7.5; 5.9	4.4; 4.9	8.2–9.3	2–3.7
PZC		3 (4)	6; 5.4		5.9–6.4	
ΔpK_a		10 (10)	3.1; 1		4.5–6.7	
ΔA_{diss} (eV)		0.6 (0.6)	0.18; 0.06		0.27–0.40	

^a Only the PZC can be directly compared to the experiment. The relevant data here are the recent experimental estimates for the 110 surface of 5.5–4.8²³ and 4.8 ± 0.3^{21} (see text).

dependence of the PZC of rutile TiO₂ using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) techniques.²³ For the rutile TiO₂(110) surface, they give a PZC of 5.5–4.8. This is consistent with the 4.8 ± 0.3 obtained by another study using second-harmonic generation spectroscopy (SHG).²¹ We conclude therefore that our DFTMD result of 4 is in fair agreement with experiment, taking the computational error margin of 2 pK_a units (100 meV) into consideration.

As discussed in the Introduction, it is not possible to compare individual pK_a values directly to experiment. However a comparison with the predictions of models is of interest in its own right because of the uncertainties involved in setting up these models. The revised 1996 version of the MUSIC model³ introduces two important refinements. The first is the use of actual bond valence computed from the length of the metal oxygen bonds. A second improvement over the older 1989 version² is the modeling of solvent effects which are taken into account by extending the expression for the actual bond valence with a term depending on hydrogen bonding. The relevant structural variables in this term are the number of hydrogen bonds donated (m) and accepted (n) by the base forms of the surface (hydr)oxide groups. m is fixed by the chemical species; $m = 0$ for Ti₂O and $m = 1$ for TiOH[−]. To determine n the MUSIC model makes the assumption that $m + n = 2$, arguing that the total H coordination of a surface O ion is decreased by two compared to the coordination in liquid water.³ One bond is replaced by the bond to the metal. Steric hindering eliminates a second bond. This means that $n = 2$ for Ti₂O and $n = 1$ for TiOH[−]. With this hypothetical H-bond coordination and the actual bond valence determined by the experimental Ti–O distances of the bulk solid, the revised MUSIC model gives a pK_a of 7.5 for TiOH₂ and 4.4 for Ti₂OH⁺ (these numbers are also listed in Table 1).³ Compared to the DFTMD calculation, we see that the estimates for the pK_a of TiOH₂ are in good agreement. The fraction of dissociated terminal water molecules is predicted to be small under pH neutral conditions (pH = 7). A Ti₂O group is however significantly more basic (5 pK_a units) in the MUSIC model compared to the DFTMD calculation with a corresponding

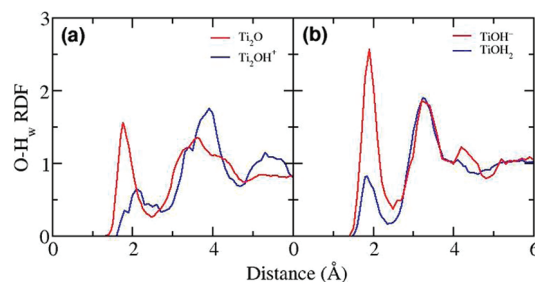


Figure 2. Radial distribution functions (RDF) between oxygen atoms of surface groups and hydrogen atoms in water. (a) The Ti₂OH⁺/Ti₂O pair and (b) the TiOH₂/TiOH[−] pair. The deprotonated and protonated states are distinguished by red and blue. Coordination numbers obtained by integrating the first peaks are 1.1 for Ti₂O, 1.0 for Ti₂OH⁺, 1.9 for TiOH[−], and 0.6 for TiOH₂, respectively.

shift of the PZC from 4 in the DFTMD calculation to 6 in the MUSIC model.

The critical structural parameters in the MUSIC model, the Ti–O bond lengths and number of hydrogen bonds, are directly accessible observables in molecular dynamics simulation. This suggests that the discrepancies between the pK_a values predicted by the MUSIC model and computed from the DFTMD simulation can be analyzed in more detail by comparing MD averages of Ti–O bond lengths and the number of hydrogen bonds to the values assumed in the MUSIC model. We can also substitute the MD estimates in the MUSIC model to see how the predicted values change. This was also the strategy followed by Machesky and co-workers in ref 13. Here, we will repeat some of this analysis using the results of our DFTMD simulation.

Coordination numbers are normally defined by the integral of the first peak of a radial distribution function (RDF). For an assessment of the variable n of the MUSIC model, the relevant RDFs are between the oxygen atoms in a Ti₂O and TiOH[−] surface group and hydrogen atoms in water. These RDFs are shown in Figure 2. The corresponding coordination numbers are $n = 1.1$ for Ti₂O and $n = 1.9$ for TiOH[−]. MD results and values used in the revised MUSIC model are compared in Table 2. Consistent with the force field model of ref 13, DFTMD finds a higher coordination number for a terminal hydroxyl than assumed in the MUSIC model and a lower coordination for a bridging oxygen. The difference is 0.9 for both surface groups, corresponding to a change in pK_a of ~ 3.6 units when substituted into the MUSIC model. More serious is that these changes go in the opposite direction, increasing the pK_a of Ti₂OH⁺ from 4.4 to 7.9 and decreasing the pK_a of TiOH₂ from 7.5 to 4. The interchange in the order of the acidity, while having a minor effect on the PZC (eq 6), leads to a negative ΔpK_a of -4 , implying that molecular absorption on TiO₂ is unstable (see eq 8).

The Ti–O bond lengths of surface groups are found to be on average somewhat shorter than the bulk values used in the MUSIC model. The precise values are 1.89 Å versus 1.95 Å for Ti₂O and 1.91 Å versus 1.98 Å for TiOH₂. The actual bond valence s is computed in the MUSIC model as $s = \exp(R - R_0)/b_0$, where R is the metal oxygen bond length, R_0 is a parameter specific to the solid oxide and $b = 0.37$ Å. The value for R_0 used in ref 3 for rutile is $R = 1.808$

Table 2. Estimation of Surface Acidity of TiO₂ Rutile (110) Using MUSIC and SBE Models from Structural Parameters Determined by the Present DFTMD Simulations^a

	TiOH ₂ /TiOH ⁻			Ti ₂ OH ⁺ /Ti ₂ O		
	<i>m</i>	<i>n</i>	p <i>K</i> _{a1}	<i>m</i>	<i>n</i>	p <i>K</i> _{a2}
this work	1	1.9	4(2)	0	1.1	8(6)
MUSIC model ³	1	1	7.5	0	2	4.4

	<i>r</i> _{M-O}	<i>s/r</i> _{M-OH}	p <i>K</i> _{a1}	p <i>K</i> _{a2}	PZC	Δp <i>K</i> _a
this work	1.91	0.2283	1.8	8.3	5.1	6.4
SBE model ⁴	1.96	0.2248	2.0	8.4	5.2	6.4

^a *m* and *n* as defined in the revised MUSIC model³ are the number of donated and accepted hydrogen bonds by the conjugate base of surface (hydr)oxide groups. p*K*_{a1} and p*K*_{a2} are the recomputed acidities according to ref 3. The numbers in parentheses are the adjustments after the change to DFTMD bond length is taken into account (see text). For convenience, the original MUSIC predictions are carried over from Table 1. The structural input as determined by DFTMD for the SBE model⁴ is given in the lower half of the table. *r*_{M-O} is the bond length in Å between the metal ion and O at the surface. *r*_{M-O} was determined in our simulation as the average Ti-O distance of a TiOH⁻ group. *s* is the Pauling bond valence of the metal ion (2/3 for Ti⁴⁺ in TiO₂). The SBE model sets *r*_{M-OH} = *r*_{M-O} + 1.01. Parameterization of the SBE model depends on the choice of the double layer model. Here, we use the p*K*_a consistent with the triple layer model.⁴

Å. With these parameters, the reduction in bond length increases the *s* of a TiO bond by about 0.1 for both groups, corresponding to a decrease in p*K*_a of 2. Applying this adjustment to the acidities in Table 2, a terminal water becomes even more acidic (p*K*_{a1} = 2), widening the gap with a DFTMD value of 9 (Table 1). The adjusted p*K*_{a2} shows a similar discrepancy with the DFTMD estimate (see Table 2).

The conclusion must be that substitution of the observed DFTMD parameters leads to unrealistic intrinsic p*K*_a values which are not matching our estimates obtained from free energy calculation based on the same DFTMD simulation. While some major inaccuracy in the DFTMD approach cannot be completely excluded (such as finite size effects, see section also section 3.2), the observation that the use of the DFTMD hydrogen bond coordination numbers can lead to a qualitative change in the picture of the surface acidity of TiO₂ seems to support the criticism by Bickmore et al.^{7,8} on the way solvation is treated in the MUSIC model (see also ref 6). In particular, these authors have questioned the direct coupling of the hydrogen bonding to the bond valence determining the undersaturation of basic oxygens as is characteristic of the MUSIC model.

Finally, we comment on the comparison to the SBE model also included in Tables 1 and 2. This comparison is of interest because the SBE approach to surface structure is more elementary, adopting the single site-two p*K*_a scheme.⁴ Acidities correspond to the free energies of the protonation states of a generic site, namely, TiOH and TiOH₂⁺ (see also section 2.1). p*K*_a in the SBE model is calculated from correlations with the electrostatic energy variable *s/r*_{M-OH}, where *s* is the formal Pauling bond valence charge of the metal ion and *r*_{M-OH} is the distance between metal ion and H atom in the OH group. The ionizable group resides at the

interface between two dielectric continua, one representing the solvent and the other the solid. The model is directly fitted to experimental surface charge curves assuming certain double layer models.⁴ Even though the identities of surface hydroxyl groups are ignored, p*K*_a's from the SBE model are fairly close to the numbers from our calculation and the MUSIC model. All three p*K*_a's of the basic component are very similar, while the SBE p*K*_a of the acidic component lies between the numbers from our DFTMD simulations and the MUSIC model (see Table 2).

Similar to the MUSIC model, we can also examine the response of the SBE model to exchange of the structural model parameters by the corresponding DFTMD averages. There is only one such parameter, namely, *r*_{M-OH}. In the model, this distance is evaluated from the equation *r*_{M-OH} = *r*_{M-O} + 1.01 where *r*_{M-O} is the length of the bond between the metal ion and O atom in the OH group. Similar to the MUSIC model, the SBE model takes the *r*_{M-O} value of the crystal. As mentioned, the time averaged value of *r*_{M-O} from our MD simulations is about 0.05 Å shorter (see also Table 2). Substituting this into the SBE model while keeping all other parameters constant yields almost the same p*K*_a's as the original SBE model. The success of the SBE model is remarkable considering its lack of structural and chemical detail. The microscopically inhomogeneous surface structure plays no role, and also the linear free energy relation is solely based on electrostatic interactions, ignoring other components of chemical bonding and replacing complicated relaxation effects at interfaces by a continuum medium model. Evidently, the combination of Pauling bond valence charge, electrostatics, and a double layer model in the SBE approach is capable of capturing all this complication in a simple linear relation, at least for the titania water interface studied here.

3.2. Dissociation Constant of Adsorbed Water. As discussed in section 2.1, the free energy change for dissociation of adsorbed water is related to the acidities of the two surface groups by eq 8. Substituting our calculated p*K*_a values of Table 1 into eq 8, we find Δ*A*_{diss} = 0.6 eV. We estimate the statistical error in this result to be less than 0.2 eV (see the Supporting Information). Unlike the PZC, the thermochemical corrections applied to the two acidities end up canceling each other. The DFTMD result for Δ*A*_{diss} is compared in Table 1 to the corresponding free energies obtained from the MUSIC and SBE model acidities. All three dissociation free energies are positive, with the DFTMD estimate the largest. This is mainly because Ti₂OH⁺ is more acidic according to DFTMD than predicted by the MUSIC and SBE models. A free energy cost for water dissociation of 0.6 eV strongly suggests that the reaction is unlikely to occur on perfect TiO₂(110). This appears to be in line with the recent work of Yamamoto et al.,³⁸ in which water adsorption was monitored by in situ XPS at ambient pressures and no noticeable water dissociation was observed except at O vacancies.

In assessing the DFTMD result for the dissociative adsorption of water, it is important to realize that Δ*A*_{diss} is known to be dependent on the number of TiO₂ layers in the model system. As has been verified repeatedly in the course of the numerous calculations under vacuum conditions,

Table 3. Variation of the Adsorption Energy (eV per molecule) of Water on Rutile TiO₂(110) in a Vacuum with the Number of TiO₂ Layers^a

no. of TiO ₂ layers	0.5 ML		1 ML		
	assoc.	diss.	assoc.	diss.	mix.
3	0.87	1.10	0.98	0.85	1.00
5	0.76	0.70	0.87	0.66	0.83
4 (from ref 35) ^b	0.86	0.64	0.82	0.63	0.77

^a The water molecules complete the six fold coordination of the five fold coordinated surface Ti ions (terminal water molecules). Adsorption is symmetric on both surfaces of the slab under full geometry relaxation. (i) assoc. denotes associative adsorption, (ii) diss. means fully dissociative adsorption, and (iii) mix. is a mixed state with half water associatively adsorbed and half water dissociatively adsorbed (see refs 26 and 27 for a detailed description of water adsorption configurations). For comparison, the last row gives the adsorption energies of the corresponding 1 × 1 or 2 × 1 structures (whichever is the more stable) as obtained in ref 35 using the same density functional (PBE) applied to a somewhat different adsorption geometry (see further discussion in section 3.2). ^b H₂O adsorption on top layer only. To improve convergence with the number of layers, the bottom layer is terminated by fractional charges and has a constrained geometry.

adsorption energies on TiO₂ show a characteristic oscillation with the number of trilayers.^{27,30,33,35} Also, the application of geometric constraints has a significant effect, which, when used appropriately, can accelerate the convergence.^{33,35} Our results were calculated using five unconstrained trilayers of TiO₂ with double sided adsorption similar to the scheme employed in the gas-phase studies of Zhang and Lindan in refs 27 and 31. According to these authors, the accuracy of the adsorption energies computed with this approach is adequate for the estimation of relative stability of molecular and dissociative adsorption. In order to obtain a rough estimate of the bias introduced in our calculation by the limited thickness of the TiO₂ slab, we have carried out static test calculations of the adsorption energy of 0.5 and 1.0 monolayer (ML) of H₂O. The results are listed in Table 3 and compared to the corresponding PBE estimates of Kowalski and co-workers.³⁵ Their 4 trilayer adsorption energies are very close to the energies for a bulk surface as a result of the use of special termination and constraint methods. With the exception of one system (the 0.5 ML molecular adsorption), our five TiO₂ trilayer slab energies are higher by approximately 50 meV, consistent with the analysis in ref 35. We are therefore inclined to consider this 50 meV (corresponding to 1 pK_a unit) as a measure of our error due to the symmetric relaxed five layer geometry applied here with a better accuracy for relative absorption energies.

The results of Table 3 also confirm that 3 layers are not enough. This is best illustrated by the 0.5 ML system. This surface density is low enough to exclude hydrogen bonding between adsorbed water molecules complicating the adsorption energies. Dissociated water is considerably more stable than molecular water on three layers of TiO₂. For five layers of TiO₂, the stability is reversed. For the 1 ML surface coverage, 100% dissociation is not the energetically most favorable adsorption mode. Instead, a mixed state with associative and dissociative adsorption is preferred as a result of stabilization by intermolecular hydrogen bonding.²⁶ Note,

however, that the data in Table 3 indicate that the tendency of a monolayer of water to dissociate on three layers of TiO₂ is still rather high.

These observations on the critical dependence of the stability of adsorbed water on the number of TiO₂ trilayers are in broad agreement with the extensive and detailed calculations on vacuum systems available from the literature.^{27,30,33,35} The question is whether they can be carried over to models of TiO₂/H₂O interfaces as studied here. A quantitative investigation of the variation of surface pK_a with the slab thickness is forbiddingly expensive. However, a single MD run of a system of three layers of TiO₂ confirmed that this system retains its reactivity in bulk solution. We found that during the 10 ps trajectory up to about 20% of H₂O adsorbed on 5-fold Ti sites lost a proton to a nearby bridging oxygen. Water adsorbed on five layers of TiO₂ appears to be stable on this time scale. In this context, it is worth recalling that because of the finite temperature in a MD simulation (330 K, see section 2.3), a finite fraction of dissociated surface water molecules on three layers of TiO₂ does not necessarily mean that water dissociation is energetically more stable. This is true only if more than half of the surface waters dissociate in equilibrium.

A further issue requiring some comment is the comparison between the dissociation free energy determined from the estimate of surface pK_a in section 3.1 and the relative adsorption energies in Table 3. The $\Delta E_{\text{ads}} = 0.1\text{--}0.2$ eV difference in adsorption energy per molecule between molecular and dissociated monolayers is significantly smaller than the $\Delta A_{\text{diss}} = 0.6$ eV of Table 1. These two measures of the stability of water adsorbed on TiO₂ have however a rather different status. First of all, ΔE_{ads} is an enthalpy difference, while ΔA_{diss} is a free energy difference including entropy contributions. Furthermore, solvent effects in ΔE_{ads} can only arise due to hydrogen bonding in the first ad-layer. ΔA_{diss} also includes interactions with the second layer in the bulk solvent. However, the ≈ 0.5 eV difference between ΔA_{diss} and ΔE_{ads} is probably too large to be explained by these effects. More important is probably the difference in thermodynamic reference state. All of the water molecules in the calculation of ΔA_{diss} are molecular except those involved in the proton transfer. In contrast, in the calculation of ΔE_{ads} , half or all of the H₂O molecules are dissociated. ΔA_{diss} is therefore calculated under conditions approaching infinite dilution, while the solvent in the calculation of ΔE_{ads} is effectively a two-dimensional ionic solution at high ionic strength.

4. Conclusion

In summary, we have applied a recently developed DFTMD method for reversible proton insertion for a calculation of acidity constants of (hydr)oxide groups on the rutile Ti₂O(110) surface, i.e., bridge OH (Ti₂OH⁺) and terminal H₂O adsorbed on 5-fold Ti sites (TiOH₂). Surface pK_a is estimated from the free energy of concerted protonation and deprotonation, equivalent to proton transfer between the surface and a H₃O⁺ or H₂O in solution. The computed pK_a's of the two groups are −1 and 9, respectively, leading to a PZC of 4, which is within 2 pK_a units of the experimental

value for TiO₂ rutile (110). Using these two acidity constants, the free energy change of water dissociation at the TiO₂/H₂O interface has been determined as 0.6 eV. The positive free energy change indicates that water dissociation is not likely on a perfect Ti₂O(110) surface. While the discrepancy with the experiment for the PZC, the only observable directly accessible to experiment, is still (just) within the uncertainties in the calculation, an acidity of -1 for Ti₂OH⁺ as obtained by DFTMD is likely an overestimation. This issue of the proton affinity of bridge oxygens clearly needs further investigation. In this context, a comparison to the 110 surface of SnO₂ which has the same structure as the TiO₂ surface studied here could be instructive.³⁴ This calculation is currently under way.

Analysis of the interfacial structure shows that some assumptions in the MUSIC model, in particular the number of hydrogen bonds to a bridging oxygen, are not justified. Using the DFTMD coordination numbers instead gave no improvement and in fact led to the prediction of a negative dissociation free energy of adsorbed water in contrast to the unambiguously positive dissociation free energy obtained in the DFTMD free energy calculation. These conflicting results can be seen as support for recent criticism of the way the MUSIC model couples explicit hydrogen bonding to the undersaturation determining the proton affinity.^{7,8} This information may be useful for further development of models for intrinsic surface acidity constants.

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Supporting Information Available: A brief summary of our methodology for computation of free energies and some technical aspects are given, together with a description of thermochemical corrections. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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