Surface Protonation at the Rutile (110) Interface: Explicit Incorporation of Solvation Structure within the Refined MUSIC Model Framework

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The detailed solvation structure at the (110) surface of rutile (α-TiO2) in contact with bulk liquid water has been obtained primarily from experimentally verified classical molecular dynamics (CMD) simulations of the ab initio-optimized surface in contact with SPC/E water. The results are used to explicitly quantify H-bonding interactions, which are then used within the refined MUSIC model framework to predict surface oxygen protonation constants. Quantum mechanical molecular dynamics (QMD) simulations in the presence of freely dissociable water molecules produced H-bond distributions around deprotonated surface oxygens very similar to those obtained by CMD with nondissociable SPC/E water, thereby confirming that the less computationally intensive CMD simulations provide accurate H-bond information. Utilizing this H-bond information within the refined MUSIC model, along with manually adjusted Ti–O surface bond lengths that are nonetheless within 0.05 Å of those obtained from static density functional theory (DFT) calculations and measured in X-ray reflectivity experiments (as well as bulk crystal values), give surface protonation constants that result in a calculated zero net proton charge pH value (pH0) at 25 °C that agrees quantitatively with the experimentally determined value (5.4 ± 0.2) for a specific rutile powder dominated by the (110) crystal face. Moreover, the predicted pH0 values agree to within 0.1 pH unit with those measured at all temperatures between 10 and 250 °C. A slightly smaller manual adjustment of the DFT-derived Ti–O surface bond lengths was sufficient to bring the predicted pH0 value of the rutile (110) surface at 25 °C into quantitative agreement with the experimental value (4.8 ± 0.3) obtained from a polished and annealed rutile (110) single crystal surface in contact with dilute sodium nitrate solutions using second harmonic generation (SHG) intensity measurements as a function of ionic strength. Additionally, the H-bond interactions between protolyzable surface oxygen groups and water were found to be stronger than those between bulk water molecules at all temperatures investigated in our CMD simulations (25, 150 and 250 °C). Comparison with the protonation scheme previously determined for the (110) surface of isostructural cassiterite (Sn–SnO2) reveals that the greater extent of H-bonding on the latter surface, and in particular between water and the terminal hydroxyl group (Sn–OH) results in the predicted protonation constant for that group being lower than for the bridged oxygen (Sn–O–Sn), while the reverse is true for the rutile (110) surface. These results demonstrate the importance of H-bond structure in dictating surface protonation behavior, and that explicit use of this solvation structure within the refined MUSIC model framework results in predicted surface protonation constants that are also consistent with a variety of other experimental and computational data.

1. Introduction

The under-coordinated cation and oxygen atoms at most oxide surfaces are reactive toward water.1 In broad terms this reactivity can be classified as dissociative if first-layer water dissociates, or associative if it does not (within the time frame and P, T conditions of the observation). One common result of this reactivity toward water is that surface relaxation and reconstruction effects are often less extensive on hydrated than corresponding vacuum-terminated oxide surfaces.2,3 Another is surface protonation whereby hydrated metal oxide surfaces adsorb or desorb protons and hence acquire charge in response to bulk solution pH.4 Formal consideration of surface proton reactions is fundamental to quantitative descriptions of important interfacial phenomena such as precipitation/dissolution and adsorption/
desorption. However, the most common surface protonation scheme used to rationalize these phenomena, specifically the 2-pK model, is generic in nature since protonation constants for arbitrarily defined surface species are derived from fitting bulk acid/base titration data, which provide no direct information about oxide–water interfacial structure. Consequently, the molecular-level details of interfacial structure obtainable from a variety of experimental and computational techniques such as infrared spectroscopy, neutron and X-ray scattering, ab initio calculations and molecular dynamics simulations is effectively ignored under the 2-pK surface protonation scheme. While hypothetical surface speciation may be sufficient for purely thermodynamic treatments of interfacial phenomena, such as ion adsorption and electrokinetics, realistic atomistic-scale surface speciation and solvent structure and dynamics will be needed to reach a fundamental understanding of interfacial reaction kinetics, heterogeneous catalysis, nanoparticle synthesis and stability, and many other dynamic interfacial processes.

At present, the most fully developed surface protonation model that explicitly considers interfacial structure is the refined MUSIC model of Hiemstra et al., which extended their original MUSIC model to include solution effects. The structural information utilized in this model consists of bulk crystal bond lengths and bulk water H-bond configurations empirically parametrized according to the bond valence method of Brown. This model can be used to estimate surface protonation constants and associated point of zero net proton charge (pH_{\text{npc}}) values for metal oxides on a crystal-face-specific basis. Additionally, it forms the basis for thermodynamically rigorous ion adsorption models that also incorporate molecular-level detail. In practice, this use usually requires slight adjustments to predicted surface protonation constants in order to match specific experimentally determined pH_{\text{npe}} values, which can vary considerably for the same metal oxide phase.

We have extended the refined MUSIC model to other temperatures, and used this extension to rationalize the pH_{\text{npc}} temperature dependence to 300 °C for several metal oxides. More recently, our group has been investigating the (110) surfaces of rutile and cassiterite using a variety of experimental and computational approaches all focused on providing an unambiguous picture of interfacial structure and dynamics. These studies have demonstrated that oxide surface and interfacial water structure are considerably different from their bulk phase counterparts. We have previously presented MUSIC model surface protonation schemes for rutile that have used DFT-derived Ti–O bond lengths, but retained bulk water H-bond configurations. However, to obtain the most unambiguous description of surface protonation it is also necessary to explicitly incorporate interfacial water structure in the form of H-bond configurations as we have recently demonstrated for cassiterite.

Here we show how interfacial H-bond configurations for the rutile (110) surface, as obtained primarily from ab-initio-optimized CMD simulations in SPC/E water, can be quantitatively incorporated into the refined MUSIC model framework. We then explicitly use this solvation structure, along with slight manual adjustments to interfacial Ti–O bond lengths that fall within the range of those determined via static DFT calculations and X-ray reflectivity measurements, to develop a surface protonation description consistent with experimentally determined pH_{\text{npe}} values (to within 0.1 pH unit) for a specific rutile powder dominated by the (110) surface to 250 °C. This protonation scheme will be used to develop thermodynamically rigorous ion adsorption models for this particular rutile powder which is used extensively in our studies. Finally, we compare the MUSIC model predicted surface protonation schemes for the isostructural rutile and cassiterite (110) surfaces. Significantly, this comparison demonstrates that explicit incorporation of solvation effects within the refined MUSIC model is necessary for the surface protonation schemes to be consistent with the associative and dissociative nature of water adsorption on the (110) rutile and cassiterite surfaces, respectively.

### 2. Methods and Materials

Many of the experimental and computational approaches used to generate results relevant to this study are detailed in previous publications. Potentiometric titration methods used to determine pH_{\text{npe}} values to 250 °C for powdered rutile samples are detailed in. Procedures used to conduct X-ray crystal truncation rod (CTR) measurements on rutile (110) single crystal surfaces in contact with bulk liquid water are given in. Many aspects of the corresponding quantum mechanical calculations and CMD simulations are provided elsewhere. New and/or modified aspects of these computational methods are presented below.

#### 2.1. Static Density Functional Theory (DFT) Calculations

All calculations were performed using the planewave pseudopotential implementation of DFT as written into the VASP code. Exchange and correlation were treated within the Perdew–Burke–Ernzerhof (PBE) functional. Ionic cores were described by the projector-augmented wave (PAW) method, which improves transferability and reduces the number of planewaves required in the expansion of the Kohn–Sham orbitals in order to improve computational

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efficiency. For Ti, a pseudopotential in which the semicore states (3s and 3p) were treated as valence electrons was used. Medium range values of the energy cutoff, 400 eV, have been applied in all calculations, and a Γ-centered Monkhorst–Pack grid of $4 \times 4 \times 6$ grid was used for the Brillouin zone sampling in bulk crystal calculations. An extended grid ($16 \times 16 \times 24$) was applied to generate the electronic density of states (DOS). For surface calculations, the number of k-points was decreased proportionally corresponding to the reduction of the Brillouin zone. The convergence criterion in the electronic cycle (i.e., computation of the electron probability density) was set to $10^{-6}$ for bulk and bare surface slabs, whereas for H$_2$O-containing systems, $10^{-4}$ was used.

To provide the precise estimation of atomic relaxations and surface adsorption energies, the lattice constants $a$ and $c$ of the tetragonal bulk unit cell of rutile were optimized. The calculated lattice parameters were 4.594 and 2.959 Å, respectively, which are very close to experimental values (4.594 and 2.959 Å).

Surfaces were modeled using slab geometries of periodically repeated supercells containing up to five Ti-layers (15 atomic planes). A layer is thus defined as consisting of three atomic planes, a Ti$_2$O$_5$ plane and the atomic O planes above and below it, that together form a stoichiometric entity. Five Ti$_2$O$_5$ layers are sufficient for reproducing the topmost atom relaxation and for correct estimation of H$_2$O adsorption energies. A vacuum width of 14 Å separated the slab from its periodic image and proved to be sufficient to avoid interactions between the adsorbed (up to third layer) H$_2$O molecules on repeated slabs. With 5 Ti-layer thick slabs, a 30 Å translation vector was sufficient to fully cover the energy of isolated H$_2$O molecules was calculated using the periodic cell of 10 Å.

Inversion symmetry (space group $P1$) was imposed on all systems containing water molecules to ensure the equivalence of both slab sides. The optimization of all atomic positions in slabs was performed except for the atoms in the middle layer. This approach allows a thin slab to better mimic the behavior of a bulk solid.

Energy minimization calculations were carried out until all forces on atoms were less than 0.01 eV/Å for bare surface slabs and 0.05 eV/Å for hydroxylated slabs.

To simulate two-layer water adsorption, 8 water molecules were placed on each side of the surface slabs. For preparing a reasonable initial structure, the previously derived force field was used in classical MD simulations of the SnO$_2$–H$_2$O system. The low-energy state was chosen for further static investigations, and that system was used to create the corresponding TiO$_2$–H$_2$O system by scaling the SnO$_2$ atomic coordinates to TiO$_2$ cell dimensions.

### 2.2. Quantum Molecular Dynamics (QMD) Simulations

The simulation cell consists of a periodic slab geometry composed of alternating rutile and vacuum slabs. The rutile slabs are oriented with their (110) direction and terminated at the bridging oxygen atoms. The dimensions of the cell in the directions parallel to the surface are 11.836 Å along the bridging oxygen rows and 12.994 Å across these rows. Perpendicular to the surface, the cell is 24 Å; this allows a vacuum slab of ~14.7 Å between bridging oxygen atoms. Each of the two surfaces of the slab contains eight bridging oxygen atoms and eight under-coordinated (5-fold coordinated) titanium atoms. On each surface we arrange 24 water molecules making a total of 48 water molecules in the simulation cell. This amount was chosen to mimic as close as possible the hydration situation determined experimentally for the rutile nanoparticles that have been measured in neutron scattering experiments by Mamontov et al. These particles predominantly expose the (110) surface and under normal conditions their hydration level corresponds to about 3.5 H$_2$O molecules per TiO$_2$ formula unit at the surface. One layer is adsorbed to the highly hydrophilic 5-fold coordinated titanium atoms and we will call this terminal water, as is commonplace in the literature.

The other two layers are prepared using CMD simulations to obtain a relaxed hydrogen bond network. The network of hydrogen bonds between water molecules is rigid enough to make the relaxation times longer than what is achievable by QMD. Thus, we prepared an initial configuration by a more efficient method and fed those already relaxed atomic positions into the QMD engine. Hence, we used CMD to generate our initial structures. First we prepared a bulk water sample by running a CMD simulation with the SPC/E water potential. A slab is formed from this bulk water system by removing the periodic boundary conditions in the $z$-direction. This slab is attached to the rutile surface, resulting in a combined structure that is used as the initial step for the CMD run. This CMD simulation takes the system to thermal equilibrium, which is determined by monitoring the total energy drift. The bulk water sample was prepared in a periodic cell with x and y dimensions being equal to the corresponding dimension of the rutile (110) slab. The $z$-direction of the periodic cell was determined to accommodate the total number of water molecules included in the system. This cell was run for 100 ps at a temperature of 2000 K in order to break any possible hydrogen bond network arbitrarily introduced by our initial positions. A temperature ramp going from 2000 to 300 K was run for another 100 ps and an additional 100 ps was used to thermalize the system at 300 K. A slab of the previously described bulk water system with its normal parallel to the $z$-direction was located on top of the rutile (110) surface already “decorated” with the layer of top water molecules. With this system we ran CMD at 300 K, with the force field of Bandura and Kubicki, for times longer than 1 ns until the total energy drift was negligible. For this run we used the General Utility Lattice Program (GULP).

We used the resulting relaxed and thermalized atomic positions as the input for the QMD simulations.

Forces for the QMD simulations were calculated within DFT with a plane wave basis set as implemented in the VASP Package. Core electrons were treated with a frozen Projector Augmented Wave scheme. The titanium 1s, 2s and 2p orbitals were treated as core electrons, hence leaving 12 valence electrons. Although our scheme used a low precision setting with the energy cutoff being 212.131 eV, we did some smaller runs with a higher cutoff and they yielded similar vibrational spectra. Moreover, as this is a rather big periodic cell, we used only one k-point at $\Gamma$ for sampling the Brillouin zone. The exchange and correlation potential was treated in the generalized gradient approximation as determined by Perdew, Burke, and Ernzerhof.

QMD simulations were performed in a NVT ensemble where the temperature was kept constant using a Nosé–Hoover thermostat as implemented in VASP. The time step was set to 0.5 fs in order to properly sample the high frequency vibrations of the hydrogen atoms. The equations of motion were integrated using the Verlet algorithm.

### 2.3. Classical Molecular Dynamics (CMD) Simulations

Simulations were performed at 25, 150 and 250 °C, and many of the details are given in previous papers, so only a brief summary is provided here. Water is modeled using the rigid, nonassociative and nonpolarizable SPC/E model and the dissolved ions as charged Lennard–Jones spheres. The surface model of rutile is based on DFT-derived potentials and structure. Simulations were performed in slab geometry in aqueous solutions sandwiched between two parallel TiO$_2$ (110) walls, periodically replicated in the lateral directions. The slab was filled with pure water with the density at

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Table 1. Bulk and DFT-Derived Bond Lengths for Bridging (BO) and Terminal (TO) Surface Oxygens, Corresponding Values Used in the CMD Simulations, and Lengths Obtained from Crystal Truncation Rod (CTR) Measurements

<table>
<thead>
<tr>
<th>bond</th>
<th>bulk DFT</th>
<th>CMD</th>
<th>DFT</th>
<th>CMD</th>
<th>CTR</th>
</tr>
</thead>
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<tr>
<td>Ti-T(OH)</td>
<td>1.98</td>
<td>1.86-2.00</td>
<td>1.96</td>
<td>2.00</td>
<td>(-0.03)</td>
</tr>
<tr>
<td>Ti-BO</td>
<td>1.87</td>
<td>1.85-1.89</td>
<td>1.85</td>
<td>1.89</td>
<td>(-0.02)</td>
</tr>
<tr>
<td>Ti-BO(OH)</td>
<td>2.02</td>
<td>2.02-1.99</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>BO(O)</td>
<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

* From Bandura et al.11,12 Bond lengths used in Prˇedota et al.19 and this study. * Bandura et al.12 Bond lengths used in two 25 °C MD simulations for this study. * Zhang et al.18 Labeling is as follows. Unprotonated bridging oxygen, BO; protonated bridging oxygen, BO(H) and similarly for the terminal group.

25 °C set to 1 g/cm³, while at 150 and 250 °C the liquid—vapor coexistence densities (0.92 and 0.80 g/cm³, respectively) were used. The 1 ns simulation length was sufficient to obtain accurate results for H-bonding due to averaging over a large number of surface species (144 bridging and 144 terminal surface sites) and water molecules (2048, including terminal hydroxyls).

Both neutral nonhydroxylated and hydroxylated surfaces were modeled. The neutral hydroxylated surface is populated solely by terminal and bridging hydroxyls, while the neutral nonhydroxylated surface is terminated by unprotonated bridging oxygens and 5-fold coordinated Ti atoms, above which is an associated water molecule. These two end member surface terminations represent strict dissociative and associative water adsorption, respectively, and correspond most closely to the pHmax condition at which the surface is neutral.

During the CMD simulations, the terminal and bridging hydroxyls/oxygens were flexible within fixed bond Ti—O—H lengths set to their average DFT-obtained values, as summarized in Table 1 and all atoms on and below the surface plane were kept rigid in the DFT-obtained relaxed structure. Most of the CMD simulations conducted for this study utilized the bond lengths given in the fourth column of Table 1, which were taken from the periodic DFT study of Bandura et al. (column three of Table 1). However, planewave DFT has been used to derive bond lengths in a more recent study.42 and values from the ranges provided in that study have been used in two 25 °C simulations presented here (column six of Table 1). The largest difference in the two sets of bond lengths used for the CMD simulations is for terminal oxygen, where the difference is about 0.1 Å. However, the DFT-derived atomic charges for the surface atoms (i.e., Ti, O, H), as given in Prˇedota et al., were the same for both sets of CMD simulations.

Also included in Table 1 are bulk crystal bond lengths and lengths observed in CTR study of Zhang et al. It is significant to note that the periodic and planewave DFT studies were conducted on rutile (110) surface slabs in the presence of water molecules, while the CTR study was conducted on rutile (110) single-crystal surfaces in bulk aqueous solutions. Consequently, because water molecules help to complete the coordination spheres of surface atoms, observed bond lengths are much closer to those found in the bulk crystal than is typically observed for vacuum-terminated surfaces.

3. Results and Discussion

3.1. Hydrogen Bonding. Intermolecular H-bonding in water is typically defined using energetic and/or geometric criteria. The energetic criterion considers each pair of water molecules to be H-bonded if their pair energy is lower than a specified value; usually about −10 kJ/mol. Geometric criteria consider various interatomic distances and/or angles.33,42 For most of the results presented in this study we used the simplest geometric criterion of a hydrogen bond which is based exclusively on intermolecular O—H distances between separate water molecules and/or surface oxygens or hydroxyl species, i.e. each OH pair is considered to be H-bonded if it is contained within the first peak of the OH pair correlation function which extends to 2.375 Å. This criterion was found to capture essentially the same hydrogen bonded configurations as the energetic criterion with a −10 kJ/mol threshold at ambient conditions,43 and reproduces the experimental average number of H-bonds per molecule. At high temperatures, both energetic and geometric distributions become less distinct, but fair agreement between both approaches is observed up to supercritical conditions.44 Our recent analysis of H-bonding on the cassiterite (110) surface employed a slightly different geometric criterion to define an H-bond; namely an O—O separation distance less than 3.5 Å, in conjunction with the angle between the OH intermolecular bond of the H-donor and the O—O vector being less than 30°.16 Consequently, for comparative purposes, H-bond results at 25 °C with this alternate geometric definition are also given in Table 2 (the Ti—O—H bond lengths from column six of Table 1 were used in these alternative simulations). In any case, both these geometric criteria are also unambiguously applicable to H-bond interactions between water and surface unprotonated oxygen and surface hydroxyl groups.

Figure 1 presents oxygen—hydrogen pair correlation functions (PCF(gOH)) for significant water—surface, water—water and surface—surface H-bonded pairs at 25 °C. The upper limit of the length scale (2.4 Å) is very near the 2.375 Å limit taken to signify an H-bonded pair. This limit corresponds to the minimum of the water—water PCF, and is close to the minima for the other PCF’s as well. The CMD PCF’s all have the same characteristic shape, i.e. a steep decrease from the peak toward shorter O—H separations due to inevitable O—O repulsion, while the decrease toward larger separations results purely from the hydrogen-bonding structure of water. This characteristic skew toward the increasing distance direction means that the peak H-bond distance (Rpeak) is about 0.1 Å less than the average H-bond distance (Ravg, examined in greater detail below). Also, terminal and bridging surface oxygen atoms both accept H-bonds that are shorter than those in bulk water. For example, the peak length for H-bonds between unprotonated bridging oxygen and water (BO—W) is 1.65 Å, versus 1.77 Å for bulk water (Table 2).

Bridging oxygen—water H-bonds (BO—W) and unprotonated oxygen—water H-bonds (TOH—W) are represented in Figure 1 by both CMD and QMD PCF’s. In the QMD simulations, water molecules were fully capable of dissociating, while the classical MD simulations utilized SPC/E water molecules which do not dissociate. However, the PCF’s for these two distinct types of MD simulations exhibit virtually identical peak H-bond distances and are generally similar in shape, although the QMD PCF’s are more symmetrical. Regardless, the similar PCF’s signify that the CMD simulations are providing accurate H-bond information. This is perhaps not too surprising since the SPC/E water model does reproduce the structural properties of bulk water accurately,45 and at much lower computational cost than dissociable water models.

Figure 2 shows the principal types of H-bond configurations formed on neutral hydroxylated and nonhydroxylated surfaces in schematic form, and which are used for MUSIC model calculations. Figure 3 presents representative snapshots of H-bond configurations for neutral hydroxylated and neutral nonhydroxy-
of water in bulk. 22 The average H-bond length for bulk water at 25°C is 0.2 Å longer than the peak distance because the distributions are positively skewed. The correlation in Figure 4 is used to convert \( r_{H-bond} \) to valence units per hydrogen bond, \( \nu u/\nu H_b \), for this purpose, the neutron diffraction H-bond lengths were fit in the important range between 1.4 and 2.375 Å as,

\[
\frac{\nu u}{\nu H_b} = 1.55 - 1.06 r_{avg} + 0.186 r_{avg}^2
\]

(3)

The resulting fit is given by the solid gray line in Figure 4. Input of the average H-bond length for bulk water at 25°C (1.90 Å, Table 2) gives \( \nu u/\nu H_b \) as the H-bond strength, which agrees with the commonly accepted value for a normal H-bond in bulk water (0.2 \( \nu u/\nu H_b \)) as given in Brown. 22 Multiplying the strength of bonds given by eq 3 by their number (eq 1), gives \( \nu u \) per surface site (or per water molecule in case of W–W hydroxylated surfaces of rutile (110) from our CMD simulations, as extracted from the large periodic structures used for those simulations. In this instance, the H-bond configurations shown are typical of those found along the surface, but are not unique.

Detailed and statistically significant H-bond data for these surfaces at 25, 150 and 250 °C are contained in Table 2. These data are categorized in “x–y” fashion (column 1) according to which O–H or H–O pairs are connected, with “x” signifying the first atom of the pair and “y” the second. When “x” is an oxygen atom, an H-bond is being accepted from an H atom bonded to a neighboring species, and when “x” is an H atom, an H-bond is being donated to an oxygen atom of an adjacent species. H-bond numbers (\( \nu H_b \)), peak and average lengths (\( r_{peak} \) and \( r_{avg} \)), and H-bond strength, as quantified in terms of valence units (\( \nu u \)) following Brown, 10 are given for relevant H-bonded pairs.

Table 2. H-Bond Data for Neutral Surfaces at 25, 150, and 250°C

<table>
<thead>
<tr>
<th>x–y</th>
<th>( \nu H_b )</th>
<th>( r_{avg} )</th>
<th>( r_{peak} )</th>
<th>( \nu u )</th>
<th>( \nu u/\nu H_b )</th>
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</thead>
<tbody>
<tr>
<td>TOH–W</td>
<td>1.03</td>
<td>1.82</td>
<td>1.71</td>
<td>0.244</td>
<td>0.237</td>
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<td>BOH–W</td>
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<td>W–W</td>
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<td>BO–W</td>
<td>1.27</td>
<td>1.83</td>
<td>1.66</td>
<td>0.296</td>
<td>0.233</td>
</tr>
<tr>
<td>BO–W</td>
<td>1.53</td>
<td>1.96</td>
<td>1.79</td>
<td>0.286</td>
<td>0.187</td>
</tr>
<tr>
<td>BO–W</td>
<td>1.23</td>
<td>1.88</td>
<td>1.68</td>
<td>0.264</td>
<td>0.215</td>
</tr>
<tr>
<td>BO–W</td>
<td>1.34</td>
<td>1.99</td>
<td>1.82</td>
<td>0.237</td>
<td>0.177</td>
</tr>
</tbody>
</table>

\( \nu u/\nu H_b \) is obtained from integrating the pair correlation functions (\( g_{OH} \)).

\[
N_{HB} = \text{Const} \int_{r=0}^{2.375} g_{OH}(r)r^2 dr
\]

(1)

where the prefactor accounts for normalization of the \( g_{OH} \). While the peak H-bond distance is simply the maximum of a particular \( g_{OH} \), the average H-bond distance (\( r_{avg} \)) is calculated as,

\[
r_{avg} = \frac{\int_{r=0}^{2.375} g_{OH}(r)r^2 dr}{\int_{r=0}^{2.375} g_{OH}(r)dr}
\]

(2)

\( r_{avg} \) is about 0.1 Å larger than the peak distance because the \( g_{OH} \) distributions are positively skewed. The correlation in Figure 4 is used to convert \( r_{avg} \) to valence units per hydrogen bond, \( \nu u/\nu H_b \); for this purpose, the neutron diffraction H-bond lengths were fit in the important range between 1.4 and 2.375 Å as,

\[
\frac{\nu u}{\nu H_b} = 1.55 - 1.06 r_{avg} + 0.186 r_{avg}^2
\]

(3)
CMD simulations conducted at 25 °C with terminal and bridging oxygen atoms (TOH and BOH) in determining H-bond configurations. Subsequently, electrostatic factors dominate small geometric differences were identical in these two sets of CMD simulations. Consequently, the insensitivity of H-bonding configurations to small changes in Ti–O bond lengths (Table 1) are similar, with intrasurface H-bonds (TOH–TOH and BOH–TOH) being most different. The relative insensitivity of H-bonding configurations to small changes in Ti–O bond lengths (±0.1 Å) relative to the 3 Å lattice spacing is primarily due to the fact that the DFT-derived atomic charges were identical in these two sets of CMD simulations. Consequently, electrostatic factors dominate small geometric differences in determining H-bond configurations.

Relative to bulk water (W–W in Table 2), the H-bonds accepted by terminal and bridging oxygen atoms (TOH–W, BO–W) are shorter and stronger at all temperatures, as is also apparent in Figure 1 for 25 °C. Moreover, as temperature increases, the accepted BO–W H-bonds are more stable relative to those in bulk water. For example, the total $u$ contribution decreases from 0.37 to 0.24 between 25 and 250 °C for W–W H-bonds, while the corresponding decrease is only from 0.33 to 0.26 for BO–W H-bonds. This relative stability is primarily due to the number of H-bonds ($N_{HB}$) remaining more constant with increasing temperature. In any case, water molecules H-bond to the terminal and bridging oxygen’s exposed at the (110) rutile surface more effectively than they do to themselves, and this relative enhancement increases with temperature.

### 3.2. MUSIC Model Surface Protonation Description

Following our previous modifications of the refined MUSIC model to include temperature effects and H-bond configurations different from bulk water, surface protonation constants are estimated using the empirical relationship,

$$\log K_{H,T} = -A_T(V + \sum \exp((r_o - r_{Me-O})/0.37 \text{ Å}) + \sum u_{Me} + \sum u_{D}) \quad (4)$$

where $A_T$ is a temperature dependent constant (the slope) obtained from regressions of log $K_{H,T}$ values of solution protonation reactions (from 0 to 300 °C) versus the “undersaturation of charge” on the respective oxygen ligands, $V$ is the formal valence of oxygen ($-2$) and $\sum \exp((r_o - r_{Me-O})/0.37 \text{ Å})$ is the sum (over 1, 2 or 3 for single, double or triple coordination, respectively, of surface oxygen’s with coordinated metal ions in the truncated crystal structure) of the bond valence values for the metal–oxygen bonds of interest. These bond valence values are estimated using the relevant metal–oxygen bond lengths ($r_{Me-O}$), a reference bond length ($r_o$) calculated from the bulk crystal structure (1.8097 Å), and an empirical constant (0.37 Å) as described by Brown. It was not necessary to adjust the $r_o$ value for our higher temperature CMD simulations (150 and 250 °C) since the thermal expansion coefficient for rutile is sufficiently small ($\sim 10^{-5} \text{ K}^{-1}$) that Ti–O bond lengthening is negligible at those temperatures. The remaining terms account for H-bonding to surface oxygen, where $u_D$ is the donating H-bond $vu$ contribution to a given surface oxygen, and $u_{Me}$ is the accepting H-bond contribution. These H-bond terms incorporate both the number of H-bonds ($N_{HB}$) and their average length ($r_{avg}$) in terms of valence units ($vu$) as specified in eqs 1–3 above.

The starting surface configuration for the MUSIC model calculations consists of terminal TOH (Ti–OH) and bridged BO (Ti–O–Ti) groups, since these groups are potentially capable of taking up an additional proton in the pH range accessible in water (0–14). In essence, this configuration is a hybrid of the hydroxylated (Ti–OH and Ti–OH–Ti), and nonhydroxylated (Ti–H$_2$O and Ti–O–Ti) surfaces. Consequently, CMD results for both types of neutral surfaces at 25 °C are utilized, and the H-bond information used explicitly is given in bold text in Table 2.

### Table 2. Average H-bond and $N_{HB}$ values for the two sets of CMD simulations conducted at 25 °C with different Ti–O bond lengths (Table 1) are similar, with intrasurface H-bonds (TOH–TOH and BOH–TOH) being most different. The relative insensitivity of H-bonding configurations to small changes in Ti–O bond lengths (±0.1 Å) relative to the 3 Å lattice spacing is primarily due to the fact that the DFT-derived atomic charges were identical in these two sets of CMD simulations. Consequently, electrostatic factors dominate small geometric differences in determining H-bond configurations.

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The bridging oxygen accepts 1.29 H-bonds from water molecules with $R_{avg}$ being 1.78 Å, resulting in a total $v(u_D)$ value of 0.33 for use in eq 4 ($v(u_D)$ is zero). The terminal oxygen accepts 1.03 H-bonds from water with $R_{avg}$ being 1.82 Å, and it accepts 0.48 H-bonds from H atoms of neighboring terminal groups, resulting in $v(u_D)$ summing to 0.36. There is also a donating H-bond contribution from the proton attached to the terminal oxygen. This bond valence contribution was taken to be 0.80, as in the original refined MUSIC model since the O–H bond length used in the CMD simulations (0.983 Å, Table 1), is very near the corresponding bulk water value (0.97 Å). Moreover, the relationship between $vu$ and O–H bond length is difficult to quantify precisely at these distances due to the steepness of the

relationship (Figure 4). In any case, accurately quantifying the length and corresponding contributions of these short H-bonds would further improve the MUSIC model approach. Input of this H-bond information into eq 4 along with Ti–O bond lengths leads to the protonation scheme depicted in Figure 5. With these protonation constants, and associated partial charges ($V + \sum \exp((r_o - r_{Me-O})/0.37 \text{ Å})$, from eq 4 plus 1 for each H atom involved), the point of zero net proton charge (pHznpc) for the rutile (110) surface can be calculated and compared to experimentally determined values. In this specific instance, the protonation scheme results in a pH$_{znpc}$ value of 5.42, which purposely matches the 25 °C pH$_{znpc}$ value of the Tioxide rutile powders we have been using extensively in our laboratories, and that are dominated (>80%) by the (110) crystal face. Matching the experimentally determined pH$_{znpc}$ value is desirable in analysis of the surface charging curves over wide ranges of pH and ionic strengths since the surface protonation constants responsible for the match can then be held constant in future surface complexation modeling efforts. This reduces model ambiguity when treating experimental surface protonation and ion adsorption experimental data obtained by titrating powder suspensions in bulk aqueous electrolytes, since surface and solvation structure is explicitly incorporated into the surface protonation description (rather than the default H-bond parameters for the refined MUSIC model), and the number of modeling fitting parameters is reduced.

The pH$_{znpc}$ match to the rutile powder titration data was obtained by manually adjusting Ti–O bond lengths, while holding the H-bond contributions determined via CMD simulations constant, and the Ti–O bond lengths used are given as the “Optimized” lengths in the table inset of Figure 5. These optimized bond lengths fall within the range of lengths found in our DFT calculations and observed in our X-ray scattering experiments, which vary from 1.90–2.05 Å for Ti–TO(H) and 1.87–1.95 Å for Ti–BO (Table 1). However, as the “DFT” and “CTR” entries in the table inset of Figure 5 illustrate, using specific Ti–O bond lengths within these ranges while keeping the H-bond contributions fixed, results in predicted pH$_{znpc}$ values that vary between 4 and 6.6. This pH$_{znpc}$ range also encompasses that determined using second harmonic generation spectroscopy (SHG) for the rutile (110) single crystal surface (4.8 ± 0.3) in contact with bulk sodium nitrate solutions, and in this specific instance decreasing the calculated pH$_{znpc}$ from 5.4 to 4.8 requires only a 0.013 Å decrease.

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decrease in both optimized bond lengths. Consequently, refined MUSIC Model predictions are extremely sensitive to small changes in bond lengths (<0.1 Å) as has been mentioned previously, and this sensitivity stems in part from the exponential relationship between bond length and corresponding bond valence inherent in the bond valence model (e.g., Figure 4 and eq 4).

Matching the 25 °C $pH_{\text{spec}}$ value is also obtainable by fixing Ti–O bond lengths and manually adjusting the bond valence contributions from H-bonds. For example, fixing Ti–O bond lengths at 1.98 and 1.89 Å for the terminal and bridged oxygen, respectively (the “DFT” entry in the table inset of Figure 5), requires corresponding $\nu u A$ contributions of 0.296 (terminal) and 0.266 (bridging) for the $pH_{\text{spec}}$ to equal 5.4. These $\nu u A$ values are only about 0.06 $\nu u$ less than those obtained from our CMD simulations, and which require “optimized” Ti–O bond lengths of 2.02 and 1.93 Å for terminal and bridged oxygen, respectively. Admittedly, whether to adjust Ti–O bond lengths, H-bond contributions, or both for a $pH_{\text{spec}}$ match remains ambiguous. However, we have chosen to fix the CMD-derived H-bond contributions for several reasons. First, our QMD simulations verify that our CMD-derived H-bond configurations are providing accurate H-bond information. Second, we have a better understanding of Ti–O bond length uncertainty (within about 0.1 Å of bulk values) than H-bond configurations at present, and we chose to make direct use of that uncertainty. Finally, a primary purpose of this contribution is to describe the methodology we have developed for quantitatively utilizing H-bond configurations to predict surface protonation constants, and that focus is best maintained by the direct use of those H-bond data obtained from the simulations.

Table 3 compares experimental $pH_{\text{spec}}$ values for our Tioxide rutile with predicted values to 300 °C. Also included are the temperature-corrected MUSIC Model constants ($A_T$) and the predicted temperature-corrected protonation constants for the terminal ($K_{HT}$) and bridged ($K_{HB}$) oxygen’s. As detailed in Machesky et al., derivation of the $A_T$ constant values to 300 °C utilized a number of log $K_{HT}$ values for solution protonation reactions (primarily the first hydrolysis constants of cations) and undersaturation of oxygen ligand charge values calculated using the H-bond configurations from Hiemstra et al. and a second factor that accounted for the observed decrease in cation hydration number with increasing temperature. Regardless, the predicted $pH_{\text{spec}}$ values agree to within 0.1 pH unit with those measured at all temperatures between 10 and 250 °C.

In principal, the H-bond configurations obtained from the MD simulations conducted at 150 and 250 °C could be used to estimate temperature-corrected protonation constants at those temperatures more directly than by using the $A_T$ values given in Table 3. However, such an approach would require revised $A_T$ values that would explicitly incorporate actual H-bond configurations observed at various temperatures for the extensive suite of solution protonation reactions used to determine those values. Additional MD simulations would be necessary to determine these H-bond configurations, but some estimate as to how $A_T$ values would change can be made from the higher temperature simulations of this study. Between 25 and 250 °C, the $\nu u A$ contributions for all types of H-bonds decrease, and explicitly accounting for this decrease would result in lower $A_T$ values since those currently used assume that H-bond $\nu u$ contributions are temperature independent. Fortunately, lower $A_T$ values are necessary to compensate for the lower $\nu u$ H-bond contributions at higher temperatures. For example, the $A_T$ value at 250 °C would have to decrease from 16.45 to about 12.4 in order for the predicted $pH_{\text{spec}}$ to remain at about 4.1 given the lower H-bond $\nu u$ contributions. This 25% decrease is not unreasonable given that the $\nu u$ decrease for W–W H-bonds between 25 and 250 °C is 35%.

### 3.3. Comparison to Cassiterite (110) Protonation.

Cassiterite and rutile are isostructural but Sn–O bonds are both slightly longer (about 0.1 Å) and more covalent than Ti–O bonds. Other important differences are the higher dielectric constant of rutile (∼120 vs 9), and the tendency for water to remain associated on the rutile (110) surface, while dissociation predominates on the cassiterite (110) surface. have developed a MUSIC model description for the cassiterite (110) surface that is also consistent with an extensive set of ab initio and CMD simulations, as well as experimental data from X-ray reflectively on single crystal surfaces in contact with bulk aqueous solutions, and potentiometric titrations of cassiterite powders. Consequently, it is informative to compare that MUSIC model description with the one developed in this study for rutile.

The comparative solvation structures of these surfaces reveals that the biggest difference is the more extensive H-bonding to the terminal oxygen on cassiterite, with the $\nu u A$ H-bond contribution being 0.46 vs 0.36 for the terminal oxygen on the rutile (110) surface. Consequently, this group is predicted to have a lower protonation constant on cassiterite than rutile under the MUSIC model framework. However, the bridged oxygen’s on these two surfaces accept H-bonds comparable in strength, with $\nu u A$ contributions being 0.35 for cassiterite and 0.33 for rutile, which results in predicted protonation being more similar. In fact, in combination within any reasonable range of corresponding Ti–O and Sn–O bond lengths (including bulk crystal values), the relative acidity of the terminal and bridged groups on these two surfaces is predicted to be reversed. That is, the bridged group is more acidic than the terminal group on the rutile (110) surface, while the reverse is true for cassiterite. This difference in relative acidity between the terminal and bridging oxygen’s is also consistent with the prevailing notion that water tends to remain associated on the rutile (110) surface, while dissociation predominates on the cassiterite (110) surface. That is, the lower log $K_{HT}$ for cassiterite corresponds to a more acidic associated water molecule which dissociates more easily.

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Table 3. MUSIC Model Constants ($A_T$), Predicted Protonation Constants, and Experimental and MUSIC Model Predicted $pH_{\text{spec}}$ Values from 0 to 300 °C

<table>
<thead>
<tr>
<th>temp (°C)</th>
<th>$A_T^a$</th>
<th>$\log K_{HT}$</th>
<th>$\log K_{HB}$</th>
<th>$pH_{\text{spec}}$ (expt)$^b$</th>
<th>$pH_{\text{spec}}$ (pred)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>23.25</td>
<td>6.361</td>
<td>5.234</td>
<td>5.81</td>
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<td>10</td>
<td>22.59</td>
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<td>5.086</td>
<td>5.7 (±0.2)</td>
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<td>25</td>
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<td>5.936</td>
<td>4.885</td>
<td>5.4 (±0.2)</td>
<td>5.42</td>
</tr>
<tr>
<td>30</td>
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<td>4.827</td>
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<tr>
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<tr>
<td>50</td>
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</tbody>
</table>

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a From Machesky et al. 12
b From Machesky et al. 17

with the released proton then being able to protonate the relatively more basic bridged oxygen, resulting in a hydroxylated surface.

This comparison illustrates the importance of accurately quantifying H-bond contributions for MUSIC model calculations. Since Sn–O and Ti–O bond lengths for both surfaces in the presence of water are close to bulk crystal values (within 0.1 Å), there is no basis for deviating greatly from bulk values for MUSIC model calculations. Conversely, the H-bond or hydration contributions are directly responsible for the predicted reversal in relative acidities of the terminal and bridged groups, with $K_{H1}$ predicted to be greater than $K_{H2}$ on the rutile (110) surface, while the converse is true for cassiterite. For rutile, that $K_{H1}$ is greater than $K_{H2}$ is also supported by the X-ray scattering results of Zhang et al., and the internal reflection IR study of Connor et al.

The importance of hydration in dictating the protonation behavior of surface functional groups has also been noted in other studies. In their large-scale CMD simulations of goethite ($\alpha$-FeOOH) nanoparticles, Rustad and Felmy observed the preferential accumulation of proton charge at edge sites, which they ascribed to the more effective solvation of the excess charge at those sites. Aquino et al. used density functional theory to compute protonation constants of reactive sites on the goethite surface and concluded that all aspects of solvation must be considered to obtain realistic values. Rustad conducted CMD simulations designed to simulate titrations of model Al-polyanions. Hydration effects for individual protolyzable functional groups were monitored and actual Al-bond lengths and H-bond configurations were used in MUSIC model calculations to predict protonation constants. It was concluded that knowledge of the specific hydration state of individual functional groups is critical for predicting their acidity. Moreover, input of this information into the refined MUSIC model resulted in generally good predictions of functional group acidity. Finally, Bickmore et al. have noted the importance of treating surface functional group hydration realistically in their critiques of the refined MUSIC model.

4. Conclusions

The refined MUSIC model framework is able to successfully incorporate the specifics of the hydration structure surrounding protolyzable surface oxygen groups on oxide surfaces into the estimation of surface protonation constants that are consistent with a variety of experimental and computational results. H-bond interactions between terminal and bridging oxygen atoms exposed at the (110) surface of rutile and water molecules, determined primarily from CMD simulations in SPC/E water as constrained using ab initio and DFT-derived surface-solution force fields, partial charges, and Ti–O bond lengths, are stronger than those between bulk water molecules, and this difference increases with temperature between 25 and 250 °C. Moreover, select QMD simulations with fully dissociable water molecules resulted in H-bond configurations very similar to those found in CMD simulations with nondissociable SPC/E water, which attests to the ability of the less computationally intensive SPC/E water simulations to provide accurate H-bond information. The resulting pH$_{npec}$ predictions, after slight manual adjustments to Ti–O bond lengths, agree with those experimentally determined for a specific rutile powder dominated by the (110) crystal face to within 0.1 pH unit between 10 and 250 °C, and with SHG measurements of bulk water in contact with rutile (110) single crystal surfaces.

Comparison of these results with those for the isostructural (110) surface of cassiterite highlights the importance of H-bonding with associated water molecules in governing surface protonation behavior. Whereas the terminal oxygen group is predicted to have a larger protonation constant than the bridged oxygen on rutile, the opposite is predicted for the cassiterite (110) surface and this predicted shift in relative acidity is due almost entirely to the terminal oxygen group on cassiterite accepting stronger H-bonds from water. This observation is consistent with DFT calculations, which indicate a stronger tendency toward first-layer water dissociation on cassiterite (110), but for first layer water to remain associated on the rutile (110) surface. Moreover, this shift in relative acidity is not predicted if H-bond contributions default to the standard refined MUSIC model values. Consequently, explicit utilization of the actual solvation structure surrounding protolyzable surface oxygen’s, represents a significant improvement to the predictive capabilities of the refined MUSIC model framework.

Future extensions and improvements to the MUSIC model framework can be envisioned. More accurate interfacial H-bond configurations, as well as valuable information concerning the dynamics of proton exchange at the interface, would result from utilizing a dissociable model for water in CMD simulations. Moreover, the results would also be more directly comparable to those from the more computationally expensive QMD simulations. An ultimate goal of these efforts should be to replace the current empirically based MUSIC model with a more theoretical construct, with surface oxygen protonation constants derived directly from atomic-scale computational modeling. In any case, these extensions and improvements will need to explicitly consider the specific hydration state of surface functional groups, as is also recognized by those concerned with predicting the aqueous protonation states of proteins, DNA and other complex organic molecules.

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