Hydrogen bonding between water molecules and the rutile (110) surface is investigated by molecular dynamics using SPC/E water model and *ab initio* derived rutile surface structure and potentials. The role of surface hydroxylation and charge is studied and the differences in bond lengths between different pairs of sites and number of bonds formed by each species are reported. Consequences of our findings on complexation modeling of rutile surface using MUSIC model are discussed. Particularly, we recognized that bridging oxygen on rutile surface does not participate in two hydrogen bonds as recently assumed, but forms a stronger single hydrogen bond instead.

1. INTRODUCTION

Mineral–aqueous electrolyte solution interfaces are of common occurrence in natural and industrial environments. The presence of a solid-fluid interface not only has the potential to modify the thermophysical properties of the neighboring fluid phase, but also the chemical nature of the mineral surface, depending on the state condition and composition of the system. The surface adsorption of ionic species from the aqueous solution generates an accumulation of net charge at the surface that must be balanced by counter-charges in the fluid vicinity of the interface, i.e., the so-called diffuse layer of counterions. Moreover, the chemical interaction of water with the mineral surface involves water dissociation and a variety of acid-base reactions involving successive surface protonation states (proton speciation at the surface).

The description of the surface charging process on metal oxides has been made traditionally through one-site/two-pK models, i.e., by assuming that the protonation (deprotonation) process characterizing the amphoteric nature of the surface takes place on a single (chemically homogeneous) type of surface site. Recently, MultiSite Complexation models (MUSIC) have been developed. In this approach, the various types of surface hydroxyl sites, as determined from structural analysis of mineral surfaces are considered explicitly. However, fitting macroscopic surface titration and ion adsorption data to surface complexation models (SCM’s) is ambiguous since the resulting ion binding constants and Stern-layer capacitance values can take on a range of plausible values. Molecular simulation
can provide detailed descriptions of the interface, and thereby help remove the arbitrariness associated with the application of SCM’s.

In principle, the ideal approach to the simulation of mineral-aqueous interfaces would be to utilize the detailed surface protonation behavior, i.e., the actual acid-base reactions and water dissociation processes occurring at the mineral surface. Currently, however, this is not a realistic simulation scenario, due to the formidable complexity behind the atomistic description of the surface chemistry. Therefore, we opt for a reasonable compromise between the realism in the atomistic description of the metal-oxide surface (as well as the aqueous electrolyte fluid phase) and the practicality of classical simulation methods based on well-characterized force fields derived from ab initio methods. Consequently, this approach provides the opportunity to fully characterize the microscopic behavior of the fluid phase in the neighborhood of the mineral surface. In our recent manuscripts\textsuperscript{10-12} we described in detail the modeling of the rutile-water interface, structure of water at the interface and adsorption of ions, Rb\textsuperscript{+}, Na\textsuperscript{+}, Sr\textsuperscript{2+}, Ca\textsuperscript{2+}, and Zn\textsuperscript{2+}, based on molecular dynamics and X-ray (XSW, CTR) experiments. Here we investigate formation of hydrogen bonds between interfacial water and rutile surface species by molecular dynamics simulations and link these results with MUSIC calculations.

2. SURFACE STRUCTURE

The bulk rutile structure is given by 6-fold coordinated Ti\textsuperscript{VI} atoms and 3-fold coordinated O atoms. Two of the O-Ti bonds are 1.946 Å long; the third one is longer, 1.984 Å. The nonhydroxylated (110) surface stems from the relaxation of the rutile bulk structure cleaved by the (110) plane. Only rows of bridging oxygens (each bonded to two underlying Ti atoms) protrude out of the layer containing surface titanium and oxygen atoms, see Figure 1. In between these rows there are rows of 3-fold coordinated O and 5-fold coordinated terminal Ti\textsuperscript{V} atoms in the same surface plane. \textit{Ab initio} calculations\textsuperscript{13,14} and X-ray experiments\textsuperscript{10,15} determined that the relaxations of atoms in the surface plane (the outermost plane containing Ti atoms) are smaller than 0.1 Å in the direction perpendicular to the surface. The length of the bond between bridging oxygen (BO) and Ti atoms was found by \textit{ab initio} calculations to be 1.87 Å\textsuperscript{11}. There is a chemisorbed water molecule above the 5-fold coordinated terminal Ti at height 2.25 Å above the surface plane\textsuperscript{11}.

The fully hydroxylated surface develops from the nonhydroxylated surface by dissociative adsorption of water molecules, with OH groups bonding to terminal Ti and becoming terminal hydroxyl, and the released H\textsuperscript{+} bonding to bridging oxygen and forming bridging hydroxyl. The Ti-BO bond length increases significantly upon protonation to 2.02 Å. The Ti-O and O-H bond lengths of surface groups are summarized in Table 1.

Each atom carries its partial charge, however as long as the numbers of terminal and bridging hydroxyls equal, the net charge of the surface is zero. The point of zero charge of
Table 1: Surface Ti-O and Ti-O-H bond lengths averaged from ab initio structures and used in MD simulations. The length of the bridging Ti-O bond changes upon protonation of the bridging oxygen.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Terminal</th>
<th>Bridging protonated</th>
<th>Bridging unprotonated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti-O</td>
<td>O-H</td>
<td>Ti-O</td>
</tr>
<tr>
<td>Length [Å]</td>
<td>1.89490</td>
<td>0.98293</td>
<td>2.02215</td>
</tr>
</tbody>
</table>

Rutile powders predominantly exposing the (110) face is pH_{zpc}=5.4 at 25°C, and thus negative surface-protonation-induced charge develops at any pH above this point. We ascribe the surface charging to dissociation of water molecules at the surface and protonation/deprotonation of bridging hydrogens and hydroxylation of terminal Ti, with negative surface charge arising from a surplus of terminal hydroxyls over bridging hydroxyls. The results presented here are for surface charge density -0.208 C/m². The relative coverages of the surface by terminal and bridging groups for both neutral and charged surfaces are given in Table 2.

3. HYDROGEN BONDING

There are two types of generally accepted definitions of the intermolecular hydrogen bond in water, with best performance given by combination of both criteria. The energetic criterion considers as bonded each pair of water molecules with pair energy lower than a specified value. Values in the range -10 to -8 kJ/mol are used as the upper limit of pair energy of bonded molecules. The purely energetic criterion fails at high-temperature conditions. The geometric
Table 2: Relative occupation of terminal and bridging groups on rutile (110) surfaces studied.

<table>
<thead>
<tr>
<th>Surface</th>
<th># of BO unprotonated</th>
<th># of BOH, BOH</th>
<th># of TOH, TOH</th>
<th># of associated H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonhydroxylated neutral</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Nonhydroxylated charged</td>
<td>1</td>
<td>0</td>
<td>1/4</td>
<td>3/4</td>
</tr>
<tr>
<td>Hydroxylated Neutral</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Hydroxylated Charged</td>
<td>1/4</td>
<td>3/4</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

criterion typically considers as hydrogen bonded a pair of water molecules with O-O and O-H separations and the angle between the OH intermolecular bond of the H-donor and the O-O vector smaller than given limits; as a typical example, the limits 3.5 Å, 2.5 Å, and 30° are used\(^{18}\). More complex geometric criteria for hydrogen bonding exist\(^{19}\). In this study, we adopt the simplest geometric criterion of a hydrogen bond, namely each OH pair within the first peak of OH pair correlation function is considered as hydrogen bonded, i.e. OH distance smaller than 2.37 Å is the only criterion for hydrogen bonding. As discussed in detail in\(^{17}\), this criterion is satisfactory at ambient temperatures, only slightly overestimating the number of hydrogen bonds (HB) compared to more restrictive definition of HB. It is a unique definition both for water-water HBs as well as for atoms of surface hydroxyls, where the energetic criterion is inapplicable without modifications.

In Table 3, the properties of all types of water-surface and water-water HBs are summarized. Atoms participating in particular HBs are marked by bold letters, the bridging and terminal atoms are distinguished the first letter B or T. Representative figure of pair correlation function (PCF) \(g_{OH}\), Figure 2, illustrates that although there are some deviations in the position of the HB peak around 1.7 Å, the location of the minimum of PCF is in all cases close to the set maximum O-H distance for HB, i.e. 2.37 Å, and therefore the definition of HB is reasonable even when surface atoms are participating. Integration of each PCF up to the maximum O-H distance 2.37 Å gives the total number of HBs of given type.

Figure 2: Oxygen-hydrogen pair correlation functions of different types for negative rutile hydroxylated surface.
In pure water, oxygen forms on average 1.72 HBs and hydrogen half of this number, 0.86. It must be expected, that generally surface atoms will form less bonds, since the approach of water molecules is restricted by the presence of the surface. Another general trend is that upon negatively charging the surface, numbers of bonds with surface oxygens increase, since hydrogens of water molecules are attracted by the negative surface. Furthermore, the charges of surface atoms vary slightly with the surface charge density. Opposite trend is observed for numbers of bonds originating from surface hydrogens, which decrease upon charging of the surface.

Table 3: Number (upper row) and length (lower row) of water-water and various types of water-surface hydrogen bonds. Bold symbols denote atoms participating in HB.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Bond</th>
<th>H$_2$O-BO</th>
<th>H$_2$O-BOH</th>
<th>H$_2$O - BOH</th>
<th>H$_2$O - TOH</th>
<th>H$_2$O - TOH</th>
<th>H$_2$O - $\cdot$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral hydroxylated</td>
<td></td>
<td>0.05</td>
<td>§</td>
<td>0.99</td>
<td>1.73</td>
<td>1.69</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Neutral</td>
<td>0.98</td>
<td>0.14</td>
<td>0.60</td>
<td>0.92</td>
<td>0.41</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>Negative</td>
<td>1.28</td>
<td>1.65</td>
<td>1.84</td>
<td>1.71</td>
<td>1.82</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>Neutral</td>
<td>1.36</td>
<td>1.68</td>
<td>1.74</td>
<td>0.66</td>
<td>2.01</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>Negative</td>
<td>1.36</td>
<td>1.68</td>
<td>1.74</td>
<td>0.66</td>
<td>2.01</td>
<td>1.77</td>
</tr>
</tbody>
</table>

* Numbers of H$_2$O-H$_2$O bonds are given per oxygen.
§ Bond length not determined due to absence of peak of corresponding PCF.
/ Surface site not present on particular type of surface.

Unprotonated bridging oxygen, BO, forms 0.98-1.36 HBs, which are significantly shorter than in pure water and therefore stronger. When protonated, bridging oxygen BOH does not participate significantly in formation of HBs, but bonds are formed by bridging hydrogen BOH, which creates on neutral hydroxylated surface 0.99 bonds, i.e. significantly more than aqueous hydrogen. The number of bonds of terminal oxygen TOH, 0.92-1.37, is rather big, considering presence of terminal hydrogen. Special situation occurs on the negative nonhydroxylated surface because of presence of neighboring terminal hydroxyls and associated water molecules above 5-fold Ti resulting in formation of H$_2$O-TOH bonds, which are much longer than ordinary HBs but numerous. The origin of these extraordinary long HBs is clear on Figure 3. The chemisorbed water is positioned above the 5-fold coordinated Ti and the distance between the two terminal sites, one with TOH and the other with adsorbed water is given by lattice spacing, i.e. 2.96 Å. This distance is bridged by a H$_2$O-TOH bond length 0.98 Å and by the 2.01 Å long hydrogen bond. This is a situation when the bond length is given by the surface structure. The directionality of the terminal hydroxyl along the surface in this case further leaves the terminal oxygen unhindered from formation of HBs with other water molecules, leading to high number of HBs formed by TOH, i.e. 1.37.
4. MUSIC MODELING

The MUSIC model\textsuperscript{5,6} generalizes the Pauling’s bond valence concept by acknowledging the effect of bond lengths on bond strengths and consequently on the partial charge of an atom. Instead of assuming that the bond valence $v$ of atoms depends only on its charge $z$ and its coordination number $CN$, $v=z/CN$, MUSIC model ascribes the actual bond valence $s$, $s=\exp[(R_0-R)/b]$, which depends on the actual bond length $R$. The atom-specific parameter $R_0$ has been obtained by analysis of the bond valence structures of many crystals; $b$ is a constant, $b=0.37$ Å. The refined version of MUSIC\textsuperscript{5} considers the effect of variation of metal-oxygen bond on the valence of surface oxygens of metal-oxides, but does not consider variations of O-H bond lengths, since valence $s_{H}=0.8$ is chosen for each donor H bond and valence of accepting H bond is then $(1-s_{H})$. Utilization of this value, which is close to that in water, is probably dictated more by the lack of information on actual bond lengths, since the dependence of the valence of HB on its length was correlated long ago\textsuperscript{20} for a variety of anions. However, when molecular simulations of metal oxide surfaces are carried out\textsuperscript{11,12}, one readily obtains information on both the numbers and lengths of various HBs, which should be compared with existing surface models and might lead to their refinement.

As an example of this approach we consider the bridging oxygen on rutile (110) surface. According to MUSIC model, the charge of surface oxygen equals $q_{O}=\Sigma s_{j}+ms_{H}+n(1-s_{H})+V$, where $\Sigma s_{j}$ is the sum of valences of metal cations bonded to oxygen, $m$ is the number of donating HBs, $n$ is the number of accepting HBs, and $V$ is the valence of oxygen, $V=-2$. The total number of hydrogen bonds of a singly coordinated oxygen to the metal is expected to be two for steric reasons, $m+n=2$. For doubly coordinated surface oxygen MUSIC does not give definitive answer and admits formation of either one or two HBs, $m+n=1$ or 2. The case of formation of two bonds by unprotonated bridging oxygen on rutile (110) surface was adopted in both known studies\textsuperscript{5,6}.

Our results do not seem to support the above premise, particularly for hydroxylated surface, since we found that unprotonated bridging oxygen BO forms 0.98 accepting HBs, i.e. $m=0$, $n=1$, and that protonated bridging hydrogen BOH forms close to zero (0.05-0.14) bonds with water molecules (accepting HB) and participates in the donating HB with BOH only, i.e. $m=1$, $n=0$. Without further modification of the MUSIC model, reduction of the number of HBs by one
accepting HB leads to reduction of the oxygen charge by $s_H$, i.e. 0.2. However, we have recognized a second factor determining the valence of bridging oxygen, namely the length of H$_2$O-BO bond, which is 1.65 Å, i.e. by 0.12 Å shorter than in water. According to$^{20}$, this shortening of HB results in the increase of actual bond valence by 0.05.

An even stronger effect might result from the shorter Ti-BO bonds of length 1.872 Å relative to the unrelaxed bond length 1.946 Å$^5$. While the latter gives rise to actual bond valence $s_{Ti} = \exp[(1.808-1.946)/0.37]=0.69$, where $R_0=1.808$ Å is the parameter of Ti bond$^5$, the ab initio derived bond length 1.872 Å$^{11}$ leads to $s_{Ti} = \exp[(1.808-1.872)/0.37]=0.84$. Considering that BO makes bonds with two Ti atoms, the shortening of Ti-BO bond results in increased valence and charge of BO by $2 \times (0.84-0.69)=0.3$.

5. CONCLUSIONS
We have investigated the bond length and number of bonds for all types of hydrogen bonds occurring at rutile (110) surface. We have demonstrated the usefulness of information obtained from hydrogen bonds analysis in application of MUSIC model. In the case studied, the number of hydrogen bonds formed by bridging oxygen was found to be only one compared to assumption of two bonds adopted in MUSIC model of rutile. At the same time the effect of shorter hydrogen bond and shorter bonds with bridging Ti atoms was found to counterbalance the lack of one hydrogen bond. As a result, the resulting charge of bridging oxygen is comparable with the previous prediction of MUSIC. However, the interpretation of that value has been re-worded. This is an example how closer collaboration of computer modeling (ab initio calculations, molecular simulations) with surface modeling might lead to better understanding of surface phenomena.

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REFERENCES