AB INITIO MOLECULAR DYNAMICS STUDY OF WATER DISSOCIATION AND PROTON DYNAMICS ON RUTILE AND CASSITERITE SURFACES

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ABSTRACT

Metal oxides have numerous applications in our everyday lives and in most of these applications their interaction with water is inevitable. Hence, it is important to understand the interactions that occur at the water/metal oxide interfaces. In this dissertation, we have used ab initio molecular dynamics simulations to study these interactions. In particular, we will study the (110) surfaces of the commonly occurring natural polymorphs of titanium dioxide (TiO$_2$) and tin dioxide (SnO$_2$) known as rutile and cassiterite, respectively.

A detailed analysis is presented for the structure of water above the rutile (110) surface. We find three distinct layers of water that are identified as L1, L2 and L3. The water molecules in L1 layer are covalently bonded with the metal atoms in the surface. The L2 layer is highly structured, which is in good agreement with the X-ray studies. The water molecules in this layer adsorb at two well-defined sites. The most prominent location is above and around the bridging oxygen. The other site is located above and between the two terminal oxygens from the L1 layer. The water molecules in the L3 layer do not show any specific adsorption preference. We show that the preferential adsorption sites, in L2 water layer, are produced by strong hydrogen bonds (H-bonds) between the surface and the water layer above the surface. The strength of these H-bonds is estimated from the broadening of the corresponding stretching mode of the vibrational band. The total vibrational spectrum from our ab initio simulations is in excellent agreement with those obtained from the inelastic neutron scattering experiments.

We compare the proton jump processes in the hydration layer on both rutile (110) and cassiterite (110) surfaces. A set of five simulations is done, for both surfaces, to remove the effect of initial configuration on the simulation results. These simulations differ in the dissociation level of the adsorbed water molecules in the initial configurations. We find that all
five simulations equilibrate to ~25% and ~60% water dissociation level on rutile and cassiterite, respectively. This dissociation level is dynamical and both surfaces exhibit proton jumping events for the whole time of the simulation and throughout the whole surface. The cassiterite surface has three times higher proton jumping events than rutile surface. The higher proton jump activity on cassiterite is produced by stronger H-bond between the surface and the water layer above the surface. We find that the stronger covalent and ionic interaction, due to the difference in the electronic structure, leads to stronger H-bond on cassiterite. In general, we find that the H-bonds are stronger on cassiterite than on rutile surface. Among these, the bridging oxygen atoms form the strongest H-bonds between the surface and the hydration layer. Thus, the cassiterite surface has the highest proton jump activity, around 10 times greater than the rutile surface.

Another surface property that provides insight into the interaction of the water with the metal oxide surface is the length of the bond between the bridging or terminal oxygen and the five fold coordinated metal atom on the surface. This metal oxygen (M-O) bond length is sensitive to its local environment. We find that the M-O bond length increases as the number of covalently bonded hydrogen atoms increase on either the bridging oxygen or the terminal oxygen, on both surfaces. The histogram of the M-O bond length is narrower on cassiterite surface indicating stronger M-O bond. The terminal water forms higher average number of H-bonds on rutile surface resulting in an additional broadening of the corresponding M-O bond length histogram. We also find that, along with the number of H-bonds, the species forming the H-bond plays an important role in determining the M-O bond length. The M-O bond length histogram for the dissociated water molecule, on rutile surface, exhibits an interestingly broad peak. A closer look at the H-bonding environment shows that the broad M-O histogram contains
two distinct peaks. We show that one of these peaks is completely due to a specific set of species that forms the H-bond with the dissociated water molecule.

Finally, we study the dependence of dissociation preference of the adsorbed water molecules on the thickness of the slab that is used to model the rutile surface. A three-layer slab shows preference for partial dissociation. But this preference changes as thicker slabs are used in the simulation. Moreover, the adsorption energy difference between the associated and partially dissociated configurations increases monotonically with the slab thickness. We find that this energy difference converges when the atoms below the first layer of the slab are kept fixed at the bulk positions. This indicates that the bulk plays an important role in determining the dissociation state of the water molecules adsorbed on the surface. The H-bond between the bridging oxygen and the water molecule weakens with the increasing slab thickness. We show that the weakening of the H-bond affects the proton transfer that is necessary for obtaining a dissociated configuration. Along with the slab thickness, we also investigate the effect of lateral size of the simulation cell on the dissociation preference. This study shows that a larger simulation cell, with sufficient slab thickness, may eventually prefer fully associated configuration for the adsorbed water molecules.
# TABLE OF CONTENTS

LIST OF FIGURES.............................................................................................................vii

LIST OF TABLES...............................................................................................................xii

ACKNOWLEDGEMENTS.......................................................................................................xiii

Chapter 1 Introduction.........................................................................................................1

Chapter 2 Computational Methods.....................................................................................6

Chapter 3 Vibrational Spectroscopy of Surface Interaction with Water on Rutile (110) Surface..................................................................................................................21

Chapter 4 Proton Transfer Events on Rutile (110) and Cassiterite (110) Surfaces.............36

Chapter 5 Surface M-O Bond Length: A Measure of the Local Environment....................48

Chapter 6 Effect of Slab Thickness on the Adsorbed Water at Rutile (110) Surface...........63

Chapter 7 Summary and Future Directions.......................................................................76

APPENDIX A: Hohenberg and Kohn Theorems.................................................................80

APPENDIX B: Proof of various equations in VDOS calculations......................................82

REFERENCES.....................................................................................................................86
LIST OF FIGURES

Figure 1 The pristine surface of rutile (110) surface with two adsorbed water molecules. The atoms shows are oxygen (red), hydrogen (white) and titanium (grey) atoms. The oxygen atoms, protruding out of the surface is called as bridging oxygen (BO). The adsorbed water molecule, on the left side of the surface, is called as terminal water (TW) and the corresponding oxygen atom is called terminal oxygen (TO). The dissociated water molecule is called as terminal hydroxyl (TH) with one of the hydrogen atom migrated and covalently bonded to neighboring bridging oxygen, which is known as bridging hydroxyl (BH). ........ 2

Figure 2 The simulation cell (Left panel) with 3 layer slab thickness (R3) with oxygen (red), hydrogen (white) and titanium (grey) atoms. The H-bonds are shown by light blue dashed line between the oxygen and hydrogen atoms in the simulation cell. Position histogram [p(z)] of oxygen (red) and hydrogen (black) atoms (Right panel) along the direction perpendicular to rutile (110) surface. The histogram was obtained as an average over 10 ps of simulation at 300K. BO denotes the surface bridging oxygen atoms. L1, L2 and L3 correspond to the three layers of water above the rutile (110) surface. Two kinds of hydrogen atoms were identified as H1 and H2. H1 corresponds to hydrogen atoms bridging between surface oxygen atoms and between hydr... 22

Figure 3 Density plot of the positions, averaged over 10 ps of simulation time, of oxygen atoms in the L2 layer along the three orthogonal directions. The most prominent peak is located around the BO atoms. The x-z and y-z panels show that these water molecules, which are H-bonded to the BO atoms, form an umbrella shaped distribution around the BO atoms indicating strong H-bonding between the surface and the water layer above the surface. The other prominent site corresponds to water molecules bridging between two TW molecules at L1. In the density plot, red corresponds to high density while yellow corresponds to lower density. .......................................................... 24

Figure 4 VDOS of all H atoms present in the simulation at three different temperatures. The peak centered at 25, 50 and 100 THz corresponds to librations, bending and stretching modes of water molecules, respectively. The vibrations of free hydroxyls produce the sharp peak at 120 THz. The rise in temperature weakens the H-bond network and results in blue shift of the stretching mode. ............................................................... 28

Figure 5 The stretching band of H1, H2 and H3 category of H atoms deconvoluted from the total VDOS calculation for three temperatures. H1 atoms are closest to the surface. These atoms form H-bonds between L1 oxygen atoms, between L1 and BO, and between BH and L2. H2 is the layer of H atoms that form H-bonds between L1 and L2, and between BO and L2. All of the remaining H atoms, including those at the interface between water and vacuum, belong to H3. The plot shows that at all temperatures, H2 dominates the lower part of the spectrum with some contribution from H1 atoms and no participation from H3 atoms. This shows that the strongest H-bonds are formed among surface species. The sharp peak at 120 THz is produced by OH bonds at the interface between water and vacuum, which belongs to H3 category. .............. 30
Figure 6 Linear relationships between the H-bond length and the stretching mode for different kind of H-bonds (symbols are described in Table 1). The insets on the upper left corner of the plot show the VDOS of three representative cases and the lower left corner shows the corresponding H-bond distance histogram. The surface-water H-bonds are shown with empty symbols, whereas, surface-surface or water-water h-bonds are shown with filled symbols. The three colors correspond to three temperatures, 280 K (black), 300 K (orange) and 320 K (red).

Figure 7 Deconvoluted VDOS of H atoms participating in three different kinds of H-bonding (pictorially shown in the top panel). The strength of H-bond between surface and water layer (Ti2O---HOH and TiHOH---HOH) is stronger as can be seen from weaker stretching band frequency.

Figure 8 Dissociation percentage of terminal water molecules on the (110) surfaces of rutile (solid line) and cassiterite (dashed line). The five different lines for each surface correspond to five different dissociation states, 0% (—), 25% (——), 50% (——), 75% (——), and 100% (——), of the equilibrated initial configurations with which the simulation was started. After first 3 ps, the system equilibrated to ~60% and ~25% for cassiterite and rutile surface, respectively. The fluctuations in dissociation percentage represent the proton jump events. Cassiterite shows more than three times faster proton jump rate than rutile.

Figure 9 Dissociation percentage curves of rutile (black) and cassiterite (red) surfaces. Left panel (a): Last 5 ps of simulation for the materials in their normal lattices. Right Panel (b): First 5 ps of simulation for the materials with exchanged cation atoms. The initial configuration for exchanged cation simulation is the last step of the normal simulation. A rise in dissociation percentage and proton jump rate is observed when tin atoms, in the rutile lattice, replace titanium atoms. An opposite trend is seen for the cassiterite lattice. This shows that electronic structure and not the lattice size affects the dissociation state and the proton jump rate.

Figure 10 Density plot of position of O atoms in the L2 layer for (a) cassiterite and (b) rutile. The horizontal dashed lines are plotted for reference. The darker regions correspond to locations where water molecules reside for longer time. For both surfaces, water molecules cluster around the BO atom, forming an umbrella like structure in the position density plot. The histogram, not shown here, for the distance between the O atom of WO in L2 and the O atom of BO shows that the L2 is 0.06 Å closer to the surface on cassiterite than on rutile.

Figure 11 H-bond lengths and corresponding weighted mean of stretching band frequency for all, statistically significant, H-bonds on the (110) surface of cassiterite (orange) and rutile (black). The symbols used are described in the inset. M symbolizes the metal atom, i.e. titanium for rutile and tin for cassiterite. The bold O and H refer to those atoms that are participating in the H-bond. The donor O atom and acceptor H atom of a H-bond are always written on left and right side, respectively, of the dash line in the symbol definition of the inset. The number 1, 2 or 3 refers to the number of H-bonds accepted by the acceptor O atom. H-bonds are, in general, stronger on cassiterite than rutile surface as shown by the smaller H-bond length and corresponding weaker stretching band frequency.
Figure 12 The energy difference between the valence states, 1b_2 and 3a_1, of water molecule as a function of the distance (d) between the O atoms of BO and WO for rutile (black) and cassiterite (orange) surface. The water molecule is positioned just above the BO with one of its H atom pointing towards the BO (shown in inset). The 3a_1 state is more stable, by 0.3 eV, on cassiterite than on rutile surface. This indicates that the covalent component of H-bond is stronger on cassiterite surface.

Figure 13 The evolution of M-O bond length with simulation time, for a TO (top panel) and a BO (bottom panel), on the rutile surface. The M-O bond length changes significantly as the number of H atoms changes from 1 to 2, for TO, or from 0 to 1, for BO. Top panel: A TO changes from TW (red) to TH (black) at around 2.5 ps, and changes back to TW at around 3.6 ps. This process is repeated as TW->TH->TW at around 5.7 and 6.9 ps. Bottom Panel: A BO changes from BH (black) to BB (red) at around 3 ps. The width of oscillation of M-O bond length appears broader for TW/TH than for BB/BH, on rutile. The surface species, TW, TH, BB and BH, are shown pictorially in the region of their existence.

Figure 14 Histograms of M-O bond length for surface species BB (o), BH (□), TH (x) and TW (Δ) on cassiterite ((A), red) and rutile ((B), black) surfaces. All of the surface species on rutile has broader histogram, which indicates that the M-O bond is, in general, weaker on rutile than on cassiterite. The peak positions of the histogram are shorter on rutile except for the TW that appears to be similar on the two surfaces.

Figure 15 Potential profiles of a TW molecule approaching the pristine (110) surface of rutile (black, •) and cassiterite (red, □) with the O atom of the water molecule pointing towards the five fold coordinated metal atom. The minimum of the potential profile is at 2.12 Å, for rutile, and 2.20 Å, for cassiterite. Moreover, the potential profile is deeper for rutile, by 0.1 eV, than cassiterite. Thus, TW will form a shorter and stronger bond with the metal atom of the surface. The curvature is similar for the two potential profiles, which indicates that the M-O histogram of the TW should be comparable for both surfaces.

Figure 16 Histogram of M-O bond length for TH (x), on rutile surface, forming 2 (◊) and 3 (*) H-bonds. The histogram for the 2 H-bond shows two distinct peaks at 1.88 Å and 2.02 Å. The dual peak indicates the possibility of two different H-bonding environments.

Figure 17 Histogram of M-O bond length for TH forming 2 H-bonds (◊) with its various neighbors on rutile (110) surface. The double peak in the TH_2 histogram originates from the differences in the H-bonding environment. The first peak at 1.88 Å appears when the TH molecule acts as donor for one and an acceptor for another H-bond. There are three different H-bonding environments that belong to this category. First, TH accepts a H-bond from a W molecule and donates another H-bond to a TW (+, TH2_aTW_dW). Second, TH accepts a H-bond from TW and donates the other H-bond to a W molecule (○, TH2_aW_dTW). Third, TH donates a H-bond to another TH and accepts a H-bond from a W molecule in the water layer above the surface (△, TH2_aTH_dW). The second peak at 2.02 Å appears when TH acts as acceptor for both of the H-bonds. In this the H atom of the TH does not participate in any H-bonding and it accepts one H-bond from the neighboring TW and the other H-bond from the W above the surface (∇, TH2_dTW_dW).
Figure 18 M-O bond length histogram for all of the surface species with various numbers of H-bonds containing different kinds of H-bonding environments. The largest curves in all of these plots are of BB_1 (a1, a2), BB_2 (b1, b2), BH_1 (c1, c2), BH_2 (d1, d2), TH_2 (e1, e2), TH_3 (f1, f2), TW_2 (g1, g2) and TW_3 (h1, h2). All other curves below the largest curve, in each plot, belongs to the various H-bonding environments that constitute the corresponding surface species with specific number of H-bonds. The plot numbering ‘1’ and ‘2’ (for e.g. a1 and a2) corresponds to cassiterite (red) and rutile (black) surface, respectively. The x-axis refers to M-O bond length and it is in the range 1.6 – 2.7 Å for all of the plots................................................................. 61

Figure 19 The two side views [(a) and (c)] of a seven-layer thick slab (R7) simulation cell, with the central layer fixed at the bulk positions, of pristine rutile (110) surface. The top view of the 2x1 surface unit cell (b) with each surface unit cell marked with the blue rectangle, containing exactly one BO and one five fold coordinated metal atom. The O-Ti-O triple layer is shown with dash lines in (a). The atoms in red and grey are oxygen and metal atoms, respectively.................................................................................................................. 64

Figure 20 The dependence of adsorption energy difference (eV/water molecule) between fully associated and partially dissociated configurations (E_{ads}^{INTACT} - E_{ads}^{PDIS} ), on rutile (110) surface, on the number of O-Ti-O triple layers (R_n). The plots with dotted lines are the geometries where either the bottom most layer (▲, from [78]) or the central layer (●) of a slab is fixed at bulk positions, to mimic the bulk behavior. The plot with solid line is the geometry, where all atoms below first triple O-Ti-O layer (■) are frozen to their bulk positions........... 66

Figure 21 H-bond lengths with increasing slab thickness, from R3 to R15, on both associated and partially dissociated configurations. The plots drawn with open symbols and dash lines are for H-bonds on geometries where only the central layer of the slab is kept fixed at crystallographic positions. The plots with filled symbols and solid lines correspond to H-bonds on slab where all atoms below first triple O-Ti-O layer are frozen to their bulk positions. The H-bonds plotted are TiO---TiOH (●, ◦), TiOH---TiHOH (●, ◦) and TiOH---TiOH on dissociated configuration (■, ◻), and TiO---TiHOH on associated configuration (▲, △). ......................................................................................................................... 68

Figure 22 Energy profile for the process of dissociation of water molecules on the rutile (110) surface with 1 ML of water coverage. The simulation cell changes from a fully associated configuration (Configuration 0) to a partially dissociated configuration (Configuration 6) on a R3 (□) and R5 (*) slab. The water dissociation occurs in steps on the two sides of the slab (Configuration 2 and Configuration 5). The energy profile shows that the R3 slab easily dissociates partially whereas the R5 has a large energy barrier for partial dissociation. The energy values of each configuration are resealed with respect to the associated configuration i.e. configuration 0 for both R3 and R5 slabs.............................................................. 69

Figure 23 Adsorption energy difference (eV/water molecule) between fully associated and a partially dissociated configurations (E_{ads}^{INTACT} - E_{ads}^{PDIS} ), where only one water molecule is dissociated on each side of the slab, on R3 (□) and R5 (*) slabs of rutile (110), with varying lateral size of the simulation cell. The ‘nxm’ lateral size corresponds to ‘n’ column
and ‘m’ rows of surface unit cells. The amount of water coverage is 1 ML, which corresponds to one water molecule per five fold coordinated titanium (Ti$^{5+}$) atom, for all surfaces. The smaller simulation cells (2x1 and 2x2) prefer associated configuration for thicker slab (R$_3$). Whereas, the larger simulation cells (4x2 and 4x4) shows preference for partially dissociated configuration on both R$_3$ and R$_5$ slabs.

Figure 24 Adsorption energy difference (eV/water molecule) between fully associated and a partially dissociated configurations ($E^{\text{INTACT}}_{\text{ads}} - E^{\text{DILS}}_{\text{ads}}$), on rutile (110) having 4x2 surface unit cells as the lateral size with slab thickness R$_3$ (□), R$_5$ (★) and R$_7$ (△). The amount of water dissociation considered are 0%, 12.5%, 25% and 37.5% that corresponds to 0, 1, 2 and 3 water molecules dissociated on each side of the slab, respectively. All possible location of water dissociation for 2 and 3 water molecules are shown diagrammatically on left and right side of the plot, respectively. The bigger rectangle represents the surface of 4x2 surface unit cell where each square box corresponds to one surface unit cell containing one TW and one BO. The dark square box represents dissociated water molecule where it contains one TH and one BH.
LIST OF TABLES

Table 1 H-bond distance and frequency for various types of H-bonds on hydrated rutile (110) surface. The frequencies (ν) and distances (d) are expressed in THz and Å, respectively. The H-bond configuration where O accepts one or two H-bonds are identified with roman numeral I or II and the column P gives the relative abundance of these two configurations. The empty cells correspond to those configurations that are not statistically significant. ... 33

Table 2 Average proton jump rate of proton transfer between BO, TO and WO in the hydration layer for (110) surfaces of rutile and cassiterite. Cassiterite exhibits higher proton jump rate in all of the categories except for TO-TO, which could be due to larger lattice spacing. The hydrated rutile surface shows no direct proton jumping events between surface species (BO and TO). ................................................................. 40

Table 3 Peak position and the half width at half maximum (HWHM) of the histogram of M-O bond lengths, for surface species BB, BH, TH and TW, on cassiterite and rutile surfaces.. 52

Table 4 Peak position and the half width at half maximum (HWHM) for surface species BB, BH, TH and TW forming 1, 2 or 3 H-bonds on cassiterite and rutile surface. ‘BB_1’ corresponds to those BB that forms 1 H-bond with its neighbors. ................................................................. 56
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Chapter 1

Introduction

Metal oxides play a crucial role in our everyday life. In particular, titanium dioxide (TiO$_2$) and tin dioxide (SnO$_2$) have applications in both industry and in households. The photo catalytic property of TiO$_2$ [1] makes it a good candidate for use in solar cells. A colloidal suspension of TiO$_2$ nanoparticles coated with dye molecules converts, economically and efficiently, solar energy into electricity [2]. The TiO$_2$ surface photo-assists the degradation of organic molecules into harmless CO$_2$ and H$_2$O. This property is used in applications such as purification of wastewater [3], as a disinfectant [4] and in making self-cleaning glasses [5]. The non-toxicity and high refractive index of TiO$_2$ makes it suitable for use as pigments in virtually every kind of paint. The ability to change the conductivity with gas adsorption leads to its use in making oxygen gas detectors [6]. SnO$_2$ is also an excellent gas sensor and it is heavily used in making carbon monoxide (CO) detectors [7]. A filament of SnO$_2$ is placed inside the CO detector and a continuous current is passed through it. The adsorption of CO decreases the resistance of the filament, which in turn can be used to monitor the CO level. Both metal oxides, TiO$_2$ and SnO$_2$, are also used in the heterogeneous catalysis [8,9]. In all of these applications water is ubiquitous. Under ambient condition, it is found that a few layers of water condenses on the surface of both metal oxides [10]. Hence, any technological advancement in the applications of these materials will depend crucially on our understanding of the interactions of water with the metal oxide surface.

We study the most commonly occurring natural polymorphs of TiO$_2$ and SnO$_2$ known as rutile and cassiterite, respectively. Both of these iso-structural metal oxides have the same tetragonal structure and belong to the same symmetry group P4$_2$/mnm. The (110) faces are found
to be dominant in both of these materials [10]. Figure 1 shows the pristine (110) surface of rutile along with the adsorbed water molecules. The pristine (110) surface, for both rutile and cassiterite, has oxygen atoms protruding out of the surface, which is known as the bridging oxygen (BO). The pristine surface also has under coordinated metal atoms that are excellent locations for the water molecules to adsorb covalently. These adsorbed water molecules are called terminal water (TW) and the corresponding oxygen atom is known as terminal oxygen (TO). The molecular water is also known as associated configuration. The water coverage is defined to be one monolayer (ML) when exactly one water molecule is present for each of the five fold coordinated metal atom. The water molecules can dissociate, known as dissociated configuration, where one of the hydrogen (H) atom from TW migrates to the neighboring BO, resulting in formation of a pair of hydroxyls i.e. terminal hydroxyl (TH) and bridging hydroxyl (BH). The BO without any covalently bonded H atom is known in the literature as bare bridging (BB).

Figure 1 The pristine surface of rutile (110) surface with two adsorbed water molecules. The atoms shows are oxygen (red), hydrogen (white) and titanium (grey) atoms. The oxygen atoms, protruding out of the surface is called as bridging oxygen (BO). The adsorbed water molecule, on the left side of the surface, is called as terminal water (TW) and the corresponding oxygen atom is called terminal oxygen (TO). The dissociated water molecule is called as terminal hydroxyl (TH) with one of the hydrogen atom migrated and covalently bonded to neighboring bridging oxygen, which is known as bridging hydroxyl (BH).
There exists a long standing discrepancy both between different theories and between theory and experiment about the percentage of water that is dissociated on the surface [11–15]. Goniakowski and Gillan [11] presented one of the earliest first-principles calculations on comparisons of water adsorption on rutile and cassiterite (110) surface. Their static calculation suggested that an unsymmetric fully dissociated configuration was energetically preferred, for 1 ML water coverage, for both surfaces. Later, Lindan et al. [16] corroborated this finding in their DFT-MD simulations on half ML coverage where it was reported that both surfaces preferred fully dissociated configuration. But, for 1 ML coverage it was shown that rutile preferred a mixed configuration [17] whereas cassiterite continued to prefer fully dissociated configuration [18]. In experiments, the presence of hydroxyl groups on the rutile surface were detected by ultraviolet photoelectron spectroscopy [19] and later confirmed in synchrotron radiation studies [20]. Later, Henderson did high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) experiments [15] to find that the rutile surface does not have any dissociated water molecules. The M-O bond length, for the bond between the TO and the five fold coordinated metal atom of the surface, is very sensitive to the hydrogenation state of the TO. Based on this M-O bond length, Allegretti et al. [14] showed that the photoelectron diffraction experiments on rutile, with 1 ML water coverage, indicated fully associated configuration for the adsorbed water molecules. Whereas, the M-O bond length obtained in the X-ray crystal truncation rod (CTR) study suggested a partial dissociation of 30 ± 15% for the rutile (110) surface covered with several layers of water. On cassiterite surface, it is generally agreed that the degree of dissociation is larger than on rutile surface [18,21,22]. The TPD experiment by Gercher and Cox [23] suggests the presence of both associated and
dissociated water molecules on cassiterite surface. The dissociation state of water on these surfaces is therefore not well established.

We have done a computational study of the water/metal oxide interface using ab initio molecular dynamics (aiMD) simulations. The quantum mechanical treatment for the interface is selected as it allows for bond breaking which is necessary for estimating the amount of dissociation and studying the proton jumping events. The aiMD simulations are computationally expensive, which in turn severely limits the system size and the duration of the simulation. Hence, with the state of the art computational resources available, we could simulate an interface of few angstroms in size, containing around 400 atoms, and explore the dynamics that are in the range of couple of picoseconds (ps).

This dissertation is organized as follows. In Chapter 2, we will introduce the theoretical methods that are used to solve the many body equations using the density functional theory (DFT). A description of the general setup of the simulations is presented thereafter. In Chapter 3, we will present the study of water above the rutile surface. We will show that aiMD predicts around 25% water dissociation for the rutile surface. The water molecules in the layer just above the surface show preferential adsorption location, which has a general agreement with the X-ray CTR measurement. In Chapter 4, we will show that the cassiterite surface exhibits around 3 times more proton jumping events than the rutile surface. The higher proton jump rate will be linked to stronger H-bond formation on cassiterite surface. In Chapter 5, we will study the M-O bond length and show that this bond length contains crucial information about the local environment. The local environment will correspond to the hydrogenation state of the oxygen atoms, the number and the kind of H-bonds formed by the corresponding oxygen atom. In Chapter 6 we will present the study of the dependence of dissociation preference of the adsorbed
water molecules on the slab thickness that is used to model the rutile surface. We will explore the
effect of increasing not only the slab thickness but also the lateral size of the simulation cell on
the dissociation state of the adsorbed water molecules. Finally, in Chapter 7, we will summarize
the results and briefly discuss future directions.
Chapter 2

Computational Methods

The aiMD simulations are based on quantum mechanical electronic structure theories. In this chapter, we will describe the fundamental theories behind solving the many-body electronic structure problems. A detailed description of the preparation of the simulation cell with appropriate selection of various parameters will be described later in the chapter. In the end, we will discuss the theory behind calculating the vibrational density of states (VDOS) from the trajectory information of the simulation.

Many-Body Equation

The non-relativistic electronic structure description of a many-body system of interacting electrons and nuclei is obtained by solving the Schrödinger’s equation:

\[ H\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R}) \]  \hspace{1cm} (2.1)

where, \( H \) is the Hamiltonian operator and \( E \) is the total energy of the system. \( \Psi(\vec{r},\vec{R}) \) is the corresponding wave function that depends on the coordinates of the electrons (\( \vec{r} \)) and nuclei (\( \vec{R} \)) in the many-body system.

Under the assumption of treating electrons and nuclei as point particles and neglecting any relativistic interactions, the Hamiltonian operator for the many-body system is given by:

\[
H = T_e + V_{ne} + T_n + V_{ee} + V_{ne} \\
= -\frac{1}{2} \sum_{A=1}^{M} \frac{1}{m_A} \nabla_A^2 + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \\
- \frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} \hspace{1cm} (2.2)
\]
where, atomic units \( (\hbar = m_e = e = [4\pi / \varepsilon_0] = 1) \) are used. Here, A and B refer to nuclei; j and i refer to electrons. The total number of electrons and nuclei are N and M, respectively. The operator \( \nabla^2 \) is the Laplacian operator.

In eq. (2.2) the first term on the right hand side \( (T_n) \) corresponds to the kinetic energy of M nuclei with each having a mass \( m_A \). The second term \( (V_{nn}) \) describes the inter-nuclear columbia repulsion between two nuclei of atomic number \( Z_A \) and \( Z_B \). The next term \( (T_e) \) is the kinetic energy of \( N \) electrons and the following term \( (V_{ee}) \) describes the interaction between electrons. The last term \( (V_{ne}) \) describes the columbia attraction between the electrons and nuclei of the system.

The mass of the nuclei is much greater than the mass of electrons (the lightest nucleus i.e. proton is \( \sim 1836 \) heavier than an electron). This means that the electrons move much faster than the nuclei and it can adiabatically adjust to any change in the position of the nuclei. This is known as the Born-Oppenheimer approximation [24]. This approximation allows us to separate the total wave function \( \Psi(\vec{r}, \vec{R}) \) into electronic and nuclear wave functions:

\[
\Psi(\vec{r}, \vec{R}) = \Psi_{e,R}(\vec{r})\Psi_n(\vec{R})
\]

(2.3)

where, \( \Psi_n(\vec{R}) \) is the nuclear wave function and \( \Psi_{e,R}(\vec{r}) \) is the electronic wave function for a fixed nuclei configuration \( (R) \). Under Born-Oppenheimer approximation the kinetic energy of the nuclei is neglected and the nuclear repulsion term \( (V_{nn}) \) is treated as a constant. Hence, the problem of finding the electronic structure description for a many-body system reduces to solving the following electronic Schrödinger equation:

\[
H_{e,R}\Psi_{e,R}(\vec{r}) = E_{e,R}\Psi_{e,R}(\vec{r})
\]

(2.4)
where, $H_{e,R}$ and $E_{e,R}$ are the electronic Hamiltonian and the electronic energy for the fixed nuclei configuration, respectively. The electronic Hamiltonian contains three terms:

$$H_{e,R} = T_e + V_{ee} + V_{ne}$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \sum_{j\neq i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|r_i - \mathbf{R}_A|}$$

(2.5)

The total energy of the system is calculated as the sum of the electronic energy and the nuclear energy. The nuclear energy component, with fixed nuclear configuration as per Born-Oppenheimer approximation, only has the nuclear repulsion term:

$$E = E_{e,R} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

(2.6)

The electronic energy can be calculated from the electronic wave function as the expectation value of the electronic Hamiltonian:

$$E_{e,R} = \frac{\langle \Psi_{e,R}(\vec{r}) | H_{e,R} | \Psi_{e,R}(\vec{r}) \rangle}{\langle \Psi_{e,R}(\vec{r}) | \Psi_{e,R}(\vec{r}) \rangle}$$

(2.7)

**Density Functional Theory**

Although the Born-Oppenheimer approximation simplifies the Schrödinger equation, it is still impossible to exactly solve for electronic wave function due to the many body terms that is encompassed in the electron-electron interaction ($V_{ee}$). Moreover, the wave function depends on the coordinates of each electron, which is a rather large number ($3N$) for any real system. Hence, an actual determination of the electronic wave function is cumbersome and computationally very expensive. In 1964, Hohenberg and Kohn [25] proposed a way to circumvent the problem of dealing with the many-body wave function by proving two key theorems in their seminal paper:
(i) for any system of interacting particles in an external potential \(V_{\text{ext}}(\vec{r})\), there exist a ground state particle density \(n_0(\vec{r})\) that uniquely identifies the \(V_{\text{ext}}(\vec{r})\), except for a constant; and (ii) the total energy of a system can be written as a functional of the particle density corresponding to a given \(V_{\text{ext}}(\vec{r})\). The global minimum of this functional, which is the ground state energy of the system, will yield the \(n_0(\vec{r})\). The proofs of these two theorems are shown in Appendix A. The total energy of the system can be written in Hohenberg-Kohn formalism as energy functional:

\[
E_{\text{HK}}[n(\vec{r})] = F_{\text{HK}}[n(\vec{r})] + \int d^3 r V_{\text{ext}}(\vec{r}) \, n(\vec{r}) \tag{2.8}
\]

The \(F_{\text{HK}}[n(\vec{r})]\) contains kinetic energy and electrostatic interaction of electrons whereas the second term results from the interaction of the electrons with an external potential \(V_{\text{ext}}(\vec{r})\), produced by the frozen nuclei.

Hohenberg and Kohn theorem promised the existence of a 3-dimensional ground state density \(n_0(\vec{r})\), which could save the tedium of dealing with a \(3N\) dimensional wave function, however it did not provide any recipe for finding \(n_0(\vec{r})\). A route to finding \(n_0(\vec{r})\) was suggested by Kohn and Sham [26]. The basic idea behind Kohn-Sham formalism is to replace the many-body interacting system with a many-body non-interacting system. The interactions are incorporated into an exchange and correlation functional. The basic assumption in preparing the auxiliary non-interacting system is that its ground state density is same as that of the interacting system. Kohn and Sham suggested that the term \(F_{\text{HK}}[n(\vec{r})]\), in Eq. (2.8), should be approximated as:

\[
F_{\text{HK}}[n(\vec{r})] = E_{\text{KE}}[n(\vec{r})] + E_{\text{H}}[n(\vec{r})] + E_{\text{XC}}[n(\vec{r})] \tag{2.9}
\]
where, $E_{KE}[n(\vec{r})]$ is the kinetic energy of a system of non-interacting electrons with the density of the interacting system, $E_H[n(\vec{r})]$ is the electron-electron columbic repulsion and $E_{XC}[n(\vec{r})]$ is the exchange and correlation. The first two terms have an explicit form:

$$E_{KE}[n(\vec{r})] = \sum_{i=1}^{N} \int d^3r \psi_i(\vec{r}) \left( -\frac{\nabla_i^2}{2} \right) \psi_i(\vec{r})$$

(2.10)

where, $\psi_i(\vec{r})$ is the wave function of electronic state $i$. The second term in Eq. (2.9) is the Hartree electrostatic energy that arises from the classical interaction between two charge densities:

$$E_H[n(\vec{r})] = \frac{1}{2} \int d^3r_1 d^3r_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|}$$

(2.11)

The Kohn-Sham formalism rewrites the ground state total energy functional of Hohenberg-Kohn of Eq. (2.8) including the ion-electron interaction as:

$$E_{KS}[n(\vec{r})] = \sum_{i=1}^{N} \int d^3r \psi_i(\vec{r}) \left( -\frac{\nabla_i^2}{2} \right) \psi_i(\vec{r}) + \frac{1}{2} \int d^3r_1 d^3r_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|}$$

$$+ E_{XC}[n(\vec{r})] - \sum_{A=1}^{M} \int d^3r \frac{Z_A}{|r_i - R_A|} n(\vec{r})$$

(2.12)

Using the definition of electronic charge density:

$$n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2$$

(2.13)

and applying the variational principle to the Kohn-Sham total energy functional, i.e. Eq. (2.12), results in the one-electron Kohn-Sham equation of the auxiliary non-interacting system:

$$\left\{-\frac{\nabla_i^2}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{|r_i - R_A|} \right) + \int d^3r_2 \frac{n(r_2)}{|r_i - r_2|} + V_{XC}(r_i) \right\} \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

(2.14)

where, $\varepsilon_i$ are the orbital energies and $V_{XC}(r_i)$ is the exchange-correlation potential that is associated with the exchange-correlation energy as:
\[ V_{xc}(\vec{r}_i) = \left( \frac{\partial E_{xc}[n(\vec{r})]}{\partial n(\vec{r})} \right) \] (2.15)

The Hohenberg-Kohn theorems and the Kohn-Sham equations developed so far, under Born-Oppenheimer approximation, are exact. The only factor, that limits the determination of exact ground state energy, is the exchange-correlation energy term \( E_{xc}[n(\vec{r})] \). The precise form of \( E_{xc}[n(\vec{r})] \) is not known and hence the success of Kohn-Sham DFT relies completely on the accuracy of the exchange-correlation functional.

The calculation for the true ground state starts with a prediction, where a pre-selected set of orbitals are used to obtain the density which is further used in calculating the potentials. This information is used to calculate a new ground state and hence a new density. Again the above procedure is repeated. This methodology is iterated until a desired convergence is achieved. This is called as self-consistent field method. The converged charge density is used to obtain the ground state energy.

**Exchange-Correlation Functionals**

Kohn and Sham [26] proposed the first guess for the exchange-correlation energy functional. It is known as Local Density Approximation (LDA). The real exchange-correlation energy is replaced with the exchange-correlation energy of a uniform electron gas \( \epsilon_{\text{unif}} \) of same density:

\[ E_{xc}[n(\vec{r})] = \int d^3r \ n(\vec{r}) \ \epsilon_{\text{unif}}^{\text{xc}}[n(\vec{r})] \] (2.16)

The corresponding exchange-correlation potential is:

\[ V_{xc}(\vec{r}) = \left( \frac{\partial E_{xc}[n(\vec{r})]}{\partial n(\vec{r})} \right) = \epsilon_{\text{unif}}^{\text{xc}}[n(\vec{r})] + n(\vec{r}) \frac{\partial \epsilon_{\text{unif}}^{\text{xc}}[n(\vec{r})]}{\partial n(\vec{r})} \] (2.17)
The exchange-correlation energy of uniform electron gas can be further separated into exchange energy and correlation energy. The exchange energy for the homogeneous gas can be calculated exactly [27] as:

\[ E_{\text{X}}^{\text{LDA}}[n(\vec{r})] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \int d^3r \ (n(\vec{r}))^{\frac{4}{3}} \]  

The exact analytical form of correlation energy is not known. It is generally obtained by fitting to highly accurate quantum Monte Carlo calculations of free electron gas [28]. There are several functionals that were developed based on the various ways of fitting the free electron gas data. The Perdew-Zunger (PZ) [29] and Perdew-Wang (PW) [30] functionals are some of the common LDA functionals. The assumption of a uniform density, in the exchange-correlation functional i.e. Eq. (2.18), possess a straightforward limitation on the range of applications of LDA. It typically underestimates the bond lengths and overestimates the binding energy. It can be significantly improved by including the gradient of the density \( \nabla n(\vec{r}) \) along with the density itself in the exchange-correlation term. These functionals are known as the generalized gradient approximation (GGA) and has the form:

\[ E_{\text{XC}}^{\text{GGA}}[n(\vec{r})] = \int d^3r \ n(\vec{r}) \epsilon_{\text{XC}}^{\text{GGA}}[n(\vec{r}),\nabla n(\vec{r})] \]  

GGAs are semi-local functionals and produce better results for many physical properties such as ground state energies, geometrical structures, bond lengths, binding energies etc. There exists several version of GGAs based on different construction of exchange-correlation functionals. The work presented here uses, as in many surface science studies, the GGA functional developed by Perdew, Burke and Ernzerhof (PBE) [31,32]. This functional produces very good structural prediction and yields much accurate bulk modulus and cohesive energy [33] than that estimated by LDA functional.
**Preparation of Simulation Cell**

The water/metal oxide interface is modeled in a periodic cell that comprises a periodic slab geometry of metal oxide and a 21 Å thick vacuum. The surfaces of both metal oxides are oriented along the (110) direction with BO termination. This result in an anhydrous surface that exposes repeating rows of under coordinated BO atoms protruding above the surface. In parallel to the row of BO atoms, there is a row of under coordinated metal atoms that provide an excellent location for an incoming water molecule to bond covalently to the surface. The available computational resources and targeted simulation time length restricted us to use simulation cells containing two columns with four \( \text{M}_2\text{O}_4 \) surface units (M = Ti or Sn) cells in each of the columns. The dimension of the simulation cell, parallel to the surface, for cassiterite is 13.399 Å and 12.746 Å. For rutile, 12.994 Å and 11.836 Å is the simulation cell dimension along the surface. The slab comprises three metal–oxygen planes of which two of the planes form the surface. The middle plane is kept fixed at the bulk positions to mimic the bulk behavior. The simulation box has a dimension of 30 Å along the direction perpendicular to the plane of the metal oxide slab. This results in a vacuum gap of 21 Å between the planes of BO atoms on the two ends of the slab. On hydrating the surfaces, an average vacuum gap of around 9 Å and 6.3 Å remains between the water layers on the cassiterite and rutile surface, respectively. A vacuum gap of 6–10 Å has been shown [11,22,34] to successfully reproduce the surface properties in a 3D slab modeling of metal oxide surfaces. Zhang and Lindan [34] showed that a vacuum gap of around 7 Å was sufficient to converge typical adsorption energy to within 1% with respect to the size of the gap. The amount of water that is used to hydrate the pristine metal oxide surfaces closely mimics the hydration level of the nanoparticles, which was determined by Mamontov *et al.* [10] using neutron scattering experiments. The nanopowder was exposed to laboratory air and
the nanoparticles were found to have predominantly (110) surfaces. The amount of water was estimated to be 4 and 3.5 H$_2$O molecules per M$_2$O$_4$ surface unit at the cassiterite and rutile surfaces, respectively. Hence, our cassiterite model contains 64 water molecules and the rutile cell has 48.

Water systems have large relaxation time that is too expensive to be reached by aiMD. Hence, the initial configuration for the aiMD simulation is obtained from a classical molecular dynamics (CMD) approach. A M$_2$O$_4$ surface unit cell with water placed at reasonable position is replicated four times in one direction and two times in other direction to obtain a super cell with eight surface unit cells. This super cell is used as the initial configuration for relaxation and thermalization with CMD at 300K. The force field of Bandura et al. [35] for cassiterite and the force field of Bandura and Kubicki [36] for rutile are used in running the CMD. The General Utility Lattice Program (GULP) [37] is used for doing the CMD. The CMD simulation is done for more than 0.5 ns until the total energy drift is negligible. The relaxed and thermalized final configuration from this CMD treatment is used as the input for the aiMD simulation.

The Vienna ab initio simulation package (VASP) [38–41] is used for doing the aiMD simulation. The forces have been calculated within DFT [25,26] with a plane wave basis set as implemented in the VASP. A frozen core projector augmented wave (PAW) [42,43] scheme is used for treating the core electrons. The 14 electrons in 4d, 5s and 5p orbitals of Sn and 12 electrons in 3d, 4s and 3p orbitals of Ti are treated as valence electrons. We use 282.8 eV as the energy cutoff for both surfaces. The large dimensions of the simulation cells suggest that it is sufficient to do one k-point, at $\Gamma$, sampling for the Brillouin zone. The exchange and correlation potential was treated in the generalized gradient approximation of Perdew et al. [31,32] A constant volume and temperature ensemble is used in doing the aiMD. The temperature is
maintained constant using the Nosé–Hoover thermostat [44,45] as implemented in the VASP. The equations of motions are integrated using the Verlet algorithm. A time step of 0.5 fs is used in the aiMD simulation to properly sample the high frequency vibrations of the H atoms. The 50 ps trajectory for both surfaces were obtained at two different centers. The simulation of cassiterite surface used 256 Cray XT cores for a total of 412 K central processing unit (cpu) hours at National Energy Research Scientific Computing Center (NERSC). The rutile surface simulation was done locally using 16 cores for a total of 101K cpu hours at the lion-X clusters at Penn State. The various analysis reported in this work was performed locally on lion-X and the Cyberstar cluster.

The 50 ps trajectory comprises a set of five simulations with each simulation being around 10 ps long. These simulations have different equilibrated initial configuration with 0%, 25%, 50%, 75% and 100% water dissociation on the surface. In 3 ps, simulations with different initial dissociation level converge to a constant dynamical dissociation level of ~60% and ~25% for cassiterite and rutile, respectively. A H-bond involves a pair of accepting and donating centers. The oxygen (O) that accepts a H-bond is called as acceptor and the O with which the H of H-bond is covalently bonded is called a donor. In simulation, a H-bond is identified as per the standard definition [46,47] using geometrical parameters. In this definition, H-bond is said to exist if the distance between the acceptor O and H is less than 2.3 Å and the angle between the acceptor O, donor O, and H is less than 30°. [27,28] We have tested other alternative definitions of H-bond and our results are found to be unaffected by the particular definition selected. [49–51]
**VDOS determination from trajectory information**

The dynamical aspect of the simulation is studied by analyzing the VDOS of H atoms. The heavier atoms like O, Ti or Sn have very low frequency vibrations, for e.g. ~2 THz for the O atom in the liquid water [52], in comparison to the lighter H atoms. The ab initio simulations are computationally expensive and thus the simulations are of generally small duration, around few picoseconds. The short simulation length and the low frequency of heavier atoms limit our analysis to vibrations of H atoms only. The stretching mode of the vibrations of H atoms contains crucial information about the strength of H-bonds formed by them. A softer stretching band corresponds to stronger H-bond and a stronger stretching band corresponds to weaker H-bond. The VDOS can be estimated from the trajectory information obtained from simulations.

The trajectory information is used to calculate the velocity autocorrelation function ($C_{vv}(t)$):

$$C_{vv}(t) = \frac{1}{N} \sum_{\alpha=1}^{N} \langle \dot{v}_{\alpha}(0) \cdot \dot{v}_{\alpha}(t) \rangle$$

(2.20)

where, $N$ is the total number of particles and the angular brackets correspond to the thermal or ensemble average. The Fourier transform of $C_{vv}(t)$ gives the corresponding frequencies of the system.

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} C_{vv}(t)$$

(2.21)

where, $G(\omega)$ is the VDOS. A method for estimating the autocorrelation function is to treat the velocities from the aiMD simulation as a discrete signal that can be modeled by an autoregressive stochastic (AR) process [53,54]. The Fourier transform of the autocorrelation function obtained from this AR model, as mentioned in (2.21), gives the VDOS. The detail of this methodology is discussed below.
The basic idea of this technique comes from the linear prediction method that has origins in the signal theory [53,55]. We will first describe this method for any general signal, and in the end replace this general signal by the velocity obtained from aiMD simulations. According to linear prediction, any output $s_n$ of an AR process can be predicted from the knowledge of past outputs ($s_{n-k}$) and inputs ($u_n$) as:

$$s_n = -\sum_{k=1}^{p} a_k s_{n-k} + G u_n$$  \hspace{1cm} (2.22)

where, $G$ is the gain parameter of the model. The z-transform of this signal ($S(z)$) is obtained as:

$$S(z) = \frac{G U(z)}{1 + \sum_{k=1}^{p} z^{-k} a_k}$$  \hspace{1cm} (2.23)

where, $S(z) = \sum_{n=-\infty}^{\infty} s_n z^{-n}$ and $U(z) = \sum_{n=-\infty}^{\infty} u_n z^{-n}$. Appendix B explains the steps to obtain $S(z)$. The autocorrelation function ($r_n$) of the output signal $s_n$ is given by:

$$r_n = \sum_{p=-\infty}^{\infty} s_p s_{p+n}$$  \hspace{1cm} (2.24)

The corresponding z-transform of the autocorrelation function ($R(z)$) can be calculated and shown to be:

$$R(z) = \sum_{n=-\infty}^{\infty} z^{-n} r_n = \frac{G^2 U(z)U(z^{-1})}{\left(1 + \sum_{k=1}^{p} z^{-k} a_k\right) \left(1 + \sum_{l=1}^{p} z^{-l} a_l\right)}$$  \hspace{1cm} (2.25)

The detailed stepwise calculation for getting equation (2.25) is shown in Appendix B. Here, we have used equation (2.23) and the relation between the z-transform of the autocorrelation...
function and the z-transform of the signal: $R(z) = S(z)S(z^{-1})$. Multiplying both sides of (2.22) with $s_n$ and then summing them over for all values of $n$ gives (Appendix B) another equation of interest:

$$r_0 = -\sum_{k=1}^{p} a_k r_k + G^2 \sum_{n=-\infty}^{\infty} u_n^2$$  \hspace{1cm} (2.26)

Now, we will introduce the velocity from the aiMD simulations as the signal of an AR process. Thus, we get the model of the signal, equivalent to equation (2.22), as:

$$v(t) = \sum_{n=1}^{p} a_n^{(P)} v(t-n\Delta t) + \epsilon_p(t)$$  \hspace{1cm} (2.27)

here, the coefficients $\{a_n^{(P)}\}$ are fitted to the aiMD data with the assumption that the velocity signal has a background noise given by $\epsilon_p(t)$, which is a Gaussian white noise with properties:

$$\langle \epsilon_p(t) \rangle = 0$$

$$\langle \epsilon_p(t) \epsilon_p(t') \rangle = \sigma_p^2 \delta(t-t')$$  \hspace{1cm} (2.28)

The variance of the noise ($\sigma_p^2$) can be calculated by multiplying equation (2.27) with $v(t)$. The result is then averaged which yields:

$$\sigma_p^2 = \psi^{(AR)}(0) - \sum_{n=1}^{p} a_n^{(P)} \psi^{(AR)}(n\Delta t)$$  \hspace{1cm} (2.29)

where, $\psi^{(AR)}(t) = \frac{\langle v(t)v(0) \rangle}{\langle v^2(0) \rangle}$ is the normalized velocity autocorrelation function. This equation is exactly same as the equation (2.26), that was obtained from the signal theory, with $G=1$, $a_n^{(P)} = -a_k$ and $u_n = \epsilon_p(t)$. Thus, we get the z-transform of the velocity autocorrelation function, as shown in equation (2.25) for the signal theory, as:
\[ \Psi^{(AR)}(z) = \frac{\sigma_p^2}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right) \left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{-l}\right)} \]  

(2.30)

Hence, if we want to calculate the VDOS we have to do a Fourier transform of \( \psi^{(AR)}(t) \) which is equivalent to using \( z = \exp(i \omega t) \) in \( \Psi^{(AR)}(z) \), i.e. in equation (2.30). But before doing that we need to find \( \sigma_p^2 \) which is related to the normalized velocity autocorrelation function \( (\psi^{(AR)}(n)) \) as shown in equation (2.29). \( \psi^{(AR)}(n) \) is obtained by doing inverse z transform of \( \Psi^{(AR)}(z) \). Before doing the inverse transformation, the denominator of \( \Psi^{(AR)}(z) \) is rewritten in the polynomial form:

\[ \Psi^{(AR)}(z) = \frac{1}{d_p^{(P)}} \frac{-z^p \sigma_p^2}{\left(z^p - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right) \left(\sum_{l=1}^{P} a_l^{(P)} z^{-l} - \frac{1}{d_p^{(P)}}\right)} \]  

(2.31)

The two polynomials in the denominator are \( p(z) = \left(z^p - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right) \) and \( q(z) = \left(\sum_{l=1}^{P} a_l^{(P)} z^{-l} - \frac{1}{d_p^{(P)}}\right) \). We can again rewrite the equation (2.31) in terms of the zeros of \( p(z) \) as \( z_k \) \((k = 1, ..., P)\) and zeros of \( q(z) \) as \( z_l^{-1} \) \((l = 1, ..., P)\) as:

\[ \Psi^{(AR)}(z) = \frac{1}{d_p^{(P)}} \frac{-z^p \sigma_p^2}{\prod_{k=1}^{P} (z - z_k) \prod_{l=1}^{P} (z - z_l^{-1})} \]  

(2.32)

The inverse z-transform to obtain \( \psi^{(AR)}(n) \) is done via contour integration:

\[ \psi^{(AR)}(n) = \frac{1}{2 \pi i} \oint_c d\zeta \zeta^{n-1} \Psi^{(AR)}(\zeta) \]  

(2.33)
where, $C$ is the region of domain of definition of $\Psi^{(AR)}(z)$. The domain of definition region is defined in Appendix B. The contour integration is done using the calculus of residues which results in the final form of $\psi^{(AR)}(n)$ as:

$$\psi^{(AR)}(n) = \sum_{j=1}^{P} \frac{1}{\alpha_p^{(P)}} \prod_{k=1,k\neq j}^{P} (z_j - z_k) \prod_{l=1}^{P} (z_j - z_l^{-1}) \frac{-z_j^{P-1} \sigma_p^2}{\prod_{j=1}^{P} (z_j - z_k)}$$  \hspace{1cm} (2.34)

Now, we can calculate the VDOS using equation (2.30) with $z$ replaced as $z = \exp(i\omega t)$ and $\sigma_p^2$ calculated from equation (2.29) with $\psi^{(AR)}(n)$ inserted from equation (2.34). This whole procedure is implemented in the nMoldyn analysis program [54] that we will use for calculating the VDOS of H atoms.
Chapter 3

Vibrational Spectroscopy of Surface Interaction with Water on Rutile (110) Surface

Introduction

Water molecules can adsorb on the surface of rutile (110) in a molecular form, known as associated configuration, or they can dissociate to form a pair of hydroxyls, which is known as dissociated configuration. In real samples, the rutile surface is covered with a hydration layer. In the experiments done by Mamontov et al. [10], where the rutile nanoparticles were hydrated under ambient condition, it was estimated that the hydration layer correspond to around 3.5 water molecules per Ti$_2$O$_4$ formula unit at the surface. This water/rutile (110) interface shows a dynamical equilibrium for the dissociation state of the water molecules adsorbed on the surface. The amount of water dissociation on water/rutile (110) interface is at the core of the long-standing discrepancy between theory and experiment and between different theories [13,14,56,57]. We have done aiMD simulations of this interface that shows a dynamical equilibrium of ~25% water dissociation [58]. The total VDOS calculated from our simulations show an excellent agreement with the vibrational spectrum measured by INS [59]. The deconvolution of the VDOS into contributions of individual atoms provides a unique tool to study the local H-bond dynamics at the surface and analyze the signature of the dissociation state on measured vibrational properties at the interface. We will also present the effect of temperature on the calculated VDOS.

Structure of Water Adsorbed on the Rutile (110) Surface

Water above the rutile (110) surface forms a layered structure. Figure 2 shows a snapshot of the simulation cell along with a profile of the H and O atom positions averaged over 10 ps of
simulation time at 300 K. The averaged position profile clearly shows the layering effect exhibited by the water above the rutile (110) surface.

![Simulation cell with 3 layer slab thickness (R3) with oxygen (red), hydrogen (white) and titanium (grey) atoms. The H-bonds are shown by light blue dashed line between the oxygen and hydrogen atoms in the simulation cell. Position histogram [p(z)] of oxygen (red) and hydrogen (black) atoms along the direction perpendicular to rutile (110) surface. The histogram was obtained as an average over 10 ps of simulation at 300K. BO denotes the surface bridging oxygen atoms. L1, L2 and L3 correspond to the three layers of water above the rutile (110) surface. Two kinds of hydrogen atoms were identified as H1 and H2. H1 corresponds to hydrogen atoms bridging between surface oxygen atoms and between hydrogenated BO and L2 (L1-L1, L1-BO and L2-BH). H2 are hydrogen atoms bridging L1-L2 and BO-L2.

Three distinct layers of water, labeled as L1, L2 and L3, are observed above the rutile (110) surface. L1 is composed of TO atoms narrowly distributed in the z-direction just next to the very narrow peak of the BO atoms. TO forms strong covalent bonds with the undercoordinated titanium atoms on the surface of rutile (110). The number of covalently bonded H-atoms affects the length of this bond. TH forms a much shorter bond with the surface than TW.
The difference in bond length contributes toward broadening of the L1 peak that can be used as an indicator of the degree of dissociation of water on the surface. The water molecules in L1 form H-bonds with adjacent water molecules in L1, with BO atoms, and with water molecules in the next layer, denoted by L2. This bonding situation is reflected in the H atom profile that is labeled as H1 and H2 in Figure 2. The peak labeled H1 collects the H atoms forming H-bonds between adjacent TOs, between TO and BO, and between BH and L2 water molecules. H atoms participating in the H2 peak form H-bonds between L1 and L2, and between BO and L2. Molecules in L2 are H-bonded to surface O and to water molecules in the outermost layer (L3). Molecules in L3 are H-bonded to other water molecules in L2 or L3, but there is also a large density of non H-bonded H atoms in L3. A similar layered structure at the water/rutile (110) interface was found in CMD simulations of both bulk SPC/E water [60] and SPC/E water at around 3 layer coverage [10].

The water molecules in L2 have preferential position of adsorption above the surface. To study this structure, the position of every O atom in L2 is recorded and folded into an irreducible quarter of the surface unit cell. Figure 3 shows the projection of the resulting density plots. The most prominent location for the L2 water molecules to adsorb is above and around BO as evidenced by the umbrella like density distribution shown in the x-z view of Figure 3. This plot shows that most of L2 water molecules form strong H-bond with the BO of the surface, moving around it while keeping the H-bond distance constant. The water in L2 visits another location, relatively infrequently, above the surface that is located above and between two TO L1 sites. This pattern is observed for the other two studied temperatures, i.e. 280 K and 320 K.
Figure 3 Density plot of the positions, averaged over 10 ps of simulation time, of oxygen atoms in the L2 layer along the three orthogonal directions. The most prominent peak is located around the BO atoms. The x-z and y-z panels show that these water molecules, which are H-bonded to the BO atoms, form an umbrella shaped distribution around the BO atoms indicating strong H-bonding between the surface and the water layer above the surface. The other prominent site corresponds to water molecules bridging between two TW molecules at L1. In the density plot, red corresponds to high density while yellow corresponds to lower density.

The water molecules in L3 layer show no specific orientation preference and do not exhibit any significant influence of the underlying rutile (110) surface. But, the H-bond structure of L3 layer does not correspond to bulk water either. This indicates that the effect of surface bonding and the distortions produced by it on the water structure are basically limited to the first and second adsorbed layers. The layering effect beyond the second layer can be due to a simple termination effect, which is found in even weakly interacting liquids [61]. The L3 molecules are clearly bound to the surface in the temperature range investigated (280 - 320 K). The ordering produced in the direction parallel to the surface, limited to only the second water layer, is the
result of weaker and subtle interactions between the surface and the water molecules above the surface.

The water molecules covalently bond with the under coordinated titanium atoms and forms the L1 layer. The dissociation state of these water molecules determines the surface adsorption properties. The H-bond structure, in both L2 and L3 layer, is affected from the dissociation state of the water molecules in L1 layer. The CMD simulations of Predota et al. [60] clearly demonstrate this effect. CMD employs a non-reactive force fields methodology that does not allow any bond breaking during the simulation. Hence, these simulations were performed at fixed pre-determined dissociation state. The first configuration was fully associated where none of the terminal water molecules are dissociated. Second configuration corresponds to complete dissociation where all of the TW molecules were dissociated. The adsorption sites of the L2 water molecules extracted from these CMD simulations were found to be different in the case of a fully associated configuration compared with a fully dissociated state. In our aiMD simulations, the amount of dissociation fluctuates around 25%. Hence the structure of water layers matches closer to the pattern corresponding to the fully associated configuration of the CMD simulation. The first adsorption site, where we found an umbrella like density distribution function around BO, is in good agreement with the L2 adsorption site of the CMD simulation [60], for the case of no dissociation. However, the secondary adsorption site between TO atoms, that is present in our simulation, is not observed in the CMD oxygen density plot. [60] In our simulations, we find that this site is mainly produced by a water molecule in L2 that accepts H-bonds from the water molecules in L1. Moreover, we find that the water molecules in L1 are strong H-bond donors because the bond with titanium weakens the OH covalent bonds. This results in donation of more charge to the O and hence making the H more positive, which in
turn forms stronger H-bond with its neighbors. Whereas, in classical simulations [10,60] the water in L1 is treated with the same SPC/E force field that is used to describe the bulk liquid water. The aiMD simulations clearly show that, because of bonding with the under coordinated surface titanium atom, L1 water molecules have different bonding characteristics than water molecules in the liquid. In spite of this detail, the density contour around the BO atom shows similar shape in both CMD and aiMD simulations.

The layering effect in water above the surface and preferential adsorption location of water molecules can be determined experimentally. X-ray CTR experiments done by Zhang et al. [62] indicated two well-defined structural layers of adsorbed water beyond the BO layer. Moreover, these experiments show similar L1 configuration as found in the aiMD simulation. The X-ray study also showed that the hydration layer L2 is highly structured with well defined absorption sites. In the analysis of the experimental information, three preferential adsorption sites were identified. The first position, labeled as AW1 by Zhang and coworkers, matches closely with our most visited adsorption site atop BO atom. The vertical position of this site above the Ti surface plane is in good agreement. But, the average lateral position indicated by the experiment is mainly atop the BO, whereas our simulations suggest that the average position of this sorption site is shifted toward the TO site. The other two sites that are obtained experimentally are not present in our aiMD simulation. The source of discrepancy between simulation and experiment can be due to the differences in the setup. The CTR experiments are done on the surface of a crystal immersed in a thick layer of water. Our simulations, instead, are designed to mimic the nanoparticles measured in neutron scattering with a much lower level of hydration. This different hydration level may influence the adsorption sites through changes in the dissociation level at the surface or through changes in the H-bond network of the liquid.
surrounding the surface. Other possible sources of this discrepancy include (a) surface defects and step-edge sorption sites, surface contamination, and other artifacts associated with the X-ray experiments involving real crystals and aqueous solutions; and (b) artifacts in the simulation results associated with the intrinsic approximations (i.e. use of DFT to parameterize the simulations and the treatment of core electrons) as well as boundary conditions imposed to make the simulations practical, including the limited lateral dimension, the thickness of the rutile slab, or the amount of vacuum between surfaces.

**Vibrational Spectroscopy of Rutile (110) Surface**

The simulation provides trajectory information for all atoms. This trajectory information can be used to compute the VDOS by calculating the Fourier transform of the velocity autocorrelation function. Figure 4 shows the VDOS of all H atoms present in the simulation. The VDOS has three characteristic peaks that are present in any water system. The peak at around 20 THz corresponds to liberations of water molecules where the whole molecule move as a rigid body due to the mutual interactions produced by H-bonds. This mode is absent in the gaseous systems. The sharp peak at around 50 THz refers to the bending mode and the broad band above 70 THz is related to the stretching mode. The stretching mode is very sensitive to the local environment and hence it can be used to characterize different kind of bonding environment for the H atoms. The small sharp peak at 120 THz is produced by the stretching mode of free water molecule OH bond with minimal influence from neighboring molecules. These water molecules are found mainly in the top most layer of water that is exposed to the vacuum space of the simulation cell. The broad stretching band between 70 THz and 120 THz results from softening
of stretching band due to various types of H-bonding environment. The stretching mode show blue shift as temperature increases due to decrease in H-bond density.

![VDOS at different temperatures](image)

Figure 4 VDOS of all H atoms present in the simulation at three different temperatures. The peak centered at 25, 50 and 100 THz corresponds to librations, bending and stretching modes of water molecules, respectively. The vibrations of free hydroxyls produce the sharp peak at 120 THz. The rise in temperature weakens the H-bond network and results in blue shift of the stretching mode.

The time scale that is achievable by aiMD simulations, at the current state of the art computing facilities, is in the range of couple of picoseconds. The dynamics that is captured at these time scales can be explored experimentally using incoherent neutron scattering (INS) experiments. Spencer et al. [59] measured the vibrational spectra of water confined on the surface of rutile nanoparticles. Fig. 1 of their paper shows the VDOS spectra extracted from the INS experiment. They find the librations to be in the range of 50-120 meV (~12-29 THz). The bending mode exhibits a sharp peak at around 200 meV (~48 THz). The stretching mode produces a broad peak with the center being at around 412 meV (~100 THz). A comparison of
these experimentally obtained peaks with our calculations (Figure 4) shows an excellent agreement between the theory and experiments. The small peak at 120 THz in our simulation does not appear explicitly in the experiments. As mentioned by Spencer et al. [59] this peak may already be present but it could be getting masked by the neighboring broad stretching band.

The simulations provide an excellent opportunity to identify the individual atom contribution to the spectrum by deconvoluting the total VDOS. This allows us to isolate and categorize various H-bonding environments that are responsible for different parts of the broad stretching band. The H1 and H2 peaks of the z position histogram (Figure 2) were associated with those H atoms that participated in forming H-bonds with BO and TO sites. H3 encompasses all other H atoms in the cell. This group includes atoms that form typical liquid water H-bonds and free OH groups at the interface between water and vacuum. Figure 5 shows the stretching band of the VDOS of H1, H2 and H3 calculated by deconvoluting the total VDOS. This figure shows that H2 dominates the lower frequency end of the stretching band and hence they participate in forming strongest H-bonds. Although, H1 atoms have some weight in the lower frequency end of the band but on average it is slightly shifted to higher energies. H3 atoms have little to no contribution to lower frequencies. Its stretching band contribution is similar to that expected from liquid water. In addition, the presence of free hydroxyl groups at the interface between water and vacuum results in a peak at around 120 THz. It is surprising that H2 atoms form stronger H-bond than H1 because same H atom when forming H-bond with other surface species is weaker than the case when it forms H-bond with the water layer above the surface. This happens because the H-bonds among the surface species get weakened due to the fact that they are bonded to the titanium atom at the surface, and are not free to move. Consequently, the H-bonds are stretched as in the case of bonds between L1 and BO, or compressed as in the case
of L1-L1 bonds. On the other hand, H2 contains bonds that are formed between a strong H-bond former at the surface and water molecules in the liquid that are free to move and adapt to maximize the strength of the H-bond. This results in H2 atoms participating in strong H-bond formation and hence dominating the lower end of the stretching band spectrum. The deconvoluted VDOS spectrum also exhibits similar temperature dependence as seen for the total VDOS. Figure 5 clearly shows that as temperature increases, from 280 K to 320 K, the stretching band of all three categories of H atoms shift to higher frequency. This is a result of decrease in H-bond density with temperature.

Figure 5 The stretching band of H1, H2 and H3 category of H atoms deconvoluted from the total VDOS calculation for three temperatures. H1 atoms are closest to the surface. These atoms form H-bonds between L1 oxygen atoms, between L1 and BO, and between BH and L2. H2 is the layer of H atoms that form H-bonds between L1 and L2, and between BO and L2. All of the remaining H atoms, including those at the interface between water and vacuum, belong to H3. The plot shows that at all temperatures, H2 dominates the lower part of the spectrum with some contribution from H1 atoms and no participation from H3 atoms. This shows that the strongest H-bonds are formed among surface species. The sharp peak at 120 THz is produced by OH bonds at the interface between water and vacuum, which belongs to H3 category.
The atomistic simulation allows a much deeper understanding to the origins of the macroscopically observed behavior. The simulations reveal that there are many different types of H-bonds at the interface that can be characterized by its donor and acceptors (Figure 6, Table 1). TW, TH, BO and BH atoms are represented by symbols TiHOH, TiOH, Ti₂O and Ti₂OH, respectively. The water molecules in the water layer are symbolized as HOH. The two atoms participating in forming the H-bond, the accepting O atom, and the donated H atom are represented in boldface. The H-bond length and the corresponding stretching mode frequency of various types of H-bonds are reported in Table 1. The number of H-bonds that O accepts affects the length and the strength of the H-bond. These are denoted in the first column of Table 1 as I, for the single bond configuration, and II, for the case of two bonds. H-bond distances are larger, and frequencies are higher in the case of configurations where the O atom is accepting two bonds. This occurs because when O accepts two H-bonds then the individual bonds get weaker.
Figure 6 Linear relationships between the H-bond length and the stretching mode for different kind of H-bonds (symbols are described in Table 1). The insets on the upper left corner of the plot show the VDOS of three representative cases and the lower left corner shows the corresponding H-bond distance histogram. The surface-water H-bonds are shown with empty symbols, whereas, surface-surface or water-water h-bonds are shown with filled symbols. The three colors correspond to three temperatures, 280 K (black), 300 K (orange) and 320 K (red).

H-bond lengths and corresponding covalent bond formed by the H participating in the H-bond show an interesting inverse relation. When the H-bond is weak, the covalent bond is stronger and the frequency is higher. The values reported in Table 1 are plotted in Figure 6. The plot clearly shows a strong correlation between the H-bond formed by acceptor O and donating H atom distance, and the vibrational frequency associated to that H-bond. The vibrational frequency spectra of three different H-bonds of varying strength are shown in the upper-left corner of Figure 6. The higher vibrational frequency exhibits a narrower peak. This is because a weak H-bond corresponds to stronger and stiff covalent OH bond, which in turn results into narrower range of frequency for the H atom. The lower right corner of figure shows the
corresponding H-bond length histogram. As expected, the width of the distribution of H-bond lengths follows a trend opposite to that of the frequency distribution.

Table 1 H-bond distance and frequency for various types of H-bonds on hydrated rutile (110) surface. The frequencies (ν) and distances (d) are expressed in THz and Å, respectively. The H-bond configuration where O accepts one or two H-bonds are identified with roman numeral I or II and the column P gives the relative abundance of these two configurations. The empty cells correspond to those configurations that are not statistically significant.

<table>
<thead>
<tr>
<th>Case</th>
<th>280 K</th>
<th>300 K</th>
<th>320 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>d</td>
<td>ν</td>
</tr>
<tr>
<td>TiO---TiOH (▲) I</td>
<td>19.5</td>
<td>1.68</td>
<td>91.6</td>
</tr>
<tr>
<td>TiO---TiOH (▲) II</td>
<td>80.5</td>
<td>1.77</td>
<td>100.3</td>
</tr>
<tr>
<td>TiO---H2O (▲)</td>
<td>1.63</td>
<td>93.9</td>
<td>1.65</td>
</tr>
<tr>
<td>TiOH---TiOH (●)</td>
<td>1.60</td>
<td>88.8</td>
<td>1.61</td>
</tr>
<tr>
<td>TiOH---H2O (○)</td>
<td>1.70</td>
<td>94.4</td>
<td>1.70</td>
</tr>
<tr>
<td>TiOH---TiOH (▼)</td>
<td>1.71</td>
<td>98.6</td>
<td>1.72</td>
</tr>
<tr>
<td>TiOH---H2O (&gt;l)</td>
<td>1.66</td>
<td>92.5</td>
<td>1.65</td>
</tr>
<tr>
<td>TiOH---H2O (▼) I</td>
<td>12.9</td>
<td>1.57</td>
<td>84.8</td>
</tr>
<tr>
<td>TiOH---H2O (▼) II</td>
<td>87.1</td>
<td>1.66</td>
<td>92.4</td>
</tr>
<tr>
<td>HOH---HOH (●) I</td>
<td>25.8</td>
<td>1.68</td>
<td>96.0</td>
</tr>
<tr>
<td>HOH---HOH (●) II</td>
<td>74.2</td>
<td>1.73</td>
<td>101.2</td>
</tr>
</tbody>
</table>

The data presented here (Figure 6, Table 1) shows an interesting fact about the H-bonds in water/rutile (110) system. The H-bonds formed by the surface species, i.e. BO and TO, is found to be stronger than the H-bonds between the water molecules. In Figure 7, we have compared the stretching band frequency of two H-bond configurations, TiO---HOH and TiOH---HOH, with the H-bond between water molecules (HOH---HOH). The vibrational contribution of each H-bond shows that the surface water H-bonds are stronger than the H-bond between water molecules. A similar trend in H-bond strength is seen for the H-bonds between
water layer and the corresponding hydroxyls (Ti$_2$OH---HOH and TiOH---HOH). The peak position of the stretching mode for Ti$_2$O---HOH and TiHOH---HOH are centered at about the same position but the band corresponding to TiHOH---HOH is wider. The broad peak indicates that the water molecule in L2 water layer that forms H-bond with the TW has significant oscillation. This weakens and strengthens the H-bond that in turn produces a wider variation in the stretching band.

Figure 7 Deconvoluted VDOS of H atoms participating in three different kinds of H-bonding (pictorially shown in the top panel). The strength of H-bond between surface and water layer (Ti$_2$O---HOH and TiHOH---HOH) is stronger as can be seen from weaker stretching band frequency.

In conclusion, we have calculated the VDOS of H atoms and used it as an estimator for measuring the strength of H-bonds on water/rutile (110) interface. The stretching band of the vibrational spectrum of H atoms in water molecules and OH groups is specifically sensitive to
the H-bonding. This interface has large variety of H-bonds between the surface species, among the water molecules, and between the water molecules and the surface species. Each type of H-bond has characteristic H-bond strength and corresponding characteristic vibrational stretching band. The molecular modeling allows us to investigate and isolate the stretching band of each individual H atoms. We identified several types of H-bonds and found that the stretching band and the H-bond length has a linear relationship as shown in Figure 6. The H-bond between the surface and water layer above the surface is stronger than the H-bond between the water molecules. This leads to softening of the VDOS, which in turn leads to a broader stretching band (Figure 4, Figure 5) as observed in the INS experiment by Spencer et al. [59] The strong H-bonding, between the surface and the water layer above the surface, results in ordering among water molecules in the L2 layer. This ordering of L2 layer leads to preferential locations for water adsorption as shown in the position density plot (Figure 3) and observed in the CTR experiment [62].
Chapter 4
Proton Transfer Events on Rutile (110) and Cassiterite (110) Surfaces

Introduction

Water molecules strongly adsorb to the under coordinated metal atoms on the (110) surfaces of rutile and cassiterite. These water molecules undergo reversible dissociation reactions forming a pair of hydroxyls (TH and BH). These reactions are the consequence of a proton transfer to a neighboring O atom either directly or through a Grotthuss process [63] via water molecules in the hydration layer. This results in a dynamical equilibrium where the surfaces achieve an average dissociation level and an average rate of proton jumping events throughout the surface [64]. In the work presented below we will show that the cassiterite surface has higher dissociation level (~60%) than the rutile surface (~25%). Both surfaces are hydrated in accordance with the experimental findings of Mamontov et al. [10] Moreover, we find that the cassiterite has around 3 times higher proton jumping events than rutile surface. We will demonstrate that the reason behind the higher proton jump rate on cassiterite surface is related to the difference in the electronic structure between the two surfaces.

Water Dissociation Percentage and Proton Jump Rate

The aiMD simulations of hydrated rutile (110) and hydrated cassiterite (110) are done with five different configurations for both surfaces. The difference between all of these configurations is the dissociation state of the initial configuration used in the simulation. We have used 0%, 25%, 50%, 75% and 100% dissociation states. This was done to ensure that the results obtained are unbiased by the initial conditions used to setup the simulation. Figure 8 shows the amount of water dissociated as a function of simulation time. It is clear that, for both
surfaces, in around 3 ps all of the five simulations, which started with different dissociation state, converged to ~60% and ~25% dissociation for cassiterite and rutile surface, respectively. The dissociation state is not fixed but it keeps fluctuating about the values mentioned earlier.

Figure 8 Dissociation percentage of terminal water molecules on the (110) surfaces of rutile (solid line) and cassiterite (dashed line). The five different lines for each surface correspond to five different dissociation states, 0% (—), 25% (—), 50% (—), 75% (—), and 100% (—), of the equilibrated initial configurations with which the simulation was started. After first 3 ps, the system equilibrated to ~60% and ~25% for cassiterite and rutile surface, respectively. The fluctuations in dissociation percentage represent the proton jump events. Cassiterite shows more than three times faster proton jump rate than rutile.

The fluctuations in the dissociation percentage are results of proton jumping events among TO, BO and the water molecules in the hydration layer above the surface. These dissociation fluctuations on the cassiterite surface are more frequent than those on the rutile surface (Figure 8). The average proton jump rate is 102.7 jumps/ps for cassiterite and 32.6 jumps/ps for rutile. This exhibits an interesting difference in the proton jump activity of the two surfaces where cassiterite appears to be more active than rutile. In order to ensure that our
observation is not an artifact of the simulation, we test for the influence of basis set convergence by doing simulations at higher cutoff energy. This is a computationally intensive calculation and hence it was run for a small time of ~1.5 ps. We find that the proton jump rate for these highly precise simulations is 42 jumps/ps and 6 jumps/ps for cassiterite and rutile, respectively. Although the proton jump rate shows strong dependence on the cutoff energy, but this expensive simulation confirms the general trend of cassiterite surface being more active than rutile surface.

**Cause of higher proton jump rate in cassiterite as compared with rutile: lattice size or electronic structure?**

Rutile and cassiterite are iso-structural metal oxides. The bigger size of the tin atom, in cassiterite, than the titanium atom, in rutile, results in larger lattice spacing for cassiterite. The other difference between the two materials is due to the chemical composition, i.e. the difference in the electronic structure. One or both of these differences can be the origin of higher proton jump rate observed on cassiterite surface. A simple computational experiment was done to study the relative importance of these two factors. In this experiment, first we run the simulation without exchanging the cations (normal simulation). After 5 ps, we exchange the cations (exchanged simulation) and run the simulation again for another 5 ps. Figure 9 shows the amount of dissociation as a function of simulation time in two panels. The left panel is for the normal simulation cell whereas the right panel shows the evolution of dissociation percentage for the exchanged simulation cell. The last step of the normal simulation cell is used as the initial configuration for the exchanged cation simulation cell. The rutile cell, with exchanged tin atoms, shows an increase in the dissociation percentage, from 25% to 40%, as simulation proceeds. Moreover, the proton jump rate also increased from 32.6 jumps/ps to 86 jumps/ps. At the same
time, the cassiterite cell with titanium atoms in the place of tin atoms, show a large drop in proton jump rate from 102.7 jumps/ps to 36 jumps/ps. The amount of dissociation changes from 60% to 30%. Moreover, when titanium atom is placed in the cassiterite cell or vice-versa, the proton jump rate did not change significantly. These results indicate that the proton jump rate and the dissociation level is significantly affected by the electronic structure and not the lattice size.

![Figure 9](image_url)

Figure 9 Dissociation percentage curves of rutile (black) and cassiterite (red) surfaces. Left panel (a): Last 5 ps of simulation for the materials in their normal lattices. Right Panel (b): First 5 ps of simulation for the materials with exchanged cation atoms. The initial configuration for exchanged cation simulation is the last step of the normal simulation. A rise in dissociation percentage and proton jump rate is observed when tin atoms, in the rutile lattice, replace titanium atoms. An opposite trend is seen for the cassiterite lattice. This shows that electronic structure and not the lattice size affects the dissociation state and the proton jump rate.

**H-bond participation in proton jump rates**

The proton jumps occur via a H-bond. As there are many kinds of H-bonds, the proton jump rates vary with the kind of H-bond involved in the transfer of the proton. The different
categories of proton transfers can be classified as jumps between BO and O atom of the water molecule (WO), TO and WO, TO and BO, TO and TO, and between WO and WO. Table 2 lists the average proton jump rates for these various categories of proton transfer. The cassiterite surface has higher proton jump rate in most of the categories. The largest difference is for the case where proton jumps between the surface species BO and WO. The ratio of proton jump rate for this category, on cassiterite with respect to rutile, is 9.8. This can be explained by the fact that BO atoms are the most basic sites on this surface [65] and thus it is an excellent location for proton transfer. The next largest difference is for protons jumping between WO and TO with a ratio of 4.0. The proton jump rate for WO-WO gets affected with the ratio being 1.9. The direct proton transfer between surface species, i.e. between BO and TO, is significant on cassiterite surface but it is completely absent in rutile surface. The only category that has lower proton jump rate for cassiterite surface, almost 2 times, is between TO and TO. This change in proton jump rate trend can be explained by the fact that the cassiterite has larger lattice spacing which in turn results into larger distances between TO atoms and hence lower probability of proton transfer.

Table 2 Average proton jump rate of proton transfer between BO, TO and WO in the hydration layer for (110) surfaces of rutile and cassiterite. Cassiterite exhibits higher proton jump rate in all of the categories except for TO-TO, which could be due to larger lattice spacing. The hydrated rutile surface shows no direct proton jumping events between surface species (BO and TO).

<table>
<thead>
<tr>
<th>Jump Type</th>
<th>SnO₂ (jumps/ps)</th>
<th>TiO₂ (jumps/ps)</th>
<th>Ratio = SnO₂/TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO-WO</td>
<td>44.2</td>
<td>4.5</td>
<td>9.8</td>
</tr>
<tr>
<td>TO-WO</td>
<td>34.6</td>
<td>8.6</td>
<td>4.0</td>
</tr>
<tr>
<td>TO-BO</td>
<td>2.3</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TO-TO</td>
<td>5.4</td>
<td>10.9</td>
<td>0.5</td>
</tr>
<tr>
<td>WO-WO</td>
<td>16.2</td>
<td>8.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Total</td>
<td>102.7</td>
<td>32.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>
The largest difference in the proton jump rate is observed for the proton transfer between the BO and the WO in the hydration layer above the surface (BO–WO). We will first focus on this category of proton transfer. Figure 10 shows the position density plot for O atoms in the L2 water layer. This shows that the water molecules in L2 have a preferential adsorption location, for both surfaces. The most preferred site is above and around BO atoms, forming an umbrella like structure in the position density plot. As, mentioned in the previous chapter, this structure indicates strong H-bonding between WO and BO. A histogram of the distance of O atoms between BO and WO of L2 layer shows that the water on cassiterite is 0.06 Å closer to the surface than on rutile. Some of the water molecules adsorb around TO atoms. These water molecules are also found to be closer, by around 0.06 Å, to cassiterite than rutile surface. These findings show that the whole L2 water layer is closer to the cassiterite surface, in comparison to rutile surface.
Figure 10 Density plot of position of O atoms in the L2 layer for (a) cassiterite and (b) rutile. The horizontal dashed lines are plotted for reference. The darker regions correspond to locations where water molecules reside for longer time. For both surfaces, water molecules cluster around the BO atom, forming an umbrella like structure in the position density plot. The histogram, not shown here, for the distance between the O atom of WO in L2 and the O atom of BO shows that the L2 is 0.06 Å closer to the surface on cassiterite than on rutile.

The umbrella like structure of O position density (Figure 10) and the fact that L2 layer is closer on cassiterite surface indicates that the H-bonds, between L2 and surface species (BO and TO), on the cassiterite surface are stronger than on rutile surface. The strength of H-bond can be independently checked, as shown in the previous chapter, by studying the correlation between the H-bond lengths and corresponding VDOS of the H atom that is participating in the H-bond. Figure 11 shows the peak position of the histogram of H-bond length, as the x-axis. The y-axis is the weighted mean of the corresponding stretching band frequency for many, statistically significant, types of H-bonds on both rutile and cassiterite surfaces. A strong H-bond corresponds to a shorter H-bond length and a lower stretching band frequency of the donating O–
H bond, whereas a weaker H-bond has longer H-bond length and higher stretching band frequency. The surface–water H-bonds for cassiterite have H-bond length between 1.55–1.60 Å and the corresponding stretching band frequency between 83–88 THz. For the rutile surface, these bonds are longer (1.61–1.66 Å) and the corresponding stretching band frequencies are higher (88–93 THz). This shows that the H-bonds, in general, are shorter and stronger on cassiterite surface, in comparison to rutile surface. A shorter and stronger H-bond reduces the distance between O atoms, and consequently decreases the potential barrier for the proton jump. Hence, stronger H-bonds can be a cause for the increase in the proton jump rate on cassiterite surface.

Figure 11 H-bond lengths and corresponding weighted mean of stretching band frequency for all, statistically significant, H-bonds on the (110) surface of cassiterite (orange) and rutile (black). The symbols used are described in the inset. M symbolizes the metal atom, i.e. titanium for rutile and tin for cassiterite. The bold O and H refer to those atoms that are participating in the H-bond. The donor O atom and acceptor H atom of a H-bond are always written on left and right side, respectively, of the dash line in the symbol definition of the inset. The number 1, 2 or 3 refers to the number of H-bonds accepted by the acceptor O atom. H-bonds are, in general, stronger on cassiterite than rutile surface as shown by the smaller H-bond length and corresponding weaker stretching band frequency.
The next logical question that arises is finding the cause for stronger H-bonds on cassiterite surface. H-bond comprises both covalent and electrostatic interaction. First, we will try to find the differences in the covalent component of the H-bond between rutile and cassiterite surface. A water molecule has three occupied states closest to the Fermi level, namely, 1b₂, 3a₁, and 1b₁, in order of increasing energy. [66,67] The 1b₂ state is very low in energy and the corresponding wave function is strongly localized. Thus, the 1b₂ state does not participate in the H-bonding. The other two states are closer to the Fermi level and are influenced by the formation of H-bond. The 3a₁ state participates from the donor side and 1b₁ state participates from the acceptor side of the H-bond. In an excellent review of water–surface interactions, Henderson [68] presented an interesting correlation between H-bond strength and the shift of the valence states of water upon H-bond formation. It was shown that stronger H-bonds are those with a larger reduction in the energy, stabilization, of the 3a₁ state with respect to the 1b₂ state. We use this criterion for finding the contribution of covalent nature of H-bond towards increasing the H-bond strength on the cassiterite surface.
Figure 12 The energy difference between the valence states, 1b$_2$ and 3a$_1$, of water molecule as a function of the distance (d) between the O atoms of BO and WO for rutile (black) and cassiterite (orange) surface. The water molecule is positioned just above the BO with one of its H atom pointing towards the BO (shown in inset). The 3a$_1$ state is more stable, by 0.3 eV, on cassiterite than on rutile surface. This indicates that the covalent component of H-bond is stronger on cassiterite surface.

A simple numerical experiment is done where a single water molecule is kept above the BO on pristine (110) surfaces of rutile and cassiterite. The orientation of this water molecule is such that one of its H atom points toward the BO atom. A pictorial illustration is given in the inset of Figure 12. The distance between the two O atoms (d), BO and WO, is changed at regular intervals from 3.5 to 2.6 Å, by moving the water molecule along the vertical direction. The electronic structure calculation is done for each value of ‘d’ to obtain the energy values of 1b$_2$ and 3a$_1$ states. Figure 12 shows the evolution of energy difference between 3a$_1$ and 1b$_2$ states as a function of ‘d’. As the distance of the water molecule to the surface diminishes and forms a H-bond as a donor, the 3a$_1$ state appears at a lower energy with respect to the 1b$_2$ state. The shift of
the 3a_1 state is 0.3 eV more on cassiterite than on rutile. This indicates that the covalent component of the H-bond is stronger on the cassiterite surface compared to rutile.

Another important component of H-bonding is the electrostatic interaction. The proton belongs to the same water molecule on the two surfaces. The other participant of the H-bond is the BO atom. This atom covalently bonds to different species on the two surfaces, titanium on rutile and tin on cassiterite, and hence it may have different electronic structure. In order to find this difference, we estimate the charge on the BO for both surfaces. The charge of a given atom in a solid is not a well-defined quantity. Hence, we use the charge partition method proposed by Bader [69] to calculate the amount of charge on BO. The Bader charge analysis [70–72] of the pristine surface shows that the BO in cassiterite has on average 0.14 more electrons than in rutile. As a consequence of this charge difference, the electrostatic potential profile, around BO, shows a minimum that is 0.05 Å closer to the surface in cassiterite compared to rutile. It is interesting to note that this difference is of the same order of magnitude as the 0.06 Å difference in the H-bond length mentioned earlier. This analysis shows that the electrostatic component of H-bond contributes significantly toward strengthening the H-bond on cassiterite surface. In conclusion, both components, covalent and electrostatic interactions, contribute in increasing the strength of H-bond between BO and WO on cassiterite surface.

The strong H-bond on cassiterite surface also explains the higher TO-WO proton jump rate (Table 2). As mentioned earlier, the L2 water is found closer to TO (Figure 10), by 0.06 Å, on cassiterite in comparison to rutile surface. The shorter H-bond results in lowering of barrier for a proton to jump and hence increases the TO-WO proton jump rate. The next category of proton jump is TO-BO, which is completely absent on rutile surface. This can be explained by the fact that TO-BO H-bond length and corresponding stretching band frequency on rutile is 1.84
Å and 99.5 THz, which is the longest and weakest among all of the H-bonds reported here (Figure 11). The proton transfer rate between TO and TO is smaller on cassiterite than on rutile. This is as expected, since the larger lattice of cassiterite hinders in forming shorter H-bonds (Figure 11). The discussion done so far on stronger H-bonds does not explain the higher proton jump rate seen for proton transfer among water molecules (WO-WO), on cassiterite surface in comparison to rutile surface. It has been shown that the H-bonds between surface and water are stronger on cassiterite surface. Moreover, it is also known [73] that the H-bond donor accepts a small amount of charge donation from the H-bond acceptor. The charge is not localized at the proton but it gets transferred to the O atom. This results in water molecules becoming strong H-bond acceptors. Hence, the H-bond strength increases that in turn leads to higher proton jump rate for WO-WO category on the cassiterite surface.

In conclusion, we showed that the simulations started with different initial configurations, with 0%, 25%, 50%, 75% and 100% dissociated surface water, equilibrated to a similar dissociation level of ~60% for cassiterite and ~25% for rutile surface. This dissociation level is dynamical and, due to the proton jumping events throughout the surface, it keeps fluctuating throughout the whole simulation. We find that the cassiterite surface has around 3 times more proton jumping events than on rutile surface. The main reason behind the difference in the proton dynamics is the difference in the electronic structure between the two surfaces and not the difference in the lattice parameters. The atomistic simulation allowed us to categorize the proton jump between different species and we find that the proton jump rate between BO and WO is around 10 times more on cassiterite than on rutile. This huge disparity in proton jump rate is the result of an increase in the covalent and ionic contributions to the H-bond between the surface O and the hydration layer on cassiterite surface.
Chapter 5

Surface M-O Bond Length: A Measure of the Local Environment

Introduction

The dissociation state of the water molecules adsorbed on the (110) surfaces of rutile and cassiterite significantly affects the M-O bond length. Consequently, information about the M-O bond length can give crucial information about the dissociation state of water molecules on the rutile surface. There have been several theoretical and experimental estimations of this M-O bond length but neither the dissociation state nor the bond length estimates agree between these different studies [14,62,74–77]. Allegretti et al. [14] showed that the photoelectron diffraction experiments on rutile (110) surface, with 1 ML water coverage, indicate a fully associated configuration for the adsorbed water molecules. They found the M-O bond length for this surface to be 2.21 ± 0.02 Å. On the other hand, Zhang et al. [62], in their X-ray CTR study, found the M-O bond length to be 2.13 ± 0.03 Å for rutile (110) surface having several layers of water coverage. They estimated the dissociation state of the surface to be around 30±15%. In a theoretical treatment, Stefanovich et al. [74] used embedded cluster calculation to show that the adsorbed water molecule, on rutile(110) surface, preferred associated configuration with the corresponding M-O bond length being 2.25 Å. The DFT calculation of Menetrey et al. [75] showed preference for partial dissociation, on rutile (110) surface, for both 0.3 ML and 1 ML coverage. They found the M-O bond length for TW and TH to be 2.28 Å and 1.85 Å, respectively. We have used our aiMD simulations to study this M-O bond length and the corresponding dissociation state of the adsorbed water molecules. We will show that our simulation is in close agreement, both in terms of the M-O bond length and the dissociation state, with the X-ray studies done by Zhang et al. [62] Moreover, we will also show that the M-O bond
length contains a unique signature of the local environment. In addition to the dependence on hydrogenation state of the O atom, of BO and TO, the M-O bond lengths are found to be sensitive to the surrounding H-bond environment. We will demonstrate that this bond length has different level of sensitivity to the local environment for the two surfaces. Cassiterite surface, as compared to rutile, forms stronger M-O bond as will be apparent from the corresponding narrower M-O bond length histogram.

**M-O bond length dependence on hydrogenation state**

The M-O bond length is an indication of the hydrogenation state of the TO and BO atoms. Figure 13 shows a pair of plots, for TO (top panel) and BO (bottom panel), of M-O bond length with the simulation time for the rutile surface. The top panel shows M-O bond length with simulation time for TO. It starts as a TW and changes to TH at around 2.5 ps. This transition results in a significant decrease of the M-O bond length. The TH continues to exist for another 1.1 ps and then it changes back to TW at 3.6 ps, resulting in an increase in the M-O bond length. This process is repeated where TW changes to TH at 5.7 ps and then back to TW at 6.9 ps. A corresponding change in M-O bond length is observed for this set of transitions. The lower panel of Figure 13 shows similar M-O bond length dependence on the hydrogenation state of the other surface species, i.e. BO. This BO starts as a BH and at around 3 ps it loses the proton to become a BB. As seen in the case of TO, the M-O bond length decreases with the loss of proton from BH. It continues to remain as a BB for the rest of the shown simulation time. The width of oscillation in the M-O bond length appears to be larger for the TO than BO on the rutile surface. It is apparent that M-O bond length gives a very clear indication for the number of H atoms that are covalently bonded to the O atom of BO or TO. The surface species on cassiterite surface
shows a similar behavior for the M-O bond length with the hydrogenation state of the corresponding O atom.

Figure 13 The evolution of M-O bond length with simulation time, for a TO (top panel) and a BO (bottom panel), on the rutile surface. The M-O bond length changes significantly as the number of H atoms changes from 1 to 2, for TO, or from 0 to 1, for BO. Top panel: A TO changes from TW (red) to TH (black) at around 2.5 ps, and changes back to TW at around 3.6 ps. This process is repeated as TW->TH->TW at around 5.7 and 6.9 ps. Bottom Panel: A BO changes from BH (black) to BB (red) at around 3 ps. The width of oscillation of M-O bond length appears broader for TW/TH than for BB/BH, on rutile. The surface species, TW, TH, BB and BH, are shown pictorially in the region of their existence.

We calculated the histograms of the M-O bond lengths obtained from the aiMD simulations, for all surface species, on both rutile and cassiterite surfaces (Figure 14) The peak corresponds to the most frequent M-O bond length and the half width at half maximum (HWHM) is a measure of the fluctuations in the bond lengths. Table 3 summarizes the peak positions and the HWHM of the histograms of M-O bond length for BB, BH, TH and TW, on both cassiterite and rutile surfaces. It is true for both surfaces that the M-O bond length increases as the number of covalently bonded H atom increases from 0 to 1 to 2. This behavior can be explained by the fact that the additional H atoms, which are covalently bonded to the BO or TO
atom, reduce the electrons availability on the corresponding O atom which could have been used in forming stronger bond to the metal atoms on the surface. For cassiterite, the peak positions of the M-O bond length for BB and BH differ by 0.05 Å whereas, for rutile, they differ by 0.14 Å. A similar trend is observed for the M-O bond length for the TW and the TH. Specifically, the TW is found to be longer than TH by 0.06 Å and 0.16 Å, for cassiterite and rutile respectively. The cassiterite surface has relatively smaller effect of the hydrogenation state of the O atom on corresponding M-O bond length. This indicates that the M-O bond is stronger on cassiterite than on rutile surface. This result is further reinforced by the study of the width of the M-O bond length histograms as discussed below.

Figure 14 Histograms of M-O bond length for surface species BB (o), BH (□), TH (x) and TW (Δ) on cassiterite ((A), red) and rutile ((B), black) surfaces. All of the surface species on rutile has broader histogram, which indicates that the M-O bond is, in general, weaker on rutile than on cassiterite. The peak positions of the histogram are shorter on rutile except for the TW that appears to be similar on the two surfaces.
The width of the M-O bond length histogram indicates the fluctuations in the M-O bond length and by extension the strength of the M-O bond. A narrower histogram corresponds to a stronger M-O bond and a broader histogram corresponds to a weaker M-O bond. The difference in HWHM between cassiterite and rutile for BB and BH is 0.06 Å and 0.04 Å, (Table 3) respectively. This difference is 0.11 Å for both TH and TW. The HWHM for BB, BH, TH and TW are much greater for rutile than for cassiterite. This shows that the surface species are weakly bonded to the rutile surface in comparison to the cassiterite surface. It is interesting to note that the M-O bond length histogram for TH, on the rutile surface, shows a bump at around 1.9 Å indicating more than one preferential M-O bond length for this surface species. Although the M-O bond length histograms are broader on rutile but the peak positions are either similar or shorter than those on cassiterite surface.

Table 3 Peak position and the half width at half maximum (HWHM) of the histogram of M-O bond lengths, for surface species BB, BH, TH and TW, on cassiterite and rutile surfaces.

<table>
<thead>
<tr>
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<th>Cassiterite</th>
<th></th>
<th>Rutile</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Peak Position</td>
<td>HWHM</td>
<td>Peak Position</td>
</tr>
<tr>
<td>BB</td>
<td>2.06 ±0.12</td>
<td></td>
<td>1.88 ±0.18</td>
</tr>
<tr>
<td>BH</td>
<td>2.11 ±0.14</td>
<td></td>
<td>2.02 ±0.18</td>
</tr>
<tr>
<td>TH</td>
<td>2.11 ±0.14</td>
<td></td>
<td>2.02 ±0.25</td>
</tr>
<tr>
<td>TW</td>
<td>2.17 ±0.16</td>
<td></td>
<td>2.18 ±0.27</td>
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</table>

The M-O bond lengths have been measured experimentally for the rutile surface. The X-ray CTR experiments done by Zhang et al. [62] found the M-O bond length to be 2.13 ± 0.03 Å for the TO on the hydrated rutile (110) surface. This bond length, as the X-ray cannot identify the H atoms, is an average over the M-O bond length for both TW and TH. In our simulation, we
find the averaged M-O bond length for the TO to be 2.16 Å. This is in close agreement with the experiments. Moreover, the amount of water dissociated was estimated to be around 30±15% in the experiment, which is in good agreement with the water dissociation ratio (∼25%) of the simulation. The small difference in the M-O bond length could be due to the fact that in the experimental setup rutile surface was hydrated with multiple layers of water whereas our simulation had 3 ML of water coverage.

The peak position of the M-O bond length histogram differs for a given surface species between the two metal oxide surfaces. Table 3 shows that the M-O bond lengths are consistently longer for cassiterite than for rutile except in the case of TW where they are almost the same for both surfaces. The difference in the peak position between the two surfaces for BB, BH and TH are 0.18 Å, 0.09 Å and 0.09 Å respectively. In contrast to this general trend, the M-O bond lengths for the TW only differ by 0.01 Å between rutile and cassiterite. For BB and BH, the larger M-O bond lengths on cassiterite can be related to its larger lattice spacing. The geometry of the M-O bond for the TW is responsible for its independence from the influence of lattice spacing. Although the peak positions are similar for TW, on rutile and cassiterite, the M-O bond length histogram is broader on rutile. This indicates that the interaction potential of the TW with the surface may be broader for rutile. But, the potential minimum depth should be similar for the two surfaces. To further understand this behavior, we study the potential profiles of a TW molecule on the pristine surfaces of the two materials.
Figure 15 Potential profiles of a TW molecule approaching the pristine (110) surface of rutile (black, •) and cassiterite (red, □) with the O atom of the water molecule pointing towards the five fold coordinated metal atom. The minimum of the potential profile is at 2.12 Å, for rutile, and 2.20 Å, for cassiterite. Moreover, the potential profile is deeper for rutile, by 0.1 eV, than cassiterite. Thus, TW will form a shorter and stronger bond with the metal atom of the surface. The curvature is similar for the two potential profiles, which indicates that the M-O histogram of the TW should be comparable for both surfaces.

We calculated the potential profile for a single water molecule with its O atom approaching a five fold coordinated metal atom in the pristine surface of rutile and cassiterite (Figure 15). The potential profile has a minimum at 2.12 Å for rutile and 2.20 Å for cassiterite. This means that the water molecule will form a shorter M-O bond on the rutile surface. Moreover, the potential profile scans results in the energy minimum being 0.1 eV deeper for rutile. This shows that the TW will form a stronger M-O bond on rutile as compared to cassiterite. On the other hand, we find that the curvature of the potential profile is similar for the two surfaces. The similarity of the curvature indicates that the M-O bond length histogram should have comparable HWHM for rutile and cassiterite. All of these conclusions are contrary
to the results obtained for the hydrated surface (Table 3). The hydrated simulation has broader HWHM (0.27 Å for rutile and 0.16 Å for cassiterite) indicating weaker M-O bond on rutile and the M-O bond length peak positions are similar for the two surfaces (2.18 Å for rutile and 2.17 Å for cassiterite). Moreover, a comparison of TW M-O bond length between the single water molecule simulation and the hydrated simulation shows an interesting behavior of bond elongation (0.05 Å) in rutile whereas bond contraction (0.02 Å) in cassiterite. The difference in the result between the hydrated surface and single water calculation suggests that the local environment plays an important role in determining the M-O bond strength.

The factors included in the study of the effect of local environment on the M-O bond length are the strength and the number of H-bonds formed by the TW. The M-O bond length histogram of the TW is wider on rutile compared to cassiterite. This indicates a broader potential profile for TW on rutile surface. However, the single water molecule simulations showed that both surfaces have similar potential profile curvature for the TW. Hence, a possible reason behind broader TW M-O bond length histogram on rutile can be the differences in interactions, where interactions correspond to H-bonds, which the TW has with its neighbors. The first difference can be that the interactions, between the TW and its neighbors, are stronger on rutile. However, we have shown in the previous chapter that, in general, the H-bonds are stronger on cassiterite than on rutile surface. The other possible difference is the number of interactions where TW may have larger number of interactions on rutile than on cassiterite. In order to find this, H-bond density analysis is done where the average number of H-bonds formed by the TW is calculated. This calculation shows that the TW forms higher average number of h-bonds on rutile (~2.3 H-bonds per TW molecule) as compared to the cassiterite surface (~2.1 H-bonds per TW molecule). Thus, the TW has higher tendency to form 3 H-bonds on rutile (38%) than on
cassiterite (14%). This may result in broadening of the potential that TW experiences on the rutile surface. We can therefore conclude that the local environment, i.e. number of H-bonds formed, has a significant effect on the M-O bond length.

Table 4 Peak position and the half width at half maximum (HWHM) for surface species BB, BH, TH and TW forming 1, 2 or 3 H-bonds on cassiterite and rutile surface. ‘BB_1’ corresponds to those BB that forms 1 H-bond with its neighbors.

<table>
<thead>
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<th>Cassiterite</th>
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<th>Rutile</th>
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<tbody>
<tr>
<td></td>
<td>Peak Position</td>
<td>HWHM</td>
<td>Peak Position</td>
<td>HWHM</td>
</tr>
<tr>
<td>BB_1</td>
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<td>2.01 ±0.18</td>
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</tr>
<tr>
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<td>2.06 ±0.19</td>
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<td></td>
</tr>
<tr>
<td>TH_2</td>
<td>2.11 ±0.14</td>
<td>1.88 ±0.11</td>
<td>2.02 ±0.22</td>
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</tr>
<tr>
<td>TH_3</td>
<td>2.12 ±0.14</td>
<td>2.01 ±0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TW_2</td>
<td>2.17 ±0.15</td>
<td>2.15 ±0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TW_3</td>
<td>2.20 ±0.18</td>
<td>2.26 ±0.26</td>
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The number of H-bonds formed by the surface species affects its M-O bond length. Table 4 shows the peak positions and the HWHM of the M-O bond length histogram for all surface species with specific number of H-bonds that it forms with the neighbors. The BB and BH mostly form 1 or 2 H-bonds whereas the TH and TW prefers 2 or 3 H-bonds, on both rutile and cassiterite surfaces. On the cassiterite surface, M-O bond length and HWHM for each of the surface species do not depend significantly on the number of H-bonds formed by them. This can be due to the fact that the M-O bond on the cassiterite surface is stronger than on rutile. Thus, the local environment has little to no effect on the M-O bond length for the cassiterite surface. On
the rutile surface, the M-O bond length and HWHM of BB remains largely unaffected as the number of H-bonds changes from 1 to 2. However, other surface species show large effects of the number of H-bonds on the M-O bond length. The BH, on rutile, has peak positions located at 2.01 Å and 2.06 Å for 1 and 2 H-bonds, respectively. The TW prefers to form 2 and 3 h-bonds with corresponding M-O bond length peak positions being 2.15 Å and 2.26 Å. These two peaks differ by 0.11 Å and hence produce a broad M-O bond length histogram for the TW on rutile surface (Figure 14, Table 3). The TH, on rutile, shows an interesting broad M-O histogram, when it forms 2 H-bonds (Figure 16). It distinctly has two peaks, one at 1.88 Å and the other at 2.02 Å. This indicates that the TH, that forms 2 H-bonds on the rutile surface, may have different local environments that are leading to the formation of the observed double peak in the corresponding M-O bond length histogram.
The difference in the local environment that may result in dual peaks in the M-O bond length histogram for the TH with 2 H-bonds is the species that are forming H-bonds with the TH molecule. Figure 17 shows the contribution of various H-bond environments toward the M-O bond length of TH molecule with 2 H-bonds. The first narrow peak at 1.88 Å appears when the TH acts as both donor and acceptor in forming the 2 H-bonds with its neighbors TH, TW or W. Three different H-bonding environment contribute toward this peak at 1.88 Å. The first type of H-bond environment is where TH donates a H-bond to a TW and accepts another H-bond from a W molecule (TH2_aTW_dW, here ‘a’ and ‘d’ refers to acceptor and donor, respectively). In the second type, TH donates a H-bond to a W molecule and accepts another H-bond from TW (TH2_aW_dTW). The third and last type of H-bond environment is where a TH donates a H-bond to another neighboring TH and accepts a H-bond from a W molecule in the water layer above the surface (TH2_aTH_dW). The second broader peak at 2.02 Å is completely due to an H-bonding environment where the H atom of TH does not participate in forming any of the two H-bonds. In this, TH only accepts H-bonds, one from a TW and the other from a W molecule in the water layer above the surface (TH2_dTW_dW). In the previous chapter, we mentioned that the H-bond donor accepts a small amount of charge donation from the H-bond acceptor [73]. Thus, when a TH accepts two H-bonds, it looses a significant amount of electrons to the donors, which results in decrease of charge density at the O atom. This in turn may lead to weakening of the M-O bond that the O forms with the five fold coordinated titanium atom in the rutile surface. On cassiterite, the TH with two H-bonds category has three kinds of H-bonding environments (Figure 18(e1)). Two of these are found on the rutile surface, TH2_aTH_dW and TH2_dTW_dW. The third H-bond configuration, that is absent on the rutile surface, is TH2_dTH_dW i.e. a TH accepting two H-bonds, one from a neighboring TH and another from a
W molecule in the layer above the surface. As mentioned earlier, these different H-bond environments, on cassiterite surface, have small effect on the M-O bond length. However, we do find that the H-bond configuration with both H-bonds accepting is weaker and has relatively longer M-O bond length than the H-bond configuration with one accepting and the other donating H-bonds.

Figure 17 Histogram of M-O bond length for TH forming 2 H-bonds (◊) with its various neighbors on rutile (110) surface. The double peak in the TH_2 histogram originates from the differences in the H-bonding environment. The first peak at 1.88 Å appears when the TH molecule acts as donor for one and an acceptor for another H-bond. There are three different H-bonding environments that belong to this category. First, TH accepts a H-bond from a W molecule and donates another H-bond to a TW (+, TH2_aTW_dW). Second, TH accepts a H-bond from TW and donates the other H-bond to a W molecule (▼, TH2_aW_dTW). Third, TH donates a H-bond to another TH and accepts a H-bond from a W molecule in the water layer above the surface (⊗, TH2_aTH_dW). The second peak at 2.02 Å appears when TH acts as acceptor for both of the H-bonds. In this the H atom of the TH does not participate in any H-bonding and it accepts one H-bond from the neighboring TW and the other H-bond from the W above the surface (∇, TH2_dTW_dW).
TH with 3 H-bonds (Figure 18(f1, f2)) always donates an H-bond and accepts two other H-bonds from its neighbors on both surfaces. On rutile, the acceptor can be a BB or a W with the two donors being TW and W (TH3_aBB_dTW_dW and TH3_aW_dTW_dW). Although both of these H-bond configurations exist on cassiterite but the configuration with BB as acceptor has much less presence than on rutile. On the cassiterite surface, the higher dissociation percentage of TW results in larger population of TH. Hence, we find higher proportion of another H-bond configuration with a TH donating one H-bond to a neighboring TH and accepting two H-bonds both from W molecules in the water layer above the surface (TH3_aTH_dW_dW). The TW, on both rutile and cassiterite, prefers to form 2 or 3 H-bonds with its neighbors. The TW with 2 H-bonds (Figure 18(g1, g2)) has both of its H atoms as donating centers with W always being one of the acceptors, on both surfaces. The other H-bond is formed with either a TH or a TW, on rutile (TW2_aTH_aW and TW2_aTW_aW). On cassiterite, TW donates the other H-bond to a neighboring TH or BB or another W molecule (TW2_aTH_aW, TW2_aBB_aW and TW2_aW_aW). TW with 3 H-bonds (Figure 18(h1, h2)) has many different H-bonding environments on the rutile surface. Among these, one of the configurations is found to be dominant where TW donates both of its H atoms to two W molecules and accepts the other H-bond from a neighboring TW (TW3_aW_aW_dTW). On cassiterite, the dominant configuration for TW with 3 H-bonds also has two of the H-bonds donated to two W molecules, but due to the higher dissociation of TW, the third H-bond is formed with a neighboring TH instead of a TW (TW3_aW_aW_dTH).
Figure 18 M-O bond length histogram for all of the surface species with various numbers of H-bonds containing different kinds of H-bonding environments. The largest curves in all of these plots are of BB_1 (a1, a2), BB_2 (b1, b2), BH_1 (c1, c2), BH_2 (d1, d2), TH_2 (e1, e2), TH_3 (f1, f2), TW_2 (g1, g2) and TW_3 (h1, h2). All other curves below the largest curve, in each plot, belongs to the various H-bonding environments that constitute the corresponding surface species with specific number of H-bonds. The plot numbering ‘1’ and ‘2’ (for e.g. a1 and a2) corresponds to cassiterite (red) and rutile (black) surface, respectively. The x-axis refers to M-O bond length and it is in the range 1.6 – 2.7 Å for all of the plots.

Other surface species, BB and BH, also have specific H-bond configuration on the two surfaces. BB with 1 H-bond (Figure 18(a1, a2)), on both surfaces, prefers to accept the H-bond from the W molecule in the water layer above the surface (BB1_dW) and not from other surface species such as TH or TW. The BB with 2 h-bonds (Figure 18(b1, b2)) has two preferential H-bonding environments. Along with accepting an H-bond with W molecule, it accepts another H-bond from a TH or a TW (BB2_dTH_dW and BB2_dTW_dW), on both surfaces. On rutile,
which has a lower dissociation state and hence larger number of TW, the BB with 2 H-bonds forms higher proportion of H-bonds with TW than with TH. The BH prefers to form 1 or 2 H-bonds. BH with 1 H-bond (Figure 18(c1, c2)) has only one dominant H-bonding environment, on rutile and cassiterite, where it donates its only H atom to a W molecule in the water layer above the surface (BH1_aW). Thus, both BB and BH, that form 1 H-bond, prefer to form H-bond with the W molecules, on both rutile and cassiterite surfaces. The dominant H-bond configuration for BH with 2 H-bonds (Figure 18(d1, d2)) has one of the H-bond donated to a W molecule, for both surfaces. The other h-bond is formed when BH accepts an H-bond from a TW (BH2_aW_dTW), on rutile, or a TH (BH2_aW_dTH), on cassiterite.

In summary, we find that the M-O bond length is representative of the local environment. The M-O bond length increases, on both rutile and cassiterite surfaces, as the number of covalently bonded H atoms increase from 0 to 1 for BO and 1 to 2 for TO. We find that the peak position is shorter, or equal for TW, and the HWHM of M-O bond length histogram is broader on rutile than on cassiterite. A comparison of the M-O bond length of TO with the X-ray CTR studies shows that our simulation is in close agreement, both in terms of the M-O bond length and the dissociation state, with the X-ray studies done by Zhang et al. [62] The analysis of H-bond density shows that the broadness of M-O bond length histogram of TW can be explained by higher H-bond density on the rutile surface. Along with the number of H-bonds, the identity of the acceptor and donor of the H-bond plays an important role in determining the M-O bond length. The broad M-O bond length histogram for TH was encompassed of two distinct peaks, one due to 2 H-bonds and the other due to 3 H-bonds formed by the TH with its neighbors. The TH with 2 H-bonds still showed a broad peak that was further resolved, only to be found that one of the peaks was coming from a specific H-bonding configuration.
Chapter 6

Effect of Slab thickness on the Adsorbed Water at Rutile (110) Surface

Introduction

It was recently shown [78] that the dissociation state of the water molecules adsorbed on the rutile (110) surface depends on the thickness of the slab that is used to model the water/rutile (110) interface. We have corroborated this calculation and found that the bulk plays a critical role in determining the dissociation state of the adsorbed water molecules on the surface of rutile. The H-bonds, between TW and BO, are affected with the slab thickness that in turn affects the proton transfer, which is crucial to obtain the dissociated configuration. The energetics study will show that proton jump on R₃ surface is preferred whereas on R₅ surface the adsorbed water molecule prefers to stay in associated configuration. Along with the slab thickness we have also analyzed the dissociation preference dependence on the lateral size of the simulation cell. A preliminary study on cassiterite surface shows that the dissociation preference, on this surface, is independent of the slab thickness. Figure 19 shows the two side views [(a) and (c)] of a R₇ simulation cell of pristine rutile (110) surface. The O-Ti-O triple layer is marked with the dashed lines. The top view of a 2x1 surface unit cell is shown with each unit cell marked by the solid blue line in Figure 19 (b). The surface unit cell contains one BO and one five fold coordinated metal atom.
Figure 19 The two side views [(a) and (c)] of a seven-layer thick slab ($R_7$) simulation cell, with the central layer fixed at the bulk positions, of pristine rutile (110) surface. The top view of the 2x1 surface unit cell (b) with each surface unit cell marked with the blue rectangle, containing exactly one BO and one five fold coordinated metal atom. The O-Ti-O triple layer is shown with dash lines in (a). The atoms in red and grey are oxygen and metal atoms, respectively.

The dependence of Energetics on layers

In a recent work by Liu et al. [78] it was shown that the calculated dissociation energy of water molecules, adsorbed on a rutile (110) surface, depends on the thickness of the slab used in the calculation (Figure 20, plot drawn with ▲). We repeated this calculation and studied the energetics of water dissociation on the rutile (110) surface as the slab thickness was increased from $R_3$ to $R_{15}$. Figure 20 (plot drawn with ◆) shows that as $R_n$ is increased from $R_3$ to $R_5$, the associated configuration gets preferred over partially dissociated configuration of the adsorbed water molecules. The adsorption energy difference for the $R_3$ surface is -0.025 eV/water molecule whereas it is +0.031 eV/water molecule for the $R_5$ surface. The energy difference
increases monotonically with \( R_n \) and it does not appear to converge even for the thickest slab considered, i.e. \( R_{15} \). Our present study and the previous work reported by Liu et al. [78] shows a similar trend of increasing energy difference with \( R_n \). The difference in the energetics of dissociation can be due to the difference in setting up the simulation. We place water molecules on both sides of the surface and fix the central layer of the slab to crystallographic positions to mimic the bulk behavior. In contrast, the calculation done by Liu et al. had water on only one side of the slab and the bottom-most layer was fixed to bulk positions. Although the adsorption energy difference for a given \( R_n \) is different in the two calculations, but the trend of the energy difference rising with \( R_n \) without any sign of convergence, even for the thickest slab (\( R_{15} \)), is seen in both set of calculations. The increasing energy difference with slab thickness suggests that the bulk may play an important role in determining the dissociation state of the water molecules adsorbed on the surface.
Figure 20 The dependence of adsorption energy difference (eV/water molecule) between fully associated and partially dissociated configurations $\left( E_{\text{ads}}^{\text{INTACT}} - E_{\text{ads}}^{\text{(PDIS)}} \right)$, on rutile (110) surface, on the number of O-Ti-O triple layers ($R_n$). The plots with dotted lines are the geometries where either the bottom most layer (△, from [78]) or the central layer (●) of a slab is fixed at bulk positions, to mimic the bulk behavior. The plot with solid line is the geometry, where all atoms below first triple O-Ti-O layer (■) are frozen to their bulk positions.

In order to determine the importance of the bulk, a computational experiment is done where all atoms below the first triple O-Ti-O layer are kept fixed to their bulk positions. The energetics studies, on these constrained geometries, show that the energy difference converges beyond $R_5$ (Figure 20 (plot drawn with ■)). The adsorption energy difference for constrained $R_5$ is found to be -0.003 eV/water molecule. This indicates that the adsorbed water molecules prefer partial dissociation on the constrained $R_5$ surface. As shown in Figure 20, all of the thicker slabs, with constraint on atoms that are deeper than the first triple layer, also show similar partial dissociation preference for the adsorbed water molecules. Moreover, the constrained geometries show converged energy difference, contrary to the monotonically increasing energy difference.
for the unconstrained geometries. The difference in the convergence of energies between the constrained and unconstrained geometries suggests that the bulk has a major role in determining the dissociation state of the adsorbed water molecules on the surface.

The H-bonds are crucial, as mentioned in the previous chapters, in determining the surface reactivity. Figure 21 shows the variation of H-bond lengths, for different type of H-bonds, with the slab thickness on both constrained (drawn with filled symbols and solid lines) and unconstrained (drawn with open symbols and dash lines) geometries. The H-bonds on the constrained geometries are very similar to the H-bonds on the R₃ slab, indicating that the bulk significantly influences these H-bonds. The length of the H-bond between the TW and BO (Ti₂O---TiHOH), on the unconstrained associated configuration (△), shows a monotonically increasing trend with Rₙ. This behavior is remarkably similar to the trend observed for the adsorption energy difference (Figure 20). The weakening of this H-bond with increasing slab thickness may increase the cost of proton transfer from TW to BO.
The study of the energetics of proton transfer shows that the proton jump on R₃ slab is preferred but the R₅ slab shows preference for fully associated configuration of the water molecules adsorbed on the surface. Figure 22 shows the energy profile for the proton transfer on the R₃ and R₅ slabs. The x-axis corresponds to the configuration number, where the Configuration 0 and 6 are the fully associated and partially dissociated configurations, respectively. The partially dissociated configuration is more stable than the associated configuration on the R₃ slab. This stability order is reversed for the R₅ slab. In this calculation, the proton dissociation on the two sides of the slab occurs in two steps and hence the two peaks,
one at Configuration 2 and the other at Configuration 5, are observed in the energy profile for both R₃ and R₅ slabs. The H-bond length study on these configurations shows that the H-bond length decreases just before the dissociation (Configuration 1 and 4), for facilitating the proton transfer, and relaxes after the proton jump (Configuration 3 and 6) on both R₃ and R₅ slabs. The large positive energy plateau, while going from fully associated to partially dissociated configuration, shows that the proton transfer will be significantly affected on the R₅ slab. Along with the slab thickness, the lateral dimension of the simulation cell also plays an important role in determining the dissociation state of the water molecules adsorbed on the surface.

Figure 22 Energy profile for the process of dissociation of water molecules on the rutile (110) surface with 1 ML of water coverage. The simulation cell changes from a fully associated configuration (Configuration 0) to a partially dissociated configuration (Configuration 6) on a R₃ (□) and R₅ (☆) slab. The water dissociation occurs in steps on the two sides of the slab (Configuration 2 and Configuration 5). The energy profile shows that the R₃ slab easily dissociates partially whereas the R₅ has a large energy barrier for partial dissociation. The energy values of each configuration are rescaled with respect to the associated configuration i.e. configuration 0 for both R₃ and R₅ slabs.
The dissociation preference of rutile (110) surface also depends on the lateral dimension of the simulation cell. Figure 23 shows the adsorption energy difference, between the associated configuration and partially dissociated configuration, with changing lateral dimension of the simulation cell, for the R₃ (□) and R₅ (★) slabs. The partially dissociated configuration, for each of the different lateral sizes of the simulation cell, has only one dissociated water molecule on each side of the slab. As shown earlier, the smallest simulation cell with 2x1 surface units prefers partially dissociated configuration for R₃ slab and fully associated configuration for the R₅ slab. This change of preference is absent in larger simulation cells. The 2x2 surface unit simulation cell prefers associated configuration for both R₃ and R₅ slabs. Whereas, the 4x2 or 4x4 cells have preference for partially dissociated configuration for both R₃ and R₅ slabs. The pattern of changing dissociation preference with lateral size of the cell, on both R₃ and R₅ slabs, is also seen in the corresponding H-bond length of the H-bond Ti₂O---TiHOH, on associated configurations. The H-bond length increases and then decreases by 0.02 Å as the lateral dimension of the simulation cell changes from 2x1 to 2x2 to 4x2. From 4x2 to 4x4 the H-bond length again increases by 0.01 Å. The adsorption energy difference (Figure 23) shows a general trend of becoming more positive as the slab thickness increases, from R₃ to R₅, for all lateral sizes of the simulation cell. This suggests that a slab thicker than R₅ may show change in dissociation preference for the larger cells.
Figure 23 Adsorption energy difference (eV/water molecule) between fully associated and a partially dissociated configurations \((E_{ads}^{\text{INTACT}} - E_{ads}^{\text{DIS}})\), where only one water molecule is dissociated on each side of the slab, on \(R_3\) (□) and \(R_5\) (★) slabs of rutile (110), with varying lateral size of the simulation cell. The ‘nxm’ lateral size corresponds to ‘n’ column and ‘m’ rows of surface unit cells. The amount of water coverage is 1 ML, which corresponds to one water molecule per five fold coordinated titanium (Ti\(^{5+}\)) atom, for all surfaces. The smaller simulation cells (2x1 and 2x2) prefer associated configuration for thicker slab (R5). Whereas, the larger simulation cells (4x2 and 4x4) shows preference for partially dissociated configuration on both R3 and R5 slabs.

The large simulation cell (4x2) shows change of preference from partially dissociated to fully associated configuration as the slab thickness is further increased from R5 to R7. Figure 24 shows the adsorption energy difference for three different slab thickness \(R_3\) (□), \(R_5\) (★) and \(R_7\) (▲) with 0%, 12.5%, 25% and 37.5% water dissociation that translates to 0, 1, 2 and 3 dissociated water molecules on each side of the slab. The dissociation of more than 1 water molecule on a 4x2 simulation cell can happen in more than one configuration. These configurations, depending upon the location of dissociation, are shown diagrammatically on the
left and the right side of the plot for 2 and 3 water molecule dissociations, respectively. This plot shows that the larger cell (4x2) starts preferring fully associated configuration of the adsorbed water molecule as a thicker slab (R₇) is used to model the surface. The configuration with 12.5% dissociation, i.e. one dissociated water molecule on each side of the slab, shows the change in dissociation preference as the slab thickness increases from R₅ to R₇. This behavior indicates that any large cell may eventually prefer fully associated configuration, if a sufficiently thick slab is used in modeling the simulation cell. A similar behavior in the dissociation preference is seen for surfaces with higher percentage of dissociation.

Figure 24 Adsorption energy difference (eV/water molecule) between fully associated and a partially dissociated configurations ($E_{ads}^{INTACT}$-$E_{ads}^{(P)DIS}$), on rutile (110) having 4x2 surface unit cells as the lateral size with slab thickness R₃ (□), R₅ (☆) and R₇ (△). The amount of water dissociation considered are 0%, 12.5%, 25% and 37.5% that corresponds to 0, 1, 2 and 3 water molecules dissociated on each side of the slab, respectively. All possible location of water dissociation for 2 and 3 water molecules are shown diagrammatically on left and right side of the plot, respectively. The bigger rectangle represents the surface of 4x2 surface unit cell where each square box corresponds to one surface unit cell containing one TW and one BO. The dark square box represents dissociated water molecule where it contains one TH and one BH.
The higher dissociation states, 25% or 37.5%, shows increasing preference towards associated configuration of the adsorbed water molecules as slab thickness is increased from $R_3$ to $R_5$ to $R_7$. The five possible arrangements of two or three dissociated water molecules, considering that the periodicity is imposed in all directions, is shown diagrammatically on the left and the right side of the plot in Figure 24, respectively. The surface of 4x2 surface unit cell is represented by the rectangle and each square box corresponds to the surface unit cell that contains one TW and one BB. The blackened square box symbolizes the surface unit cell with dissociated water molecule, i.e. it contains a TH and a BH. In both dissociation states, i.e. 25% or 37.5%, the adsorption energy difference increases continuously for all of the five configurations. At 25% dissociation, the configurations 1, 2 and 3 have very similar energies and it is significantly lower than configurations 4 and 5 for all three slab thickness. The crucial distinction between these two sets of configurations is the location of the two dissociated water molecules on the 4x2 surface unit simulation cell. In configurations 1, 2 and 3 the two dissociated water molecules are present on two different rows of TW molecules. But, configurations 4 and 5 have both dissociated water molecules on the same row of TW molecules. A similar behavior is observed in the configurations for three dissociated water molecules. The configuration 4', which has all three dissociated water molecules arranged one after another in the same row, is around 0.05 eV/water molecule higher in energy than other configurations. But, all other configurations, with two dissociated water molecules in the same row and the third dissociated water molecule in the other row, have similar energies.

The change in the dissociation preference as thicker slab is considered for the larger 4x2 cell indicates that a broader cell with sufficient slab thickness may eventually lead to associated configuration being preferred for the adsorbed water molecules. The results reported in previous
chapters are for a 4x2 cell with R₃ slab thickness. We find that it is sufficient to use R₃ slab geometry for modeling the water/rutile (110) interface since it has been shown to give consistent results with the experiments. The VDOS calculated from our simulations is in excellent agreement with the INS experiment by Spencer et al. [59] Zhang et al. in their X-ray CTR experiment [62] could precisely measure the position of titanium and O atoms. They used the covalent bond between the 5-fold coordinated titanium and the O atom of the adsorbed water molecule to estimate the partial dissociation of water on the rutile (110) surface to be around 30 ± 15%. The aiMD simulation of hydrated rutile (110) interface, with R₃ slab geometry, shows that the surface is at dynamical equilibrium of around 25% dissociation. In the same experiment, it was found that the water layer just above the surface has high degree of ordering and it forms H-bond with the surface that is stronger than the H-bonds between the water molecules. The R₃ slab simulation complied with these experimental findings. As shown in the previous chapters, the water above the surface was found to form stronger H-bond with the surface where the stretching frequencies of the H atoms were used to determine the strength of the h-bonds. And as seen in experiments and reported in the previous chapters, the stronger H-bond also gave high degree of ordering to the water layer above the surface.

In conclusion, we showed that the thickness of slab significantly affects the dissociation preference for the rutile surface as reported by Liu et al. [78] For a 2x1 surface unit cell, the adsorption energy difference increases monotonically with the slab thickness. This energy difference is found to converge when the atoms deeper than the first triple O-Ti-O layer is kept fixed to their bulk positions. The difference in the energy convergence suggests that the bulk plays a crucial role in determining the dissociation state of the adsorbed water molecules. A closer look at the H-bonds shows that the H-bond between TW and BO weakens significantly as
the slab thickness in increased from R₃ to R₁₅. This in turn increases the cost of proton transfer, which is needed to obtain the dissociated configuration, as observed in the energetics study for R₃ and R₅ slabs. The simulation cell with larger lateral size of the rutile surface, 4x2 and 4x4, is found to prefer partially dissociated configuration for R₃ and R₅ slabs. This preference is found to change for a thicker slab, i.e. R₇. This indicates that a larger cell with sufficient slab thickness may eventually prefer associated configuration for the adsorbed water molecules on the surface.

It was further shown that the R₃ slab geometry, as reported in the previous chapters, can model and predict the system to some extent as can be seen from results, such as amount of dissociation, high degree of ordering in the water layer just above the surface and stronger H-bond of water molecules with the surface, being consistent with the experiments. The reason for this consistency could be the fact that all of the analysis presented in this chapter, on the layer dependence, is related to 1 ML water coverage. But, the experiments and the analysis reported in the previous chapters are for the case where 3 ML water coverage is present on the rutile surface. The presence of this additional water layer may facilitate dissociation events leading to a partially dissociated surface for even a thick slab of rutile surface. The aiMD simulation of a thick slab, say R₇, for a larger lateral size simulation cell, such as 4x2, with 3 ML water coverage is computationally very expensive and is under consideration.
Chapter 7

Summary and Future Directions

We used ab initio simulations to investigate the water/metal oxide interface. In particular, we dealt with the naturally dominant (110) face of commonly occurring natural polymorphs of TiO$_2$ and SnO$_2$ called as rutile and cassiterite, respectively. The amount of water used on both surfaces was in accordance with the experimental findings [10]. The water molecules adsorbed on the surface can remain in molecular form or they can dissociate to form a pair of hydroxyls. The actual amount of water dissociation is a controversial topic and it continues to remain a matter of discussion in the scientific community.

We started our investigation of the water/metal oxide interface with the rutile surface. aiMD simulations predicted the dissociation level to be $\sim$25%. The water above rutile showed layering effect and three layers were identified as L1, L2 and L3. The L2 layer was found highly structured with two preferred adsorption sites that were in general agreement with the X-ray CTR studies. The VDOS of H atom was studied to capture the dynamical aspect of the water/rutile (110) interface. These dynamics can be explored experimentally with INS experiments. The total VDOS spectrum from simulations showed an excellent agreement with experimental data extracted from INS [59]. After this, we used our atomistic simulation to identify the VDOS of individual H atoms. The stretching band of the VDOS spectrum contains crucial information about the strength of H-bond. A softer stretching band corresponds to stronger H-bond and vice-versa. This study revealed that the H-bond was stronger between the surface and water than between water molecules in the water layer above the surface. This explained the high degree of ordering in the L2 layer and absence of any specific orientation in the L3 layer. It will be interesting to do a similar layer analysis for the cassiterite surface.
We expanded our study of water/metal oxide interface by including the cassiterite (110) surface along with the rutile (110) surface. In this investigation, we did a set of five simulations, for both surfaces, where each simulation differed in the amount of dissociation of the initial configuration. Interestingly, all of the five simulations equilibrated to ~60% and ~25% water dissociation for cassiterite and rutile, respectively. These dissociation amounts were dynamical as the proton jumping events were observed for the whole length of the simulation and throughout the whole surface. We find that the cassiterite surface has around 3 times more proton jumping activities than the rutile surface. The two main difference between these surfaces, lattice size and electronic structure, were investigated to identify the source of the difference in the proton jump rate. A computational experiment was done where the metal atoms were exchanged for the two surfaces, i.e. titanium atoms were replaced with tin atoms in rutile and tin atoms were replaced with titanium atom in cassiterite. The aiMD simulation of these exchanged ion simulation cells revealed that the proton jump rate was highly dependent on the type of ion. This suggested that the electronic structure difference plays a critical role in determining the proton jump rate. The proton jump rate was categorized based on the species involved in the proton-jumping event. It was seen that the proton jump rate between BO and WO is around 10 times more on cassiterite than on rutile. This huge disparity in proton jump rate was the result of an increase in the covalent and ionic contributions to the H-bond between the surface O and the hydration layer on cassiterite surface. This resulted in stronger H-bond and hence higher proton jump rate on cassiterite surface. In general, the H-bonds are found to be stronger on cassiterite surface.

The study of proton jump rates was followed by the investigation of the M-O bond length. We showed that M-O bond length is sensitive to its local environment. It increased as the
number of covalently bonded H atom increases from 0 to 1 for BO and from 1 to 2 for TO, on both surfaces. The narrower M-O bond length histogram, for all surface species (BB, BH, TH and TW), on cassiterite surface indicated stronger M-O bonds. A comparison of the M-O bond length of TO with the X-ray CTR study showed that our simulation was in close agreement, both in terms of the M-O bond length and the dissociation state, with the X-ray studies done by Zhang et al. [62] TW had similar peak positions on both surfaces but the HWHM was smaller for the cassiterite surface. This indicated that the interaction potential profile of the TW with the surface might be narrower for cassiterite. A computational experiment was done where the interaction potential profile was calculated for a single water molecule approaching the surface. The potential profile curvature was found to be similar for the two surfaces. We showed that the difference in the potential profile curvature was actually coming from the difference in the H-bond density. The rutile surface has higher H-bond density that could be resulting in the broadness of the corresponding potential profile curvature and hence broader M-O bond length histogram. Moreover, it was shown that along with the number of H-bonds, the identity of the acceptor and donor of the H-bond might also play an important role in determining the M-O bond length. In the end, we presented M-O bond lengths corresponding to all, statistically significant, H-bonding environments on both surfaces.

In the end, we presented our work on the dependence of dissociation preference of the adsorbed water molecules on the slab thickness that is used to model the rutile surface. This study was motivated by a recent study by Liu et al [78]. Firstly, we corroborated their energetics results for the 2x1 surface unit cell. A similar study on cassiterite surface indicated no dependence of the slab thickness on the dissociation state of the adsorbed water molecules. In rutile, the adsorption energy difference between the associated and partially dissociated
configuration was observed to be increasing monotonically. This energy difference was found to converge when the atoms below the first triple O-Ti-O layer was kept fixed to the bulk positions. This indicated that the bulk plays a critical role in determining the dissociation state of the water molecules adsorbed on the surface. The H-bonds between TW and BO, in the fully associated configuration, weakened with the increasing slab thickness. This affected the proton transfer, which is necessary to obtain the partially dissociated configuration, as seen in the energetics study of the proton transfer. Along with the slab thickness, we studied the dependence of lateral size of the simulation cell on the dissociation preference of the adsorbed water molecules on the surface. We found that simulation cells with larger lateral size of the rutile surface, 4x2 and 4x4, preferred partially dissociated configuration for R₃ and R₅ slabs. But, this preference changed back to fully associated configuration when thicker slab, i.e. R₇, was used. This indicated that a larger simulation cell, with sufficient slab thickness, might eventually prefer adsorbed water molecules to be in the associated configuration. Lastly, we defended our previous studies, which were done with R₃ slabs, by pointing out the excellent agreement between several experimental findings, such as results from X-ray CTR [62] and INS [59], and our simulations. Moreover, the results presented with R₃ slab had additional water layers above the surface. This layer could facilitate proton transfers even for thicker slabs. It will be interesting to do an aiMD simulation of a R₇ surface for a simulation cell with 4x2 surface unit cell and 3 ML water coverage. A comparison of this simulation with the results reported in this dissertation will give an insight into the influence of slab thickness on several results that can be directly compared with experiments.
APPENDIX A: Hohenberg and Kohn Theorems

Theorem I: A ground state particle density \( (n_0(\vec{r})) \) uniquely identifies the external potential \( V_{\text{ext}}^{(1)}(\vec{r}) \). This in turn uniquely identifies the Hamiltonian and hence all of the ground and excited state.

Proof: This theorem is proved by method of contradiction. We assume that there exist two external potentials \( V_{\text{ext}}^{(1)}(\vec{r}) \) and \( V_{\text{ext}}^{(2)}(\vec{r}) \) which give the same ground state particle density \( n_0(\vec{r}) \).

The two external potential corresponds to two different Hamiltonians, \( H_{e,R}^{(1)} \) and \( H_{e,R}^{(2)} \), and correspondingly there are two different ground state wave functions \( \Psi_{e,R}^{(1)}(\vec{r}) \) and \( \Psi_{e,R}^{(2)}(\vec{r}) \). As \( \Psi_{e,R}^{(2)}(\vec{r}) \) is not the ground state wave function for \( H_{e,R}^{(1)} \):

\[
E_{e,R} = \langle \Psi_{e,R}^{(1)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(1)}(\vec{r}) \rangle < \langle \Psi_{e,R}^{(2)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(2)}(\vec{r}) \rangle
\] (A.1)

The two Hamiltonians differ only in the external potential and hence we can rewrite the last term of Eq. (A.1) as:

\[
\langle \Psi_{e,R}^{(2)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(2)}(\vec{r}) \rangle = \langle \Psi_{e,R}^{(2)}(\vec{r}) | H_{e,R}^{(2)} | \Psi_{e,R}^{(2)}(\vec{r}) \rangle + \langle \Psi_{e,R}^{(2)}(\vec{r}) | H_{e,R}^{(1)} - H_{e,R}^{(2)} | \Psi_{e,R}^{(2)}(\vec{r}) \rangle
\]

\[
= E_{e,R}^{(2)} + \int d^3r \left[ V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r}) \right] n_0(\vec{r})
\] (A.2)

As \( E_{e,R}^{(2)} \) is not the ground state energy for \( H_{e,R}^{(1)} \), using (A.1) and (A.2),

\[
\langle \Psi_{e,R}^{(1)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(1)}(\vec{r}) \rangle < \langle \Psi_{e,R}^{(1)}(\vec{r}) | H_{e,R}^{(2)} | \Psi_{e,R}^{(2)}(\vec{r}) \rangle
\]

\[
E_{e,R}^{(1)} < E_{e,R}^{(2)} + \int d^3r \left[ V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r}) \right] n_0(\vec{r})
\] (A.3)

An exact same approach for \( E_{e,R}^{(2)} \) yields:

\[
E_{e,R}^{(2)} < E_{e,R}^{(1)} + \int d^3r \left[ V_{\text{ext}}^{(2)}(\vec{r}) - V_{\text{ext}}^{(1)}(\vec{r}) \right] n_0(\vec{r})
\] (A.4)

addition of (A.3) and (A.4) leads to the contradiction:

\[
E_{e,R}^{(1)} + E_{e,R}^{(2)} < E_{e,R}^{(2)} + E_{e,R}^{(1)}
\] (A.5)
This proves that the two different external potentials cannot produce the same particle density and hence a given particle density uniquely identifies the external potential.

**Theorem II:** The total energy of a system can be written as functional of particle density corresponding to a given $V_{\text{ext}}(\vec{r})$. The global minimum of this functional, which is the ground state energy of the system, will yield the $n_0(\vec{r})$.

**Proof:** The total energy of the system in Hohenberg-Kohn formalism (from Theorem I) can be written as:

$$E_{HK}[n(\vec{r})] = F_{HK}[n(\vec{r})] + \int d^3r V_{\text{ext}}(\vec{r}) \ n(\vec{r}) \quad (A.6)$$

We consider a system with ground state density $n^{(1)}(\vec{r})$ corresponding to a fixed external potential $V_{\text{ext}}^{(1)}(\vec{r})$. The ground state energy can be evaluated with the ground state wave function $\Psi_{e,R}^{(1)}(\vec{r})$ that gives the same Hohenberg-Kohn energy functional:

$$E^{(1)} = \langle \Psi_{e,R}^{(1)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(1)}(\vec{r}) \rangle = E_{HK}[n^{(1)}(\vec{r})] \quad (A.7)$$

Let us consider a different density, $n^{(2)}(\vec{r})$, which corresponds to a different wave function $\Psi_{e,R}^{(2)}(\vec{r})$. The total energy corresponding to $\Psi_{e,R}^{(2)}(\vec{r})$ state $E^{(2)}$ will be larger than $E^{(1)}$ as:

$$E^{(1)} = \langle \Psi_{e,R}^{(1)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(1)}(\vec{r}) \rangle < \langle \Psi_{e,R}^{(2)}(\vec{r}) | H_{e,R}^{(1)} | \Psi_{e,R}^{(2)}(\vec{r}) \rangle = E^{(2)} \quad (A.8)$$

This shows that the Hohenberg-Kohn functional evaluated at the correct ground state density is actually lowest than the value calculated for any other density.
APPENDIX B: Proof of various equations in VDOS calculations

The calculation of \( S(z) \):

We have the equation for the signal coming from an AR process:

\[
s_n = -\sum_{k=1}^{p} a_k s_{n-k} + Gu_n
\]  

(B.1)

Taking the z-transformation on both sides:

\[
\sum_{n=-\infty}^{\infty} z^{-n} s_n = -\sum_{n=-\infty}^{\infty} z^{-n} \sum_{k=1}^{p} a_k s_{n-k} + G \sum_{n=-\infty}^{\infty} z^{-n} u_n
\]

(B.2)

\[
S(z) = -\sum_{k=1}^{p} a_k \sum_{n=-\infty}^{\infty} z^{-n} s_{n-k} + G \sum_{n=-\infty}^{\infty} z^{-n} u_n
\]

here, we have used the definition of z-transform of signal \( S(z) = \sum_{n=-\infty}^{\infty} z^{-n} s_n \). We can change the indices in the first term on the right hand side, \( n - k = t \):

\[
S(z) = -\sum_{k=1}^{p} a_k \sum_{t=-\infty}^{\infty} z^{-t} s_{t} + G \sum_{n=-\infty}^{\infty} z^{-n} u_n
\]

(B.3)

\[
= -\sum_{k=1}^{p} a_k \sum_{t=-\infty}^{\infty} z^{-t} s_{t} + GU(z)
\]

\( U(z) \) is the z-transform of the input signal \( u_n \), \( U(z) = \sum_{n=-\infty}^{\infty} z^{-n} u_n \). ‘t’ or ‘n’ are the dummy indices. So, we can rewrite the above equation as:

\[
S(z) = -S(z) \sum_{k=1}^{p} z^{-k} a_k + GU(z)
\]

(B.4)

and, hence we finally get the equation (2.23) as:

\[
S(z) = \frac{GU(z)}{1 + \sum_{k=1}^{p} z^{-k} a_k}
\]

(B.5)
**The calculation of** \( R(z) \):

The autocorrelation function \( (r_n) \) of the output signal \( s_n \) is given by:

\[
r_n = \sum_{p=-\infty}^{\infty} s_p s_{p+n}
\]  

(B.6)

The corresponding z-transform of the autocorrelation function \( (R(z)) \) can be calculated as:

\[
R(z) = \sum_{n=-\infty}^{\infty} z^{-n} r_n
\]

\[
= \sum_{n=-\infty}^{\infty} z^{-n} \left( \sum_{p=-\infty}^{\infty} s_p s_{p+n} \right)
\]

(B.7)

\[
= \sum_{p=-\infty}^{\infty} s_p \left( \sum_{n=-\infty}^{\infty} z^{-n} s_{p+n} \right)
\]

Interchanging the indices as \( p + n = t \):

\[
R(z) = \sum_{p=-\infty}^{\infty} s_p \left( \sum_{t=-\infty}^{\infty} z^{-t} s_t \right)
\]

\[
= \sum_{p=-\infty}^{\infty} z^p s_p \left( \sum_{t=-\infty}^{\infty} z^{-t} s_t \right)
\]

(B.8)

\[
= \left( \sum_{t=-\infty}^{\infty} \left( z^{-1} \right)^t s_t \right) \left( \sum_{p=-\infty}^{\infty} z^{-p} s_p \right)
\]

Using the definition of the z-transform of the signal \( S(z) \), we can rewrite the above equation as:

\[
R(z) = S(z^{-1})S(z)
\]

(B.9)

Now using the expression for \( S(z) \) we finally get the equation (2.25):

\[
R(z) = \frac{G^2 U(z) U(z^{-1})}{\left( 1 + \sum_{k=1}^{\beta} z^{-k} a_k \right) \left( 1 + \sum_{l=1}^{\beta'} z^{l} a_l \right)}
\]

(B.10)
Proof of equation (2.26):

The signal theory model gives:

\[ s_n = -\sum_{k=1}^{p} a_k s_{n-k} + Gu_n \]  \hspace{1cm} (B.11)

Multiplying both sides with the signal \( s_n \) and taking the average as:

\[ \sum_{n=-\infty}^{\infty} s_n s_n = -\sum_{k=1}^{p} a_k \sum_{n=-\infty}^{\infty} s_{n} s_{n-k} + G \sum_{n=-\infty}^{\infty} s_n U_n \]  \hspace{1cm} (B.12)

Using the definition of autocorrelation function \( r_n \) we can write:

\[ r_0 = -\sum_{k=1}^{p} a_k r_k + G \sum_{n=-\infty}^{\infty} u_n s_n \]  \hspace{1cm} (B.13)

Again introducing the signal theory equation (B.11):

\[ r_0 = -\sum_{k=1}^{p} a_k r_k + G \sum_{n=-\infty}^{\infty} u_n \left( -\sum_{k=1}^{p} a_k s_{n-k} + Gu_n \right) \]  \hspace{1cm} (B.14)

The second term inside the bracket corresponds to correlation between the input signal at time 'n' with the outputs as times lower than 'n'. Thus from causality this expectation value is 0. Thus, we finally get the equation (2.26):

\[ r_0 = -\sum_{k=1}^{p} a_k r_k + G^2 \sum_{n=-\infty}^{\infty} u_n^2 \]  \hspace{1cm} (B.15)

Determination of domain of definition for the contour integration of \( \Psi^{(AR)}(z) \):

The \( z \)-transform of the velocity autocorrelation function \( \Psi^{(AR)}(z) \) with the denominator written with the zeros of the corresponding polynomials in the denominator, \( p(z) \) and \( q(z) \), is:
\[
\Psi^{(AR)}(z) = \frac{1}{d_p^{(p)}} \frac{-z^p \sigma_p^2}{\prod_{k=1}^{P} (z - z_k) \prod_{k=1}^{P} (z - z_k^{-1})}
\] (B.16)

This expression can be formally decomposed into partial fraction as:

\[
\Psi^{(AR)}(z) = \sum_{j=1}^{P} \left\{ \frac{A_j}{z - z_j} + \frac{B_j}{z - z_j^{-1}} \right\}
\] (B.17)

The stability and causality of AR process is guaranteed by considering that \(|z_j| < 1 \) (j = 1,...,P) [79]. The two parts of the fraction can be expanded in a Laurent and Taylor series as:

\[
\frac{1}{z - z_j} = \frac{1}{z} \frac{1}{1 - (z_j / z)} = \frac{1}{z} \sum_{n=0}^{\infty} \left( \frac{z}{z_j} \right)^n, \quad |z| > |z_j|
\] (B.18)

and,

\[
\frac{1}{z - z_j^{-1}} = \frac{1}{z_j^{-1}} \frac{1}{1 - (z / z_j^{-1})} = -z_j \sum_{n=0}^{\infty} \left( z z_j \right)^n, \quad |z| < |z_j^{-1}|
\] (B.19)

These expansions defines the domain of definition for \( \Psi^{(AR)}(z) \) as:

\[
|z_j|_{\text{max}} < |z| < \frac{1}{|z_j|_{\text{max}}}
\] (B.20)
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