AN AB INITIO STUDY OF ALPHA-QUARTZ (0001) SURFACE AND WATER-SILICA INTERFACE INTERACTION

By

YUN-WEN CHEN

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2010
To my parents and siblings
ACKNOWLEDGMENTS

I acknowledge Dr. Hai-Ping Cheng for her advice in all this work and her great patience. None of this would be done without her teaching and inspiring tutelage in Physics. I also thank my former colleagues, Dr. Chao Cao and Dr. Alexander Kemper for their help in programming and technological suggestions. In particular, Dr. Cao shared diverse knowledge in Physics and numerous strategies in computational science. I would also like to thank my colleagues and peers in my group for their helpful questions and discussions in the long journey of developing my research.

Funding from NSF under Grant No. DMR-0325553 and DMR-0804407 has supported my PHD study for past 5 years. The DOE/NERSC and UF/HPC centers have provided computing resources for this work.

I would like to show my appreciation to Dr. Samuel B. Trickey for his extensive help with editing this work.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION AND BACKGROUND</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Two Important Ingredients in Human Life</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Silica Surfaces</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>Water at Interfaces and Water-Silica Interaction</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>COMPUTATIONAL METHODS</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Classical Molecular Dynamics</td>
<td></td>
</tr>
<tr>
<td>2.1.1</td>
<td>Newtonian Equations</td>
<td></td>
</tr>
<tr>
<td>2.1.2</td>
<td>Computational Algorithm (for NVE ensemble)</td>
<td></td>
</tr>
<tr>
<td>2.1.3</td>
<td>Extension to Thermostats and Barostats</td>
<td></td>
</tr>
<tr>
<td>2.1.3.1</td>
<td>Berendsen thermostats and barostats</td>
<td></td>
</tr>
<tr>
<td>2.1.3.2</td>
<td>Nosé-Hoover thermostats and barostats</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Density Functional Theory</td>
<td></td>
</tr>
<tr>
<td>2.2.1</td>
<td>Hartree-Fock approximation</td>
<td></td>
</tr>
<tr>
<td>2.2.2</td>
<td>Kohn-Sham Ansatz and Local Density Approximation</td>
<td></td>
</tr>
<tr>
<td>2.2.3</td>
<td>Generalized Gradient Approximation</td>
<td></td>
</tr>
<tr>
<td>2.2.4</td>
<td>Pseudopotential</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ALPHA-QUARTZ (0001) SURFACES</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Perfect Surface Reconstruction</td>
<td></td>
</tr>
<tr>
<td>3.1.1</td>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>3.1.2</td>
<td>Method</td>
<td></td>
</tr>
<tr>
<td>3.1.3</td>
<td>Results</td>
<td></td>
</tr>
<tr>
<td>3.1.4</td>
<td>Discussion and Conclusion</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Fully Hydroxylated Surface</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Defective Surfaces</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>WATER CLUSTER ADSORPTION ON SILICA SURFACES</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Methods</td>
<td></td>
</tr>
</tbody>
</table>
4.3 Water Adsorption on Surfaces 1 and 2 ((1X1) and (2X1) Perfect Surface)...... 59
4.4 Water Adsorption on Surface 3 (the Fully Hydroxylated Surface).............. 62
4.5 Water Adsorption on Surfaces 4 and 5 (Oxygen Vacancy Defect)............. 64
4.6 Water Adsorption on Surfaces 6 and 7 (Oxygen Displacement)............... 66

5 WATER LAYER(S) ADSORPTION ON SILICA SURFACES......................... 94

5.1 Introduction.................................................................................. 94
5.2 Methods..................................................................................... 95
5.3 Water Adsorption on Surfaces 1 and 2 ((1X1) and (2X1) Perfect Surface) 95
5.4 Water Adsorption on Surface 3 (the Fully Hydroxylated Surface)......... 100
5.5 Water Adsorption on Surfaces 4 and 5 (Oxygen Vacancy Defect)....... 102
5.6 Water Adsorption on Surfaces 6 and 7 (Oxygen Displacement)......... 105

6 HYDROXYLATION OF ALPHA-QUARTZ (0001) SURFACES.................... 145

6.1 Introduction................................................................................. 145
6.2 Methods................................................................................... 146
6.3 Results...................................................................................... 146
6.3.1 Hydroxylation on Surfaces 1 and 2 ((1x1) and (1x2) Pefect Surface) 146
6.3.2 Hydroxylation on Defective Surfaces................................. 148

7 SUMMARY ................................................................................... 156

REFERENCES ............................................................................... 159

BIOGRAPHICAL SKETCH ................................................................. 164
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Experimental and calculated structure of bulk alpha-quartz.</td>
<td>49</td>
</tr>
<tr>
<td>3-2</td>
<td>The surface energies $\varepsilon$ (in meV/Å$^2$) of five reconstructed surfaces and the freshly cleaved surface, and the energy barriers (in meV/Å$^2$) for transition from type I ($E_{Ib}^I$) or type II ($E_{IIb}^{II}$) surface to others.</td>
<td>49</td>
</tr>
<tr>
<td>3-3</td>
<td>The average charge on each atom species of surface type I, type III and $\alpha$-quartz bulk.</td>
<td>49</td>
</tr>
<tr>
<td>3-4</td>
<td>The average charge on each atom species of a hydroxylated quartz slab.</td>
<td>50</td>
</tr>
<tr>
<td>3-5</td>
<td>The formation energy of a defective surface with respect to (1x1) perfect surface.</td>
<td>50</td>
</tr>
<tr>
<td>3-6</td>
<td>The average charge transfer onto Si/O atoms at and around the defect site.</td>
<td>50</td>
</tr>
<tr>
<td>4-1</td>
<td>The adsorption and bonding energy of water molecules on silica surface.</td>
<td>69</td>
</tr>
<tr>
<td>4-2</td>
<td>Charge transfer analysis of water molecules on surface.</td>
<td>69</td>
</tr>
<tr>
<td>4-3</td>
<td>The charge redistribution of water cluster adsorption systems.</td>
<td>70</td>
</tr>
<tr>
<td>5-1</td>
<td>The adsorption and bonding energy of water layer(s) on a silica surface.</td>
<td>107</td>
</tr>
<tr>
<td>5-2</td>
<td>The charge transfer analysis of water layer(s) on a silica surface (Positive means gaining electrons).</td>
<td>108</td>
</tr>
<tr>
<td>5-3</td>
<td>The charge redistribution of water layer(s) adsorption systems.</td>
<td>109</td>
</tr>
<tr>
<td>6-1</td>
<td>Hydroxylation energy of surfaces 1.</td>
<td>151</td>
</tr>
<tr>
<td>6-2</td>
<td>Hydroxylation energy of surfaces 2.</td>
<td>151</td>
</tr>
<tr>
<td>6-3</td>
<td>Hydroxylation energy of defective surfaces.</td>
<td>151</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>3-1</td>
<td>Top and side views of reconstructed alpha-quartz (0001) surfaces</td>
<td>51</td>
</tr>
<tr>
<td>3-2</td>
<td>Transformations from one surface type to another. a) From type I (left) to type II (right); b) from type I (left) to type III (right)</td>
<td>51</td>
</tr>
<tr>
<td>3-3</td>
<td>Statistics of bond length and bond angles of all perfect surfaces</td>
<td>52</td>
</tr>
<tr>
<td>3-4</td>
<td>Top view of the large-scale structure of a reconstructed alpha-quartz surface from MD simulation</td>
<td>52</td>
</tr>
<tr>
<td>3-5</td>
<td>Top view (a) and side view (b) of a full hydroxylated alpha-quartz (0001) surface</td>
<td>53</td>
</tr>
<tr>
<td>3-6</td>
<td>Top view (a) and side view (b) of detective surface 1 (oxygen vacancy)</td>
<td>54</td>
</tr>
<tr>
<td>3-7</td>
<td>Top view (a) and side view (b) of detective surface 2 (oxygen vacancy)</td>
<td>54</td>
</tr>
<tr>
<td>3-8</td>
<td>Top view (a) and side view (b) of detective surface 3 (oxygen displacement)</td>
<td>55</td>
</tr>
<tr>
<td>3-9</td>
<td>Top view (a) and side view (b) of detective surface 4 (oxygen displacement)</td>
<td>55</td>
</tr>
<tr>
<td>4-1</td>
<td>One water molecule adsorbed on surface 1 ((1x1) perfect surface) at the hollow site</td>
<td>71</td>
</tr>
<tr>
<td>4-2</td>
<td>One water molecule adsorbed on surface 2 ((2x1) perfect surface)</td>
<td>72</td>
</tr>
<tr>
<td>4-3</td>
<td>One water molecule adsorbed on surface 1 ((1x1) perfect surface) at the silicon atom site</td>
<td>73</td>
</tr>
<tr>
<td>4-4</td>
<td>Two water molecules adsorbed on surface 1 ((1x1) perfect surface)</td>
<td>74</td>
</tr>
<tr>
<td>4-5</td>
<td>Two water molecules adsorbed on surface 2 ((2x1) perfect surface)</td>
<td>75</td>
</tr>
<tr>
<td>4-6</td>
<td>Two water molecules adsorbed on two silicon sites of surface 1 ((1x1) perfect surface)</td>
<td>76</td>
</tr>
<tr>
<td>4-7</td>
<td>Three water molecules adsorbed on surface 1 ((1x1) perfect surface)</td>
<td>77</td>
</tr>
<tr>
<td>4-8</td>
<td>Three water molecules adsorbed on surface 2 ((2x1) perfect surface)</td>
<td>78</td>
</tr>
<tr>
<td>4-9</td>
<td>One water molecule adsorbed on surface 3 (fully hydroxylated surface)</td>
<td>79</td>
</tr>
<tr>
<td>4-10</td>
<td>Two water molecules adsorbed on surface 3 (fully hydroxylated surface)</td>
<td>80</td>
</tr>
<tr>
<td>4-11</td>
<td>Three water molecules adsorbed on surface 3 (fully hydroxylated surface)</td>
<td>81</td>
</tr>
</tbody>
</table>
4-12 One water molecule adsorbed on surface 4 (oxygen vacancy defect).............. 82
4-13 One water molecule adsorbed on surface 5 (oxygen vacancy defect).............. 83
4-14 Two water molecules adsorbed on surface 4 (oxygen vacancy defect).............. 84
4-15 Two water molecules adsorbed on surface 5 (oxygen vacancy defect).............. 85
4-16 Three water molecules adsorbed on surface 4 (oxygen vacancy defect).............. 86
4-17 Three water molecules adsorbed on surface 5 (oxygen vacancy defect).............. 87
4-18 One water molecule adsorbed on surface 6 (oxygen vacancy displacement)........... 88
4-19 One water molecule adsorbed on surface 7 (oxygen vacancy displacement)........... 89
4-20 Two water molecules adsorbed on surface 6 (oxygen vacancy displacement).................................................................................................................. 90
4-21 Two water molecules adsorbed on surface 7 (oxygen vacancy displacement)........ 91
4-22 Three water molecules adsorbed on surface 6 (oxygen vacancy displacement).................................................................................................................. 92
4-23 Three water molecules adsorbed on surface 7 (oxygen vacancy displacement).................................................................................................................. 93
5-1 One water layer adsorbed on surface 1 ((1x1) perfect surface) with protons pointing up........................................................................................................................................ 110
5-2 One water layer adsorbed on surface 1 ((1x1) perfect surface) with protons pointing down........................................................................................................................................ 111
5-3 One water layer adsorbed on surface 2 ((2x1) perfect surface) with protons pointing up........................................................................................................................................ 112
5-4 One water layer adsorbed on surface 2 ((2x1) perfect surface) with protons pointing down........................................................................................................................................ 113
5-5 Two water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing up in the first water layer........................................................................................................................................ 114
5-6 Two water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing down........................................................................................................................................ 115
5-7 Two water layers adsorbed on surface 2 ((2x1) perfect surface) with protons pointing up in the first water layer........................................................................................................................................ 116
5-25 Two water layers adsorbed on surface 4 (oxygen vacancy defect) with protons pointing down. ................................................................. 134

5-26 Two water layers adsorbed on surface 5 (oxygen vacancy defect) with protons pointing up in the first water layer. ......................................................... 135

5-27 Two water layers adsorbed on surface 5 (oxygen vacancy defect) with protons pointing down. ................................................................. 136

5-28 One water layer adsorbed on surface 6 (oxygen displacement) with protons pointing up.............................................................................. 137

5-29 One water layer adsorbed on surface 6 (oxygen displacement) with protons pointing down. .............................................................................. 138

5-30 One water layer adsorbed on surface 7 (oxygen displacement) with protons pointing up.............................................................................. 139

5-31 One water layer adsorbed on surface 7 (oxygen displacement) with protons pointing down. .............................................................................. 140

5-32 Two water layers adsorbed on surface 6 (oxygen displacement) with protons pointing up in the first water layer. ......................................................... 141

5-33 Two water layers adsorbed on surface 6 (oxygen displacement) with protons pointing down. .............................................................................. 142

5-34 Two water layers adsorbed on surface 7 (oxygen displacement) with protons pointing up in the first water layer. ......................................................... 143

5-35 Two water layers adsorbed on surface 7 (oxygen displacement) with protons pointing down .............................................................................. 144

6-1 Two examples of the initial configurations for surface hydroxylation. ............... 152

6-2 The hydroxylation sites on surface 1................................................................ 152

6-3 Two types of hydroxylation on surface 1.......................................................... 153

6-4 Two types of hydroxylation of surface 2 with higher hydroxylation energy. ...... 154

6-5 Hydroxylation on surface 4 and surface 6......................................................... 155
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>B88</td>
<td>Becke 88</td>
</tr>
<tr>
<td>BKS</td>
<td>van Beest, Kramer, and van Santen</td>
</tr>
<tr>
<td>CPMD</td>
<td>Car-Parrinello Molecular Dynamics</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>GEA</td>
<td>Gradient Expansion Approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
</tr>
<tr>
<td>HSC</td>
<td>Hamann, Schluter and Chiang</td>
</tr>
<tr>
<td>LDA</td>
<td>Local density approximation</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>NPT</td>
<td>Constant particle number, system pressure, and system temperature</td>
</tr>
<tr>
<td>NVE</td>
<td>Constant particle number, system volume, and total energy</td>
</tr>
<tr>
<td>NVT</td>
<td>Constant particle number, system volume, and system temperature</td>
</tr>
<tr>
<td>OPW</td>
<td>Orthogonalized Plane Wave</td>
</tr>
<tr>
<td>PAW</td>
<td>Projector Augmented-Wave</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew, Burke, and Enzerhof</td>
</tr>
<tr>
<td>PW91</td>
<td>Perdew and Wang 91</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab initio Simulation Package</td>
</tr>
</tbody>
</table>
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

AN AB INITIO STUDY OF ALPHA-QUARTZ (0001) SURFACE AND WATER-SILICA INTERFACE INTERACTION

By

Yun-Wen Chen

December 2010

Chair: Hai-Ping Cheng
Major: Physics

Silica is an important mineral for many applications in our daily life. Thus, numerous studies have been done to understand its properties and its interaction with other materials/molecules. In this work, we apply first-principles density functional theory (DFT) calculations to the investigation of alpha-quartz (0001) surfaces and water clusters and water layer(s) adsorbed on those surfaces. Ten different surfaces are studied for exploring alpha-quartz (0001) surface properties. They include five reconstructed surfaces, one fully hydroxylated surface, and four defective surfaces. Water molecule(s) and layer(s) were deposited on seven of the surfaces to examine how surface character can affect the behavior of water molecule(s) or layer(s) adsorbed on the surface.

A newly cleaved silica surface generally is thought to be hydroxylated quickly in atmosphere and become hydrophilic. However, the surface can be dehydrated under an Ultra High Vacuum (UHV) environment and the siloxane surface is then hydrophobic. We will discuss the five perfect surface reconstruction patterns of the alpha-quartz (0001) surface (called perfect surfaces frequently in the following text) and how they can explain the observed (2 x 2) diffraction spectrum in experiments. A fully hydroxylated
alpha-quartz (0001) surface will be discussed in detail regarding its formation energy, structure and charge distribution. Two oxygen vacancy and two oxygen displacement defective surface patterns on (1 x 1) perfect surface were considered in this work. Their formation energies, structures, charge distributions and hydroxylation on the defect sites will be discussed.

Water molecule adsorption on surfaces was investigated by depositing molecules one by one. The hydroxylated surface exhibits highly hydrophilic properties. Conversely, perfect surfaces are hydrophobic or interact with water molecules quite weakly. A defect on the surface does enhance water adsorption on that surface. However, the strong hydrogen bonds within a water cluster have a tendency to compromise the water-silica interaction. Ice XI sub-layers were deposited one by one on surfaces. The highly stable bilayer structures which result effectively shield the interaction between water and the silica surface.
CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 Two Important Ingredients in Human Life

Water and silica, two important ingredients involved in daily human life, both play irreplaceable roles in many aspects of biology, chemistry, geology, weathering, etc. The water-silica interaction is a topic of extensive scientific attention from ancient times. It is our research interest in this work.

Water is definitely recognized as the most important material affecting all living beings on the Earth because it is involved in many life-essential chemical processes. The existence of water on a remote planet is always the first index of hypothesizing other life forms on said planet. Of course, the value of water is not just in biology; it is involved in myriad phenomena happening around us (on Earth, at least). The daily weather we must accommodate, the erosion of Earth’s crust, the rotting of food, and even the types of volcanic eruptions are all examples wherein the character of water plays a role. On the other hand, a clean water resource is so important to human activities, that we can say that water also affects phenomena happening in civilization and economics.

Scientists have exerted themselves for over a hundred of years to understand the behavior of water and its interaction with other materials. Water in solid phase has multiple polymorphs under different pressure and temperature conditions [1, 2]. Various crystal types built by the complex network of hydrogen bonds have drawn enormous scientific effort to investigate their properties and the research progress continues. Salzmann et al. found a new ice phase, Ice XV, in 2009 by neutron diffraction [3]. Ice XV is the hydrogen-ordered form of ice VI and has antiferroelectric property. The trouble
makers, hydrogen bonds, are also responsible for the strange behavior of water in liquid and gas phase [4]; superheated, supercooled water and supercritical fluid phenomena enticed researchers to repeat experiments again and again. Because most life-essential chemical processes always involve liquid water in participating or mediating, the interaction between water and other materials and the behavior of liquid water itself comprise one of the most important modern fields of study. Another reason for investing so much scientific effort in this topic is the potential for numerous applications in biology and industry to make human lives better.

Silica is one of the most abundant minerals in the Earth's crust. Its various polymorphs and many applications in industry have attracted sustained research on this material. Silica exists in various solid forms in the Earth’s crust: quartz, cristobalite, tridymite, coesite, stishovite, and also amorphous silica. In principle, they are constructed from rigid SiO$_4$ tetrahedron units with shared corners [5, 6]. However, each has its special properties in density, bulk modulus, dielectric constant, etc. Silica appears not only as a mineral in nature but is also found in cell walls of diatoms. The amazing structure of the diatoms cell walls not only draws biologists’ attention but also compels scientists to study its application in nanotechnology [7]. Human kind already uses silica in many applications, such as a substrate in the semiconductor industry, lenses, glass, silica gel and nano-particles. Similar to water, silica has been studied for a very long time in human history. Such study becomes more conspicuous in contemporary time because of growing applications. Recently, for example, silica-based devices have been developed for DNA/RNA sequencing [8-10].
Understanding the water-silica interaction thus is an important subject to which many research groups have devoted prodigious efforts. For understanding how erosion of the Earth’s crust occurs and also for industrial applications, it is important to know the mechanism of interaction between water molecules and silica, the key procedure to prevent silica erosion with coating, etc. It also helps to understand the formation process of a diatom cell wall, the etiology of silicosis [11] and perhaps the application of silica in DNA/RNA sequencing.

1.2 Silica Surfaces

Since at room temperature, silica is in solid phase and water is liquid or vapor phase for many biological and chemical processes of high interest, investigating silica surface structures will be the first step to take. Surface properties of crystalline silica, amorphous silica and amorphous silica combined with other chemical components all have been the subjects of study by experiments or theory. Basically, these surfaces are defined as either hydrophilic or hydrophobic depending on how they are prepared. There are many strategies in chemistry that can change the hydrophilic properties of silica surfaces by coating or chemically terminating the surface with other molecules. In this work, we only consider surfaces terminated with hydroxyl groups (Si-OH, or silanol group) and bare surfaces with or without defects.

In atmosphere, a newly cleaved silica surface will interact exothermically with water molecules and form hydroxyl groups because of the dangling bond left after cleavage. The resulting surface has been shown to be hydrophilic in many studies [5, 6]. On the other hand, if the surface is carefully prepared in an Ultra High Vacuum (UHV) environment, the silica surface is dehydrated and hydrophobic [12-16]. Many investigations have been done both experimentally [17-19] and computationally [20-22]
to answer various questions about how water is adsorbed on silica surface, how weathering phenomena proceed, etc. Because silica has so many polymorphs with different symmetries on each facet, and the structures of silica surfaces vary from one type to the other, the surface properties could vary greatly among them. Amorphous silica is the form with the most numerous applications. Its surface properties and defect populations are main objects for the experimental studies. Yet a local description of the structure and feature of amorphous silica surface has not been completed by either experiments or first-principle calculations. The crystalline silica surface could provide a relatively simple model for understanding the effects of silica surface on water molecules and the hydrogen bonding network. In this work, we investigate several alpha-quartz (0001) surfaces, and water cluster/layer(s) adsorption on the surface.

1.3 Water at Interfaces and Water-Silica Interaction

Because many natural phenomena and technological applications depend upon the interfaces of water and other materials, it is a prominent research topic. The hydrophilic/hydrophobic properties of a surface can dramatically alter the hydrogen bonds network of water near the surface and add complexity to the numerous known anomalies in the water phase diagram [1, 2, 4]. The interaction strength varies from weak bonding between hydrophobic surfaces and water molecules to strong chemical bonding of hydroxylation of surface or partially dissociation of water adsorbed on the surface [23]. Recently, water confined in a nano-scale space has commanded intense scrutiny from researchers, especially in biological science. Castellana and Cremer reported that a water layer can exist between lipid bilayers and a solid substrate at a thickness of 10 to 20 Å. The existence of this water layer is important for hydration of lipids and for enhancing lipid bilayers stability [24]. Janiak and Scharmann reported a
neutron diffraction study on nearly two-dimensional water and ice layers confined between organic layers of nickel(II) chelate complexes [25]. Temperature dependence studies on the water/ice layers, ranging from 20 K to 278 K, showed both liquid-solid and solid-solid transitions. Antognozzi et al. measured the viscoelastic force of confined water layers on mica surface with transverse dynamic force microscopy [26]. They measured the relationship between amplitude and phase of the oscillating force and observed a step-like behavior; the elastic and viscous forces of the water layer were evaluated.

For water- silica interfaces, many groups investigated the mechanism of weathering (hydroxylation) of a silica surface, water adsorbed on a silica surface, and water confined in silica nanopores in experiments and also theoretical simulation via density functional theory (DFT) or classical molecular dynamics (MD) methods. A summary of these methods is given in Chapter 2. Du et al. studied the hydroxylation of the silica surface with a combination of classical MD and DFT calculations [27]. They concluded that water will attack regions with high local strain. Du et al. [21] and Adeagbo et al. [28] studied the dissolution of an Si(OH)$_4$ unit on fully hydroxylated alpha-quartz (0001) surfaces by using classical MD and DFT calculations respectively. On the other hand, Du et al. [14] and Rignanese et al. [15] showed that the perfectly reconstructed alpha-quartz (0001) surface is hydrophobic; further, Rignanese et al. showed this surface is very hard to hydroxylate.

Asay and Kim studied water layers adsorbed on a hydrophilic silica surface with attenuated total reflection-infrared spectroscopy [17]. They suggested that icelike water will grow up to three layers at room temperature. Optiz et al. measured the friction force
of a water thin film on silica surfaces. The measurement showed dramatically different tendencies on hydrophilic and hydrophobic surfaces with high and low friction forces respectively [29]. Ostroverkhov and Shen et al. studied a series of phase-sensitive sum-frequency spectroscopies of the water-quartz interface [18, 19]. Through that technology, they analyzed the icelike and liquidlike peaks in the spectrum and the polar orientation of water at the interface for different pH values. Yang et al. found water could form an icelike layer on full hydroxylated beta-cristobalite (100) and alpha-quartz (0001) surfaces in their DFT calculations [22, 30]. Several groups studied the density distribution, dipole orientation, and drift velocity of water molecules on silica surfaces with classical MD [31-33]. Their result showed water layers forming on the silica surface, and some of them showed that hydroxylation conditions can greatly alter the behavior of water.

Many groups experimentally observed confined water in silica nanopores [34-36]. The melting point of water is lowered depending on the size of the nanopores. In principle, there may be two or three types of water existing in the pores: quasi-liquid (or non-freezing) water layer with low mobility next to the silica wall, core water at the central region of the pore, and perhaps shell water between the former two types. The thickness of the quasi-liquid water layer was not well-determined in these experiments but it was suggested to be between one to three monolayers in most of the papers. Liu et al. clearly suggested that there will be three types of water, core water, shell water and bound non-freezing water [36]. From their experimental results, they suggested that non-freezing water formed a bilayer film next to the pore wall when water completely filled the nanopores. Confined water in a silica tube also was studied with classical MD
by some groups [20, 37, 38]. Their observations agree with the proposed model for experimentally confined water in silica nanopores. Both bound non-freezing water and core water exist in the silica tube model.

So far, first-principle studies on the adsorption of water on silica surface only focused on one or two water molecules, and one monolayer adsorption [14, 15, 22, 30]. More effort is warranted to investigate water-silica interfacial properties and answer a long-standing question. Is there an ice or quasi-liquid film at the interface and, if so, what is the thickness of such a film [17]?
CHAPTER 2
COMPUTATIONAL METHODS

In this chapter, we are introduce the computational methods used in this work. Classical molecular dynamics (MD) and density functional theory (DFT) methods are included.

2.1 Classical Molecular Dynamics

2.1.1 Newtonian Equations

In MD, the many-body dynamics of the simulated system are solved by Newton’s equations of motion.

\[ \frac{d\vec{p}_i}{dt} = \vec{F}_i = -\nabla U(\vec{r}_1, \vec{r}_2, \vec{r}_3, ...) \]  \hspace{1cm} (2-1)

Here, \( \vec{p}_i, \vec{F}_i \) and \( \vec{r}_i \) are the momentum, force and position vectors of atom \( i \).

\( U(\vec{r}_1, \vec{r}_2, \vec{r}_3, ...) \) is the potential energy of the system, which is a function of the positions of all atoms. The corresponding Hamiltonian is:

\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(\vec{r}_1, \vec{r}_2, \vec{r}_3, ...) \] \hspace{1cm} (2-2)

Here, \( m_i \) is the mass of atom \( i \) and \( N \) is the total number of atoms in the system. The first term, \( \frac{p_i^2}{2m_i} \), is the kinetic energy of atom \( i \). It is related to system temperature via

\( N_f k_B T = E_k = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \). \( N_f \) is the total number of degrees of freedom and \( k_B \) is the Boltzmann constant. In principle, the potential energy \( U(\vec{r}_1, \vec{r}_2, \vec{r}_3, ...) \) can be expanded into the sum of an external potential \( U_{ext} \), two-body potentials \( U_{ij} \), three-body potentials \( U_{ijk} \), etc.

\[ U = \sum_i U_{ext}(\vec{r}_i) \]

\[ \quad + \sum_{i<j} U_{ij}(\vec{r}_i, \vec{r}_j) + \sum_{i<j<k} U_{ijk}(\vec{r}_i, \vec{r}_j, \vec{r}_k) \]
In practical applications, only the external potential and first few low-order interaction potentials are considered. This choice arises both because of the capability of contemporary computational power and because the system usually can be well described without the higher-order terms. In our classical MD simulations, we used two-body potentials for pure silica systems and included three-body potentials as well if water molecules were involved.

2.1.2 Computational Algorithm (for NVE ensemble)

To solve Newton’s equations of motion computationally, it is necessary either make some approximation except in the rare cases that they can be solved analytically. When simulating a system with hundreds or thousands of atoms, in general, it is not feasible to solve such huge linear combinations of equations exactly. Thus, in the contemporary classical MD simulation they are solved in a discrete time sequence with a tiny time step \( \delta t \). Verlet [39] proposed a particular algorithm which in modified form has been widely applied in classical MD simulations. The original version has a problem of accumulating numerical error in the \( \delta t^2 \) term. It has been modified in two ways to eliminate the problem. The first way is the Verlet Leapfrog algorithm [40]:

\[
\begin{align*}
\mathbf{v}_i \left( t + \frac{1}{2} \delta t \right) &= \mathbf{v}_i \left( t - \frac{1}{2} \delta t \right) + \mathbf{a}_i(t) \delta t \\
\mathbf{r}_i(t + \delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t + \frac{1}{2} \delta t) \delta t \\
\mathbf{v}_i(t) &= \frac{1}{2} [\mathbf{v}_i \left( t - \frac{1}{2} \delta t \right) + \mathbf{v}_i \left( t + \frac{1}{2} \delta t \right)]
\end{align*}
\]

(2-4)

The second way is the Velocity Verlet algorithm [41]:

\[
\mathbf{v}_i \left( t + \frac{1}{2} \delta t \right) = \mathbf{v}_i(t) + \frac{1}{2} \mathbf{a}_i(t) \delta t
\]
\[ r_i(t + \delta t) = r_i(t) + v_i(t + \frac{1}{2} \delta t) \delta t \]
\[ v_i(t + \delta t) = v_i \left( t + \frac{1}{2} \delta t \right) + \frac{1}{2} a_i(t + \delta t) \delta t \] (2-5)

In above equations, \( v_i \) and \( a_i \) are the velocity and acceleration of atom i. These two algorithms are basically equivalent. In both, the numerical error in the \( \delta t^2 \) term is eliminated. In our classical MD simulations, we always use the Verlet Leapfrog algorithm.

2.1.3 Extension to Thermostats and Barostats

The algorithms just given are for the microcanonical ensemble. They keep the total number of particles, volume of the system, and total energy constant. If the chosen time step \( \delta t \) is small enough, the total energy will display minute fluctuations around the constant with almost unnoticeable error. To make the simulation resemble practical experiments, the algorithm should be extended to simulate ensembles with constant temperature and/or pressure (NVT and NPT). Two kinds of algorithms are implemented most widely in contemporary classical MD simulation packages.

2.1.3.1 Berendsen thermostats and barostats

As noted, the system temperature is related to the summation of atoms’ kinetic energies via \( N_f k_B T = E_k \). It is very straightforward to modify the system temperature to a target value by just linearly rescaling the atomic velocities:

\[ v_i'(t) = v_i(t) * \chi(t) \]

\[ \chi(t) = \frac{T_0}{\sqrt{T(t)}} \] (2-6)

Here, \( T_0 \) is the target temperature, \( T(t) \) is the temperature at time t. However, this simple rescaling is crude in that it does not correspond to any physical process of
heating or cooling. Berendsen [42] therefore introduced a modified $\chi(t)$ to modulate the system temperature:

$$
\chi(t) = \sqrt{1 + \frac{\delta t}{\tau} \left( \frac{T_0}{T(t)} - 1 \right)}
$$

(2-7)

Here, $\tau$ is a constant which characterizes the response time of the system to temperature changes. If the system is a non-interacting ideal gas, then it is easy to see that the analytical solution of $T(t)$ will be:

$$
T(t) - T_0 = (T(t_0) - T_0) e^{-t/\tau}
$$

(2-8)

This results from taking $\delta t$ to be infinitesimal and takes $T(t + \delta t) = T(t)\chi^2(t)$. The equation (2-7) now transforms into:

$$
\frac{dT(t)}{dt} = \frac{(T_0 - T(t))}{\tau}
$$

(2-9)

So the ideal gas is following Newton’s law of cooling in contact with a reservoir of constant temperature $T_0$. However, in the real simulation systems, the potential $U(r_1, r_2, r_3, \ldots)$ is not zero. Over time the temperature will be modulated by the system potential as well and become much more complicated than Newton’s law of cooling.

If we consider how to change the pressure of a free ideal gas system and maintain the temperature, the simplest way would be by changing the volume of the gas because of the ideal gas law, $PV=NRT$, namely

$$
V'(t) = V(t) \ast \chi_p(t)
$$

$$
\chi_p(t) = \frac{p(t)}{p_0}
$$

(2-10)

As a result, all of the particle coordinates will be scaled by $\chi_p^{1/3}$

$$
r'(t) = \chi_p^{1/3} r(t)
$$

(2-11)

To mimic the real system’s response, the Berendsen barostat follows a similar concept
to that of the Berendsen thermostat. Specifically, it assumes that the instant pressure change is proportional to its difference with a pressure reservoir

\[
\frac{dP(t)}{dt} = \frac{(P_0 - P(t))}{\tau_P}
\]

\[
\chi_p(t) = 1 - \frac{\delta t}{\tau_p} \left(1 - \frac{P_0}{P(t)}\right)
\]

(2-12)

Here, \(\tau_p\) is a constant which characterizes the response time of the system to pressure changes.

### 2.1.3.2 Nosé-Hoover thermostats and barostats

The idea of the Nosé-Hoover algorithm is more sophisticated. In it, the variables representing the temperature or pressure reservoir also fluctuate as well when heat is transferred between the simulation system and the reservoir. In the Berendsen algorithm, on the other hand, the temperature and pressure of the reservoir are kept constant and the transfer rates are controlled by \(\tau\) and \(\tau_p\) only.

Consider the thermostats first [43]. The central parameter \(\chi(t)\) is changed to

\[
\frac{d\chi(t)}{dt} = \frac{N_f k_B}{Q} (T(t) - T_0).
\]

(2-13)

Here, \(Q = N_f k_B T_0 \tau^2\) is the effective thermal mass of the reservoir and \(\tau\) is a specified time constant that reflects the response time of the reservoir. The heat transfers to the simulation system by accelerating the atoms,

\[
\frac{d\mathbf{v}_i(t)}{dt} = \mathbf{a}_i(t) - \chi(t)\mathbf{v}_i(t)
\]

(2-14)

The result is an extended Hamiltonian which is a conserved quantity

\[
H_{NVT} = E_k + U + \frac{1}{2} Q \chi^2(t) + \frac{Q}{\tau^2} \int_0^t \chi(s) ds
\]

(2-15)

This equation represents a combined Hamiltonian of the simulated system and reservoir.
For the barostat [44], \( \chi(t) \) and \( \chi_p(t) \) both are changed to read

\[
\frac{d\chi(t)}{dt} = \frac{N_f k_B}{Q} (T(t) - T_0) + \frac{1}{Q} (W \chi_p^2(t) - k_B T_0)
\]

\[
\frac{d\chi_p(t)}{dt} = \frac{3}{W} V(t)(P(t) - P_0) - \chi(t) \chi_p(t).
\] (2-16)

Here, \( W = N_f k_B T_0 \tau_p^2 \) and \( Q \) is the same as before. The equations for changing the system volume, atomic velocities and accelerations then are

\[
\frac{dV(t)}{dt} = 3V(t)\chi_p(t)
\]

\[
\frac{dr_i(t)}{dt} = v_i(t) + \chi_p(t)(r_i(t) - R_0)
\]

\[
\frac{dv_i(t)}{dt} = a_i(t) - \left( \chi(t) + \chi_p(t) \right) v_i(t)
\] (2-17)

The extended Hamiltonian

\[
H_{NPT} = E_k + U + P_0 V(t) + \frac{1}{2} \left( Q \chi^2(t) + W \chi_p^2(t) \right) + \int_0^t \frac{Q}{T^2} \chi(s) + k_B T_0 ds
\] (2-18)

is conserved.

**2.2 Density Functional Theory**

Density Functional Theory (DFT) is a powerful tool for investigating nano-scale systems properties and behaviors in computational study today. It replaces the problem of solving for the many-electron ground-state wave function with the problem of solving for the electron density distribution. In practice, it produces structural parameters and system cohesive energies of high accuracy in many successful cases. We will start from the Hartree-Fock approximation and then introduce Density Functional Theory.

**2.2.1 Hartree-Fock approximation**

The Hamiltonian of a many-electron system within the Born-Oppenheimer non-relativistic approximation can be written as
\[ \hat{H} = \sum_\alpha \frac{p^2_a}{2m_\alpha} + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \sum_i \left( \frac{p^2_i}{2m_e} - \sum_\alpha \frac{Z_\alpha q_e}{r_{\alpha i}} \right) + \sum_{i<j} \frac{q_e}{r_{ij}} \]  

(2-19)

Here, the indices \( \alpha \) and \( \beta \) are for ions, \( i \) and \( j \) are for electrons. \( Z_\alpha \) is the charge of ion \( \alpha \) and \( r_{\alpha\beta} \) is the distance between the \( \alpha \) and \( \beta \) ions. Similarly, \( r_{\alpha i} \) is the distance of electron \( i \) from \( \alpha \). The electron mass and charge are \( m_e \) and \( q_e \) respectively. In the Born-Oppenheimer non-relativistic approximation, the ions are treated as point charges while the electrons are treated as charge density distributions which adjust instantaneously to the ionic positions. Under this approximation, the problem can be separated into solving first for the electronic ground state, then solving for the ionic motion. The effective many-electron Hamiltonian then is

\[ \hat{H}_e = \sum_i \left( -\frac{\hbar^2}{2} - \sum_\alpha \frac{Z_\alpha}{r_{\alpha i}} \right) + \sum_{i<j} \frac{1}{r_{ij}} \]  

(2-20)

in Hartree atomic units (\( \hbar = m_e = q_e = 1 \)). According to the Pauli Exclusion Principle, the overall electron wave function has to be antisymmetrized. The simplest possible form is a Slater determinant of \( N \) single-electron orbitals,

\[ \Psi = \frac{1}{\sqrt{N!}} \det [\psi_1 \psi_2 \ldots \psi_N] \]  

(2-21)

Then the expectation value of the electronic Hamiltonian is:

\[ H_F = \langle \Psi | \hat{H}_e | \Psi \rangle = \sum_i H_i + \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij}) \]

\[ H_i = \int \psi_i^*(x) \left[ -\frac{\hbar^2}{2} - \sum_\alpha \frac{Z_\alpha}{r_{\alpha i}} \right] \psi_i(x) \, d^3x \]

\[ J_{ij} = \iint \psi_i(x_1) \psi_j^*(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j(x_2) \, d^3x_1 \, d^3x_2 \]

\[ K_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j^*(x_2) \, d^3x_1 \, d^3x_2 \]  

(2-22)

Here, \( r_{\alpha} \) means the distance from ion \( \alpha \) to the position \( x \). In this expression, the electron-electron potential energy is partitioned into two contributions. \( J_{ij} \) are called
Coulomb potential energies and $K_{ij}$ are called exchange potential energies. $J_{ij}$ has the form of a classical Coulomb interaction (or Hartree energy) wherein electrons $i$ and $j$ with charge distribution $n_i = \psi_i^* \psi_i$ and $n_j$ interact with each other. However, $K_{ij}$ originates from the antisymmetry of the overall electron wave function and has no direct classical analogue. It is essential, however, for the stability of matter.

2.2.2 Kohn-Sham Ansatz and Local Density Approximation

Hohenberg and Kohn [45] proved that the electron density distribution $n(r)$ alone determines the system ground state and hence the positions of ions. They also demonstrated that the ground state energy can be obtained by minimizing a suitable electron density functional

$$E[n] = T[n] + V_{\text{ext}}[n] + V_{\text{ee}}[n]$$

$$E_0 = \min_n [E[n]]. \tag{2-23}$$

Here, $T$ is the total electron kinetic energy, $V_{\text{ext}}$ includes the energy from the interaction between electrons and ions and any other external potential, and $V_{\text{ee}}$ is the energy of electron-electron interaction. The proof penned by Hohenberg and Kohn is really simple. Consider that there are two external potentials $V_{\text{ext}}^{(1)}$ and $V_{\text{ext}}^{(2)}$ which differ by only a constant. Suppose the two corresponding Hamiltonians $H^{(1)}$ and $H^{(2)}$ have two different ground state wave functions $\Psi^{(1)}$ and $\Psi^{(2)}$. These will lead to the same charge density $n(r)$, since the two Hamiltonians just differ by a constant. If the ground states of two Hamiltonians are non-degenerate and $\Psi^{(1)}$ is not the ground state of $H^{(2)}$ and vice versa, then the following inequality is true:

$$E^{(1)} = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle$$

$$\langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | H^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | H^{(1)} - H^{(2)} | \Psi^{(2)} \rangle$$
A corresponding inequality can be derived for $E^{(2)}$, and then we get the contradictory inequality $E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$. This means there cannot be two external potentials differing by only a constant which give the same non-degenerate ground state density.

Although Hohenberg and Kohn proved the existence of the universal electron density functional to determine the ground state, they did not give a construction. The universal functional still needs to be determined. DFT did not become a feasible tool, until Kohn and Sham [46] proposed an ansatz to make the whole theory practical with two assumptions:

1. The exact ground state electron density can be found as the ground state electron density of a non-interacting reference system with an auxiliary potential.
2. The auxiliary potential of the non-interacting reference system is local.

Hence, the Kohn-Sham ansatz simplifies the ground state problem of the original many-body system into an independent particle system problem with an auxiliary potential.

In equation (2-23), the $V_{ee}[n]$ term can be decomposed into $V_{Hartree}[n]$, $V_x[n]$ and $V_c[n] = V_{ee}[n] - V_{Hartree}[n] - V_x[n]$. $V_{Hartree}[n]$ is the functional for the Coulombic electron-electron potential, $V_x[n]$ is for the exchange energy, and $V_c[n]$ is for the Coulombic correlation energy. Compared with equation (2-22), the forms of $V_{ext}[n]$ and $V_{Hartree}[n]$ are rather straight forward.

\[
V_{ext}[n] = \int d^3r \ V_{ext}(r)n(r)
\]

\[
V_{Hartree}[n] = \frac{1}{2} \int \int d^3r d^3r' \ \frac{n(r)n(r')}{|r-r'|}
\] (2-25)
However, the explicit forms of the kinetic energy $T[n]$, exchange energy $V_e[n]$, and Coulombic correlation energy $V_c[n]$ are not known in general. The next step in the Kohn-Sham ansatz is to introduce $T_s[n]$ and rearrange the true kinetic energy $T[n]$.

$$T[n] = \langle \psi | \sum_i^{N} -\frac{\psi_i^2}{2} | \psi \rangle = T_s + \Delta T$$

$$\Rightarrow T_s[n] = \frac{-1}{2} \int \sum_i^{N} \psi_i^*(\mathbf{r})v_i^2[\mathbf{r}]\psi_i(\mathbf{r}) d^3r \quad (2-26)$$

Combining the exchange and Coulombic correlation energies with the difference of $T[n]$ and $T_s[n]$, $\Delta T$, into the exchange-correlation energy, the energy functional becomes:

$$E[n] = T_s[n] + V_{ext}[n] + V_{Hartree}[n] + V_{xc}[n]$$

$$V_{xc}[n] = \Delta T + V_{ee}[n] - V_{Hartree}[n] \quad (2-27)$$

All of the trouble in finding the universal functional is shifted over to the exchange-correlation energy which will be expressed as the auxiliary potential of a non-interacting reference system. However, until now there is no exact expression for this part. Note that Kohn and Sham provided a method to solve the complicated many-body equations by replacing an interacting $V$-representable potential into a non-interacting $V$-representable potential. It is known that this is not always possible. Fortunately, the success of Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) made the Kohn-Sham ansatz the most widely used approach today in DFT calculations for solving electronic structure.

The recent studies for improving the accuracy of DFT approximations are devoted to find better exchange-correlation functionals which are feasible in a wide range of applications. The simplest successful functional approximation is the Local Density Approximation (LDA). LDA simply represents the exchange-correlation energy
as that of a homogeneous electron gas at each spatial point. That is, the exchange-correlation potential energy just depends on the local density of charge.

\[ V_{\text{xc}}[n^\alpha, n^\beta] = \int d^3 r \ n(r) \mu_{\text{xc}}(n^\alpha(r), n^\beta(r)) \]  \hspace{1cm} (2-28)

Here \( n^\alpha(r) \) and \( n^\beta(r) \) are spin \( \alpha \) and \( \beta \) electron densities at position \( r \). The exchange-correlation potential can be further divided into exchange and correlation parts. The exchange potential of a homogeneous electron gas has an explicit form from the Hartree-Fock approximation, namely

\[ v_x(n^\sigma) = \frac{-3}{4} \left( \frac{6}{\pi} n^\sigma \right)^{1/3} \]  \hspace{1cm} (2-29)

The correlation part has been calculated to a high accuracy with Monte Carlo methods [47].

### 2.2.3 Generalized Gradient Approximation

The next step to improve LDA is to introduce density gradients into the exchange-correlation energy. The idea of expanding the exchange-correlation energy in terms of local density gradient (GEA, gradient expansion approximation) was suggested in the original Kohn and Sham paper and was developed by Herman et al. [48] However, the simple GEA does not improve upon LDA results consistently and can even leads to worsened results because it violates the sum rules and the large density variation in real materials causes the expansion to fail.

Instead, generalized gradient approximations (GGA) were developed. A GGA exchange-correlation energy can be expressed as:

\[ E_{\text{xc}}^{\text{GGA}}[n^\alpha, n^\beta] = \int d^3 r \ n(r) \ v_{\text{xc}}(n^\alpha, n^\beta, |\nabla n^\alpha|, |\nabla n^\beta|, ...) \]

\[ \equiv \int d^3 r \ n(r) \ v_{\text{x}}^{\text{hom}}(n)F_{\text{xc}}(n^\alpha, n^\beta, |\nabla n^\alpha|, |\nabla n^\beta|, ...) \]  \hspace{1cm} (2-30)
For the exchange energy, only the spin-unpolarized form is necessary. The enhancement factor $F_x(n, |\nabla n|, \ldots)$ is naturally expressed in terms of the dimensionless reduced density gradients

$$S_m = \frac{|p^m n|}{(2kp)^m n} = \frac{|p^m n|}{2^m(3\pi^2)^{m/3}(n)^{(1+m/3)}}$$

(2-31)

The low order expansion of $F_x$ is known analytically [49].

$$F_x = 1 + \frac{10}{81}s_1^2 + \frac{146}{2025}s_2^2 + \cdots$$

(2-32)

Numerous forms of $F_x(n, s_1)$ have been proposed, notably the widely used forms of Becke (B88) [50], Perdew and Wang (PW91) [51], and Perdew, Burke, and Enzerhof (PBE) [52]. In the range of $0 < s_1 < 3$, these three forms of $F_x$ have values close to each other. This range corresponds to most of the environments in physical and chemical applications, and this is why different GGA forms give similar results in many cases (see the review of Martin [53] in section 8.2). But in the range of $s_1 > 3$, which is relevant to large density gradients, the three forms converge to different limiting values with different choice of physical conditions. B88-GGA chooses to give the correct exchange energy density, PW91-GGA and PBE-GGA exchange obey the Lieb-Oxford bound but PBE-GGA approaches a constant for large $s_1$, while PW91-GGA decreases to zero asymptotically. The differences occur because not all asymptotic constraints on $E_{xc}^{GGA}$ can be satisfied by a GGA. One form successfully predicts the energy and structure of some systems, but may fail in other cases.

Correlation energy is typically much smaller in magnitude than the exchange energy but more difficult to express. The lowest order expansion has been calculated by Ma and Brueckner [54].
At large density gradient limit, the correlation energy diminishes to zero as $s_1 \to \infty$.

### 2.2.4 Pseudopotential

The motivation for using with a pseudopotential is to replace the problem of solving the all-electron Kohn-Sham problem with either LDA or GGA with the task of diagonalizing only an effective valence Hamiltonian. The latter task needs smaller basis expansions. Since in most of the environments (either in a molecule or in a solid), the distribution of core electrons is almost unchanged compared to the distribution in an individual atom, only the valence electrons will contribute to chemical bonding or Van der Waals interactions.

An important idea for simplifying an one-electron wave function is the orthogonalized plane wave (OPW) approach [55, 56]. It decomposes the eigenvalue problem by separating the valence wave functions into smooth parts and core-like functions. Consider a wave function $u_j(r)$ and a plane wave $e^{iqr}$. Then a wave function orthogonal to each $u_j(r)$ can be formulated as

\[
\chi_q^{OPW}(r) = \frac{1}{\Omega} [e^{iqr} - \Sigma_j (u_j|q)u_j(r)]
\]

\[
\langle u_j|q \rangle = \int_\Omega u_j^*(r)e^{iqr}dr
\]

Here, $\Omega$ is the volume of the integration space. From the Kato cusp condition, an one-electron orbital will approach to zero in a form of $r^{n-1}e^{-Zr/n}a_0$ ($n$, $Z$, and $a_0$ are the principal quantum number, atomic number and Bohr radius) and the radial part of the orbital has high radial derivatives localized near the nucleus. If the $u_j(r)$ are chosen to be well localized, then the wave function can be partitioned into a smooth part and a
localized part. Herring [55] suggested that the eigenfunction in a crystal can be approximated by a linear combination of a few plane waves, plus a linear combination of a few functions centered around each nucleus and obeying the wave equations:

$$\frac{1}{2} \nabla^2 u_j + (E_j - V_j) u_j = 0$$

(2-35)

Note that the OPWs are not orthonormal:

$$\langle \chi_q^{\text{OPW}} | \chi_q^{\text{OPW}} \rangle = 1 - \sum_j |(u_j | q)|^2$$

(2-36)

Thus, expansion of orbitals in OPWs will lead to a generalized eigenvalue problem with a non-diagonal overlap matrix.

In modern DFT calculations, several popular forms of pseudopotential are available, like HSC [57], Troullier-Martins [58], Ultrasoft [59] and PAW [60]. Different types of pseudopotentials follow from different criteria, thus pseudopotentials are classified as hard or soft, and as transferable or not. Hard or soft means that the pseudo wave functions must be expanded in plane waves including many high frequency terms or just a few low frequency terms respectively. If the pseudopotential is suitable for every environment, then it is transferable. Usually, a harder pseudopotential is more transferable than a soft one. In general, there are two important aspects to consider in constructing a pseudopotential. One is shape-consistency and the other is norm-conservation. In the paper of Hamann, Schluter and Chiang (HSC) [57], their pseudopotential obeys the following properties (in their original words):

1. Real and pseudo valence eigenvalues agree for a chosen “prototype” atomic configuration.

2. Real and pseudo atomic wave functions agree beyond a chosen “core radius”, $r_c$. 
3. The integrals from 0 to $r_c$ of the real and pseudo charge density agree for each valence state (norm conservation).

4. The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r > r_c$.

Here $r_c$ plays an important role for offering flexibility to make a pseudopotential harder or softer. It will be easy to choose a large $r_c$ and keep norm conservation, since atomic wave functions fluctuate less at large distance from the nucleus. However, the price for choosing a large $r_c$ and making the pseudopotential soft is that the pseudopotential is made non-transferable.

Ultrasoft and PAW pseudopotentials are two powerful and widely used forms implemented in the popular DFT software “Vienna Ab initio Simulation Package (VASP)” [61]. The ultrasoft pseudopotential does not respect norm conservation criterion because it uses a larger $r_c$. However, it uses auxiliary functions and overlap operators to maintain high accuracy. On the other hand, the PAW method reformulates the OPWs equations and keeps the full wave functions with some auxiliary transformation.
CHAPTER 3
ALPHA-QUARTZ (0001) SURFACES

Alpha-quartz, the most stable structure among numerous silica polymorphs, has its SiO$_4$ tetrahedra units arranged in a trigonal symmetric crystal. Among facets of alpha-quartz, the (0001) surface is the most stable one. A newly cleaved alpha-quartz (0001) surface will be hydroxylated quickly under atmosphere condition and is hydrophilic. However, if the surface is prepared under UHV conditions, the surface can reconstruct itself and result in a hydrophobic surface.

In section 3.1, we present our study on the reconstruction of alpha-quartz (0001) surfaces using combined classical molecular dynamics and density functional theory. Five reconstruction patterns are identified, including three (2x1) patterns and two (1x1) patterns [62]. The energetically most stable surface structure is found to be a (2x1) reconstruction pattern, though several patterns can coexist on a large-scale surface. A combination of structures can explain the experimentally observed (2x2) diffraction pattern [62].

In section 3.2, we analyze a fully hydroxylated alpha-quartz (0001) in respect to its structure and charge distribution. The system is found to form alternating strong and weak hydrogen bond chains within the surface.

In section 3.3, we study four defective alpha-quartz (0001) (1x1) surfaces. Two of them have non-equivalent oxygen vacancy point defects, while the other two have non-equivalent oxygen displacement point defect. Their structure and charge distribution are discussed.
3.1 Perfect Surface Reconstruction

3.1.1 Introduction

Silica is an important mineral that has wide application in various fields in industry [5, 6, 63]. Due to the close relationship between the structure of a surface and its chemical activity, it is crucial to determine the silica surface structure accurately so that one can understand its interactions with other molecules, such as water, oxide compounds, or proteins [5, 6].

Although, as mentioned, a newly cleaved silica surface will be hydroxylated rapidly when it is exposed to atmospheric moisture [5], a dry surface (not hydroxylated) can be prepared either in vacuum or via heat treatment. The activity of dry silica surfaces is considered to be important for its biological toxicity [11]. Among all different dry surfaces, the alpha-quartz (0001) surface has been widely studied in experiments and theoretically [12-14, 16, 64-67] because of its stability. Previous low-energy electron diffraction (LEED) experiments claimed a (1x1) pattern for alpha-quartz (0001) surfaces [12, 64], which undergoes a ($\sqrt{84} \times \sqrt{84}$) reconstruction with a $R11^\circ$ rotation at a temperature above 600 °C [12]. A dense surface with a (1x1) pattern (which from now on we call surface type I), identified and studied using density functional theory (DFT) calculations [14, 65, 66] or classical molecular dynamics (MD) calculations [13, 14, 66], can explain the (1x1) pattern in the LEED experiments well. In recent helium atom scattering experiments, Steurer et al. [16] observed weak (2x2) diffraction peaks, which also appear in the LEED pattern of Bart and Gautier [12] but were not explicitly mentioned. On the other hand, atomic force microscopy (AFM) studies of the surface
failed to give further detail about the surface structure due to its limited resolution [16, 67].

3.1.2 Method

This section presents a combined classical MD and first-principles study of the alpha-quartz (0001) surface reconstruction. We find five stable surface patterns with similar surface energies. Two of them are dense surfaces with (1x1) patterns, while the other three possess (2x1) patterns. All are different from the semi-dense surface in the work of Rignanese et al. [65] Classical MD simulations [68] using the potential [69] developed by van Beest, Kramer, and van Santen (BKS) were employed to provide a reasonable initial approximation of the reconstructed surface structure. To simulate the surface reconstruction, a 4x4x5 supercell and 720 atoms were included in MD simulations. The resulting structures have either a (1x1) pattern or a (2x1) pattern in the X-Y plane. These are truncated into a supercell of 2x2x5 for further optimization via DFT calculations. We used the VASP package, which employs a plane-wave basis set and the projector augmented wave potential [60, 61]. The PW91 generalized gradient approximation [51] (GGA) was used as the exchange-correlation energy functional. A kinetic energy cutoff of 400 eV and a 2x2x1 Γ-centered K-grid were used to ensure energy convergence. The lattice constant was optimized in bulk simulations. The result is in good agreement with the experimental value (see Table 3-1). To form the surface, the system was cleaved between two oxygen sublayers to maintain stoichiometry. This is done for both top and bottom surfaces, and consequently the supercell has no dipole moment. A vacuum layer of 50 Å was inserted in the z-direction between two adjacent
slabs. We fixed the middle of the slab (1 unit cell thick) at a geometry which mimics the quartz bulk and let the top and bottom layers relax (each side two unit cells thick).

3.1.3 Results

The type I surface observed at low temperature \( T \sim 100 \) K is obtained in a constant particle number, system volume and temperature (NVT) ensemble in classical MD calculations (Figure 3-1 (a)). To generate other surfaces, we heated the system (using the Berendsen thermostat [42]) with relaxation constant 0.1 ps from 100 to above 1400 K with an increment of 100 K and a duration of 20 ps at each stage. For each 100 K, we performed a separate calculation to quench the system to 0 K and analyze the structure. Three more surface structures were identified via this procedure (type III, IV and V). The type II surface is constructed by manual tuning the orientations of the topmost layer \( \text{SiO}_4^{4-} \) tetrahedra (Figure 3-1 (b), (c) and 3-2). Type I and II surfaces can transform between each other through rotating all \( \text{SiO}_4^{4-} \) tetrahedra in the topmost layer \( \sim 35^\circ \) about the z-axis, as shown in Figure 3-2 (a). The underlying alpha-quartz bulk feature (right-handed helix) distinguishes these two as different surfaces without ambiguity.

All five surfaces feature six-membered rings in the topmost layer and three-membered rings right below it, and have the same topological character. The stability of these surface structures is confirmed through DFT optimization calculations until the total energy converges within 0.2 meV. Their surface energies, given by \( \varepsilon = (E_{\text{surface}} - E_{\text{bulk}}) / \text{area} \), are listed in Table 3-2. The statistical variations among the five surfaces (Figure 3-3) show that the changes in O–Si–O bond angles and Si–O bond lengths are less than 4%, but the Si–O–Si bond angles reach 18%. This analysis suggests that the
$\text{SiO}_4^{4-}$ tetrahedra are rigid, and that the different surface structures can be regarded as rotations of $\text{SiO}_4^{4-}$ tetrahedral units.

The type III surface has the lowest surface energy, 27.3 meV/Å$^2$, in our calculations. It features zigzag shaped six-membered rings in the topmost layer and three-membered rings underneath (Figure 3-1 (b) and (c)). As shown in Figure 2(b), the type III surface can be regarded as rotating the topmost $\text{SiO}_4^{4-}$ tetrahedra of the type I surface in certain lines along the [110] direction. As a result, the type III surface undergoes a (2x1) reconstruction that has two-unit cell patterns in the [100] and [010] directions, but one-unit cell pattern in the [110] direction. The type IV surface has a surface energy similar to type I and II. It can be regarded as rotating the $\text{SiO}_4^{4-}$ tetrahedra in the topmost layer of type I surface in a similar way as for the type III surface, but along the [100] direction. Correspondingly, the type IV surface undergoes a different (2x1) reconstruction pattern that has a one-unit cell pattern in the [100] direction and two-unit cell patterns in the other two directions. The type V surface also has a (2x1) reconstruction pattern but has the highest surface energy, 34.3 meV/Å$^2$, in the series of surfaces. It can be regarded as rotating the topmost $\text{SiO}_4^{4-}$ tetrahedra of type I surface along [010] direction in a similar way as with the type III and IV surfaces. Hence, it has a one-unit cell pattern in the [010] direction and a two-unit cell pattern in the other two directions. Even though the types III–V surfaces have very similar (2x1) reconstruction patterns, the underlying alpha-quartz bulk feature (right-handed helix) distinguishes their orientations (Figure 3-1(c)).
3.1.4 Discussion and Conclusion

To determine the energy barriers between surface structures, we performed nudged elastic band calculations [70] in VASP with five intermediate images. The results are listed in Table 3-2. The barrier from type II to III is the lowest, 5.67 meV/Å² relative to type II. The number of degrees of freedom ($N_f$), the barrier height $\Delta E$, and the temperature $T$ of a structural transition are related by $N_f/2k_B T=\Delta E$, where $k_B$ is the Boltzmann constant. As we mentioned above, the SiO$_4^{4-}$ tetrahedra are essentially rigid, therefore the rigid-unit mode model [71] can be used. In our simulations, 24 tetrahedra (56 O and 24 Si) are involved in the structural change. However, 24 Si and 4 O atoms remain rigid and all interatomic bonds are unchanged. This leads to $N_f=12$. The energy barrier corresponds to a transition temperature of 913 K.

Steurer et al. [16] proposed that the combination of the dense surface and semi-dense surfaces [65] can explain the (2x2) observed diffraction patterns. However, the transition from a dense surface to a semi-dense surface will include a bondbreaking process since the semidense surface has three-membered rings in the topmost layer, hence has different topological character from the dense surface. Therefore this transition will occur only at a much higher temperature. Conversely, the transformations between the five surface patterns in our study involve no bond-breaking process, similar to the alpha-beta incommensurate phase transform in which a quartz twinning phenomenon was observed. [72] Bart and Gautier [12] also explained the observed ($\sqrt{84}x\sqrt{84}$) surface reconstruction pattern using the quartz twin argument. Since the surface energies of these five surfaces are very close to each other, coexistence of several surface types is very probable, as seen in our large-scale classical MD
calculations (a 10x10x5 supercell with 4500 atoms). In a MD simulation, types I–III surfaces coexist at 400 K (Fig. 3-4). On the one hand, the coexistence of surface types III–V provides a good explanation of the (2x2) pattern in experiments in a defect-free condition. On the other hand, Steurer et al. [16] observed flat terraces oriented 60° relative to each other in their AFM image, which can be explained by different steps in alpha-quartz due to imperfect cutting of the surface. Such steps offer three different surface orientations automatically. Therefore a combination of type III surfaces along three orientations also can explain the experimental results. Based on energetic, we argue that the latter explanation is more convincing. Due to computational restrictions, it is not feasible to examine the stability of such large-scale structure in a DFT calculation.

In summary, we have studied the reconstruction of alpha-quartz (0001) surfaces through DFT and classical MD calculation. Three surfaces with a (2x1) pattern and two surfaces with a (1x1) pattern are found in our calculation. Two of the (2x1) pattern surfaces are energetically more stable than the dense surfaces. The experimentally observed (2x2) pattern can be explained by combinations of (2x1) surfaces.

### 3.2 Fully Hydroxylated Surface

As noted earlier, a newly cleaved silica surface will be hydroxylated quickly under atmosphere with a varying degree of hydrophilicity depending on surface preparation [5, 6]. Multiple groups have studied the mechanics of silica surface hydroxylation by using DFT or Classical MD. Du et al. combined two to study possible hydroxylation pathways of the amorphous silica surface [27]. They concluded that the highly strained sites such as two-membered rings, are much easier to interact with water. They mapped the energy landscape along the interaction pathway and observed a barrier-free hydroxylation process. Adeagbo et al. used Car-Parrinello molecular dynamics (CPMD)
combination with a coordination constraint to study the dissociation of one Si(OH)$_2$ unit on fully hydroxylated alpha-quartz (0001) surface [28]. The calculated energy barrier height is about 186 kJ/mol which is roughly comparable to experimental data if apply a temperature dependence with an Arrhenius slope. Ma et al. [73] and Rimola et al. [74] studied the hydroxylation process of silica surface by using silica cluster models. They both observed that the presence of more than one adsorbed water molecule could accelerate the hydroxylation of a defective surface.

The fully hydroxylated alpha-quartz (0001) surface had been studied by Murashov [75] and Yang et al. [22] with DFT. Yang et al. found that the hydroxyl groups (silanol groups) will form hydrogen-bond chains with alternating strength on the surface itself. However, Murashov’s calculations did not find the same phenomenon: the weak hydrogen bonds were not formed. Yang et al. had reported the geometry of this surface and also studied the adsorption of water molecules and one water layer on it. In this section, we will only report how the fully hydroxylated alpha-quartz (0001) surface is prepared for the water adsorption study which will be discussed in the following chapters, and also give a charge analysis of the surface.

In our simulation, the newly cleaved silica surface has a 2x2x5 supercell and is cut in a way that maintains its stoichiometry on the top and bottom surfaces as described in section 3.1.2. We hydroxylated the newly cleaved surface by attaching a proton to each dangling oxygen bond and a hydroxyl radical to each dangling silicon bond. The structure is optimized by using DFT calculations with the same parameters used in section 3.1.2; the center layer of the silica slab is still fixed during optimization.
The optimized structure has a (1x1) symmetry pattern and the hydrogen-bond chains with alternating strength form on the surface (Figure 3-5). The hydroxylation energy is -14.5 meV/Å² calculated from \( E_{\text{surf}} = (E_{\text{tot}} - E_{\text{AQ}} - n \times E_{\text{H}_2\text{O}})/\text{area} \). Here, \( E_{\text{tot}} \) is the total energy of the surface system; \( E_{\text{AQ}} \) is the Alpha Quartz bulk energy with a 2x2x5 supercell and \( E_{\text{H}_2\text{O}} \) is the energy of a single structure-optimized water molecule. \( n \) is 8 and the value of the area is 169.8 Å² for both top and bottom surfaces in total. The calculated hydroxylation energy is larger than Murashov’s result in absolute value (-10.0 meV/Å²) [75]. This is reasonable since weak hydrogen bonds form in our model but not in Murashov’s. It is unfortunate that Yang et al. did not give the hydroxylation energy in their work for comparison with. The hydrogen bond lengths (O···H distances) of strong and weak groups are 1.78 Å and 2.14 Å, both are slightly longer than Yang’s results since we use a larger lattice constant set. The charge on each atom was calculated by using Bader analysis with a program developed by Henkelman et al. [76, 77] The silicon atoms on the topmost layer have an average charge similar to silicon atoms on perfect surface, but the average charge on those oxygen atoms in hydroxyl group is obviously smaller than that of oxygen atoms on perfect surfaces (Table 3-3, 3-4). We note that the charge on hydroxyl groups has slight variation depending on its proton is involved in a strong or weak hydrogen bond. Table 3-4 gives a summary of the charge analysis.

3.3 Defective Surfaces

Defects in silica (especially in amorphous silica) draw attention because they affect many properties: stiffness, transparency, refraction index, generation of additional defects, etc [78, 79]. In optics, high energy radiation and astronomy, equipment with lenses demand high accuracy and long lifetime. Recognizing and controlling the number
and properties of defects is important. In the semiconductor and telecommunication business, the quality of wafers, optical fibers, and optical lenses as well also depend upon by the defect population in silica. Researchers in biochemistry and the medical field are concerned with the quality of glassware and its chemical activity with respect to other atoms/molecules.

The point defect types of silica have been studied and classified for years [78, 79]. Roughly they can be categorized as Frenkel defects, dangling bonds, strained bonds, and dopants [79]. Each category includes more detailed classification of defect types and each has its special properties and population in different silica forms. Among those defect types, the E'-center (dangling silicon bond), the oxygen vacancy, and the NBOCH (dangling oxygen bond) have been studied extensively and are much better understood than are other defects. Many investigations have been devoted to the optical adsorption spectra in different charge state, defect formation energy, defect structure and the diffusion of defects [80-87].

In this section, we report our study of the point defect on the (1x1) perfect surface (surface type 1 in section 3.1). Those surfaces will be involved in the study of water adsorption in subsequent chapters. Two types of point defect are studied and two surfaces with non-equivalent point defect site are prepared for each type. The first type of defect is an oxygen vacancy which is made by dropping one bridge oxygen atom from the surface. Depending on the environment of the oxygen vacancy, two kinds of defective surface are prepared. Defective surface 1 has the oxygen vacancy involved in a three-membered ring, while defective surface 2 does not (Figure 3-6, 3-7). The second type of defect is oxygen displacement, made by moving one bridge oxygen
atom to the other bridge oxygen site next to the original one. In another words, it consists of one oxygen vacancy and one peroxy linkage [79]. Depending on the defect environment, there are three non-equivalent surfaces. However, in this work, we treat just two of them. The oxygen vacancy on each surface is not involved in a three-membered ring. Defective surface 3 has its peroxy linkage involved in a three-membered ring and defective surface 4 does not (Figure 3-8, 3-9).

To reduce the spurious interaction between defects under periodic boundary conditions, the size of the quartz slab was increased compared to previous calculations to contain a 3x3x5 supercell. Total of 403 or 405 atoms are included as a result. The center layer still was fixed to mimic the alpha-quartz bulk. All of the DFT calculation parameters used were the same as in section 3.1.2. The optimized surface structures are shown in Figure 3-6 to 3-9. Table 3-5 lists the defect formation energies.

It is necessary to consider the defect involved in a three-membered ring because the local strain will be higher in such rings than in six-membered rings. Prior studies showed that water will more likely attack the high strain sites [27, 74]. Even though they were investigating the high strain sites of two-membered rings, it is important to consider the effect of a three-membered ring on the formation of defects and the subsequent effect on water adsorption. The defect involved in a three-membered ring does enhance the formation energies (less stable) when compared to its counterpart of the same defect type, but the energy difference between surfaces 1 and 2 is not so big as between surfaces 3 and 4 (Table 3-5). Note that the oxygen atoms in the peroxy linkage on defective surface 3 are not at the same heights in Z direction for they are involved in a three-membered ring with a higher strain than the peroxy linkage on
defective surface 4. Charge transfer analysis is given in Table 3-6. Silicon atoms at the
defect site generally gain 0.77 to 0.79 more electrons compared to the silicon atoms on
the (1x1) perfect surface. This charge is gained from other atoms on the surface and
bulk as well. On defective surfaces 1 and 2, the charges on the oxygen atoms around
the defect do not differ from those on the (1x1) perfect surface so much. On the other
hand, the peroxy linkage on surface 3 and 4 tend to lose electrons. Those losses
compensate for the electrons gained by silicon atoms of the oxygen defect site.
Table 3-1. Experimental and calculated structure of bulk alpha-quartz

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>GGA PW91</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a(c)$ (Å)</td>
<td>4.916 (5.405)</td>
<td>4.950 (5.445)</td>
</tr>
<tr>
<td>$d_{\text{Si-O}}$ (Å)</td>
<td>1.605</td>
<td>1.623, 1.627</td>
</tr>
<tr>
<td>$&lt;\text{Si-O-Si}&gt;$ (deg)</td>
<td>143.73</td>
<td>142.83, 142.96</td>
</tr>
<tr>
<td>$&lt;\text{O-Si-O}&gt;$ (deg)</td>
<td>110.52, 108.81, 108.93, 109.24</td>
<td>110.72, 108.66, 108.75, 109.22, 110.67</td>
</tr>
</tbody>
</table>

Table 3-2. The surface energies $\epsilon$ (in meV/Å$^2$) of five reconstructed surfaces and the freshly cleaved surface, and the energy barriers (in meV/Å$^2$) for transition from type I ($E^I_b$) or type II ($E^{II}_b$) surface to others. The transition between surface type I and II is mediated by type III, and is therefore not listed.

<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
<th>Type V</th>
<th>Cleaved</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>31.0</td>
<td>30.8</td>
<td>27.3</td>
<td>29.8</td>
<td>34.3</td>
<td>166.6</td>
</tr>
<tr>
<td>$E^I_b$</td>
<td>N/A</td>
<td>N/A</td>
<td>5.71</td>
<td>6.16</td>
<td>7.55</td>
<td>...</td>
</tr>
<tr>
<td>$E^{II}_b$</td>
<td>N/A</td>
<td>N/A</td>
<td>5.67</td>
<td>6.57</td>
<td>8.67</td>
<td>...</td>
</tr>
</tbody>
</table>

Table 3-3. The average charge on each atom species of surface type I, type III and $\alpha$-quartz bulk. The unit is in electron.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Surface</td>
</tr>
<tr>
<td>Surface Type I</td>
<td>0.81</td>
<td>0.84</td>
</tr>
<tr>
<td>Surface Type III</td>
<td>0.81</td>
<td>0.83</td>
</tr>
<tr>
<td>$\alpha$-Quartz Bulk</td>
<td>0.81</td>
<td>0.83</td>
</tr>
</tbody>
</table>
Table 3-4. The average charge on each atom species of a hydroxylated quartz slab. The unit is electrons.

<table>
<thead>
<tr>
<th></th>
<th>Si Bulk</th>
<th>Si Surface</th>
<th>O Bulk</th>
<th>O Strong acceptor</th>
<th>O Weak acceptor</th>
<th>H Weak donor</th>
<th>H Strong donor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxylated surface</td>
<td>0.80</td>
<td>0.83</td>
<td>7.60</td>
<td>7.45</td>
<td>7.50</td>
<td>0.32</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table 3-5. The formation energy of a defective surface with respect to (1x1) perfect surface. \( E_{defect} = E_{total} - E_{perfect\ surface} - nE_o \). Here \( E_{total} \) is the total energy of the defective surface system, \( E_{dry\ surface} \) is the total energy of (1x1) perfect surface. \( E_o \) is the energy of one oxygen atom. \( n \) is 1 on defect 1 and 2, it is 0 on defect 3 and 4. The unit is eV.

<table>
<thead>
<tr>
<th>E_{defect}</th>
<th>Defect 1</th>
<th>Defect 2</th>
<th>Defect 3</th>
<th>Defect 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Bulk</td>
<td>0.79</td>
<td>0.77</td>
<td>0.78</td>
<td>0.77</td>
</tr>
<tr>
<td>O Bulk</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-0.32</td>
<td>-0.31</td>
</tr>
<tr>
<td>O peroxy linkage (‡)</td>
<td>N/A</td>
<td>N/A</td>
<td>-0.79</td>
<td>-0.77</td>
</tr>
</tbody>
</table>
Figure 3-1. Top and side views of reconstructed alpha-quartz (0001) surfaces. The larger spheres represent silicon and the smaller ones, oxygen. The positions of some atoms in three-membered rings are circled. The arrow shows the [110] direction. a) Top view of a type I surface. b) Top view of a type III surface. c) Side views of the surfaces. From top to bottom: type I and II; type III; type IV; type V. The blue circles in the top views indicate the location of three-membered ring underneath.

Figure 3-2. Transformations from one surface type to another. a) From type I (left) to type II (right); b) from type I (left) to type III (right). The circled atoms are shifted along the [\bar{1}10] direction.
**Figure 3-3.** Statistics of bond length and bond angles of all perfect surfaces. a) Si-O bond length distribution. b) O-Si-O bond angle distribution. c) Si-O-Si bond angle distribution.

**Figure 3-4.** Top view of the large-scale structure of a reconstructed alpha-quartz surface from MD simulation. The shaded areas are types I (pink) and II (blue), as indicated in the figure, and the unshaded area is type III. A 10x10x5 supercell is included in this system.
Figure 3-5. Top view (a) and side view (b) of a full hydroxylated alpha-quartz (0001) surface. The silicon and oxygen atoms in the second level are represented in thinner lines in the panel b. One of the hydrogen-bond chains on the surface is shown in blue dashed lines; dark blue means stronger hydrogen bonding and light blue is for weaker bonding. The big blue arrow indicates the direction of side view.
Figure 3-6. Top view (a) and side view (b) of detective surface 1 (oxygen vacancy). The defect site (Si-Si) is presented as yellow-colored spheres.

Figure 3-7. Top view (a) and side view (b) of detective surface 2 (oxygen vacancy).
Figure 3-8. Top view (a) and side view (b) of detective surface 3 (oxygen displacement).

Figure 3-9. Top view (a) and side view (b) of detective surface 4 (oxygen displacement).
CHAPTER 4
WATER CLUSTER ADSORPTION ON SILICA SURFACES

Water molecules were deposited one by one on seven of alpha-quartz (0001) surfaces. These were the (1X1), (2X1) perfect surface (type I, type III surface in Chapter 3), the fully hydroxylated surface and four defective surfaces. For convenience, they are named as surfaces 1 through 7 in the discussions and in Chapter 5. The structures of one, two and three water molecules adsorbed on surfaces were optimized by DFT calculations. The adsorption energies and bonding energies of water for all these systems were calculated to reveal the interaction strength of the water-silica interface. The charge density difference of each system was calculated to serve as an indicator for the location of the water-silica interaction. Though the net charge transfer between water and a silica surface is tiny, the charge redistribution is obvious. On perfect surfaces, the bonding energies of water dimer adsorption were obviously enhanced as compared to one- or three-water molecule adsorption and it exhibits a quadrupole pattern in charge density difference on each perfect surface.

In Chapter 4 and Chapter 5, the methods section skips most of the details of using classical MD and DFT because most of the parameters and criteria are the same as in Chapter 3. We will only mention the equations and the changed parameters if it is necessary.

4.1 Introduction

Asay and Kim studied water layers growing on a hydrophilic silica surface and suggested that there will be about three icelike layers built on a silica surface [17]. Ostroverkhov and Shen et al. measured phase-sensitive sum-frequency spectroscopy of the water-quartz interface. They observed both icelike and liquidlike peaks in the
spectra [18, 19]. Water confined in silica nanopores has been studied experimentally by many groups [34-36]. In the theory, it is believed that two or three types of water exist in the pores. A quasi-liquid layer with low mobility stays next to the silica wall, core water with bulk-water-like behavior stays in the central region, and there may be shell water existing between the quasi-liquid layer and core water. Many groups did computational studies of the hydroxylation mechanism of silica surfaces [27, 28, 73, 74], water molecule/layer adsorption on silica surfaces [14, 15, 22, 30, 88] and the statistical behavior of bulk water when it is adsorbed on a silica surface and fills in a silica nanopore [20, 21, 31, 32, 37, 38, 89]. After those studies, it was recognized that surfaces having hydroxyl groups (Si-OH, silanol groups) are hydrophilic and siloxane surfaces (bare silica surfaces) are hydrophobic. Silica surfaces with defects of dangling bonds and high local strain are hydroxylated easily, while a dry surface with perfect reconstruction (like surface 1 and 2) will be hydrophobic and hydroxylation is not energetically preferred [15]. Yang et al. studied water molecule(s)/layer adsorption on a fully hydroxylated alpha-quartz (0001) surface with DFT methods and found an icelike layer to form the surface [22, 30, 88].

First-principle studies of the water adsorption on silica surfaces had only been done for one or two water molecules and one monolayer adsorption. More effort was needed regarding multi-water-layer adsorption on more species of silica surfaces. Thus we studied water adsorption on seven alpha-quartz (0001) surfaces. This Chapter 4 addresses the water molecules adsorption and Chapter 5 treats water layers adsorption.
4.2 Methods

We used classical MD to look for possible adsorption sites on surfaces for water molecules, then optimized those target structures by DFT calculations. Instead of using the BKS potential [69] used in Chapter 3, we used the CLAFF interaction developed by Cygan et al. [90], which allows the simulation of a system with coexisting water, hydroxyl groups and silica.

In this chapter, the adsorption and bonding energies are calculated according to

\[ E_{amw} = -(E_{total} - E_0 - E_{H_2O}) \]  \hspace{1cm} (4-1)

\[ E_{bmw} = -(E_{total} - E_{unrelaxed}^{surface} - E_{H_2O-cluster}^{unrelaxed}) \]  \hspace{1cm} (4-2)

In equation (4-1), \( E_{amw} \) is the adsorption energy of the \( m \)th water molecule, \( E_{total} \) is the total energy of the optimized system with \( m \) water molecules adsorbed, \( E_0 \) is the total energy of the optimized system with \((m-1)\) water molecules adsorbed, and \( E_{H_2O} \) is the energy of one optimized water molecule. In equation (4-2), \( E_{bmw} \) is the bonding energy of the \( m \) water-molecule cluster, and \( E_{unrelaxed}^{subsystem} \) is the energy of the individual surface or water cluster subsystem which has the same configuration as in the optimized total system.

The charge density difference is calculated with the definition

\[ \Delta n(r) = n(r) - n_{sur}^{unrelaxed}(r) - n_{H_2O-cluster}^{unrelaxed}(r) \]  \hspace{1cm} (4-3)

Here, \( n(r) \), \( n_{sur}^{unrelaxed}(r) \) and \( n_{H_2O-cluster}^{unrelaxed} \) represent the total charge of the optimized system, the charge of the unrelaxed surface only and the charge of the unrelaxed water cluster only.

The charge redistribution is defined as the sum of the absolute value of charge density difference.
\[ \int |\Delta n(r)| \, d^3r = \frac{\sum_{i,j,k} |\Delta n_{i,j,k}|}{\text{total grids}} \]  

Here, the indices i, j and k are indices of real space grids in DFT calculations.

**4.3 Water Adsorption on Surfaces 1 and 2 ((1X1) and (2X1) Perfect Surface)**

When one water molecule is adsorbed on a perfect surface, two kinds of adsorption sites are observed in the calculation. One is the silicon atom site, the other is the hollow site. In our calculations, one water molecule adsorbed on a hollow site is preferred more than on a silicon atom site on both surface 1 and 2. This result is different from what Du et al. reported [21]. They claimed that the silicon site is the most stable adsorption site. In our calculations, the bonding energy on the hollow site is 18.8 meV, 2.9 meV lower than on the silicon atom site on surfaces 1 and 2. The adsorption energies are smaller than bonding energies (Table 4-1) because of the energy cost for deformation of the perfect surfaces and the water molecule. The bonding energy is only about 19% of one hydrogen bond in Ice XI (350 meV in DFT calculation) [91]. In Figures 4-1 and 4-2, we show the side views and top views of the relaxed structures as well as the charge density difference. The charge transfer from the water molecule to each surface (Table 4-2) is small, but the charge redistribution is large (0.45 e on surface 1 and 0.31 e on surface 2, Table 4-3) and concentrated around the water molecule and the adsorption site. The charge density difference indicates that the proton(s) of water is/are attracted to the bridge oxygen atom(s) on the silica surfaces. The bonding energy, charge transfer and charge redistribution values all indicate that surface 1 has a stronger interaction with a water molecule (the difference between bonding energies is tiny). However, the adsorption energy of one water molecule on surface 1 is smaller than for surface 2. This is because surface 1 is less stable than
surface 2 and the deformation of surface 1 is larger when adsorbing a water molecule on it. On the other hand, the charge density difference for one water molecule adsorbed on the silicon site of surface 1 (Figure 4-3) shows another kind of charge redistribution. The oxygen atom in the water molecule gains electrons and the silicon atom on the adsorption site loses electrons. The charge transfer to the water molecule is smaller than for the hollow site adsorption (-1.4 x E^3 e) and with opposite sign. The charge density difference indicates that the oxygen atom of water is attractive to the silicon atom on the surface and that the hydrogen atom has an interaction with the bridge oxygen atom on the surface as well. The charge redistribution is smaller (0.31 e) than for the hollow site adsorption.

When the second water molecule is adsorbed on the surfaces, the first water molecule stays on the hollow site and the second one is absorbed on the silicon atom site with one hydrogen bond formed between two water molecules (Figure 4-4, 4-5). The bonding energy is greatly enhanced compared to single-water molecule adsorption (Table 4-1), so that the average bonding energy is also much higher than E_b1w on both perfect surfaces. Consideration of the adsorption energy and bonding energy (E_a2w and E_b2w) indicates that the water-silica interaction is comparable with the strength of one hydrogen bond in Ice XI (E_b2w on either surfaces is about 50 to 60% of one hydrogen bond of Ice XI). The charge density difference shows a much larger range of redistributions on both surface 1 and 2 than for one-water molecule adsorption. The charge density difference is characterized by a quadrupole-like distribution, the alternating enriched and depleted zones lying in the Z direction (Figure 4-4 (c),(d) and 4-5 (c), (d)). This special phenomenon is observed in water layer(s) adsorption on silica
surfaces also, and it could be the reason for the enhanced water-silica interaction. The charge transfer on water molecules is still small (Table 4-2) but changes the sign of the total (the first one is positive and the second one is negative). The total charge redistribution is 0.85 e on surface 1 and 0.68 e on surface 2. Each of them shows again a significant charge redistribution happening when water is adsorbed on the silica surface. On the other hand, if two water molecules are adsorbed on two adjacent silicon sites, the bonding energy is lower. On surface 1, we obtained a result that the first water molecule was slightly dragged off the silicon site and the total bonding energy is 53 meV lower (Figure 4-6). The charge density difference shows that the interaction between the oxygen atom of the first water molecule and the silicon site is weaker than that of one water molecule adsorbed on a silicon site due to the displacement of water molecule from the original position. On the other hand, the interaction between the proton of the first water molecule and the bridge oxygen atom is unaltered or slightly strengthened (with a larger isosurface region near the atoms). Interestingly, the charge density difference still shows a quadrupole pattern after structural relaxation.

When a third water molecule is adsorbed on the surfaces after the adsorption of a water dimer in the most stable state, three water molecules form hydrogen bonds with each other, and the third water molecule is absorbed on the other silicon site (Figure 4-7, 4-8). Contradicting intuitive thinking, the total bonding energies are decreased and the average bonding energies are even lower than the bonding energies of one water molecule adsorption on both perfect surfaces. Compared to the adsorption energies, the bonding energies are much smaller. This indicates that the strength of hydrogen bonds overwhelms the water-silica interaction and directs the optimization of a water cluster.
adsorbed on the perfect surfaces. On the other hand, the charge density difference on each surface also shows smaller distribution ranges than in the dimer adsorption case. Similar to the two-silicon site adsorption case, the second water molecule is lifted from the silicon site, and the water-silica interaction between the second, third water molecules and silica surfaces is much smaller than the case of dimer adsorption in the most stable state (considering the distribution of charge density difference). However, the first water molecule still has a strong interaction with the silica surface.

The bonding energies of one water molecule adsorbed on both surfaces are similar. However, the bonding energies in two and three water molecules adsorption cases on surface 2 are obviously smaller than those on surface 1. There could be two reasons. One is because surface 2 is more stable than surface 1, hence surface 2 deforms less when water-water and water-surface interactions compete each other during structural optimization. The other reason could be that surface 1 has (1x1) hexagonal symmetry which is more preferred for water molecules’ arrangement, since they tend to form hexagonal arrangements akin to in one sub-layer of Ice XI.

Because of the similarity between six-membered ring geometry on surface 1 and the hexagonal arrangement of one Ice XI sub-layer, we suggest that there are two kinds of one-water-layer adsorption on surface 1. One arrangement has all of the oxygen atoms of water molecules are adsorbed on silicon atom sites. The other arrangement has half on silicon atom sites and half on hollow sites (Figure 5-1, 5-2). We discuss water layer adsorption in Chapter 5.

**4.4 Water Adsorption on Surface 3 (the Fully Hydroxylated Surface)**

Water adsorption on a fully hydroxylated surface has been studied by Yang *et al.* already [22]. They studied the adsorption of one, two water molecules and one-water-
layer on surface 3. We describe the results of our calculations in the following. When one water molecule is adsorbed, the water molecule will break one weak hydrogen bond formed within the hydroxyl groups on the surface and form two strong hydrogen bonds with two of them (Figure 4-9 and Ref. [22]). The bond length we found differs slightly different from Yang's result because we use a set of larger lattice constants and also a larger energy cutoff in the calculations (recall Chapter 3). The adsorption energy of one water molecule adsorbed on the surface is 618.9 meV which is ~14% larger than Yang's result [22]. The charge density difference (Figure 4-9 (c), (d)) shows a much larger range of charge redistribution than the same case on perfect surfaces and indicates a much stronger water-silica surface interaction. The adsorption and bonding energies are about 14 and 12.5 times larger respectively than those on surface 1. Table 4-2 shows that the water molecule tends to lose some electrons to the surface. There is 0.68 e of charge redistribution in the system, a value which is larger than that of one water molecule adsorption on perfect surfaces. It is surprising that the charge redistribution does not show a much larger number than for perfect surfaces since the water-silica interaction on the fully hydroxylated surface is much stronger than on the perfect surfaces.

When the second water molecule is adsorbed, the existing hydrogen bonds on the first water molecule do not break as Yang et al. reported. The second water molecule donates one proton to form a weak hydrogen bond with the surface and forms one slightly stronger hydrogen bond with the first water molecule (Figure 4-10). We also tried to optimize a structure which Yang reported [22]. The adsorption energy of water dimer is slightly less by 5.4 meV. The charge density difference shows that the second
water molecule does not have as strong an interaction with the surface as the first water molecule does, since the charge redistribution range is much smaller around the second water molecule.

When the third water molecule is adsorbed, it forms three hydrogen bonds in total with the second water molecule and hydroxyl groups on the surface. Its position relative to the second water molecule is similar to the first one (Figure 4-11). The charge density difference shows there are strong interactions between the first, third water molecules and the surface. The interaction of the second water molecule with the surface is enhanced compared to two-water-molecule adsorption. Because of the hydrogen bonds formed between water molecules and the silica surface, the bonding energies on the fully hydroxylated surface are always much higher than for water molecule adsorption on perfect surfaces (Table 4-1). The total charge redistribution is increased to 0.98 e, which is somewhat larger than the cases on perfect surfaces.

4.5 Water Adsorption on Surfaces 4 and 5 (Oxygen Vacancy Defect)

The strongest one-water-molecule adsorption site on defective surfaces with one oxygen vacancy is the center of the defect formed by two silicon atoms (Figure 4-12, 4-13). The oxygen atom of the water molecule is almost equally distant to the two silicon atoms. The adsorption energies on surface 4 and 5 are about 4 to 4.8 times larger than that those on surface 1 (Table 4-1) and about 50 to 60% of the strength of one hydrogen bond in Ice XI (in DFT calculations). In our calculation, surface 5 has a larger bonding energy for a water molecule than surface 4 by 39 meV, even though surface 5 is a little more stable than surface 4. To test the effect of a defect on neighbor adsorption sites, we optimize the structure of one water molecule adsorbed on hollow and silicon atom sites as well (hollow site next to the defect and silicon atom on defect).
The bonding energies are 52.3 and 5.6 meV higher than for the low energy state. However, the hollow site adsorption still has higher adsorption and bonding energy than those on surface 1 by 84.1 and 78.7 meV. The distance between oxygen atoms of water molecules adsorbed on the hollow site and the defect site is about 1.8 Å. This indicates that the oxygen vacancy defect does enhance water molecule attraction to the silica surface. The interaction strength is about 50 to 60% of one hydrogen bond with ~ 2 Å interaction range. The charge density difference of the low energy state shows a larger range of charge redistribution than on surface 1 as well. The silicon-silicon bond of the defect gains electrons, but just above the defect there is a large region of electron depletion. The charge redistributes around the water molecule in a large range as well. Some electron transfers from the water molecule to the surface, which is in opposite sign with that of the water molecule adsorbed on perfect surfaces (Table 4-2). There are 0.75 e and 0.83 e charge redistributions on surface 4 and 5, which is reasonable, since the bonding energies are larger than on the perfect surfaces.

When the second water molecule is adsorbed, it is at the hollow site and forms a hydrogen bond with the first one (Figure 4-14, 4-15). The bonding energies are weakened to being slightly smaller than that of a water dimer adsorbed on perfect surfaces. The adsorption energies of the second water molecule obviously are smaller than the counterpart on perfect surfaces. The charge density difference shows the second water molecule on each surface has a very weak interaction with the surface compared to the first water molecule. Compared with surface 1, the lowered bonding energy and adsorption energy indicate the silica-water interaction is compromised for the strong hydrogen bond within the water dimer. As in the one-water-molecule
adsorption case, the water clusters lose electrons and surfaces gain electrons, but the absolute value is smaller than before. The charge redistributions are reduced to 0.59 e and 0.76 e respectively. On the other hand, the adsorption and bonding energies of water dimer adsorbed on perfect surfaces are much enhanced after one-water-molecule adsorption. The charge density difference shows quadrupole pattern on each perfect surface (Figure 4-4, 4-5) which may be the reason for the interaction strengthening. We will discuss the quadrupole pattern later in Chapter 7.

When the third water molecule is adsorbed, it forms hydrogen bonds with the two previous water molecules on both surfaces (Figure 4-16, 4-17). The third water molecule is not adsorbed on the silicon atom site or on the hollow site. The total bonding energies are increased compared to the previous cases. The isosurfaces of charge density difference show that the first water molecule still has a strong interaction with the defect on surfaces, but the interaction of the other two is much smaller. The interaction between the second water molecule and the surface is increased slightly. This could be the reason for the rise in bonding energy. The charge redistributions are increased to 1.02 e and 1 e respectively. Compared with the second water molecule adsorption energy, the third adsorption energy is much higher. This is because there are two new hydrogen bonds formed within the water trimer.

4.6 Water Adsorption on Surfaces 6 and 7 (Oxygen Displacement)

When one water molecule comes near to the surface, it will be attracted to the peroxo linkage of the defect with one of the protons pointing to the oxygen atom of the peroxo linkage (Figure 4-18, 4-19). The bonding energy on surface 6 is ~73% larger than that on surface 1; but on surface 7, it is about the same value. Because the peroxo linkage on surface 6 is involved in a three-membered ring (which has a higher strain
environment than in six-membered rings and quartz bulk), the interaction between the peroxy linkage and the proton in the water molecule is stronger. Du. et al. studied the relationship of the water-silica interaction with the surface structure and reached a similar conclusion [27]. The charge density difference shows the interaction is located at the peroxy linkage and the proton of water on each surface. There are 0.43 e and 0.39 e charge redistribution for the two systems respectively.

When the second water molecule is adsorbed, it is located on the hollow site. On surface 6, the second water molecule forms a hydrogen bond to the first water molecule (Figure 4-20). On surface 7, the second water molecule interacts with the oxygen peroxy linkage and alters the orientation of the first water molecule to form a hydrogen bond within the water dimer (Figure 4-21). Compared to water dimer adsorption on surface 4 and 5, the total energies are not reduced but increased. The reason could be that the defect has a larger interaction area than the oxygen vacancy defect on surfaces 1 and 2, since this defect type is composed of one oxygen vacancy and one peroxy linkage. The average bonding energies are decreased by about 10% of one-water-molecule adsorption. The effect of hydrogen bonds making the water-silica interaction to compromise does not appear yet, it will be revealed in three water molecules adsorption. The charge redistributions are increased with values of 0.69 e and 0.68 e respectively.

When the third water molecule is adsorbed, it forms a hydrogen bond to the second one on surface 6 and to both preceding molecules on surface 7 (Figure 4-22, 4-23). The bonding energies are decreased and the adsorption energies are increased, similar to the water trimer adsorption on perfect surfaces (Table 4-1). The charge
density difference still shows that the water-silica interactions on each surface are located at the first water molecule and peroxy linkage. The charge redistributions are slightly reduced to 0.59 e and 0.56 e.

In table 4-1, we can see that the adsorption energies on surfaces increase with increasing number of adsorbed water molecules. However, the total bonding energies rise a little or descend. This behavior is an indication that the interaction of hydrogen bonds within the water entity gradually controls the optimization direction when more water molecules accumulate. We notice that the charge transfer behaviors are different on two types of silica defects. The oxygen vacancy always will gain electrons from water molecule(s), while the oxygen displacement defect always gives electrons to water molecule(s). On the other hand, the perfect surface loses electrons at one water molecule adsorption and gains electrons when more water molecules are adsorbed.
Table 4-1. The adsorption and bonding energy of water molecules on silica surface. Adsorption energy, $E_{amw} = -(E_{total} - E_o - E_{H_2O})$, $E_{total}$ is total system energy, $E_o$ is total energy of a system with one fewer water molecule. Bonding energy, $E_{bmw} = -(E_{total} - E_{unrelaxed}^{quartz} - E_{unrelaxed}^{H_2O-cluster})$, All energies are given in meV.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{a1w}$</th>
<th>$E_{a2w}$</th>
<th>$E_{a3w}$</th>
<th>$E_{b1w}$</th>
<th>$E_{b2w}$</th>
<th>$E_{b3w}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.8</td>
<td>343</td>
<td>481</td>
<td>67.0</td>
<td>207</td>
<td>146</td>
</tr>
<tr>
<td>2</td>
<td>58.8</td>
<td>327</td>
<td>485</td>
<td>66.9</td>
<td>176</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>619</td>
<td>365</td>
<td>779</td>
<td>838</td>
<td>1148</td>
<td>2120</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>224</td>
<td>597</td>
<td>198</td>
<td>175</td>
<td>267</td>
</tr>
<tr>
<td>5</td>
<td>213</td>
<td>183</td>
<td>590</td>
<td>237</td>
<td>192</td>
<td>251</td>
</tr>
<tr>
<td>6</td>
<td>108</td>
<td>248</td>
<td>414</td>
<td>116</td>
<td>184</td>
<td>158</td>
</tr>
<tr>
<td>7</td>
<td>63.0</td>
<td>291</td>
<td>523</td>
<td>70.3</td>
<td>125</td>
<td>118</td>
</tr>
</tbody>
</table>

Table 4-2. Charge transfer analysis of water molecules on surface (Positive means gaining electrons). Units: (electron number/1000). The number is given as the electrons transferred onto the whole water molecule(s) cluster. The charge on surface means the charge transferred on the topmost layer of the surface, not including the whole slab. The charge transfer is calculated from the charge distribution of [whole system – static surface alone – static cluster of water molecule(s)].

<table>
<thead>
<tr>
<th>Surface</th>
<th>1 water molecule</th>
<th>2 water molecules</th>
<th>3 water molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water surface</td>
<td>water surface</td>
<td>water surface</td>
</tr>
<tr>
<td>1</td>
<td>8.9</td>
<td>-3.9</td>
<td>-3.3</td>
</tr>
<tr>
<td>2</td>
<td>2.9</td>
<td>-7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>3</td>
<td>-27</td>
<td>-31</td>
<td>31.3</td>
</tr>
<tr>
<td>4</td>
<td>-15.7</td>
<td>-12.3</td>
<td>7.7</td>
</tr>
<tr>
<td>5</td>
<td>-22.9</td>
<td>-18.5</td>
<td>16.9</td>
</tr>
<tr>
<td>6</td>
<td>5.9</td>
<td>6.7</td>
<td>-4.9</td>
</tr>
<tr>
<td>7</td>
<td>4.4</td>
<td>8</td>
<td>-8.7</td>
</tr>
</tbody>
</table>
Table 4-3. The charge redistribution of water cluster adsorption systems. See equation (4-4). The values are in electrons.

<table>
<thead>
<tr>
<th>Surface</th>
<th>1 water molecule</th>
<th>2 water molecules</th>
<th>3 water molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.45</td>
<td>0.85</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>0.31</td>
<td>0.68</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>0.68</td>
<td>0.89</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>0.59</td>
<td>1.02</td>
</tr>
<tr>
<td>5</td>
<td>0.83</td>
<td>0.76</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>0.43</td>
<td>0.69</td>
<td>0.59</td>
</tr>
<tr>
<td>7</td>
<td>0.39</td>
<td>0.68</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Figure 4-1. One water molecule adsorbed on surface 1 ((1x1) perfect surface) at the hollow site. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³. The yellow balloon is the zone gaining electrons and blue is that losing electrons.
Figure 4-2. One water molecule adsorbed on surface 2 ((2x1) perfect surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-3. One water molecule adsorbed on surface 1 ((1x1) perfect surface) at the silicon atom site. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of $\pm 0.003/\text{Å}^3$. 
Figure 4-4. Two water molecules adsorbed on surface 1 ((1x1) perfect surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005 Å³.
Figure 4-5. Two water molecules adsorbed on surface 2 ((2x1) perfect surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005 Å⁻³.
Figure 4-6. Two water molecules adsorbed on two silicon sites of surface 1 ((1x1) perfect surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-7. Three water molecules adsorbed on surface 1 ((1x1) perfect surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-8. Three water molecules adsorbed on surface 2 ((2x1) perfect surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-9. One water molecule adsorbed on surface 3 (fully hydroxylated surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.03/Å³.
Figure 4-10. Two water molecules adsorbed on surface 3 (fully hydroxylated surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.03/Å³.
Figure 4-11. Three water molecules adsorbed on surface 3 (fully hydroxylated surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of $\pm 0.03/\text{Å}^3$. 
Figure 4-12. One water molecule adsorbed on surface 4 (oxygen vacancy defect). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-13. One water molecule adsorbed on surface 5 (oxygen vacancy defect). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-14. Two water molecules adsorbed on surface 4 (oxygen vacancy defect). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-15. Two water molecules adsorbed on surface 5 (oxygen vacancy defect). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-16. Three water molecules adsorbed on surface 4 (oxygen vacancy defect). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-17. Three water molecules adsorbed on surface 5 (oxygen vacancy defect). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-18. One water molecule adsorbed on surface 6 (oxygen vacancy displacement). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005 Å⁻³.
Figure 4-19. One water molecule adsorbed on surface 7 (oxygen vacancy displacement). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-20. Two water molecules adsorbed on surface 6 (oxygen vacancy displacement). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.005/Å³.
Figure 4-21. Two water molecules adsorbed on surface 7 (oxygen vacancy displacement). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density distribution drawn on isosurface of ±0.005/Å³.
Figure 4-22. Three water molecules adsorbed on surface 6 (oxygen vacancy displacement). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density distribution drawn on isosurface of ±0.005/Å³.
Figure 4-23. Three water molecules adsorbed on surface 7 (oxygen vacancy displacement). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density distribution drawn on isosurface of ±0.005/Å³.
CHAPTER 5
WATER LAYER(S) ADSORPTION ON SILICA SURFACES

After the test of water cluster adsorption on alpha-quartz (0001) surfaces, we deposited Ice XI sub-layers one layer at one time onto the surfaces. We tried two strategies of water layer deposition on both perfect surfaces and defective surfaces. According to the observation of water cluster adsorption on perfect surfaces in Chapter 4, one arrangement could be that all of the water molecules are absorbed on silicon atom sites; the other one is half on silicon atom sites and half on hollow sites. Regarding water layer adsorption on hydroxylated surface, we followed the ice-layer structure proposed by Yang et al. [22] and then deposited more water layers on it.

5.1 Introduction

In the introduction of Chapter 4, we reviewed briefly the recent studies of water adsorption on silica surfaces in experiment and in computational calculations. So far, the first-principles studies on water-silica interaction were focused on the hydroxylation of silica by water molecules [27, 28, 73, 74], water molecule adsorption on the (1x1) perfect surface and the fully hydroxylated surface [14, 15, 22, 30, 88], and one water layer adsorption on the fully hydroxylated surfaces [22, 30, 88]. More efforts still is needed on water multi-layer adsorption on silica surfaces. The most important issue may be the understanding of the water-silica interaction on an amorphous silica surface. While a full understanding of an amorphous silica surface is not available experimentally or theoretically, the alpha-quartz (0001) surface offers a simplified model for investigating water-silica interaction and its effect on the water hydrogen bonding network.
5.2 Methods

The methods used are the same as in Chapter 4 except for the equations for calculating the adsorption and bonding energies, namely

\[ E_{anL} = \frac{-E_{total} - E_o - mE_{H_2O}}{area} \]  \hspace{1cm} (5-1)

\[ E_{bnL} = \frac{-E_{total} - E_{unrelaxed} - E_{H_2O-layer}}{area} \]  \hspace{1cm} (5-2)

In equation (5-1), \( E_{anL} \) is the adsorption energy of the \( n \)th water layer, \( E_{total} \) is the total energy of the optimized system with \( n \) water layers adsorbed, \( E_o \) is total energy of the optimized system with \((n-1)\) water layers adsorbed, and \( E_{H_2O} \) is the energy of one optimized water molecule. \( m \) is the number of water molecules in one water layer, thus it is 8 on surfaces 1 through 3 and 18 on surfaces 4 through 7. The area is 84.89 Å\(^2\) for surface 1 through 3 and is 191.01 Å\(^2\) for surfaces 4 through 7. In equation (5-2), \( E_{bnL} \) is the bonding energy of \( n \)-water layer, and \( E_{unrelaxed}^{surface} \) is the energy of the individual surface or water layer(s) subsystem which has the same configuration as in optimized total system.

5.3 Water Adsorption on Surfaces 1 and 2 ((1X1) and (2X1) Perfect Surface)

According to the discussion in section 4.3, there are two kinds of water molecule adsorption sites: silicon atom sites and hollow sites. All of the silicon atom sites form a hexagonal 2D matrix and all of the hollow sites combined with half the silicon atom sites also form the same arrangement. Because one sub-layer of the most stable ice structure (Ice XI) and surface 1 have the same hexagonal geometry, we deposited the sub-layer of Ice XI one by one onto the surfaces to see how the surface interacts with the water layer. Figure 5-1 and 5-2 show the optimized structures of two types of one water layer deposition on surface 1. Each of the relaxed water layers adsorbed on
surface 1 has a flat-ice feature with two groups of hydrogen bond lengths (~1.75 Å and ~1.96 Å). In each water layer, half of the water molecules have two protons forming hydrogen bonds in the water layer plane. The other halves have one proton forming hydrogen bonds and one proton pointing out of the water layer plane. For the water layer with the proton pointing up, the water molecules prefer to be adsorbed on all silicon sites. For the proton pointing down structure, the water molecules with proton pointing down will be adsorbed on hollow sites, while the other water molecules are adsorbed on silicon atom sites. The ground state is the water layer with the proton pointing down. It has a total surface energy lower than pointing up system by 3.58 meV/Å². The bonding energy of the low energy state is about twice of its isomer but the adsorption energies of two states are similar (Table 5-1). The proton pointing down case is considered as a hydrophilic adsorption case, which has an average bonding energy (divided by the number of water molecules) of 40.8 meV. The distance between the water monolayer to the surface is shortened in the proton pointing down case by ~16% compared to the proton pointing up case (isomer case). Comparing the charge density difference of these two cases, the proton pointing down structure has a larger range of charge redistribution (low energy state: 0.71 e, isomer state: 0.11 e) which also forms quadrupole matrix on the surface (Figure 5-2). The proton pointing up case has a smaller range of charge redistribution and the distribution is not equivalent on the adjacent silicon atom sites. In section 4-3, we discussed the two cases of water dimer adsorption on surface 1. One case has water molecules adsorbed on one hollow and one silicon site, the other has both water molecule adsorbed on adjacent silicon sites. The resulting charge density difference forms quadrupole arrangements for both cases.
However, in the two-silicon-sites case, the oxygen atom of one water molecule is lifted off the silicon site and one proton has an interaction with the oxygen atom on the surface (Figure 4-6). The charge density difference for the water layer isomer case shows alternating interaction strength of water molecules to silica surface (Figure 5-1). Adsorption of water molecules on adjacent silicon sites seems not preferred according to the two cases described. On the other hand, the average bonding energy of the water layer adsorption in proton pointing down case is obviously lower than that of the water dimer adsorption, even though the charge density difference forms a hexagonal quadrupole matrix. Because the hydrogen bonds are much stronger than the water-silica interaction, the best adsorption position for the individual water molecule is compromised. We will see this point much clearer in adsorption on defective surfaces.

We also treated two types of water monolayer adsorption on surface 2. Compared to the counterparts on surface 1, in the surface 2 case, each water monolayer is deformed a little with a larger variation on the longer hydrogen bond group (1.93 ~ 2.01 Å in Figure 5-3, 1.95~1.98 Å in Figure 5-4). The distance between the water layer and silica surface is similar to cases on surface 1 but the water molecules on silicon sites deviate from the silicon sites. The charge density difference of each case is different from the counterpart on surface 1, but a quadrupole matrix still formed in the proton pointing down case. The low energy state is still the proton pointing down configuration and the proton pointing down case is isomer state. The charge redistributions of the proton pointing down and up cases are 0.58 e and 0.11 e respectively. The adsorption and bonding energies are a little bit weaker than for the corresponding cases with surface 1 for dissimilar symmetries of surface 2 and water
layer. Because the hydrogen bonds are much stronger than the interaction of water-silica interface, the water-layer hexagonal structure is deformed just a little on surface 2 and the adsorption energy is surprisingly similar.

For the second water layer adsorption on surface 1, we deposit a corresponding Ice XI sub-layer on top of the first layer structures. The optimized structures of water layers are very different for the two adsorption cases. For the proton pointing up case, the out-of-plane protons in the second layer will reverse their orientations to pointing down. The up and down water layers form a membrane-like bilayer thin film and all hydrogen bonds of the water thin film are saturated within itself (Figure 5-5). The thickness of the thin film is 2.71 Å, and the distance between the water film and surface are similar to the isomer state of monolayer adsorption case. The charge density difference is localized at the interface, which indicates that the second water layer does not have a strong (or observable) interaction with the silica surface. The bonding energy is only increased by 6.8% from monolayer adsorption. In the proton pointing down case, there is no direction reversal for protons out of the water plane (Figure 5-6). The charge density difference is also localized at the interface as in the bilayer adsorption case, but it still forms a quadrupole matrix as with the proton pointing down case in monolayer adsorption. Not like the bilayer adsorption case, the bonding energy decreases by 15% from monolayer adsorption. The charge redistributions are 0.11 e and 0.54 e for the systems with protons pointing up and down in first water layer.

The ground state of two-water-layer adsorption is now switched to the bilayer adsorption case, not the case with proton pointing down. The bilayer adsorption is 37.9 meV/Å² lower than the proton pointing down configuration in total surface energy. The
main energy gain is from the formation of more hydrogen bonds. In the bilayer structure, all protons form hydrogen bonds with the other water molecules but in the proton pointing down case, they are not saturated. Although the bonding energy is still larger in the proton pointing down case, the hydrogen bonds strongly direct the total energy minimization and the ground state should be the bilayer adsorption case. On surface 2, the bonding energies of the adsorption of two water layers are similar to those on surface 1. The deviation of the hydrogen bond lengths within water layers become smaller compared to the monolayer cases. The lower energy state is the bilayer adsorption case as well. The charge redistributions are 0.12 e and 0.46 e for the bilayer and the protons pointing down case.

For the third and fourth water layer adsorption, the same way of Ice XI sub-layer deposition is applied onto two adsorption cases on each perfect surface (Figure 5-9 to 5-16). When the third layer is added on top of the bilayer structure, hydrogen bonds form and break between the second and third water layers (Figure 5-9, 5-11). The water layers pucker in the vertical direction. But for the proton pointing down case, there is no hydrogen bond breaking; only the third layer forms hydrogen bonds with the second layer. The result is like a piece of Ice XI placed on a silica surface. The ground state is still the case with the first layer pointing up which has a total surface energy lower than the proton pointing down configuration on surface 1 by 35.3 meV/Å². The result for the fourth water layer adsorption is similar to that for the third water layer adsorption (Figure 5-10, 5-12). The first layer pointing up case has a total surface energy 47.1 meV/Å² lower than the proton pointing down configuration on surface 1. The adsorption energies
of the water monolayer to four layers (ground state) show an odd-even oscillation on both surfaces.

It is remarkable that the adsorption and bonding energies are so similar on both perfect surfaces, even though their surface symmetries are different. The other phenomenon which deserves notice is that the bonding energies increase a large amount for four water layer with proton pointing down on defect surfaces when compared to the adsorption of ewer water layers (~5.3 eV vs ~3.0 eV). The charge density difference shows that a small amount of charge redistribution is localized at the fourth layer. The weird phenomenon of charge accumulation at the topmost water layer actually starts from the third water layer adsorption (see Table 5-2). At the same time, the total charge redistributions are also increased (from 0.58 e to 1.7 e, see Table 5-3). This behavior seems to be originating from the interaction between the surface and the dipole of Ice XI. Even though the proton pointing down arrangements are not the ground states for 2, 3, 4 water layers adsorption, it is still interesting to study the existence of a stable dipole moment of ice adsorbed on a silica surface and the interactions within. But in this dissertation we do not go beyond four water layers adsorption, and further efforts need to be done in the future work.

5.4 Water Adsorption on Surface 3 (the Fully Hydroxylated Surface)

The interaction of the hydroxyl groups with water molecules is very strong and comparable with hydrogen bonds between water molecules in Ice XI. The hydrogen bond network could be complicated and without any symmetry. There are many ways for water molecules to be absorbed on the fully hydroxylated quartz surface. For one water layer adsorption, the way Yang reported [22] will saturate all of the hydrogen bonds of water molecules and hydroxyl groups on the surface (Figure 5-17). We did not
find another way for water layer adsorption to occur with the same coverage and lower total system energy. However, we point out that this mode of water layer adsorption has three kinds of polymorphic states with different dipole orientations (Figure 5-18). The adsorption energies are 61.5, 62.2, 61.7 meV/Å² respectively. The energy differences are not big, but the relative dipole orientations differ by 120° relative to each other. The existences of these three types of adsorption need to be clarified experimentally. In this work, we only pick the first configuration for discussion and consider the adsorption of more water layers. The charge density difference shows a large range of charge redistribution at the interface again, and it forms a hexagonal quadrupole matrix on the surface (Figure 5-17 (c), (d)). The charge transfer is much larger than that on perfect surfaces, but it is still a small amount in absolute value. The total charge redistribution is 1.85 e which is also much larger than for perfect surfaces, and about double the value for three-water-molecule adsorption on surface 3 (8 water molecules in one water layer for water layer adsorption).

When the second water layer is deposited on the first layer, there is no strong bonding between those two as indicated by the adsorption energy of the second water layer and also the slight increase in bonding energy. The adsorption energy is slightly larger than that of 1 water layer adsorption on perfect surfaces. The main contribution to the adsorption energy is from the formation of hydrogen bonds within the second water layer. We tried several water layer deposition positions for the second water layer adsorption. Figure 5-19 shows the structure with the lowest total energy in which the second layer forms weak (long, ~2 Å) hydrogen bonds to the first water layer. The charge density difference is still localized at the interface and is not even disturbed
when compared with the monolayer adsorption. To look for the possible adsorption site, we deposited one water molecule at several positions on top of the first water layer. The bonding energies are about 100 meV/molecule, which is much lower than the hydrogen bonds within Ice XI. These data show that the hydrophilic property of the surface is shielded by the bilayer structure which consists of the first water layer and the hydroxyl groups. On surface 1 and 2, the first two water layers also form a membrane-like bilayer and all of the hydrogen bonds are saturated. The second water layer adsorption on surface 3 is similar to the third water layer adsorption on surface 1 and 2. However, the adsorption energy is dramatically different. The third water layer adsorption on surface 1 or 2 results in hydrogen bonds forming and breaking at the second and third water layers. It also causes the whole water film to pucker. On the other hand, the bilayer structure on surface 3 almost does not deform for the adsorption of the second water layer. This is because the oxygen atoms of hydroxyl groups are almost fixed by the silicon-oxygen chemical bond on the surface and make the bilayer structure much more stable and inert.

We deposit one and two more water layers onto the second water layer and the optimized structures consist of surface-the first layer structure and water bilayer, trilayer structures on perfect surfaces. The adsorption energies are similar to those for the second, third water layer adsorption on perfect surfaces (Table 5-1). This test proved that the bilayer structure formed by the hydroxyl groups and the first water layer is truly inert and stable.

5.5 Water Adsorption on Surfaces 4 and 5 (Oxygen Vacancy Defect)

Even though the interaction between the surface defect and one water molecule is stronger than water-silica interaction on perfect surfaces, the interaction decays
quickly as the distance between water and defect increases. In section 4.5, we discussed the adsorption of water molecules on defective surfaces and the water-silica interaction compromises for the strong hydrogen bonds within the water cluster. Since the hydrogen bonds are very strong and affect the structure of water cluster so much in the previous test of adsorption of water molecules, we deposited Ice XI sub-layers on defective surfaces and then studied the effect of the defect on the adsorption of water layer(s). Monolayer and two water layer adsorption are included. For one water-layer adsorption, the proton pointing down structure is still more stable than the proton pointing up structure on both surfaces (Figure 5-20 to 5-23) and the total surface energy difference between two states are 3.31 meV/Å$^2$ on surface 4 and 3.16 meV/Å$^2$ on surface 5; which are slightly smaller than that on surface 1 (3.58 meV/Å$^2$). The adsorption and bonding energies of the proton pointing down state on defective surfaces are slightly smaller than for the perfect surface as well, which may result from the competition between the minimum energy of the water layer and the water-silica defect interaction. As a result, the water layer distorts a little from the one adsorbed on surface 1. The water molecules adsorbed on the defect sites are pulled slightly closer to the surface because of the stronger interaction.

The data of adsorption and bonding energies (Table 5-1) show that the effect of the defect is compromised for the appearance of the hydrogen bonds network. The strong hydrogen bonds will control the direction of energy minimization. On both defective surfaces, the charge density difference of the proton pointing down state forms a hexagonal quadrupole matrix (Figure 5-21, 5-23) as well as on perfect surfaces, even though the distributions are distorted near the surface defects. On the other hand,
the charge density difference of each isomer state has an arrangement (Figure 5-20, 5-22) similar to the counterparts on perfect surfaces except the region near the water molecules adsorbed on the defect. In particular, there is a large zone of electron enrichment between two water molecules on the defect on both defective surfaces. The effect of the defect is a short-range interaction for each the charge density difference that quickly recovers to the corresponding distribution on (1x1) perfect surface (Figure 5-1, 5-2) about 2 to 3 Å away from the defect site. One special phenomenon is that the observed charge enrichment on the defect (Si-Si bond) in water molecule(s) adsorption cases disappears or diminishes very much in the water layer adsorption on both defective surfaces.

In the two-water-layer adsorption case, the bilayer structures on surfaces are the lower-energy states again on both defective surfaces with total surface energy 37.6 meV/Å² and 37.7 meV/Å² lower than the proton pointing down states. As on perfect surfaces, even though the bonding energy is higher for the proton pointing down states, the minimum of total energy requires that the structure transform to a bilayer state. The existence of defects did not change the water layer(s) adsorption tendency; and the adsorption and bonding energies are very similar to the numbers on perfect surfaces (Table 5-1). The charge density difference in each case is localized at the silica-water interface as well (Figure 5-24 to 5-27). Similar to water monolayer adsorption cases, the disappearance of charge enrichment on defect for both water layer states and electron enrichment between two water molecules on defect for bilayer cases are also observed.
5.6 Water Adsorption on Surfaces 6 and 7 (Oxygen Displacement)

We use the same strategy for depositing Ice XI sub-layer(s) on surface 6 and 7 and optimize the structures to see the effect of defects on the water film. The low-energy state for one water adsorption is still the one with the proton pointing down structure and the other one is the isomer state on both surfaces. Compared to the water films on surface 1, two types of adsorbed water film have some distortion near the defect as well. The water molecule close to the defect will be pushed up or pulled down a little bit. The adsorption energies show similar values to those of surface 1. The bonding energy on surface 7 is slightly lower than that on surface 1. However, on surface 6 it is apparently lower by 27% of the value on surface 1. The charge density difference shows the water-silica interaction is concentrated at the peroxy linkage of the defect for two states of adsorption on surfaces. Unlike on surface 4 and 5, the large range charge redistribution above oxygen vacancy disappears, and the charge redistribution is more concentrated on the peroxy linkage now (Figure 5-28 to 5-31). Again, the interaction with the defect is a short range effect; the pattern of charge redistribution recovers quickly to the corresponding distributions on surface 1 just as with surfaces 4 and 5.

In the water cluster adsorption sections, surface 6 has larger water molecules bonding energies than surface 7; however, it is reversed for 1 water layer adsorption. The optimization follows the energy minimum of the total system, so the strong hydrogen bonds tend to keep the hexagonal structure of the water layer but compromise the interaction between silica surface and water molecules at the same time. Though surface 6 has higher tension on peroxy linkage and should attract the
water molecules more. One oxygen atom of the peroxo linkage is out of the surface plane which will make the water layer to distort more than on surface 7. The result is the bonding energy has to be weakened for maintaining water layer hexagonal structure.

For two water layers adsorption, the water bilayer is still more stable than the proton pointing down configuration. Again, the adsorption energies on two surfaces are similar to those on surface 1, but the bonding energies are smaller than those on surface 1. On surface 6 the number is even smaller. We can use the same reason to explain the similar tendency for the bonding energies as in 1 water layer adsorption case.
Table 5-1. The adsorption and bonding energy of water layer(s) on a silica surface. Adsorption energy, $E_{\text{anL}} = -(E_{\text{total}} - E_o - mE_{H_2O})/\text{area}$, $E_{\text{total}}$ is total system energy, $E_o$ is total energy of one fewer water-layer system. $m$ is the number of water molecules in one water layer. Bonding energy, $E_{\text{bnL}} = -(E_{\text{total}} - E_{\text{unrelaxed}}^{\text{unrelaxed}} - E_{n-H_2O\text{-layer}}^{\text{unrelaxed}})/\text{area}$. The numbers out/in parentheses are for proton pointing up/down systems. All energies are given in meV Å$^2$.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{\text{a1L}}$</th>
<th>$E_{\text{a2L}}$</th>
<th>$E_{\text{a3L}}$</th>
<th>$E_{\text{a4L}}$</th>
<th>$E_{\text{b1L}}$</th>
<th>$E_{\text{b2L}}$</th>
<th>$E_{\text{b3L}}$</th>
<th>$E_{\text{b4L}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.3</td>
<td>68.7</td>
<td>46.9</td>
<td>56.5</td>
<td>1.48</td>
<td>1.58</td>
<td>1.51</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>(46.1)</td>
<td>(48.0)</td>
<td>(48.2)</td>
<td>(50.6)</td>
<td>(3.84)</td>
<td>(3.26)</td>
<td>(3.35)</td>
<td>(5.60)</td>
</tr>
<tr>
<td>2</td>
<td>43.9</td>
<td>68.8</td>
<td>47.0</td>
<td>58.3</td>
<td>1.43</td>
<td>1.44</td>
<td>1.56</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>(45.6)</td>
<td>(48.4)</td>
<td>(48.0)</td>
<td>(51.5)</td>
<td>(3.01)</td>
<td>(2.70)</td>
<td>(2.85)</td>
<td>(5.15)</td>
</tr>
<tr>
<td>3</td>
<td>62.2</td>
<td>48.5</td>
<td>64.1</td>
<td>56.5</td>
<td>34.6</td>
<td>35.9</td>
<td>36.4</td>
<td>36.4</td>
</tr>
<tr>
<td>4</td>
<td>44.4</td>
<td>68.9</td>
<td>1.42</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(46.0)</td>
<td>(48.4)</td>
<td></td>
<td></td>
<td>(3.53)</td>
<td>(3.04)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>44.4</td>
<td>68.9</td>
<td>1.43</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(46.0)</td>
<td>(48.4)</td>
<td></td>
<td></td>
<td>(3.33)</td>
<td>(2.79)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>44.4</td>
<td>68.9</td>
<td>1.41</td>
<td>1.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(45.6)</td>
<td>(48.6)</td>
<td></td>
<td></td>
<td>(2.81)</td>
<td>(2.58)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>44.4</td>
<td>68.9</td>
<td>1.45</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(46.0)</td>
<td>(48.4)</td>
<td></td>
<td></td>
<td>(3.22)</td>
<td>(2.82)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5-2. The charge transfer analysis of water layer(s) on a silica surface (Positive means gaining electrons). Unit: (electron number/1000). The number given is the electrons transferred to the whole water layer(s) system. The charge on surface means the charge transferred to the topmost layer of the surface, not including the whole slab. The charge transfer is defined as the charge distribution of [whole system – static surface alone – static water layer(s)]. The numbers out/in parentheses are for proton pointing up/down systems. For systems with more than two water layers, the charge transfer is presented in a way of charge transfer in first layer, second layer...

<table>
<thead>
<tr>
<th>Surface</th>
<th>1 water layer</th>
<th>2 water layers</th>
<th>3 water layers</th>
<th>4 water layers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>surface</td>
<td>water</td>
<td>surface</td>
</tr>
<tr>
<td>1</td>
<td>-5.7 (-18.2)</td>
<td>5 (15.5)</td>
<td>-5.4, 0.2 (-16.2, 0.2)</td>
<td>5 (14.3)</td>
</tr>
<tr>
<td>2</td>
<td>-5.4 (-16.1)</td>
<td>4.7 (14.4)</td>
<td>-4.5, -0.9 (-15.1, 0.2)</td>
<td>4.3 (13.5)</td>
</tr>
<tr>
<td>3</td>
<td>-21</td>
<td>17.3</td>
<td>-46, 19.1 (-16.2, 0.2)</td>
<td>22.8</td>
</tr>
<tr>
<td>4</td>
<td>-12.1 (-42.7)</td>
<td>11.1 (35.1)</td>
<td>-10.4, 0.4 (-32.5, 0.4)</td>
<td>9.4 (26.1)</td>
</tr>
<tr>
<td>5</td>
<td>-13.7 (-43.6)</td>
<td>12.1 (39.2)</td>
<td>-10.5, 1.1 (-32.7, 0.1)</td>
<td>9.5 (28.4)</td>
</tr>
<tr>
<td>6</td>
<td>-13.6 (-55.7)</td>
<td>13.6 (50.6)</td>
<td>-12.2, 0.7 (-40.3, -0.3)</td>
<td>10.9 (35.6)</td>
</tr>
<tr>
<td>7</td>
<td>-13.9 (-42)</td>
<td>13.6 (35.5)</td>
<td>-11.5, 0.1 (-32.5, 0)</td>
<td>10.4 (28.1)</td>
</tr>
</tbody>
</table>
Table 5-3. The charge redistribution of water layer(s) adsorption systems. The definition is at equation (4-4) with units in electron. The numbers out/in parentheses are for proton pointing up/down systems.

<table>
<thead>
<tr>
<th>Surface</th>
<th>1 water layer</th>
<th>2 water layers</th>
<th>3 water layers</th>
<th>4 water layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.11 (0.71)</td>
<td>0.11 (0.54)</td>
<td>0.15 (0.83)</td>
<td>0.15 (1.61)</td>
</tr>
<tr>
<td>2</td>
<td>0.11 (0.58)</td>
<td>0.12 (0.46)</td>
<td>0.18 (0.89)</td>
<td>0.18 (1.70)</td>
</tr>
<tr>
<td>3</td>
<td>1.85</td>
<td>2.05</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>4</td>
<td>0.29 (1.58)</td>
<td>0.30 (1.26)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>0.27 (1.44)</td>
<td>0.25 (1.10)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>6</td>
<td>0.33 (1.21)</td>
<td>0.33 (1.06)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>0.33 (1.37)</td>
<td>0.31 (1.09)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 5-1. One water layer adsorbed on surface 1 ((1x1) perfect surface) with protons pointing up. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-2. One water layer adsorbed on surface 1 ((1x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.003/Å³.
Figure 5-3. One water layer adsorbed on surface 2 ((2x1) perfect surface) with protons pointing up. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-4. One water layer adsorbed on surface 2 ((2x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-5. Two water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-6. Two water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-7. Two water layers adsorbed on surface 2 ((2x1) perfect surface) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-8. Two water layers adsorbed on surface 2 ((2x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of \( \pm 0.002/\text{Å}^3 \).
Figure 5-9. Three water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005 Å³.
Figure 5-10. Three water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å$^3$. 
Figure 5-11. Three water layers adsorbed on surface 2 ((2x1) perfect surface) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-12. Three water layers adsorbed on surface 2 ((2x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of $\pm0.002/Å^3$. 
Figure 5-13. Four water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-14. Four water layers adsorbed on surface 1 ((1x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-15. Four water layers adsorbed on surface 2 ((2x1) perfect surface) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-16. Four water layers adsorbed on surface 1 ((2x1) perfect surface) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-17. One water layer adsorbed on surface 3 (fully hydroxylated surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of $\pm 0.03/\text{Å}^3$. 
Figure 5-18. The other two possible orientations of one water layer adsorbed on surface 3 (fully hydroxylated surface). a) and b) are the top and side view of the first orientation. c) and d) are the top and side view of the second orientation.
Figure 5-19. Two water layers adsorbed on surface 3 (fully hydroxylated surface). a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.03/Å³.
Figure 5-20. One water layer adsorbed on surface 4 (oxygen vacancy defect) with protons pointing up. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-21. One water layer adsorbed on surface 4 (oxygen vacancy defect) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.003/Å³.
Figure 5-22. One water layer adsorbed on surface 5 (oxygen vacancy defect) with protons pointing up. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-23. One water layer adsorbed on surface 5 (oxygen vacancy defect) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-24. Two water layers adsorbed on surface 4 (oxygen vacancy defect) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-25. Two water layers adsorbed on surface 4 (oxygen vacancy defect) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-26. Two water layers adsorbed on surface 5 (oxygen vacancy defect) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-27. Two water layers adsorbed on surface 5 (oxygen vacancy defect) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-28. One water layer adsorbed on surface 6 (oxygen displacement) with protons pointing up. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of $\pm 0.0005/\text{Å}^3$. 
Figure 5-29. One water layer adsorbed on surface 6 (oxygen displacement) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of $\pm 0.002/\text{Å}^3$. 

Figure 5-30. One water layer adsorbed on surface 7 (oxygen displacement) with protons pointing up. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-31. One water layer adsorbed on surface 7 (oxygen displacement) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002/Å³.
Figure 5-32. Two water layers adsorbed on surface 6 (oxygen displacement) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005 Å³.
Figure 5-33. Two water layers adsorbed on surface 6 (oxygen displacement) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002 Å³.
Figure 5-34. Two water layers adsorbed on surface 7 (oxygen displacement) with protons pointing up in the first water layer. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.0005/Å³.
Figure 5-35. Two water layers adsorbed on surface 7 (oxygen displacement) with protons pointing down. a) Top view. b) Side view. c) and d) are the top view and side view of the system with charge density difference drawn on isosurface of ±0.002 Å³.
CHAPTER 6
HYDROXYLATION OF ALPHA-QUARTZ (0001) SURFACES

6.1 Introduction

We have already mentioned the easy hydroxylation of a newly cleaved silica surface under atmosphere conditions [5, 6] and the contrast hydrophilic properties with the hydrophobic properties of such a surface prepared in high vacuum[12, 16]. In simulation, the hydroxylation of silica surfaces has been studied by several groups by using silica cluster models [73, 74], and amorphous, hydroxylated or crystalline silica slabs [13-15, 22, 27, 28, 30, 75, 88]. On a newly cleaved silica surface, the oxygen and silicon dangling bonds interact exothermically with water and form hydroxyl groups [13-15, 28, 75]. Du et al. concluded that the high-strain sites like two-membered rings are easy to be hydroxylated [27]. Rignanese et al. studied the hydroxylation of a perfect reconstructed alpha-quartz (0001) surface (as surface 1 in this work) with DFT calculations [15]. They concluded that surface 1 is hydrophobic and stable, since surface hydroxylation by one water molecule is not energetically preferred. Rimola and Ugliengo studied the hydroxylation mechanism of a two-membered ring defect with a cluster model [74]. The vibrational spectrum of the defect and the hydroxyl groups were calculated to compare with experiment. They also found that the hydroxylation had been speeded up when there was more than one water molecule adsorbed.

Each of the silica polymorphs possesses different chemical properties and defects in silica bulk and on silica surfaces increase the variety of chemical activity. There is still need for effort devoted to the understanding of the silica hydroxylation mechanism at atomic scale. In this chapter, we report on the hydroxylation of six alpha-quartz (0001) surfaces studied in the preceding chapters. Two perfect surfaces and four
defective surfaces are included. The same nomenclature as used in Chapter 4 and 5 still applies in this chapter.

### 6.2 Methods

The initial configurations were prepared by breaking some selected Si-O, Si-Si or O-O bonds on surfaces and insertion of one piece of a dissociated water molecule (a proton or a hydroxyl radical) onto the dangling bonds created. Here are the examples.

\[
\equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{H}_2\text{O} \rightarrow \equiv \text{Si} - \text{OH} \cdots \text{HO} - \text{Si} \equiv \quad (6-1)
\]

\[
\equiv \text{Si} - \text{Si} \equiv + \text{H}_2\text{O} \rightarrow \equiv \text{Si} - \text{OH} \cdots \text{H} - \text{Si} \equiv \quad (6-2)
\]

\[
\equiv \text{Si} - \text{O} - \text{O} - \text{Si} \equiv + \text{H}_2\text{O} \rightarrow \equiv \text{Si} - \text{OH} \cdots \text{HOO} - \text{Si} \equiv \quad (6-3)
\]

Figure 6-1 shows two examples of the initial configurations for two surfaces. DFT optimization calculations were done on those prepared initial configurations and the hydroxylation energy is calculated by the following equation

\[ E_{\text{hydro}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{H}_2\text{O}} \quad (6-4) \]

Here, \( E_{\text{total}} \) is the total energy of the hydroxylated surface system, \( E_{\text{surface}} \) is the energy of one optimized alpha-quartz (0001) surface (See Table 3-2, 3-5), and \( E_{\text{H}_2\text{O}} \) is the energy of one optimized water molecule. The supercell vectors of the systems were the same as those surface systems in Chapter 3 and all of the DFT parameters for optimization calculations were the same as reported in section 3.2.

### 6.3 Results

#### 6.3.1 Hydroxylation on Surfaces 1 and 2 ((1x1) and (1x2) Perfect Surface)

On surface 1, there are three inequivalent hydroxylation sites. One of them is involved in a three-membered ring, the other two are not. On surface 2, there are six inequivalent hydroxylation sites. Two of them are involved in two separated three-
membered rings and the others are not. In Figure 6-2, we label the hydroxylation sites on surface 1 and 2 for the calculations.

For each site, two or three slightly different initial configurations of hydroxylation are tried. Different kinds of optimized configurations were observed. Some have one hydroxyl group with its oxygen atom three-coordinated, some have two of them, and some recover the status of separate surface and water molecule. Tables 6-1 and 6-2 give the hydroxylation energies of those systems which keep hydroxyl groups.

According to Table 6-1, all of the optimized hydroxylation processes are endothermic and most of the hydroxylation energies range from 1.29 eV to 1.68 eV, except that the larger energies corresponding to site 3 on surface 2 (~2.5eV). There are two major types of hydroxylation structures. One type has two hydroxyl groups with their oxygen atoms bonding to the same two silicon atoms. In this type, the oxygen atoms of the hydroxyl groups are three-coordinated and the both bonded silicon atoms are five-coordinated. The other type has just one hydroxyl group behaving this way (Figure 6-3) and only one silicon atom is five-coordinated. Figure 6-4 shows the other two types of hydroxylation observed on site 3 of surface 2 with higher hydroxylation energies. The first one has one hydroxyl group bonding to the two silicon atoms on site 3 of surface 2. The other hydroxyl group transfers to site 2, which results in two silicon atoms on site 2 being five-coordinated. In the second hydroxylation type, the proton of one hydroxyl group is transferred to the oxygen atom on site 4; only one silicon atom on site 3 is five-coordinated.

There is no obvious difference between the hydroxylation on a site involved in a three-membered ring and not. It seems that the three-membered rings are not highly
strained compared to other six-member rings on surface 1 and 2. Rignanese et al. reached the same conclusion in their investigation [15]. They reported that the hydroxylation structure has two hydroxyl groups without three-coordinated oxygen atom and five-coordinated silicon atoms on surface 1 and their hydroxylation energy (4.69 eV) is much higher than our calculations. The discrepancy remains to be clarified, but our results and those of Rignanese have the same conclusion namely that the hydroxylation on perfect surfaces is not energetically preferred. And indeed, in many cases which we tried, the optimized systems recovered the states with the separate surface and water molecule. The charge on each atom varies a little at the hydroxylation site. In general, the three-coordinated oxygen atom of the hydroxyl group has charge ranging from 7.43 e to 7.47 e, but not the three-coordinated oxygen atom, which of hydroxyl group has less charge, ranging from 7.38 e to 7.40 e.

6.3.2 Hydroxylation on Defective Surfaces

We set up the initial configurations for surface 4 and 5 according to equation (6-2) that breaks the Si-Si bond of the defect and attaches a hydroxyl radical and a proton onto the silicon dangling bonds. For surface 6 and 7, we set up the initial configurations according to equation (6-3); we did not try the setup of equation (6-2), since we already showed that the peroxy linkage is more active than the oxygen vacancy site (see the charge density difference of water adsorption on surface 6 and 7).

On surface 5 and 7, the optimized structures relaxed to separate surfaces and water molecules. In particular, the defect on surface 7 was repaired and surface 7 relaxed to surface 1. This phenomenon had been discussed by Lee et al. and Lockwood et al. [92, 93] In their studies, water played an important role in mediating the processes of defect repair. On surface 4, the hydroxylation is stable with hydroxyl group and proton
terminated silicon coexisting after optimization (Figure 6-5 (a) and (b)). The hydroxylation is still not energetically preferred (note its positive hydroxylation energy), but it has much smaller hydroxylation energies than for perfect surfaces (more than 10 times smaller). This indicates that an oxygen vacancy is a potential site for hydroxylation. The charge on the hydroxyl group is about 0.1 to 0.2 e more than the three-coordinated hydroxyl group on the perfect surface. On the other hand, the H-Si terminated group possesses 2.6 e. It seems that most of the electrons residing in the Si-Si defect site transfer to H-Si group after hydroxylation and the silicon atom on hydroxyl group gains only 0.85 e, which is slightly higher than the average charge gained by silicon atoms in alpha-quartz bulk (0.81 e).

On surface 6, the optimized structure has both hydroxyl and hydroperoxyl groups bonding to the same pair of silicon atoms. Two oxygen atoms are three-coordinated and two silicon atoms are five-coordinated (Figure 6-5 (c) and (d)). The hydroxylation energy shows that this is an exothermic process and it is much more preferred compared to water molecules adsorption on surface 6 (Table 4-1). The three-coordinated hydroxyl group gains similar charge as on surface 4. On the other hand, the oxygen atoms on the hydroperoxyl group gain only 6.6 and 6.8 e respectively, which is less than the average number of electrons on the bridge oxygen of the surface (7.59 e). One of the five-coordinated silicon atom gains 0.84 e and the other one involved in the Si-Si site gains 1.44 e. The other silicon atom on the Si-Si site gains more electrons (1.75 e) than before hydroxylation.

The defect on each surface 4 and 6 is involved in a three-membered ring; the defects on surface 5 and 7 are not. On the other hand, surfaces 4 and 6 are individually
less stable than surfaced 5 and 7 when comparing their defect formation energies (Table 3-5). Combining the results in this section, we conclude that the defect involved in a three-membered ring on (1x1) perfect surface is less stable and likely to trigger the hydroxylation with water molecules.
### Table 6-1. Hydroxylation energy of surfaces 1. Unit: eV.

<table>
<thead>
<tr>
<th>Site/type</th>
<th>1/two three-coordinated O atoms</th>
<th>1/one three-coordinated O atom</th>
<th>2/two three-coordinated O atoms</th>
<th>3/two three-coordinated O atoms</th>
<th>3/one three-coordinated O atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{hydro}}$</td>
<td>1.49</td>
<td>1.41</td>
<td>1.38</td>
<td>1.41</td>
<td>1.68</td>
</tr>
</tbody>
</table>

### Table 6-2. Hydroxylation energy of surfaces 2. Unit: eV.

<table>
<thead>
<tr>
<th>Site/type</th>
<th>1/two three-coordinated O atoms</th>
<th>2/two three-coordinated O atoms</th>
<th>2/one three-coordinated O atom</th>
<th>3/two three-coordinated O atoms*</th>
<th>3/one three-coordinated O atom*</th>
<th>5/two three-coordinated O atoms</th>
<th>6/one three-coordinated O atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{hydro}}$</td>
<td>1.29</td>
<td>1.31</td>
<td>1.35</td>
<td>2.54</td>
<td>2.49</td>
<td>1.32</td>
<td>1.54</td>
</tr>
</tbody>
</table>

### Table 6-3. Hydroxylation energy of defective surfaces. Unit: eV.

<table>
<thead>
<tr>
<th>Surface/type</th>
<th>4/separate hydroxyl group and proton termination</th>
<th>6/ three- coordinated O atoms in hydroxyl and hydroperoxyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{hydro}}$</td>
<td>0.12</td>
<td>-0.33</td>
</tr>
</tbody>
</table>
Figure 6-1. Two examples of the initial configurations for surface hydroxylation. a) an attempt site for hydroxylation on surface 1 which is involved in a three-membered ring. b) an attempt site for hydroxylation on the surface 4 which is the oxygen vacancy site. The silicon atoms are represented in yellow balls, oxygen in red, and hydrogen in light grey.

Figure 6-2. The hydroxylation sites on surface 1 (a) and surface 2 (b). a) Site 1 is involved in a three-member ring underneath the surface; the other two sites are not. b) Site 1 and 4 are involved in separate three-member rings, other sites are not.
Figure 6-3. Two types of hydroxylation on surface 1. a) and b) are the side view and top view of the first type in which the oxygen atoms of two hydroxyl groups bond to the same two silicon atoms. c) and d) are the side view and top view of the second type in which only one hydroxyl group bonds to two silicon atoms.
Figure 6-4. Two types of hydroxylation of surface 2 with higher hydroxylation energy. a) and b) are the side view and top view of the first type; in which, the oxygen atoms of two hydroxyl groups bond to two silicon atoms (not the same pair). c) and d) are the side view and top view of the second type in which only one hydroxyl group bonds to two silicon atoms and two hydroxyl groups do not bond to the same silicon atom.
Figure 6-5. Hydroxylation on surface 4 and surface 6. a) and b) are the side view and top view of hydroxylation on surface 4. c) and d) are the side view and top view of hydroxylation on surface 6.
CHAPTER 7
SUMMARY

With the power of DFT and Classical MD computational calculations, we have investigated the properties of several alpha-quartz (0001) surfaces and water-silica interaction on those surfaces. There are five dehydrated surface reconstructions found with close surface energies. Two of the surfaces have (1x1) symmetry and the other three possess (2x1) symmetry on the surface plane. All of them are characterized by six-membered rings on the topmost layer and three-membered rings underneath. The SiO$_4$ tetrahedra within surface slabs are perfectly connected without any defects. These five surfaces possess the same topological structure such that they can transform among each other without bond breaking. The low energy state of the perfect surface with (2x1) symmetry can explain the observed (2x2) diffraction pattern on alpha-quartz (0001) surface when combined with what Steurer et al. proposed [16]. That is a surface cleavage may not be perfect and may, instead, consist of several steps which display three orientations of the (2x1) surface. The energy barriers from (1x1) to (2x1) perfect surfaces were calculated. The lowest one explains well why the (2x2) diffraction spectrum was observed after heat treatment at a temperature roughly higher than when quartz twinning happens [62].

Water adsorption was investigated on one (1x1), one (2x1) perfect surfaces, one hydroxylated and four defective surfaces. Water molecules were dropped onto surfaces one by one to observe the variation of water-silica interaction. The interaction between water molecule(s) and hydroxyl group(s) on the fully hydroxylated surface is much stronger than other types of surface and is comparable to the strength of hydrogen bonds between water molecules. The water-silica interaction on perfect surfaces is
much weaker than on the fully hydroxylated surface, but an enhancement was observed when two water molecules were adsorbed. The charge density difference shows a quadrupole pattern on the perfect surfaces with two water molecules adsorbed. The defects made on the (1x1) perfect surface do enhance water molecule adsorption. However, on both perfect surfaces and four defective surfaces, the water-silica interaction will compromise to hydrogen bonds forming within water cluster.

The water-silica interaction investigation was done in another way by depositing water layers (one sub-layer of Ice XI) one by one onto surfaces. On perfect surfaces and defective surfaces, two types of water layer deposition were tested. One has out-of-plane protons pointing down and the other has protons pointing up. The ground state of water layer adsorption changes from protons pointing down depositing to protons pointing up when there are two or more water layers adsorbed. The hydrogen bonds between water layers strongly affect the optimization direction and result in the formation of a stable water bilayer [94]. As a consequence, the silica surface property changes from hydrophilic (protons pointing down) to hydrophobic (protons pointing up). The charge density difference shows that the effect of defects on water adsorption is short-range and will be shielded by water layer/molecules. The interaction between one water layer and a full hydroxylated surface is much stronger than on other surfaces. However, the first water layer and hydroxyl groups on the surface form a stable bilayer structure which effectively shields the interaction between the silica surface and more following adsorbed water molecules. We believe that the icelike spectrum in Asay’s experiment [17] must result from the vicinity of the surface [94].
The hydroxylation on perfect surfaces was tested on many oxygen sites. All of the results show that the perfectly reconstructed alpha-quartz (0001) surfaces are stable and not easily hydroxylated. The hydroxylation energies on defective surfaces are much lower than that on perfect surfaces. In particular, an exothermic process is observed on the hydroxylation of a peroxy linkage which is involved in a three-member ring. The surface defects are the possible triggers for surface hydroxylation. However, many cases of the hydroxylation on defective surfaces were not successful; the optimized systems with separate surface and water molecule were observed. The mechanism of silica surface hydroxylation/repair will need more careful molecular dynamics modeling. A system consisting of two defects and more than one water molecules would be a modeling candidate for investigating the complex interactions.
REFERENCES

C. Herring, Physical Review 57, 1169 (1940).
G. Kresse, and J. Furthmüller, VASP, http://cms.mpi.univie.ac.at/marsweb/ (Institut für Materialphysik, Universität Wien, Vienna, Austria, 1999)


BIOGRAPHICAL SKETCH

Yun-Wen Chen was born in Taipei, Taiwan, Republic of China in 1975. He was highly interested in nature science since his childhood and loved to read the stories about Newton, Einstein, Curie, Bell, Stephenson, and also Edison. Somehow before he knew who made more money, he chose to register in the physics department for his bachelor degree because he thought physics looks more fun than engineering and it did. He was working with Dr. Yu on a topic of the quantum interference of electromagnetic field to cold $^{87}$Rb spectroscopy and then he got his master degree in physics in Tsing-Hua University, Taiwan.

After another couple years of military service and working experience, Yun-wen joined the Department of Physics in UF in 2004 to pursue his Ph.D degree. He met Dr. Hai-Ping Cheng and started working on the computational simulation on water-silica interface. He learned the nature of water and silica interaction via simulation and also other scientists’ works. At the same time, he gained various computational skills and tools that apply physics and chemistry ideas in simulations. He will like to devote himself in computational applied physics or chemistry for future academic research.