UNDERSTANDING THE STRUCTURE OF WATER, ICE, AND AQUEOUS SOLUTIONS NEXT TO SOLID SURFACES

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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December, 2015
ABSTRACT

The phase change of water into ice on solid surfaces has significant impact on infrastructure and human activity. In this thesis, we have set out to understand the structure of water as it is systematically cooled to form ice next to solid surfaces. We have coupled a novel heating and cooling device with surface sensitive sum frequency generation spectroscopy (SFG) to observe molecularly how water interacts with solid surfaces as temperature is decreased. This we believe can lead to a better understanding of how to delay ice formation or reduce ice adhesion to surfaces. SFG (used mainly in the total internal reflection geometry) is a nonlinear optical technique which detects the orientation and molecular arrangement at surfaces and interfaces. We used sapphire and mica as model surfaces for our experiments.

In the first part of this research, we have performed experiments on a neutral sapphire surface. We have observed that the SFG signal intensity increased considerably when ice was formed. This shows that the water molecules in ice interact strongly with each other and with the solid surface. When temperature was further decreased, the ice peak intensity increased, indicating the increased coherence length of the water molecules in ice. SFG spectra of ice during heating show gradual signal attenuation. Contrary to ice surfaces, no interface premelting of ice was observed during the heating cycle.
In the second part, we studied freezing of water next to charged surfaces. The effect of charge or electric field on water has been shown in the literature. Recently, it was indicated that negative and positive charges have opposing effects on the freezing of water; negative charges delayed freezing, while positive charges enhanced it. In this part, we sought to understand the molecular origin of this finding. Our results showed no considerable difference in the freezing temperature of water on both surfaces. However, the structure of water was different. Just like the neutral surface, intense SFG ice signal was observed for positively charged sapphire whereas signal intensity drastically decreased for ice next to negatively charged sapphire and mica surfaces. The signal attenuation observed for negatively charged surface is attributed to the disordering of water molecules at the interface. This could indicate that ice adhesion to negatively charged surfaces should be less than neutral and positively charged surfaces.

The third part of this thesis deals with the freezing of a sodium chloride solution next to a sapphire surface. Of interest is how the solution phase separates. Our results show that the brine stays close to the sapphire surface, while the ice segregates away from the sapphire. Despite the presence of a surface, the solution freezes above the equilibrium freezing temperature of sodium chloride solution possibly due to supercooling. The freezing of the salt solution into a hydrate is acknowledged by an intense peak, about three orders of magnitude higher than water signal. No premelting of the hydrate is observed during the heating cycle. The intensity of the hydrate peak, however, decreased significantly until the eventual melting at -22°C.
DEDICATION

To my parents:

Martin and Mary Anim-Danso
ACKNOWLEDGEMENTS

No one is an Island. So says an old proverb. But this is truly the case in the life of a graduate student. There are people who without them my life here will literally be difficult if not flat out impossible. I would like to take this opportunity to thank them all.

My sincere gratitude goes to my advisor, Dr. Ali Dhinojwala, for his support in both academic and personal matters. His love for research is infectious and he has thought me to always question everything, even my own results and to delve deeper into problems by asking more questions. It is a life changing attitude that will always be part of me. I would like to also thank Dr. Mesfin Tsige, my committee chair. He has been like a second advisor to me. I really enjoyed all the discussions we had. I am appreciative of his interest in my research and his willingness to run molecular dynamics simulation (MD) to help explain my experimental results. Many thanks goes to the rest of my research committee members, Dr. Tianbo Liu, Dr. Toshikazu Miyoshi, and Dr. Adam W. Smith for their time and very important insights. I am thankful for their feedback during my research presentation and for reading this dissertation. I also thank Dr. Azar Alizadeh of General Electric (GE) for helpful scientific discussions during the early part of my work.
I would like to thank Edward Laughlin (Ed) for his help throughout my PhD career. He helped build the temperature stage and made various adjustment throughout the years. Without his ingenious ideas, this work would have been very difficult to accomplish. Thank you again for also being a friend. You dropped everything to help me fix even the menial stuff. I thank Dr. Anish Kurian for initiating and getting the temperature stage together. I also would like to thank Dr. Liehui Ge for help with sealing water inside the steel cells used in this work. I would like to thank Dr. Ping Hsu and Dr. Anish Kurian for teaching me the basic operating procedure of the sum frequency generation (SFG) spectroscopy. I would like to thank The University of Akron and National Science Foundation GOALI Grant for Financial assistance. Without the financial help this work would not have been possible. I am also thankful for the financial support by GE in building the temperature stage.

I would like to thank my current and past group members for their help and support. If it takes a village to raise a child, then it takes group members to make a better scientist. I am thankful for all the discussions at group meetings. I thank He ‘Parker’ Zhu for help with running SFG. We started our PhD career at the same time working on SFG. He shares the pains of aligning SFG and joys of obtaining a clean spectrum. I thoroughly enjoyed my collaborations with Yu Zhang, Nishad Dhopatkar, Yang Zhou, Chao Peng, and Jing Zhou. I would like to thank Mena Klittich, Saranshu Singla, Nishad Dhopatkar, Yu Zhang, Parker and Dr. Gary Leuty for proofreading my papers and this dissertation. I would also like to thank my friends who have made living in Akron a wonderful experience. Since our first semester of graduate school, Ajay Amrutkar, Kaushik Mishra, Dr.
Yeneneh Yelaw (and wife, Elizabeth Gebretsadik), Dr. Attila Gergely (and wife, Andrea Bokor), and I bonded like family and have helped each other to be successful. Thank you guys. I also thank Nishad Dhapatkar for his friendship and have enjoyed talking about our cosmic perspectives. I would also like to thank Mark Rich for our interesting discussions about life and martial art. I would like to thank Dr. Zhorro Nikolov (and wife Galia) for their friendship and love of music. It was always a pleasure to attend classical music concert at Severance Hall and folk and rock music at Kent and Akron. I thank Parker and Jia Khang for inviting me to their home on multiple occasions and for attempting to teach me Chinese language and food. I will always remember our fun times together.

I would like to thank Melissa Bowman and Jacqueline 'Jacqui' Clark for their help throughout my time in Akron. They have been very good to me and it has been my pleasure to know them. I also thank Cheryl Westfall for her help while she was here. She is one of the most wonderful human beings I have ever met. Thank you for being there to listen to all my blabbing.

This dissertation was written using LaTex and would have been difficult without the help of Dr. Yeneneh Yelaw and Dr. Gary Leuty. They taught me tricks with using the graduate thesis compiler. I also thank Tammy Stitz from the University of Akron Science Library for various workshop on LaTex and being available for consultation anytime I had problems with the code.

I would like to take this opportunity to thank several individuals from my undergraduate program at both Mercer County Community College (MCCC) and Rutgers University. I thank Prof. Diane Hilker whole-heartedly for believing in me. Her consistent push for me to do semester research at Rider University
(NJ) and Hamilton Diagnostic Laboratory (NJ) brought me in contact with great scientists and advanced instruments. This ignited a love for research in me that I never knew existed. I owe all that to her. I thank Dr. Joachim Kohn (Rutgers) for giving me a place to do research as an undergraduate. I thank Dr. Abraham Joy for being a great mentor to me while at Rutgers University. He took my ragged interest in science and refined it. I am indebted to him for his patience and also for his friendship. He continued to help me here at Akron. I also would like to thank Dr. Kathryn Uhrich for her help and support while at Rutgers.

Finally, I would like to express my profound gratitude to my parents. Their belief in me never wavered. They allowed me free range to explore as a child. They have spent a lot of time and money on giving me and my siblings a great education. I am grateful for everything they have done and continue to do. I also thank my sister, Adelaide Harris, for her love and support throughout my time in graduate school.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. BACKGROUND</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Water</td>
<td>5</td>
</tr>
<tr>
<td>2.1.1 Hydrogen bonding</td>
<td>6</td>
</tr>
<tr>
<td>2.2 Water/solid interface</td>
<td>17</td>
</tr>
<tr>
<td>2.3 Ice interfaces</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Polymer/water interface</td>
<td>29</td>
</tr>
<tr>
<td>2.5 Sum frequency generation spectroscopy</td>
<td>35</td>
</tr>
<tr>
<td>III. EXPERIMENTAL</td>
<td>45</td>
</tr>
<tr>
<td>3.1 Sample preparation</td>
<td>45</td>
</tr>
<tr>
<td>3.2 Sum frequency generation set up and measurement</td>
<td>48</td>
</tr>
<tr>
<td>3.3 Thickness measurements</td>
<td>52</td>
</tr>
<tr>
<td>3.4 Contact angle</td>
<td>53</td>
</tr>
<tr>
<td>IV. FREEZING AND MELTING OF WATER NEXT TO SOLID SURFACES. ADAPTED WITH PERMISSION FROM REF. [1]. ©2013 AMERICAN CHEMICAL SOCIETY.</td>
<td>54</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>54</td>
</tr>
<tr>
<td>4.2 Results and Discussions</td>
<td>56</td>
</tr>
</tbody>
</table>
4.3 Conclusion .................................................. 63

V. FREEZING AND MELTING OF WATER NEXT TO CHARGED SURFACES ........................................... 65
   5.1 Introduction ............................................. 65
   5.2 Results and Discussions ............................... 68
   5.3 Conclusions ............................................. 78

VI. FREEZING AND MELTING OF MONOVALENT SALT SOLUTION NEXT TO SOLID SURFACE. ADAPTED WITH PERMISSION FROM REF. [2]. ©2013 AMERICAN CHEMICAL SOCIETY. ........................................... 79
   6.1 Introduction ............................................. 79
   6.2 Results and Discussions ............................... 80
   6.3 Conclusions ............................................. 89

VII. THE EFFECT OF WATER ON THE REORIENTATION OF POLYMER CHAINS ........................................... 90
    7.1 Introduction ............................................. 90
    7.2 Results and Discussions ............................... 93
    7.3 Conclusion ............................................. 105

VIII. CONCLUSIONS .................................................. 107
REFERENCES .......................................................... 110
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for SSP polarization in the cooling cycle</td>
<td>81</td>
</tr>
<tr>
<td>6.2</td>
<td>SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for PPP polarization in the cooling cycle</td>
<td>83</td>
</tr>
<tr>
<td>6.3</td>
<td>Comparison of NaCl dihydrate peak assignments for IR,[3] Raman,[4] and SFG spectroscopy.</td>
<td>84</td>
</tr>
<tr>
<td>6.4</td>
<td>SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for SSP polarization in the heating cycle</td>
<td>85</td>
</tr>
<tr>
<td>6.5</td>
<td>SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for PPP polarization in the heating cycle</td>
<td>86</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The basic H-bond nomenclature. 10</td>
</tr>
<tr>
<td>2.2</td>
<td>The Coulson Valence Bond Formalism. 13</td>
</tr>
<tr>
<td>2.3</td>
<td>A chemical classification of the H-bond. The different types of shared-proton interactions are shown in the first category. Class 1 H-bonds involving the main-group elements were the first to be discovered. However, quite recently, metal centers have been discovered to be able to form true H-bond. The field is still new. The second category represent interactions that are H-bond-like but are not true H-bonds. 16</td>
</tr>
<tr>
<td>2.4</td>
<td>The physiochemical properties of weak, moderate and strong H-bonds. 17</td>
</tr>
<tr>
<td>2.5</td>
<td>SFG spectra collected from quartz/water interface at pH (a) 1.5; (b) 3.8; (c) 5.6; (d) 8.0; (e) 12.3. (f) SFG spectrum from quartz/ice interface. These water spectra were the first to be collected on a solid surface. Due to the low isoelectric point of quartz (≤2), the surface OH groups become ionized as pH is increased. Reprinted with permission from Ref. [5]. ©1994 by the American Physical Society. 21</td>
</tr>
<tr>
<td>2.6</td>
<td>SFG spectra collected at various temperatures at water/air interface. Reprinted with permission from Ref. [6]. ©1994, American Association for the Advancement of Science. 22</td>
</tr>
</tbody>
</table>
2.7 SFG spectra collected from water/air interface. Fits to the data are shown by the solid lines. Simulated data for the 'icelike' and 'waterlike' hypothesis are shown by the dotted line. Peak positions are indicated in the graph. For pure D₂O [ratio D/(D + H) = 1, closed circles], two resonances are clearly identified in the O-D stretch region. For a sample with D/(D + H) = 0:33 (open circles), the contribution from D₂O modes is less than 10%, and HDO modes dominate the spectrum. (b) Energy level diagram for D₂O and HDO water molecules. The fundamental O-D stretch vibration is coupled intramolecularly, giving rise to symmetric (ss) and asymmetric (as) modes. Because of Fermi resonance with the overtone of the bending mode (δ₂), the ss mode is further split into a low and a high frequency band (labeled here ν₁ and ν₂). For an HDO water molecule, the intramolecular modes are decoupled, allowing the determination of the fundamental O-D stretch vibration. The corresponding frequency of each energy level is specified, except for the as mode, in cm⁻¹.

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2.8 SFG (|χ(2)|) and Imaginary SFG (Imχ(2)) spectra collected from water/air interface (A) OH (B) OD stretch regions. Reprinted with permission from Ref. [8]. ©2009 American Chemical Society.

2.9 SFG spectra collected at ice/air (0001) interface at various temperatures. Reprinted with permission from Ref. [9]. ©2002 by the American Physical Society.

2.10 Side view of an ideal (0001) basal surface of ice Ih. Note that the free (or dangling) OH bonds are perpendicular to the surface due to the tetrahedral hydrogen bonding geometry. Also note that the adjacent layers A and B do not repeat each other by a simple spatial translation but are rotated by 180° with respect to each other in the surface plane. Reprinted with permission from Ref. [9]. ©2002 by the American Physical Society. (b) Molecular dynamics simulation of the (0001) basal surface of ice Ih at 265K. Reprinted with permission from Ref. [10]. ©2004, AIP Publishing LLC.

2.11 Schematic of the hydrogen bond configurations on the ice surface. In the top half bilayer: (i) d-OH (dangling or free OH) bonds or donor, donor, acceptor dAA; (ii) d-O(dangling O) or ddA; and (iii) H-bonded companion to the d-OH or the donor bond of a dAA. In the lower half bilayer: (iv) OH of water molecule hydrogen bonded to a d-O, (v) OH of a water molecule hydrogen bonded to a d-OH, and (vi) the bilayer stitching OH bonds hydrogen bonded to the next bilayer. Reprinted with permission from Ref. [11]. ©2005 American Chemical Society.
2.12 An illustration of a block copolymer of poly(ethylene glycol) (PEG) and poly(dimethyl siloxane) (PDMS) in water. Reprinted with permission from Ref. [12]. ©2005 American Chemical Society.


2.14 SFG spectra collected in SSP and SPS polarizations of PMMA before, during, and after coming in contact with water. Reprinted with permission from Ref. [14]. ©2001 American Chemical Society.

2.15 SFG spectra collected in SSP and SPS polarizations of PBMA before, during, and after coming in contact with water. Reprinted with permission from Ref. [14]. ©2001 American Chemical Society.

2.16 (a) Time dependence of $\theta$ (contact angle) for PMMA films annealed at different temperatures. Open symbols and solid curves denote the experimental data and ones fitted by eq. 7.1 (b) Annealing temperature dependence of $\theta_{ini}$, $\theta_{ter}$, and $R_{rms}$ of each film. Reprinted with permission from Ref. [15]. ©2012 American Chemical Society.

2.17 SFG spectra collected in SSP and SPS polarizations for unannealed PMMA film (empty squares) and one annealed at 433 K: (a) in air (b) and in water. Reprinted with permission from Ref. [15]. ©2012 American Chemical Society.

2.18 The interface between two media that is probed by SFG. The subscripts i and r denotes incident and reflected directions. Here $n_1 > n_2$.

2.19 The relationship between the molecular coordinate system (a,b,c) and the laboratory coordinate system (x,y,z) through the Euler angles ($\psi, \theta, \phi$).

3.1 Diagram of the temperature stage and the sample geometry for SFG measurements. The water is sealed from one side by a sapphire prism while the other side is in contact with a heating or cooling stage purchased from Instec Inc. The top part of the temperature cell was machined to hold CaF₂ and SiO₂ optical windows for the input and the output of the laser beams. The cell was held under vacuum to prevent water condensation on the sapphire prisms and to maintain the temperature uniformity.
3.2 Schematic of the picosecond SF spectrometer. The meanings of the symbols are as follows: H, half wave plate; B, calcium fluoride plate beam splitter; M, mirror; DM, dichroic mirror; P, polarizer; F, Raman notch filter; C, IR chopper; PMT, photomultiplier tube detector. ......................................................... 52

4.1 SFG spectra of water collected in SSP (a) and PPP (b) polarization. .......................... 58

4.2 SFG spectra collected in SSP (a) and PPP (b) polarization. The data were collected with temperature increment of 1°C (using a 4°C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (filled circles) near the freezing and melting transition temperatures are shown. The freezing transitions temperature is between -4 and -6°C ............................................................. 58

4.3 SFG spectra collected in SSP (a) and PPP (b) cooling cycles. The data were collected with a temperature increment of 1°C (using a 4°C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (open squares) and ice (filled circles) are shown. The SSP spectra has been offset for clarity whereas the PPP spectra is only offset between water and ice. ................................................................. 61

4.4 SFG spectra collected in SSP (a) and PPP (b) heating cycles. The data were collected with temperature increment of 1°C (using a 4°C/min heating rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (filled circles) are shown. The SSP spectra has been offset for clarity whereas the PPP spectra is only offset between water and ice. ................................................................. 63

5.1 SFG spectra collected in SSP polarization during cooling of hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution. The changes in the SFG spectra were measured for pH 3.3 (a) and 9.8 (b). The data were collected with temperature increment of 1°C (using a 4 °C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. SFG spectra collected in SSP polarization during cooling of cesium hydroxide solution (CsOH) (c) and tetramethylammonium hydroxide solution (N(CH₃)₄OH) (d). The data were collected with temperature increment of 1°C (using a 0.3 °C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (solid circles) are shown with their corresponding temperatures. The freezing transitions temperatures for the two pH conditions were between -5 and -6 °C. ................................................................. 71
5.2 SFG spectra collected in PPP polarization during cooling of tetramethylammonium hydroxide solution (N(CH$_3$)$_4$OH). The changes in the SFG spectra were measured for pH 10. The data were collected with temperature increment of 1°C (using a 0.3 °C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (solid circles) near the freezing are shown. The freezing transition temperatures were between -5 and -6 °C.

5.3 SFG spectra collected in SSP polarization during cooling of ammonia-water solution. The changes in the SFG spectra were measured for pH 10. Two freezing rates are presented; 5 °C/min (empty circles) and 10 °C/min (solid circles). For each rate, the solution is cooled from 20 °C to -40 °C. This figure shows that the incorporation of ammonia into the ice structure at the sapphire surface is rate dependent.

5.4 Illustration of NH$_3$-doped ice near sapphire/ice interface. The bound ammonia molecules are able to polar order water molecules significantly increasing the SFG signal intensity. This conformation also changes the dipole alignment of what would be on a negatively charged surface.

5.5 (a) SFG spectra of water on mica collected in SSP (empty circles) and PPP (empty squares) polarizations. (b) SFG spectra collected in SSP polarization during cooling of water. The data were collected with temperature increment of 1°C (using a 0.3 °C/min cooling rate) and a 30 minute equilibration time, before collecting the spectra. The spectra for water (empty squares) and ice (solid circles) near the freezing are shown. (c) Variation in SFG intensity are plotted using SSP polarization and IR frequency of 3150 °C during the cooling (blue curve) and heating (red curve) cycles. These measurements were done at cooling and heating rate of approximately 0.3°C/min.

6.1 SFG spectra collected in SSP (A) and PPP (B) polarizations during the cooling cycle. The empty squares and filled circles correspond to temperatures where salt solution or NaCl hydrate are in contact with the sapphire substrate, respectively. The solid lines are the fits using the Lorentzian equation and the fitting results are summarized in the supporting information (Tables 1 and 2). The freezing transition temperatures for the hydrate formation are between -25°C and -30°C.
6.2 SFG spectra collected in SSP (A) and PPP (B) polarizations during the heating cycle. The empty squares and filled circles correspond to temperature where salt solution or NaCl hydrate are in contact with the sapphire substrate, respectively. The solid lines are the fits using the Lorentzian equation and the fitting results are summarized in the supporting information (Tables 4 and 5). The melting transition temperatures for the hydrate formation is -22°C.

6.3 Phase diagram of NaCl solution reconstructed from CRC Handbook. [16] In the SFG experiments the salt solution was cooled below 0°C following the blue dashed line. Near -10°C (Point A), the ice freezes and we expect increase in the concentration of brine (Point B). As the temperature is decreased further, the concentration of NaCl increases as indicated by the blue dashed lines, until the eutectic point is reached. The hydrate freezes around 6°C below the temperature expected for bulk freezing of hydrates (Point C). On heating the path is reversed and the hydrates melt between -23°C and -22°C. Finally, the ice melts near zero (Point D).

7.1 Time dependence of \( \theta \) for PHNB film. Open symbols are solid lines denote the experimental data and fit by eq. 7.1, respectively.

7.2 SFG spectra for PHNB in PPP polarization with varying environment. The experimental data is fitted by Lorentzian function.

7.3 SFG spectra for PHNB in PPP polarization with varying environment. The experimental data is fitted by Lorentzian function.

7.4 SFG spectra for PHNB in SPS polarization.

7.5 Water contact angle for PVNODC and PHNB with heating under water protocol. Pristine means as annealed; H\(_2\)O-anneal suggests heating and cooling under water followed by N\(_2\) jet drying; Reannealed stands for heating under vacuum above ODT and Tg for PVNODC and PHNB respectively.

7.6 Time dependence of \( \theta \) for PnBA film. Open symbols are solid lines denote the experimental data and fit by eq. 7.1, respectively.

7.7 SFG spectra in PPP polarization for PHNB at air (red) as annealed; with D\(_2\)O (yellow) at R.T.; heated to 90°C under D\(_2\)O (green); cooled down to 25°C under D\(_2\)O (blue); N\(_2\) dried (purple); and reannealed under vacuum at 110°C and spectrum obtained at R.T. (black).

7.8 SFG spectra for PnBA in SSP polarization at air (red); in D\(_2\)O (blue); and at air after drying off the D\(_2\)O by a stream of N\(_2\) (black).
CHAPTER I

INTRODUCTION

Over the years, the study of interfaces have garnered increasing interest in both academia and industry. This was preceded by the understanding that interfaces govern the physical and chemical properties of any particular material.[17] An interface is generally defined as the boundary region between two immiscible bulk phases.[18] Surface, usually used interchangeably with interface, refers to the physical boundary of one phase with air (vacuum). Of all interfaces, liquids are ubiquitous, with the most abundant and important of all, water, getting most attention. The water interfaces, which can be easily perturbed, directly control many aspects of science and technology. One of those effects of water interfaces, in this case solids, is ice adhesion.

When water next to solid surfaces (including roads, vehicles, aircraft wings and engines, ship superstructure, transmission lines, and various machinery and infrastructure) is cooled below the equilibrium freezing temperature, it freezes.[19, 20] The adhered ice becomes very problematic for the energy sector, transportation, and human activity. It can lead to the loss of lives and significantly affect efficiency and safety of various machinery. Interestingly, the active methods of ice mitigation rely on melting and breaking of ice. This is inefficient and, especially in the airline industry, cost and energy intensive.[19, 20] For over a half a century, passive low ice adhesion (specifically hydrophobic and super-
hydrophobic) coatings (also known as icephobic coatings) have been proposed to mitigate ice accretion to surfaces. This is based on the fact that hydrophobic and superhydrophobic coatings can repel water. Hence, it can be extrapolated that they delay ice formation or lower ice adhesion strength.[21] However, currently no successful icephobic material is available on the market. This is due to conflicting experimental reports presented in the literature. There seem to be complicated parameters which affect freezing of water. For example, it was found that, in low humidity environments, ice nucleation can be significantly delayed.[20] Others have reported that the time a water droplet spends on a superhydrophobic surface[22] and the size of textures on superhydrophobic surfaces[23] can impact freezing. Interestingly, it was reported that ice adhesion on superhydrophobic surfaces actually increased.[24] Moreover, on a flat hydrophilic silica surface, ice nucleation was found to be delayed.[25, 26] All these examples show the complexities involving water interactions with surfaces. If we are to gain a better understanding of the ice nucleation process at solid surfaces, it is imperative that we study the fundamental molecular interactions of water with solid surfaces during cooling.

New probes capable of studying water interfaces have diversified in the past decade. These includes atomic force microscopy, neutron reflection and absorption, X-ray diffraction and reflection, and sum frequency generation spectroscopy (SFG). The X-ray and neutron measurements require special geometries that make them less versatile.[27, 28] SFG has established itself as a powerful and most successful tool for probing water interfaces. SFG is a second order nonlinear optical technique that involves mixing a short-pulse high intensity visible laser ($\omega_{vis}$) with a tunable infrared laser ($\omega_{IR}$). Based on the dipole approximation,
the SFG signal, at the sum of $\omega_{SFG}=\omega_{vis} + \omega_{IR}$, is only generated at interfaces in systems where the symmetry is broken. By combining SFG with a total internal reflection geometry, this technique offers the ability to study the structure and phase change of water into ice next to solid surfaces. The probe depth in SFG experiments is the distance from the surface to the position where the anisotropic molecular orientation becomes isotropic. This means few layers of water freezing next to a solid surface can be observed throughout the phase change process.

In this work, SFG has been employed to study the "buried" water/solid interface as the water is cooled to form ice. Before jumping to water (or ice) next to icephobic materials, water (or ice) next to simple solids should be first fully understood. A new methodology and instrumental setup were devised in order to study the molecular interactions of water and ice with solid surfaces.

This thesis is divided into seven chapters, including this introductory note. The background chapter (Chapter 2) follows this one. There, hydrogen bonding is examined. More light is shed on its history and the nature of the bond. Detailed discussions of the state of the art of water and ice next to solid surfaces are given. Chapter 3 describes the experimental techniques, devices, materials, and procedures developed and used in this work. Details of the SFG setup, along with in-house built cooling and heating stage are provided.

Chapter 4 is the start of the experimental results section. Here, the structure of water and ice next to a sapphire surface is examined. We first discuss the structure at water/sapphire interface. The structure of ice next to sapphire surface is then examined. Additionally, answers to questions as to the nature and strength of ice interactions with sapphire are attempted.
In Chapter 5, freezing of water is performed on charged sapphire and mica surfaces. This is particularly intriguing because recent data shows that charge has enormous effect on the structure of water and has been used to delay freezing of water.\cite{29} The structure of water and ice is discussed as a function of temperature. Predictions are attempted on the ice adhesion on positively and negatively charged surfaces.

Chapter 6 presents data from cooling sodium chloride (NaCl) solution next to sapphire surface. Salt is known to thermodynamically depress the melting temperature of water. Of interest in this study, is to ascertain the process of ice nucleation. Will ice form or will brine segregate next to the sapphire surface? Is the migration of brine or ice surface driven or some other process? What is the structure of water as the solution is cooled? This chapter attempts to answer all of these questions.

In Chapter 7, another important interface in science and technology, polymer/water interface, is examined. A polymer with both hydrophobic and hydrophilic side chains is studied; poly($n$-butyl $\alpha$-hydroxymethyl acrylate) (PHNB) is examined in conjunction with contact angle and SFG measurements. The molecular rearrangement of the side chain is shown at both room temperature and above the glass transition of the polymer.
2.1 Water

Water has relatively a simple geometric structure: two hydrogens and one oxygen, H$_2$O, forming a tetrahedral structure. However, this simple structure gives rise to complex interactions that makes it difficult to predict the behavior of water. There are currently about forty-one (and counting) anomalies found in water. Albert Szent-Gyorgi, the 1937 Noble prize winner, put it succinctly: 'water is the most extraordinary substance! Practically, all its properties are anomalous.' An example is the existence of the triple point: water as solid, liquid, and gas at the same temperature and pressure. The culprit of these anomalous properties of water is the physio-chemical bond known as hydrogen bonding (H-bond). This H-bond is responsible for the fundamental role water plays in science and technology. H-bond allows water to be a highly collective liquid with strong electrostatic intermolecular interactions between the partially charged hydrogen (-0.24e) atoms and partially charged oxygen (-0.48e) atom. Our lives revolve round water even before we are born and dictates the behavior of many important processes on earth and across the universe. Water, initially thought as a simple universal solvent, is now known to influence almost every aspect of science. It is important to interstellar transport of materials, adhesion, wetting, corrosion, colloidal stability, weathering, lubrication, and cloud formation. This means it is
imperative that detailed molecular understanding of water be known in order to fully comprehend the afore mentioned processes.

In the next subsection, we will take a detailed look at hydrogen bonding to understand what makes water behavior so anomalous. In the subsequent sections, we will discuss water and ice interactions with various surfaces.

2.1.1 Hydrogen bonding

The understanding of chemical bonding and electronic structures of molecules in the last century has helped put to rest disputes among scientists on the forces that hold atoms together. Hence, molecules became the fundamental building blocks of matter, a denotation that was once given to atoms. Van der Waal interactions, a non-bonded interactions that results from electric attractions of permanent dipoles and induced molecular multipoles, was used to explain the aggregation of molecules (gases, liquids, crystals). However, these weak interactions of molecules could not explain the newly discovered intermediate interactions that were disputed to exchange protons now called hydrogen bonds (H-bonds). Chemical or covalent bonds occur within a strict range of distances and energies, while non-bonded interactions are beyond the sum of van der Waals radii. Hydrogen bonding, on the other hand, covers the range between chemical and non-bonded interactions. As expected, any rules governing this intermediate interactions should be complicated. The difficulties come from the fact that H-bonds undergo large variations in their energetic and geometrical parameters, sometimes even for the same interacting molecules with no apparent reason. This has been dubbed the H-bond puzzle. Since its ‘discovery’ in 1902, it wasn’t until mid-1970s when sophisticated techniques like neutron diffraction - which made
possible a reliable localization of the H-bonded proton to be observed—were developed. The first calculation using the Hartree-Fock limit was done around this time. However, only with great theoretical and computational advances of the following decades has it been made possible to perform \textit{ab-initio} or DFT calculations that fully account for electron correlation effects and that can correctly simulate H-bonds of any strength formed by molecules of reasonable complexity. This section deals with the discovery of the hydrogen bond, the empirical and theoretical understanding, and the character of hydrogen bond as a chemical and physical bond.

By the late nineteenth century, van der Waals had already formulated his laws of corresponding states accounting for deviations from the ideal gas laws based on the earlier introduced concepts of attractive and repulsive molecular interactions.\cite{30} At the same time, the laws of ideal solutions in both vapor tension and osmotic pressure were put forth by Raoult and van’t Hoff, respectively, to explain the deviation from ideality of liquid state from gas. In the later years, it was discovered that molecules having certain hydrogenated functional groups associated better than others. Moreover, the physical properties of gases, liquids, and solids can be quite significant. Water is one such example, whose actual melting and boiling points are in complete disagreement with the properties of other hydrides in Group 6 of the periodic table.

The discovery of the H-bond is difficult to attribute to one person as it emerged out of this scientific era of great discovery. In their book, \textit{The Hydrogen Bond}, Pimentel and McClellan recognized a number of scientists as perhaps the pioneers of the H-bond idea. The first is Alfred Werner, who around 1902 sug-
gested that the properties of ammonium salts can be better explained by assuming that the proton lies in between the ammonia molecule and the anion, as symbolized by his \((\text{H}_3\text{N} \cdot \cdot \cdot \text{H})X\) notation. He called this *Nebenvalenz* (secondary valence). This same term was used by Hantzsh in 1910 to explain properties of ammonium salts of acetic acids. Actually, the first intramolecular H-bond was suggested by Oddo and Puxeddu in 1906 to explain the properties of some o-hydroxyazo derivatives of eugenol. They called it the mesohydric form. However, the final H-bond concept is attributed to Maurice Loyal Huggins and, independently, to Wendell Latimer and Worth Rodebush. All three were then working in the laboratory of G.N. Lewis at the University of California, Berkeley around 1920. Latimer and Rodebush wrote a paper in which they used H-bond to rationalize the properties of highly associated liquids such as water and hydrogen fluoride. In explaining this H-bond, they used Lewis’ dot formalism ‘a free electron pair on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecules to bind the two molecules together. Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a *weak bond.*’[31] The role of Huggins is less documented although he claimed to have discovered and written about it first in his thesis in 1919 before Latimer and Rodebush (though his thesis has disappeared). However, Lewis, Huggins’ adviser, corroborated his claim to have been the first person to propose the idea and concept of H-bond. Meanwhile, the descriptor *hydrogen bond* was first used by Linus Pauling in 1931 to interpret the structure of the \([\text{F}:\text{H}:\text{F}]^-\) ion in his first general paper on the nature of the chemical bond. Other scientists including Huggins, Bernal, and Megaw used the term to describe similar ionic features but
it wasn’t until Pauling published his book, *The Nature of the Chemical Bond* in 1939 that the H-bond was brought into mainstream science.[32]

In order to understand the H-bond, basic nomenclature is needed. The nucleus of H-bond nomenclature is the distinction between donor and acceptor. In any D–H···:A bond, D-H is the H-bond donor (and also a Bronsted acid, a Lewis acid, and an electron acceptor) and :A is the H-bond acceptor (and also a Bronsted base, a Lewis base, and an electron donor). Figure 2.1 shows the many ways the donor and acceptor can be combined. From a general chemical point of view, there are two main types of H-bonds; homonuclear and heteronuclear. The homonuclear is further divided into homomolecular and heteromolecular depending on whether the substituents are equal or less. Normal D–H···:A bonds are referred to as two-center or monodentate (Figure 2.1 C2.1b1) while the multiple H-bond acceptor is indicated by the terms three-center, bifurcated or bidentate, and four center (Figure 1). H-bonds also differ wildly for the geometry of the D–H···:A between the two extreme configurations *dissymmetric and bent* and *symmetric and linear* which are typical situations for weak and very strong bonds, respectively. The symbols used in Figure 2.1 and rest of this subsection are $d_1 = d(D–H)$, $d = d_2 = d(H···:A)$, $D = d(D···:A)$ for distances and $\theta = \alpha(D–H–A)$ for angles. They are essentially adopted from Gilli and Gilli’s book, *The Nature of Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory.*[30]

Since the inception of the H-bond, many authors have given different definitions on what H-bond should be, however they all can be traced to two main definitions given based on purely empirical considerations and a general theory of the chemical bond.
Pimentel and McClellan’s definition from their book *The Hydrogen Bond* is probably the best empirical definition available. It states: *A H bond \([A-H\cdots B]\) exists between a functional group \(A-H\) and an atom or a group of atoms \(B\) in the same or a different molecule when (a) there is evidence of bond formation (association or chelation) and (b) there is evidence that this new bond linking \(A-H\) and \(B\) specifically involves the hydrogen atom already bonded to \(A\).* The authors continued, ‘It is convenient to separate parts (a) and (b) because there are many physical measurements that provide information relative to (a) but only a few substantiating (b). It is specifically criterion (b) that differentiates the H bond from other types of associative interaction.’ This statement obviously underlies its purely empirical definition.

The second theoretical definition was first proposed by Latimer and Rodenbush in the first known paper on H-bond in 1920. It was completed by Vinogradov...
and Linnell in their book *Hydrogen Bonding* in 1971. They made reference to Lewis’ theory of chemical bonding, which later became known as the valence bond theory (VB). It states: *Hydrogen bonding occurs between a proton-donor group A-H and a proton-acceptor group B, where A is an electronegative atom, O, N, S, X (F, Cl, Br, I) or C, and the acceptor group is a lone pair of an electronegative atom or a π bond of a multiple bond (unsaturated) system. Generally, a H-bond can be characterized as a proton shared by two electron pairs.*[34]

The difference between these two definitions is clear: One is empirical while the other ignores experiments. The first can be called upon a posteriori to explain what is experimentally observed due to H-bond formation. The second is strictly based on the electronic structure of the interacting moieties, and can predict H-bond formation as well as justify it. The first stage where the first definition starts to break down has to do with how the proton is shared. According to Pimentel and McClellan’s definition, any sort of attractive interactions where the proton is involved is considered H-bond. In essence the B-H-B bond in boranes should be considered as true H-bond. Here, only the second definition can discriminate boranes from being a true H-bond due to its precise description of the acceptor atom carrying lone pair of electrons. The second stage has to do with the correct bond polarity in true H-bonds. The first definition does not even consider this polarity issue, while the second includes atomic electronegativity conditions assessing the correct polarity to be $A^{\delta-} - H^{\delta+} \cdots B^{\delta-}$, so in effect excluding other interactions with reversed $A^{\delta+} - H^{\delta-} \cdots B^{\delta+}$ polarity such as agostic interactions (Agostic interactions occur when an electron-deficient metal makes a close approach to an electron-rich C–H bond giving rise to a nearly T-shaped
M····(H–C) contact). These two considerations seem to indicate that Vinogradov and Linnell’s definition is preferred. However, the rules in their definitions are not without confusion. Firstly, the H-bond polarities do not depend on atomic but rather on group electronegativities as modified by all other surrounding atoms. Secondly, extensive work on weak H-bonds by Desiraju and Steiner in 1999 shows that the polarity rule is more strictly obeyed on the donor than on the acceptor side.[35] This is obvious when dealing with a π-bond acceptors where the accepting multiple bond can be defined as an electron-rich rather an electronegative moiety. In a way, the H-bond is better understood not as a bond in the normal sense. It can be thought of as a dual or multiple bond made by a single proton with two or more electron pairs located on the surrounding ligands. This makes it clear that the true H-bond polarity must be A:δ−····H+····Bδ−.

To effectively avoid excessive mixing of the above definition with the the Bronsted-Lowry acid-base theory, Gilli and Gilli in their book, The Nature of Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory provide a minor modification to Vinogradov and Linnell’s H-bond definition. It becomes: The H-bond is a three-center-four-electron (3c-4e)shared-proton interaction having the general form R–D–H···:A–R’, where D is the proton donor (an electronegative atom, such as F, O, N, C, S, Cl, Br, and I) and :A the proton acceptor or lone-electron-pair carrier (a second electronegative atom or the π-bond of a multiple bond). The H-bond can also be seen as a single proton sharing two lone-electron pairs from two adjacent electronegative atoms or groups: R–D:···H···:A–R’. In order to simplify this definition or prevent calling H-bond merely an acid-base interactions, the H-bond donor is always a neutral acid D-H and never a
protonated base A-H$^+$, and the H-bond acceptor is always a neural base :A and never a deprotonated acid :D$^-$

From the above definition, it might appear that the H-bond is solely a chemical bond. However that is not the case. Linus Pauling, who led the way in using theory to understand H-bond was misquoted as saying H-bonds are only physical. As a matter of fact, he noted that the covalent character becomes predominant only in very short and symmetric bonds that, being extremely rare, are exceptions and then can be reasonably neglected in the treatment of the more copious H-bonds of normal strength. As a result, early theoretical H-bond models by noted authors such as Bernal and Fowler, Lennard-Jones and Pople, and Rawlinson, were purely electrostatic in nature. We know today that strong H-bonds are not as rare as was originally thought. Even back then, the sentiment of the purely electrostatic nature was not shared by all.

Figure 2.2: The Coulson Valence Bond Formalism.
Charles A. Coluson (whose PhD advisor was Lennard-Jones) was the first to re-examine the electrostatic model through VB theory by way of the now termed Coulson formalism.[36] He started by suggesting four main concepts for understanding the H-bond: 1. electrostatic interaction is derived from the purely electrostatic forces acting among undeformed charged clouds 2. delocalization effects associated with charge-transfer are associated with large-scale deformations of these clouds, that is charge-transfer effects are able to induce a partial covalent character in the H-bond formed 3. repulsive forces associated with the Pauli exclusion principle are produced by the physical overlapping of closed-shell charge clouds 4. dispersion forces, that is London forces associated with small-scale coordinate motion of the electron. In 1954, Coulson and Danielson evaluated the amount of the covalent contribution to the O–H⋅⋅⋅O bond by considering a mixture of three main VB canonical wavefunctions as illustrated in Figure 2.2.[37, 38] These wavefunctions also mixed with their respective coefficient \( \omega_1(\psi_{COV1,NCT}) \), \( \omega_2(\psi_{IONIC,NCT}) \), and \( \omega_3(\psi_{COV2,CT}) \) (CT and NCT means with or without charge transfer). An essentially electrostatic bond would have \( \omega_1 > \omega_2 \gg \omega_3 \) while a purely covalent bond will be characterized by \( \omega_1 = \omega_3 \gg \omega_2 \). Since the mixing between two canonical wavefunctions is larger, their energy difference is smaller. These two extreme types of bond H-bond can be represented on a semiquantitative energy scale as shown in Figure 2.2. The representation in Figure 2.2 is in general form. It is simply the probabilities of the valence shells forming a bond. As expressed, it shows that the true nature of H-bond is twofold and can be switched from electrostatic to covalent simply by changing the relative energy order of the three VB resonance form. Basically, any argument about whether the H-bond is
physical or covalent is purely academic. The H-bond can perfectly be explained from the standpoint of a chemical and physical approach. The scheme in Figure 2.2b, stresses the importance of symmetry in H-bond formation because the energy equivalence, \( E(\psi_{COV1,NCT}) = E(\psi_{COV2,CT}) \) of the two mixing O–H···O and O···H–O forms require that they are also geometrically identical, that is symmetry related by a mirror plane perpendicular to the bond. This generally suggests that very strong H-bonds must be symmetric from both a geometrical and a chemical point of view. Apart from showing the mixing of the wavefunctions on the energy diagram, Coulson and Danielson calculated the percent weights of the coefficient. As it was shown above, the \( \omega_3(\psi_{COV2,CT}) \) is responsible for measuring the covalent character of the O–H···O bond. They observed that as the O–O distance was shortened, the covalent character percent increased. This confirmed the fact that a strong H-bonds can be characterized by some covalency while weak H-bond are physical or electrostatic in nature. Figures 2.3 and 2.4 shows the chemical and physical classifications of the H-bond respectively.
Figure 2.3: A chemical classification of the H-bond. The different types of shared-proton interactions are shown in the first category. Class 1 H-bonds involving the main-group elements were the first to be discovered. However, quite recently, metal centers have been discovered to be able to form true H-bond. The field is still new. The second category represent interactions that are H-bond-like but are not true H-bonds.

H-bond systems have been extensively studied since their discovery. There is an extremely wide literature concerning the role played by H-bonds in a great number of chemical and biochemical systems. This is deservedly so because this 'bond' is the most important of any kind ever known to man. However, the understanding of the H-bond system is far from over. Many processes occurring at surfaces and interfaces that have direct impact on our lives are still not understood. However, with advances in instruments that are sensitive to hydrogen
bonding at surfaces such as second harmonic generation (SHG) and sum frequency generation (SFG) spectroscopy, the behavior of various solvents at interfaces can be elucidated. The goal of this thesis is to shed light on the water structure at surfaces and interfaces. This can only be done by understanding the origin of water’s anomaly. That is hydrogen bonding.

2.2 Water/solid interface

For many years, the solid/water interface has captured the attention of researchers. There are chemical, physical, and biological processes that occur at these interfaces that are relevant to various industries. Some of these processes involve heterogeneous catalysis, tribology, corrosion science, nanoparticle stabilization, colloidal system stabilization, geochemistry, electrochemistry, soil and aquifer chemical reactions, and ore beneficiation. [39, 40] In the current atmo-
sphere of cheap and efficient energy ideas, the solid/water interface is serving as a platform for such purpose. Dye molecules grafted to solid surfaces in contact with electrolyte solutions are seen as potential source of solar energy.[41] In biology, the water/membrane/lipids/protein interactions are enormously important to the functioning of the cell. Understanding the solid/water interface is therefore crucial and fundamental. Unfortunately, the atomistic picture of water next to solid surfaces has not fully being realized. This is because of a two part problem. The first is the limited tools specifically available for ”viewing” the interfacial region and secondly, the complexities that exists at the solid/water interface due to various chemical and physical reactions that occur of their contact with each other.[40, 41]

Current experimental surface techniques use electrons, ions, and atoms as probes.[17] In this setup, an ultra high vacuum (UHV) environment is needed for efficient and distortion free experiments. Some of these techniques include ion-scattering spectroscopy, X-ray photoelectron spectroscopy, scanning tunneling spectroscopy, Auger spectroscopy, and low-energy electron diffraction.[39] These techniques, to some extent, have provided details of water clusters on surfaces. Its apparent limitation is obvious in the sense that large amount of water cannot be probed. Moreover, the water structure in UHV is more likely dissimilar to water encountered in ambient environment. On the other hand, there are surface techniques that can observe water interfaces. For example, attenuated total internal reflection IR spectroscopy, time-resolved spectroscopy, Raman spectroscopy, and ellipsometry have been used to provide surface information. However, they are not inherently surface specific. X-ray diffraction and reflection can be used in situ
to provide information about ordered molecular arrangements but lack the ability to provide information on molecular orientation and conformation at surfaces.[17]

The development of optical nonlinear spectroscopy has made it possible to obtain orientational, conformational, and detailed arrangements of molecules at interfaces. Sum frequency generation spectroscopy (SFG) is one example of a nonlinear technique and has been established as a powerful technique for monitoring interfaces in situ. It is intrinsically surface specific in the sense that signal from the centrosymmetric bulk is forbidden. In the dipole approximation, SFG, which is a second-order nonlinear technique, is only active where there is a breakdown in inversion symmetry. This selection rule makes it possible to use SFG to study the structure of molecules near surfaces and interfaces. It has been used to study water next to hydrophobic, lipid, glass, sapphire, quartz, protein, and air surfaces.[42–46]

The solid/water spectrum was first obtained by Du et al., in the Shen laboratory at University of California, Berkeley, using SFG.[5] Figure 2.5 shows the SFG spectrum of water next to quartz as a function of pH. Two main peaks are observed at 3200 and 3400 cm$^{-1}$. Before assigning these peaks, the water/air SFG spectrum should be first discussed. This is because the assignments at the water/air set precedent over how the peaks are attributed in the hydrogen bonded region. In Figure 2.6, the spectrum for water/air interface is presented.[6] There are three main peaks; two broad peaks at 3200 cm$^{-1}$ and 3400 cm$^{-1}$, and a sharp peak at 3690 cm$^{-1}$. The peak at 3690 cm$^{-1}$ is assigned to free OH. The existence of free OH at the water/vapor interface should be expected. In the bulk, water molecules form tetrahedral structures with neighbouring water
molecules. The molecules at the air interface however, faces air. No matter how much it tries to reduce surface energy by attaining different conformation, there will always be a broken bond. It has been estimated that free OH groups cover \(~20\%\) of a given water surface. The redshifted peak (3200 cm\(^{-1}\)) is attributed to the strong tetrahedrally bonded OH group. Due to the characteristic resemblance to the peak position of ice in IR and Raman spectroscopy, it is often referred to as icelike.\[6, 17\]. The 3400 cm\(^{-1}\) peak is attributed to relatively weaker hydrogen bonding water molecules. It is also commonly referred to as liquidlike due to the similarity in peak position with water spectrum of IR and Raman spectroscopy. These broad peaks are controversial. Other researchers have attributed them to either symmetric and asymmetric peaks or to bifurcated hydrogen bonds.\[47, 48\] Recently, however, research in the Bonn laboratory has challenged the icelike and liquidlike assignments. It is argued that when the H\(_2\)O is isotopically diluted with D\(_2\)O, the two peaks merge into one at 2510 cm\(^{-1}\) (experimentally viewing the D\(_2\)O region).\[7\] If the peaks did indeed belong to these icelike and liquidlike components at the water surface, then they should be present in the spectrum. Since it wasn’t present in the isotopic diluted water, the two peaks were attributed to the splitting of the symmetric mode with the bending overtone and other intermolecular effects (see Figure 2.7).\[7, 43\]. In a sense, the isotopic dilution significantly decreased the intramolecular and intermolecular interactions. It should be noted that, up until now, the SFG (\(|\chi^{(2)}|\)) spectra obtained were a combination of the real(Re\(\chi^{(2)}\)) and imaginary parts (Im\(\chi^{(2)}\)). To obtain orientational information of water, the Im\(\chi^{(2)}\) had to be calculated. The Shen laboratory responded to the assertion that the icelike and liquidlike assignments might not be correct by performing phase-
Figure 2.5: SFG spectra collected from quartz/water interface at pH (a) 1.5; (b) 3.8; (c) 5.6; (d) 8.0; (e) 12.3. (f) SFG spectrum from quartz/ice interface. These water spectra were the first to be collected on a solid surface. Due to the low isoelectric point of quartz (≤2), the surface OH groups become ionized as pH is increased. Reprinted with permission from Ref. [5]. ©1994 by the American Physical Society.

Sensitive SFG on the water surface (phase-sensitive SFG can directly measure the orientation of molecules at surfaces and interfaces).[8] They observed that, while conventional $|\chi^{(2)}|$ showed convergence of the two peaks during isotopic dilution, the Im$\chi^{(2)}$ spectra had two peaks; a positive band around $\sim 3200$ cm$^{-1}$ and a negative band at $3450$ cm$^{-1}$. This showed that the icelike and liquidlike peaks were still present even after isotopic dilutions.[8] Figure 2.8 shows results from the phase-sensitive SFG experiment. In the past 3-4 years, computer simulations of water the interface have become powerful counterparts to SFG experiments. At the moment, however, there is no consensus over the icelike and liquidlike nature of water surface from the viewpoint of computer simulations.[42–44, 49]

Two main peaks are observed at 3200 and 3400 cm$^{-1}$ in Figure 2.5 correspond to the icelike and liquidlike water molecules. There is no free OH peak because quartz has a low isoelectric point (IEP) ($\sim 1.5$) which means most of the surface OH groups are deprotonated or engaged in hydrogen bonding with water molecules.[50] This is not the case for Al$_2$O$_3$ (sapphire)/water interface.
Figure 2.6: SFG spectra collected at various temperatures at water/air interface. Reprinted with permission from Ref. [6]. ©1994, American Association for the Advancement of Science.

Figure 2.7: SFG spectra collected from water/air interface. Fits to the data are shown by the solid lines. Simulated data for the 'icelike' and 'waterlike' hypothesis are shown by the dotted line. Peak positions are indicated in the graph. For pure D₂O [ratio D/(D + H)= 1, closed circles], two resonances are clearly identified in the O-D stretch region. For a sample with D/(D + H)= 0:33 (open circles), the contribution from D₂O modes is less than 10%, and HDO modes dominate the spectrum. (b) Energy level diagram for D₂O and HDO water molecules. The fundamental O-D stretch vibration is coupled intramolecularly, giving rise to symmetric (ss) and asymmetric (as) modes. Because of Fermi resonance with the overtone of the bending mode (δ₂), the ss mode is further split into a low and a high frequency band (labeled here ν₁ and ν₂). For an HDO water molecule, the intramolecular modes are decoupled, allowing the determination of the fundamental O-D stretch vibration. The corresponding frequency of each energy level is specified, except for the as mode, in cm⁻¹. Reprinted with permission from Ref. [7]. ©2008 by the American Physical Society.
Here, free OH groups are observed but are attributed to surface OH groups of the sapphire.[40, 51–53] These free surface OH groups form very strong bonds and hence do not fully participate in hydrogen bonding with the interfacial water molecules.[40] These groups are only deprotonated at relatively high pH.[?] Recently, it was reported that while the assignment for the sapphire surface free OH is correct, some portion of the peak should be attributed to free water OH oscillators at the sapphire surface.[54] The assignment at the solid/water interface is less controversial. This is because there is the understanding that when water molecules meet an abrupt hard interface, they tend to layer to ∼1.2 nm.[55, 56] This view has also been supported by atomistic molecular dynamics simulation,[55] density functional theory (DFT) calculations,[57] and Monte Carlo simulations.[58]

The structure of water at a charged solid/water interface has been studied by both SFG and simulation.[40, 52, 55?] Due to the electrostatic field from surface charge, an orientational order is induced in the water molecules at the in-
terface. This order can persist in the bulk over a certain depth.[55] Interestingly, only the icelike peak is observed past the IEP of sapphire (6-7).[46] This is because of the structured water next to the solid surface. In the field of atmospheric science, some believe that highly ordered water molecules on solid surfaces tend to freeze faster, and hence are better ice nuclei for cloud seeding.[59–61] However, recently, Ehre et al.[29] reported that the freezing of water was delayed on a negatively charged surface whereas a positively charged surface enhanced freezing. Using specular X-ray diffraction (XRD) on frozen water droplets, the authors contended that the nucleation of ice was different for negatively and positively charged surfaces. Due to the local electric field emanating from the substrate, water molecules were able to preferentially polar order either with their dipoles pointing towards the interface (negatively charged surface) or dipole pointing into the bulk (positively charged surface). Since the experiments conducted on both positively and negatively charged surfaces were the same, it seemed that the orientation of water molecules at the surface was the cause of the difference in the freezing temperatures.[29] This showed that the structural order of water next to solids is not necessarily a precursor for faster ice nucleation. In Chapters 4 and 5, the water and ice structures next to neutral sapphire and charged substrates are examined in detail, respectively.

2.3 Ice interfaces

The study of ice interfaces has many implications in science. It has been said that our ability to study ice will allow us to understand how life started on earth and to predict the future of our planet. This stems from the fact that ice is
present everywhere in our solar system and possibly across the universe.\cite{62} Data from the New Horizons space probe shows mountains as high as the Rockies made of ice on Pluto. This has led to the interesting questions as to whether life could exist in solid ice. On Earth, the polar ice caps reflects about 90% of the sun’s incoming light. About 7% and 10% of ocean’s and land’s surfaces are covered with ice, respectively.\cite{62} Through this, ice insulate land and ocean and controls ocean current. More importantly, ice surfaces serves as reactors for various chemical reactions that are detrimental to earth’s atmosphere.

In 1850, Michael Faraday postulated that the surface of ice might be liquidlike.\cite{63–65} It was largely ignored until the later part of the 20th century when advances in surface techniques and theoretical calculations made it possible to investigate the surface of ice. Fletcher, who picked up after Faraday, calculated (using electrostatic interactions) that the surface of ice slowly disorders and diverges as temperature is increased. This is called surface ‘premelting’.\cite{66} It has now become apparent that surface premelting is rather common in many solids, including germanium, gallium, lead, and aluminum.\cite{9} However, when it comes to water, nothing is ever easy. The search for a quasi-liquid (as it has been discussed that this liquid layer might be different from liquid water) layer has spun a whole scientific field. Numerous experimental techniques including photoemission, nuclear magnetic resonance, low energy electron diffraction, atomic force microscopy, proton backscattering, and ellipsometry have been used to study ice surfaces. Extensive computational power has also been utilized to calculate and simulate the ice surface.\cite{10, 66–68} The conclusions from these measurements and calculations
are similar, in that the ice surface premelts as temperature increases. However, the formation, onset, and nature of the liquidlike layer is still under debate.

With the advent of surface sensitive SFG, an attempt has been made to resolve such controversy. This is because SFG is more tuned to the surface arrangements of molecules than most of the surface techniques available. Wei et al. (Shen laboratory in Berkeley) first used SFG to study the ice surface.[9, 69] Figure 2.9 shows spectra of an ice surface as a function of temperature. There are two main visible peaks. The redshifted peak at 3150 cm$^{-1}$ is attributed to the tetrahedral bonding of water molecules in ice. This is also similar to the strong ice peak obtained for Raman. The focus of this Figure, however, is on the peak around 3695 cm$^{-1}$ which is associated with the free OH of water. Following this peak as temperature is increased, the emergence of a liquidlike layer on ice surface was deduced. The authors found that the onset temperature of the liquidlike layer was $\sim$200K (-73°C). This is much lower that what has been found by other experimental techniques and simulations.[10] The structure of the free OH and the premelting layer (disordered water molecules) at the ice surface is shown in Figure 2.10.

In the above work, the assignments of the hydrogen bonded water in ice were not the focus of the paper. The origin of the SFG signal at the ice surface is not obvious. This is because, due to residual entropy during cooling, the hydrogen orientation in bulk ice is disordered. This is usually referred to as proton disorder. The SFG experiments and theoretical models by Buch et al.[68, 70] and Shultz et al.[11, 71] for the ice/air interface have suggested that the strong ice peak is due to water molecules that have one non-hydrogen-bonded
Figure 2.9: SFG spectra collected at ice/air (0001) interface at various temperatures. Reprinted with permission from Ref. [9]. ©2002 by the American Physical Society.

Figure 2.10: Side view of an ideal (0001) basal surface of ice Ih. Note that the free (or dangling) OH bonds are perpendicular to the surface due to the tetrahedral hydrogen bonding geometry. Also note that the adjacent layers A and B do not repeat each other by a simple spatial translation but are rotated by 180° with respect to each other in the surface plane. Reprinted with permission from Ref. [9]. ©2002 by the American Physical Society. (b) Molecular dynamics simulation of the (0001) basal surface of ice Ih at 265K. Reprinted with permission from Ref. [10]. ©2004, AIP Publishing LLC.

free OH exposed to the vapor interface and the other OH that is part of a strong tetrahedrally coordinated hydrogen-bonded network. They also attributed the
intense peak to the water molecules connecting the different bilayers (also called stitching bilayer). Groenzin et al.\cite{71} used this model to explain experimental data from the basal ice face. This assignment was also supported by Barnett et al.\cite{11} using the polarization angle null SFG technique. Recently, Ishiyama and Morita used molecular dynamics simulations to explain the high intensity of the ice peak at the ice/air interface.\cite{72, 73} They emphasized that the charge transfer between the bilayer stitching molecules and the bonded water molecules below is very important in explaining the intense ice peak in the SFG spectra for ice/air interface. See Figure 2.11 for an illustration of the different possible hydrogen bonding modes present at the ice surface.

Currently, while there is still more to be known, the ice surface is fairly understood. The solid/ice interface, however, has largely being ignored.\cite{61, 62} This is puzzling because the solid/ice interface has significant impact on both climate and human activity. Understanding ice nucleation on dust particles can
help predict rainfall and other phenomena involving cloud formation. Ice adhesion on solids can be problematic and a burden on the transportation industry. This thesis attempts to fill the void in our understanding of solid/ice interfaces. Ice nucleation has been studied on neutral and charged surfaces and we hope the results obtained can lead to the design of low ice adhesion materials.

2.4 Polymer/water interface

The integration of polymeric materials in various biomedical, technological, and environmental applications is steadily increasing. Interestingly, most of these applications rely on the interface with water. For example, in the field of biomedical science, polymers are currently being used in drug deliveries, stents, nerve conduits, and scaffolds for generation of partial or whole organs. In such situations, the interaction of water with these polymeric materials determines their utility. The diffusion of water through a polymer coating is very important to the interfacial adhesion, lubrication, and corrosion.[74–79] Polymers are used as coating on various electrical systems. Most importantly, the ability of polymers to change their conformation when they come in contact with external stimulus has aided their use as mechanical and electrical triggers.[13] Very recently, the Los Angeles Department of Water and Power used polyethylene balls (Shade balls) to cover its reservoirs in an attempt to slow down the evaporation of water and the growth of algae. This further shows the environmental importance of polymers. However, despite the obvious significance of polymer/water interface, detailed studies are limited.
In this thesis, we are concerned with the structural changes of polymer surfaces. As such, a brief review will be given. The ability of a polymer to change its conformation at the polymer/water interface depends on the type of functional groups present on the side chains. The presence of hydrophilic and hydrophobic moieties on a polymer side chain will facilitate the surface restructuring in and out of water. For example, the contact angle of a droplet of water will decrease when in contact with a polymer with polar and non-polar groups.[14, 15] This is because the hydrophobic segments of the polymer orient in air to reduce the interfacial energy. However, in water, such such conformation is unfavorable, so the polar groups migrate to the interface to reduce the surface free energy. Such restructuring of polymer chains is recognized when observing the advancing and receding contact angle. This is one cause of contact angle hysteresis on polymer surfaces.[80] In most of the earlier studies, multicomponent systems (end-grafted or copolymers) were used.[81] Inutsuka et al. studied end-grafted PDMS-PEG components using neutron reflectivity.[12] They observed that in water, the PEG component was ordered at the water interface while the PDMS part moved inward, away from the interface. This is shown in the illustration in Figure 2.12.

Figure 2.12: An illustration of a block copolymer of poly(ethylene glycol) (PEG) and poly(dimethyl siloxane) (PDMS) in water. Reprinted with permission from Ref. [12]. ©2005 American Chemical Society.
In a pioneering study of surface restructuring as a function of time, Crowe et al.[13] studied the surface responsiveness of modified poly(vinylmethylsiloxane) (PVMS) networks using contact angle measurements. The authors reacted the vinyl moieties on PVMS via AIBN-initiated thiolene radical addition of HS(CH$_2$)$_n$OH ($n = 2, 6,$ and $11$) to obtain PVMS-C$_n$-OH. They observed a fast contact angle drop as a function of time for $n = 2$ and $6$. In contrast, the degree of change was much lower for $n = 11$ (see Figure 2.13). For $n = 2$ and $6$, the polymer behaves like a liquid although it is crosslinked. Moreover, the glass transition temperatures (Tg) of $n = 2$ and $6$ are -58 and -65 °C, respectively.[82] This means at room temperature, the polymer segments are highly mobile. Upon contact with water, segmental motion occurs to bring the hydrophilic groups to the surface. On the contrary, when $n = 11$, the Tg increases considerably. Due the long chain of the linker, it forms crystalline units that prevent segmental motions. In a sense, when the flexibility of the chain is compromised, the fast surface reconstruction kinetics are lost or drastically reduced.[13]

It should be noted that in the above studies, the Tg of the polymers was far below room temperature and hence surface mobility was occurring. However, what will happen if the Tg of the polymer under study is higher but is composed of both hydrophilic and hydrophobic functional groups? Wang et al attempted to answer that with their study of poly(methacrylate)s using surface-sensitive sum frequency generation spectroscopy (SFG).[14, 83]

In the study of poly(methyl methacrylate) (PMMA), the authors observed no surface restructuring in water at room temperature (Figure 2.14). However, poly($n$-butyl methacrylate) (PBMA) restructured when it came in contact with
Figure 2.13: Time dependence of the deionized water wettabilities for PVMS-C<sub>n</sub>-OH surfaces. Inset: ATR-FTIR for the PVMS-C<sub>6</sub>-OH and PVMS-C<sub>11</sub>-OH substrates. The lower frequencies for the methylene asymmetric and symmetric stretches in PVMS-C<sub>11</sub>-OH are a signature of a semicrystalline surface. Reprinted with permission from Ref. [13]. ©2005 American Chemical Society.

Figure 2.14: SFG spectra collected in SSP and SPS polarizations of PMMA before, during, and after coming in contact with water. Reprinted with permission from Ref. [14]. ©2001 American Chemical Society.
water (Figure 2.15). The authors explained that due to the difference in Tg (105 °C for PMMA and 17 °C for PBMA) the side chains were able to respond to the presence of water differently.[14]

Interestingly, literature from the Tanaka Laboratory presents a different picture at the polymer/water interface.[15, 84] Recently, Horinouchi et al. reported on the surface dynamics of PMMA in contact with water (Figures 2.16 and 2.17).[15] The authors observed the reorientation of the ester methyl side chain by placing the more hydrophilic carbonyl group to the interface with water. The measured activation energy for surface reorganization was found to be much lower than in air and in bulk.[15] The water acting as a plasticizer and the need to decrease surface energy were both used to explain the segmental chain motions observed here even at room temperature. However, these results contradict what was observed before.[83] This shows that despite the inroads made in understanding polymer surfaces, there still remains unresolved issues that are key to various applications in science.

To obtain useful information from the curve, the authors used eq. 7.1 to fit the experimental θ-t relation.
Figure 2.16: (a) Time dependence of $\theta$ (contact angle) for PMMA films annealed at different temperatures. Open symbols and solid curves denote the experimental data and ones fitted by eq. 7.1 (b) Annealing temperature dependence of $\theta_{\text{ini}}$, $\theta_{\text{ter}}$, and $R_{\text{rms}}$ of each film. Reprinted with permission from Ref. [15]. ©2012 American Chemical Society.

$$\theta(t) = (\theta_{\text{ini}} - \theta_{\text{ter}}) \exp(-t/\tau) - kt + \theta_{\text{ter}}$$

(2.1)

Here, $\theta_{\text{ini}}$ and $\theta_{\text{ter}}$ are $\theta$ values at $t = 0$ and the terminal value of $\theta$ in a quasi-equilibrium state over an exponent, respectively. $\tau$ is the time constant for the $\theta$ decay in the initial stage and $k$ is a constant over the corresponding monotonic $\theta$ decrease due to evaporation.

In Chapter 7, we have used SFG and contact angle measurements to elucidate the molecular structure of poly($n$-butyl $\alpha$-hydroxymethyl acrylate) (PHNB) in contact with water. Unlike the multicomponent systems mostly studied for surface restructuring in water,[81] PHNB is a single component system with hydrophilic and hydrophobic side chains in each repeating unit, giving it a unique amphiphilic character. The pendant chains are composed of ester butyl and hy-
droxymethylene groups. Due to this amphiphilic nature, a decrease in water contact angle is expected over time.[15] In air at room temperature, the surface should be rigid (Tg of 80°C) and dominated by the ester butyl group. However, in the presence of water, the hydroxymethylene groups should migrate to the surface to reduce surface free energy and interact with water. Since SFG and contact angle measurements are sensitive to the surface, any changes in the molecular structure should be observed. This polymer is especially synthesized for biomedical application and the surface reorientation of this polymer in water will determine its utility. The synthesis of this polymer has already been published.[85]

2.5 Sum frequency generation spectroscopy

This section is adapted in part from refs. [18, 86–89].

Many excellent review have been published up to date.[89–93] Hence, the review of the fundamental of sum frequency generation spectroscopy here is to give the reader enough basics to understand the work in this thesis.
When an oscillating intense electric field is applied to a molecule, it induces a dipole whose strength is proportional to the applied electric field. Considering a condensed medium, the relation between the dipole per unit volume (polarization), and electric field is

\[ P = \chi^{(1)} E + \chi^{(2)} : EE + \chi^{(3)} : EEE + \ldots \] (2.2)

where \( E \) is the electric field vector and \( \chi^{(1)} \), \( \chi^{(2)} \) and \( \chi^{(3)} \) are the first-, second-, and third-order susceptibility tensors of the medium, respectively. The contribution from higher order susceptibilities are usually negligible. It is assumed that the medium has zero or negligible static polarizability and the intermolecular interactions have no effect on the induced dipole moment. Then the linear and second order nonlinear susceptibilities are expressed in terms of the number of molecules per unit volume (\( N \)), molecular polarizability (\( \alpha \)) averaged over all orientations, and second order hyperpolarizability (\( \beta \)),

\[ \chi^{(1)} = N \langle \alpha \rangle \chi^{(2)} = N \langle \beta \rangle \] (2.3)

The applied electric field is oscillating with time, \( t \), at a certain frequency, \( \omega \) and \( E \) can be replaced by \( E \cos \omega t \). The corresponding polarization will also be oscillating and thus will emit light at an intensity, \( I \), that is proportional to the square of the polarizability,

\[ I = [\chi^{(1)}E \cos \omega t + \chi^{(2)} : E E \cos^2 \omega t + \chi^{(3)} : E E E \cos^3 \omega t + \ldots]^2 \] (2.4)
Concentrating only on the second term and using \( \cos^2 \omega t = 1 + \cos 2\omega t \),

\[
I = [\chi^{(2)} : EE(1 + \cos 2\omega t)]^2 \tag{2.5}
\]

The first term represents the static polarization while the second represents the oscillating polarization at a frequency of \( 2\omega \) which emits light at \( 2\omega \). This process is known as second harmonic generation (SHG).

When the applied electric field consists of two separate electric fields, \( E_1 \) and \( E_2 \) with frequencies \( \omega_1 \) and \( \omega_2 \) the intensity in eq. 2.5 becomes,

\[
I = (\chi^{(2)} : EE(\cos \omega_1 t \cos \omega_2 t))^2 \tag{2.6}
\]

In this case, the emitted light has components at the sum \( (\omega_1 + \omega_2) \) and difference \( (\omega_1 - \omega_2) \) frequencies along with the fundamental frequencies, \( \omega_1 \) and \( \omega_2 \). The electromagnetic radiation at \( \omega_1 + \omega_2 \) is the SFG signal. \( \chi^{(2)} \) in the SFG expression is a third rank tensor and changes sign after an inversion symmetry operation, \( \chi^{(2)} = -\chi^{(2)} \). However, a media with inversion symmetry (centrosymmetry) is invariant under this operation which indicates that \( \chi^{(2)} \) must be zero and under the electric dipole approximation SFG signal is forbidden. This is a significant characteristic of SFG because the bulk of most polymers whether amorphous or semicrystalline is centrosymmetric. The centrosymmetry breaks down at the surface and interface and the SFG signal can be generated. As a result, SFG is surface/interface specific.

In infrared-visible SFG, one of the two incident electric fields has a frequency, \( \omega_{vis} \) in the visible region and the other a frequency, \( \omega_{IR} \) in the infrared
region. When these two light beams are incident from medium 1 into medium 2 and are overlapped in time at interface, an SFG signal of frequency $\omega_1 + \omega_2$ is generated in the reflected and transmitted directions (Figure 2.18). The angles of incidents for the visible and IR beams from the surface normal (z-axis) are $\theta_i(\omega_{vis})$ and $\theta_i(\omega_{IR})$ the angles of reflection are $\theta_r(\omega_{vis})$ and $\theta_r(\omega_{IR})$ and, the angles of transmission are $\theta_t(\omega_{vis})$ and $\theta_t(\omega_{IR})$ respectively. The reflected and transmitted SFG beams propagate with an angle $\varphi_r$ in medium 1 and $\varphi_t$ in medium 2, respectively. The refractive indices of the medias depend on the frequencies and are indicated in parenthesis. Some basic relationships are,

$$\theta_i(\omega_{vis}) = \theta_i(\omega_{vis}), \theta_i(\omega_{IR}) = \theta_i(\omega_{IR})$$

(2.7)

$$\omega_{vis}n_1(\omega_{vis})\sin\theta_r(\omega_{vis}) + \omega_{IR}n_1(\omega_{IR})\sin\theta_r(\omega_{IR}) = \omega_{SFG}n_1(\omega_{SFG})\sin\phi_r(\omega_{vis})$$

(2.8)

$$\omega_{vis}n_2(\omega_{vis})\sin\theta_t(\omega_{vis}) + \omega_{IR}n_2(\omega_{IR})\sin\theta_t(\omega_{IR}) = \omega_{SFG}n_2(\omega_{SFG})\sin\phi_t(\omega_{vis})$$

(2.9)

The polarization of the beams in Figure 2.18 forget determines which components of $\chi^{(2)}$ are active. A light beam is either S polarized, $E_s$, if in the plane of the interface or P polarized, $E_p$ if in the plane of incidence. Then the overall polarization of SFG is a combination of the SFG beam, visible beam, and IR beam polarizations in this order. The expressions for SSP and PPP polarization combi-
Figure 2.18: The interface between two media that is probed by SFG. The subscripts \( i \) and \( r \) denotes incident and reflected directions. Here \( n_1 > n_2 \).

Equations are given in eq. 2.2 where \( \chi^{(2)} \) is replaced with an effective susceptibility, \( \chi^{(2)}_{\text{eff}} \). It can also be shown as \( \chi^{(2)}_{ijk} \) because it is a sum of the nonvanishing \( \chi^{(2)} \) components. Here \( i, j, k = x, y, z \) and \( x, y, \) and \( z \) are the laboratory coordinates.

For an azimuthal isotropy at the interface the seven nonvanishing components of \( \chi^{(2)}_{ijk} \) and the relation among them are \( \chi^{(2)}_{xxz} = \chi^{(2)}_{yyz}, \chi^{(2)}_{xxz} = \chi^{(2)}_{yzy}, \chi^{(2)}_{zzx} = \chi^{(2)}_{zyy}, \) and \( \chi^{(2)}_{zzz} \).

\[
\chi^{(2)}_{\text{eff,SSP}} = L_{yy}(\omega_{SFG})L_{yy}(\omega_{vis})L_{yy}(\omega_{IR})\sin \varphi \omega_{ir} \chi_{yyz} \tag{2.10}
\]

\[
\chi^{(2)}_{\text{eff,SPS}} = L_{yy}(\omega_{SFG})L_{yy}(\omega_{vis})L_{yy}(\omega_{IR})\sin \varphi \omega_{ir} \chi_{yzy} \tag{2.11}
\]
\[ \chi_{eff,PPP}^{(2)} = -L_{xx}(\omega_{SFG})L_{xx}(\omega_{vis})L_{zz}(\omega_{IR})\cos\omega_{sf}\cos\omega_{vis}\sin\omega_{ir}\chi_{zzz} \]
\[ - L_{xx}(\omega_{SFG})L_{zz}(\omega_{vis})L_{xx}(\omega_{IR})\cos\omega_{sf}\sin\omega_{vis}\cos\omega_{ir}\chi_{zzy} \]
\[ + L_{zz}(\omega_{SFG})L_{xx}(\omega_{vis})L_{xx}(\omega_{IR})\sin\omega_{sf}\cos\omega_{vis}\cos\omega_{ir}\chi_{xxx} \]
\[ + L_{zz}(\omega_{SFG})L_{zz}(\omega_{vis})L_{zz}(\omega_{IR})\sin\omega_{sf}\sin\omega_{vis}\chi_{zzz} \]  
\[ (2.12) \]

The \( L \) values are the optical Fresnel coefficients that relate the magnitudes of the electric fields at the interface to those of the input electric fields. They basically depend on the optical properties of the media that form the interface and therefore have a frequency dependence.

The total SFG intensity reflected from a surface is given by,

\[ I(\omega_{SFG}) = \frac{8\pi^3\omega^3 \sec^2\theta_{SFG}}{c^3 n_1(\omega_{SFG})(\omega_{vis})(\omega_{IR})} |\chi_{eff}^{(2)}| I(\omega_{vis}) I(\omega_{IR}) \]  
\[ (2.13) \]

Where \( n_1 \) and \( n_2 \) are the refractive index of air and the medium respectively and \( c \) is the speed of light. The nonlinear susceptibility of the surface \( \chi_{ijk}^{(2)} \) can be broken down into two components:

\[ \chi_{ijk}^{(2)} = \chi_{eff}^{NR} e^{i\Phi} + \sum_{q=1}^{Q} \frac{A_{ijk,q}}{\omega_{IR} - \omega_q + i\Gamma_q} \]  
\[ (2.14) \]

The first term is the nonresonant component and is wavelength independent. It may be originated from the bulk of a material or from the substrate that the material is coated on. The second term is the resonant component which is the sum of \( Q \) resonances of each chemical species at the surface or interface.
When the frequency of the incident IR beam, IR, matches the frequency of the $q^{th}$ molecular vibration of a specific chemical group, energy is absorbed from the IR beam. In eq. 2.14, $A_{ijk,q}$, $\omega_q$, and $\Gamma_q$ are the amplitude, frequency, and width of this molecular vibration, respectively. $\Phi$ is the relative phase of the nonresonant term with respect to the resonant term. It takes into account the destructive or constructive interference of the SFG signals generated from the nonresonant and resonant components.

The important result from eq. 2.14 is that chemical information of the surface or interface can be deduced from an SFG signal. This is provided by the molecular hyperpolarizability, $\beta$ which has characteristic resonance peaks corresponding to vibrational modes of the molecules. The component of $\beta$ for a vibrational mode $q$ is given by,

$$\beta_{lmn} = \frac{\alpha_{lmn,q} \mu_{q,n}}{\omega_{IR} - \omega_q + i \Gamma_q}$$

(2.15)

where $l, m, n = a, b, c$ and $a, b, c$ are axes of the molecule fixed coordinate system. $\alpha_{q,lm}$ is the Raman tensor and $\mu_{q,n}$ is the infrared transition dipole moment vector. As a consequence, only Raman- and IR- active vibrational modes contribute to $\beta$ and are SFG-active.

The $\beta_{q,lmn}$ can be projected on the lab axis (xyz) from the molecular axis (abc) by using Euler transformation coefficients which are functions of Euler angles, $\psi$, $\theta$, and $\varphi$ (Figure 2.19). This is different than the beam angles in Figure 2.18 and $\chi$ in ref [94] is replaced here with $\varphi$ to avoid confusion with the susceptibility tensor. The coordinate transformation is performed by first rotating the z-axis by $\varphi$, second the x-axis by $\theta$, and then rotating the z-axis once again.
by $\psi$. The transformation makes it possible to express $\beta_{lmn}$ in the molecular reference frame with the $\beta_{ijk}$ in the laboratory frame. Due to the symmetry of the molecule, many components of the molecular hyperpolarizability tensor vanish which simplifies the calculations. Finally, the summation of the $\beta_{ijk}$s for each molecule at the surface or interface gives the resonant component of eq. 2.14,

$$\frac{A_{ijk,q}}{\omega_{IR} - \omega_q + i\Gamma_q} = \sum_{all\text{molecules}} = N \int \beta_{ijk} f(\psi, \theta, \phi) d\Phi d\theta d\phi \quad (2.16)$$

where $f(\psi, \theta, \phi)$ is the probability distribution function of the molecular orientation. The Euler angle $\psi$ is in the plane of the surface and angle $\phi$ describes the rotational degree of freedom as seen in Figure 2.19. Generally the orientations of the SFG-active groups at the surface or interface are isotropically distributed in these angles causing $\langle \psi \rangle$ and $\langle \phi \rangle$ to be zero. Therefore, eq. 2.16 depends only on the averages of the polar angle $\theta$ which is the angle that the molecule makes with the surface normal (z-axis). This result is very important because by analyzing $\theta$ from the total SFG intensity reflected from a surface given in eq. 2.13 through its contribution in eq. 2.16 it is possible to tell the degree of orientational order of molecules at the surface or interface with respect to the surface normal. The SFG intensity also indicates the number of molecules, $N$, that contribute to the SFG signal since the orientation factor is multiplied with $N$ in eq. 2.16.

In an infrared-visible SFG experiment, the SFG signal intensity (eq. 2.13) is measured as an output when the visible and IR input beams are overlapped in space and time on a surface or interface. The frequency of the visible beam, $\omega_{vis}$ is fixed while that of the IR beam, $\omega_{IR}$ is scanned over a certain range. Depending on
Figure 2.19: The relationship between the molecular coordinate system \((a, b, c)\) and the laboratory coordinate system \((x, y, z)\) through the Euler angles \((\psi, \theta, \phi)\).

The relationships between the macroscopic and microscopic hyperpolarizabilities and the vibrational resonant frequencies of the chemical species an SFG spectrum is obtained. Since the SFG intensity is enhanced at an SFG-active vibrational mode, the spectra is composed of peaks unless one peak destructively interferes with another due to opposite phases. A vibration may also appear as a dip for the same reason. This SFG spectrum is fit to a simplified version of eq. 2.13 to determine the resonant and non-resonant components of \(\chi_{eff}\),

\[
I_{SFG} \propto [\chi_{eff}^{NR} e^{i\Phi} + \sum_{q=1}^{Q} \frac{A_{ijk,q}}{\omega_{IR} - \omega_q + i\Gamma_q}]^2
\]  

(2.17)

Here \(\omega_q\) provides the chemical information directly. To obtain the orientational information, the fitted value of \(A_q\) has to be related to the true macroscopic hyperpolarizability tensor elements by using priory known fresnel coefficients. The macroscopic hyperpolarizability tensor is calculated through the molecular hyperpolarizability tensor for various molecular orientations in order to find the one that matches the experimentally determined macroscopic hyperpolarizability tensor. While \(\beta\) can be estimated it is difficult to obtain an accurate value of \(N\). The intensity of a spectrum may be effected from the experimental variables such as the alignment of incidence beams on the sample, the beam quality, the alignment...
of the SFG beam into the detector, or the detector quality. It is safer to compare relative peak intensities belonging to two different vibrational modes of the same molecule within one spectrum. This eliminates N, avoids the Fresnel coefficients and provides tilt information. If it is crucial to measure N in order to know the complete structure of the surface or interface especially when different molecules are involved, the ratio of the peaks in the same SFG spectrum can be used as a reference spectrum of a well characterized surface or interface.
CHAPTER III
EXPERIMENTAL

3.1 Sample preparation

Ultrapure water from a Millipore filtration system with deionizing and organic removal columns and a resistance of 18.2 MΩ·cm was used in these experiments. CsOH (≥ 99.9% purity, Sigma-Aldrich), N(CH₄)₄OH (25wt% in H₂O, Sigma-Aldrich), NH₃OH (≥ 28-30% NH₃ basis, Sigma-Aldrich), NaOH (≥ 97.0 % pellets, Sigma-Aldrich) or HCl (37 wt%, Sigma-Aldrich) were used as obtained for pH adjustments. The pH measurements were performed with an Oakton pH meter with an epoxy-body pH electrodes. NaCl (purity ≥ 99.0 %, purchased from Fisher Scientific) was used to make 0.1 M solution for the salt experiment in Chapter 6. D₂O was purchased from Cambridge Isotopes (D 99.9%) for experiments in Chapter 7.

Sapphire has a high surface energy hence it is easy for adventitious carbon to adsorb on the surface. Due to this, care was taken to use freshly clean surface for every experiment. The sapphire prisms were purchased from Meller Optics. They are custom cut 60° equilateral (c-axis ± 2° parallel to the prism face) prisms. For all sapphire/water experiments, the sapphire prisms were sonicated (Branson model 610 sonicator) for 1 h in acetone, methanol, and deionized water. This was followed by thorough rinsing with deionized water. This cleaning method has been used to remove surface organic residues in previous studies and has been shown
to give consistent results.[40, 95–97] The stainless steel components of the sample cell were also cleaned by the same method. The sapphire prisms and the water cell were blow-dried using dry N\textsubscript{2} (Praxair grade 2). The prisms and cells were then plasma (air plasma) treated for 4 min right before an experiment. The plasma treatment was done with a Harrick PDC-32G scientific plasma cleaner with the intensity set high (100 W). The vacuum inside the plasma chamber was stabilized around 75 Torr with a Varian 3201 direct drive rotary vane pump.

Muscovite mica was obtained from Lawrence Company, New Bedford, MA. Since we wanted to perform total internal reflection geometry experiment, mica was adhered onto a sapphire prism by a spuncoated polystyrene interlayer. We first spincoat polystyrene on a clean sapphire prism. Then a drop of toluene is put on top of the film. Thin sheet of mica, cut to the size of the sapphire is carefully placed on the film. The sample is then annealed at 120\degree C for 12 h. The integrity of the mica layer is tested by cleaving. If the adhesion between the mica and sapphire prism is strong, the mica layer doesn’t delaminate. Prior to performing an experiment, a new mica surface is cleaved and immediately placed in water. This prevented adventitious carbon in air from contaminating the clean new mica surface.

All glassware used to clean and make solutions were first cleaned with soap and washed thoroughly. They were then immersed in a base bath (300 g of KOH pellets in 4 L of isopropyl alcohol and 2 L of DI water) for about 3 h. They were subsequently first rinsed with distilled water and then thoroughly with DI water. The glassware was blow-dried with N\textsubscript{2}. They were further dried in the oven at 120\degree C and taken out right before the experiment.
Poly(n-butyl α-hydroxymethyl acrylate) (Mn = 25.4 kg/mole PDI = 1.2) was obtained from Joy laboratory, Polymer Science, The University of Akron. It was synthesized by Chao Peng and details of this polymer have been published.[85]. A film (about 300 nm thick) was prepared from a 3.8 wt% solution of dissolved polymer in tetrahydrofuran (THF), which was spin coated at 2000 rpm for 1 min. The films were spin coated on sapphire prims and silicon wafers for SFG and contact angle measurements, respectively. The films were then annealed under vacuum at 100°C for a minimum of 12 h in a vacuum oven at a pressure of about 75 torr. Spin coating was done by using a Specialty Coating Systems model P6700 spin coater. Prisms were mounted by using a custom 60° screw tightened mechanical chuck and silicon wafers were mounted by a standard chuck via a vacuum seal to the chuck using a rubber O-ring.

Water condensation is a major issue when cooling the SFG sample cell below 0 °C, and thus, we designed a sample cell with a vacuum chamber as shown in Figure 3.1. The inside chamber containing the water is sealed to prevent any loss of water due to vacuum. The temperature stage was purchased from Instec Inc. and modified in-house to hold the sapphire prisms. An aluminum dome was designed with a CaF₂ window to introduce the visible and IR beams and SiO₂ window to collect the output SFG beam. The sample cell was designed with the flexibility to change the orientation of the windows to maintain the normal incidence of the input and output beams. A vacuum pressure of 8 Torr was used to prevent water condensation and to maintain temperature uniformity inside the sample chamber. The heating and cooling rate for each experiment is noted clearly in each chapter where the stage is used.
Figure 3.1: Diagram of the temperature stage and the sample geometry for SFG measurements. The water is sealed from one side by a sapphire prism while the other side is in contact with a heating or cooling stage purchased from Instec Inc. The top part of the temperature cell was machined to hold CaF$_2$ and SiO$_2$ optical windows for the input and the output of the laser beams. The cell was held under vacuum to prevent water condensation on the sapphire prisms and to maintain the temperature uniformity.

3.2 Sum frequency generation set up and measurement

The schematic layout of the SFG instrument is shown in Figure 3.2. Excellent reviews on this technique have been discussed in many publications.[89–93] Also, it has been covered in Chapter 2 so only the experimentation and instrumentation setup is explained here.

The SFG experiments were performed using a picosecond Spectra Physics laser system with a $\sim$3.5 $\mu$J tunable IR beam (2000–3800 cm$^{-1}$, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 100–200 $\mu$m) and a $\sim$70 $\mu$J visible beam (800 nm wavelength, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 1 mm).[98, 99] The IR beam energy used in this work had negligible effect on
laser heating of the ice or hydrate. The measured transition temperature of ice into water at the surface occurred at 0°C. The SFG measurements involved spatial and temporal overlap of the two laser beams on the sample. A motorized, computer-controlled delay stage was used to ensure that the temporal delay was maintained while scanning IR frequencies from 2800 to 3800 cm⁻¹.

The Millenia is a diode-pumped solid state green laser with a continuous output at 532 nm and power of 5W which is directed into the Tsunami. The Tsunami is a Ti:Sapphire laser cavity with regenerative mode locking. The pulsed beam leaving Tsunami (800 nm, 100 fs, 82 MHz, red beam) enters the Spitfire as a seed. The Spitfire stretches the input pulse and amplifies it with Empower, a diode-pumped pulsed green light at 527 nm and power of 10 W and 1 KHz repetition rate. Both the stretched seed and the pump beam overlap on the Ti: Sapphire crystal in the Regen cavity. After multiple passes through the Regen cavity, the pulse builds up in intensity and is released by the pockels cell to a compression stage in the pulse compressor part of the spitfire. The amplified pulse is compressed back (1 ps, 1 KHz, ~1 W, 800 nm) and sent into the optical parametric amplification (OPA).

The beam entering the OPA-800 is split into two, with one used to generate a broadband white light (this becomes the seed during the OPA process). The rest of the 800 nm input pulse (pump) is further divided into two paths: a second and third path. The seed beam is later combined with the pump beam from the second path and passed through a barium borate (BBO) non-linear crystal. This combination of the two beams separate the pump beams into signal and idler beams through optical parametric generation. The idler is sent to a diffraction
grating with is reflected back to the BBO crystal. Here, it combines with the pump beam from the third path to generate signal and idler beams. The tilt angle of the BBO crystal and diffraction grating controls the wavelength of the idler beam.

These beams are directed to an AgGaS$_2$ crystal where difference frequency mixing (DFM) takes place to generate an IR pulse of 1 ps in a frequency range of 1800 to 3800 cm$^{-1}$. The crystal is rotated to the optimal phase matching condition between the signal and idler beams. While the IR beam is generated, the remainder of the pump intensity is taken to a separate path for the visible beam output. The IR wavelength output from the OPA is tuned by rotating the BBO crystal and the diffracting grating. The DFM crystal is then rotated for maximum IR output intensity. A Labview program, written by Hasnain Rangwalla (a former student) is used to control the motor (ESP-6000 motor system manufactured by Newport) positions. The Labview program controls the optimum motor positions (that decide the tilt angles) of the diffraction grating, BBO crystal, and DFM crystal for each IR output wavelength. A base file for the optimum motor positions is generated and is tuned regularly for the optimum OPA performance by optimizing the IR output intensity. The motor positions are periodically calibrated by optimizing the output power of the OPA, while the IR wavelength is calibrated at the beginning of every experiment day based on an IR absorption spectrum from a standard poly(styrene).

The IR and visible beams are then taken out of the OPA from separate exits to be overlapped on a sample in both space and time. The visible beam is passed through a half-wave plate in order to control its polarization. Then it is
reflected through a series of mirrors and a delay stage. Since it takes a shorter path inside the OPA, its path length outside the OPA has to be adjusted to ensure the time overlap with the IR beam. After the delay, the visible beam is sent to the dichroic mirror. The IR beam first passes through a filter to remove the remnants of the signal and idler wavelengths. Then it is taken to a CaF$_2$ beam splitter where a small part of it is sent to a pyroelectric photodetector through a chopper. The rest of the IR beam is transmitted and then focused on the dichroic mirror by a lens where the IR beam is transmitted and the visible beam is reflected. The two beams are kept separate on this mirror to avoid SFG generation from its optical coating. They are spatially overlapped on the sample surface by tilting the dichroic mirror. This overlap, in time and space, produces an SFG beam which is reflected by two mirrors into the path of the photomultiplier tube (PMT). In this path, it is focused by a lens, passed through optical notch filters to reduce the noise and a polarizer to control its polarization. The SFG beam is taken through a 0.5 m triple grating Acton Research Spectrapro 500i spectrometer to the PMT which is attached to the exit of the spectrometer. The spectrometer is controlled with the same SFG program that controls the wavelength of the IR beam because the 1200 groove/mm holographic visible grating inside the spectrometer has to be synchronously tuned to direct the expected SFG wavelength to the PMT. The SFG signals from the PMT (Hammatsu 928P) are detected by a Stanford Research Systems SR400 gated photon counter. At the same time, the signals from the IR photodetector are detected by a Stanford Research Systems SR850 DSP lock-in amplifier that is triggered by the chopper. These two outputs are recorded simultaneously by the Labview computer program as the number of photon counts and the average IR
intensity. Then the SFG intensity (number of photon counts) is normalized with the average IR intensity and plotted as a function of the IR wavenumber which is the SFG spectrum.

Figure 3.2: Schematic of the picosecond SF spectrometer. The meanings of the symbols are as follows: H, half wave plate; B, calcium fluoride plate beam splitter; M, mirror; DM, dichroic mirror; P, polarizer; F, Raman notch filter; C, IR chopper; PMT, photomultiplier tube detector.

3.3 Thickness measurements

Thickness measurements were performed with a J. A. Woolam Co. Inc. Spectroscopic Ellipsometer (control module: VB-400, monochromator: HS-190 high speed monochromator) from Dr. Cheng’s laboratory in the Department of Polymer Science, The University of Akron. For the thickness calculations, refractive indices of $n = 1.47$ for PVNODC, $n = 1.5894$ for PHNB, and $n = 1.4830$ for PnBA were used. All polymer films were coated on silicon wafers whose oxide
layer thicknesses were measured prior to coating with the same technique. The laser was shone on each film within the center region and a thickness value was obtained from three different places of the same surface.

3.4 Contact angle

The static and dynamic contact angle of water on PHNB was measured based on the sessile-drop method. The apparatus is a Rame-Hart goniometer (model 100-07-00, Rame-Hart, Inc.) from the Department of Polymer Science, The University of Akron. All contact angles were measured in an enclosed quartz cuvette chamber by equilibrating the atmosphere of the chamber with the liquid in use. A small drop of about 5 L was slowly dropped on the surface using a micropipette. Then the static contact angle was measured within a few seconds. For dynamic contact angle experiments, a test droplet was aligned. Once, this has been done, the experiment began with a droplet placed parallel to test droplet within a second of the droplet touching the polymer surface. The different surface dynamic experiments that were performed are clearly mentioned in the chapters in which they were performed. Multiple samples were tested. The final value reported is the arithmetic mean of all these contact angles.
4.1 Introduction

Ice formation at solid interfaces is responsible for interstellar transport, cloud formation, catalysis of reactions for ozone destruction, and generation of lighting storms.[100–103] The state of water or ice layers next to solid surfaces is also of geological consequence in understanding friction between glaciers, as well as being correlated with climate and life on earth. Questions regarding the freezing and melting of water next to solid surfaces have technological significance in preventing ice formation and adhesion to surfaces of wind turbines and high-altitude aircrafts. Recently it was shown that freezing of water can be enhanced or delayed on positively or negatively charged surfaces, respectively.[29] Although this phenomena is of wide importance in many fields, there have been few experiments on the freezing of the first few layers of water molecules next to solid surfaces. Previous work on the freezing of ice next to silica surface has been performed by Wei et al.,[9, 69] In these experiments water was first frozen and then brought in contact with the silica surface. The authors found no pre-melting layer present at the interface. However, this geometry could not be used to study the freezing of water in direct contact with the solid surface. In this work, we have extended the
use of infrared-visible sum frequency generation (SFG) spectroscopy in conjunction with a unique sample cell to study the freezing of water next to Al$_2$O$_3$ (sapphire) surface.

SFG is a powerful surface sensitive-spectroscopic tool for studying water interfaces. In the dipole approximation, SFG, which is a second-order nonlinear technique, is only active where there is a breakdown in inversion symmetry. This selection rule makes it possible to use SFG to study the structure of molecules near surfaces and interfaces. Excellent reviews on this technique have been discussed elsewhere.[89–93] It has also being discussed in Chapter 2. In brief, two incident beams, one visible ($\omega_{\text{vis}}$) and the other a tunable IR beam ($\omega_{\text{IR}}$), are temporally and spatially overlapped on the sample. Because of the non-zero second order effects, a small fraction of the incident light is converted to sum frequency signal ($\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$) at the interface. The SFG signals are enhanced when the tunable IR frequency overlaps with Raman and IR vibrational bands of molecules at the interface, making it possible to use this technique to identify the interfacial chemical groups. The intensity of the SFG signal, as a function of polarization of the incident and outgoing light, carries information on the orientation of the interfacial molecules. For these reasons, SFG is an important tool to study orientation of interfacial water molecules, the hydrogen bonding of interfacial water next to solid surfaces, and phase transition temperatures next to solid surfaces. It has been used to study water-solid [40, 46, 51, 52, 96, 104, 105] and ice-vapor surfaces.[9, 11, 69–71, 106]

Sapphire surfaces in aqueous solutions have been the focus of study by several research groups because of their importance in both natural and indus-
trial environments.[40, 46, 51, 52, 96, 97, 107] These surface OH groups can be de-protonated at high pH and protonated at low pH; the increase in SFG intensity due to surface charges have been used to measure the isoelectric point (IEP) of the sapphire substrate.[40, 46, 52] Here, we have used sapphire prisms with isoelectric points between pH of 5–6 as solid substrates to study water-ice transition temperatures using SFG spectroscopy. A unique sample cell under vacuum allowed us to monitor the freezing and melting transitions in situ during both cooling and heating cycles between -50 °C and 25 °C. This work offers a unique insight on how water freezes on solid surfaces, which in turn is crucial in understanding the friction and adhesion of ice.

4.2 Results and Discussions

Figure 4.1 shows the SFG spectra in SSP (a) and PPP (b) polarizations. The water peaks are expected in the range of 3000–3800 cm\(^{-1}\); typically, methyl and methylene assignments are in the range of 2700–3000 cm\(^{-1}\). The absence of methyl and methylene hydrocarbon peaks validates the effectiveness of the cleaning process used for removing organic residues from the prism and sample cells. The spectral assignments for water have been discussed in previous publications.[50, 52, 93, 104, 105] The peaks at 3200 and 3450 cm\(^{-1}\) in the liquid spectra are assigned to strongly tetrahedrally coordinated (icelike) and lower coordination (liquidlike) hydrogen-bond stretch, respectively.[50, 52, 93, 105] These peaks are referred to as ”icelike” and ”liquidlike” because they resemble the dominant peaks in IR and Raman spectra of ice and bulk water, respectively.[104, 105]. However, alternate assignments for the icelike peak near 3200 cm\(^{-1}\) have been discussed
recently in the literature. [7, 108–111]. Detail of the water assignments is covered in Chapter 2.

The peak at \( \sim 3700 \text{ cm}^{-1} \) has been assigned to surface hydroxyl groups on the sapphire surface.[16, 40, 107] Hass et al. [112] have shown that the sapphire surfaces have, on average, ten OH groups per \( \text{nm}^2 \). These surface OH groups can be de-protonated at high pH and this observation has been used to measure the isoelectric point (IEP) of the sapphire substrate.[40, 46, 52] However, it is puzzling why the 3700 cm\(^{-1}\) peak in the water spectra is not shifted or diminished (due to hydrogen bonding with the water next to it) after contact with water. There have been two different explanations for the origin of the OH peak at the (0001) crystal plane. One study concluded that the \((\text{Al})_n\text{OH}\) species are accessible to water, but some of the groups do not form hydrogen bonds with water molecules due to strong bonds with aluminum.[40] Another study concluded that most of the OH groups may be in nanopores and do not interact with water and that these OH groups are only accessible after annealing these surfaces at high temperature.[96] Our results indicate that the surface hydroxyl groups on the sapphire prisms are in contact with water and are de-protonated at conditions above the IEP (see Chapter 4). Recently, it was reported that while the assignment for the sapphire surface free OH is correct, some portion of the peak should be attributed to free water OH oscillators at the sapphire surface.[54]

In both Figure 4.1(a) and (b), the magnitude of the icelike and liquidlike peaks are similar. That is because the water used in this experiment has a pH (5.6) that is within the IEP of the sapphire (5-7). It should be noted that no acid was added to the solution. The low pH is as a result of carbon dioxide in
Figure 4.1: SFG spectra of water collected in SSP (a) and PPP (b) polarization.

Figure 4.2: SFG spectra collected in SSP (a) and PPP (b) polarization. The data were collected with temperature increment of 1°C (using a 4°C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (filled circles) near the freezing and melting transition temperatures are shown. The freezing transitions temperature is between -4 and -6°C.

The icelike peak here is the result of the abrupt shift in gradient as the water ‘touches’ the solid surface. It has been shown that at the solid/water interface, water molecules structure even in the absence of charge.[55, 57] The sapphire free OH peak at 3700 cm$^{-1}$ is higher in SSP than PPP. This could be due to the symmetric nature of the SSP polarization.
In the ice spectra (Figures 4.2, 4.3, and 4.4) the peak at ~3150-3180 cm\(^{-1}\) is assigned to hydrogen-bonded stretching modes of the water molecules. [9] However, the origin of the high intensity SFG ice peak is not obvious. The SFG experiments and theoretical models by Buch et al.[70] and Shultz et al.[11, 71] for ice-vapor interface have suggested that the strong ice peak is due to water molecules that have one non-hydrogen-bonded free OH exposed to the vapor interface and the other OH that is part of a strong tetrahedrally coordinated hydrogen-bonded network. They also attributed the intense peak to the water molecules connecting the different bilayers (also called stitching bilayer). Groenzin et al.[71] used this model to explain experimental data from the basal ice face. This assignment was also supported by Barnett et al.,[11] using the polarization angle null SFG technique. Recently, Ishiyama et al. used molecular dynamics simulations to explain the high intensity of the ice peak at ice-air interface.[72] They emphasized that the charge transfer between the bilayer stitching molecules and the bonded water molecules below is very important in explaining the intense ice peak in the SFG spectra for ice-air interface. We note that the orientation and strength of the hydrogen bonds present at the interface influences the signal intensity attenuations in ice. In bulk ice (ice Ih), the order obtained comes from the ordered arrangement of oxygen molecules. However, due to residual entropy in ice during the freezing process, the protons in ice are disordered. This is usually referred to as proton disorder in ice. Pauling[113] produced a statistical model of hydrogen atom positions as suggested by Bernal and Fowler. This model is referred to as Bernal-Fowler[114] ice rule:(1) Oxygen is covalently bonded to two hydrogens making the structure H-O-H with an angle of 105°. (2) Each oxygen atom is tetrahedrally coordinated.
with two covalently bonded hydrogens and two hydrogen-bonded hydrogens. (3) Only one hydrogen lies between oxygen-oxygen axis. This is usually perturbed at interfaces resulting in an SFG signal. (4) A large number of configurations exist in ice Ih due the many different distribution of hydrogens in relation to oxygen atoms. So in a sense, obtaining a strong intense signal in ice is a combination of a proton ordered stitching-layer and charge transfer. As mentioned above, at surfaces and interfaces, protons are ordered, whereas disordered protons mainly exist in the bulk. It has, however, been shown that bulk ice can also be ordered via a dopant[9] or epitaxial effect.[115] Because there is no direct theoretical work on ice-solid interface, we believe that the high intensity of the SFG peak observed for ice-sapphire interface could be also related to the combination of charge transfer and stitching bilayer concept introduced for explaining the results for the ice-air interface.

Based on the assignments for the ice peak in the SFG spectra, we will discuss the structure of ice at the sapphire surfaces. We note that, to our knowledge, we are the first group to use SFG to observe the cooling of water next to a solid substrate. Figure 4.2(a) and (b) shows the freezing of water (empty squares) to ice (filled circles) at the transition point. The ice SFG signal is significantly more intense than that of water. This, as mentioned earlier is due to the ordered protons and charge transfer at the interface. The freezing transition temperature was found to be between -4 and -6°C. Freezing is kinetic; different freezing rates produce different freezing temperatures. Hence, the delay in freezing is due to the supercooling of water and has nothing to do with the effect of the sapphire surface. Due to the volume (250 µL) of the cell used in our experiment, we believe
the ice nucleation is heterogenous and begins from the bulk or the steel side of the cell. We have proved this hypothesis by designing a low volume cell (11 µL) and measuring the freezing temperature. We found water to consistently freeze at -10°C. This shows that (in the low volume cell), the ice nucleation is initiated from the sapphire surface. The SSP and PPP spectra are very similar. A shoulder peak seen at $\sim 3000 \text{ cm}^{-1}$ (more prominent in all PPP spectra and SSP heating scans in Figure 4.4(a)), is associated with stronger hydrogen bonding of the water molecules at the sapphire/ice interface.\[104\]

Recently, it has been reported that ice adhesion increases with a decrease in temperature.\[116\] This is not very obvious because one could imagine that once ice is frozen next to a solid surface, the bond that exist at that interface is set. However, this report shows that something more is happening on a molecular level once the water is frozen. With SFG, we have investigated the effect of
temperature on the interaction of ice with sapphire surface. Figure 4.3 shows the cooling of water in SSP and PPP polarizations. The SSP spectra has been offset for clarity while the PPP spectra are only offset between ice and water spectra. It is quite clear that as temperature decreases, the SFG signal intensity increases. Similar signal attenuation has been observed for bulk ice at low temperature using Raman spectroscopy and is assigned to an in-phase collective mode.[67] This is in agreement with what we observe here. By decreasing the thermal energy of the system, the coherence length of the water molecules increases. In other words, the crystalline regularity of ice increases with decreasing temperature (collectivity extends over more OH vibrational modes). This means that the hydrogen bond strength at the interface increases for all the water molecules present. That will in turn, increase the interaction of water with the solid surface, and adhesive energy. The results in Figure 4.3 could explain the increasing adhesion strength with decreasing temperature.

Finally, the heating of frozen water is discussed. From the above data, we know that the coherence length increases with decreasing temperature. However, a question that could be asked is what happens to the ice structure as temperature is increased? Figure 4.4 shows the heating spectra of ice to liquid in SSP and PPP polarizations. The SSP spectra has been offset for clarity while the PPP spectra are only offset between ice and water spectra. It is observed that the signal intensity decreases slowly as temperature is increased. This is the exact reverse of the cooling spectra. As thermal energy is injected to the system, coherence length decreases, which can be interpreted as a decrease in signal intensity. In these measurements, close attention was paid to whether surface premelting occurred.
Figure 4.4: SFG spectra collected in SSP (a) and PPP (b) heating cycles. The data were collected with temperature increment of 1°C (using a 4°C/min heating rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (filled circles) are shown. The SSP spectra has been offset for clarity whereas the PPP spectra is only offset between water and ice.

However, at -1°C the spectral feature of the ice is still considerably different from water spectra. Hence we conclude that there is no observable surface premelting of ice next to sapphire surface. If there is, it would be very close to the bulk melting temperature of water (0°C).

4.3 Conclusion

For the first time, freezing of water next to sapphire surface is examined using SFG. We observe that water is structured next to the solid surface even without a surface charge. The SFG signal intensity increases with decreasing temperature. This shows that there is increase in the in-phase collective vibration at the interface. This could explain the increase in adhesion as temperature is decreased. Interestingly, no surface premelting of ice next to the sapphire surface is observed. We believe that the premelting could be very close to the bulk melting
temperature. A computer simulation could help further our understanding in this respect.
CHAPTER V

FREEZING AND MELTING OF WATER NEXT TO CHARGED SURFACES

5.1 Introduction

Water is the most important liquid on earth and its interaction with charged surfaces influences key processes in biology, electrochemistry, geology, and technology. [41, 117, 118] For biomolecular self-assembly, it has been shown that aggregation of protein molecules is controlled by the orientation of water molecules, which is influenced by the net charge on the protein surface and not by the protein-protein interactions.[118] Interestingly, the interaction of water molecules next to positively and negatively charged surfaces are not the same. In a dielectric continuum, the strength of an electric field should not depend on the orientation or the sign of the charge. However, these studies point that the orientation of water does make a difference and coincidently, most macromolecules and lipid bilayers in the cells are partially negatively charged. In addition, the other most important interface, oil-water or hydrophobic-water interfaces are also negatively charged due to migration of OH\(^-\) groups to the interface.[42, 119] Scheu et al.[45] recently reported an intriguing asymmetry for tetraphenylborate (TPB\(^-\)) and tetraphenylarsonium (TPA\(^+\)) ions in water. Although these two ions are very similar in size and hydrophobic character, because of the charge differences, water molecules forms stronger hydrogen bonds with negatively charged TPB\(^-\) ions compared with TPA\(^+\).[45]
Recently, Ehre et al.\cite{29} specifically explored the role of charged surface on freezing of water and showed using specular X-ray diffraction (XRD) that the nucleation of ice was different for negatively and positively charged surfaces. These differences resulted in lower freezing temperature of water next to negatively charged surfaces. This experiment also points out that the water molecules pointing with hydrogen facing towards or away from the surface also influences the formation of ice and the differences in freezing temperatures.\cite{29} We also reported recently on directly measuring the freezing of water next to charged Al$_2$O$_3$ (sapphire) surface using sum frequency generation (SFG) spectroscopy.\cite{p} SFG, a second-order nonlinear technique, is only active where there is a breakdown in inversion symmetry, which makes this technique useful to study the structure of water molecules near surfaces and interfaces.\cite{6, 46, 50, 80, 93, 105, 115, 120} In these studies NaOH was used to adjust the pH so that we could measure the freezing behavior of water next to both negative and positively charged sapphire surfaces without having to change the surface chemistry. We observed that the SFG intensity of ice was attenuated in comparison with water signals before freezing. This was opposite to what was observed next to positively charged sapphire surfaces. We concluded that protons are disordered in the ice crystals next to negatively charged surfaces. However, the origin of proton disorder was not identified. Two hypothesis were suggested. First, there is a possibility of Na$^+$ ions migrating to the sapphire interface and influencing the ordering of frozen water molecules. The second possibility could be due to orientation of water and the fact that freezing of water when the hydrogen atoms pointing towards the surface is inherently different than for hydrogen pointing inwards. Both these arguments
were supported by the fact that the influence of ions on water structure has been well studied with the ranking arranged based on the Hofmeister series. Na⁺ ion is one of the ions that disturb the structure of water the most based on the size and charge density of ions. Experiments using phase sensitive SFG (PS-SFG), which is sensitive to the average orientation of water molecules at interfaces, observed a flip of the OH bonds towards the silica surface after melting of ice. [69, 106] Therefore, in a situation where the water molecules are strongly bonded to a negatively charged surface, such a flip of the water dipoles during freezing could also cause the protons to disorder. In other words, such an orientation of water can create a barrier to forming proton ordered ice crystals because it has to overcome the strong electrostatic interactions to rearrange the water molecules.

To distinguish whether the ions or orientation of water is a dominant factor in attenuation of the ice signals, we present here experimental data on two other ions which are known to be weak disrupters of water structure based on the Hofmeister series, cesium (Cs⁺) and tetramethylammonium (N(CH₃)₄⁺) ions. We used hydroxides of these two ions to adjust the pH such that the sapphire surfaces is negatively charged. In addition, we studied ammonia-water solution next to sapphire surface because it is known that ammonia is able to bond to the aluminol groups and polar order water molecules with the OH groups of the ice facing towards the bulk.[69] This control of water orientation should exhibit strong proton ordered ice structure and a high intensity of the ice peak. Finally, we will discuss SFG spectra for water and ice next to negatively charged mica surface. Since mica is negatively charged, there is no need to use hydroxide solutions to adjust pH and the structure of ice should be directly related to the surface charge.
5.2 Results and Discussions

Figure 5.1 shows the spectra of water and ice next to positively (a) and negatively (b, c, and d) charged sapphire surfaces. The empty squares and solid circles represent spectra of water and ice, respectively. The positively charged sapphire was prepared using HCl solution to adjust the pH to 3.3. The negatively charged sapphire surfaces were prepared using NaOH, CsOH, and tetramethylammonium hydroxide. The data for HCl and NaOH were discussed in our previous publication and here we briefly describe the peak assignments for water and ice next to the sapphire interface. The water spectrum (Figure 5.1a) has two peaks in the hydrogen bonded region (3000–3600 cm\(^{-1}\)). The peak at 3200 cm\(^{-1}\) corresponds to strong hydrogen bonding OH stretching modes of water molecules at the solid surface and the 3450 cm\(^{-1}\) peak is assigned to weak hydrogen bonding OH stretching modes of water near the interface.[50, 54, 121] These peaks are similar to those observed at the water/air interface. The only difference is the peak at 3720 cm\(^{-1}\). At water/air interface, this peak is assigned to ‘dangling’ OH stretching mode.[122] However, on sapphire/water interface, such a peak is attributed to free surface OH groups.[40, 51–53] These free surface OH groups form very strong bonds hence do not participate in hydrogen bonding with the interfacial water molecules.[40] These groups are only deprotonated at relatively high pH.[? ] This is very unlike silica silanol groups which when immersed in water, even at low pH, are easily deprotonated (due to low isoelectric point for silica).[50] Recently, it was reported that while the assignment for the sapphire surface OH is correct, some portion of the peak should be attributed to free water OH oscillators at the sapphire surface.[54] We would like to note that there are various interpretations
of the water peaks, especially at the water/air interface. [7, 109–111] However, at the solid/water interface, water molecules have been shown to structure even in the absence of charge.[55] In the presence of charge, the local electric field extends further and orients water molecules deeper in the bulk.[55, 57]

For CsOH system, the water spectrum is similar to that of NaOH solution, and the 3450 cm$^{-1}$ peak is absent (Figure 5.1c). There is however, a small rise at around 3720 cm$^{-1}$ due to partial deprotonation of alumino groups at pH 10. Figures 5.1d and 5.2 show the SFG spectra for N(CH$_3$)$_4$OH solution with a soft cation N(CH$_3$)$_4^+$ using SSP and PPP polarizations, respectively. The liquid spectra in both polarization are similar except the shoulder at 3450 cm$^{-1}$. In general SSP polarization shows stronger symmetric vibration in comparison to asymmetric vibration. When we freeze the solution, four peaks are observed in the PPP spectrum at 2933 cm$^{-1}$, 3026 cm$^{-1}$, 3200 cm$^{-1}$, and 3450 cm$^{-1}$. The first two peaks, 2933 cm$^{-1}$ and 3026 cm$^{-1}$, are tentatively assigned to CH$_3$ symmetric and asymmetric stretch, respectively.[123] For the SSP, these two peaks are not clear and they are merged with the shoulder of the broad water peaks. It is possible that the water signal overshadowed any signal from the C-H stretch of N(CH$_3$)$_4^+$ in the water spectrum. It became apparent only after the significant signal attenuation in ice.

Upon freezing, the ice peak (Figure 5.1a) which appears at 3150 cm$^{-1}$ is assigned to hydrogen-bonded stretching modes of the water molecules. The exact nature of the water molecules contributing to this intense peak was not known until quite recently. Through seminal work by Buch et al.[70] and Shultz et al.,[11, 71] bilayer stitching bonds between water layers on the basal face (ice/vapor interface)
were found to be responsible for this peak. MD simulations by Ishiyama and Morita et al.[72, 73] on ice/vapor interface also found that charge transfer between the bilayer stitching water molecules are important for the SFG signal. We note that there are currently no MD calculations for the solid/ice interface. However, due to spectral similarities, we have used the same assignment for the ice formed next to the sapphire surface.

Based on the above assignment, it is clear that ice spectra in Figure 5.1a are quite different for the spectra collected next to the negative charged surfaces (Figures 5.1b, c, and d). While signal intensity is expected to increase (Figure 5.1a), on negatively charged sapphire surfaces, the ice SFG signal intensity is about an order of magnitude lower than that of water. This indicates that the ice is proton disordered at the interface. Ice formed at atmospheric pressure exists as hexagonal ice (Ice Ih). Though this ice Ih is crystalline, there remains some residual entropy that allows the water molecules to rotate. This leads to protons being disordered in the ice crystal. Pauling[113] produced a statistical model of hydrogen atom positions as suggested by Bernal and Fowler.[114] According to the Bernal-Fowler ice rule, a large number of configurations exist in ice Ih due to the many different distribution of hydrogens in relation to oxygen atoms. Based on the SFG results we conclude that the protons are ordered next to positively charged surfaces while they are disordered next to the negatively charged surfaces. Since these results are similar for both strong and weak ions, this shows that the surface disorder of ice is not due to specific cation effect.

We believe that the decrease in the SFG signal for ice suggests an intriguing possibility that the orientation of protons towards the negatively charged
Figure 5.1: SFG spectra collected in SSP polarization during cooling of hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution. The changes in the SFG spectra were measured for pH 3.3 (a) and 9.8 (b). The data were collected with temperature increment of 1°C (using a 4 °C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. SFG spectra collected in SSP polarization during cooling of cesium hydroxide solution (CsOH) (c) and tetramethylammonium hydroxide solution (N(CH$_3$)$_4$OH) (d). The data were collected with temperature increment of 1°C (using a 0.3 °C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (solid circles) are shown with their corresponding temperatures. The freezing transitions temperatures for the two pH conditions were between -5 and -6 °C.
Figure 5.2: SFG spectra collected in PPP polarization during cooling of tetramethylammonium hydroxide solution (N(CH₃)₄OH). The changes in the SFG spectra were measured for pH 10. The data were collected with temperature increment of 1°C (using a 0.3 °C/min cooling rate) and a 30 minute equilibration time, before collecting the SFG spectra. The spectra for water (empty squares) and ice (solid circles) near the freezing are shown. The freezing transitions temperatures were between -5 and -6 °C.

Sapphire substrate may result in surface ice layer with disordered proton. Ehre et al.[29] reported on the freezing of water molecules on negatively and positively charged LiTaO₃ surface. Using XRD, the authors observed that freezing was initiated at the water/vapor and water/LiTaO₃ interfaces on negatively and positively charged surfaces, respectively. They attributed this difference in nucleation sites to the orientation of water molecules on the LiTaO₃ surface. Although we have not directly measured the orientation of the water molecules next to the sapphire substrate, Wei et al.[9] have used a phase sensitive SFG to show that upon melting the hydrogen molecules that were facing the bulk flip to point to the silica substrate. This implies that for negative charged surfaces, the water has to flip its
orientation upon freezing. We believe this would lead to a proton disorder and this is reflected in weaker SFG intensity for ice next to negatively charged surfaces.

To confirm that orientation is playing an important role and not the cations used to increase pH of the solution, we have collected SFG spectra for freezing of water for two additional systems; ammonia/water solution and negatively charged mica surface. Wei et al. reported that when ammonia/water solution was frozen next to silica surface, there was a three-fold increase in the ice SFG signal intensity.[9] This was explained due to ammonia molecules hydrogen bonding with the surface silanol groups and orienting the water molecules with the protons facing the bulk. Su et al. used similar explanation to describe the strong SFG signal observed for ice grown on Pt(111) surface.[115] Figure 5.3 shows the ammonia/water solution and ice spectra next to sapphire surface. The water spectrum (empty squares) shows highly ordered water molecules. In aqueous solution, ammonia deprotonates a small amount of water to form ammonium hydroxide. These OH$^-\ $ions deprotonate some of the sapphire hydroxyl groups to make the surface negatively charged. When the solution is cooled to form ice, the ice SFG signal intensity rises contrary to what is observed on negatively charged surfaces. This further suggest that for the strong ice peak at 3150 cm$^{-1}$ to be observed, water molecules have to orient with their OH bonds pointed towards the bulk. This is consistent with the hypothesis that some of the NH$_3$ molecules are able to hydrogen bond to aluminol groups and orient water molecules at the interface.[9] We also find that the incorporation of ammonia molecules into the ice is rate dependent and the SFG intensity for ice was higher at faster freezing rate (Figure 5.3).[9] We have not directly observed the N-H symmetric peak
Figure 5.3: SFG spectra collected in SSP polarization during cooling of ammonia-water solution. The changes in the SFG spectra were measured for pH 10. Two freezing rates are presented; 5 °C/min (empty circles) and 10 °C/min (solid circles). For each rate, the solution is cooled from 20 °C to -40 °C. This figure shows that the incorporation of ammonia into the ice structure at the sapphire surface is rate dependent.

(at 3312 cm\(^{-1}\) [124]) possibly due the high intensity of the ice signal which may have overshadowed the N-H peak. In Figure 5.4, we show an illustration of how ammonia is able to order water molecules in ice at the sapphire surface.

To emphasize the role of negatively charged surface in controlling the ice formation, we performed experiments on muscovite mica surface. Mica is atomically smooth surface with an intrinsic negative charge density of -0.33 C/m\(^2\) due to the isomorphic substitution of silicon by aluminum atoms.[125] In air, the charge is compensated by potassium and to a lesser extent, sodium ions. In aqueous solution, the surface charge is considerably less than -0.33 C/m\(^2\) due to the adsorption of counterions to the surface charge sites.[125] However, in water
Figure 5.4: Illustration of NH₃-doped ice near sapphire/ice interface. The bound ammonia molecules are able to polar order water molecules significantly increasing the SFG signal intensity. This conformation also changes the dipole alignment of what would be on a negatively charged surface.

with considerable less ions (deionized water), potassium ions become hydrated and dissociate from the mica surface.[126, 127] The surface charge decreases with decreasing pH. The point of zero charge (PZC) for mica is still under debate but it is generally assumed to be 3.[128] Based on this, we studied both the water and ice structures on muscovite mica using deionized water of pH around 6. The slight acidity is derived from dissolved carbon dioxide in the solution. Figure 5.5a shows the spectra of water on mica in SSP and PPP polarizations. There are two main peaks. The red-shifted peak at 3150 cm⁻¹ is attributed to strong hydrogen bonded water molecules normally referred to as icelike and the peak at 3450 cm⁻¹ is assigned to the weak three or low coordinated liquidlike water molecules, similar to water on sapphire surface. The PPP polarization (empty squares), which is sensitive to both symmetric and asymmetric water stretching modes shows both icelike and liquidlike water molecules. The SSP polarization (emptry circles) which corresponds to molecules normal to the surface shows highly ordered water next to the mica surface. This assessment is in line with data.
from scanning polarization force microscopy (SPFM)[129, 130] and first principle molecular dynamics simulation (MD)[59] where water molecules adsorbed on mica forms stable icelike monolayers.

SFG measurement of adsorbed water molecules was first performed by Miranda et al.[131] The authors observed that at 90% RH (relative humidity), the monolayer formed on the mica surface was an ordered icelike structure similar to what was predicted by molecular dynamics simulation.[59, 131] A recent study of water/muscovite mica interface using SFG also reported on the observation of icelike water molecules next to mica surface and is consistent with the results reported here.[60] Figure 5.5b shows the SFG results for water and the ice structure next to the mica surface using SFG. Upon freezing the SFG signal intensity decreases and the peak is slightly blue-shifted. This sudden decrease in signal intensity is consistent with the hypothesis that proton disordering next to negatively charged surfaces surface reduces the intensity of ice. It is interesting that liquid water next to negatively charged surfaces are highly ordered due to the surface electric field. However, molecules in ice are proton disordered due to the strong interaction of water with the surface and the mechanism of ice formation. Finally, we would like to comment on the structure of water next to mica just before freezing. Very recently, Abdelmonem et al. reported that water next to mica increases it structural order before the freezing transition.[61] We show in Figure 5.5c the SFG signal intensity at mica/water interface as a function of temperature during cooling (blue curve) and heating (red curve) at 0.3°C/min. Our experiment shows no apparent increase in signal intensity as the temperature is decreased. This is different from what has been reported using second harmonic
Figure 5.5: (a) SFG spectra of water on mica collected in SSP (empty circles) and PPP (empty squares) polarizations. (b) SFG spectra collected in SSP polarization during cooling of water. The data were collected with temperature increment of 1°C (using a 0.3 °C/min cooling rate) and a 30 minute equilibration time, before collecting the spectra. The spectra for water (empty squares) and ice (solid circles) near the freezing are shown. (c) Variation in SFG intensity are plotted using SSP polarization and IR frequency of 3150 °C during the cooling (blue curve) and heating (red curve) cycles. These measurements were done at cooling and heating rate of approximately 0.3°C/min.

generation technique.[61] In all conditions reported here, the melting temperature of ice is close to 0°C.
5.3 Conclusions

Water and ice in contact with charged surfaces are ubiquitous on earth and here we show how that the orientation of water molecules next to negatively charged surfaces have a profound effect on the surface structure of ice. By using surface sensitive infrared-visible sum frequency generation spectroscopy (SFG) we show that at high pH the ice signals are attenuated compared to the water signals. This attenuation is not due to the cations added to increase the pH. However, it is due to the orientation of water molecules in contact with negatively charged surfaces, which leads to proton disordered ice phase. We have shown using ammonia that if this orientation of water was reversed and in the same direction as neutral and positively charged surfaces, then the ice signals are actually enhanced several orders of magnitude compared to water. On mica, which is inherently negatively charged, the ice signals were again attenuated compared to liquid water, indicating that it is negative charge which is responsible for the attenuation rather than the cations added to increase the pH. In comparison the ice signals are much larger than water signals next to positively charged surfaces. These results have important implications in designing surfaces to reduce ice adhesion\textsuperscript{[29]}, understanding processes involved in cloud seeding, and movement of glaciers.
6.1 Introduction

Salt and water interactions are of great significance to climatology, geology, biology, and many other fields of science. For example, hydrated NaCl particles are better nuclei for cloud formation than non-hydrated salt particles.\[132, 133\] Ozone depletion in the stratosphere has been linked to interactions of nitric acid salts with ice.\[62\] Magnesium sulphate hydrates found within the saline deposits on Mars has provided information on the history of water on Mars.\[134\] In geology, identifying the salinity of various fluid inclusions can lead to greater understanding of diagenesis, metamorphism, and hydrothermal processes.\[135, 136\] The formation of salt hydrate clusters has been studied using infrared (IR)\[3, 137, 138\] and Raman spectroscopy.\[4, 136\] Frequency shifts and the absorption strength of the O-H stretching vibrations observed in the IR measurements have been used to study the nature or strength of hydrogen bonds.\[138, 139\] and IR spectroscopy has been used to measure the relaxation time of O-H stretching in NaCl hydrate to study the behavior of confined water.\[140\] Raman spectroscopy has also been used extensively to study fluid inclusions in minerals and rock formations.\[4, 135, 136, 141–144\]
Although many studies have enumerated the importance of studying the freezing of salt solutions near surfaces, there has been no direct experimental measurement of hydrates freezing near solid surfaces.\cite{62, 145} Here, we report for the first time the use of infrared-visible sum frequency generation (SFG) spectroscopy to study the freezing of salt solutions next to sapphire substrates. Sapphire is a model substrate for studying geochemical \cite{146} and catalytic processes,\cite{147} and is transparent in visible and IR spectral region, and serves as a good substrate for SFG measurements. We have observed the segregation of salt solution in the coexisting phase region of ice and brine, and the subsequent freezing of NaCl hydrates next to sapphire substrates. The position of the hydrate peaks in the SFG spectra of the surface hydrates are similar to those reported for NaCl dihydrate crystals using IR and Raman spectroscopy. The similarities in the melting transition temperatures suggest that the concentration of NaCl salt solutions in contact with sapphire substrates before freezing must be similar to the eutectic concentration of NaCl salt solution. We believe that this study increases our understanding of the influence of solid surfaces on the nucleation and freezing of salt solutions and the effect of salt ions on the structure of interfacial ice.

6.2 Results and Discussions

Figure 6.1(a and b) shows the SFG spectra collected during the cooling of 0.1 M NaCl solution in contact with a sapphire substrate using SSP and PPP polarizations. The SSP and PPP polarizations provide complementary information and could be useful in interpreting the orientation of molecules. For the salt solution in the liquid state (empty squares), three main peaks are observed, at
Table 6.1: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for SSP polarization in the cooling cycle

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3200 cm⁻¹, 3450 cm⁻¹, and 3720 cm⁻¹. The peak at 3720 cm⁻¹ has been assigned to hydroxyl groups on the sapphire surface.[40, 107] The peaks at 3200 and 3450 cm⁻¹ were attributed to strongly tetrahedrally coordinated (ice-like) and lower coordination (liquid-like) hydrogen-bond stretch, respectively.[6, 50] However, alternate assignments for the hydrogen bonded region have been discussed recently in the literature. [7, 108, 109, 111] The SFG spectra of 0.1 M NaCl solution show stronger ice-like peak at 3200 cm⁻¹ in comparison to the liquid-like peak at 3450 cm⁻¹. For spectra collected at -10°C, the ratio of ice-like and liquid-like peaks changed and the SFG intensity dropped (Figure 6.1). Upon further cooling, we observed a very sharp peak near 3410 cm⁻¹. This sudden change in structure indicates crystallization of hydrates.

Table 6.3 summarizes the assignments for NaCl dihydrate crystals using IR and Raman spectroscopy. There are four main peaks observed at 3530–3540 cm⁻¹,
Figure 6.1: SFG spectra collected in SSP (A) and PPP (B) polarizations during the cooling cycle. The empty squares and filled circles correspond to temperatures where salt solution or NaCl hydrate are in contact with the sapphire substrate, respectively. The solid lines are the fits using the Lorentzian equation and the fitting results are summarized in the supporting information (Tables 1 and 2). The freezing transition temperatures for the hydrate formation are between -25°C and -30°C.

3430–3440 cm$^{-1}$, 3420–3425 cm$^{-1}$, and 3405 cm$^{-1}$. These peaks correspond to four different positions of OH groups in the hydrate crystals, and the magnitudes of these peaks in IR spectroscopy are related to the composition and type of crystal structure. [148] The peak positions determined after fitting the SFG spectra using a Lorentzian function are also summarized in Table 1. There is one dominant peak at 3410 cm$^{-1}$ with spectral widths of 10 cm$^{-1}$ and 14 cm$^{-1}$ in SSP and PPP polarizations, respectively. The second, smaller peak is at 3530 cm$^{-1}$ with SSP and PPP spectral widths of 10 cm$^{-1}$ and 10 cm$^{-1}$, respectively. The resolution of these hydrate peaks is limited by the resolution of the infrared laser and the SFG spectrometer (8-10 cm$^{-1}$) used in these experiments. The narrow spectral
width and the similarity in the spectral signatures between IR, Raman, and SFG spectroscopy indicate the formation of NaCl dihydrate crystals next to sapphire substrates.

To measure the melting transition temperature of the NaCl dihydrate crystals, we heated the frozen sample at a heating rate of 0.033°C/min. Interestingly, around -23°C (for both polarizations, see Figure 6.2), we observed a decrease in the hydrate signal intensity, suggesting a pre-melting layer or possibly a loosening of the hydrogen bonding network in the hydrate crystals before the melting transition. When the temperature was increased further by only 1°C, the hydrate crystals melted (-22°C), showing the previously observed water peaks in the cooling experiments. The melting temperature is similar to the eutectic temperature of bulk NaCl dihydrate crystals at -21.2°C.

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Table 6.3: Comparison of NaCl dihydrate peak assignments for IR,[3] Raman,[4] and SFG spectroscopy.

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Figure 6.2: SFG spectra collected in SSP (A) and PPP (B) polarizations during the heating cycle. The empty squares and filled circles correspond to temperature where salt solution or NaCl hydrate are in contact with the sapphire substrate, respectively. The solid lines are the fits using the Lorentzian equation and the fitting results are summarized in the supporting information (Tables 4 and 5). The melting transition temperatures for the hydrate formation is -22°C.

Interestingly, we observe no ice peak at 3150 cm$^{-1}$ as one would expect upon heating and freezing ice adjacent to a sapphire substrate. [?] Additionally,
Table 6.4: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for SSP polarization in the heating cycle

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Table 6.5: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for PPP polarization in the heating cycle

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the spectral features shifted dramatically near -10°C in the cooling cycle. These observations suggest that the sample starts out with a uniform 0.1 M (0.6% NaCl) concentration of salt solution. As we cool the salt solution, we cross the phase boundary shown in the phase diagram of NaCl solution in Figure 6.3.[16] This results in the freezing of ice and the formation of brine which is more concentrated than the original salt solution at -10°C. The concentrated brine is segregated next to the sapphire interface; therefore, no ice peak is observed in the SFG spectra. This may be analogous to the freezing of water on the surface of Antarctic Ocean and the cascade of higher-density brine pushed down towards the ocean floor. For our system, the segregation of brine next to the sapphire substrate is driven by surface effects rather than gravity. As we lower the temperature below -10°C, we expect the salt concentration to increase and to follow the phase diagram (indicated by the arrows in Figure 6.3) as more water molecules are incorporated in the growing ice crystals. Eventually, the salt concentration will reach the eutectic concentration and the solution will crystallize to form hydrates. The freezing point of the hydrate crystals in our experiment is about 6°C lower than the transition reported from bulk measurements (-21.2°C). Using mass conservation we estimate that the thickness of the brine layer next to the sapphire substrate is \( \sim (c_i \ast t_c)/c_e \), where \( c_i \), \( t_c \), and \( c_e \) are the initial brine concentration, the thickness of sample cell (0.04 cm), and the concentration at the eutectic point, respectively. We estimate that there is \( \sim 10 \ \mu m \) thick layer of brine next to the sapphire substrate at the eutectic point, and the ice layer is considerably thicker than the concentrated brine layer. During the heating cycle, we observed pre-melting around 1°C before the actual melting transition of hydrate crystals at -22°C. Immediately after melting,
we expect the salt concentration to be near the eutectic concentration and then continue to decrease as we heat the solution (corresponding to the arrows on the phase diagram). The SFG spectra collected at 0°C during the heating cycle recovers back to the spectra that we obtained before the cooling cycle, indicating that after the ice melted upon heating and the solution concentration next to the sapphire substrate returned to the starting concentration of 0.1 M NaCl.

Figure 6.3: Phase diagram of NaCl solution reconstructed from CRC Handbook. [16] In the SFG experiments the salt solution was cooled below 0°C following the blue dashed line. Near -10°C (Point A), the ice freezes and we expect increase in the concentration of brine (Point B). As the temperature is decreased further, the concentration of NaCl increases as indicated by the blue dashed lines, until the eutectic point is reached. The hydrate freezes around 6°C below the temperature expected for bulk freezing of hydrates (Point C). On heating the path is reversed and the hydrates melt between -23°C and -22°C. Finally, the ice melts near zero (Point D).
6.3 Conclusions

The use of NaCl solution in cooling and heating experiments allowed us to study the effect of salt concentration on water structure at the sapphire surface. In the phase region that corresponds to the coexistence of ice and brine, the temperature can be related to the change in the concentration of the brine in contact with the sapphire substrate. After transition to the coexistence curve, there is a shift in the SFG peaks and a strong attenuation of the SFG signals. The attenuation of the SFG signal in the salt solution has already been observed at solid surfaces [149, 150] and has been explained to be due to the formation of the double layer that screens the surface charge.[151] For concentrated brine there is a decrease in intensity of the 3200 cm$^{-1}$ peak, while the 3450 cm$^{-1}$ peak increases in intensity. This could be attributed to the presence of sodium ions at the interface.[110, 152]

These experimental results raise some very interesting questions. The relative intensities of various hydrate peaks in the IR and Raman spectra are characteristic of the crystal structure. However, the selection rules of SFG are different from the IR and Raman spectroscopy and the intensity of the SFG signals depends on orientation of molecules. The microscopic susceptibility of the four hydrate sites and their relative orientation with respect to the surface need to be understood before interpreting the ratio of the different hydrate peaks in the SFG spectra. Additionally, the pre-melting layer observed here suggests one intriguing possibility that the surface transition temperatures could be different from those in the bulk.
CHAPTER VII

THE EFFECT OF WATER ON THE REORIENTATION OF POLYMER CHAINS

7.1 Introduction

Water interaction with polymeric materials have become ubiquitous in our everyday life. Polymer surface is important in membrane separation of oil and water and in recent years, biomaterial applications. Polymers are currently being used as stents, conduits, and scaffolds for generation of part or whole organs. Hence the ability to obtain molecular level information at water/polymer interface is key to the development and performance of polymeric materials.[74, 153, 154] One significant aspect of polymer/water interactions is the reorientation of the polymer chains or segments in contact with water. Contact angle measurement is usually used to characterize such reorientation due to its sensitivity to the underlying molecular structure. For example, the contact angle of a droplet of water will decrease when in contact with a polymer with polar and non-polar groups.[14, 15] This is because the hydrophobic segments of the polymer orients in air to reduce the interfacial energy.[12, 155, 156] However, in water, it is unfavorable so the polar groups migrate to the interface to reduce the surface free energy. Such restructuring of polymer chains are amplified when observing the advancing and receding contact angle. This is the cause of contact angle hysteresis on polymer surfaces.[80] The ability for surfaces to restructure can also be due to the plasticizing effects of
water. As a small molecule, water can interpenetrate the space between polymer chains allowing for segmental motions at the surface of polymers.[15]

In order to observe the polymer/water interactions, several groups have employed the use of X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), surface plasmon resonance (SPR), attenuated-total reflection Fourier transform IR (ATR-FTIR), and sum frequency generation (SFG) spectroscopy.[14, 15, 80, 157, 158] The latter technique, SFG, has established itself as a powerful and most successful tool for probing surfaces and interfaces. SFG is a second order nonlinear optical technique that involves mixing a short-pulse high intensity visible laser ($\omega_{\text{vis}}$) with a tunable infrared laser ($\omega_{\text{IR}}$). Based on the dipole approximation, the SFG signal, at the sum of $\omega_{\text{SFG}}=\omega_{\text{vis}}+\omega_{\text{IR}}$, is only generated at interfaces in systems where the bulk is centrosymmetric.[89–93] By combining SFG with a total internal reflection geometry, this technique offers the ability to study the structure of polymers at surfaces and buried interfaces.[98, 99]

Wang et al., were the first to use SFG to observe surface restructuring or lack thereof of poly(methacrylates)s in contact with water.[14] For example, the authors observed no surface restructuring for poly(methyl methacrylate)(PMMA) in water. However, when poly(n-butyl methacrylate) (PBMA) was brought in contact with water, the surface structure was significantly different from that of PBMA/air interface. It is argued that the differences in surface restructuring for these two polymers stems from the difference in glass transition ($T_g$). PMMA has a $T_g$ of about 105°C while $T_g$ of PBMA is 17°C. In this case, PBMA is mobile at the experimental temperature (room temperature) and can respond to the presence of water while PMMA has a rigid structure at room temperature. Several publica-
tions coming from the Chen Laboratory have reinforced the relationship between water-induced restructuring and polymer Tg.\cite{83} Interestingly, literature from the Tanaka Laboratory presents a different picture at polymer/water interface.\cite{15, 84} Recently, Horinouchi et al. reported on the surface dynamics of PMMA in contact with water.\cite{15} The authors observed the reorientation of the ester methyl side chain by placing the more hydrophilic carbonyl group to the interface with water. The measured activation energy for surface reorganization was found to be much lower than in air and in bulk. The water as a plasticizer and the need to decrease surface energy was used to explain the segmental chain motions observed here even at room temperature. However, these results contradict what was observed before.\cite{83} It has been suggested that the contact angle change observed in PMMA could be due to water absorption.\cite{159, 160} This shows that despite the inroads made in understanding polymer surfaces, there still remains unresolved issues that are key to various applications in science.

In this work, we have used SFG and contact angle measurements to elucidate the molecular structure of poly(n-butyl α-hydroxymethyl acrylate) (PHNB) in contact with water. Unlike the multicomponent systems mostly studied for surface restructuring in water,\cite{12, 81} PHNB is a single component system with hydrophilic and hydrophobic side chains in each repeating unit, giving it a unique amphiphilic character. The pendant chains are composed of ester butyl and hydroxymethylene groups. Due to this amphiphilic nature, a decrease in water contact angle is expected over time.\cite{15} In air at room temperature, the surface should be rigid (Tg of 80°C) and dominated by the ester butyl group. However, in the presence of water, the hydroxymethylene groups should migrate to the surface to
reduce surface free energy and interact with water. Since SFG and contact angle measurements are sensitive to the surface, any changes in the molecular structure should be observed. This polymer is especially synthesized for biomedical application and the surface reorientation of this polymer in water will determine its utility. The synthesis of this polymer has already been published.[85]

7.2 Results and Discussions

One of the directs methods of studying surface restructuring of polymer thin films is contact angle measurements. For a film of a multicomponent polymer, the surface is understandably covered with more hydrophobic component in air.[12, 80, 81, 155, 156] However, once the film is exposed to water, the hydrophilic moieties tend to segregate at the water interface in order to minimize the interfacial energy, hence decreasing the contact angle. Monitoring the contact angle changes with time gives the idea about dynamics involved in surface restructuring. Figure 7.1 shows the time dependence of contact angle ($\theta$) for PHNB film. The $\theta$ value shows an initial exponential decrease, followed by a power curve (a monotonous decrease of contact angle with time). The power law decrease in $\theta$ is assumed to be due to changes in the surface tension of the probe liquid with time, with water evaporation dominating.[15, 161, 162] This means that this decrease has no connection with the effect of surface restructre. To minimize the evaporative loss from changing the surface tension with time, the substrate containing droplet was kept under a quartz cuvette enclosure. The enclosure contained a small water reservoir to keep relative humidity constant.
To obtain useful information from the curve, we have used eq. 7.1 to fit the experimental $\theta$-t relation, a treatment given previously for contact angle dynamics on polymer surfaces.[13, 15]

$$\theta(t) = (\theta_{ini} - \theta_{ter}) \exp(-t/\tau) - kt + \theta_{ter}$$  \hspace{1cm} (7.1)

Here, $\theta_{ini}$ and $\theta_{ter}$ are $\theta$ values at $t = 0$ and the terminal value of $\theta$ in a quasi-equilibrium state over an exponent, respectively. $\tau$ is the time constant for the $\theta$ decay in the initial stage and $k$ is a constant over the corresponding monotonic $\theta$ decrease due to evaporation. Fitting of the experimental data using eq. 7.1 shows the $\theta_{ini} = 77.6$, $\theta_{ter} = 76.8$, and $\tau_{\text{quasi-equilibrium}} = 2.1$ min. We hypothesize that this small change in contact angle over ca. 2 min is due to slow restructuring of PHNB. The reason for the slow dynamics could lie in the glassy nature of the polymer at room temperature. We will elaborate on this point later in the in the text.

To provide direct evidence of surface restructuring and identify the molecular origin of the contact angle decrease, we used sum frequency generation spectroscopy to probe the polymer/water interface. Figure 7.2 shows SFG spectra.
in PPP polarization for PHNB at air, in D$_2$O, and again at air interface after drying by N$_2$ gas. The peaks seen at air surface are 2885 cm$^{-1}$, 2945 cm$^{-1}$, and 2975 cm$^{-1}$. They are assigned to symmetric, Fermi, and asymmetric vibrations of ester butyl CH$_3$ group. The peak at 2910 cm$^{-1}$ is assignable to asymmetric vibrations of ester butyl CH$_2$ group. It can be argued that the peak at 2910 cm$^{-1}$ could also be associated with the $\alpha$-CH$_2$ attached to -OH group. However, the presence of -OH groups shifts the symmetric and asymmetric vibrations of CH$_2$ groups to 2880 cm$^{-1}$ and 2940 cm$^{-1}$, respectively, as identified form IR assignments for ethylene glycol.[163]. Moreover, the absence of any features in the region corresponding to -OH stretching vibrations (3000-3200 cm$^{-1}$) suggest that -CH$_2$-OH pendant group is not showing up at the air interface. When the polymer is exposed to D$_2$O, different peaks appear in the spectrum. A peak at 2875 cm$^{-1}$ could be from symmetric vibrations of $\alpha$-CH$_2$ group attached to -OH. The negative peak at 2970 cm$^{-1}$ is from asymmetric vibrations of ester butyl CH$_3$ group. There is also
a broad peak in the -OH stretching vibrations region centered around 3120 cm$^{-1}$. We attribute this to the presence of the hydroxylmethylene at the polymer/water interface. This region was featureless at the air interface and since we are using D$_2$O, any peak in to OH vibration region can only be from the -OH groups present in polymer. When the polymer is dried by blowing a N$_2$ jet over the sample, identical spectral features to that of original polymer/air interface is obtained. Peaks at 2885 cm$^{-1}$, 2945 cm$^{-1}$, and 2960 cm$^{-1}$ are assigned to symmetric, Fermi, and asymmetric vibrations, respectively, of CH$_3$ group and a peak at 2910 cm$^{-1}$ is assigned to asymmetric vibrations of CH$_2$ group present in ester butyl side chain.

Figure 7.3 shows SFG spectra in SSP polarization for PHNB under identical conditions as of Figure 7.2. At air interface, peaks at 2875 cm$^{-1}$ and 2940 cm$^{-1}$ are assigned to symmetric and Fermi (CH$_3$(s) and CH$_3$(F)) stretches, respectively. A shoulder at 2850 cm$^{-1}$ and a peak at 2910 cm$^{-1}$ can be attributed to the symmetric and asymmetric vibrations of CH$_2$ present in ester butyl side chains.[158, 164] Since SSP polarization is sensitive to the molecular groups oriented normal to the surface, it appears that the ester butyl group tends to orient upright at the
air interface to minimize the interfacial energy.[14] The SFG spectrum of poly(n-butyl acrylate) (PnBA) in SSP polarization, shows exactly the same peaks. Since PnBA has a similar structure as of PHNB except the α-hydroxymethyl group, identical SFG spectra for these two polymers suggest that PHNB has an ordered n-butyl pendant group instead of the hydroxymethylene pendant group at the air surface.[158] When D$_2$O is introduced, the spectral features change substantially. There appears a peak at 2870 cm$^{-1}$ along with a negative peak at 2980 cm$^{-1}$. No apparent changes are observed in the -OH stretching region in the SSP polarization. The peak at 2870 cm$^{-1}$ could be assigned to symmetric hydroxymethylene vibrations and a negative 2980 cm$^{-1}$ to asymmetric vibrations of ester butyl CH$_3$ group. Upon drying, peaks in the SSP spectrum revert back to that obtained at the air interface, suggesting that surface restructuring is reversible. A weak peak is seen at 3150 cm$^{-1}$ perhaps due to some population of -OH groups still appearing at the surface.

Figure 7.4 shows SFG spectra in SPS polarization for PHNB under identical conditions as that of Figure 7.2. SPS polarization is sensitive to asymmetric
vibrations and likewise dominant peaks at 2910 cm\(^{-1}\) and 2960 cm\(^{-1}\) are identified as asymmetric stretches of ester butyl CH\(_2\) and CH\(_3\) groups, respectively. Changing the environment to D\(_2\)O causes a peak at 2930 cm\(^{-1}\) to show up, tentatively assigned to asymmetric vibrations of \(\alpha\)-CH\(_2\). Peaks at 3090 cm\(^{-1}\) and 3150 cm\(^{-1}\) are assigned to different modes of H-bonded -OH groups from the polymer with surrounding D\(_2\)O. Again upon drying, peaks at 2905 cm\(^{-1}\) and 2960 cm\(^{-1}\), similar to those seen at the polymer/air interface reappears.

Based on these results, we believe that the arrangement of the molecules at the interface is governed by interfacial energy. At polymer/air interface, hydrophobic ester butyl group has a preference to form a low energy interface, as suggested by dominant symmetric and asymmetric stretches in SSP and SPS polarizations, respectively. When water is introduced, the hydrophilic hydroxymethylene group is placed at the surface to minimize the interfacial energy. Other than the appearance of -OH peak, the presence of symmetric CH\(_2\) of the hydroxymethylene and increased contribution of the negative CH\(_3\) asymmetric peak from the ester butyl pendant chain supports the idea of surface restructuring. Upon just removal of water, without any annealing, exact reverting of the spectral features, does bolster the argument about thermodynamically driven surface restructuring.

Although the SFG data suggests the presence of surface -OH groups in the aqueous environment, the macroscopic manifestation of hydrophilicity, i.e. change in contact angle, is very subtle. As mentioned earlier, the drop in \(\theta\) over the quasi-equilibrium \(t (\tau)\) of 2 min is only c.a. 0.8\(^\circ\). We hypothesize that significant restructuring is not observed in water because the polymer is in a rigid glassy state at room temperature (Tg of 80\(^\circ\)C).[14, 83] To test this hypothesis, we heated the
polymer film above its Tg in water. As the mobility of the polymer increases, the driving force to place the more hydrophilic hydroxymethylene groups at the surface should also increase. The details of the experiment is as following: Thin films of polymer (≈300 nm) were spin coated on silicon wafers and annealed overnight at 110° under vacuum. The initial contact angle is measured. The wafers were then placed in beakers containing water and then heated to 90°C ( > bulk Tg of PHNB) (water-annealing). After 15 min at 90°C in water, the films were allowed to cool down to room temperature under water so that the extent of surface restructuring is preserved as the orientation of chains is locked up below its Tg. Then the substrates were taken out of water, gently dried by a jet of N₂ gas and then the contact angle is measured. The reversibility of the surface restructuring was checked by measuring the contact angle after 2 h of annealing in a 110°C oven under vacuum.

In Figure 7.5 we compare results of PHNB films to a another acrylate polymer, poly(vinyl n-octyl carbamate-co-vinyl acetate) (PVNODC). PVNODC
is a semi-crystalline polymer with a long side chain and is useful for creating hydrophobic surfaces for pressure sensitive adhesives. Work of Rangwalla et al. [80] has shown that the SFG spectrum of PVNODC/water interface (at room temperature in SSP polarization) has a dominant symmetric CH$_3$ (r$^+$ - 2875 cm$^{-1}$) peak over symmetric CH$_2$ (d$^+$ - 2850 cm$^{-1}$) peak that is consistent with the crystalline packing of the side chains resulting in high water contact angle. It should be noted that, r$^+$ peak corresponds to the n-octyl carbamate side group whereas the d$^+$ peak is from the backbone of the polymer. With increasing temperature, the ratio r$^+$/d$^+$ decreases and at 81°C the r$^+$ peak vanishes showing only d$^+$ peak. This was understood as order-to-disorder (ODT) temperature for side chains driven by a reduction of interfacial energy in the presence of water. When the same system was cooled down below ODT to room temperature, the intensity of r$^+$ peak did not recover suggesting the irreversible disordering of alkyl side chains in the presence of water. We decided to test the macroscopic manifestation of this phenomenon by measuring the water contact angle with the same heating-cooling treatment under water as described earlier. The pristine PVNODC showed a contact angle of 112°, a characteristic for a crystalline well packed hydrophobic alkyl side chains. After annealing under water, the contact drops down to $\approx$74° which is consistent with the irreversible disordering of the alkyl side chains to minimize the free energy at polymer/water interface. The PVNODC surface regaining its high contact angle (107°) after vacuum annealing at 90°C. This indicated that side chains had again attained an ordered crystalline packing at air interface and the polymer thin film did not degraded due to heating cycles performed under water. Corroboration between the SFG and contact angle data builds the confidence on our testing pro-
tocol of activating the surface restructuring by heating above the Tg (or ODT) of polymer and locking the structure by cooling it down to room temperature.

Based on the above success and confidence, we performed the experiment for PHNB. For PHNB, the pristine contact angle is \( \approx 78^\circ \), similar to what has been observed in the dynamic contact angle measurements at \( t = 0 \). After water-annealing, the contact angle decreased to \( \approx 63^\circ \). This change in contact angle (\( \approx 15^\circ \)) is significantly higher than the contact angle change observed in the dynamic contact angle experiment in Figure 7.1 (\( \approx 0.8^\circ \)). After reannealing in air, the contact angle reverts back to 80\(^\circ\) which may suggest that heating under water did not cause hydrolysis of the acrylate polymer and the film integrity is maintained. This proves our hypothesis that the extent of surface restructuring for the amphiphilic PHNB, with changing environment, is limited at room temperature. This is because the glassy nature acts as a kinetic barrier to the equilibrium state of -CH\(_2\)-OH group to ordering at the interface with water. However, raising the temperature above Tg results in overcoming the barrier due to enhanced segmental motion of the polymer. To validate this claim, we performed the dynamic contact angle measurements on poly(\( n \)-butyl acrylate) (PnBA), a hydrophobic analogue for PHNB with Tg of -50\(^\circ\)C (see Figure 7.6). After fitting the curve using eq. refequ:CADynamics, the \( \theta_{ini} \approx 81.9 \), \( \theta_{ter} \approx 79.5 \) over \( \tau_{quasi-equilibrium} \) of only 44.6 s. Even in this case the change in contact angle is not large. However, the timescale of surface restructuring is much shorter than the PHNB which is glassy at room temperature.

To shed light on the molecular origin of the dramatic surface restructuring observed by contact angle measurements using the water-annealing method,
we carried out SFG experiments on PHNB films with a parallel water-annealing protocol in the presence of water. In Figure 7.7, the spectrum of PHNB/air and PHNB-D/2O in PPP polarization at room temperature have been discussed earlier and are been shown here to compare the spectra taken following the water-annealing protocol. Upon to heating to 90°C, there seems to be predominantly one peak in hydrocarbon region i.e. at 2970 cm\(^{-1}\) assignable to r\(^{-}\) vibrations. There is no clear peak in -OH stretching region. At 90°C in D\(_2\)O, we would have expected rapid surface restructuring and hence a distinct polymer -OH peak. However, above Tg the polymer surface may not be well ordered and the CH\(_2\)-OH group could be completely solvated by the surrounding D\(_2\)O molecules. SFG is an order sensitive technique and not just susceptible to the number density of surface groups. Although there could be surface enrichment by polymer -OH groups under these conditions, the solvation by D\(_2\)O can disorder them. After cooling down to
Figure 7.7: SFG spectra in PPP polarization for PHNB at air (red) as annealed; with D$_2$O (yellow) at R.T.; heated to 90°C under D$_2$O (green); cooled down to 25°C under D$_2$O(blue); N$_2$ dried (purple); and reannealed under vacuum at 110°C and spectrum obtained at R.T. (black).
25°C, the PHNB-D$_2$O spectrum shows a $r^-$ peak at 2970 cm$^{-1}$ and a broad peak in the -OH vibration region centered at 3070 cm$^{-1}$ corresponding to hydrophilic pendant group of PHNB. The experimental condition for this spectrum is actually analogous to the contact angle experiment. When the surface is frozen in its reorganized state by cooling under water the SFG spectrum at polymer/water interface clearly shows dominance of polymer -OH peak. This hydrophilic nature of the surface is correctly captured by the reduced contact angle of $\approx 63^\circ$ as shown in Figure 7.7. After drying the surface with a jet of N$_2$ gas, the surface recovers to equilibrium conformation at air as characteristic by the 2880 cm$^{-1}$, 2915 cm$^{-1}$, and 2965 cm$^{-1}$ peaks. Presence of $r^+$ and $r^-$ peaks from ester butyl group is an evidence that heating the polymer above its T$_g$ under water did not cause the hydrolysis of ester linkage and the integrity of polymer is preserved. A weak peak at 3060 cm$^{-1}$ could be due to a fraction of -OH group still ordered at the surface as the complete migration away from the surface is not possible in a glassy state at room temperature. Once annealed at 110°C under vacuum, the surface regains the optimum configuration at air surface as indicated by the identical shape of the spectra in black and red.
To support our arguments about mobility of polymer surface above its Tg and how it facilitates the surface restructuring driven by thermodynamics, we perform similar SFG experiments with PnBA, which is a structural analogue of PHNB without the hydroxymethylene pendant. Figure 7.8 shows the SFG spectra for PnBA in SSP polarization with varying conditions. At air interface, peaks at 2875 cm\(^{-1}\), 2910 cm\(^{-1}\), and 2945 cm\(^{-1}\) account for r\(^+\), d\(^-\), and \(r^{fermi}\) vibrations, respectively. Lack of r\(^-\) and a very weak d\(^-\) peaks in SSP polarization suggest highly ordered n-butyl ester group perpendicular to the surface. As soon as D\(_2\)O is introduced, the spectrum at polymer/water interface shows no discernible features. In a sense, the surface is completely randomized. Upon drying by N\(_2\) stream, the spectral features are reappear at polymer/air interface, however, with much reduced signal intensity. Similar behavior was observed on the SFG measurement of poly(n-octyl methacrylate) (POMA) which has a Tg of -70°C by Wang et al.\[14\]. The authors explained that due to the increased mobility of this polymer at room temperature, the polymer backbone moved to disorder the surface when it was in contact with water. However, upon removal of water, it was found to be irreversible due to the complete nature of the disordering.\[14\] This may be what is happening to PnBA. The polymer should be very mobile at room temperature and complete segmental motion of the backbone should be expected. This is rather obvious in the rapid restructuring of the surface in water (Figure 7.6).

7.3 Conclusion

We have investigated the surface restructuring phenomenon of an amphiphilic glassy polymer, poly(n-butyl α-hydroxymethyl acrylate) (PHNB), using
contact angle and surface sensitive sum frequency generation spectroscopy (SFG). We have seen that at air surface, the polymer has an equilibrium surface structure with well ordered hydrophobic \( n \)-butyl ester pendant group. This corresponds to the instantaneous (static) contact angle of \( \approx 80^\circ \). When exposed to water, the polymer surface has a thermodynamic drive to restructure and increase the surface concentration of hydrophilic hydroxymethylene pendant group. However, this process is stalled by the kinetic barrier of the glassy nature of the polymer at room temperature resulting in change in contact angle of only \( \approx 0.8^\circ \) over two minutes. When heated to a temperature above its Tg in presence of water, the polymer surface shows dramatic restructuring as seen by a distinct peak in hydroxyl stretching vibrations region and the macroscopic manifestation of this phenomenon is decrease in contact angle by 15°. The role of kinetic barrier is also verified by demonstrating SFG and contact angle experiments on a structurally similar hydrophobic polymer, poly(\( n \)-butyl acrylate) (PnBA), with a Tg of -50°C. Change in contact angle of 2° over a few seconds and complete disordering of surface structure in water as indicated by SFG spectra, highlighted the predominance of thermodynamics in the absence of kinetic barrier.
CHAPTER VIII
CONCLUSIONS

The significance of any scientific experiment is to further the understanding of that particular field. This dissertation is no different. We believe that the results presented here will help researchers studying ice adhesion to develop better surfaces that can delay freezing or decrease ice adhesion to solid surfaces. Each results and discussion chapter has a conclusion at the end so in this concluding chapter, I shall present perspectives on our results and what they may mean.

We have coupled a temperature stage with surface-sensitive sum frequency generation (SFG) to study solid/water interfaces as temperature is decreased. This is to understand how water molecules in ice interacts with solid surfaces in order to mitigate ice adhesion to solid surfaces. SFG, a nonlinear optical technique, has been established as a versatile and powerful tool for monitoring surface molecules. Our interest in molecularly observing the interactions of water with solid surface stems from the fact that water frozen on solid surfaces present a lot of problems to transportation and infrastructure. Moreover, there isn’t effective and efficient method of getting rid of accreted ice on solid surfaces.

In Chapter 4, we show for the first time the systematic freezing of water into ice next to a neutral sapphire surface. We observe an intense ice peak at the solid/ice interface. This signifies ordered and strongly interacting water molecules are present. Moreover, as temperature decreases, the signal intensity also increases
indicating stronger interactions with the surface. This could explain the increase in ice adhesion to solid surfaces as outside temperature decreases.[19] Numerous studies on ice surfaces have shown that there exists a premelted layer below the equilibrium melting temperature. Such has been suggested for solid/ice interface. However, our results indicate that might not be the case. As we heat the ice, the spectral features become less finer but still resembles that of ice. Our results here sets the baseline for water/ice interaction with a solid surface. Any study going forward will attempt to disrupt or delay the onset of this strong solid/ice interactions.

We next discuss the freezing of water next to charged surfaces. We observe a surprisingly weak SFG ice signal next negatively charged mica and sapphire surfaces. This is contrary to what we see on positively charged surfaces. It may seem that the orientation that the water molecules adopt on negatively charged surfaces can affect the strength of ice interaction. We believe that with the lone electron pairs on the oxygen and the difference in electron density of oxygen and the two hydrogens, one should expect, at least to some level, a varied interaction with oppositely charged surfaces.[29] This could indicate that the ice adhesion on negatively charged surfaces may be less. We did not perform any ice adhesion measurements. However, experiments could be done in the future to test our prediction.

The effect of impurities on ice adhesion is enormous. This is because ice adhesion strength scales linearly with contact area. Hence, anything that can decrease the ice contact with a solid surface will also decrease ice adhesion. In Chapter 6, we observe that brine segregates to the sapphire surface during the
freezing of sodium chloride solution. The observation of brine solution present between ice and a solid surface could mean that ice adhesion strength might be significantly low. This study is the first of its kind and it provides valuable data as to the process of brine expulsion as water in the salt solution slowly (following the equilibrium phase line in the phase diagram[16]) phase separates.[19]

Finally, we discuss the implications of our results on the surface restructuring of surface polymer groups in the presence of water. The polymer in question, poly(n-butyl α-hydroxymethyl acrylate) (PHNB), has both hydrophilic and hydrophobic side groups. We expect that there will be a strong thermodynamic driving force for surface rearrangement by placing more hydrophilic groups at the water interface. We also anticipate that the kinetics of interfacial polymer rearrangement should be fast.[15] It is, however, surprising that little restructuring takes place at room temperature. The polymer surface only restructures in water above the polymer’s Tg (80°C). Our experimental protocol sets up a new platform for studying the behavior of polymer surfaces in water. The implications are important for polymeric medical devices that are autoclaved before use. Such a process could change the polymer surface functional groups, and hence its intended function.

In summary, the experiments and data presented in this dissertation are intended to further the understanding of ice interaction with solid surfaces. The studies here set up the platform allowing experiments to be performed on various published icephobic/hydrophobic surfaces in order to monitor their utility.
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