Fathoming ice

Using non-linear ultrafast spectroscopy to look at interfacial properties

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Chapter 1

Water and Ice – structure and properties

Water, a ubiquitous substance on Earth, is chemically one of the simplest compounds, yet a contentious topic of scientific research. An accurate theoretical model of water remains elusive; notably one of the top 125 questions of the 125th anniversary of Science\textsuperscript{1,2} was ‘what is the structure of water?’ Constituting three atoms, the water molecule has four sp\textsuperscript{3}-hybridized electron pairs, giving it a tetrahedral arrangement. The partial charge on the oxygen and hydrogen atoms gives the water molecule its polar character; which in turn leads to a water molecule being able to form hydrogen bonds with up to four of its closest neighbours. Hydrogen bonds can be 10-100 times weaker than covalent bonds, making quick rearrangements possible for water molecules whilst maintaining a three-dimensional cohesive structure.

Hexagonal ice, Ice I\textsubscript{h}, is the most commonly encountered solid phase of water. Ice currently is known to have 19 different crystalline structures\textsuperscript{3} under conditions of varying temperature and pressure.

Structure of water molecule

The structure of an isolated water molecule, in its gaseous state, is represented in Figure 1.1. The equilibrium O-H distance is 0.96 Å and the H-O-H angle is 104.5\textdegree; these values were deduced from the rotational components of the rotation-vibration spectrum\textsuperscript{4}. As apparent from Figure 1.1, the water structure is bent, and not linear (like CO\textsubscript{2}), and this form gives it a dipole moment.

The two H atoms and an O atom covalently bond together to form a water molecule. In its condensed states, water molecules interact to form a cohesive network via hydrogen bonds. This is a distinct type of chemical bonding that occurs when an H atom lies between two of the highly electronegative atoms like F, O, or N. Interestingly, hydrogen bonding is effective only for the first row of the electronegative atoms in the periodic table – explaining why HCl due to its larger molecular weight is not able to form hydrogen bonds and is thus a gas at room temperature. This hydrogen bonding between water molecules is what ‘binds’ the molecules together into a liquid; and accounts for the arrangements of molecules in ice.
Figure 1.1: dimensions of an isolated water molecule

A hydrogen bond, represented as O-H…O, is weaker than a covalent bond H–O. Thus the O…H distance is larger than the O-H distance. A hydrogen bond donor is the molecule to which the hydrogen is covalently bonded, and the other molecule is the hydrogen bond acceptor. Water, because of its polar nature is very effective at transferring additional charges by rearrangement of molecular configurations, by the Grotthuss hopping mechanism. This mechanism is based on the ‘relay’ of protons by a series of water molecules, instead of a single proton diffusing through water. The solvation of excess protons occurs in two limiting forms: the Eigen – where the proton is associated with one central water molecule H₂O⁺, and Zundel – where the proton is equally shared with two neighbouring water molecules forming a complex H₅O₂⁺. Proton hopping involves cooperative efforts of water molecules upto the second solvation shell for a periodic isomerization of the Eigen and Zundel structures.

Structure of ice

The structure of ice in its stable state under ordinary conditions is known as Ice-I (one), which exists in two different crystalline forms – hexagonal, which is called Ice-Ih; and cubic, called Ice-Ic. Both these forms of ice are represented in the phase diagram of water shown in Figure 1.2. Ice-Ih forms under normal pressure and temperature conditions, and is thus also the most widely-existing terrestrial form of ice – in the form of snowflakes, ice crystals in the atmosphere, ice sheets and glaciers, etc. Ice-Ic is formed by depositing vapour at very low temperatures (below 120 K). Besides these, another 15 different crystalline structures of ice have been shown to exist under varying temperature and pressure conditions; and three different types of amorphous ice (low density, high density, and very high density) have been characterized. Ice-Ih is the focus of this thesis and all references to ice in the thesis are directed to Ice-Ih, unless explicitly mentioned otherwise.

The crystalline structure of ice is comprised of oxygen atoms arranged on a hexagonal lattice, where it has four nearest neighbours at the corners of a tetrahedron. Each H₂O molecule donates two hydrogen bonds, and also accepts two hydrogen bonds, hence making a tetrahedral arrangement of hydrogens around the oxygen atom. Although a crystalline structure, a long-ranging orientational order in ice is absent.
Crystalline structure

The hexagonal crystal representation of ice is shown in Figure 1.3. Part b shows a hexagonal lattice system, with the unit cell marked in bold lines. The unit cell is enough to represent the lattice symmetry, the ‘full’ hexagonal prism arrangement comprised of three unit cells is marked in dotted lines. The water molecules with the oxygen atoms corresponding to the hexagonal unit cell are shown coloured in part a of the figure, and as is apparent from the figure, the unit cell contains 4 water molecules. When looking down perpendicular to the c-axis, the oxygen atoms stack in the sequence ABAB, the A and B layers marked on the left figure. The hexagonal rings have a puckered shape, giving the stacking sequence a bi-layered form. The unit cell elucidates that the two sides of the cell have an equal length with an enclosed angle of 120 degrees. When this property is translated to the hexagonal prism, it gives it a 6-fold rotation axis. A hexagonal system is usually referenced by Miller-Bravais lattice notation, introducing a 4th direction, written as the 3rd index. The Miller-Bravais system hence uses 4 instead of 3 indices as in the Miller notation. The usage of 4 indices makes it easier in terms of crystallographic representation to deduce plane and direction symmetry as a permutation of lattice indices.

Three different planes, that correspond to the basal, primary prism, and secondary prism planes are highlighted and indexed in Figure 1.4. The space group of hexagonal ice is P63/mmc; where the first and the second m denote the mirror plane perpendicular and parallel to the c-axis; c denotes glide planes; 6s denotes the multiplicity and screw of the pitch axes, P denotes Primitive instead of Centred structure.
The bi-layered arrangement of the oxygen atoms can be appreciated better in Figure 1.4 which shows the side views of the different plane orientations of the crystal system. It was shown that the interfacial molecules at the basal plane of ice melt in a bilayer-by-bilayer manner\(^9\), whereas those at the secondary prism plane melt in a layer-by-layer manner; and Figure 1.4 is a pictorial explanation behind that. The figure also illustrates clearly the different plane orientations of the ice crystal with molecular and crystalline representations.

**Ice rules and orientational disorder**

In 1921, Dennison, was the first person to determine unit cell parameters, and in 1922, Bragg used them to propose the structure of ice as we know now, based on positions of oxygen atoms. The determination of hydrogens atoms had to wait until 1949 using neutron diffraction. There is an inherent orientational disorder present in ice, which can be explained as follows: every individual water molecule can share its two covalently-bonded hydrogens to only two other water molecules when there are four to choose from. This
constrained arrangement can have 6 different directional configurations. The concept of disorder can be better visualized in Figure 1.5: in the left figure, the central water molecule donates two hydrogen bonds to the two water molecules above it; in its disordered phases one of them shown on its right side, it would donate to any two of the water molecules available.

Figure 1.5: left: proton ordered arrangement wherein the central water molecule donating two hydrogen bonds to water molecules above it, and accepting two hydrogen bonds from water molecules below it; right: one of the disordered phases shown; Image adapted\textsuperscript{10}.

Bernal and Fowler, in 1933, laid down basic ice rules that govern the arrangement of atoms in ice. The rules state that each oxygen atom is covalently bonded to two hydrogen atoms, and an oxygen atom in each water molecule is hydrogen bonded to other oxygen atoms, leading to precisely only one hydrogen atom between each pair of oxygen atoms. Pauling in 1935 estimated that there are \((3/2)^N\) different ways to arrange H-bonds of \(N\) water molecules, subject to the ice rules formulated by Bernal and Fowler. A disorder in the structure, thermodynamically introduces entropy in the system, which would be \(R \ln 3/2 = 0.806\) cal K\(^{-1}\) mol\(^{-1}\). This orientational disorder in the ordered lattice gives rise to distinct properties like electrical polarizability and conductivity, because of which ice is often described as a protonic semiconductor.

The presence of a disordered state also postulates the existence of an ordered equilibrium state at or before 0 K. This concern was solved in the 1980s when KOH-doped ice exhibited a proton-ordering transition at 72 K. This proton-ordered structure was called Ice-XI. The transition temperature from Ice-Ih to Ice-XI was independent of the KOH concentration, suggesting that it was required only as a catalyst. However, the requirement of ‘defects’ for the transformation process is also thought of as a violation of the ice rules.

At the surface where there is a break in symmetry, the disorder in the orientation of molecules in the ice crystal is suspected to change for electrostatic stability. Quantum chemical simulations have shown that proton ordering affects the surface energies by an order of magnitude more than the effect on bulk energies\textsuperscript{11}. The ice surface was thought to have a ferroelectric ordering, determined from neutron diffraction\textsuperscript{12} data and simulations\textsuperscript{13}, but the idea was challenged and the surface of ice subsequently is claimed to be antiferroelectric\textsuperscript{14}. Computational studies expect the surface to be proton-ordered in specific alternate arrangements, known as Fletcher pattern. Experimentalists have been in the hope of being able to confirm or negate this hypothesis. Chapter 5 is an attempt towards answering this question, using SFG spectroscopy to explore ways to characterize proton ordering, if any, at the surface of ice.
Water – absorption spectrum

This thesis is about studying the structure and dynamics of water in its liquid and solid states, using its interaction with light as the measurement tool. Water absorbs light across a wide range of frequencies, being transparent only in the visible region. Light in the UV frequency range is absorbed by water through excitation of electronic modes; in the visible region, the weak absorption of red light is caused by various combinations of overtones of intramolecular bands, giving water a slightly blue tinge. The strongest vibrational mode of water is at ~3400 cm⁻¹. Going further to the red side, the bend mode appears around 1640 cm⁻¹, followed by wagging and librational modes, and finally the intermolecular vibrations and collective motion of water molecules. At very low frequencies, corresponding to wavelengths longer than 10 m, the water starts becoming transparent again, making radio communication possible in water by sub-marines.

Vibrational modes of ice

For an ice crystal with N molecules, there would be 3 N normal modes of vibration. In a perfect crystal, the normal vibrations can be described as standing waves with a constant amplitude through the crystal and can be described by a wave vector. In an orientationally-disordered crystal-like ice, as has been described before, the intermolecular coupling constants are not periodic in space and so vibrational amplitudes are not periodic either. There are no selection rules applying in terms of the wave vector, and hence all vibrations are spectroscopically active. This explains why the Infrared and Raman spectra of ice, as shown in Figure 1.7, show an almost continuous response throughout the range displayed.

The fundamental frequencies of an isolated H₂O molecule, and H₂O and D₂O ice are presented in table 1.1, and represent the intramolecular vibrations of the water molecule. ν₁ and ν₃ depend on the force constant for stretching the covalent O-H bond: where a symmetric stretch vibrates at ν₁=3652, and the asymmetric
stretch $\nu_2=3756$ cm$^{-1}$. $\nu_2$ depends on the force constant for changing the bond angle, thereby leading to the H-O-H bending motion at $\nu_2=1595$ cm$^{-1}$. For ice, the intricate intermolecular coupling between the molecules results in a band of vibrations, which are severely complicated to disentangle and interpret. Essentially the spectrum can be divided into four distinct regions: a) intramolecular O-H stretching vibrations around 3300 cm$^{-1}$ derived from $\nu_1$ and $\nu_3$ of the isolated H$_2$O molecule; b) intramolecular bending vibration at 1600 cm$^{-1}$ derived from $\nu_2$; c) intermolecular rotational vibrations around 840 cm$^{-1}$; and d) intramolecular translational vibrations peaking at 230 and 165 cm$^{-1}$.

The stretch mode of ice has been extensively studied, because of easier acquisition of signal. Recently there is attention starting to be paid to the bend mode of ice, and chapter 4 will focus on the bend mode of interfacial ice, with an extensive temperature-dependent and polarization-dependent study. The aim is centred around finding how the bend mode responds to temperature changes, and how the differences in polarization-dependent signals can be explained.

| Table 1.1: Vibrational peak assignments for an isolated water molecule and hexagonal ice$^7$: |
|---------------------------------|----------------|----------------|----------------|
|                                 | H$_2$O vapour | H$_2$O ice     | D$_2$O ice     |
| $\nu_1$ (cm$^{-1}$)             | 3652          | 3143           | 2347           |
| $\nu_2$ (cm$^{-1}$)             | 1595          | 1640           | 1210           |
| $\nu_3$ (cm$^{-1}$)             | 3756          | 3252           | 2440           |

In chapter 6, we come back to the stretch mode, and look at the dynamics of the oscillators in the stretch mode. So far, we have only talked about static information received from spectroscopic data, but using ultrafast lasers and pump-probe experiments, time-resolved molecular information on a femtosecond scale can be measured. Methods are discussed on how these results can be modelled and interpreted, and what can we gain from them in a bigger picture.
Preparation of single-crystalline ice

Multiple methods have been reported in the literature to produce single-crystalline ice samples: surface cooling of water by rapid evaporation under reduced pressure, variants of the Czochralski technique involving elevation of a seed crystal, and growing ice via a capillary into a wider glass tube using the Sapporo or the Bridgeman techniques. Ice for all the measurements in this thesis was grown using the Czochralski method, for which the starting seed was procured using the Lake ice technique.

Lake ice

This method propagates the growth of single-crystalline ice as it would naturally on a cold undisturbed lake surface. Treated milliQ water is poured into a cleaned Petri-dish, covered and kept undisturbed in a freezer at -20°C. Over time, nucleation of ice should start, and the water starts freezing, usually from the surface, down to the bottom. Often times an eruption of the surface was seen when water at the bottom would start to freeze beneath the already-frozen surface. Under conditions of undisturbed nucleation of ice, a few centimetre-wide cubes of single-crystalline ice blocks in an overall polycrystalline sample would be formed. The largest of such a single, or poly-crystalline areas was cut off using a bandsaw in the freezer. This would act as a seed crystal for the Czochralski process to grow much larger single-crystalline boules.

In Chapter 7, the role of structural order in the efficiency of a biologically-relevant ice-nucleating agent, cholesterol, is explored using experimental and simulation methods.

Czochralski method

The Czochralski method, which involves the extraction of a seed from the melt, is widely used to produce single crystals of metals, semiconductors, salts, and synthetic gemstones. The method established in our laboratory, was applied to obtaining single-crystalline ice boules, inspired by the work of S. Roos\textsuperscript{18}. The setup involves a water bath maintained at around 0.5°C, a copper finger maintained at -14°C that acted as a heat sink and was adjustable in height and tilt angle, and a seed crystal, approximately 4 x 4 cm and 2-4 cm thick to start with. The water bath is constantly stirred to promote agitation and constant movement for thermal equilibrium and also to prevent bubble formation at the air-water interface. The copper finger is attached to a Peltier element with liquid back-cooling, allowing temperature control. Temperatures of both the bath and the copper finger are monitored throughout. The seed is melt-attached to the copper finger: the copper finger is cooled at a rate of ~5°C/minute from room temperature conditions; at ~5°C, the seed placed flat on a Teflon substrate is pressed against the copper finger, the cooling rate of which is increased to 10-15°C/minute, to avoid complete melting of the seed. The seed attaches as the surface of the seed touching the finger melts, and there is subsequent freezing as the temperature goes down. An image of the attached seed to the copper finger is presented in Figure 1.8a.

After seed attachment, the temperature of the copper finger is maintained at -14°C. Thereafter, the bottom surface of the attached seed is melted using a heat gun to create a molten layer of water, and it is translated immediately to the top of the bath using the adjustable height and tilt settings of the copper finger setup. The seed is lowered slowly to immerse only a couple of millimetres into the water bath, maintained at a temperature of around 0.5°C. The seed is allowed to stay in that position for half an hour or more depending
on the size of the boule one aims to produce. In that period, the seed stabilizes into a wider block of ice, that continues to get bigger the longer it stays. The seed is then pulled out of the water bath at an optimized rate using an automated height adjustment system that the copper finger is mounted to. The rate of extraction depends on the dimensions of the final boule size. We would like our boules to be around 8-10 cm in wide, and 10 cm long cylindrically shaped, to slice out 5 cm thick samples for experiments. For these dimensions, we had optimized the pulling rate to be nearly 5 mm per hour. Ice would usually grow over a period of 24 hours.

![Image](image1.png)

Figure 1.8: steps to making single-crystalline ice

When the boule looks satisfactory in size, the process is stopped and the ice is extracted by raising the boule out of the bath; an example of the boules produced is shown in Figure 8b. At this point, to release the boule from the copper finger, the temperature of the finger is raised to above the melting point of water to let the boule just drop from the finger, which is caught by gloved hands. The boule was kept in the freezer immediately after release from the finger, undisturbed for equilibration reasons, and to avoid immediate cracks or defects because of sudden temperature changes and handling.

Characterization of single crystals

**Cross-polarizer setup**

Ice is birefringent, thereby having an ordinary wave that has the same velocity in all directions, and an extra-ordinary wave that travels with a different speed of light in different directions, producing a phase shift. At the optical axis the two waves meet, the optical axis of ice coincides with its c-axis. Therefore, using a cross-
polarizer setup, it is possible to determine the c-axis of the ice sample. A cross-polarizer setup, also called a Rigsby stage, consists of two orthogonal polarizers. In between the two polarizers there is space to insert and rotate a sample. Without any sample between the first polarizer and the second polarizer (called the analyser), the transmitted light is completely extinguished by the two orthogonal polarizers. With a polycrystalline sample within the polarizer and analyser, light incurs a phase shift between the ordinary and extra-ordinary waves when passing through ice, changing the polarization. This causes the sample to appear bright, and the brightness varies for differently oriented domains of the polycrystalline sample, an example of which is shown in Figure 1.8c. The outgoing light is completely extinguished for the cases when the optical axis of the ice is aligned with either the polarizer or the analyzer, or when the c-axis is parallel to the line of sight. When the c-axis is indeed parallel to the line of sight, rotation in that axis should remain dark at all angles. This would be the basal or 0001 plane of ice.

The accuracy of using a Rigsby stage is a user-dependent process. Although it can offer complete information, it was used only to roughly estimate the basal plane, and to check the single-crystallinity of the sample. For a more quantitative determination of the crystal-orientation, Formvar etching was performed.

Formvar etching

Crystallographic information from the ice surface can be obtained in the form of etched pits using thermal and anisotropic etching, known as Formvar etching. A thin slice of ice (10-20 mm thick) is obtained using a bandsaw, it is vital to pay attention to the viewing plane of the cut slice in reference to the boule to pinpoint the correct axis. The ice slice is melt-attached onto a glass cover slip: the ice slice is rubbed over the glass slide to initiate melting of the contact surface of ice, after which it is placed in the centre of the slide and moved to the freezer to attach. After attachment, the sample is placed in a microtome holder to produce a flat and smooth surface for the etching process. Thereafter, the cover slip is mounted onto a microscope holder. A 2% solution of polyvinyl formal (Formvar) in ethylene dichloride is used to cover the surface of the thin ice slice using a clean cotton swab. After the solvent evaporates, a polymer film forms on the sample.

Figure 1.9: a) etch pits shapes for different orientation plane cut, from reference\(^{15}\); b) basal, and the prism planes of ice depicted in the hexagonal crystalline structure.
The polymeric film causes the formation of etched pits as water starts to evaporate through small randomly distributed holes of the film. The etched pits take the shape associated with the lattice structure dependent on the crystal orientation, and start from tiny pits and increase in size with time due to continuous evaporation of water. From the shape of the pits, it is thus possible to determine the orientation of the axis. The basal plane leaves hexagonally-etched pits, an example of which is shown in Figure 1.8d. Other shapes of the pits are shown in Figure 1.9a, corresponding to the plane orientations of the crystal shown in Figure 1.9b. The microscope used was Olympus BX40, at a magnification of 40X, and Nikon Digital Sight DS-U2 camera was used to take photographs.

When starting with a crystal seed not already basal-oriented, the sample orientation can be far from that desired. The etch pit images help to obtain the degree to which the orientation plane is off. Having an estimate of the angles, based on the shadows of the etched pits in one or multiple directions, the boule is cut at the respective angle in a direction referenced to the slice of ice being observed for etched pits. This can be a tedious, iterative process, based on trial and error in the beginning. Once the desired plane orientation is obtained, enough ice is grown to always have a seed for the next growth process of the correct orientation.

Sample preparation for measurements

After an ice boule is correctly oriented to the desired plane, a parallel disc of ice (~5 mm), maintaining the same orientation, is cut from the boule using a bandsaw. A stainless steel device, with high mass concentration at one end, and very thin features in the shape of a circle (4.4 mm) on the other end, is used as a ‘cookie cutter.’ The thick side helps to take up the heat when heated before usage, and transfer it while cutting the disc using the thin sharp side, assisting the cut with some melting from the heat. Once the disc is cut in the right dimensions, it is melt-attached to a pin in the centre of an aluminium ice cell. The ice cell with ice attached to it can be seen in Figure 1.10 b and c, with the aluminium pin with grooves in the middle.

After attachment to the cell, the cell is screwed to a microtome holder, as shown in Figure 10a. The microtome used was an adapted version of a Swift and Anderson Rotary Microtome. The ice attached to the cell is microtomed, by moving the ice cell up and down in reference to the microtome blade. The microtome blade chosen after trying at least 15 different types, was a Leica three-faceted blade. When the ice cell is positioned above the blade, it is moved in minimal distance steps over the microtome blade position, and then lowered to scrape off the ice. This is an extremely important step that determines the ice surface quality.

To obtain an optically-flat ice sample, the step sizes of ice scraping are kept small, and the cell is moved slowly and smoothly while scraping to avoid line ridges. An optically flat shining sample after microtoming is shown in Figure 1.10b. The reflectivity of some direct light was a good check of the sample surface. After microtoming, the ice cell is then closed air-tightly within a Calcium Fluoride window, and a plastic cap is threaded closed to retain air-tightness, shown in Figure 1.10c. The ice cell is left overnight for annealing so the surface can reach an equilibrium state.
The ice cell is subsequently transferred to the setup in the lab for measurements. The ice cell in the setup rotates over a copper cooling stage using a crank-shaft mechanism and an additional wobbling. The ice cell is rotated at a rate so that every pulse from the laser (assuming a ~100 μm diameter) hits a subsequent new spot on the ice, thus avoiding the accumulation of heat in the sample and preventing it from melting. The copper plate can be cooled down to 218 K, and the aluminium cell being a good thermal conductor can attain temperatures almost as close. The temperatures of the ice (by drilling a hole in the ice and placing a sensor), and the ice cell corresponding to the temperature of the copper block were recorded for reference to the ice temperature later. The setup was purged to avoid condensation over the cell or copper block, and a nitrogen jet pipe placed close to the cell would avoid condensation over the cell window.

Outline

Having had a general overview so far about the structure, properties, and synthesis of crystalline ice, the subsequent chapters are outlined as follows. Chapter 2 and 3 give an overview on the theory of non-linear light-matter interaction, ultrafast lasers and Sum Frequency Generation spectroscopy, followed by a brief explanation of the experimental setup, and data analysis. Chapter 4 to 6 present experimental results pertaining to the ice surface, discussing specifically the vibrational bend mode, proton order, and dynamics of the vibrational stretch mode, respectively. Finally, Chapter 7 showcases experimental and simulation results on the ice-nucleating properties of cholesterol monolayers.

A brief summary of the PhD work closes the thesis.