The cool state of water: Infrared insights into ice

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Citation for published version (APA):
1 Introduction

Ice is the coolest state of water. It only remains frozen at temperatures below 0°C. Whereas a change from 23 to 21 °C is hardly noticeable, a transition from +1 to −1 °C can transform an entire landscape: canals and lakes freeze over and snow covers everything with a white blanket. For a long time, winter was a challenging season, when less food was available and people had to rely on their reserves. However, the ice-cold also has its upsides. Ever since prehistoric times, ice and snow made it possible to travel great distances for migration, hunting, commerce, or leisure, as beautifully illustrated by the winter landscape from Hendrick Avercamp on the cover of this thesis. Over the years ice has even been a saviour: during the Spanish siege of Haarlem in the winter of 1572–1573, the frozen Haarlemmermeer enabled the Dutch to supply the city, damsel in distress, with sledges over the ice. When the ice melted again after seventeen weeks, the city inevitably had to surrender.[1] Nowadays winters in the Netherlands are less severe and the ice over lakes and ditches only occasionally grows past the 3–4 cm required to support the weight of a single person.[2–4]

Ice floats on water, and only the top part of the water needs to freeze in order for us to skate on ice. This property that makes ice float on water is actually rather peculiar. Most substances become more dense when they freeze and would therefore sink. The origin of this property and of many other anomalies of water lies in its special molecular structure. In spite of its simple molecular formula H₂O, water is surprisingly complex. It consists of one oxygen atom to which two hydrogen atoms are bonded in a triangular shape (Fig. 1.1).

\[\text{Figure 1.1: Schematic picture of the water molecule: an oxygen atom (red) with two covalently-bonded hydrogen atoms (white). In total the water molecule is charge neutral, but a charge separation is present within the molecule. This charge separation corresponds to a net point charge of } +0.3 \, e \text{ at the hydrogen atoms and a negative charge of } -0.6 \, e \text{ at the oxygen atom.}^5\]

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^5These values are derived by a goniometric calculation based on an electric dipole moment of $6 \cdot 10^{-30}$ C m and the electron clouds assumed to be point charges.
The bonds between the atoms are covalent, which means that the hydrogen and oxygen atoms share their electrons. This allows them to attain the equivalent of a full outer shell, corresponding to a more stable electronic configuration. The sharing is not fair: in its greed for electrons, oxygen hogs the electrons like a selfish lover claiming most of the duvet. As a result, the oxygen atom becomes partly negatively charged and the hydrogen atoms are left with a slight positive charge. These partial charges in the water molecule give rise to an attractive interaction between water molecules, called hydrogen bonds (see Fig. 1.2). This hydrogen bond is about ten times stronger than the van der Waals force that keeps “regular” liquids together, but 10–100 times weaker than a covalent bond. The presence of hydrogen bonds between water molecules is the cause of the relatively high congealing and boiling temperatures, and the origin of exceptional behaviour. Hydrogen bonds have a large capacity to store energy, giving water its unusually high heat capacity, which causes sea climates to be more temperate than land climates.

Every water molecule can form up to four hydrogen bonds: two involving their own hydrogen atoms plus an additional two involving the hydrogen atoms of neighbouring water molecules. In liquid water the structure of the hydrogen bonds is very dynamic and continuously reforms on the timescale of a picosecond ($10^{-12}$ s). When liquid water freezes and forms ice, the arrangement of the hydrogen bonds becomes fixed and an ordered, spacious structure of water molecules is formed. The density of water decreases by 8.3 % upon freezing. As a result, ice floats on water. The structure of normal ice is depicted in Fig. 1.3. The oxygen atoms are found at the summits of non-planar hexagons that have the shape of a chair. A projection of the ice crystal in the basal plane gives a regular hexagonal structure similar to honeycombs in a beehive. The hexagonal structure of ice is the origin of the sixfold symmetry of snowflakes.
In his *Les météores* (1637) Descartes details his observations on Amsterdam’s snowfalls of 4, 5, 6, and 9 February 1635:

But what astonished me above all was that among the grains which fell lately I noticed some which had around them six little teeth, like clockmakers’ wheels.

These were little plates of ice, very flat, very polished, very transparent, about the thickness of a sheet of rather thick paper, ... so perfectly formed in hexagons, and of which the six sides were so straight, and the six angles so equal, that it is impossible for men to make anything so exact.\cite{10}

Today we continue to marvel at and unravel the properties of ice. Its surface structure and the reason why ice is slippery, for instance, are still not fully understood.\cite{11} The low friction of ice is closely linked to a well-established premelting, which results in a water layer at the surface of ice at temperatures

\footnote{Mais ce qui m’étonna le plus de tout, fut qu’entre ceux de ces grains qui tombèrent les derniers, j’en remarquai quelques-uns qui avaient autour de soi six petites dents semblables à celles des roues des horloges.

C’étaient de petites lames de glace, toutes plates, fort polies, fort transparentes, environ de l’épaisseur d’une feuille d’assez gros papier, ... si parfaitement taillées en hexagones, et dont les six côtés étaient si droits, et les six angles si égaux, qu’il est impossible aux hommes de rien faire de si exact.}
close to the melting point.\textsuperscript{[12,13]} Premelting is not unique to ice, but occurs for all types of crystalline materials.\textsuperscript{[14,15]} However, for ice it stands out due to the ubiquity and importance of the geophysical effects. Our understanding of the properties of the premelted layer on ice remain very limited, especially at the most fundamental level. Very little is known about the molecular properties of the surface layer.\textsuperscript{[12]} The small size of water molecules in combination with their ultrafast dynamics makes further study challenging. Only few techniques can be deployed to acquire precise insights. This thesis uses spectroscopy to shine light on the molecular properties of ice and other related systems.

**Spectroscopy** Light is made up of wavelengths, and each wavelength corresponds to a particular colour. White light contains all colours of the rainbow, as can be demonstrated by shining it through a prism. Our eyes are sensitive to a small range of wavelengths, namely the range (in vacuum) from 390 nm (violet) to 700 nm (red).\textsuperscript{[17]} This region coincides with the maximum of the emission spectrum of the sun,\textsuperscript{[18]} which is — from an evolutionary point of view — unlikely to be a coincidence.

![Figure 1.4: The refractive index (blue) and the absorption spectrum (green) of ice at 266 K.\textsuperscript{[16]} The vibrational and librational normal modes are indicated by their abbreviation (see text).](image-url)
Introduction

Matter consists of atoms, which in turn comprise charged species like electrons and an ion core. When light is incident in matter, significant interactions can take place with the charged constituents. The light–matter interaction can be used as a measurement tool. This field of study is called spectroscopy. Spectroscopic data is often depicted by a spectrum: a plot of the absorbed or emitted light as a function of wavelength or frequency. For historic reasons, in spectroscopy the frequency is often denoted in wavenumbers in units of cm$^{-1}$.

The wavenumber $\tilde{v}$ is related to the frequency $f$ by the speed of light $c$:

$$\tilde{v} \ [\text{cm}^{-1}] = \frac{1}{100} \frac{f \ [\text{s}^{-1}]}{c \ [\text{m s}^{-1}]}.$$

The absorption spectrum of ice from the extreme ultraviolet up to the far infrared is shown in Fig. 1.4. The spectrum has both regions of weak and strong absorptions. At a wavelength of 3 $\mu$m (3300 cm$^{-1}$), a slice of ice of 10 $\mu$m (thinner than a human hair) is already enough to absorb 99% of the light, whereas at a wavelength of 500 nm this requires a sheet of ice of more than a kilometre. Ice is almost perfectly transparent to visible light and appears to us colourless. Only the tail of the red side of the visible spectrum is absorbed giving ice and water their intrinsic bluish shine.[19]

The features of the absorption spectrum have various origins. The absorptions in the ultraviolet part of the spectrum are caused by electronic transitions and those in the infrared are caused by molecular vibrations and rotations. In this thesis we study molecular vibrations, which field of study is called vibrational spectroscopy. The water molecule vibrates in several ways. The normal mode vibrations are illustrated in Fig. 1.5. There are symmetric and antisymmetric stretching vibrations, usually denoted as $v_1$ and $v_3$, respectively, in which the length of the covalent OH bonds oscillates. The bending vibration ($v_2$) is a scissor-like movement in which the angle between the two covalent OH bonds oscillates. Lastly, water molecules rotate. In the condensed phase this motion is restricted by hydrogen bonds giving rise to hindered rotations or librations ($L$). Each of these modes has its own oscillation frequency. The vibrations give rise to several peaks in the absorption spectrum, as marked in Fig. 1.4. The other features in the infrared spectrum are associated with overtones and combinations of vibrations.

The vibrational modes of water are very sensitive to the local environment. The spectral position, width, and amplitude of the vibrational bands depend on
the hydrogen-bond network.\textsuperscript{[20]} Especially the stretching modes are sensitive to the strength of the hydrogen-bond interaction.\textsuperscript{[7]} The hydrogen bond exerts a force on a hydrogen atom in opposite direction to the covalent OH bond, thereby lowering the effective restoring force of the hydrogen atom. As a result, the hydrogen bond lowers the oscillation frequency of the stretching mode. The absorption spectra of the H$_2$O stretching modes in ice and liquid water are shown in Fig. 1.6. Comparing these spectra we note that the stretching modes of ice have a lower frequency than the stretching modes of liquid water. This reflects the hydrogen bonds to be on average stronger in ice than in liquid water. The sensitivity of the stretching vibrations can be of great use as a probe for the molecular landscape.

OUTLINE In this thesis we investigate several properties of ice and ice-related systems by taking advantage of the sensitivity of the stretching vibrations to the hydrogen-bond structure. In Chapters 2 & 3 we first provide a theoretical introduction and an overview of the employed spectroscopic techniques. We will investigate aspects of the vibrational dynamics of water molecules in ice and hydrated salts in Chapters 4 & 5. Subsequently, we study the surface properties of ice and the surface premelting in Chapters 6 & 7. Chapter 8 deals with the effects of resonant molecular couplings at the surfaces of ice and liquid water. In the last two chapters we study the surface properties of water and oil emulsions. The effect of freezing water at the surface of oil droplets in water is investigated in Chapter 9. The surface structure of water droplets and ice nanocrystals immersed in a hydrophobic environment is discussed in Chapter 10.