The cool state of water: Infrared insights into ice
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7 Observation of liquid water at the surface of ice at temperatures far below the melting point

We employ phase-resolved sum-frequency generation (SFG) spectroscopy to study the molecular properties of the premelted layer on ice. We observe that even at temperatures far below the melting point (<245 K), the surface of ice is covered by a liquid layer, that is indistinguishable from supercooled liquid water.

7.1 Introduction

It has been well-established that the surface of ice is covered by a liquid-like layer. This layer governs processes as diverse as glacier motion, frost heave, the occurrence of lightning and chemical reactions at the surface of ice particles in the atmosphere. In spite of its importance, the precise nature of the liquid-like layer is still under debate. For decades, the surface properties of ice have been the subject of numerous studies employing a large variety of experimental techniques. Much of this previous work reached seemingly inconsistent conclusions about the structure of the liquid-like layer and the temperature at which it forms. For example, the top surface layer has been reported to resemble bulk liquid water, but also to have a much higher viscosity than liquid water. The onset temperature for the formation of a liquid-like layer reported from experiments varies between 200 and 271 K.

SFG spectroscopy is an ideal tool to provide information on the molecular structure at the surface of ice as it combines surface-selectivity with molecular sensitivity. In the previous chapter we have studied the surface structure of ice using phase-resolved SFG between 150 and 245 K. In this chapter we employ the same technique at higher temperatures to probe the molecular nature of the premelting layer at the surface of ice.
7.2 Experimental methods

The preparation of the ice sample and the experimental configuration of the phase-resolved sum-frequency setup have been described in the previous chapter. The spectra are obtained in an ssp-polarization configuration and divided by a reference spectrum taken from z-cut quartz. The Fresnel factors are calculated using literature values for the optical constants of ice,\textsuperscript{[16]} water,\textsuperscript{[158,192]} and quartz,\textsuperscript{[159]} and calculating the effective refractive index of the interfacial layers by the use of a slab model.\textsuperscript{[44]} For an accurate determination of the phase of $\chi^{(2)}$, it is essential that the sample and reference are measured at the same height. The heights of the sample and reference are set to a precision of 10 μm, resulting in a phase inaccuracy of 10°. Following previous work, the obtained $\chi^{(2)}$ spectra are precisely phased such that the imaginary part is zero in the off-resonance part of the spectrum between 3800–3900 cm$^{-1}$.\textsuperscript{[73]} During the SFG experiment, the ice sample is continuously moved to prevent the accumulation of heat and damage of the crystal. The heating effect of the laser pulses is found to be negligible (see Fig. 7.5).

7.3 Results

In Fig. 7.1 we present the phase-resolved SFG response of the ice surface at different temperatures in the range 245–270 K for an ssp-polarization configuration. The imaginary part of $\chi^{(2)}$ contains direct information at the surface resonances. The real part of $\chi^{(2)}$ complements the imaginary part, and additionally contains a negative non-resonant background contribution.\textsuperscript{[163]} The constructed $|\chi^{(2)}|^2$ spectra allow for a direct comparison with conventional intensity SFG measurements. At 245 K the spectrum is dominated by an intense band at 3230 cm$^{-1}$ with a shoulder around 3400 cm$^{-1}$. With increasing temperature the 3230 cm$^{-1}$ band decreases in amplitude and the shoulder around ~3400 cm$^{-1}$ increases in amplitude. The Im $\chi^{(2)}$ spectrum also shows a clear band at ~3580 cm$^{-1}$. The low amplitude of this band makes it hardly visible in the constructed $|\chi^{(2)}|^2$ spectra. This band can be assigned to water molecules with 2 donor and 1 acceptor hydrogen bonds and a lone pair.\textsuperscript{[73,172]} These molecules are oriented with both hydrogen atoms pointing towards the bulk, which implies that the antisymmetric mode will be oriented nearly parallel to the surface. Nevertheless, this mode contributes with a positive sign to the Im $\chi^{(2)}$ in the ssp-polarization combination.\textsuperscript{[73]} This mode shows a very small blue shift when the temperature increases reflecting a weakening of the hydrogen bonds. The resonance at ~3700 cm$^{-1}$ is assigned to free OH groups sticking out of surface. The positive sign of the imaginary part reflects their outward orientation from the bulk. The amplitude of the free OH band changes only moderately with temperature, which is in agreement with previous work.\textsuperscript{[152]}

In Fig. 7.2a we show the Im $\chi^{(2)}$ spectra of ice at 245 K, ice at 270 K, and supercooled liquid water at 270 K. To facilitate the comparison, the amplitude of the ice spectra are multiplied by 1.6. The lower amplitude of the ice spectrum
Figure 7.1: Second-order susceptibility of the basal ice surface as a function of temperature. The top panel shows the imaginary component (\(\text{Im} \chi^{(2)}\)), the central panel the real component (\(\text{Re} \chi^{(2)}\)), and the bottom panel the squared amplitude (\(|\chi^{(2)}|^2\)).
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Figure 7.2: (a) Comparison of the imaginary parts of the second-order susceptibility ($\text{Im} \chi^{(2)}$) of the surfaces of basal ice and supercooled water. (b) Bulk absorption spectra of ∼0.5 mm polycrystalline ice and supercooled liquid water.

is likely caused by some remaining surface roughness resulting from the ice sample preparation, which causes SFG light to be scattered outside the range of detection angles (the detection path has a numerical aperture of ∼0.1). It is clearly seen that the surface spectrum of ice at 270 K is more similar to that of supercooled liquid water than to that of ice at 245 K. This conclusion is not influenced by the applied corrections for the Fresnel factors (see Fig. 7.6).

The bottom panel of Fig. 7.2b shows bulk infrared absorption spectra of equivalent systems that were shown in Fig. 7.2a. The absorption bands of ice at 245 K and ice at 270 K are quite similar. Ice at 245 K has its maximum infrared absorption at 3255 cm$^{-1}$, and ice at 270 K has its maximum absorption at 3265 cm$^{-1}$. Hence, the strength of the hydrogen bonds in bulk ice decreases only slightly going from 245 to 270 K. For supercooled water at 270 K the infrared absorption maximum is found at a frequency of 3390 cm$^{-1}$, much higher than is observed for ice at 270 K, which implies that the hydrogen bonds are significantly stronger in bulk ice at 270 K than in bulk liquid water at 270 K. It is thus clearly seen that for ice at 270 K the bulk response is similar to that of ice at much lower temperatures, whereas the surface response is similar to that of liquid water. This result indicates that the surface response of ice at 270 K has a large contribution from a layer that resembles liquid water.
To obtain more quantitative information on the properties of the ice surface we perform a spectral decomposition (Fig. 7.3). First we fit the Im $\chi^2$ spectrum of supercooled water by 3 Gaussian bands of which 2 have asymmetric widths to account for the inhomogeneity in hydrogen-bond strengths. The broad band with the maximum at 3407 cm$^{-1}$ corresponds to hydrogen-bonded OH modes of liquid water, the band at 3587 cm$^{-1}$ corresponds to the mode involving 2 donor and 1 acceptor hydrogen bonds and a lone pair,\cite{73,172} to be denoted as the lone-pair band, and the band at 3702 cm$^{-1}$ corresponds to the free OH mode. Next we fit the ice spectra with these three bands plus another asymmetric Gaussian-shaped band to account for the response around 3230 cm$^{-1}$, which represents the OH vibrations of crystalline ice. In this fit of the ice spectra we keep the spectral shapes and widths of the four bands constant. Furthermore, the peak position of the lone-pair band is kept constant and obtained from a global fit. The peak position of the band corresponding to liquid water is taken to be 3407 cm$^{-1}$ at 270 K and to shift by 1 cm$^{-1}$/K. This latter shift per Kelvin is determined from the liquid water spectra at 270 and 295 K (Fig. 7.7). The peak position of the crystalline ice band is also fitted globally to all ice spectra and is also set to shift by 1 cm$^{-1}$/K. The fitting of the ice spectra yields the amplitudes of the 4 bands. The areas of the fitted bands as a function of temperature are shown in Fig. 7.4.

The results of Fig. 7.3 show that at all measured temperatures the Im $\chi^2$ spectrum of ice can be well described with the four bands described above. This implies that the surface response of ice contains a contribution of (supercooled) liquid water, even at 245 K, i.e. at 28 K below the melting point. It also follows from Fig. 7.4 that the liquid water band still shows a significant amplitude at 245 K, that is only $\sim$3 times smaller than the amplitude of the liquid water band of ice at 270 K. This observation indicates that the surface of even very cold ice (at $-28^\circ$C) is covered with a water layer. In contrast, the amplitude of the crystalline ice response strongly depends on temperature, and vanishes when approaching the melting point at 273 K (Fig. 7.4). The amplitudes of the free OH band and the lone-pair band involving the OH groups of water molecules with a lone pair change only moderately with temperature. The frequency position of the lone-pair band is shifted 30 cm$^{-1}$ to lower frequencies in comparison to the spectrum of supercooled liquid water. This frequency shift indicates that the two OH groups of the water molecule on which this mode is located, are pointing into the bulk of crystalline ice instead of liquid water. This means that the observed lone pair modes are likely located at the water molecules in the top layer of the crystalline ice phase, i.e. at the boundary of the crystalline ice phase and its overlying liquid water layer.

### 7.4 Discussion

The surface properties of ice have been studied before with conventional intensity SFG spectroscopy.\cite{69,152} In this study it was found that the free OH groups sticking out the ice–air interface show orientation disorder at tempera-
Figure 7.3: Spectral decomposition of the imaginary part of the susceptibility \( \text{Im} \chi^{(2)} \) of the surface of supercooled water at 270 K and basal ice at temperatures between 245 and 270 K. The supercooled water spectrum (top) is fitted by a sum of two asymmetric Gaussian-shaped bands and one symmetric Gaussian-shaped band. The ice spectra are fitted with the three bands resulting from the fit to liquid water and an additional asymmetric Gaussian-shaped band (see text). The data are represented by the symbols and the fitted spectra by the solid lines. The four spectral bands that together form the fitted spectra are indicated by shaded areas.
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Temperatures $\geq 200$ K,\[^{69,152}\] pointing at a disordered character of the top surface layer of ice. However, the exact nature of this disorder was not revealed, in particular to what extent the disordered surface would resemble liquid water. In this study we measure the spectrum of the ice surface with phase-resolved SFG, and we find that the spectrum of the premelted layer is indistinguishable from the spectrum of supercooled liquid water at the same temperature.

As the premelted layer is indistinguishable from supercooled water, the hydrogen-bond structure and dynamics of this layer will also likely be similar to the structure and dynamics of supercooled liquid water. In view of this finding it seems unlikely that the viscosity of the premelted layer would be 300–4000 times larger than the viscosity of (supercooled) water, as has been reported in interfacial and atomic force microscopy studies of the ice surface.\[^{184–186}\] The observed extremely high viscosity may find its origin in the strong confinement of the liquid-like layer between the probing tip of the atomic force microscope and the ice crystal surface.\[^{12}\] Indeed, in an interfacial force microscopy study it was reported that the measurements may be affected by the formation of a frustrated capillary between the probing tip and the ice surface.\[^{186}\]

7.5 Conclusions

We studied the surface of ice between 245–270 K using phase-resolved SFG spectroscopy. At all temperatures in this range, we find the ice surface to be covered with a layer of supercooled liquid water. We observe that the magnitude of the water signal decreases only by a factor of 3 when the temperature is decreased from the melting point down to 245 K.
FIGURE 7.5: SFG spectra at various IR intensities and moving speeds of the ice sample. Both a reduction in IR intensity from $5 \, \mu J$ to $2 \, \mu J$ as well as a reduction in the scanning speed from $4 \, \text{mm/s}$ to $2 \, \text{mm/s}$ do not affect the spectral shape. From this we conclude that the laser pulses used in the experiment lead to a negligible heating effect.
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Figure 7.6: The imaginary part of the second-order susceptibility ($\text{Im} \chi^{(2)}$) of the surfaces of basal ice and supercooled water. The top panel shows the division of the sum-frequency field generated from ice/liquid water ($E_{\text{SF, sample}}$) by the sum-frequency field generated from z-cut quartz ($E_{\text{SF, quartz}}$). The bottom panel shows this division and a correction for the Fresnel effects.
Figure 7.7: Spectral decomposition of the $\text{Im} \chi^{(2)}$ spectrum of the liquid water–air interface at 270 and 295 K. The spectra are decomposed in two asymmetric Gaussian bands and one symmetric Gaussian band. The maximum of the negative imaginary band is found to be located at 3407 cm$^{-1}$ for 270 K and at 3430 cm$^{-1}$ for 295 K, corresponding to a shift of $\sim$1 cm$^{-1}$/K.