Fathoming ice

*Using non-linear ultrafast spectroscopy to look at interfacial properties*

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Chapter 4

Interfacial Vibrational Spectroscopy of the Water Bending Mode on Ice Ih

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ABSTRACT: We study the molecular-level properties of the single-crystal ice Ih surface using interface-specific Sum Frequency Generation spectroscopy. We probe the water vibrational bend region around 1650 cm\(^{-1}\) of the basal plane of hexagonal ice, to understand the interfacial structure from vibrational properties. As opposed to the stretch mode of ice, the bend mode response depends very weakly on temperature. The large linewidth of the bending mode response, relative to the response on water, is inconsistent with inhomogeneous broadening, and points to ultrafast pure dephasing. The bend mode of ice provides an excellent means to study adsorbate-ice interactions and understand differences in ice and water reactivity.

Introduction

The water-air and ice-air interfaces act as active sites for chemical reactions in both natural and engineering settings. Water molecules at the surface are different from those in bulk, owing to the truncation of the hydrogen bond network. The properties of interfacial water molecules have been extensively studied owing to relevance in atmospheric\(^{41,42}\), biological\(^{43}\), electrochemical\(^{44,45}\), and geological sciences\(^{46}\). Ice interfaces have raised particular scientific interest owing to their reported high catalytic activity\(^{47,48}\), and implications in frost heave, supraglacial chemistry\(^{49}\), and exchange of trace gases establishing atmospheric concentrations of species\(^{50}\). Information on the molecular properties of specifically the interface can be obtained with surface-specific vibrational spectroscopic methods, such as Sum Frequency Generation (SFG) spectroscopy\(^{24,51}\). As a second-order nonlinear technique, SFG is inherently interface-specific owing to its selection rule that inversion symmetry must be broken for the signal to be generated. In this method, two laser beams, an infrared beam in resonance with a vibrational transition, and a visible beam for upconversion
are overlapped in space and time. An SFG signal is generated at the sum of the frequencies of the two incoming laser beams. When the infrared beam is vibrationally resonant with surface molecules, the signal is enhanced. The SFG intensity as a function of infrared frequency thus provides the vibrational spectrum of specifically the interfacial molecules.

SFG research has traditionally focused on the ~3300 cm\(^{-1}\) OH stretch mode of water in the study of interfacial properties of aqueous systems. The stretch mode frequency is correlated to hydrogen bond strength\(^{52,53}\), allowing access to molecular structure information from spectroscopic observables. The stretch-mode region of water gives a relatively high intensity compared to other vibrational modes, simplifying signal detection. Despite the clear advantages, water vibrational stretch mode spectra can be challenging to interpret due to the strong effects of inter- and intra-molecular couplings on the spectral lineshape\(^{54}\). This coupling causes delocalization of vibrational OH stretch quanta, affecting the vibrational response. Further complications appear in the presence of other moieties with OH groups due to interference of the vibrational OH-stretch of water with that of alcohols, other biomolecules, etc. The HOH bend mode of water can act as an insightful alternative to the stretch mode: as it avoids such complications. The weaker inter-molecular coupling for the bend mode and the correlation of the bend mode frequency to the hydrogen-bonding strength can complement the stretch mode results\(^{55,56}\). Due to its smaller transition dipole moment, the bend mode is expected to be less influenced by intermolecular dipole-dipole coupling, which was recently experimentally verified for water interfaces\(^{57}\). Furthermore, the bend mode of water is spectrally separate from the C-O-H and C-N-H bending modes of alcohols and biomolecules, making such composite systems simpler to study. The vibrational bend region has thus recently gained interest to obtain molecular information of both bulk and interfacial systems.

The first SFG measurements of the vibrational bend mode of interfacial water, at ~1650 cm\(^{-1}\), dates back to 2012\(^{58}\), but has not yet been reported for ice. Previous theoretical work has shown that, for ice, the total dipole moment is reduced due to anti-correlated effects of permanent and induced dipole moments, indicating it is more challenging to determine the bending mode response from the surface of ice than of water\(^ {59,60}\). Nevertheless, the bend mode region of interfacial ice is of fundamental importance, as its lineshape may provide information on the low-frequency excitations and bend-libration coupling mechanisms\(^ {61}\) at interfaces, and on the bending overtone, which determines the rate of vibrational energy relaxation\(^ {62}\). As the bending mode is expected to be a more ‘local’ probe than the stretch mode, it can be important for studies of adsorbate-based systems on the surface of ice, allowing to observe spectral changes without intermolecular coupling effects\(^ {59}\).

Results and Discussion

Here, we report vibrational bend mode spectra of the basal plane of interfacial ice Ih, measured using SFG spectroscopy. Figure 4.1 a and b show SFG spectra of ice in the vibrational stretch and bend mode regions, respectively, at comparable temperatures in the SSP polarization combination (S-polarized SFG, S-polarized visible, and P-polarized infrared). The stretch mode spectrum is dominated by a signal at roughly 3200 cm\(^{-1}\) assigned to O-H modes hydrogen-bonded to neighbours. The signal at 3700 cm\(^{-1}\) originates from so-called free OH groups, while the 3500 cm\(^{-1}\) could be mainly attributed to the asymmetric stretch mode of fully coordinated water molecules\(^ {53}\).
As apparent from figure 4.1a, the ice surface exhibits a strong temperature-dependence in the OH-stretch region, with a ~100% intensity increase for a ~7% temperature decrease from 260 to 243 K. A straightforward explanation for this signal increase would be the enhanced orientation of interfacial water molecules at lower temperatures. However, MD simulations, shown in Figure 4.2, reveal that the orientational ordering of water molecules in the top two bilayers on the surface of ice can only account for a ~10% increase in the SFG intensity over this limited temperature interval. Thus, the major change in the stretching mode intensity for interfacial ice is attributed to temperature-dependent intermolecular coupling in the stretch region.

In contrast, Figure 4.1b shows no indication of a similar intensity increase for the interfacial ice bend mode region upon lowering the temperature, in line with the notion that bending modes are weakly coupled. The response in the bend region is, however, less straightforward than in the stretch region. For the stretch region, several clear peaks can be identified. In contrast, the bend mode response appears derivative-like, due to a relatively sizeable non-resonant contribution to the overall signal, as apparent from the high baseline relative to the signal size.

Figure 4.1a reveals a redshift of the stretch mode upon a decrease in temperature, as reported before. A redshift in the stretch mode region is associated with stronger hydrogen bonding. Conversely, stronger hydrogen bonding is reflected by a blueshift of the bend mode frequency, as first shown by Falk. For the given temperature interval, the ~15 cm$^{-1}$ redshift of the low-frequency peak of ice in the stretch region translates to a negligible frequency shift in the bending region, as per the empirically inferred relationship between the frequencies of the two modes. Indeed, no shift is apparent from the data in Figure 4.1b. Having established that the bend mode is less affected by intermolecular coupling, we further analyze the bending mode response at the ice interface, and compare it with the response of water. The polarizations of the incoming visible beam and the SFG beam were varied to generate signals in SSP and PPP polarization combinations. The three letters indicate the polarization of the SFG, Visible, and IR beams, respectively.
Figure 4.2: Probability distributions of water molecules with the OH-group pointing up ($\cos \theta = 0.3$) and with the OH pointing down ($\cos \theta = -0.3$) for the top two bilayers on the surface of basal ice Ih. The figures are obtained from MD simulations, from the work of Sanchez et al. Both the bilayers show certain asymmetry between the peaks representing the up and down pointing OH groups, which eventually leads to generation of an SFG signal. To elucidate the contribution of orientational ordering of water molecules to the increasing SFG intensity upon lowering the temperature in the stretch region, we evaluate the difference in probability distribution of the water molecules at the two temperatures. We integrated the Probability*\cos \theta within the range of -0.5 to 0.5 for both bilayers and compared the difference at the temperatures 240 and 260 K. We find an increase of 5.7% in the value for 240 K compared to 260 K, meaning an intensity increase to be $(1.057)^2 = 11\%$. Thus we expect that the ordering of water molecules would lead to an intensity increase of roughly 10% upon lowering the temperature from 260 to 240 K.

The bend mode of interfacial ice compared to water

Figures 4.3 a and b represent the bend mode SFG intensity obtained from the interfaces of ice and water for the polarization combinations SSP (left column) and PPP (right column) as a function of the IR frequency. From the raw data, it is apparent that the bending mode response of ice is blueshifted and substantially broadened compared to water.

Both effects are qualitatively also present in the bulk infrared response (Figure 4.3e), but the blueshift is more pronounced at the interface. Perhaps remarkably, the SFG intensity for ice and water in the bend mode region is comparable. This observation is remarkable for two reasons: First of all, the intensities in the stretch mode region are strikingly different, with interfacial ice having a considerably higher intensity than water, as shown in Figure 4.4. This difference is in line with the strong intermolecular coupling present in the stretch region for ice\textsuperscript{64}, and its absence in the bend region. Secondly, the bulk infrared response of the ice bending mode is substantially weaker (by a factor 2-3) than that of liquid water (see Figure 4.3e). Nonetheless, the SFG bend mode intensities are very similar for ice and liquid water.
Figure 4.3: a) and b): Experimental SFG measurements (dots) and fits (solid lines) in the vibrational bend mode region of interfacial ice (blue) and water (red) with SSP measurements depicted in the left column, and PPP in the right. Water and ice spectra, also SSP and PPP are plotted on the same scale; see the Appendix for correction due to intensity alteration on the window of the ice cell. c) and d): Imaginary $\chi^{(2)}$ for both polarization combinations obtained from the spectral fits. e) Linear infrared absorption spectra for bulk ice and water in the H-O-H bending region.

The bend spectra display dispersive lineshapes for both polarization combinations. The PPP spectra are less intense for both ice and water, compared to the SSP spectra. The SSP response is most insightful since it is determined by one independent $\chi^{(2)}_{xxz} = \chi^{(2)}_{yyz}$ element of the $\chi^{(2)}$ second rank tensor; the PPP response, in
contrast, contains contributions from two ($\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zzz}$) independent tensor elements, as explained in the Appendix. To quantify the observed spectral changes, the SSP spectra are fitted using a purely real non-resonant contribution and two complex resonant Lorentzian contributions (see Table 4.1 for the fitting parameters). The interfacial water SSP spectrum was described in accordance with previously reported parameters in agreement with the reported heterodyne measurements of the water-air interface. The high-frequency resonance is attributed to a DD-type water molecule, which donates two hydrogen bonds. The low-frequency resonance corresponds to a D-type molecule having one H-bond donating OH group and a dangling, free OH group. Thus, the low- and high-frequency contributions correspond to water molecules having a free-OH and the strongly hydrogen-bonded water molecules at the surface, respectively.

Figure 4.4: SFG spectra in the OH-stretch region of ice at 243 K and of water close to melting temperature

**Ice and water – fit comparisons**

To fit the interfacial ice SSP spectrum, the center frequency and linewidth of the low-frequency feature, corresponding to interfacial molecules with a free-OH, are kept similar to the fit for water. This assumption is based on the observation that the free-OH groups at the interface of water and ice have a very similar stretch frequency (Figure 4.4). The amplitude, central frequency, and linewidth of the high-frequency bend feature are allowed to vary between ice and water spectra. The SFG spectra in the bend-mode region are fitted using the expression:

$$I_{SFG}(\omega) = \left| \chi^{(2)}(\omega) E_{\text{VIS}}(w) E_{\text{IR}}(\omega) \right|^2$$

Eq. 4.1

wherein $\chi^{(2)}$ is a sum of resonant and non-resonant contributions, related with a phase difference $\Phi$, as follows:

$$I_{SF} \propto \left| \chi^{(2)}_R + \chi^{(2)}_{NR} \right|^2$$

or,

$$\chi^{(2)} = A_{NR} e^{i\phi} + \sum_j \left( \frac{A_j \Delta \omega_j}{\Delta \omega_j^2 + \sigma_j^2} + \frac{-iA_j \sigma_j}{\Delta \omega_j^2 + \sigma_j^2} \right)$$

Eq. 4.2
where $A_{NR}$ is the non-resonant amplitude related to the resonant signal by a phase difference $\Phi$; $A$ is the strength of the vibrational mode, $\Delta \omega$ is the difference in the resonant and excited frequency, $\sigma$ is the HWHM of the Lorentzian peak, and $j$ is an integer representing number of Lorentzian resonances.

From fitting the interfacial ice SSP spectrum, a strong correlation between the position and width of the high-frequency peak was observed. The peak frequency varied between 1706 to 1689 cm$^{-1}$, when varying the peak width between 200 and 300 cm$^{-1}$; Table 4.1 shows the fitting parameters, and Figure 4.3c shows the imaginary part of the fitted response function.

A comparison of the interfacial ice and water spectra of the SSP polarization combination reveals that the ice bending mode is blueshifted by $\sim35$ cm$^{-1}$, (taking an average peak position of 1697 cm$^{-1}$ for the ice SSP response). This blueshift for the bend-mode feature represents stronger hydrogen bonding. From the empirical relationship between the bend and stretch frequencies, a blueshift of 35 cm$^{-1}$ for the bending mode of ice corresponds very well with the $\sim200$ cm$^{-1}$ redshift observed, Figure 4.4 displays the stretch mode in ice compared to water.

Table 4.1: Fitting parameters for the bend mode spectra of SSP and PPP polarization combinations for both ice and water. Values in brackets for ice denote alternative fitting parameters.

|       | Ice SSP | Water SSP | Ice PPP | Water PPP |
|-------|---------|-----------|---------|-----------|
| NR Amp| -0.14   | -0.16     | 0.1     | 0.13      |
| $\omega_1$ cm$^{-1}$ | 1612 | 1612 | 1612 | 1612 |
| $2\sigma(\omega_1)$ cm$^{-1}$ | 130 | 130 | 130 | 130 |
| $A(\omega_1)$ | 0.9 (2.57) | 1.3 | -0.54 (-1.5) | -0.78 |
| $\omega_2$ cm$^{-1}$ | 1706 (1689) | 1661 | 1706 (1689) | 1661 |
| $2\sigma(\omega_2)$ cm$^{-1}$ | 200 (300) | 110 | 200 (300) | 110 |
| $A(\omega_2)$ | -7.3 (-13.8) | -3.6 | 4.38 (8.28) | 2.16 |
| $\omega_3$ cm$^{-1}$ | 1646 | 1679 | 1646 | 1679 |
| $2\sigma(\omega_3)$ cm$^{-1}$ | 60 | 60 | 60 | 60 |
| $A(\omega_3)$ | 1.1 | -0.8 | | |

The vibrational bend bandwidth is roughly doubled for interfacial ice (200-300 cm$^{-1}$) compared to water (110 cm$^{-1}$), as is apparent from the raw data in figure 4.3a and the fits presented in Figure 4.3c and Table 4.1. This is in strong contrast to the OH-stretch lineshape being much narrower for interfacial ice than for interfacial water as seen in Figure 4.4, further narrowing upon lowering the temperature of ice$^{71}$. If the ice surface bend mode were inhomogeneously broadened, the observed bandwidth $>200$ cm$^{-1}$ would translate to an extremely broad band of more than a 1000 cm$^{-1}$ in the stretch region, using the empirical relationship mentioned above. This is clearly not observed, indicating that the bend mode of ice is predominantly homogeneously broadened, with a short dephasing time of the ice bend mode, which would include the pure dephasing time, population and orientational relaxation. Ultrafast studies of the bulk water bend mode report a vibrational lifetime of $\sim170$ fs$^{57,72}$, and ultrafast anisotropy decay of 80 fs$^{73}$. The $>200$ cm$^{-1}$ bandwidth of the bend mode of ice compared to water, and the incompatibility with inhomogenous broadening mechanism, suggest sub-25 fs vibrational dephasing times for the bend mode of ice. Consistent with the interfacial spectra, the bulk bend mode spectrum also has a broader lineshape for ice, as seen from Figure 4.3e, also opposite to the stretch mode$^{74}$. 
Comparison of the SSP and PPP spectra

Fitting for the PPP spectra was conducted keeping the SSP parameters corresponding to the effective (i.e. including the Fresnel factors) $\chi^{(2)}_{xxx}$ consistent (the amplitudes were adjusted according to prefactors as per equation 2.18), and adding an additional peak representing an effective $\chi^{(2)}_{zzz}$ as the additional tensor element in PPP spectra. The non-resonant signal contribution is kept purely real. Both PPP spectra can be very well fitted in (see Fig. 4.3b) and result in an additional peak at 1646 and 1679 cm$^{-1}$ for ice and water, respectively.

From a comparison of the raw data for the two polarization combinations, we observe a spectral shift to the red side for the PPP spectrum compared to the SSP spectrum for both ice and water (Figure 4.5). Considering the complications of direct comparison from the data fits according to tensor elements described before, the spectral shift was quantified using simple sigmoidal fits to the ice and water spectra. For water, the PPP spectrum shift is quantified to be ~20 cm$^{-1}$ to the red side. This shift is in line with the 15 cm$^{-1}$ shift reported before\textsuperscript{70}, explained by the authors as an interference effect of two types of hydrogen bonding populations giving the same resonances in both the PPP and SSP response. However, we observe that an additional peak is needed to describe the PPP response; solely the SSP response is not enough. Interestingly, we observe an even larger frequency redshift for PPP compared to SSP in the case of interfacial ice, amounting to ~50 cm$^{-1}$ as per the sigmoidal fit. This 50 cm$^{-1}$ shift is in good agreement with the frequency difference between $\omega_2$ and $\omega_3$ in Table 4.1 indicating that for ice the PPP signal is dominated by the $\chi^{(2)}_{zzz}$ tensor element. A section in the Appendix elaborates on effects due to Fresnel factors, showing that optical effects due to setup geometry are not causing the differences.

Figure 4.5: Sigmoidal fits to ice and water spectra in SSP and PPP polarization combinations. The fitting was performed to extract x-axis positions for the bend bands from the raw data to illustrate frequency shifts between the SSP and PPP spectra. From the fits, for water, the PPP (1634 cm$^{-1}$) spectrum shifts to the red side by ~20 cm$^{-1}$ compared to the SSP spectrum (1656 cm$^{-1}$). For ice, a larger shift of ~50 cm$^{-1}$ is observed between the PPP (1649 cm$^{-1}$) and SSP (1699 cm$^{-1}$) spectra.
Conclusions

In conclusion, this work has shed light upon the observed contrasting features of the bend mode spectra for ice and water, compared to the stretch mode. Stronger hydrogen bonding for ice manifests as a redshift in the stretch-mode region, and a blueshift in the bend mode region, as was empirically predicted and experimentally confirmed by our measurements. A comparable intensity of the bend mode for ice and water (unlike for the stretch mode), and little or no temperature dependence in our range of temperature variation, points towards negligible intermolecular coupling for the bend mode region. The anomalously increased bandwidth of ice in the bend mode compared to water points towards the line broadening mechanism to be predominantly homogeneous, unlike in the stretch mode. Also, polarization-dependent studies in the bend mode region indicate an inherent 20 and a 50 cm\(^{-1}\) frequency shift between the SSP and PPP spectra, for ice and water respectively, the origins of which remain incompletely understood.
Appendix

Intensity alteration due to CaF₂ window

Ice samples were measured inside a cell, with a CaF₂ window to allow equilibration of the ice sample in a closed environment, and to avoid evaporation to facilitate long-time measurements of the sample. However, to make a fair comparison of the SFG intensities on ice for SSP and PPP polarization combinations, one has to take into account the different reflectivity of P and S polarized light when interacting with a CaF₂ surface. An analysis for the Visible and SFG wavelengths is done below, as the Infrared remains constant for the SSP and PPP polarization combinations.

Figure 4.A1: left column: reflection coefficients of 800 nm S and P polarized light at the CaF₂ interface; right column: transmission accounted for incoming visible and outgoing SFG beams at the air-CaF₂ and CaF₂-air interfaces.

Figure 4.A1 left column shows the different reflectivity for S and P polarized light as a function of the incoming angle at an air-CaF₂ interface. The figure is depicted for an incoming visible beam of 800 nm wavelength. The refractive index of CaF₂ for the visible beam of 800 nm and the SFG outgoing beam of ~704 nm was taken as 1.4306 and 1.4317, respectively. The incoming angle of the visible beam was 64° and the SFG beam was calculated to be reflecting at 60°. The S and P reflection coefficients were calculated using the Fresnel equations for reflection and transmission. From Figure 4.A1 left column, it is apparent that at an angle of ~65°, there is a ~20-fold difference in the reflectivity coefficients of S and P polarized light. Using Fresnel equations for intensity reflectance and transmission coefficients, the transmission (or 1 – reflectance) of Visible light at the air-CaF₂ interface (P=0.98, S=0.81), and at the CaF₂-air interface (P=0.98, S=0.81), coupled with the reflection loss of SFG light at the air-CaF₂ interface (P=0.99, S=0.84), and then at the CaF₂-air interface (P=0.99, S=0.84), as depicted in the right column of Figure 5.A1, the subsequent light transmission out of the window is 0.94 for the PPP, and 0.45 for the SSP beams. Therefore, for fair comparison between SSP and PPP spectra, the SSP spectra were multiplied by a factor 2 to account for the reflection losses due to the CaF₂ window.
Contributions due to setup geometry: influence of Fresnel factors

The lineshape of an SFG spectrum can be adversely affected by the local electric fields of the incoming/outgoing beams at the interface. An introduction to Fresnel factors was made in Chapter 2. For the experiment, the refractive index of air $n_1$ was taken as 1, for $n_2$ (refractive index of second medium: water or ice), the value was taken from Warren (1984) for Visible wavelength 800nm and SFG wavelength 704 nm. For the infrared light, the values were taken from Zasetsky et al, for ice at 235 K and water at 273 K.

Figure 4.A2: Imaginary $\chi^{(2)}$ responses of the SSP and PPP spectra obtained from fitting SFG intensity data shown in red and green respectively, and of the calculated $\chi_{yyz}$ and $\chi_{zzz}$ tensor elements shown in blue and orange respectively. Left column displays spectra for ice, and right for water.

To analyse the effects of incoming beam angles and polarizations, Fresnel-corrected spectra are obtained for the $\chi^{(2)}$ tensor elements corresponding to SSP and PPP polarizations. The complex $\chi_{eff}^{(2)}$ required for the Fresnel factor analysis, are obtained from fitting the measured SFG intensity spectra in SSP and PPP polarization combinations; the fitting parameters are mentioned in the main text. The imaginary part of the $\chi_{eff}^{(2)}$ obtained from fits to the SSP and PPP data are plotted in green and red respectively, for ice (left column) and water (right column), in Figure 5.A1. These responses were used to calculate the $\chi_{yyz}^{(2)}$ and $\chi_{zzz}^{(2)}$ for the two systems, also plotted in Figure 4.A1 in blue and orange respectively. $\chi_{yyz}^{(2)}$ is calculated using equation 2.18 where the $\chi_{eff,SSP}^{(2)}$ is obtained from fitting the measured SFG intensity in SSP polarization combination. The $\chi_{yyz}$ thus obtained is then used to calculate $\chi_{zzz}^{(2)}$ from equation 2.19. $\chi_{yyz}^{(2)}$ and $\chi_{zzz}^{(2)}$ are the $\chi^{(2)}$ responses without influence of the Fresnel factors. Clearly, the differences between ice and water also remain in the $\chi_{yyz}^{(2)}$ and $\chi_{zzz}^{(2)}$ spectra. Therefore, we conclude that the differences between ice and water in spectral features observed for the SSP and PPP polarization spectra are not an optical artefact, but an inherent feature.

Figure 4.A3 is a direct comparison of the $\chi_{yyz}^{(2)}$ for ice and water (in solid and dashed lines, respectively). The blue-shift for the ice spectrum compared to water for the Fresnel-corrected SSP spectrum, reinstates the frequency shift observed in the measured intensity spectra to be indeed a physical phenomenon, and not an optical ’illusion’ seen in the intensity spectra.
Figure 4.A3: direct comparison of the $\chi_{yyz}^{(2)}$ responses of ice and water.