Observation and Identification of a New OH Stretch Vibrational Band at the Surface of Ice

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Supporting Information

ABSTRACT: We study the signatures of the OH stretch vibrations at the basal surface of ice using heterodyne-detected sum-frequency generation and molecular dynamics simulations. At 150 K, we observe seven distinct modes in the sum-frequency response, five of which have an analogue in the bulk, and two pure surface-specific modes at higher frequencies (∼3530 and ∼3700 cm⁻¹). The band at ∼3530 cm⁻¹ has not been reported previously. Using molecular dynamics simulations, we find that the ∼3530 cm⁻¹ band contains contributions from OH stretch vibrations of both fully coordinated interfacial water molecules and water molecules with two donor and one acceptor hydrogen bond.

Ice plays a key geophysical role. Glaciers shape the Earth’s surface, and ice particles in the atmosphere play a crucial role in lightning and the depletion of the ozone layer. Ice has at least 16 distinct crystalline phases, but the only thermodynamically stable phase that naturally occurs on the Earth’s surface is hexagonal ice (ice Ih). For ice Ih, the oxygen atoms lie on a wurtzite lattice and the hydrogens are located in-between the oxygen atoms following the Bernal–Fowler ice rules. These rules state that each oxygen is covalently bonded to two hydrogen atoms and in the crystal structure is terminated, leaving the outermost water molecules oriented in such a way that only one hydrogen atom lays between each pair of oxygen atoms. At the surface, the crystal structure is terminated, leaving the outermost water molecules with an incomplete hydrogen bond configuration.

At low temperatures, the surface of ice is highly ordered; the basal plane of ice Ih has full-bilayer termination, and the outer molecules have either a free OH group or an oxygen atom with a free lone electron pair. At somewhat elevated temperatures (reported to be 180–200 K), surface disorder sets in, finally resulting in premelting of the surface. This premelted layer has been reported to be important for processes such as glacier motion, frost heave, and chemical reactions taking place at the surface of ice particles in the atmosphere.

It is highly challenging to acquire detailed molecular-scale insights into the properties of the surface of ice. In most practical situations, the surface region is very thin compared to the bulk, which implies that a technique with high surface-specificity is needed to obtain unambiguous information on the surface. Furthermore, the technique should be minimally invasive because the ice surface can be easily melted and irreversibly deformed.

Sum-frequency generation (SFG) spectroscopy is a suitable technique for studying the surface of ice as it is noninvasive, highly surface-specific, and selective to molecular groups. Because SFG is an even-order (χ(2)) nonlinear optical process, SFG is bulk-forbidden for water and ice under the electric dipole approximation. As the frequency of the OH stretch vibrations is strongly correlated with the strength of the hydrogen bonds, the SFG spectrum of vibrations of water molecules at the ice surface can provide insight into the molecular configuration of the surface. The surface properties of ice have thus been studied with conventional intensity SFG spectroscopy, and the results have been compared with molecular dynamics (MD) simulations.

In this Letter, we report on a study of the ice surface with heterodyne-detected SFG (HD-SFG). In this technique, the sum-frequency signal is interfered with a local oscillator field. The SFG electric field, thus enabling a direct determination of the amplitude and phase of the generated sum-frequency electric field. The SFG electric field can be directly related to the amplitude and phase of the
second-order susceptibility $\chi^{(2)}$ (in conventional intensity SFG, $|\chi^{(2)}|^2$ is measured). As a result, HD-SFG provides not only the response spectrum of the molecular vibrations at the surface but also their orientation. Here, we specifically make use of the fact that HD-SFG allows access to the imaginary part of $\chi^{(2)}$, to which different modes simply contribute additively. This allows a straightforward analysis of the surface vibrational response in terms of different modes. In combination with MD simulations, we thus investigate the properties of the basal surface of ice between 150 and 245 K through its different vibrational modes.

The basal surface of ice $I_b$ is schematically depicted in Figure 1. The water molecules can be classified into different categories following the number of hydrogen bonds that a water molecule donates (D) or accepts (A); for instance, DAA molecules are water molecules of which one of the OH groups donates a hydrogen bond and of which the oxygen atom accepts two hydrogen bonds. For a perfectly structured basal face, the topmost water layer consists of 50% DAA and 50% DDA water molecules.

The growth and handling of single-crystal ice and the experimental setup are described in the Supporting Information. In Figure 2a, we present the real and imaginary parts of the $\chi^{(2)}$ of the basal face of ice at 150 K. The imaginary part of $\chi^{(2)}$ contains direct information on the vibrational resonances. The real part of $\chi^{(2)}$ complements the imaginary part and also contains a small negative nonresonant background contribution.

Below 3500 cm$^{-1}$, five resonances are clearly distinguishable in the $\text{Im}\chi^{(2)}$ response. From low to high frequency, the first resonance shows up as a dispersive-like feature at 3110 cm$^{-1}$ (discussed in more detail below); the additional four appear at 3150, 3228, 3350, and 3420 cm$^{-1}$ (as indicated by the vertical dashed lines). The Raman and infrared absorption spectra of bulk ice presented in Figure 2b,c show similarities with the $\chi^{(2)}$ spectrum of Figure 2a. Note that the $\chi^{(2)}$ associated with a vibrational resonance is proportional to the product of its Raman transition polarizability and its infrared transition dipole moment. Together, the Raman and infrared bulk spectra reproduce the five main resonances, which we label from low to high frequency by I–V. Bands I, III, IV, and V are visible in the Raman spectrum, and bands II and III are observable in the infrared spectrum. All of these bands have been assigned to delocalized OH vibrations and can thus not be assigned to particular water molecules with specific hydrogen bond configurations. According to the simulation results of Li and Skinner, bands II and V result from strong intermolecular coupling between OH stretch vibrations on neighboring water molecules for which no other hydrogen atom is located in-between the coupled OH groups. Bands III and IV result from the weaker intermolecular coupling between OH stretch vibrations for which there is one other hydrogen atom located in-between the two OH groups. The infrared spectrum contains an additional shoulder in-between the frequency positions of bands IV and V. According to the simulation results of Li and Skinner, this shoulder has the same origin as band IV in the Raman spectrum.

Bands II, III, IV, and V all appear as peaks with negative amplitudes in the $\text{Im}\chi^{(2)}$ spectrum. In contrast, band I does not coincide with a maximum or minimum in the $\text{Im}\chi^{(2)}$ spectrum but rather with a strong peak in the $\text{Re}\chi^{(2)}$ spectrum. The strong Raman band I has been assigned to a collective in-phase OH stretch vibration, and SFG experiments using the polarization null-angle method have shown that band I (with a frequency of 3098 cm$^{-1}$ at 113 K) contains a significant quadrupole contribution. As a result, mode I has been assigned to water molecules forming bilayer-stitching hydrogen bonds, which thus constitute neighboring oppositely aligned dipoles. The significant quadrupole bulk response leads to a 90° phase shift of this mode in the $\text{Re}\chi^{(2)}$ response with respect to a pure surface mode. As a result, band I leads to a maximum negative amplitude at 3100 cm$^{-1}$ in the real part of $\chi^{(2)}$ and a dispersive line shape for $\text{Im}\chi^{(2)}$ around 3100 cm$^{-1}$. The quadrupolar character of the signal of band I implies that the
generated SFG light can originate from both the bulk and the interface. It has been theoretically shown that a bulk quadrupolar contribution can be distinguished from an interfacial contribution by varying the optical geometry of the experiment.\textsuperscript{39} This will be the subject of future study.

In Figure 3, we present HD-SFG spectra of the basal ice surface at different temperatures in the range of 150–245 K.

Figure 3. \(\chi^{(2)}\)-Component of the experimental second-order susceptibility \(\chi^{(2)}\) of the basal ice–air interface at different temperatures. 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 \((|\chi^{(2)}|^2)\).

From the measured real and imaginary \(\chi^{(2)}\), we construct \(|\chi^{(2)}|^2\) spectra. The spectral features of the \(\chi^{(2)}\) spectrum become less pronounced at higher temperatures. Modes I–III merge into a single broad band. A similar effect is observed for modes IV and V. These modes broaden and merge into a single broad band at higher temperatures. The overall spectrum shifts to higher frequencies when the temperature increases, which can be explained from a weakening of the hydrogen bonds. The amplitude of the low-frequency modes I–III decreases when the temperature rises. In particular, the bilayer-stitching mode (1) exhibits a strong temperature dependence and has been reported to even gain further strength below 150 K.\textsuperscript{22} The decrease in the \(\chi^{(2)}\) response of mode I with increasing temperature can be explained from a decrease in vibrational coupling due to an increase of the thermal fluctuations.\textsuperscript{36,22} As a result, the depth over which the SFG signal is generated decreases with increasing temperature, thereby weakening the signal.

The \(\text{Im} \chi^{(2)}\) spectra also exhibit two bands at \(\sim3530\) and \(\sim3700\) cm\(^{-1}\) (as indicated by the vertical solid lines in Figures 2 and 3) that are not apparent from the infrared and Raman bulk spectra. The resonance at \(\sim3700\) cm\(^{-1}\) has been assigned to the stretching vibration of free OH groups sticking out of the surface.\textsuperscript{22} The low amplitude of the band at \(\sim3530\) cm\(^{-1}\) in the \(\text{Im} \chi^{(2)}\) spectra makes it difficult to distinguish this band in the constructed \(|\chi^{(2)}|^2\) spectra. As a result, this band has not been reported previously.

To assign the band at \(\sim3530\) cm\(^{-1}\), we performed MD simulations of the ice–air interface using a slab model (see the Supporting Information for details), focusing on the spectral region of 3400–3800 cm\(^{-1}\). The simulation cell contains 1344 water molecules, which form 12 bilayers. Water molecules are modeled with the POLI2VS force field,\textsuperscript{40} which can reproduce the SFG signatures of the liquid water–air interface including a shoulder band at \(\sim3600\) cm\(^{-1}\).\textsuperscript{41} SFG spectra are generated by computing the time correlation function of the dipole moment and the polarizability\textsuperscript{42} obtained from the MD simulations. The surface response of the 3400–3800 cm\(^{-1}\) region is found to be scarcely influenced by intermolecular couplings (see Figure S5 in the Supporting Information).\textsuperscript{43} As such, SFG spectra are calculated without cross-correlation terms in order to allow for a decomposition of the spectral response in this frequency region into the responses of different hydrogen-bonded types of water molecules.

In Figure 4, we show a comparison of the experimental and simulated spectra and the contributions of different hydrogen-bonded types of water molecules to the spectral response. Water molecules with a dangling OH group (DAA and DA) are responsible for the peak at \(\sim3700\) cm\(^{-1}\). The broad band at around 3530 cm\(^{-1}\) is composed of contributions to \(\text{Im} \chi^{(2)}\) from fully coordinated DDAA molecules and from DAA water molecules with opposite sign. The positive contribution from DDAA molecules is located at around 3475–3500 cm\(^{-1}\) and has a slightly higher frequency than the negative contribution from DAA water molecules at around 3440–3480 cm\(^{-1}\). In addition, the amplitude of the DDAA molecules dominates over the amplitude of the DDA molecules, finally resulting in a net positive band near 3530 cm\(^{-1}\).

Both the experiment and the simulation show that the amplitude of the \(\sim3530\) cm\(^{-1}\) band decreases when the temperature increases. The MD simulations show that this temperature dependence is caused by a decrease in amplitude of both the positive DDAA band as well as the negative DDA band. The amplitude of the DDA band exhibits a stronger decrease with temperature than the amplitude of the DDAA band, which follows from the fact that the DDA molecules are located in the outermost layer of the ice surface (see Figure 1) and thus are more strongly affected by an increase in surface disorder than the DDAA molecules. With increasing temperature, the 3530 cm\(^{-1}\) band shifts to higher frequency as a result of a weakening of the hydrogen bonds of both the DDA and the DDAA water species.\textsuperscript{14}

The \(\text{Im} \chi^{(2)}\) contribution of the DDAA molecules to the \(\sim3530\) cm\(^{-1}\) band arises from their asymmetric OH stretch vibration, whereas the \(\text{Im} \chi^{(2)}\) response of the DDA molecules results from their symmetric OH stretch vibration. The negative sign of the latter response reflects the net orientation of the DDA molecules with both OH groups pointing toward the bulk. The DDA molecules also have an asymmetric stretch vibration that leads to a positive \(\text{Im} \chi^{(2)}\) signal at \(\sim3590\) cm\(^{-1}\). This band has zero amplitude at 150 K but acquires strength at elevated temperatures. For a perfectly ordered ice surface, the antisymmetric mode would be oriented parallel to the surface (see Figure 1) and would thus not contribute to the \(\chi^{(2)}\).
The observation of a nonzero amplitude of this mode and an increase of its amplitude with temperature can be well explained from an increasing disorder of the surface and thus of the orientation of the DDA water molecules. This result is consistent with the observations for the liquid water−air surface, for which a positive Imχ(2) band has been observed at ~3620 cm$^{-1}$ and that has been attributed to the same mode.$^{44-46}$

In conclusion, we studied the surface structure of the basal surface of ice by combining HD-SFG spectroscopy with MD simulations. We measured spectra in the OH stretch frequency range in the temperature range of 150−245 K. At 150 K, the experimentally obtained sum-frequency spectra exhibit five distinct bands in the range of 3000−3450 cm$^{-1}$, which correspond well to bands in the infrared and Raman bulk spectra. The sum-frequency spectrum also contains two bands with positive amplitude at ~3530 and ~3700 cm$^{-1}$. The MD simulations show that these bands can be identified as surface modes. We find that the ~3530 cm$^{-1}$ band contains contributions of the symmetric OH stretch vibrations of DDA water molecules and the asymmetric OH stretch vibrations of DDAA water molecules that have opposite signs. With increasing temperature, this band decreases in amplitude and shifts to higher frequency.

ASSOCIATED CONTENT

 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01295.

Experimental details: single-crystal ice growth and temperature cell, experimental SFG setup and data analysis, effect of laser-induced heating, and measurement of bulk Raman and infrared spectra; Simulation protocols: MD simulation, calculation of SFG spectra, effects of intermolecular vibrational coupling on the SFG spectra, decomposition of SFG spectra, and hydrogen bond definition (PDF)

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