Reduced Near-Resonant Vibrational Coupling at the Surfaces of Liquid Water and Ice

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Supporting Information

ABSTRACT: We study the resonant interaction of the OH stretch vibrations of water molecules at the surfaces of liquid water and ice using heterodyne-detected sum-frequency generation (HD-SFG) spectroscopy. By studying different isotopic mixtures of H2O and D2O, we vary the strength of the interaction, and we monitor the resulting effect on the HD-SFG spectrum of the OH stretch vibrations. We observe that the near-resonant coupling effects are weaker at the surface than in the bulk, for both water and ice, indicating that for both phases of water the OH vibrations are less strongly delocalized at the surface than in the bulk.

Water and ice are remarkable substances owing to the presence of a spatially extended network of strong hydrogen bonds. This network is truncated at the surface, which gives rise to unique properties like an extremely high surface tension. The surface properties of water and ice govern a broad variety of biological and environmental processes.1–7 Therefore, a detailed understanding of the physical properties of the surface structure of water and ice at the molecular level is of broad scientific interest. Studying the surface properties of water and ice is challenging, as the surface region is typically very thin compared with the bulk. Few techniques are capable of probing the surfaces of water and ice with sufficient surface specificity.8

Over the last three decades, sum-frequency generation (SFG) spectroscopy has emerged as an extremely useful tool to study the molecular structure of water surfaces.9–11 SFG is a second-order (χ(2)) optical process that is dipole-forbidden in centrosymmetric media like bulk water but dipole-allowed at its surface. The method involves the frequency mixing of an infrared and a visible laser pulse, yielding a signal at the sum frequency. The SFG response is strongly enhanced when the infrared frequency matches a vibrational resonance, making it a selective probe for surface vibrations. The imaginary part of the second-order susceptibility χ(2) can be interpreted as a surface absorption spectrum with the additional feature that, unlike a bulk absorption spectrum, Im χ(2) can be positive or negative. The sign of Im χ(2) reflects the net orientation of the transition dipole moment of the probed interfacial vibrational mode. In conventional SFG spectroscopy, the intensity of the sum-frequency signal is measured, yielding a signal that is proportional to the squared magnitude of the second-order susceptibility (|χ(2)|2). The real and imaginary parts of χ(2) can be obtained using the recently developed heterodyne-detected SFG approach.12–16

The spectral response of the OH stretch vibrations of water depends on the strength of the hydrogen-bond interactions and on near-resonant intra- and intermolecular couplings. In neat H2O, the stretching vibration of an OH group couples both to the other OH group located on the same H2O molecule (intramolecular coupling) and to OH oscillators located on other water molecules in the vicinity (intermolecular coupling). This coupling takes the form of a dipole–dipole coupling at longer distances ( Förster energy transfer). At shorter distances higher electrical moments and even mechanical interactions may contribute. As a result of these couplings, the vibrational modes are delocalized over many OH oscillators, which leads to a broadening and red shift of the overall vibrational spectrum and precludes a direct connection between the hydrogen-bond strength and the OH vibrational frequency.17,18

We examine the effect of near-resonant coupling to the OH stretch vibrations at the surface of liquid water and ice by studying different isotopic mixtures of H2O and D2O using heterodyne-detected SFG spectroscopy. For isotopically dilute HDO in D2O, the OH oscillator is decoupled from the surrounding water molecules containing predominantly OD oscillators, owing to the large frequency mismatch between the OH and OD oscillators. As a result, the Im χ(2) spectrum of
HDO:D_2O can be interpreted in terms of localized OH stretch oscillators.

A detailed description of the heterodyne-detected SFG setup and the data analysis is provided in the Supporting Information. In short, the SFG experiments in the OH stretch vibrational region are performed in an ssp-polarization configuration, which implies that the sum-frequency and visible beams are polarized perpendicular to the plane of incidence, whereas the infrared beam is polarized parallel to the plane of incidence. The sum-frequency signal is generated at the sample surface with sum-frequency light generated from a gold surface (local oscillator) allows for the determination of the real and imaginary χ^(2) components of the second-order susceptibility χ^(2).

The Im χ^(2) of the liquid water–air interface is presented in Figure 1 for different isotopic mixtures at room temperature (295 K). The signal scales with the number of chromophores and accordingly decreases with increasing isotopic dilution. The spectra shown in Figure 1 further reveal a shoulder at ~3620 cm⁻¹, of which the amplitude strongly decreases with isotopic dilution. For this band different explanations have been proposed. In one explanation, this response has been assigned to water molecules with two donor and one acceptor hydrogen bond.22,24,27 The OH groups of these molecules are oriented, on average, with their hydrogen atoms toward the bulk, and intramolecular coupling gives rise to an antisymmetric stretching mode with a positive Im χ^(2) response in an ssp-polarization configuration.28 In a more recent study, the shoulder at ~3620 cm⁻¹ has been assigned to a Fermi resonance between the free OH stretch (at ~3700 cm⁻¹) and a combination mode of a hydrogen-bonded OH stretch vibration (~3450 cm⁻¹) and a low-frequency intermolecular hydrogen-bond vibration (~200 cm⁻¹).23 Both explanations would account for the observed dependence on isotope composition. With increasing isotopic dilution, the concentration of H_2O decreases, and the intensity of a band resulting from either intramolecular coupling or a Fermi resonance involving closely spaced OH stretch vibrations will decrease accordingly.

To compare the shapes of the H_2O and HDO:D_2O spectra in more detail, we plot in Figure 2 a the spectra normalized to the number of OH groups present. For H_2O, the negative Im χ^(2) band is broader (fwhm of 269 cm⁻¹) than for HDO:D_2O (fwhm of 208 cm⁻¹). In addition, the first spectral moment of the OH mode is smaller than for the free OD mode because the natural frequency is a factor of ~√2 larger for the free OH mode, which increases the frequency mismatch with the other hydrogen-bonded OH mode on the same water molecule. Accordingly, the frequency shift resulting from the coupling is reduced for the free OH mode compared with the free OD mode. In addition, the intramolecular coupling is somewhat weaker in H_2O than in D_2O.24,25 The positive amplitude of the free OH mode in the Im χ^(2) spectrum reflects its orientation with the hydrogen atom pointing away from the bulk. The Im χ^(2) spectrum of H_2O shows a small positive offset above 3750 cm⁻¹. The small positive offset is most likely due to the experimental error in the determined phase of χ^(2) of ~10°.

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(295 K). The signal scales with the number of chromophores and accordingly decreases with increasing isotopic dilution. The spectra show a main negative band centered at ~3425 cm⁻¹ and a positive band near 3700 cm⁻¹. The Im χ^(2) spectra of the liquid water–air interface shown in Figure 1 are very similar to other recently reported spectra.19–21 All spectra show a zero-crossing near ~3570 cm⁻¹. The negative imaginary band below 3570 cm⁻¹ corresponds to hydrogen-bonded OH groups. The negative value of Im χ^(2) implies that the hydrogen-bonded OH groups have a net orientation of their hydrogen atoms pointing toward the bulk. The peak position is ~3425 cm⁻¹ and does not change with isotopic concentration.

The frequency of the free OH mode is affected by intramolecular coupling: We find that the position of the free OH mode shifts from ~3701 cm⁻¹ in pure H_2O to ~3692 cm⁻¹ for diluted HDO by decomposing the Im χ^(2) of the free OH mode by two Gaussian bands. The frequency of the free OH peak of H_2O is 4 cm⁻¹ higher than the value of 3697 cm⁻¹ that was reported by Suzuki et al.23 This difference is within the experimental uncertainty of our experiment. In a previous study by Stiopkin et al.24 a shift of ~17 cm⁻¹ has been observed for the free OD mode. The observed shift of ~9 cm⁻¹ for the free OH mode is smaller than for the free OD mode because the natural frequency is a factor of ~√2 larger for the free OH mode, which increases the frequency mismatch with the other hydrogen-bonded OH mode on the same water molecule. Accordingly, the frequency shift resulting from the coupling is reduced for the free OH mode compared with the free OD mode. In addition, the intramolecular coupling is somewhat weaker in H_2O than in D_2O.24,25 The positive amplitude of the free OH mode in the Im χ^(2) spectrum reflects its orientation with the hydrogen atom pointing away from the bulk. The Im χ^(2) spectrum of H_2O shows a small positive offset above 3750 cm⁻¹. The small positive offset is most likely due to the experimental error in the determined phase of χ^(2) of ~10°.

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this band is red-shifted by \(\sim 19 \text{ cm}^{-1}\). These differences result from the resonant coupling of the OH oscillators for pure \(\text{H}_2\text{O}\); for \(\text{HDO}:\text{D}_2\text{O}\) this effect vanishes.\(^{22,29}\)

The broadening and red shift of the spectrum can be explained from the near-resonant interactions between the OH stretch vibrations. The near-resonant coupling of the OH stretch vibrations in pure \(\text{H}_2\text{O}\) leads to the formation of a band of delocalized exciton OH vibrations that is broader than the inhomogeneous distribution of uncoupled OH-stretch vibrational frequencies, thus explaining the larger width of the negative \(\text{Im } \chi^{(2)}\) band of \(\text{H}_2\text{O}\) compared with dilute \(\text{HDO}:\text{D}_2\text{O}\). The OH vibrations are in-phase for the lower-frequency exciton modes in this band and out-of-phase for the higher frequency exciton modes in this band. As a result, the low-frequency exciton modes have a larger absorption cross-section than the high-frequency exciton modes, leading to a red shift of the first spectral moment. Recent molecular dynamics simulations confirmed that the near-resonant coupling of the OH stretch vibrations leads to a broadening and red shift of the OH stretch \(\chi^{(2)}\) spectrum.\(^{22}\) The calculated results are in qualitative but not quantitative agreement with the experimental findings; for example, the calculated red shift of the spectrum is larger than is experimentally observed.

To compare the surface \(\text{Im } \chi^{(2)}\) spectra with the bulk response, one should note that the SFG response is the product of the infrared transition dipole moment and the Raman polarizability. We therefore plot in Figure 2b the constructed \(\sqrt{\alpha_{\text{IR}}/\alpha_{\text{Raman}}}\) spectra of \(\text{H}_2\text{O}\) and isotopically diluted water (\(\text{HDO}:\text{D}_2\text{O}\)) (with \(\alpha_{\text{IR}}\) and \(\alpha_{\text{Raman}}\) as the bulk infrared and Raman signals, respectively; see the Supporting Information for experimental details). For dilute \(\text{HDO}:\text{D}_2\text{O}\), the surface and bulk spectra show a quite similar width and shape, and the experimental details). For dilute \(\text{HDO}:\text{D}_2\text{O}\), the surface and bulk spectra show a quite similar width and shape, and the experimental details). For dilute \(\text{HDO}:\text{D}_2\text{O}\), the surface and bulk spectra show a quite similar width and shape, and the experimental details). For dilute \(\text{HDO}:\text{D}_2\text{O}\), the surface and bulk spectra show a quite similar width and shape, and the experimental details). For dilute \(\text{HDO}:\text{D}_2\text{O}\), the surface and bulk spectra show a quite similar width and shape, and the experimental details). For dilute \(\text{HDO}:\text{D}_2\text{O}\), the surface and bulk spectra show a quite similar width and shape. The near-resonant coupling of the OH stretch vibrations in pure \(\text{H}_2\text{O}\) leads to the formation of a band of delocalized exciton OH vibrations that is broader than the inhomogeneous distribution of uncoupled OH-stretch vibrational frequencies, the inhomogeneous distribution of uncoupled OH-stretch vibrational frequencies, thus explaining the larger width of the negative \(\text{Im } \chi^{(2)}\) band in \(\text{H}_2\text{O}\) compared with dilute \(\text{HDO}:\text{D}_2\text{O}\). The OH vibrations are in-phase for the lower-frequency exciton modes in this band and out-of-phase for the higher frequency exciton modes in this band. As a result, the low-frequency exciton modes have a larger absorption cross-section than the high-frequency exciton modes, leading to a red shift of the first spectral moment. Recent molecular dynamics simulations confirmed that the near-resonant coupling of the OH stretch vibrations leads to a broadening and red shift of the OH stretch \(\chi^{(2)}\) spectrum.\(^{22}\) The calculated results are in qualitative but not quantitative agreement with the experimental findings; for example, the calculated red shift of the spectrum is larger than is experimentally observed.

The \(\text{H}_2\text{O}\) bulk spectrum is strongly affected by intra- and intermolecular coupling,\(^{17}\) leading to a substantial broadening from 306 to 413 cm\(^{-1}\) (full width at half maximum) and a red shift of the first spectral moment by \(\sim 34 \text{ cm}^{-1}\) with respect to the first spectral moment of the \(\text{HDO}:\text{D}_2\text{O}\) spectrum. The shift of the first spectral moment due to the near-resonant coupling of the OH stretch vibrations is thus about two times larger for the bulk spectrum than for the surface spectrum. These observations show that the hydrogen bonds at the surface are quite comparable in strength to the hydrogen bonds in the bulk, in line with the observation of a remarkably fast onset of a bulk-phase hydrogen-bond structure when entering the surface of water.\(^{11,24,30,31}\)

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Next, we compare the surface of water with the surface of ice. The growth and processing of single-crystal ice samples are described in ref 33. In Figure 3a we show the \(\text{Im } \chi^{(2)}\) spectrum of the basal faces of \(\text{H}_2\text{O}\) and \(\text{H}_2\text{O}:3\text{D}_2\text{O}\) ice single crystals at 245 K. Recently, the SFG spectrum of \(\text{H}_2\text{O}\) ice at ca. 130 K was reported by Nojima et al.\(^{34}\) This SFG spectrum contains a positive band at 3100 cm\(^{-1}\) for which we observed a dispersive line shape in the imaginary part,\(^{33}\) that is, \(\pi/2\) phase shifted in comparison with the band reported in ref 34. The band at 3100 cm\(^{-1}\) likely represents the response of water molecules deeper buried in the ice crystal. At temperatures above 200 K, this bulk band becomes small,\(^{33}\) and the SFG spectrum is dominated by the band near 3200 cm\(^{-1}\) that has an absorptive imaginary response at all temperatures and that represents the response of water molecules at the surface. Otsuki et al.\(^{35}\) measured the spectrum of \(\text{HDO}:\text{D}_2\text{O}\) ice at 120 K. This spectrum has a different shape from the spectrum shown here, which can be explained from the fact that the previous study was performed at a much lower temperature and for a different polarization combination. It has been shown that the SFG spectrum of ice strongly depends on temperature.\(^{33,36}\)

Above 3500 cm\(^{-1}\), the \(\text{Im } \chi^{(2)}\) spectrum is positive and contains a resonance at \(\sim 3700 \text{ cm}^{-1}\), corresponding to non-hydrogen-bonded free OH groups sticking out of the ice surface, and a broad positive response below 3500 and 3600 cm\(^{-1}\). The latter response has been assigned to the antisymmetric stretch vibration of \(\text{H}_2\text{O}\) molecules near the surface.\(^{33}\) This signal decreases less upon isotopic dilution than expected, probably because of the narrowing of the strong negative signal between 3150 and 3450 cm\(^{-1}\). The position of the free OH is \(\sim 8 \text{ cm}^{-1}\) higher for \(\text{H}_2\text{O}\) ice than for \(\text{HDO}:\text{D}_2\text{O}\) ice, which can be explained from the intramolecular coupling of
H$_2$O, similar to what is observed for the surface of liquid H$_2$O (see above). The observed frequency shift for ice is slightly smaller than the ∼9 cm$^{-1}$ shift observed for liquid water, which can be well explained from the larger frequency difference between the free OH oscillator and the other hydrogen-bonded OH group located on the same H$_2$O molecule for H$_2$O ice. The spectral shapes of the Im $\chi^{(2)}$ response for H$_2$O and HDO:D$_2$O ice are very different below 3500 cm$^{-1}$ (Figure 3a). The negative imaginary band of the H$_2$O spectrum is dominated by a band at 3230 cm$^{-1}$. A small shoulder band is located near ∼3450 cm$^{-1}$. The Im $\chi^{(2)}$ spectrum of HDO:D$_2$O ice is dominated by a single negative imaginary band at ∼3310 cm$^{-1}$. For H$_2$O ice the negative Im $\chi^{(2)}$ is broader (fwhm of 168 cm$^{-1}$) than for HDO:D$_2$O ice (fwhm of 91 cm$^{-1}$). In addition, the first spectral moment of this band is red-shifted by ∼33 cm$^{-1}$ compared with HDO:D$_2$O. The effect of near-resonant coupling of the OH stretch vibrations is thus stronger at the surface of H$_2$O ice than at the surface of H$_2$O liquid water, for which we observed a red shift of ∼19 cm$^{-1}$. Recent molecular dynamics simulations by Ishiyama and Morita also found the OH stretch vibrations at the surface of H$_2$O ice to be strongly delocalized. However, the shapes of the calculated spectra of both H$_2$O and HDO:D$_2$O are not in agreement with the measured spectra.

The stronger coupling of the OH stretch vibrations at the surface of ice can be explained from the fact that ice has a narrower distribution of uncoupled OH stretch vibrational frequencies than liquid water. Because of this narrower distribution, the resonant dipole–dipole interactions result in a stronger mixing of the OH vibrations in ice than in water, both in bulk and at the surfaces. In addition, the OH stretch transition dipole moment is ∼20% larger for ice than for liquid water, leading to a stronger intra- and intermolecular dipole–dipole coupling and thus to a larger degree of delocalization of the OH stretch vibrations for H$_2$O ice than for H$_2$O liquid water.

In Figure 3b we present, for comparison, bulk $\sqrt{\alpha_{IR} f_{Raman}}$ spectra of H$_2$O and H$_2$O:3D$_2$O ice at 245 K. The isotopically diluted spectrum is dominated by a single band at ∼3300 cm$^{-1}$. This band is at a lower frequency for HDO:D$_2$O ice than for liquid HDO:D$_2$O, reflecting the larger average strength of the hydrogen bonds in ice than in the liquid. The band is also narrower for HDO:D$_2$O ice than for liquid HDO:D$_2$O, which indicates that the distribution of hydrogen-bond strengths is narrower in ice than in liquid water. For HDO:D$_2$O ice, the bulk resonance frequency is close to the maximum of the sum-frequency spectrum, red-shifted by only ∼10 cm$^{-1}$. Hence, the hydrogen bonds have a similar strength at the surface of ice surface as in the bulk of ice, in line with the observations for liquid water.

The bulk spectra of HDO:D$_2$O and H$_2$O ice strongly differ, which can be explained from the strong effects of near-resonant coupling and the resulting delocalization of the OH oscillators in H$_2$O ice. The H$_2$O bulk spectrum is broader (fwhm of 357 cm$^{-1}$) than the bulk spectrum of HDO:D$_2$O (fwhm of 170 cm$^{-1}$) and has a first spectral moment that is red-shifted by ∼63 cm$^{-1}$ with respect to the first spectral moment of the HDO:D$_2$O bulk spectrum. This shift is about two times larger than for the surface of H$_2$O ice. Clearly, the near-resonant coupling of the OH stretch vibrations results in much stronger spectral broadening and stronger spectra red shift for bulk H$_2$O ice than for the surface of H$_2$O ice.

We observe the relative decrease in spectral red shift going from the bulk to the surface to be quite similar for water and ice. For both phases of water we find a decrease in the red shift of the first spectral moment by a factor of 1.9: from 34 to 19 cm$^{-1}$ for liquid water and from 63 to 33 cm$^{-1}$ for ice. This similarity in the decrease in the red shift suggests that the reduction of the near-resonant coupling of the OH stretch vibrations at the surface is mainly a geometrical effect. For both water and ice, the density of OH oscillators decreases by a factor of ∼2 going from the bulk to the surface, with the result that the vibrational exciton modes at the surface involve a smaller number of local OH oscillators than the vibrational exciton modes in the bulk. This smaller degree of delocalization at the surface reduces the broadening and red shift of the surface spectrum.

In summary, we studied the effects of near-resonant intra- and intermolecular interactions at the surfaces of liquid water and ice using heterodyne-detected SFG experiments. For both liquid water at 295 K and ice at 245 K, we observed a broadening and a red shift of the first spectral moment of the hydrogen-bonded Im $\chi^{(2)}$ spectrum of neat H$_2$O with respect to isotopically diluted (HDO:D$_2$O) water. The red shift is stronger for ice than for water, which indicates that the OH vibrations are more strongly delocalized at the ice surface than at the water surface. By comparing the Im $\chi^{(2)}$ spectra with the bulk response, we conclude that the near-resonant coupling effects are weaker at the surface than in the bulk, for both water and ice, indicating that for both phases of water the OH vibrations are less strongly delocalized at the surface than in the bulk.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b03359.

Description of the sample preparation, experimental setup, and analysis. (PDF)

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Notes

The authors declare no competing financial interest.

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