Direct Evidence for a Surface and Bulk Specific Response in the Sum-Frequency Generation Spectrum of the Water Bend Vibration

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Direct Evidence for a Surface and Bulk Specific Response in the Sum-Frequency Generation Spectrum of the Water Bend Vibration

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ABSTRACT

Spectroscopic studies of aqueous surfaces can provide a fundamental understanding of interfacial processes. These studies have largely focused on the OH stretch vibrations of water, which is unfortunate as the bending mode is an attractive feature to probe as it is relatively free of inter- and intramolecular couplings. However, the origin of the response of the bending mode is highly debated and has been assigned to either surface-specific or to bulk effects. Here, we study the bending mode of pure water and charged aqueous surfaces using heterodyne-detected vibrational sum frequency generation spectroscopy (HD-VSFG) to quantify the two effects. Our results show a low - (1626 cm^{-1}) and a high - (1656 cm^{-1}) frequency component which can be unambiguously assigned to an interfacial dipole and a bulk quadrupolar response, respectively. We thus demonstrate that probing the bending mode provides structural and quantitative information on both the surface and the bulk.

Introduction

The structure and dynamics of aqueous interfaces is of high relevance for many different scientific fields.^{1–9} Many important chemical and biological processes take place at aqueous interfaces, like for instance molecular recognition at bio-membranes, protein folding, and energy conversion and storage.^{10–15} The structural properties of the neat water/air interface^{16,17} and charged aqueous interfaces have been extensively studied with vibrational sum-frequency generation spectroscopy (VSFG) in the frequency region of the water OH stretch vibrations.^{11,18–20} The frequency region of the water bending vibrations has been much less investigated, even though this region can provide unique information on the hydrogen-bond structure, because, in contrast to the stretching mode, the water bending mode is hardly influenced by intermolecular coupling due to its small transition dipole moment.^{21–23} Furthermore, there is only one water bending mode per water molecule, thus strongly decreasing the effects of intramolecular coupling on the spectrum.²¹ The first measurements of the water bending mode of the neat water/air interface were performed with conventional VSFG, for which the response is proportional to the modulo squared of the second-order susceptibility ($|\chi^{(2)}|^2$), by Vinaykin and Benderskii²². These authors reported the observation of an inhomogeneously broadened line shape centered at 1650 cm^{-1} . They assigned the low- and high-frequency wing of this band to weakly hydrogen bonded water molecules sticking out of the surface, and to fully hydrogen-bonded interfacial water molecules, respectively. Furthermore, they found evidence for the presence of a large orientational inhomogeneity by measuring the $|\chi^{(2)}|^2$ spectrum with different polarization combinations (SSP and PPP)²². These findings have been confirmed by recent computational studies by Nagata et al.²³, and Ni and Skinner²¹, that showed that the different hydrogen-bonded water species correlate with different net orientations of the bending mode transition dipole moment.

Kundu et al. reported the first heterodyne detected VSFG (HD-VSFG) measurements of the neat water/air interface in the bending mode region.²⁴ In this technique the real and imaginary part of the second-order susceptibility $\chi^{(2)}$ are determined. The measured $\text{Im}[\chi^{(2)}]$ showed a single positive peak centered at 1650 cm^{-1} . In the same work it was also reported that charging the interface negative with iodide ions leads to an enhancement of this signal. This observation strongly contrasts with observations in the OH stretching mode region, for which a change of the sign of the band is observed when the surface gets negatively charged.^{18,20} The accompanying calculations indicated that the observed $\text{Im}[\chi^{(2)}]$ signal would originate mainly from a quadrupole response from the bulk.²⁴ In the most recent intensity VSFG measurements of Benderskii¹⁵ it was found that the interfacial water molecules orient in different directions depending on the charge of the surface. This dependence of the orientation of the interfacial water molecules on the charge of the surface, suggests that the observed signal primarily results from a surface dipolar response. This explanation is consistent with the $|\chi^{(2)}|$ measurements of the group of Bonn and Nagata.²⁵ The results of the $|\chi^{(2)}|^2$ measurements of the groups of Benderskii and Bonn and Nagata thus strongly disagree with the interpretation of the $\text{Im}[\chi^{(2)}]$ measurements by Kundu et al.²⁴, who reported that the signal in the bending mode region

would mainly originate from a bulk quadrupolar response . Here we perform HD-VSFG measurements to investigate the sum-frequency response of aqueous systems in the frequency region of the bending mode. By measuring both the phase of the sum-frequency light and the effect of surface charge on the signal, we observe and distinguish both a dipolar contribution of the surface and a quadrupolar contribution of the bulk to the signal. We thus arrive at a consistent picture of the response of the water bending mode for different aqueous systems, and we can clear up the existing inconsistencies between earlier reports.^{15,21,22,24,25}

Results

In Figure 1 we present $|\chi^{(2)}|^2$ (intensity VSFG) spectra of the neat water surface water/air (dark blue), the water/DTAB/air (darkcyan) and the water/SDS/air interface (magenta) in the frequency region of the water bend vibration. For pure water we observe that the $|\chi^{(2)}|^2$ spectrum has the shape of a step function, in agreement with previous findings.²² The addition of a charged surfactant leads to strong changes of the response. Adding the positively charged DTAB leads to an enhancement and a redshift of the response, adding the negatively charged SDS leads to a redshift of the maximum of the SFG intensity.

Figure 1. $|\chi^{(2)}|^2$ spectra of the neat water surface water/air (dark blue), the water/DTAB/air (darkcyan) and the water/SDS/air interface (magenta) in the frequency region of the water bend vibration. The concentration of the SDS and DTAB solution is 10 mM and the measurements are performed in SSP polarization configuration (S-SFG, S-VIS, P-IR). The solid curves are the result of model calculations, as described in the text. Note that the spectra are not offset with respect to each other, the signal observed for the DTAB solution is much stronger than that of pure water and the SDS solution.

In Figure 2a the experimental $\text{Im}[\chi^{(2)}]$ spectra of neat water (dark blue) in the frequency region of the water bend vibration is presented. We observe a symmetric positive peak centered at 1656 cm^{-1} that we assign to the water bending mode. The observed spectrum agrees with previous HD-VSFG measurements of the water bending mode of Kundu et al.²⁴. We find that this $\text{Im}[\chi^{(2)}]$ response can be fitted well with a single lorentzian curve (cyan). In Figure 2b we show a comparison of the calculated $\text{Im}[\chi^{(2)}]$ spectrum of neat water over a broad frequency region (cyan) combined with the experimental data (dark blue) in the frequency region of the water bending mode. In addition to the water bending mode, the model includes the resonances of the OH stretch vibrations of hydrogen-bonded and non-hydrogen-bonded water molecules (red dotted line, $\chi_{\sigma,OH}$). The OH stretch band of the hydrogen-bonded water molecules is modeled with two lorentzian curves with maxima at 3250 cm^{-1} and 3450 cm^{-1} , and the response of the non-hydrogen-bonded water molecules is modeled with a single lorentzian centered at 3700 cm^{-1} . In addition to the resonances in the stretching mode region, we included a frequency-independent non-resonant background χ_{NR} (orange dotted). The comparison of the model and the experimental data shows that the resonances of the OH stretch band have a negligible influence on the observed $\text{Im}[\chi^{(2)}]$ in the bending mode region. However, the $\text{Re}[\chi^{(2)}]$ in the bending mode region does show significant contributions from both the different OH stretch vibrations $\chi_{\sigma,OH}$ and the non-resonant background χ_{NR} , as illustrated in Figure 2c,d. The low-frequency wing of the real response of the stretching band (red dotted) adds a negative value to the real part of the response of the bending mode χ_{δ} (green dotted). In Figure 2d we show the $\text{Re}[\chi^{(2)}]$ over a broad frequency range. This figure clearly shows that the χ_{σ} contribution also induces a slight tilt of the total $\text{Re}[\chi^{(2)}]$ in the frequency region of the bending mode. From the analysis of Figure 2 it is clear that the observed step in the intensity SFG spectrum of pure water of Figure 1 can be well explained from the interference with the stretch vibrations. The $\text{Re}[\chi_{\sigma}^{(2)}]$ of the stretch vibrations compensates the positive $\text{Re}[\chi_{\delta}^{(2)}]$ of the bending vibration at frequencies $< 1650 \text{ cm}^{-1}$, and

Figure 2. (a) $\text{Im}[\chi^{(2)}]$ spectrum of neat water (dark blue) in the frequency region of the bending mode. The solid line represents the result of a fit, explained in the text. (b)–(d) modeled $\text{Im}[\chi^{(2)}]$ and $\text{Re}[\chi^{(2)}]$ spectra of neat water ($\chi_{tot,the}$, cyan) compared to the experimental data (dark blue). The figures also show the decomposition of the total response $\chi_{tot,the}$ in different contributions: the non-resonant background χ_{NR} (dotted orange), the bending mode response χ_{δ} (dotted green), and the response of the OH stretch vibrations χ_{σ} (dotted red).

enhances the negative $\text{Re}[\chi_\delta^{(2)}]$ of the bending vibration at frequencies $>1650 \text{ cm}^{-1}$. As a result, the total intensity ($|\chi^{(2)}|^2$) shows a step-like shape.

In Figure 3, we present experimental $\text{Im}[\chi^{(2)}]$ spectra of the water/DTAB/air (dark-cyan) and the water/SDS/air interface (magenta) in the frequency region of the water bend vibration. The $\text{Im}[\chi^{(2)}]$ spectrum of the water/DTAB/air interface shows a positive band centered at 1640 cm^{-1} . This band is stronger, broader and somewhat redshifted in comparison to the $\text{Im}[\chi^{(2)}]$ spectrum of water/air. The $\text{Im}[\chi^{(2)}]$ spectrum of the water/SDS/air interface shows a clear negative feature at lower frequencies. At this point it should be noted that we can exclude phase distortions in the HD-VSFG spectra, as the electric double layer (EDL) has a thickness $<10 \text{ nm}$ for ionic strengths $>1 \text{ mM}$.^{26–28} The spectra observed for water/DTAB/air and water/SDS/air can be well explained from the presence of an additional low-frequency band in the $\text{Im}[\chi^{(2)}]$ spectra that is negligibly present for neat water/air, and that has a different sign for the water/DTAB/air and the water/SDS/air interface. We thus find that the $\text{Im}[\chi^{(2)}]$ response of neutral and surface-charged water can be well explained with two bands of which one changes sign depending on the sign of the surface charge. To check that the lower-frequency band truly depends on the sign of the surface charge, we also performed measurements with a different negatively charged surfactant sodium monododecyl phosphate (SMP) (see supporting figure 2 in the Supporting Information). These measurements also show the presence of a negative band centered at 1626 cm^{-1} , thus confirming that this band results from the bending mode of water and the presence of negative charge at the surface. To quantify the different contributions to the $\text{Im}[\chi^{(2)}]$ spectra we decompose the spectra observed for water/DTAB/air and water/SDS/air into lorentzian-shaped bands centered at 1656 cm^{-1} (blue) and 1626 cm^{-1} (red). The band at 1656 cm^{-1} does not depend on the charge of the surface and is assigned to the quadrupolar response of the bulk. The sign and amplitude of the 1626 cm^{-1} band are determined by the charge at the surface and can be assigned therefore to a dipolar surface contribution. The exact frequencies of the dipolar and quadrupolar contributions are extracted from the fitting procedure. For neat water we find that the experimental data can be well described with a single lorentzian line that only represents the quadrupolar contribution of the bulk (Figure 2). In our fitting procedure for the water/DTAB/air and water/SDS/air (10 mM) interfaces presented in Figs. 3a,b we use the same quadrupolar contribution. In the Supplementary Information we show the measured $\text{Re}[\chi^{(2)}]$ responses of water/DTAB/air and water/SDS/air, and the decomposition of the $\text{Im}[\chi^{(2)}]$ and $\text{Re}[\chi^{(2)}]$ spectra (Supporting Information Figures S3 (DTAB) and S4 (SDS)), as was done for neat water/air, which was shown in Figure 2. The thus obtained $\text{Re}[\chi^{(2)}]$ and $\text{Im}[\chi^{(2)}]$ responses account very well for the observed effects in the $|\chi^{(2)}|^2$ spectra of the three studied systems shown in Figure 1. The solid lines in Figure 1 are the result of the complete analysis of the $\chi^{(2)}$, as is shown in Figure 2, and Figures S3 and S4 of the SI, and include the interference effect of the bending mode with the stretch vibrations and the nonresonant background, and the quadrupolar bulk and dipolar interface contributions to the bending mode response. We find that for water/DTAB/air and water/SDS/air the $\text{Re}[\chi^{(2)}]$ response is again strongly affected by the interference with the response of the OH stretch vibrations, as was the case for neat water.

For the positively charged DTAB/air surface the interfacial water molecules are oriented with their hydrogen atoms towards the bulk. For the stretch vibration this orientation leads to a negative contribution to $\text{Im}[\chi^{(2)}]$, because for the stretch vibration

Figure 3. Spectral decomposition of the $\text{Im}[\chi^{(2)}]$ spectra of the water/DTAB/air (dark cyan) and the water/SDS/air interface (magenta), each modeled with two lorentzian-shaped spectral components. The two lorentzian-shaped components are assigned to the quadrupolar contribution of the bulk (blue, centered at 1656 cm^{-1}), and to the surface dipolar contribution (red, centered at 1626 cm^{-1}), of the water bending mode. The DTAB and SDS solution have a concentration of 10 mM.

Figure 4. The $\text{Im}[\chi^{(2)}]$ spectra of the water/DTAB/air (4(a)) and the water/SDS/air (4(b)) interface at different concentrations in the range of 0.05 to 5 mM including fits presented with dashed lines. 4(c)-(d) show the absolute amplitude of the dipole contribution extracted from the fitting procedure in respect to the concentration of DTAB 4(c) and SDS 4(d).

the dipole and the polarizability have the same dependence on the phase of the stretch vibration (when the hydrogen atoms move away from the oxygen atom, the dipole moment increases and the size and polarizability of the water molecules also increase). For the bending vibration the dipole moment and polarizability have an opposite dependence on the phase of the bending vibration (when the atoms move together, the dipole moment increases while the size and polarizability of the water molecule decreases). As a result, the surface dipolar contribution to the $\text{Im}[\chi^{(2)}]$ of the bending mode is positive for water molecules with their hydrogen atoms oriented towards the bulk. For the negatively charged water/SDS/air interface, the water molecules have their hydrogen atoms oriented towards the surface and the surface dipolar contribution to the $\text{Im}[\chi^{(2)}]$ of the bending mode is negative.

In Figure 4 we present the $\text{Im}[\chi^{(2)}]$ spectra of water/DTAB/air (4a) and water/SDS/air (4b) at different concentrations in the range of 0 mM to 5 mM. For water/DTAB/air we observe that the positive peak centered at 1656 cm^{-1} assigned to the water bending mode is increasing with increasing concentration of DTAB. Furthermore, we observe a broadening and a slight red shift of the $\text{Im}[\chi^{(2)}]$ spectra. Increasing the SDS concentration leads to an ingrowth of a negative peak at lower frequencies. These observations confirm the assignment of the band at 1626 cm^{-1} to a surface dipolar contribution. In the case of DTAB, the positive surface charge is increasing with increasing concentration, thus causing an enhanced ordering of the interfacial water molecules with their hydrogen atoms towards the bulk, which leads to an increase of a positive dipolar band at 1626 cm^{-1} to $\text{Im}[\chi^{(2)}]$. The increase of the concentration of SDS increases the negative charge density at the surface, thereby inducing an enhanced orientation of the water molecules with their hydrogen atoms towards the surface, and thus to an increase of a negative dipolar contribution at 1626 cm^{-1} to the $\text{Im}[\chi^{(2)}]$ response.

To quantify the results, we decompose the responses measured at different concentrations of DTAB and SDS in two lorentzian bands centered at 1626 cm^{-1} and 1656 cm^{-1} , for the dipole and quadrupole contribution, respectively. While keeping the quadrupolar contribution and the width of the dipolar contribution constant, we allow the amplitude of the dipole contribution to change with varying concentration. The fits are shown in Figure 4 (a-b) with dashed lines. The decompositions for the different concentrations are presented in the Supporting Information (Supporting Figures 5 (DTAB) and 6 (SDS)). In

Figure 4c,d we present the amplitude of the dipolar band extracted from the fitting procedure as a function of the surfactant concentration. For both DTAB and SDS, the amplitude of the dipolar band increases nonlinearly with concentration, showing saturation behavior at a bulk concentration of a few mM. From the fitting procedure we find that at a surfactant concentration of 10 mM the absolute ratio of the amplitudes of the dipolar interfacial and the quadrupolar bulk contribution is 1:0.7, both for the water/DTAB/air interface and the water/SDS/air interface. It is also seen that at zero surfactant concentration the dipolar contribution is negligible.

Discussion

Recently Ahmed et al.²⁹ reported HD-VSFG measurements of water with charged surfactants and lipid monolayer/water interfaces in which they did not find evidence for an interfacial dipole contribution of the water bending mode. Their $\text{Im}[\chi^{(2)}]$ spectra show a positive band, independent on the sign of the charge of the headgroup. Therefore, Ahmed et al. argued that the $\text{Im}[\chi^{(2)}]$ response of the water bending mode arises only from a quadrupolar response, even for charged surfaces.²⁹ At first sight this finding appears to disagree with the results of Figure 3. However, the measurements of Ahmed et al. were performed with a surfactant concentration of only 0.1 mM, while the measurements shown in Figure 3 are performed with a surfactant concentration of 10 mM. As is clearly illustrated in Figure 4, for a surfactant concentration of 0.1 mM, the dipolar contribution is negligibly small. At these low concentrations the contribution of the dipolar surface concentration merely induces a small change in amplitude and shift in frequency of the overall measured $\text{Im}[\chi^{(2)}]$ response. An interesting observation is that the dipolar contribution has a significantly lower frequency than the quadrupolar contribution. For the bending mode, the vibrational frequency increases with increasing strength of the hydrogen-bond interaction.²² Hence, the lower frequency of the dipolar contribution indicates that the hydrogen bonds of the contributing water molecules are weaker than those of the water molecules giving rise to the quadrupolar contribution. This finding agrees with the fact that the molecules giving rise to the quadrupolar contribution are predominantly located in the bulk of the liquid, whereas the molecules giving rise to the dipolar contribution will be located at the surface. In summary, we performed heterodyne detected vibrational surface sum-frequency generation (HD-VSFG) measurements of pure water, and of aqueous solutions of ionic surfactants, i.e. of a dodecyltrimethylammonium bromide solution (DTAB), and of a sodium dodecyl sulfate solution (SDS) solution. We find that the sum-frequency generation response in the frequency region of the bending mode of water is strongly affected by the interference with the low-frequency wing of the OH stretch vibrations of water. The different contributions of the bending mode and the stretching modes can be distinguished and quantified.

By comparing the measured $\text{Im}[\chi^{(2)}]$ spectra of differently charged water surfaces, we demonstrate the presence of a surface-specific dipolar response of the water bending mode centered at 1626 cm^{-1} . This response changes sign when the sign of the surface charge changes, and increases with increasing surface charge, i.e. increasing concentration of ionic surfactant. In addition to this dipolar surface contribution, the bending mode of water shows a quadrupolar bulk contribution centered at 1656 cm^{-1} . This contribution is not surface-charge dependent and dominates the $\text{Im}[\chi^{(2)}]$ response of neat water in the frequency region of the bending mode. We thus demonstrate that HD-VSFG involving the bending mode of the water molecules can provide important information on the hydrogen-bond structure of both the surface and the bulk of aqueous solutions.

Methods

The technique of HD-VSFG has been developed and successfully used by several groups.^{20,30,31} Here we give a brief description of our implementation of HD-VSFG. A more detailed description of the setup can be found in previous work.³² We use an amplified Ti:Sapphire laser system (1 kHz, 35 fs, 6.5 mJ/pulse) to generate a narrow 800 nm beam and a tunable, broadband mid-infrared beam. The two beams are spatially and temporally overlapped at the surface of a gold mirror to generate light at the sum-frequency that serves as a local oscillator (LO-SFG). The 800 nm beam (s-polarized), the IR beam (p-polarized) and the LO-SFG signal (s-polarized) are all sent onto a concave mirror. Before the beams are focused on the sample surface, the LO-SFG signal is passing through a silica plate to delay it in time (~ 1.6 ps). The 800 nm and IR beam are generating a second SFG signal at the sample surface. Both the SFG signal of the sample and the LO-SFG signal are sent into a spectrometer and detected with a thermoelectrically cooled charged-coupled device (CCD, Princeton Instruments). From the interference spectrum of the two SFG signals the real (Re) and the imaginary (Im) $\chi^{(2)}$ spectra can be extracted, providing direct information on the orientation of the vibrational transition dipole moments, and thus on the absolute orientation of the molecules at the surface.³³ We also perform a reference experiment in which the sample is replaced by a z-cut quartz crystal. The typical acquisition time of a single HD-VSFG spectrum is 600 seconds. The water bending mode has a small transition dipole moment and therefore yields a ~ 5 times smaller signal than the OH stretching modes. Therefore, the measurement of a clean signal confronts us with several technical challenges. In particular, in the frequency region of the water bending mode an etaloning effect occurs on the CCD camera, which introduces a systematic modulation on the signal. A detailed explanation of how we were able to remove this systematic modulation can be found in the Supporting Information (Noise reduction and

measurement procedure and Supporting figure 1). For all measurements we used water from a Millipore Nanopure system (18,2 M Ω). Both DTAB and SDS are purchased from Sigma Aldrich and used without further purification. In all experiments we observe a small frequency-independent positive offset that we assign to background noise of which the amplitude varies between different experiments. We extract the amplitude of this background noise from our fitting procedure. In all presented data this background noise has been subtracted.

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Author contributions statement

C.J. Moll, J. Versluis designed research idea; C.J. Moll performed the experiments; C.J. Moll, J. Versluis, H.J. Bakker analyzed and discussed the data; and C.J. Moll, J. Versluis, H.J. Bakker wrote the paper.

Additional information

The authors declare no competing interest.

Figures

Figure 1

$|x(2)|^2$ spectra of the neat water surface water/air (dark blue), the water/DTAB/air (darkcyan) and the water/SDS/air interface (magenta) in the frequency region of the water bend vibration. The concentration of the SDS and DTAB solution is 10 mM and the measurements are performed in SSP polarization configuration (S-SFG, S-VIS, P-IR). The solid curves are the result of model calculations, as described in the text. Note that the spectra are not offset with respect to each other, the signal observed for the DTAB solution is much stronger than that of pure water and the SDS solution.

Figure 2

(a) $\text{Im}[\chi^{(2)}]$ spectrum of neat water (dark blue) in the frequency region of the bending mode. The solid line represents the result of a fit, explained in the text. (b)-(d) modeled $\text{Im}[\chi^{(2)}]$ and $\text{Re}[\chi^{(2)}]$ spectra of neat water ($\chi_{\text{tot,the}}$, cyan) compared to the experimental data (dark blue). The figures also show the decomposition of the total response $\chi_{\text{tot,the}}$ in different contributions: the non-resonant background χ_{NR} (dotted orange), the bending mode response χ_{δ} (dotted green), and the response of the OH stretch vibrations χ_{σ} (dotted red).

Figure 3

Spectral decomposition of the $\text{Im}[\chi^2]$ spectra of the water/DTAB/air (dark cyan) and the water/SDS/air interface (magenta), each modeled with two lorentzian-shaped spectral components. The two lorentzian-shaped components are assigned to the quadrupolar contribution of the bulk (blue, centered at 1656 cm⁻¹), and to the surface dipolar contribution (red, centered at 1626 cm⁻¹), of the water bending mode. The DTAB and SDS solution have a concentration of 10 mM.

Figure 4

The $\text{Im}[\chi(2)]$ spectra of the water/DTAB/air (4(a)) and the water/SDS/air (4(b)) interface at different concentrations in the range of 0.05 to 5 mM including fits presented with dashed lines. 4((c)-(d)) show the absolute amplitude of the dipole contribution extracted from the fitting procedure in respect to the concentration of DTAB 4(c) and SDS 4(d).

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