The Influence of Electrolyte Concentration on the Depth-Dependent Structural Anisotropy of Water at Charged Interfaces

Supplementary Information

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This supplementary information provides additional details on the data analysis procedure and the experiment. This includes: the removal of magnetic dipole contributions which is described in (section A), more data showing the extracted BIL and DL spectra for more NaCl concentrations (section B), and details on the analysis procedure for the determination of the error bars shown in Figures 2 and 3 in the main text (section C). Section D and E present additional details on the sample preparation and the SFG/DFG spectrometer used in this work.

A) Removal of magnetic dipole contributions

Apart from the desired electric dipole signals, the measured spectra presented in this work also contain small contributions from magnetic dipole transitions. As recently shown,[1] one part of the magnetic dipole contributions intrinsically generates different SFG and DFG amplitudes, even though they originate directly from the interface where beam propagation effects on their SFG and DFG responses are negligible. These signals almost exclusively appear in the C-H stretching region, however, as a consequence from their intrinsic amplitude differences, these sharp spectral features do not entirely cancel when taking the difference between SFG and DFG spectra. The resulting raw DL spectra therefore show small residual C-H resonances although their source is clearly located at the phase boundary (the surfactants are highly insoluble in water). In order to correct for these contributions, we remove them by subtraction of the SFG/DFG difference spectrum at the NaCl concentration of 10^{-1} M where the thickness of the anisotropic water layer is on the order of 1 nm and thus any deviations must originate from the magnetic dipole contribution. A detailed discussion of this procedure is given in the supplementary information of publication.[2]

B) Isolated spectra from BIL and DL

Figure S-1 shows the resulting BIL and DL spectra obtained by the decomposition of the measured SFG/DFG data, including the spectra for $10^{-3.5}$ M and 10^{-3} M NaCl concentration (which are not shown in the main text). Inspection of the spectra shows that the accuracy of the decomposition decreases with increasing salt concentration. This phenomenon originates from the fact that SFG and DFG become nearly equal for small Debye lengths, which makes the extracted DL contribution increasingly influenced by noise. The resulting noise from the DL spectrum then propagates into the BIL spectrum by the decomposition procedure. For this reason, BIL and DL spectra for 10^{-2} M NaCl concentration or higher offer little reliability and are therefore not extracted.

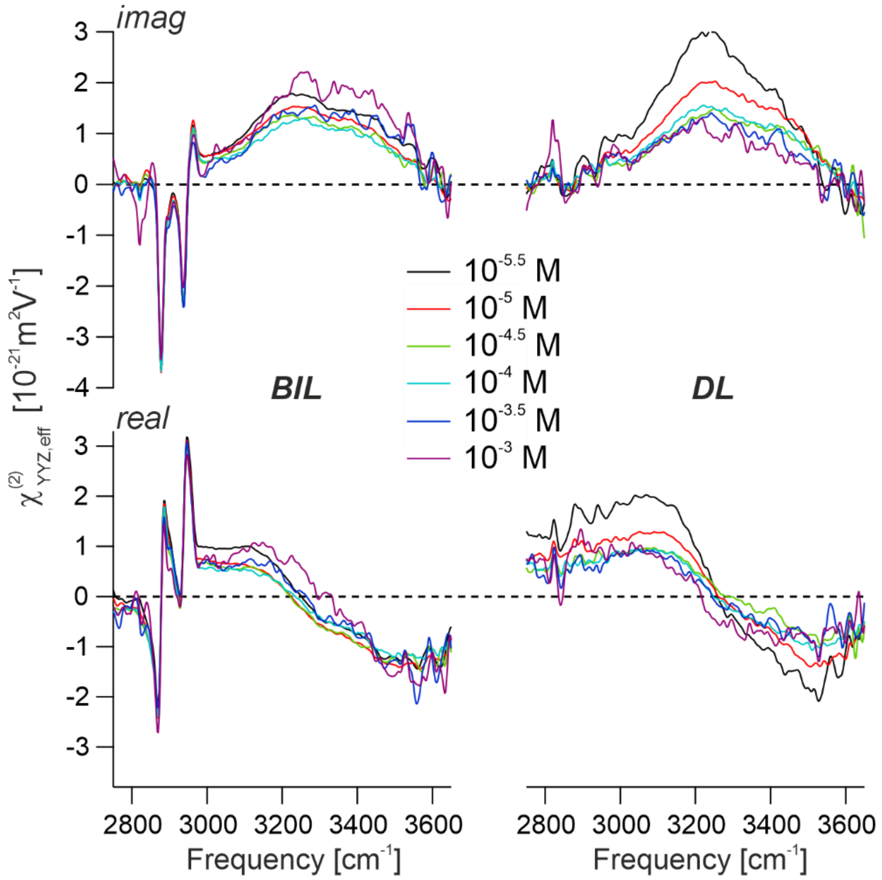

Figure S-1. Decomposition of the SFG/DFG spectra into the spectra from BIL (left side) and DL (right side) for NaCl concentrations $10^{-5.5}$, 10^{-5}, $10^{-4.5}$, 10^{-4}, $10^{-3.5}$, 10^{-3} M. Spectra are divided into their imaginary (top) and real (bottom) parts.

C) Calculation of relative amplitudes and error bars

The spectral amplitude deviations shown in Figure 2(e) as well as the relative Stern potentials shown in Figure 3 in the main text are obtained by analyzing the relative amplitudes of the water signals in the BIL and DL, respectively. In this analysis, all imaginary spectra are first divided by the respective spectrum obtained for 10^{-5} M NaCl concentration, yielding a spectrally flat line in the O-H stretching region. The choice of the 10^{-5} M data as reference is because this concentration offers the smoothest BIL and DL spectra that contain the smallest amount of spectral noise of all measurements. The relative amplitude of the responses is then determined by taking the mean value in the range from 3100 to 3400 cm^{-1}, with the presented error bars representing the standard deviation of the normalized amplitude within this range. For the deviations in the C-H amplitudes shown in Figure 2(e), the relative amplitude of the ss-CH_3 mode is determined from the normalized spectrum by taking the value at its peak frequency (at 2877 cm^{-1}). Because this method uses a single point in the spectrum error bars could not be determined using the method described above and are consequently not included in the plot.

D) Sample preparation

The sample preparation procedure follows closely that previously reported.[2] The investigated systems consist of monolayers of dihexadecyl phosphate (DHP, Sigma-Aldrich), an insoluble and negatively charged surfactant, deposited onto the surface of aqueous electrolytes with different ionic strengths. Electrolyte solutions are prepared by dissolving sodium chloride (NaCl, >99% purity, Sigma-Aldrich) in deionized water (Milli-Q) to obtain concentrations ranging from 10^{-1} to $10^{-5.5}$ M. Prior to monolayer deposition, DHP is dissolved in chloroform to prepare spreading solutions with a concentration of 1 mg mL^{-1}, which are stored at -20 °C until use. Monolayers are formed by dropwise deposition of the chloroform solution onto the aqueous interface using a micropipette (2 µL per drop) until saturation is reached. Full surface coverage is essential for the presented measurements, since infrared-induced heating generates surface convection, that drags surfactant molecules out of the spectroscopically probed illumination area. Saturation is identified using two complementary indicators: (i) the appearance of the terminal methyl (CH_3) stretching vibrations around 2800 cm^{-1} in the SFG/DFG spectra, and (ii) an abrupt change in surface height and in the oscillation frequency of surface ripplons resulting from the reduction of surface tension at full coverage. These surface changes are monitored continuously in real time using a position-sensitive photodiode, which detects beam-pointing variations caused by vertical motion of the liquid surface. The simultaneous appearance of the CH_3 vibrational signatures and the abrupt change in surface height then indicates the complete formation of the monolayer.

E) SFG/DFG measurements

The SFG/DFG measurements are carried out using a home-built spectrometer that combines heterodyned time-domain spectral acquisition with a fully collinear beam geometry. The spectrometer employs broadband mid-infrared and visible upconversion pulses (690 nm) from the outputs of two individual OPAs (LightConversion TOPAS) that are pumped by an amplified Ti:Sa laser system (Coherent Astrella,, 7W output, 800 nm pulses of ca. 30 fs duration at a repetition rate of 1 kHz). Phase-resolved SFG and DFG spectra from the sample interfaces are measured simultaneously and referenced to the SFG/DFG spectra obtained from the surface of a z-cut quartz crystal. During the measurements the sample height is maintained by an automized, home-built height control system that compensates for height changes originating from water evaporation. Full details of the spectrometer can be found in a previous publication.[2]

References

1 L. Lehmann, M. R. Becker, L. Tepper, A. P. Fellows, Á. D. Duque, M. Thämer and R. R. Netz, arxiv: 2505.19856.

2 Á. Diaz-Duque, V. Balos, M. Wolf, A. P. Fellows and M. Thämer, arxiv: 2508.06912.