

Supporting Information:
Electrolytes Change the Interfacial Water
Structure but not the Vibrational Dynamics

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Measurement of Time Resolution

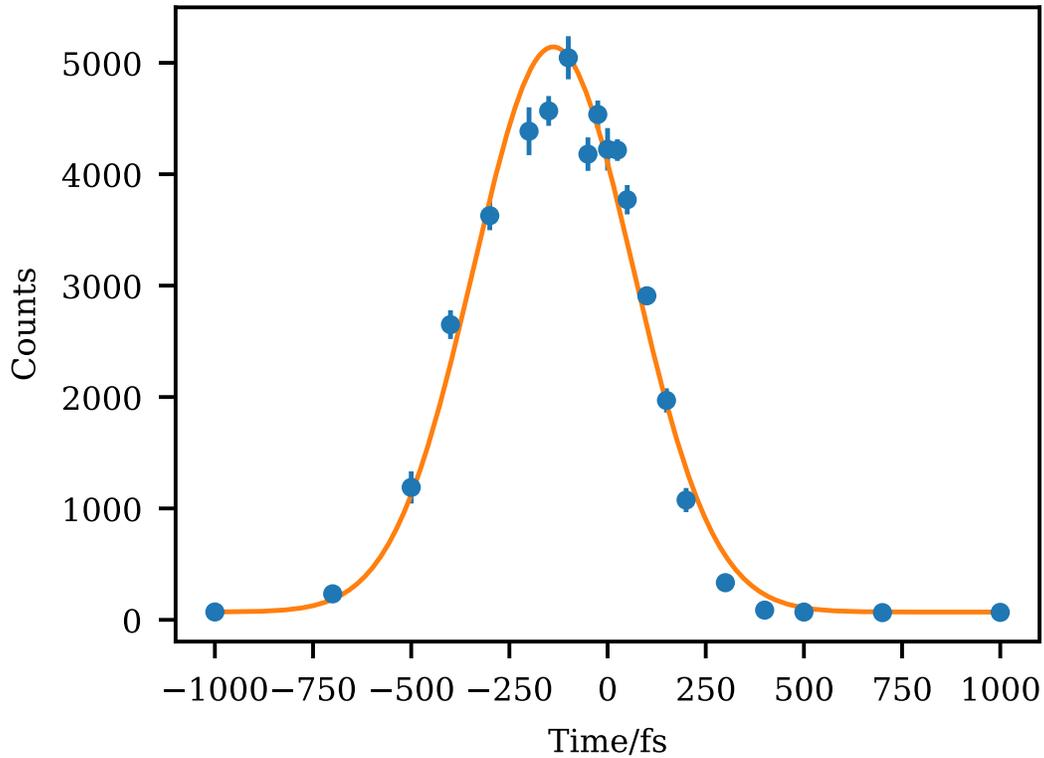


Figure S1: Cross-correlation measured on gold, mean pump frequency of 2600 cm^{-1} , mean probe frequency of 2500 cm^{-1} and mean visible frequency of 812 nm .

Figure S1 depicts a cross-correlation measurement. The cross-correlation is measured by recording the SFG signal of the visible, pump and probe pulses and has a center frequency of about 570 nm depending on the precise pump, probe and visible laser frequency. The time dependency of the cross-correlation is measured by tuning the pump-probe time delay. The line shows a Gaussian fit with a width of $\sigma = 200\text{ fs}$ at a central position of $\mu = -140\text{ fs}$. The width of the cross-correlation is an estimator for the time resolution of the setup and accounted for within the analysis. The position of the cross correlation is used to calibrate a $t = 0$ time.

$\chi^{(3)}$ Induced SFG Response

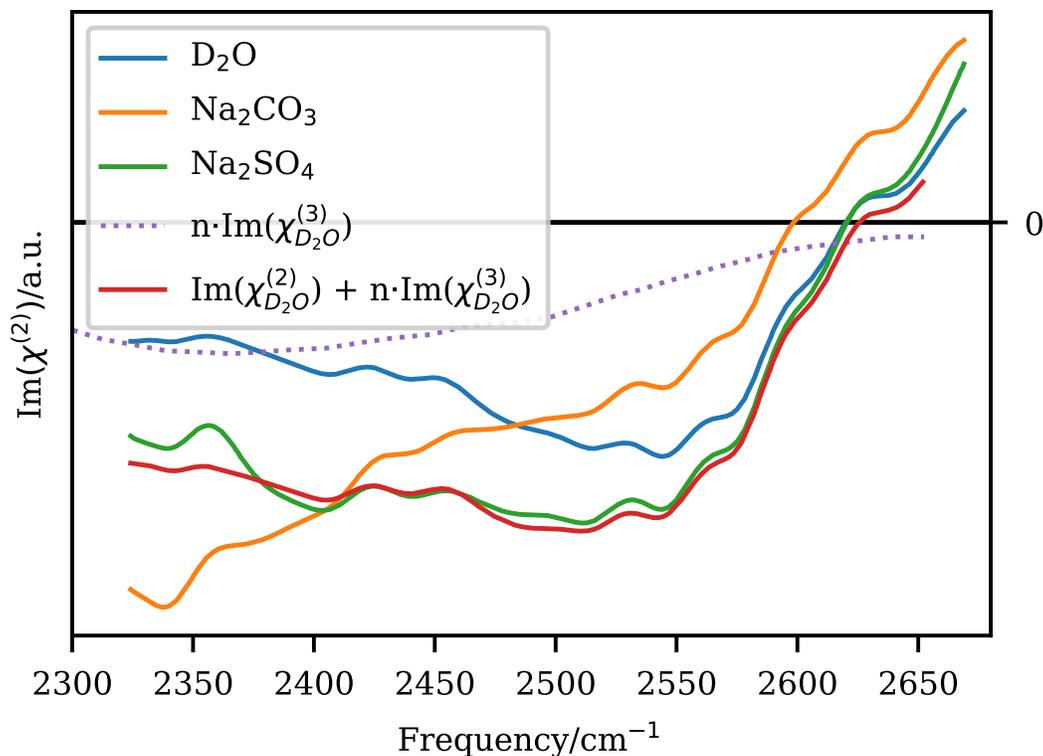


Figure S2: $\chi^{(3)}$ multiplied by an arbitrary number can be used to describe the difference between D_2O and Na_2SO_4 PS-SFG data. For Na_2CO_3 such a scaling factor can not be found.

Figure S2 shows that $\chi^{(3)}$ contributions of water are a possible candidate for the differences between $\text{Im}(\chi^{(2)})$ of Na_2SO_4 and $\text{Im}(\chi^{(2)})$ of D_2O . $\text{Im}(\chi_{\text{D}_2\text{O}}^{(3)})$ was taken from^{S1} $\chi^{(3)}$ data of H_2O and transformed into D_2O region using the harmonic approximation. To match the difference, a scaling factor of $n = -7$ was used. The exact number of the scaling factor is arbitrary, but the negative sign hints towards a downwards pointing electric field. Meaning that Na^+ is closer to the surface than SO_4^{2-} as it was e.g. discussed in.^{S2,S3}

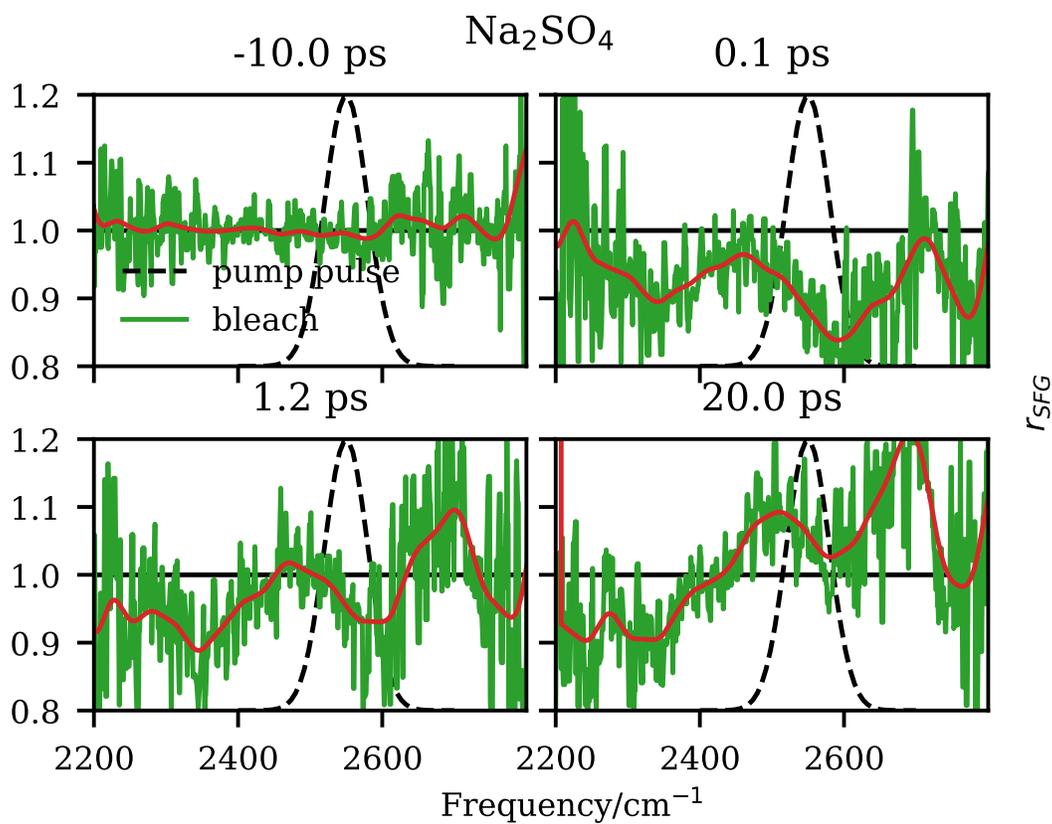


Figure S3: Ratio of pumped/unpumped SFG spectra (green) at four different pump-probe time delays (-10 ps , 0.1 ps , 1.2 ps , 20 ps) of $2\text{ M Na}_2\text{SO}_4\text{-D}_2\text{O}$ solution. The dashed black line denotes the spectral shape of the pump pulse and the red line is a guide to the eye.

Bleach Spectra

Figure S3 shows the ratio of pumped/unpumped SFG spectra at pump-probe time delays of -10 ps, 0.1 ps, 1.2 ps and 20 ps exemplarily for $2\text{M Na}_2\text{SO}_4$ pumped at 2550 cm^{-1} . The red line is a guide to the eye; the black dashed line denotes the spectral shape of the pump pulse. At negative pump-probe time delays, the probe pulse arrives at the sample before the pump pulse. Thus the ratio for negative times is a flat line around 1. At 0.1 ps the pump pulse depletes the ground state, and we see a reduction in the ratio around the mean pump frequency. At later times, i.e. after the excitation due to the pump pulse, the system relaxes, and therefore the ratio recovers back to 1. However one notes, that the spectrum after 20 ps has a distinct shape and shows frequency-dependent features. To understand this, turn towards Figure S5.

IR Absorption Spectra

Figure S4 shows ATR spectra of Na_2SO_4 , Na_2CO_3 , and D_2O with the same concentrations as the SFG spectra. The ATR spectra show the highest absorbance for Na_2SO_4 and the smallest for Na_2CO_3 with D_2O in between. Surprising is the long tail of Na_2CO_3 between 2200 cm^{-1} and 2300 cm^{-1} , that does not have a counterpart in the SFG spectrum of the same ionic solutions.

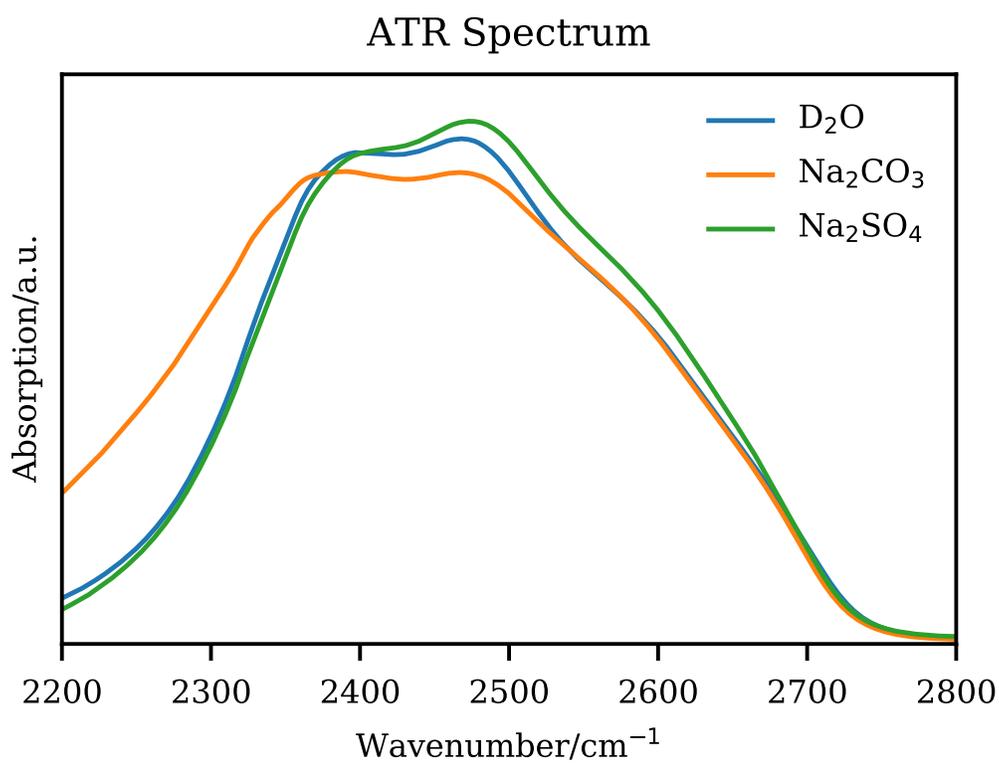


Figure S4: IR absorption of Na₂SO₄, Na₂CO₃, and D₂O within the probed frequency range.

Spectral Heat Effects

The top panel of Figure S5 shows static SFG spectra for Na_2SO_4 at 24 °C (Hot) and 14 °C (Cold). Heat leads to an overall loss of orientation throughout the hydrogen bond network, in particular, the strongly hydrogen bonded region with its intermolecular coupling around 2380 cm^{-1} is affected by this. For a better visibility, the middle panel shows the ratio of the hot and the cold spectrum, while the bottom panel shows the ratio of the pumped and unpumped SFG signals for relatively large 20 ps pump-probe time delays. If the signal at 20 ps is solely given by a temperature difference, the spectra in panel b) and panel c) should be the same. While the overall slope of the ratios is indeed the same, the bottom panel exhibits a more complex structure. Apparently, the state reached after 20 ps is not yet fully thermalized.

Na₂SO₄

SFG Spectrum

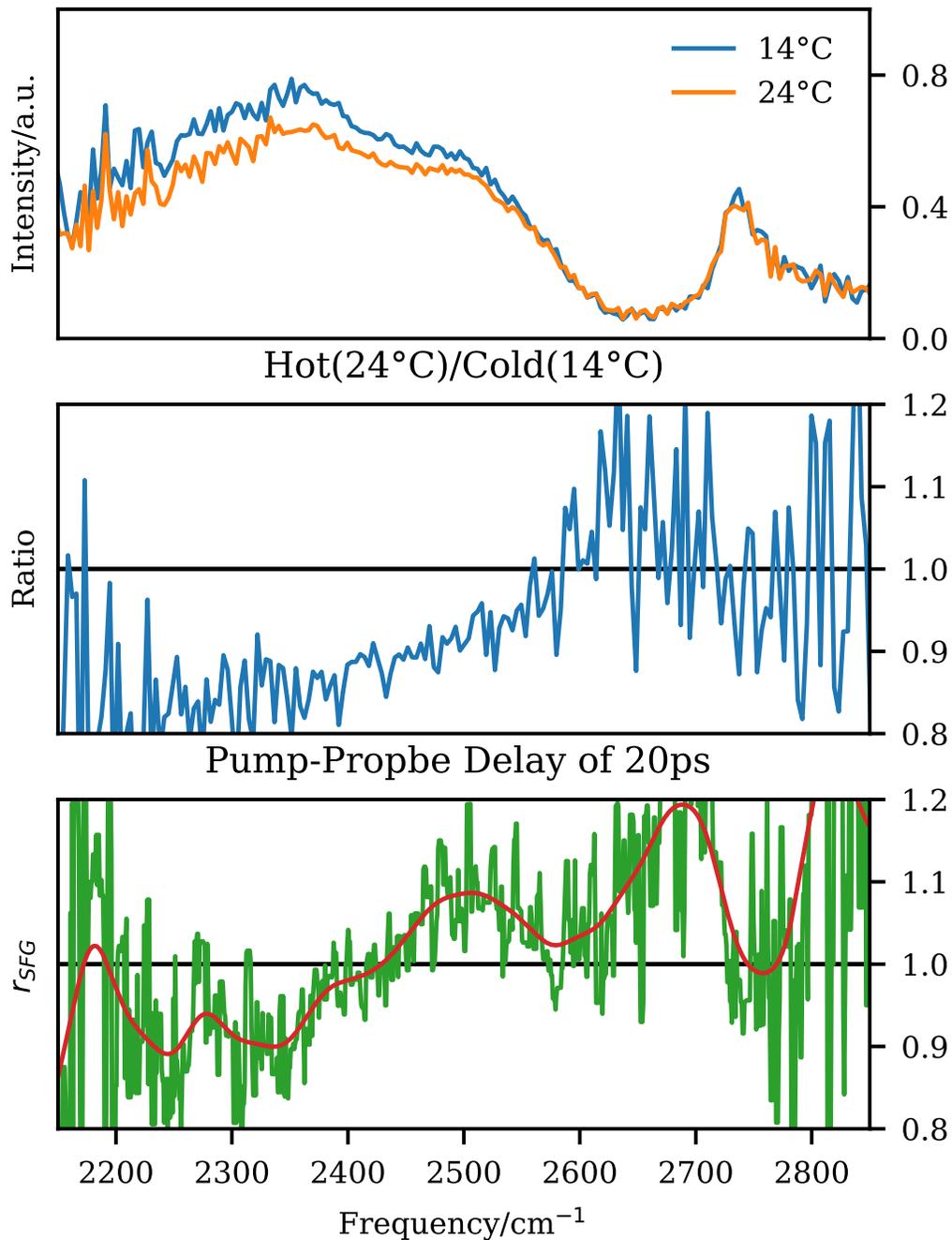


Figure S5: SFG Spectra of Na₂SO₄. Top panel shows the SFG spectra of cold (14°C) and hot (24°C) Na₂SO₄. The middle panel shows the ratio of hot/cold. Bottom panel shows pumped/unpumped for a pump-probe time delay of 20 ps.

Bibliography

References

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