# Supporting Information: Lifetime-Associated Two-Dimensional Infrared Spectroscopy Reveals the Hydrogen-Bond Structure of Supercooled Water in Soft Confinement

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#### Experimental details

#### Sample preparation

The sample was prepared by mixing sorbitol (99.9% purity, Sigma-Aldrich) with water up to a molar fraction of  $c \simeq 0.19$  ( $\simeq 70$  sorbitol wt %). In order to obtain an isotope diluted solution, the hydroxyl groups of sorbitol were deuterated by OH/OD exchange (the process occurs on a timescale  $\ll$ s). The poly-alcohol was then dissolved in water consisting of 98% D<sub>2</sub>O (99.9% purity, Sigma Aldrich) and 2% Milli-Q water. Sorbitol homogeneously dissolved in water after having been sonicated for 10 minutes. The samples for IR measurements consisted of  $2\mu$ L of liquid placed in between two CaF<sub>2</sub> windows separated by a Teflon spacer of 25  $\mu$ m. The tempeature of the sample was controlled using a liquid-nitrogen cryostat (Optistat DN, Oxford Instruments). To ensure rapid and complete thermalization the sample chamber was filled with 1 bar of He. The temperature of the sample was measured using a PT100 thermocouple.

#### Linear absorption measurements

Perkin-Elmer Spectrum-Two FTIR spectrometer was used to measure the FTIR spectra. Measurements were performed with a resolution of 4 cm<sup>-1</sup>. The sample waas cooled with a rate of 1.5K/min and a spectrum is collected every 20 s. Small baseline fluctuations in the FTIR spectrum were corrected by subtracting the baseline at 4500 cm<sup>-1</sup>, where the sample absorption is negligible, individually for each FTIR measurement.

#### **2D-IR** measurments

The 2D-IR measurements were conducted using the experimental setup described in S1,S2. Transient absorption measurements were performed using broad-band pulses with a spectra width of  $\simeq 150 \text{ cm}^{-1}$ , while for the 2D-IR measurements the FWHM of the pump pulse is reduced down to  $\simeq 25 \text{ cm}^{-1}$  (see Fig. for comparison with the spectral width of the OH-



Figure S1: Blue solid line: FTIR spectrum measured at T = 280 K. Black solid line: Pump power spectrum

stretch band). The pump-probe cross correlation is approximately a single-sided exponential with a FWHM of  $\simeq 200$  fs at the liquid layer positions. The transient absorption and 2D-IR spectra were measured with the pump and probe polarization at the magic angle (54.7°).

#### Absence of crystallization during FTIR measurements

The absence of crystallization was cautiously monitored during measurements. No sign of crystallization was observed both on cooling and re-heating the sample and the spectral features of the sample result to be completely reversible upon re-heating (see for example Fig. S2). The small hysteresis which can be observed in the temperature dependence of the central position of the OH-stretching band (see Fig. S2) is probably due to the non-direct thermal contact between the PT100 sensor and the liquid and the higher cooling rate used during the re-heating of the sample. However, once corrected for this temperature offset, the



Figure S2: (a): IR spectra of a water-sorbitol solution (sorbitol wt% 70, H/D $\simeq$ 2%) upon cooling the sample at 1.5 K/min. IR-spectra of the same solution upon re-heating (10 K/min). (c): position of OH-stretch band as a function of temperature during cooling and reheating as indicated by the arrows. A small, hysteresis ( $\simeq$  10K) is present, probably due to the higher rate used during the heating cycle.

IR-spectra collected upon cooling or heating are identical (see Fig.S3).

# T-dependence of the OH-stretching band

The temperature dependence of the position of the OH-stretching band maximum  $\nu_{\rm OH}(T)$ can be fitted by accounting for three different temperature regions (see Fig. S4). A first change in the slope of  $\nu_{\rm OH}(T)$  can be observed at  $\simeq 206$ K, that is, close to the calorimetric glass-transition temperature of the sample ( $T_{\rm g} \simeq 200$  K). A further modification in the *T*dependence occurs around  $T_{\rm g}^{\beta} \simeq 169$  K, as highlighted in the inset of Fig. S4. This second



Figure S3: FTIR spectra of water-sorbitol mixture (sorbitol wt% 70, H/D $\simeq$ 2%) at 158K and 230K measured while cooling (solid lines) and re-heating (dashed lines) the sample with a rate of 1.5K/min and 10 K/min respectively. Temperatures have been re-calibrated according to the observed hysteresis.



Figure S4: Blue solid line: temperature dependence of the OH-stretching absorption frequency ( $v_{\text{OH}}$ ). Red dashed lines: linear fits of the  $v_p$ : three different slopes can be identified at T < 169K, 169 < T < 206K and T > 206K. Inset: highlight of the temperature region between 77K and 200K.

"kink" at  $T_{\rm g}^{\beta}$ , also observed in THz measurements, <sup>S3</sup> could be related, as discussed in the main text, to the vitrification of the Johari-Goldstein relaxation, <sup>S4</sup> a secondary process characteristic of glass-formers liquids. So,  $T_{\rm g}^{\beta}$  may indicate the "glass transition temperature" at which the  $\beta_{JG}$ -relaxation arrests, <sup>S5,S6</sup> in analogy to the change in the thermal expansion occurring at  $T_{\rm g}$ . The presence of a second glass-transition temperature and its effect on several observable, such as the OH-stretching mode, has been already observed in several other glass-formers, including sorbitol. <sup>S5,S6</sup>

#### HOH bending mode of water

The temperature dependence of the spectrum of the HOH bending mode of water was also investigated to confirm that the spectral changes observed in the OH-stretching band upon cooling do not involve only the sorbitol molecules but the water ones as well. For instance,



Figure S5: a):IR absorption spectra of sorbitol solution (molar fraction  $c \simeq 0.19$ ) in H<sub>2</sub>O during cooling (2 K/m). (b): Temperature dependence of the peak position of the HOHbending mode shown in (a) during the cooling.

the HOH-bending mode of water is also sensitive to changes in the H-bond network and when the H-bond strength increases, contrarily to what observed for the OH-stretching mode, its vibrational frequency increases.<sup>87</sup> The reason for this opposite behavior is that, while hydrogen-bonding decreases the restoring force for the OH-stretching mode, it increases that for the HOH-bending.<sup>87</sup> The IR absorption spectra of the HOH-bending mode can be investigated in water-sorbitol solution without isotope dilution as the HOH-bending mode is less subjected to vibrational coupling.<sup>88</sup> As can be clearly observed in Fig. S11, the HOH-bending mode shifts toward higher frequencies upon cooling, reflecting the increase in the H-bond strength, as already suggested by the behavior of the OH-stretching mode. Also in the case of the HOH-bending mode a change in the T-dependence can be observed on crossing the glass-transition temperature  $T_g \simeq 200$ K and at a lower temperature  $T_g$  and  $T_g^{\beta}$  extracted from the T-dependencies of isotopic diluted (OH-stretching mode measurements) or fully protonated solutions (HOH-bending mode) may be due to isotopic effects.<sup>89</sup>

#### H/D exchange between water and sorbitol

The OH-stretching band of our samples comprises both OH-stretching modes from sorbitol and water, as a result of the fast OD/OH exchange between sorbitol (with deuterated hydroxyl groups), D<sub>2</sub>O and H<sub>2</sub>O. This H/D exchange can be observed by comparing the FTIR spectra from a water-sorbitol mixture (sorbitol wt % 70) with H/D=100% and with isotopic dilution H/D $\simeq$  2%. The FTIR spectrum of H<sub>2</sub>O and d-sorbitol (no isotopic dilution) shows a clear peak at 1650 cm<sup>-1</sup>, due to the HOH-bending mode (see red curve in Fig. S6). At 2200 cm<sup>-1</sup> there is a broad contribution arising from the combination of the bending and libration mode of H<sub>2</sub>O. while at lower frequencies, between 1200 cm<sup>-1</sup> and 1500 cm<sup>-1</sup>, the peaks corresponding to the CH<sub>2</sub> and COH bending modes of sorbitol can be observed. Concerning the isotopic diluted spectrum (blue curve in Fig. S6), the peaks at 1460 and 1212 cm<sup>-1</sup> are HOD and DOD bending modes, respectively. In the same region the sorbitol peaks described above can be also observed, partially over imposed with the bending modes. This



Figure S6: FTIR spectra of the water-sorbitol solution (sorbitol wt% 70) without (red curve) and with isotopic dilution  $H/D\simeq 2\%$  (blue curve).

shows that the H/D exchange occurs not only between the  $D_2O$  and  $H_2O$  molecules but also between  $H_2O$  and the deuterated hydroxyl groups of sorbitol.

## Examples of fitting curves of transient absorption data



Figure S7: Isotropic absorption change resulting from the excitation by a broad band min-IR pulse (FWHM $\simeq 150 \text{ cm}^{-1}$ ) centered at  $v_{\text{pump}} = 3250 \text{ cm}^{-1}$ . The absorption changes are shown for different probe frequencies (dots with errorbars) as a function of the pump-probe delay time. The black solid line are the curves obtained from fitting a bi-exponential model to the experimental data.

Both the broad band transient absorption (TA) spectra and the time-dependent 2D-IR spectra were modeled using a bi-exponential model, accounting for the (slow) sorbitol and water components:

$$\Delta \alpha = \Delta \alpha_{HOD} \exp\left[-\frac{t}{T_1^{HOD}}\right] + \Delta \alpha_S \exp\left[-\frac{t}{T_1^S}\right] + c \tag{1}$$

The use of this simple model for the time dependence of the transient absorption (TA) spectra is also justified by singular-value-decomposition analysis which for instance identifies, in the case of the data shown in Fig.S7, two main components accounting for  $\simeq 97\%$  of the signal, with the remaining 3% arising from noise (see also Fig.S8). Fig. S7 and Fig. S9 show some examples of the time-dependent absorption changes observed during TA and 2D-IR



Figure S8: First eight singular values obtained from singular-value-decomposition analysis on the data shown in Fig. S7.



Figure S9: Isotropic absorption changes for different narrow band pump pulses (FWHM $\simeq$  25 cm<sup>-1</sup>). The absorption changes are shown for different probe frequencies (dots with errorbars) as a function of the pump-probe delay time. The solid lines are the curves obtained from fitting a bi-exponential model to the experimental data.

measurements, respectively. In the case of the 2D-IR spectra, the vibrational lifetimes of the HOD and sorbitol components have been fixed according to the values obtained from the

analysis of the TA data, as discussed in the main text. This is a simplifying assumption, as the transient absorption measurements were performed with pulses with a larger bandwidth with respect to the homogeneous broadening of the vibrational band. As a consequence, the frequency dependence extracted from the TA experiments might be slightly smeared out. However, our assumption remains still valid given i) the weak frequency dependence of the  $T_1$  of sorbitol and water, smaller than the difference between the two timescales, and ii) the rather long duration of the pump pulse pulse envelope in the narrow-band experiments. Few examples of reconstructed 2D-IR spectra, compared with the experimental data can be observed in Fig. S10. It can be clearly observed that in both cases the model well describe



Figure S10: 2D-IR spectra measured at a temperature T = 165K and two different pumpprobe delays  $\Delta t = 0.7$  ps (a) and 2 ps (b). Panel (c) and (d) show instead the spectra reconstructed from the fitting parameters

the experimental data.

# Spectral components from transient absorption measurements.



Figure S11: Position of the bleaching signal for the spectral components of water (a) and sorbitol (b) as extracted from transient absorption measurements. The blue squares show the results obtained from exciting the solution with a broad pump pulse centered at 3380 cm<sup>-1</sup> while the red diamonds corresponds to an excitation at 3280 cm<sup>-1</sup>.

The position of the bleach of the spectral components corresponding to the vibrational lifetime plotted in Fig. 2-(c,d) are reported in Fig. S11. Both the sorbitol and water bleaches move toward lower wave-numbers upon cooling, signaling an increase in the H-bond strength. Furthermore, it can also be noticed that the temperature dependence of the red-shift changes upon crossing the glass transition temperature. The accuracy of the experimental data does not allow to asses whether a further change in the temperature dependence occurs also at lower temperatures.

### Absence of spectral diffusion

In the deeply supercooled state the investigated water-sorbitol solutions show negligible spectral diffusion even at the highest temperatures that were probed, as can be observed in Fig. S12. This observation justifies the procedure used to decouple the water and sorbitol



Figure S12: Isotropic 2D-IR spectra measured from a water-sorbitol mixture (70 wt %) at a temperature of 240K and 270K and for two diffrent pump-probe delay times: 0.7ps (a,c) and 2.5 ps (b,d). The red errorbars show the position of minima of the transition lobes and the red curves are lines with slope 1 ( $\nu_{probe} = \nu_{pump}$ ).

contributions to the 2D-IR spectra.

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