

Supporting Information

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Difference in Relaxation Time of ASW and LDA Water

Comparison of relaxation times obtained for LDA water and ASW (Fig. 1) reveals a difference of almost one order of magnitude at the same temperature, with the ASW sample showing slower relaxation for both H-ASW and D-ASW. LDA is a compact material of surface area $<1 \text{ m}^2/\text{g}$, whereas ASW is a highly microporous, fluffy material with a surface area of several hundred square meters per gram at low temperatures ($<77 \text{ K}$) that can efficiently take up impurities from the background gas (1, 2). The network of the micropores in ASW then collapses upon heating to $>130 \text{ K}$, and some impurities remain irreversibly trapped within the bulk of ASW (3). This difference in surface-to-volume ratio and some impurities may be at the origin of the observed differences between LDA and ASW (Fig. 1).

Estimates of T_{onset} from Rate-Dependent Dielectric Measurements of LDA

To compare the dielectric results with the DSC measurements the complex permittivity ϵ^* of protonated and deuterated LDA was recorded not only at constant temperatures (Fig. S2) but, in addition, at a constant frequency of 1 Hz for various heating rates q . In Fig. 2 and Fig. S3 the results for the imaginary part of ϵ^* , normalized by its maximum value, $\epsilon''/\epsilon''_{\text{max}}$, are plotted as a function

of temperature. Using a procedure similar to the one used for estimating T_g from calorimetric data, we extracted dielectric onset temperatures, T_{onset} , as the intersection point of the linear increase of $\epsilon''/\epsilon''_{\text{max}}$ at $T > T_{\text{onset}}$ with a baseline, $\epsilon''/\epsilon''_{\text{max}} = 0$, taken to characterize the loss behavior at low temperatures. The linear increase of ϵ'' was obtained from a linear fit of the dielectric data in the range $0.5 < \epsilon''/\epsilon''_{\text{max}} < 0.9$. The resulting fits, extrapolated to $\epsilon''/\epsilon''_{\text{max}} = 0$, are shown in Fig. 2 and Fig. S3. The error bars for ΔT_{onset} (Fig. 2G) account for the small deviations from the linear regression and for deviations occurring when the fitting range varies between $0.3 < \epsilon''/\epsilon''_{\text{max}} < 0.9$ and $0.7 < \epsilon''/\epsilon''_{\text{max}} < 0.9$. The data in Fig. S3 also show that the maximum in ϵ'' vs. T is broad and smooth at high heating rate q . This maximum reflects that the condition $2\pi\nu\tau \sim 1$ is fulfilled before the transformation to the cubic ice phase sets in. This dielectric loss maximum thus signals the presence of a relaxation process. The decay in ϵ'' observed at higher T gets sharper at heating rates $q \leq 0.2 \text{ K/min}$, thereby precluding a consistent determination of ϵ''_{max} (Fig. S3). Thus, the maximum at slow heating rate might not reflect a relaxation maximum, but rather a crystallization-related loss maximum. Hence, we refrain from using the data obtained with heating rates slower than 0.2 K/min in our analysis of ΔT_{onset} .

1. Li J (1996) Inelastic neutron scattering studies of hydrogen bonding in ices. *J Chem Phys* 105(16):6733–6755.
2. Mayer E, Pletzer R (1986) Astrophysical implications of amorphous ice – a microporous solid. *Nature* 319(6051):298–301.

3. Mitterdorfer C, et al. (2014) Small-angle neutron scattering study of micropore collapse in amorphous solid water. *Phys Chem Chem Phys* 16(30):16013–16020.

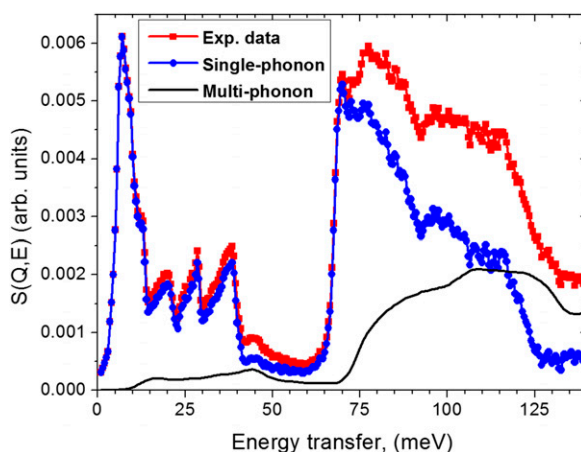


Fig. S1. Dynamical structure factor $S(Q,E)$ for an LDA sample obtained from the INS spectra measured at $T = 15 \text{ K}$: the experimental spectrum (1) (red curve), calculated multiphonon (black line), and single-phonon (blue curve) contributions.

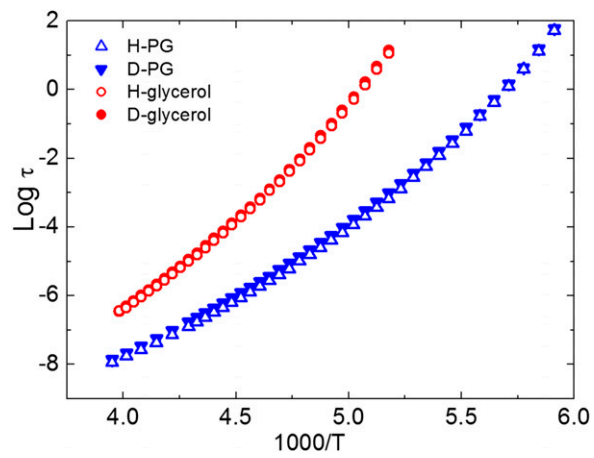


Fig. 57. Structural dynamics in propylene glycol and glycerol. An isotope effect on the glass transition in these hydrogen bonding liquids is very small, $\Delta T_g \approx 0.1$ K for PG and $\Delta T_g \approx 0.4$ K for glycerol (2).