

Supplementary Information

**Spectral Diffusion in Glycerol-Water Mixtures from Theoretical
Two Dimensional Infrared Spectroscopy: Varying Effects of
Concentration for Different Solvation Environments**

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Table S1: Timescales extracted from the 2DIR metrics of the slope of nodal line (SNL) and frequency time correlation function (FTCF) using triexponential fits (Eq. 11) for all water molecules present in the systems studied. The a_1 and a_2 are the weights of τ_1 and τ_2 , respectively. The subscript in τ_3 is the uncertainty in the last digit(s).

x_{GLC}	metric	All Water				
		τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2
0.03	SNL	0.08	0.47	1.45 ₂	0.35	0.38
	FTCF	0.03	0.37	1.33 ₀	0.54	0.28
0.045	SNL	0.08	0.51	1.62 ₂	0.34	0.38
	FTCF	0.03	0.38	1.54 ₁	0.54	0.28
0.06	SNL	0.08	0.49	1.74 ₃	0.33	0.35
	FTCF	0.03	0.42	1.78 ₂	0.54	0.28
0.075	SNL	0.08	0.52	1.94 ₂	0.32	0.36
	FTCF	0.03	0.44	2.01 ₁	0.54	0.28
0.08	SNL	0.08	0.49	1.96 ₁	0.33	0.34
	FTCF	0.03	0.46	2.05 ₁	0.54	0.28
0.083	SNL	0.08	0.50	1.98 ₁	0.32	0.36
	FTCF	0.03	0.46	2.10 ₃	0.54	0.28
0.09	SNL	0.08	0.51	2.01 ₃	0.31	0.33
	FTCF	0.03	0.46	2.15 ₃	0.54	0.28
0.105	SNL	0.07	0.52	2.20 ₄	0.30	0.32
	FTCF	0.03	0.50	2.38 ₂	0.54	0.28
0.12	SNL	0.08	0.55	2.41 ₆	0.31	0.32
	FTCF	0.03	0.53	2.65 ₂	0.55	0.27

Table S2: Timescales extracted from the decay of the orientational correlation functions of the OH and dipole vectors (single molecule orientation relaxation (SMOR)) of water for all water molecules present in the systems studied using triexponential fits (Eq. 11). The a_1 and a_2 are the weights of τ_1 and τ_2 , respectively. The subscript in τ_3 is the uncertainty in the last digit(s).

x_{GLC}	Vector	All Water				
		τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2
0.03	OH	0.02	0.50	3.02 ₅	0.20	0.22
	Dipole	0.03	0.79	3.14 ₀	0.26	0.30
0.045	OH	0.02	0.49	3.30 ₄	0.20	0.22
	Dipole	0.03	0.81	3.40 ₂	0.26	0.30
0.06	OH	0.02	0.54	3.62 ₄	0.21	0.23
	Dipole	0.03	0.85	3.66 ₃	0.26	0.29
0.075	OH	0.02	0.62	3.89 ₂	0.20	0.24
	Dipole	0.03	0.82	3.96 ₂	0.26	0.29
0.08	OH	0.02	0.59	3.97 ₂	0.20	0.23
	Dipole	0.03	0.92	4.07 ₁	0.26	0.30
0.083	OH	0.02	0.56	4.01 ₂	0.21	0.23
	Dipole	0.03	0.66	4.12 ₁	0.26	0.29
0.09	OH	0.02	0.61	4.13 ₂	0.21	0.23
	Dipole	0.03	0.89	4.27 ₃	0.27	0.28
0.105	OH	0.02	0.64	4.45 ₁	0.21	0.23
	Dipole	0.03	0.94	4.61 ₄	0.27	0.29
0.12	OH	0.02	0.67	4.76 ₂	0.21	0.23
	Dipole	0.03	0.87	4.92 ₆	0.27	0.27

Table S3: Timescales extracted from the decay of $S_{\text{HB}}(t)$ for water-glycerol hydrogen bonds using triexponential fits (Eq. 11). The a_1 and a_2 are the weights of τ_1 and τ_2 , respectively. The subscript in τ_3 is the uncertainty in the last digit(s). Note that bulk water does not form any hydrogen bond with glycerol.

x_{GLC}	Metrics	Trapped water					Hydration Water				
		τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2
0.03	$S_{\text{HB}}(t)$	0.06	0.56	1.95 ₁	0.11	0.28	0.07	0.52	1.82 ₁	0.07	0.26
0.045	$S_{\text{HB}}(t)$	0.08	0.57	2.11 ₄	0.09	0.25	0.08	0.55	1.92 ₂	0.08	0.29
0.06	$S_{\text{HB}}(t)$	0.08	0.62	2.21 ₃	0.12	0.32	0.08	0.62	2.05 ₂	0.10	0.28
0.075	$S_{\text{HB}}(t)$	0.08	0.62	2.36 ₁	0.12	0.33	0.08	0.69	2.15 ₂	0.08	0.25
0.08	$S_{\text{HB}}(t)$	0.08	0.62	2.37 ₄	0.09	0.23	0.08	0.66	2.19 ₂	0.11	0.34
0.083	$S_{\text{HB}}(t)$	0.08	0.64	2.40 ₅	0.10	0.29	0.08	0.64	2.20 ₁	0.12	0.29
0.09	$S_{\text{HB}}(t)$	0.08	0.65	2.44 ₀	0.10	0.25	0.08	0.65	2.25 ₅	0.10	0.31
0.105	$S_{\text{HB}}(t)$	0.08	0.67	2.55 ₁	0.10	0.32	0.08	0.64	2.34 ₁	0.11	0.36
0.12	$S_{\text{HB}}(t)$	0.09	0.71	2.65 ₆	0.12	0.37	0.09	0.71	2.49 ₆	0.12	0.32

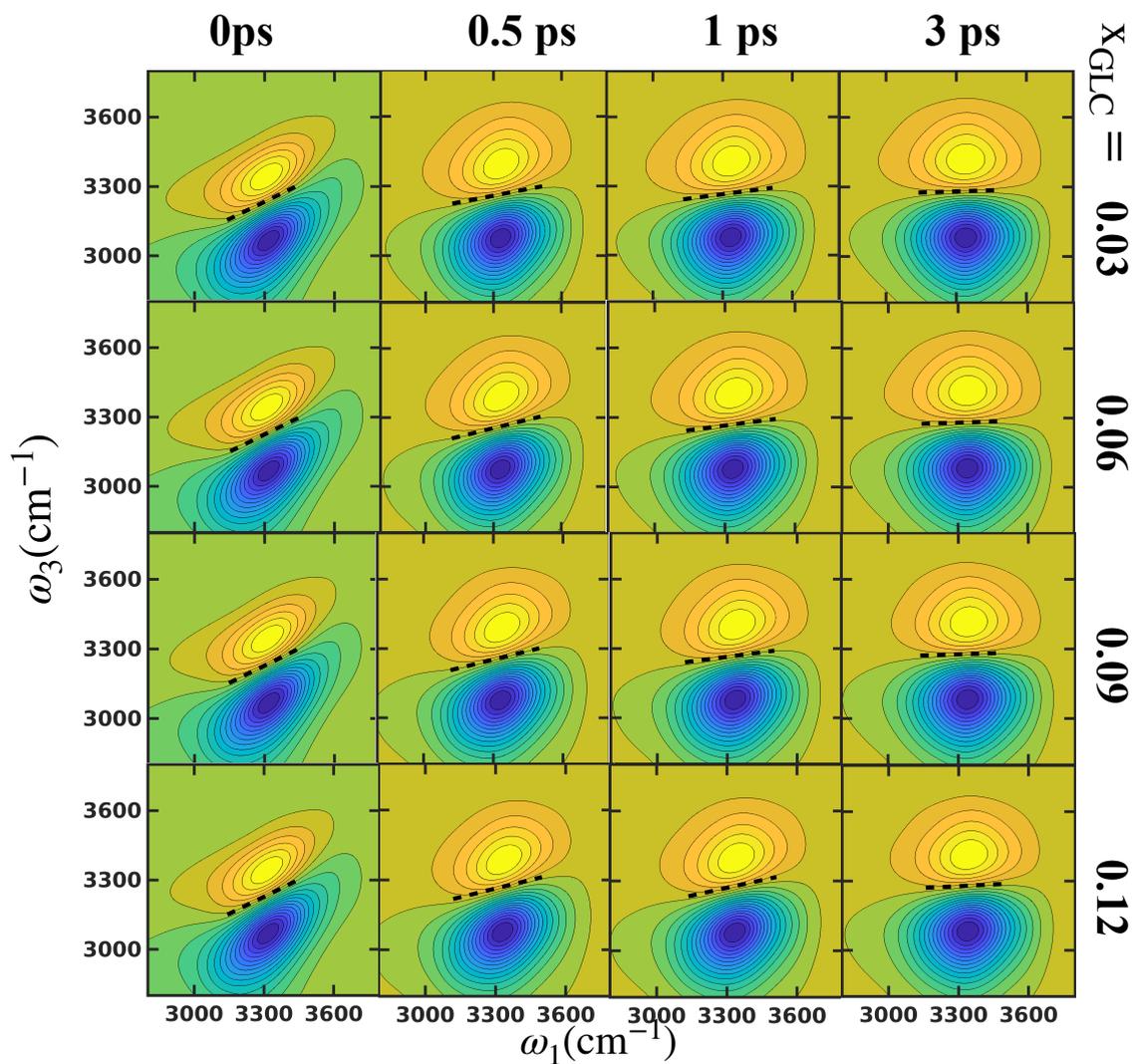


Figure S1: 2DIR spectra of bulk water molecules for a few representative glycerol-water mixtures.

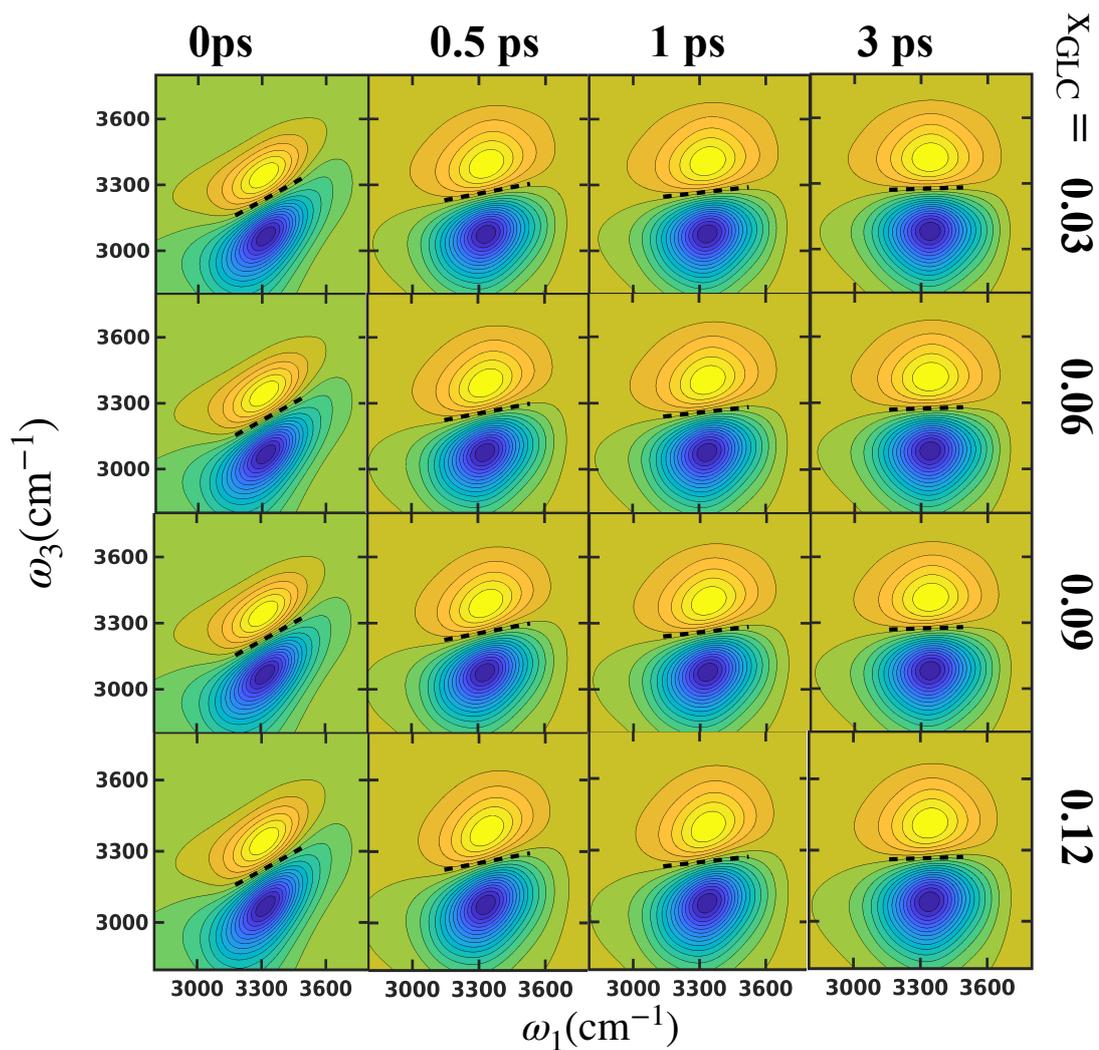


Figure S2: 2DIR spectra of all water molecules for a few representative glycerol-water mixtures.

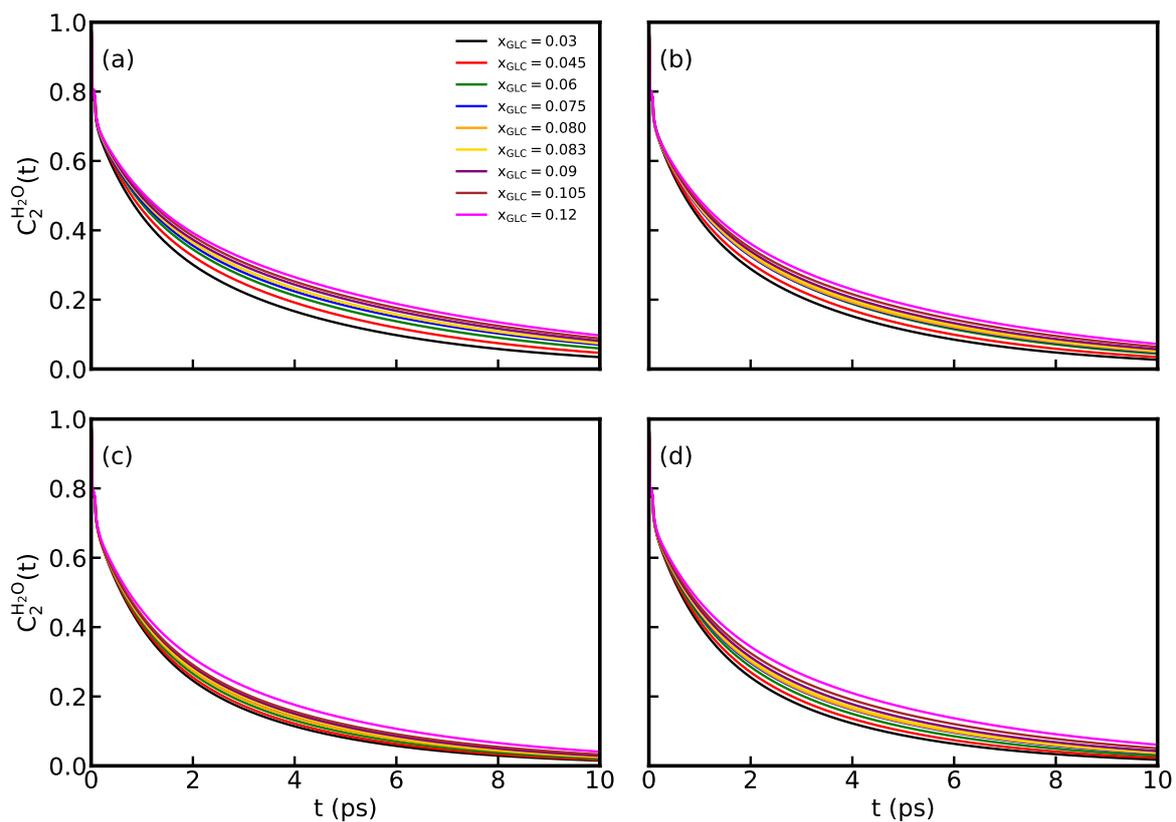


Figure S3: Decay of the SMOR function for different categories of water: (a) Trapped water, (b) hydration water, (c) bulk water, and (d) all water present in a system.

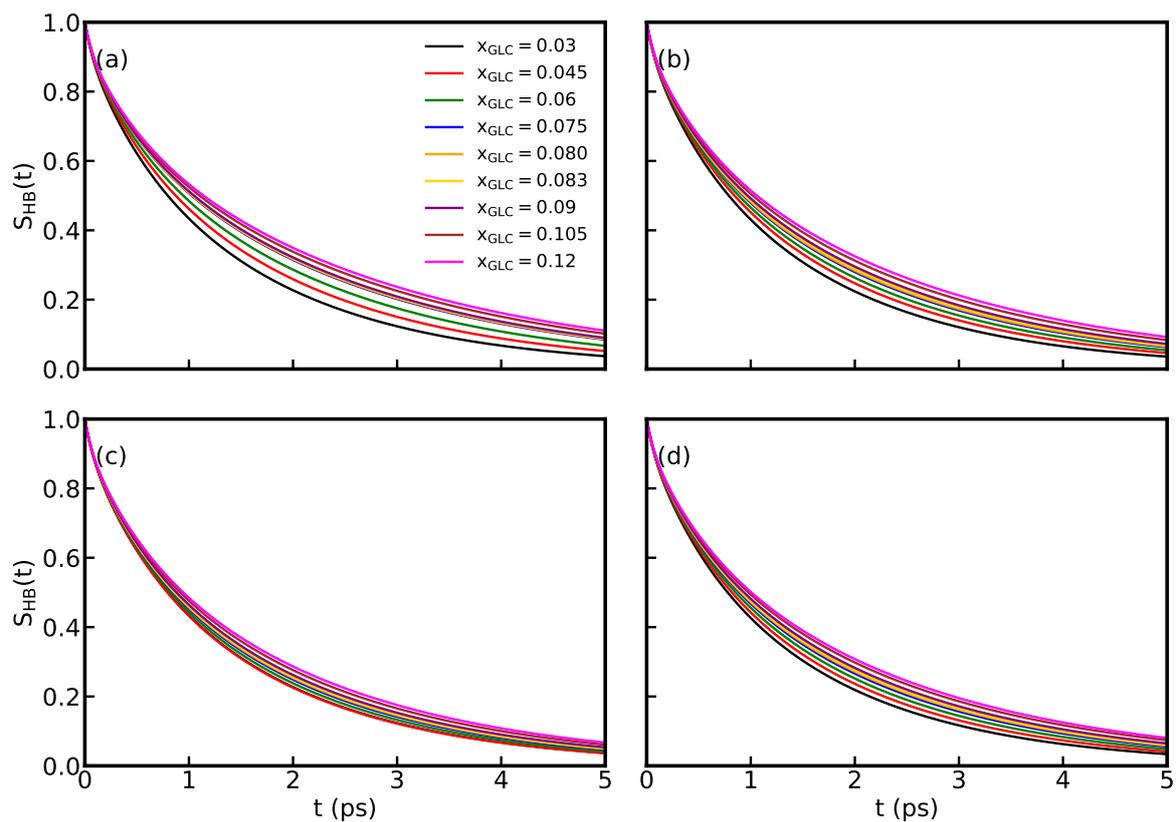


Figure S4: Decay of $S_{HB}(t)$ for water-water hydrogen bonds for different categories of water: (a) Trapped water, (b) hydration water, (c) bulk water, and (d) all water present in a system.

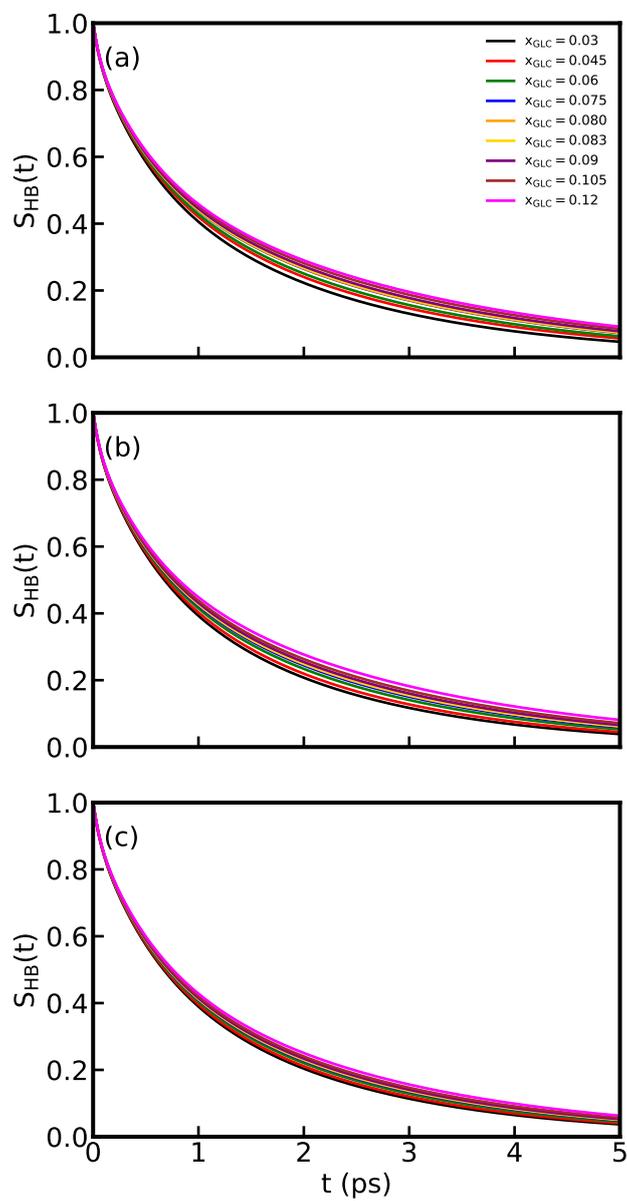


Figure S5: Decay of $S_{HB}(t)$ for water-glycerol hydrogen bonds for different categories of water: (a) trapped water, (b) hydration water, and (c) all water present in a system.

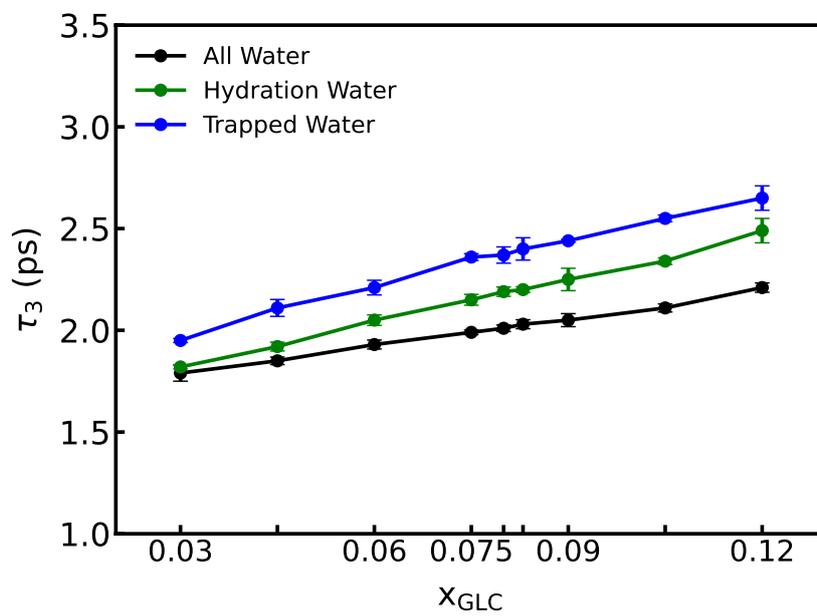


Figure S6: Plot of the slowest timescale (τ_3) of $S_{\text{HB}}(t)$ for water-glycerol hydrogen bonds as a function of glycerol concentration for trapped, hydration, and all water molecules. Error bars represent the uncertainties in the values of τ_3 .

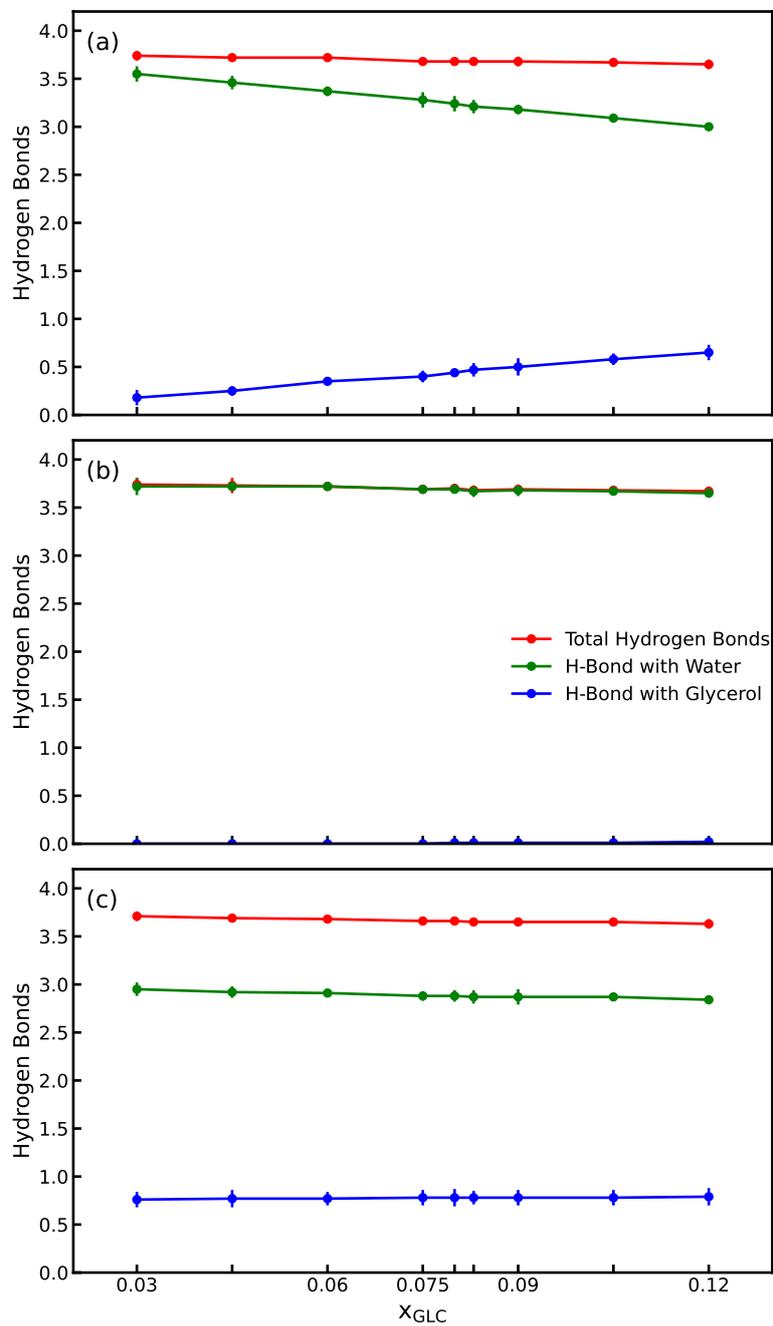


Figure S7: Average number of hydrogen bonds per water molecule for different categories of water molecules: (a) all water, (b) bulk water, and (c) hydration water.

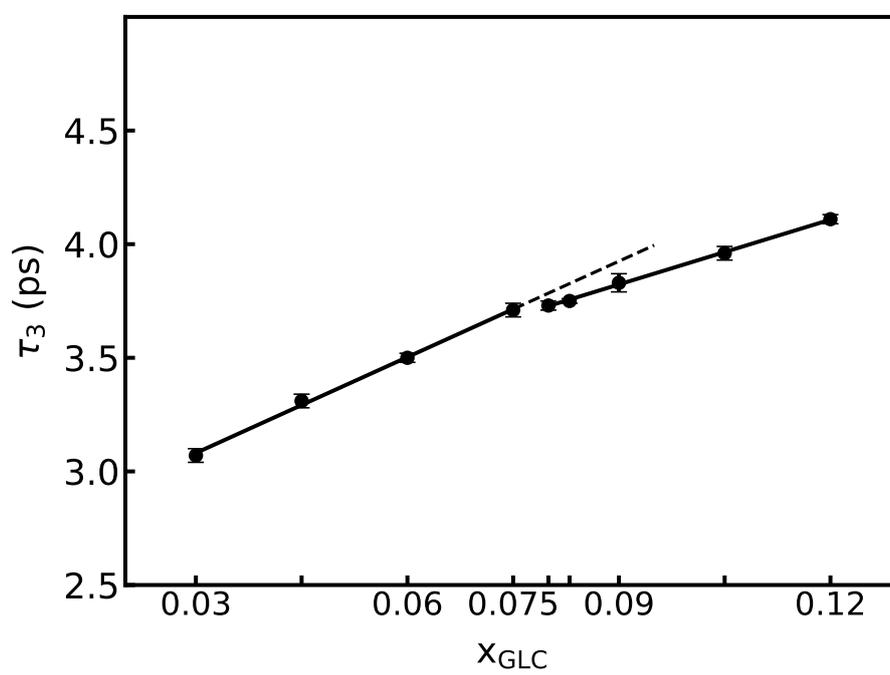


Figure S8: Variation of the slowest timescale (τ_3) of FTCF for the OH modes of glycerol as a function of glycerol concentration.

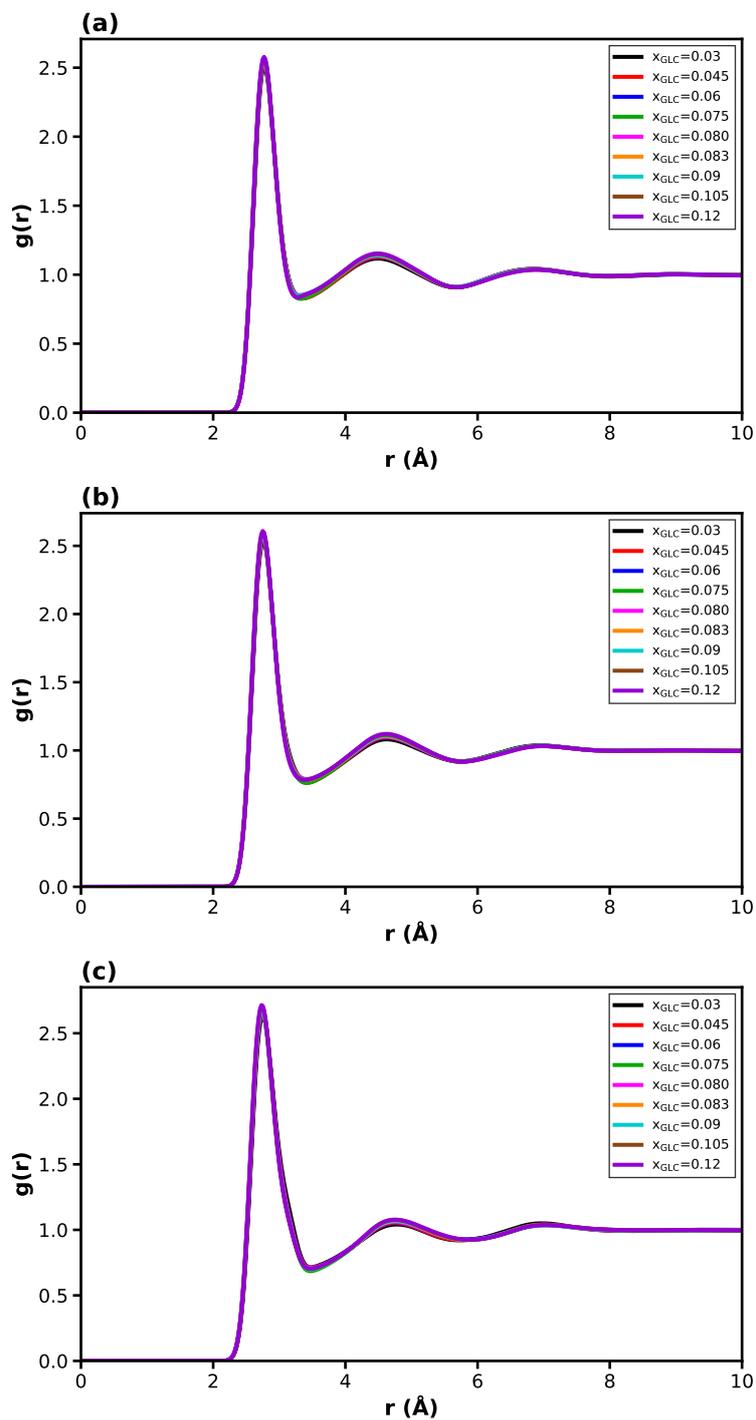


Figure S9: Radial distribution functions (RDFs) between the oxygen atoms of water molecules present in different regions, as (a) bulk water, (b) hydration water, and (c) trapped water, and all oxygen atoms present in the system, irrespective of glycerol or water.