Supporting Information

Toward Theoretical Terahertz Spectroscopy of Glassy Aqueous Solutions: Partially Frozen Solute–Solvent Couplings of Glycine in Water

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Table S1. Decomposition of the total harmonic kinetic energy in terms of the separate contributions due to glycine's center of mass, overall rotation, and vibrational motion as well as motion of the considered H–bonded water molecules (reported in percent, deviations from 100 % due to rounding errors) associated to the THz modes of the supermolecular solvation complex SSC(+), Gly(3 H_2O), in "free" (red) and "fixWAT" (blue) solvation environments, see main text.

Mode	Frequency	Intensity	Gly-COM	Gly-Rot	Gly-Vib	Water
cage rattling I	58 cm^{-1}	47 cm^{-1}	84.04	<1	2.03	13.88
cage rattling I	112 cm^{-1}	111 cm^{-1}	92.42	3.76	3.82	–
cage rattling II	66 cm^{-1}	15 cm^{-1}	72.83	<1	2.05	24.23
cage rattling II	103 cm^{-1}	59 cm^{-1}	68.16	22.09	9.75	–
cage rattling III	59 cm^{-1}	<2 cm^{-1}	75.96	<1	1.39	22.21
cage rattling III	135 cm^{-1}	21 cm^{-1}	81.49	14.62	3.89	–
cage libration I	71 cm^{-1}	49 cm^{-1}	14.10	46.01	2.24	37.65
cage libration I	118 cm^{-1}	83 cm^{-1}	37.98	57.63	4.39	–
cage libration II	73 cm^{-1}	260 cm^{-1}	6.57	69.82	2.70	20.91
cage libration II	193 cm^{-1}	109 cm^{-1}	3.76	93.25	2.99	–
NCCO open/close	307 cm^{-1}	313 cm^{-1}	1.66	1.92	92.27	4.15
NCCO open/close	336 cm^{-1}	435 cm^{-1}	1.57	<1	97.79	–
Cα out-of-plane	139 cm^{-1}	21 cm^{-1}	4.77	7.27	72.55	15.41
Cα out-of-plane	179 cm^{-1}	363 cm^{-1}	9.85	35.69	54.46	–
C-C twist + HB stretch	219 cm^{-1}	186 cm^{-1}	13.86	31.83	21.30	33.01
C-C twist	127 cm^{-1}	239 cm^{-1}	1.91	60.27	37.82	–
HB stretch I	181 cm^{-1}	76 cm^{-1}	11.16	21.94	4.51	62.39
HB stretch I	–	–	–	–	–	–
HB stretch II	190 cm^{-1}	13 cm^{-1}	17.99	3.26	5.08	73.67
HB stretch I	–	–	–	–	–	–
HB bend I	91 cm^{-1}	28 cm^{-1}	<1	31.28	<1	67.43
HB bend I	–	–	–	–	–	–
HB bend II	81 cm^{-1}	<2 cm^{-1}	6.27	<1	<1	92.57
HB bend II	–	–	–	–	–	–

Table S2. Decomposition of the total harmonic kinetic energy in terms of the separate contributions due to glycine's center of mass, overall rotation, and vibrational motion as well as motion of the considered H–bonded water molecules (reported in percent, deviations from 100 % due to rounding errors) associated to the THz modes of the supermolecular solvation complex SSC(−), Gly(1 H_2O), in "free" (red) and "fixWAT" (blue) solvation environments, see main text.

Mode	Frequency	Intensity	Gly-COM	Gly-Rot	Gly-Vib	Water
cage rattling I	53 cm^{-1}	25 cm^{-1}	88.31	1.16	3.46	7.07
cage rattling I	110 cm^{-1}	16 cm^{-1}	84.37	8.61	7.02	–
cage rattling II	55 cm^{-1}	12 cm^{-1}	87.59	6.69	2.44	3.28
cage rattling II	94 cm^{-1}	75 cm^{-1}	74.18	17.44	8.37	–
cage rattling III	54 cm^{-1}	66 cm^{-1}	87.36	<1	2.28	9.73
cage rattling III	175 cm^{-1}	38 cm^{-1}	68.35	25.94	5.71	–
cage libration I	82 cm^{-1}	146 cm^{-1}	8.02	79.63	5.08	7.27
cage libration I	171 cm^{-1}	128 cm^{-1}	10.56	86.53	2.92	–
cage libration II	66 cm^{-1}	24 cm^{-1}	<1	93.67	4.61	1.08
cage libration II	93 cm^{-1}	67 cm^{-1}	39.06	54.60	6.34	–
NCCO open/close	304 cm^{-1}	291 cm^{-1}	<1	<1	99.15	<1
NCCO open/close	337 cm^{-1}	412 cm^{-1}	1.53	1.83	96.63	–
Cα out-of-plane	140 cm^{-1}	92 cm^{-1}	2.82	19.74	77.10	<1
Cα out-of-plane	186 cm^{-1}	305 cm^{-1}	10.68	37.25	52.07	–
C-C twist	70 cm^{-1}	230 cm^{-1}	10.54	67.41	19.54	2.51
C-C twist	154 cm^{-1}	184 cm^{-1}	10.09	52.54	37.37	–
HB stretch I	201 cm^{-1}	33 cm^{-1}	9.32	11.88	1.75	77.05
HB stretch I	–	–	–	–	–	–
HB bend I	65 cm^{-1}	14 cm^{-1}	8.85	<1	<1	89.92
HB bend I	–	–	–	–	–	–
HB bend II	64 cm^{-1}	4 cm^{-1}	2.06	6.21	<1	91.47
HB bend II	–	–	–	–	–	–

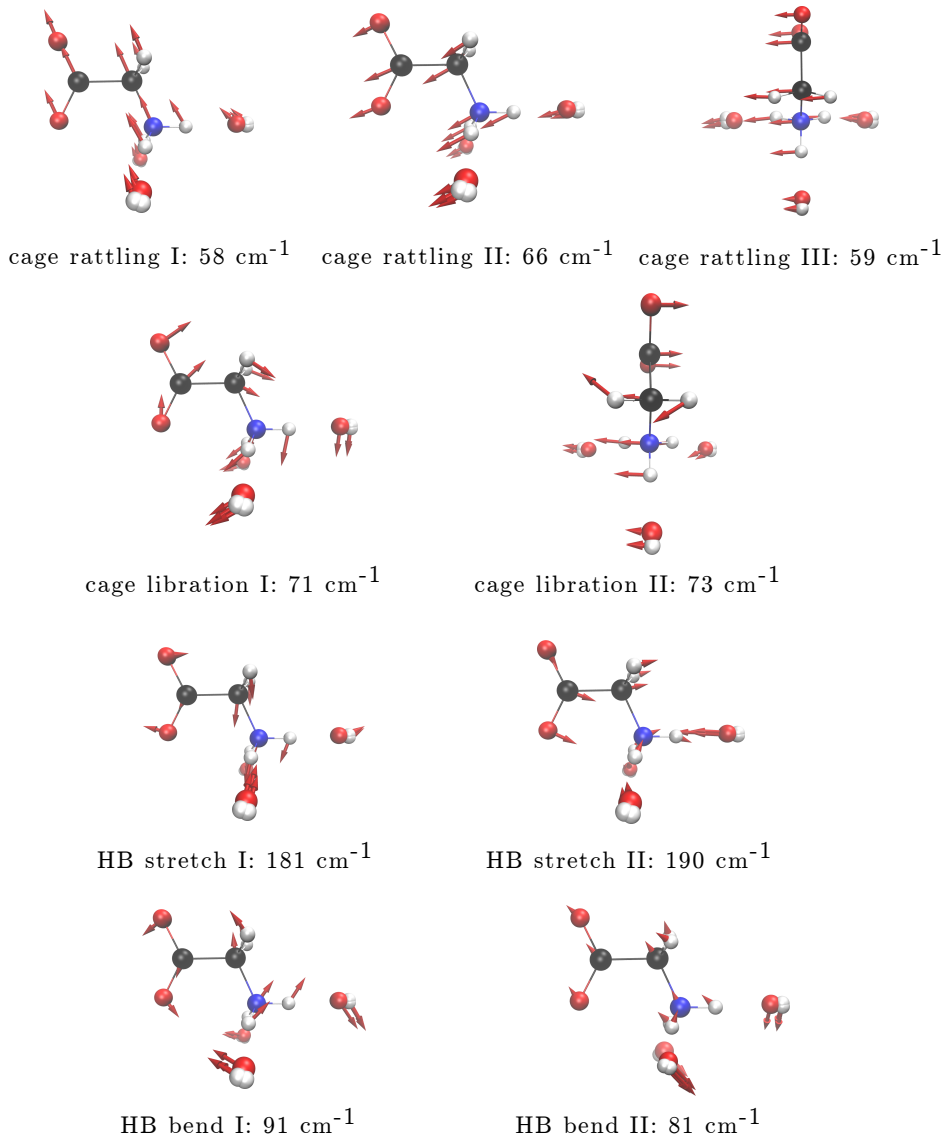
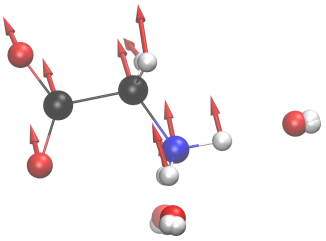
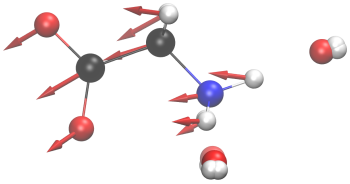


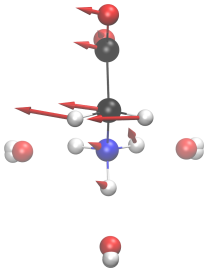
Figure S1. Atomic displacement patterns corresponding to the intermolecular THz modes of the supermolecular solvation complex SSC(+), Gly(3 H_2O), in the "free" solvation environment; the reported frequencies correspond to the peak maxima of the mode-specific IR spectra presented in Fig. 5a.



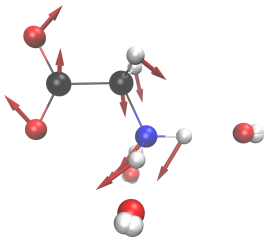
cage rattling I: 112 cm^{-1}



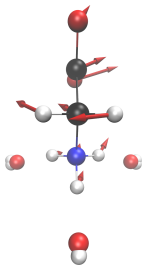
cage rattling II: 103 cm^{-1}



cage rattling III: 135 cm^{-1}

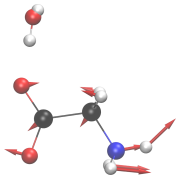


cage libration I: 118 cm^{-1}

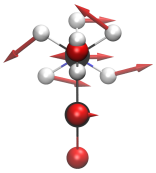


cage libration II: 193 cm^{-1}

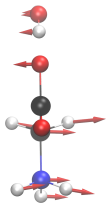
Figure S2. Atomic displacement patterns corresponding to the intermolecular THz modes of the supermolecular solvation complex SSC(+), Gly(3 H_2O), in the "fixWAT" solvation environment; the reported frequencies correspond to the peak maxima of the mode-specific IR spectra presented in Fig. 5b.



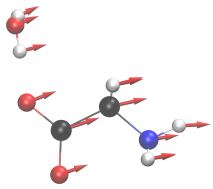
NCCO: 304 cm-1



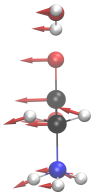
C_α OOP: 140 cm-1



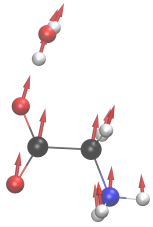
C-C twist: 70 cm-1



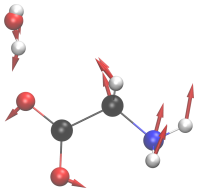
cage rattling I: 53 cm-1



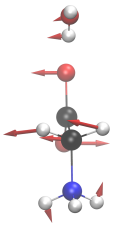
cage rattling II: 55 cm-1



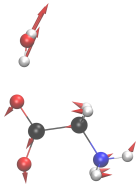
cage rattling III: 54 cm-1



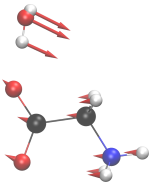
cage libration I: 82 cm-1



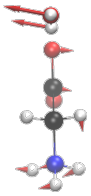
cage libration II: 66 cm-1



HB stretch I: 201 cm-1

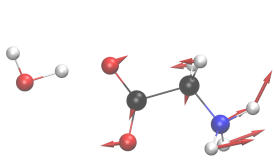


HB bend I: 65 cm-1

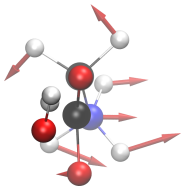


HB bend II: 64 cm-1

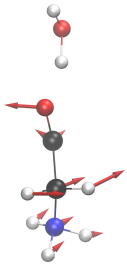
Figure S3. Atomic displacement patterns corresponding to the intermolecular THz modes of the supermolecular solvation complex SSC(−), Gly(1 H_2O), in the "free" solvation environment; the reported frequencies correspond to the peak maxima of the mode-specific IR spectra presented in Fig. 7a.



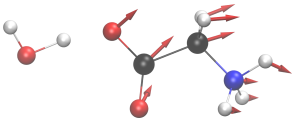
NCCO : 337 cm^{-1}



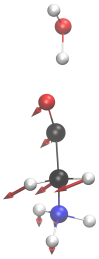
C_α OOP : 186 cm^{-1}



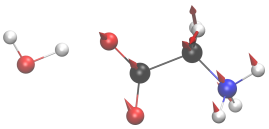
C-C twist : 154 cm^{-1}



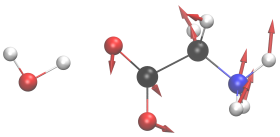
cage rattling I : 110 cm^{-1}



cage rattling II : 94 cm^{-1}



cage rattling III : 175 cm^{-1}



cage libration I : 171 cm^{-1}

cage libration II : 93 cm^{-1}

Figure S4. Atomic displacement patterns corresponding to the intermolecular THz modes of the supermolecular solvation complex SSC(−), Gly(1 H_2O), in the "fixWAT" solvation environment; the reported frequencies correspond to the peak maxima of the mode-specific IR spectra presented in Fig. 7b.

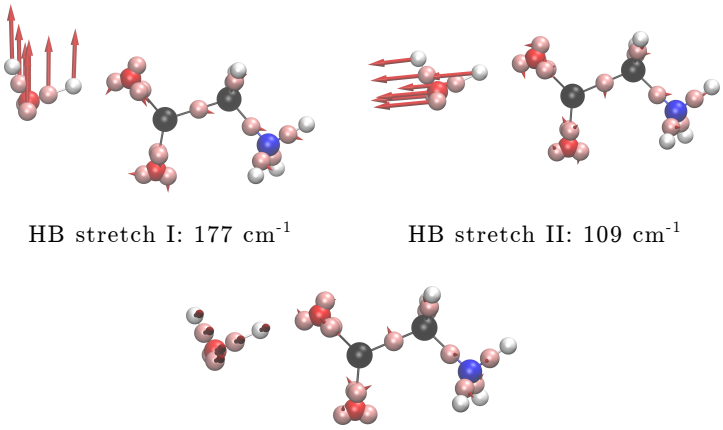


Figure S5. Atomic displacement patterns corresponding to the intermolecular THz modes of the supermolecular solvation complex SSC(−), Gly(1 H_2O), when glycine is frozen whereas all water molecules are mobile (fixGLY scenario); the reported frequencies correspond to the peak maxima of the mode-specific IR spectra presented in Fig. 9a. The displacement vectors of the Wannier centers belonging to the glycine molecule are very small and thus hardly visible.