Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Dynamics of Water in Conical Solvation Shells around a Benzene Solute under Different Thermodynamic Conditions

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Supplementary Information

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TABLE S1. Values of average interaction energy (in kJ/mol) of water molecules (non-polarizable model) present in the 0-30 ° and 60-90 ° conical regions, solvation shell and bulk. The interaction energy of a water molecule is calculated as the sum of Lennard-Jones and Coulomb interactions with the benzene and all other water molecules in the benzene-water systems.

Density	E_{0-30°	E_{60-90°	$E_{Solv.Shell}$	E_{Bulk}
1.0 g cm^{-3} $(298K)$	-44.07	-47.83	-46.58	-45.28
0.87 g cm^{-3} $(473K)$	-32.22	-34.47	-33.85	-33.51
0.7 g cm^{-3} $(673K)$	-22.62	-22.75	-22.65	-22.63
0.35 g cm^{-3} $(673K)$	-13.21	-13.01	-13.11	-14.76

TABLE S2. Values of the residence times (τ_R) of the hydration shell water molecules in different conical shells around a benzene solute molecule. Residence times are expressed in the units of ps. $\tau_R^{x_1-x_2\,^\circ}$ means the τ_R of water in a conical shell characterized by the conical angles $x_1\,^\circ$ and $x_2\,^\circ$. Results are included for both non-polarizable and polarizable models.

System/Model	$\tau_R^{0-30\,^\circ}$	$\tau_R^{30-60\,^\circ}$	$\tau_R^{60-90\,^\circ}$	τ_R^{solv}
System 1				
Non-polarizable	2.76	5.14	6.05	12.36
Polarizable	3.31	6.21	8.31	15.49
System 2				
Non-polarizable	0.28	0.26	0.24	0.19
Polarizable	0.34	0.31	0.26	0.21
System 3				
Non-polarizable	0.08	0.09	0.09	0.10
Polarizable	0.11	0.12	0.12	0.15
System 4				
Non-polarizable	0.05	0.05	0.05	0.05
Polarizable	0.06	0.06	0.06	0.06

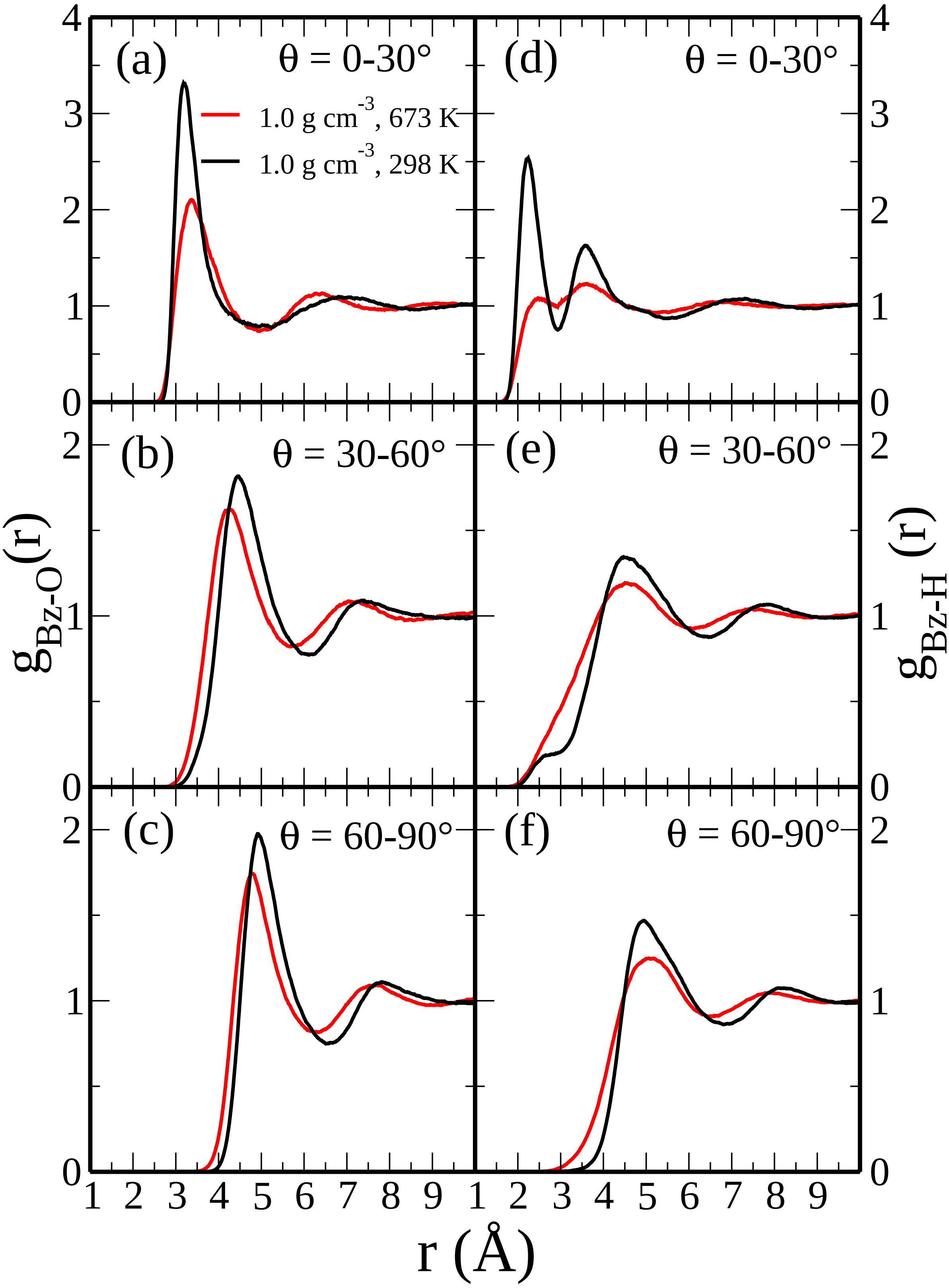

Fig.S1. Radial distribution functions (RDFs) for Systems 1 and 5. RDFs between the centre of mass of benzene (Bz) and oxygen atoms of water are plotted in figures (a)-(c) for 0-30°, 30-60° and 60-90° conical shells of the benzene solvation shell, respectively. The corresponding plots for Bz-H RDFs are shown in figures (d)-(f). The results are for the non-polarizable models.

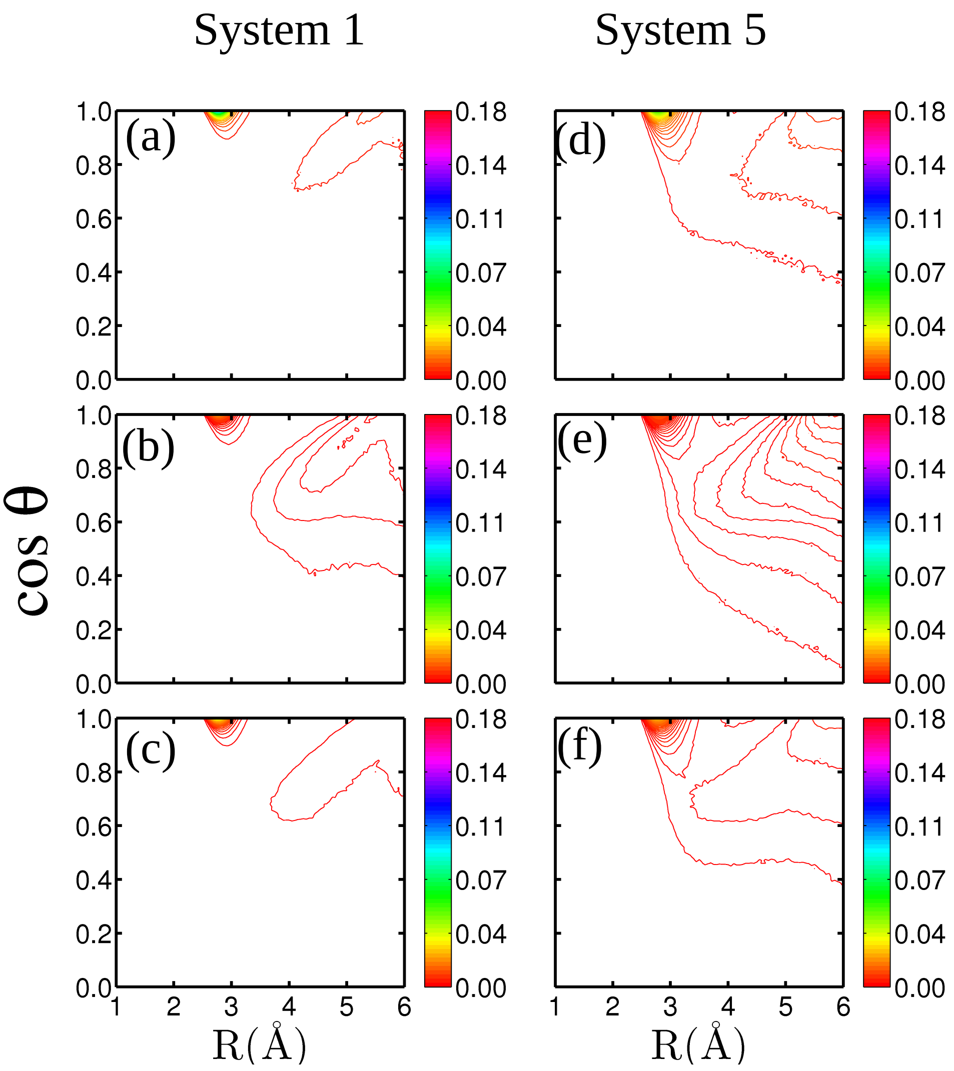

Fig.S2. Water-water interparticle distribution function, $\rho_{OO}(R, cos\,\theta)$, is plotted for Systems 1 and 5. Figures (a)-(c) are for water molecules inside the solvation shell (solv-solv); solvation shell-bulk water (solv-bulk) and for water molecules in the bulk (bulk-bulk) for System 1 and the corresponding figures (d)-(f) are for System 5. The results are for the non-polarizable models.

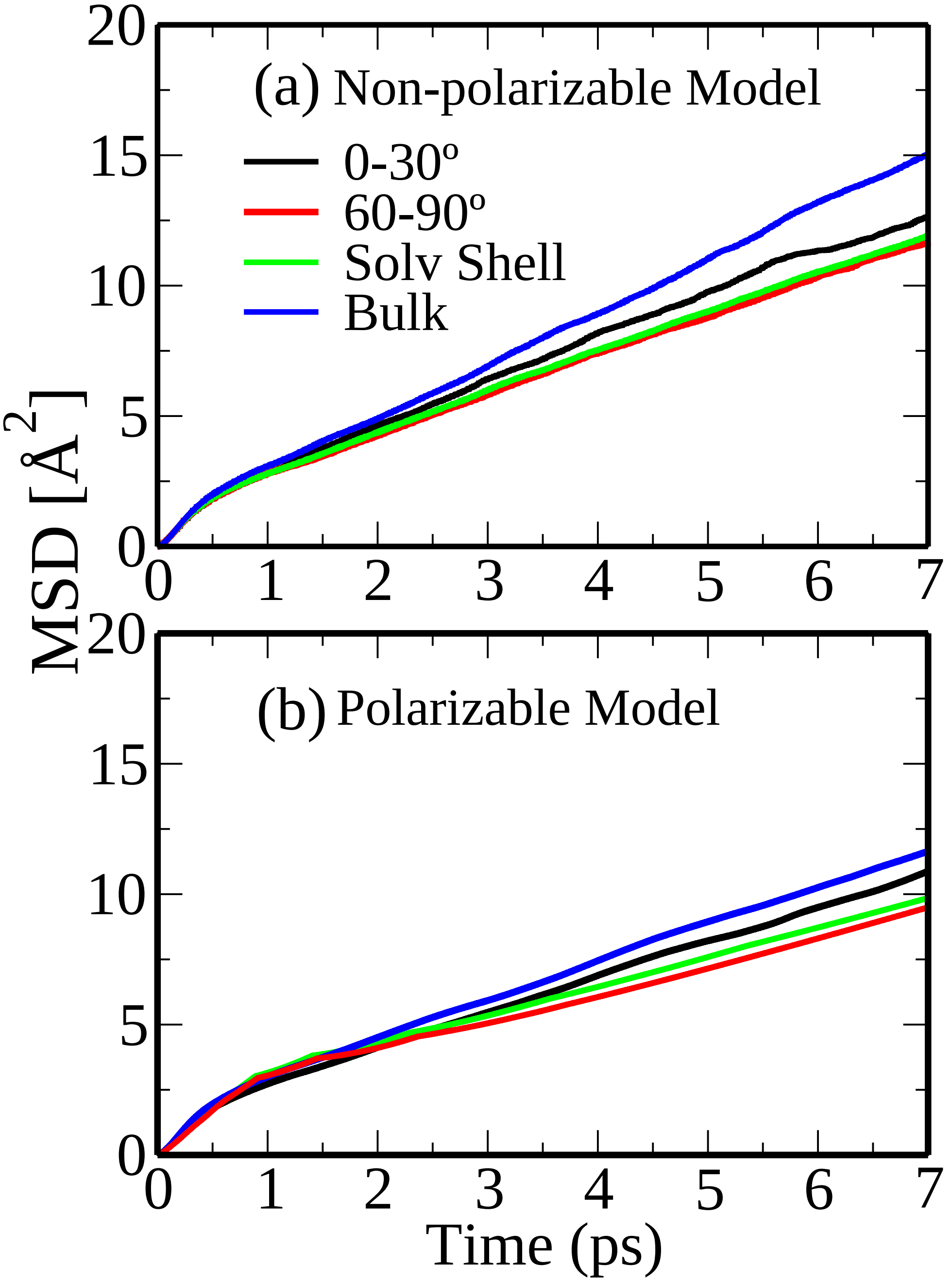

Fig.S3. Mean square displacement plots for water in different regions of System 1 for the (a) Non-polarizable and (b) polarizable models of the benzene-water system.

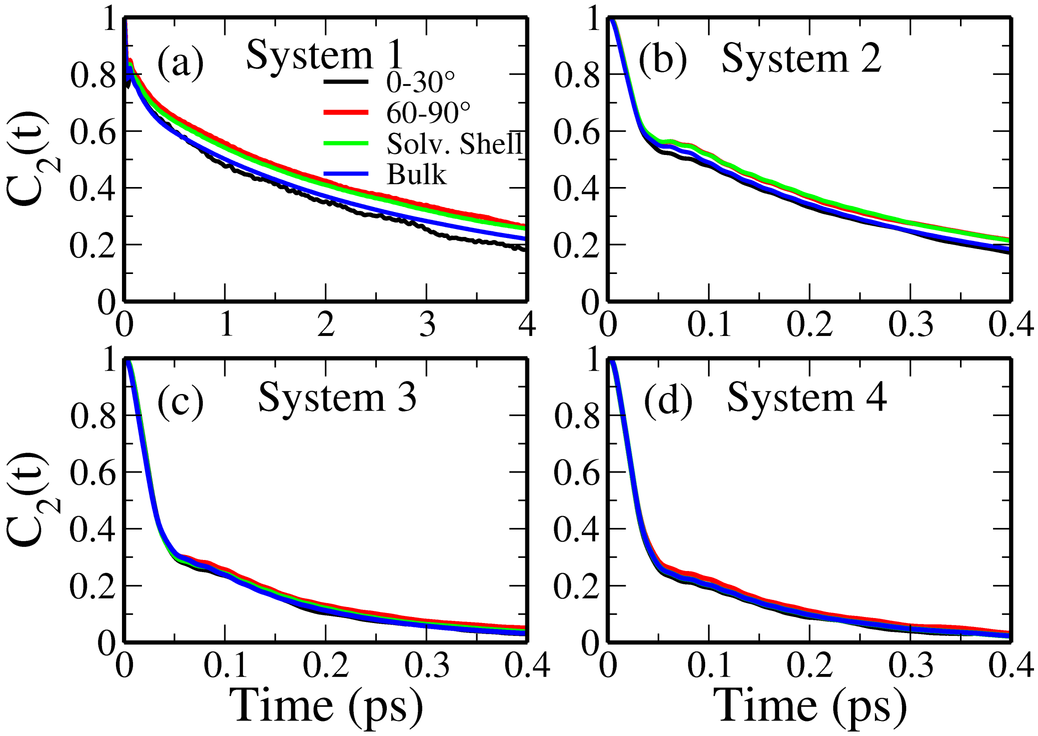

Fig.S4. The second rank orientational correlation function, $C_2(t)$, of OH vectors of water molecules in the solvation shell of benzene and bulk regions for Systems 1-4 are shown in figures (a)-(d), respectively. The results are for the polarizable models of benzene-water systems.

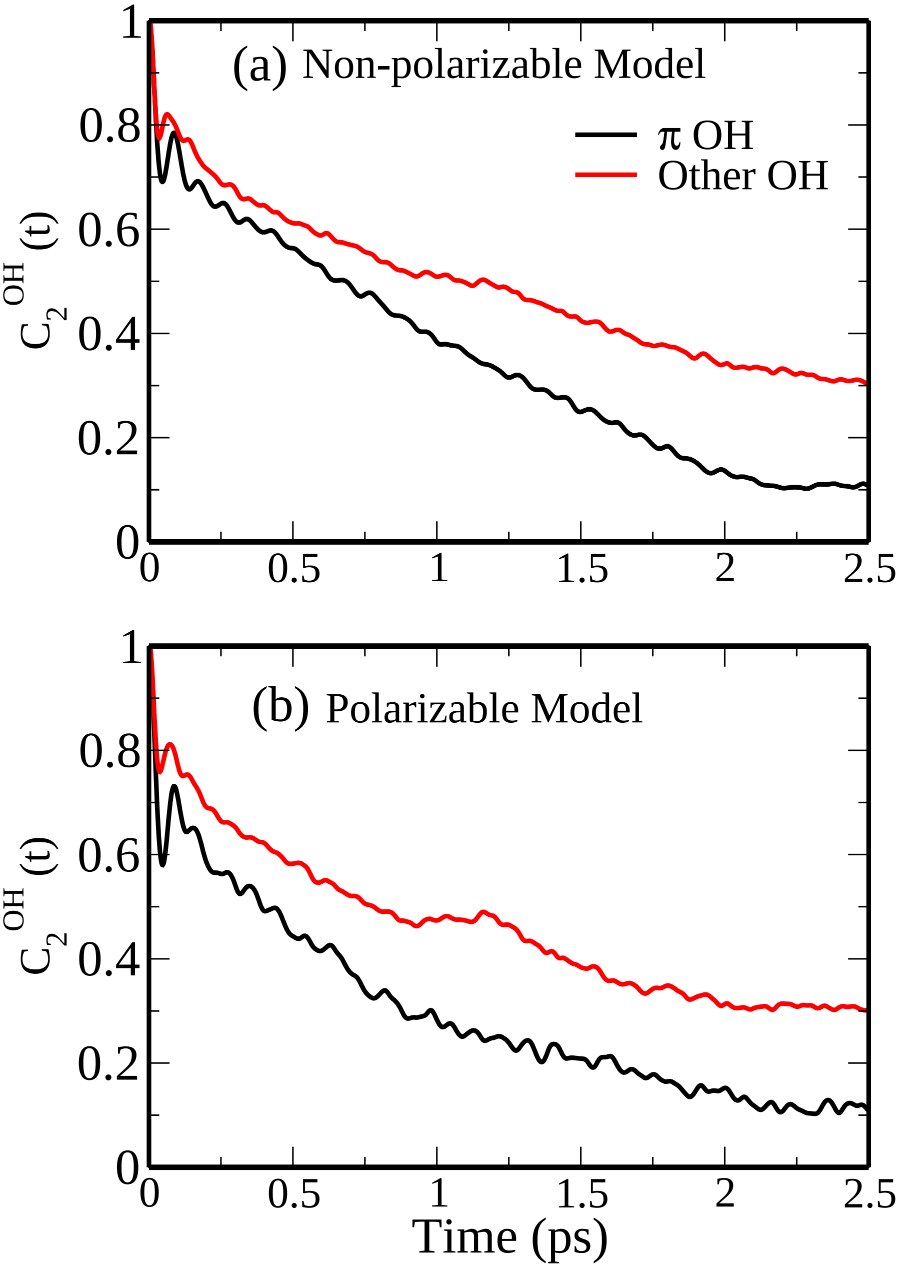

Fig.S5. The second rank orientational correlation function, $C_2(t)$, of two OH bonds of a water in the axial region in System 1. The orientational relaxation is shown separately for the πH-bonded OH bond and for the other OH bond which is hydrogen bonded to another water. Figures (a) and (b) are for non-polarizable and polarizable models of the benzene-water system, respectively.

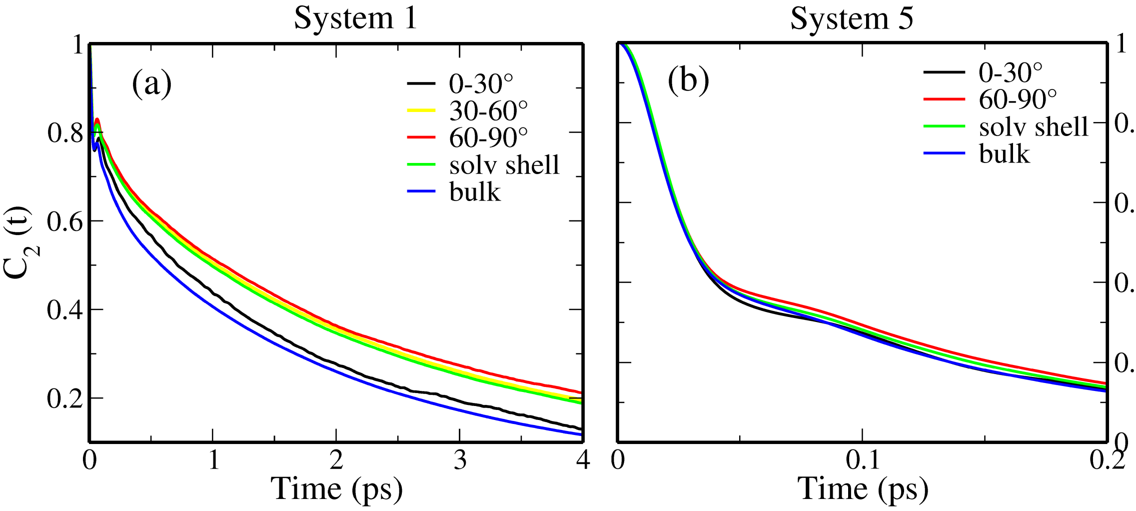

Fig.S6. The second rank orientational correlation function, $C_2(t)$, of OH vectors of water for Systems 1 and 5. The results are for the non-polarizable models.

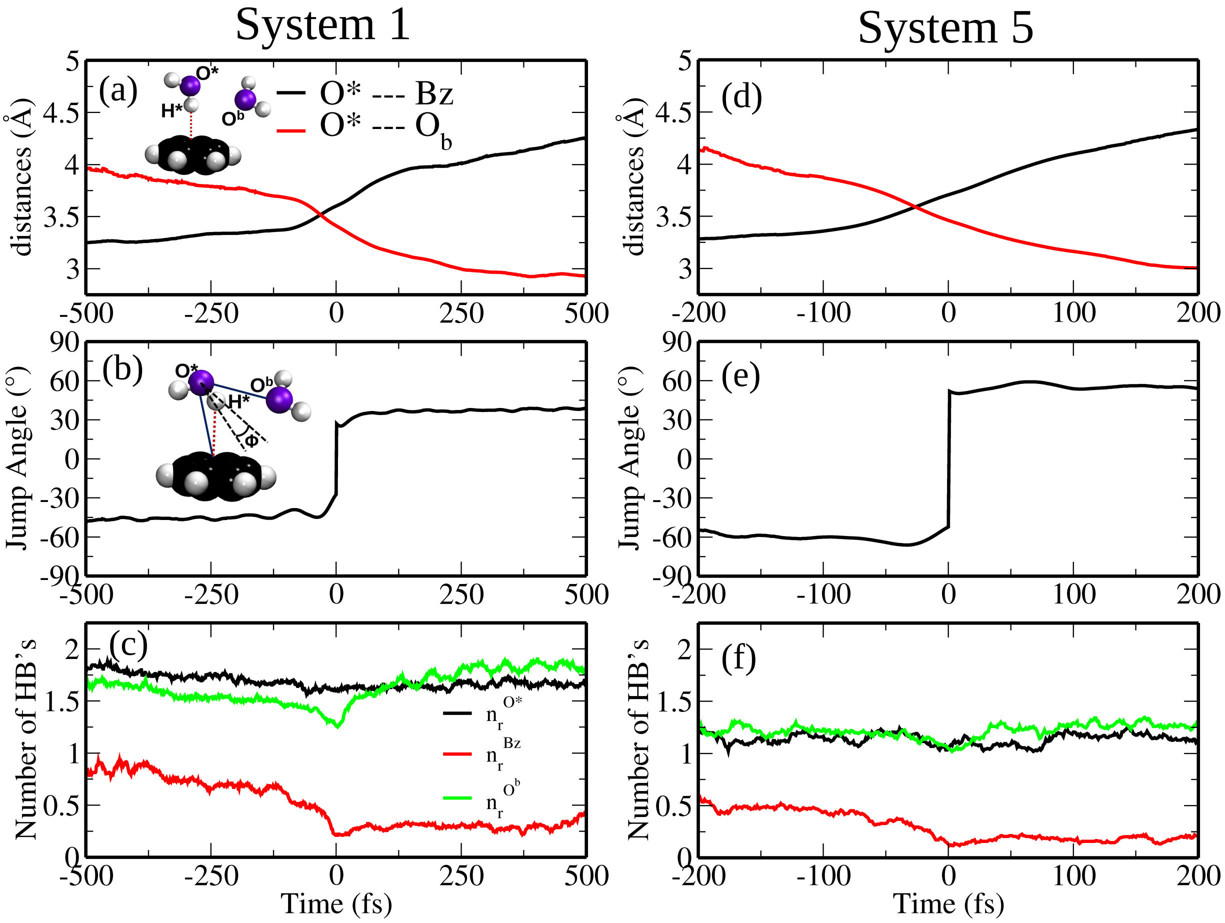

Fig.S7. The changes in distances and angles on breaking of a benzene-water π-Hydrogen bond and formation of a water-water hydrogen bond for Systems 1 and 5. The results are for the non-polarizable models.

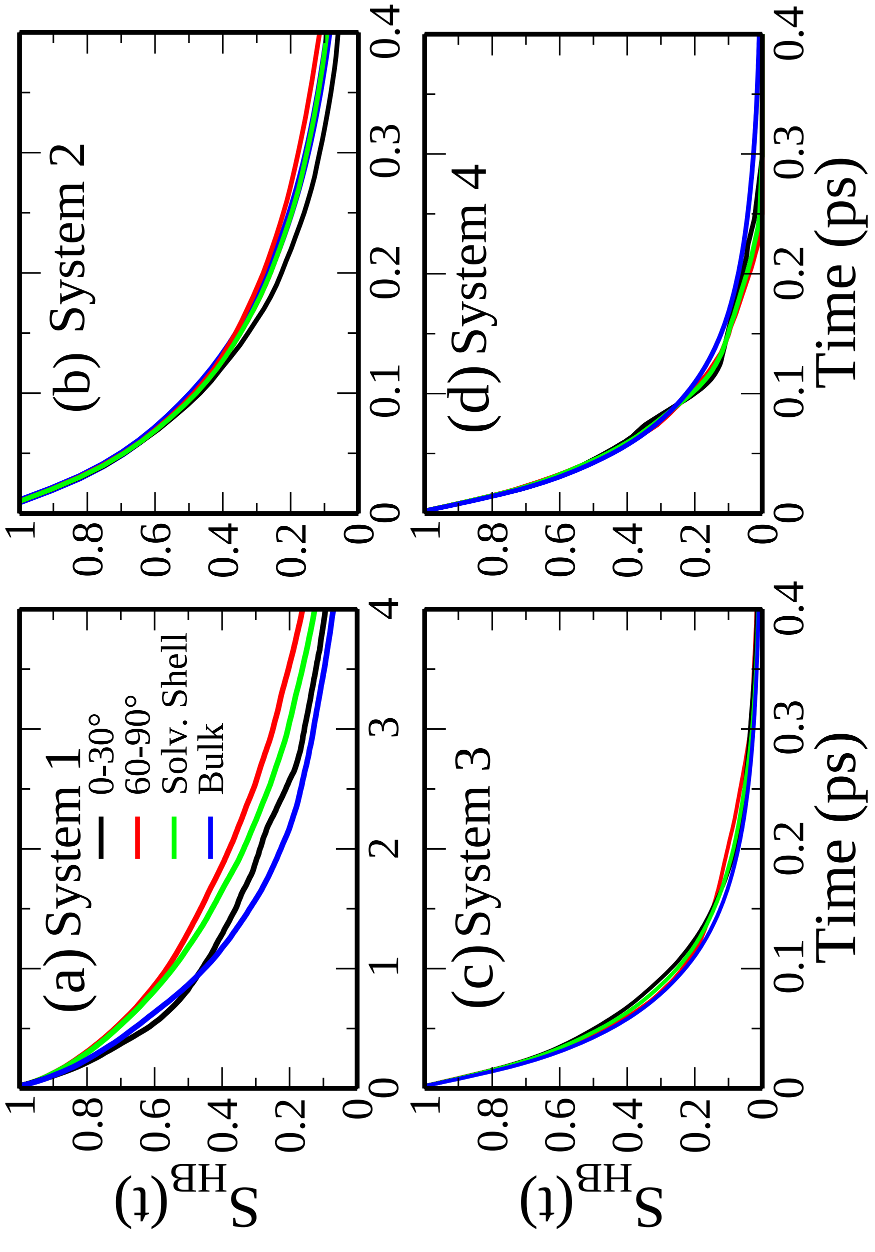

Fig.S8. The time dependence of the continuous hydrogen bond time correlation functions calculated for water-water hydrogen bonds in 0-30° and 60-90° conical shells and also in the entire solvation shell and bulk region for Systems 1 and 4. The results are for the polarizable models of benzene-water systems.

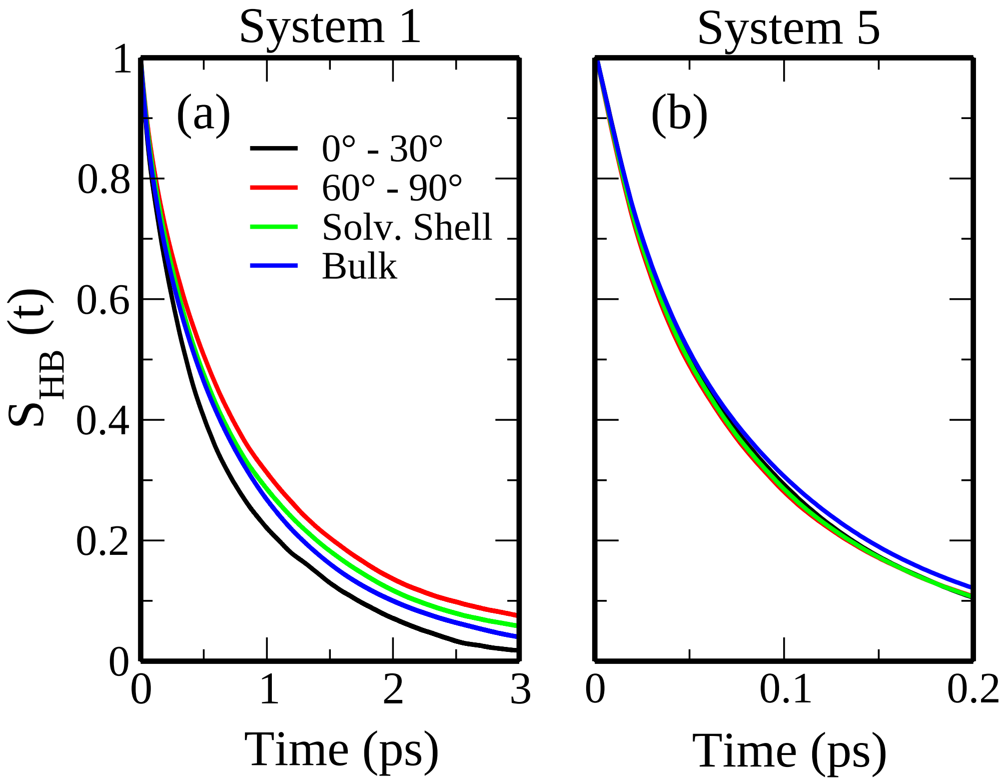

Fig.S9. Time dependence of the continuous hydrogen bond time correlation functions calculated for water-water hydrogen bonds in the 0-30° and 60-90° conical shells and also in the entire solvation shell and bulk region for Systems 1 and 5. The results are for the non-polarizable models of benzene-water systems.