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Anisotropic structure and dynamics of the solvation shell of a benzene solute in liquid water from *ab initio* molecular dynamics simulations

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Supporting Information

1 Structure and binding energy of the benzene-water dimer: Performance of the BLYP and BLYP-D functionals

In the current work, we have employed BLYP and the corresponding dispersion corrected BLYP-D functionals[1–4]. Another popular exchange-correlation functional belonging to the same category of the so-called generalized gradient approximation (GGA) functionals is the PBE functional[5]. Although it was not feasible to carry out additional *ab initio* simulations with the PBE and the corresponding dispersion corrected PBE-D functionals due to the length and size of the simulations, we have performed additional quantum chemical calculations of the binding energy and structural parameters of the optimized geometry of benzene-water dimer for BLYP (BLYP-D) and PBE (PBE-D) functionals using the same CPMD code[6] with a plane wave basis set cut-off of 80 Ry. The results of these calculations are shown in Table S1. It may be noted that both BLYP-D and PBE-D incorporate dispersion corrections at Grimme-D2 level. As can be seen from the Table, the structural parameters remain quite close for the BLYP and PBE functionals and also for their dispersion corrected variants. The binding energies, however, change significantly with incorporation of the dispersion corrections. Further calculations as discussed below show that the dispersion corrected binding energies provide more reliable description of the benzene-water interaction than the results of the corresponding dispersion uncorrected functionals.

In order to further test the importance of the dispersion corrections, we carried out additional all-electron quantum chemical calculations of the optimized geometry and binding energies of benzene-water dimer at MP2 perturbative level and also at the density functional theory (DFT) level with BLYP and B2PLYPD functionals using the GAUSSIAN09 software[7]. It may be noted that the B2PLYPD functional uses dispersion corrections at the same Grimme-D2 level. All calculations are done using the cc-pVTZ basis set. The binding energies are calculated by incorporating the basis set corrections using the counterpoise method. The results of these calculations are presented in Table S2. As can be seen, the binding energy of the dimer for the dispersion corrected density functional is closer to the MP2 result than the dispersion uncorrected BLYP functional. Rather, with the pure BLYP functional, the benzene-water interaction is far from correct. Thus, it is important that the dispersion corrections are used in *ab initio* simulations of benzene-water systems.

2 Maintenance of electronic adiabaticity and energy conservation during simulation

We also note that the current *ab initio* simulations were performed by using a fictitious orbital mass of μ=800 a.u. for the electronic degrees of freedom, deuterium mass for all hydrogen atoms of water and benzene molecules and a time step of 5 a.u. for numerical integration of the equations of motion. The choice of D_2O and C_6D_6 in place of H_2O and C_6H_6, respectively, ensured that electronic adiabaticity and energy conservation were maintained during the simulations. It may be noted that the choices of proper values of the electronic mass parameter and time step are important issues in carrying out Car-Parrinello simulations. While a value of 800 a.u. for the fictitious orbital mass is not expected to be reliable for H_2O[8] for maintaining electronic adiabaticity, it appears to be acceptable for the present D_2O/C_6D_6 systems in maintaining the adiabaticity and energy conservation reasonably well. In Fig.S1, we have shown the results of fictitious electronic temperature, ionic temperature and the extended Hamiltonian for the last 50 ps of the production run of the simulation with the BLYP-D functional. Similar results were also found for the BLYP functional, hence are not shown here. As can be seen from this figure, no significant drifts in these quantities are observed during the trajectory generation which ensure that the Car-Parrinello simulations were run in the proper manner in the current study.

3 Basis set cut-off of plane waves

We used a cut-off of 80 Ry for the plane wave basis functions. The use of any higher cut-off will make the already expensive simulations even more challenging. Nevertheless, it is also important to quantify the quality of the basis set used in the current calculations from its convergence point of view. In order to judge the quality of the current basis set cut-off, we performed additional calculations of frequencies of benzene-water dimer using basis set cut-offs of 80, 100 and 120 Ry. The frequencies were calculated using the normal mode method on optimized geometries obtained with the three different basis set cut-offs and for both the BLYP and BLYP-D functionals. All frequencies are found to be real positive without any significant changes as we increased the size of the basis set. On going from 80 to 120 Ry cut-off, typical changes in normal mode frequencies of the benzene-water dimer are found to be less than 4% (less than 1% in most cases) while the changes in the average frequency of all the modes are found to be less than 0.04 (0.07)% for the BLYP (BLYP-D) functional. Thus, the basis set cut-off of 80 Ry appears to be acceptable for the current systems of interest.

4 Coordination and πH-Bond numbers in different conical regions

The details of πH-bond and coordination numbers of different conical shells in the axial and equatorial regions are presented in Fig.S2. The relevant discussions of these results are available in Section 3.1 of the main text.

5 Benzene-water radial/angular distributions involving water dipole and OD tilt angles

In Fig.S3, we have shown schematic representations of (a) water dipole and (b) OD tilt angles of a deuterated water molecule. These angles are taken into consideration in calculations of benzene-water radial/angular distributions which are presented in Figs. S4 and S5. The results of the distributions involving dipole tilt angle (ω) are discussed in Section 3.2 of the main text. In the current section of SI, we include a brief discussion of the distributions involving the OD tilt angle α.

The radial/angular distribution functions of the OD tilt angle α [Fig.S5] of the smaller axial regions reveal that water molecules which are in the πH-bonded distance range from benzene center of mass have higher probabilities of two distinct ranges for the tilt angles of their OD vectors around $\alpha = 0^\circ$ to 20° and 90° to 120°. The water molecules in the 15° axial region align one of their OD towards benzene and the second OD is pointed away from benzene. The range of πH-bonded OD vector tilt angle suggests enough rotational freedom of πH-bonded water molecules.

On increasing the conical angle of the axial and equatorial regions, two maxima are found to occur at distances above 3.5 Å with the angular range of $\cos\alpha$ = 0.5 to 0.0

and -0.9 to -1.0 corresponding to $\alpha = 60\,^\circ$ to $90\,^\circ$ and $160\,^\circ$ to $180\,^\circ$. These results show that the water molecules in the larger axial regions of the solvation shell of benzene, in particular water molecules in the equatorial region, align their one OD vector tangential to the solute and other OD opposite to the solute surface. The probability densities are slightly different for the OD vector tilt angle distribution for the BLYP-D and BLYP functionals. Therefore, on the basis of the radial/angular distribution functions, one can conclude that water molecules in the solvation shell of a benzene solute in the smaller axial regions align their one OD vector toward the benzene center with the other OD pointing away from benzene. However, water molecules in the equatorial regions align their one OD tangential to the benzene ring and other opposite to the benzene surface.

6 Water-water inter-particle distance/angle distributions

The results of water-water inter-particle distributions resolved in both oxygen-oxygen distance and the smallest oxygen-oxygen-deuterium angle are shown in Fig.S6. The corresponding discussions of the results are presented in Sec.3.3 of the main text.

7 Diffusion of water molecules in the solvation shell of benzene

In order to compare the translational dynamics of water molecules in different conical regions around a benzene solute molecule, we have calculated the translational diffusion of water molecules in different conical regions of the solvation shell. The diffusion coefficients are calculated from the long time limit of mean square displacement (MSD) by using the following relation

$$D = lim_{t\to\infty} \frac{< [r(t) - r(0)]^2 >}{6t} \ , \tag{1}$$

where $r(t)$ is the position of the centre of mass of the molecule at time t. To calculate MSD in a particular angular conical region, we take water molecules in the first solvation shell of benzene which were initially (at t = 0) in that particular conical region of interest. The values of diffusion coefficients for different angular regions are included in Table S3 for both BLYP-D and BLYP functionals. It is found that the diffusion coefficient value in the $15\,^\circ$ axial conical region is the greatest and that in the $15\,^\circ$ equatorial conical region is found to be the smallest for both the functionals. It is found that the diffusion coefficient decreases for larger axial conical regions and it increases for the larger equatorial conical regions. This shows that the equatorial water molecules have slower translational dynamics. The trend of the diffusion of solvation shell water molecules is found to be similar for the BLYP and BLYP-D functionals although the absolute values of the diffusion coefficients are noticeably different for the two functions in all the regions.

TABLE S1. The optimized structural parameters and binding energies of the benzene-water dimer with water in the axial πH-bonded geometry. The optimizations are done using the CPMD code[6] with a plane wave basis set cut-off of 80 Ry. Bz stands for the centre of mass of benzene.

Functional→	BLYP	BLYP-D	PBE	PBE-D
Bz-H Distance (Å)	2.89	2.73	2.85	2.67
Bz-O Distance (Å)	3.50	3.41	3.44	3.49
$\angle$OBzH (°)	13.54	13.16	14.35	9.89
$\angle$BzHO (°)	122.31	126.93	119.10	142.08
$\angle$HOBz (°)	44.14	39.90	46.53	28.02
Binding Energy (kcal/mol)	-0.84	-3.22	-1.92	-4.09

TABLE S2. The optimized structural parameters and binding energies of the benzene-water dimer with water in the axial πH-bonded geometry. The optimizations are done using the GAUSSIAN09 code[7] at MP2 perturbative level and also at the density functional theory (DFT) level with BLYP and B2PLYPD functionals. All calculations are done using the cc-pVTZ basis set. The binding energies are calculated by incorporating the basis set corrections using the counterpoise method.

Functional	MP2(cc-pVTZ)	BLYP(cc-pVTZ)	B2PLYPD(cc-pVTZ)
Bz-H Distance (Å)	2.57	2.86	2.54
Bz-O Distance (Å)	3.22	3.52	3.19
$\angle$OBzH ($^\circ$)	14.09	13.01	14.42
$\angle$BzHO ($^\circ$)	125.45	125.45	124.30
$\angle$HOBz ($^\circ$)	40.63	41.53	41.28
Binding Energy (kcal/mol)	-2.66	-0.61	-3.03

TABLE S3. Values of diffusion coefficients (D) of water molecules in the axial and equatorial conical regions of the hydration shell of a benzene solute molecule for both BLYP-D and BLYP functionals. The diffusion coefficients are expressed in units of 10^{-5} $\text{cm}^2\ \text{sec}^{-1}$. D_{x° means the diffusion coefficient (D) of water in a conical region of the solvation shell characterized by the conical angle of $x\,^\circ$. The standard deviations in the diffusion coefficient values are found to be in the range of 1.7% (for D_{bulk}) to 3.5% (for D_{15°) of the respective average values reported in the Table.

Diff. Coeff.		$D_{15\,^\circ}$	$D_{30\,^\circ}$	$D_{45\,^\circ}$	$D_{60\,^\circ}$	$D_{75\,^\circ}$	$D_{90\,^\circ}$	D_{bulk}
BLYP-D	Axial	1.26	1.21	1.02	0.94	0.90	0.87	0.92
	Equatorial	0.76	0.80	0.83	0.84	0.85		
BLYP	Axial	0.89	0.85	0.78	0.67	0.56	0.47	0.61
	Equatorial	0.28	0.32	0.37	0.43	0.46		

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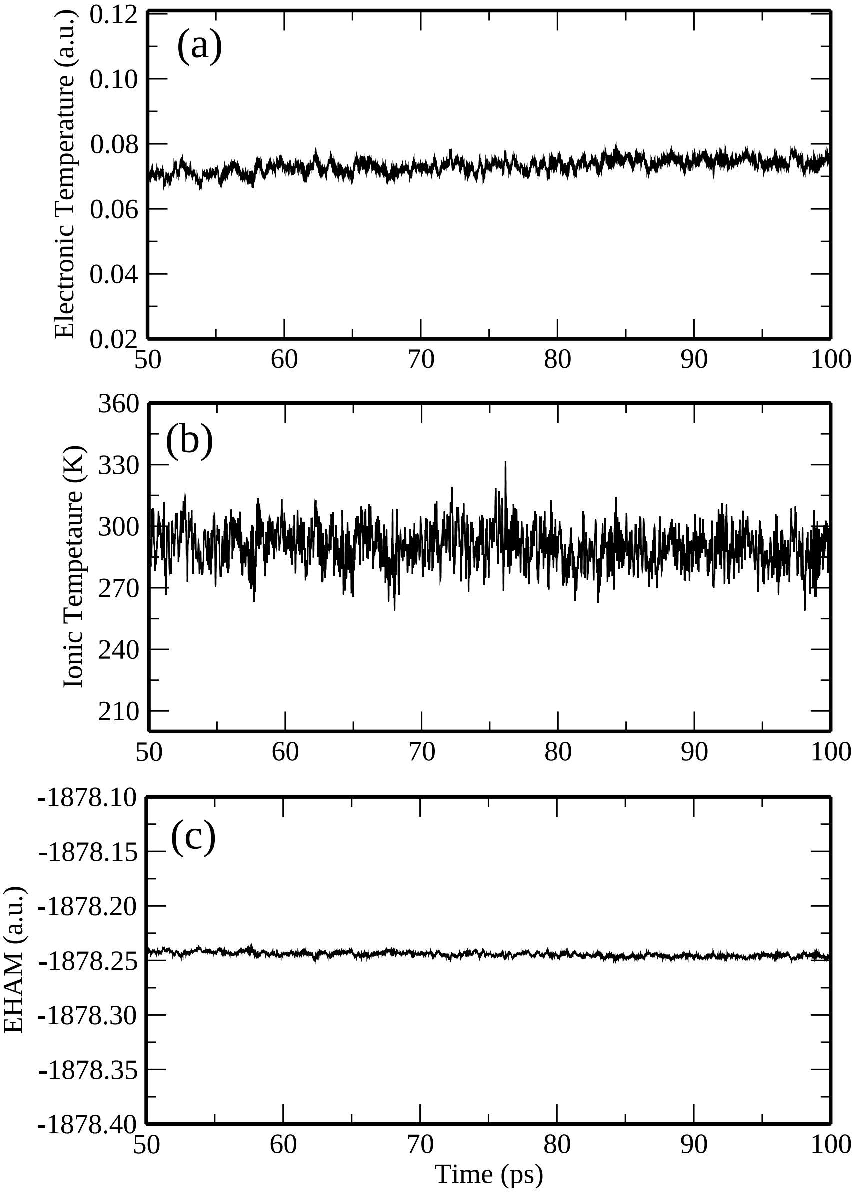

Fig.S1. (a) Temperature of fictitious electrons, (b) Temperature of ions, and (c) Extended Hamiltonian of the simulation system for last 50 ps of the BLYP-D run.

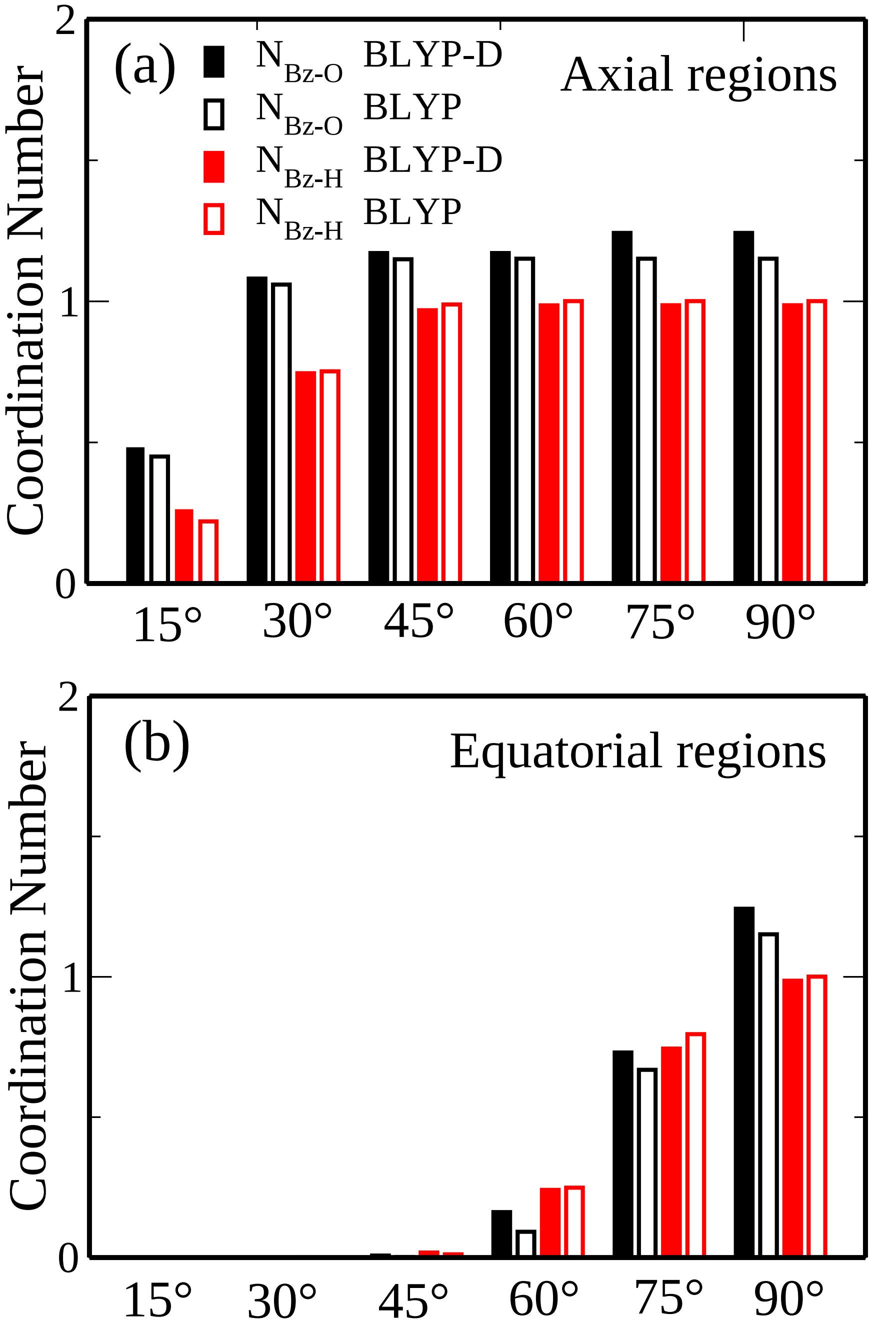

Fig.S2. The coordination numbers for Bz-O and Bz-D pairs in the π-hydrogen-bonded cutoff range of 3.6 Å for $g_{\mathrm{Bz-O}}(\mathrm{r})$ and 3.0 Å for $g_{\mathrm{Bz-H}}(\mathrm{r})$. The color filled bars are for the BLYP-D functional and the empty bars are for the BLYP functional.

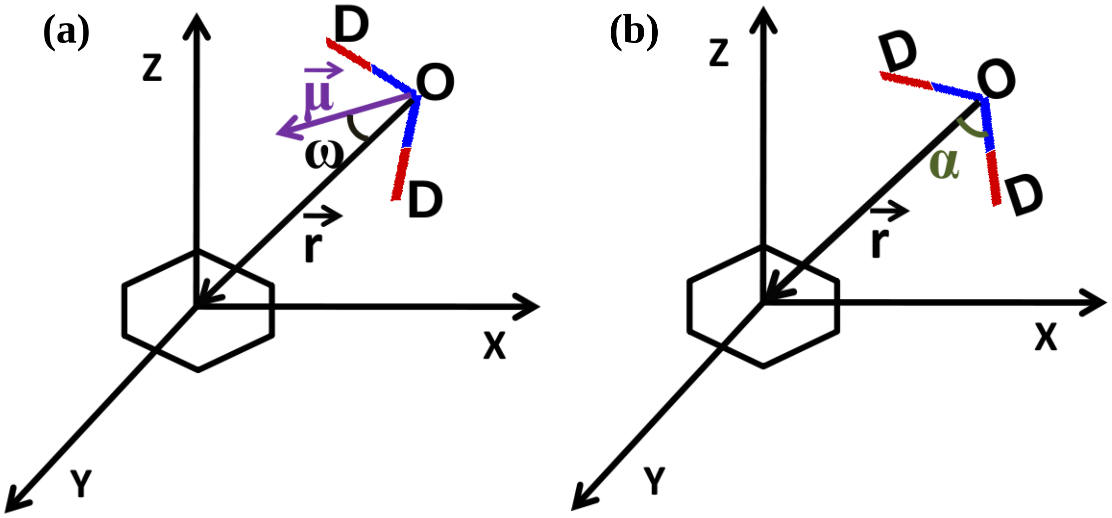

Fig.S3. Definition of the dipole and OD vector tilt angle upon taking the centre of mass of Bz as the reference point, the vector $\vec{r}$ is defined as the vector which connects the water oxygen to the benzene centre of mass and $\vec{\mu}$ is the dipole vector of the water molecule. (a) The water dipole tilt angle ω is the angle between the $\vec{r}$ and $\vec{\mu}$ vectors. (b) Water OD vector tilt angle α is defined as the angle between the $\vec{r}$ and OD vectors.

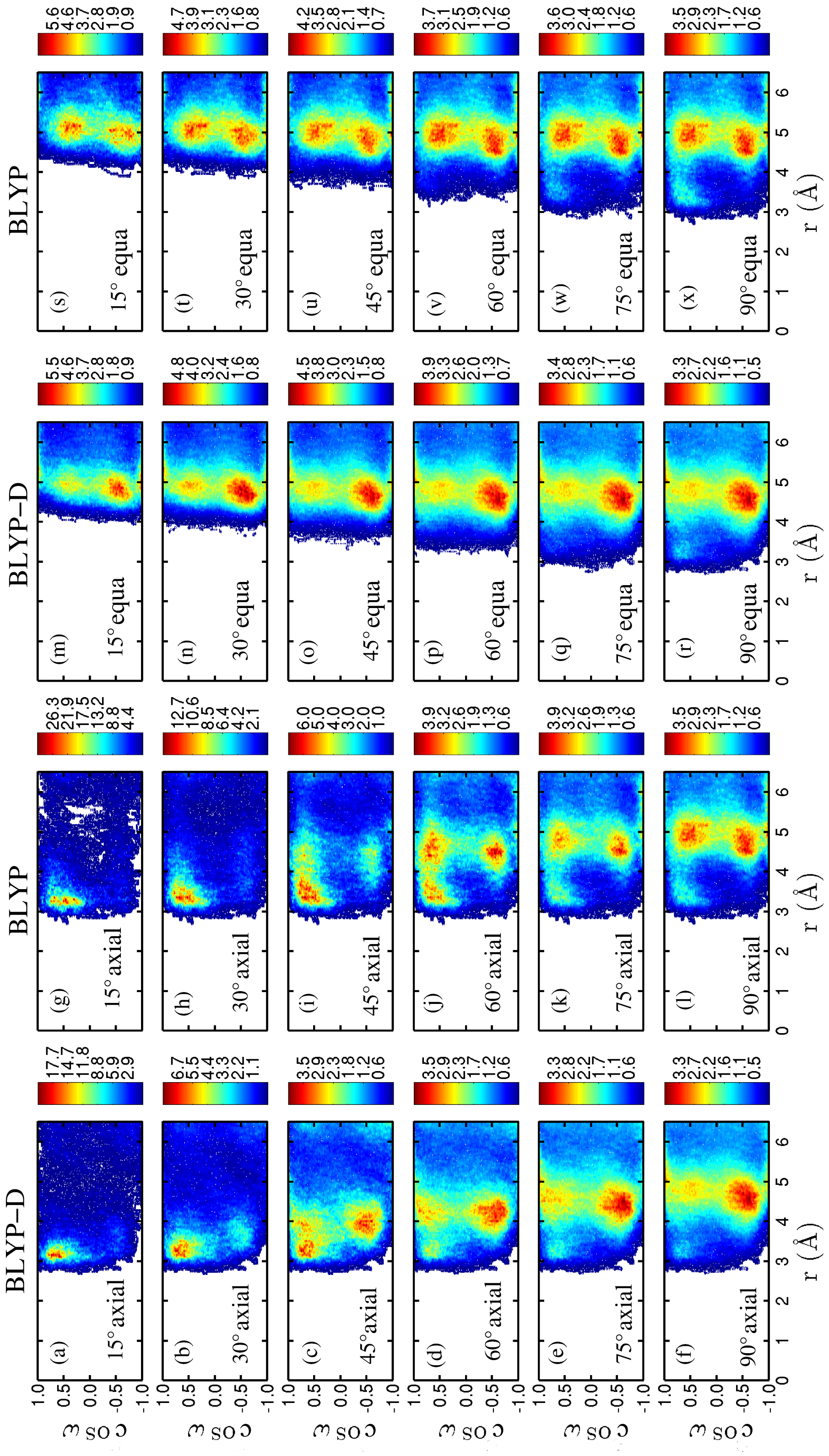

Fig.S4. Radial/Angular distribution functions of water, $g_{Bz-O}(r, \cos\omega)$, in the axial and equatorial conical regions of the benzene solvation shell where ω refers to dipole tilt angle as defined in Fig.S3 . Results are shown for both BLYP-D and BLYP functionals.

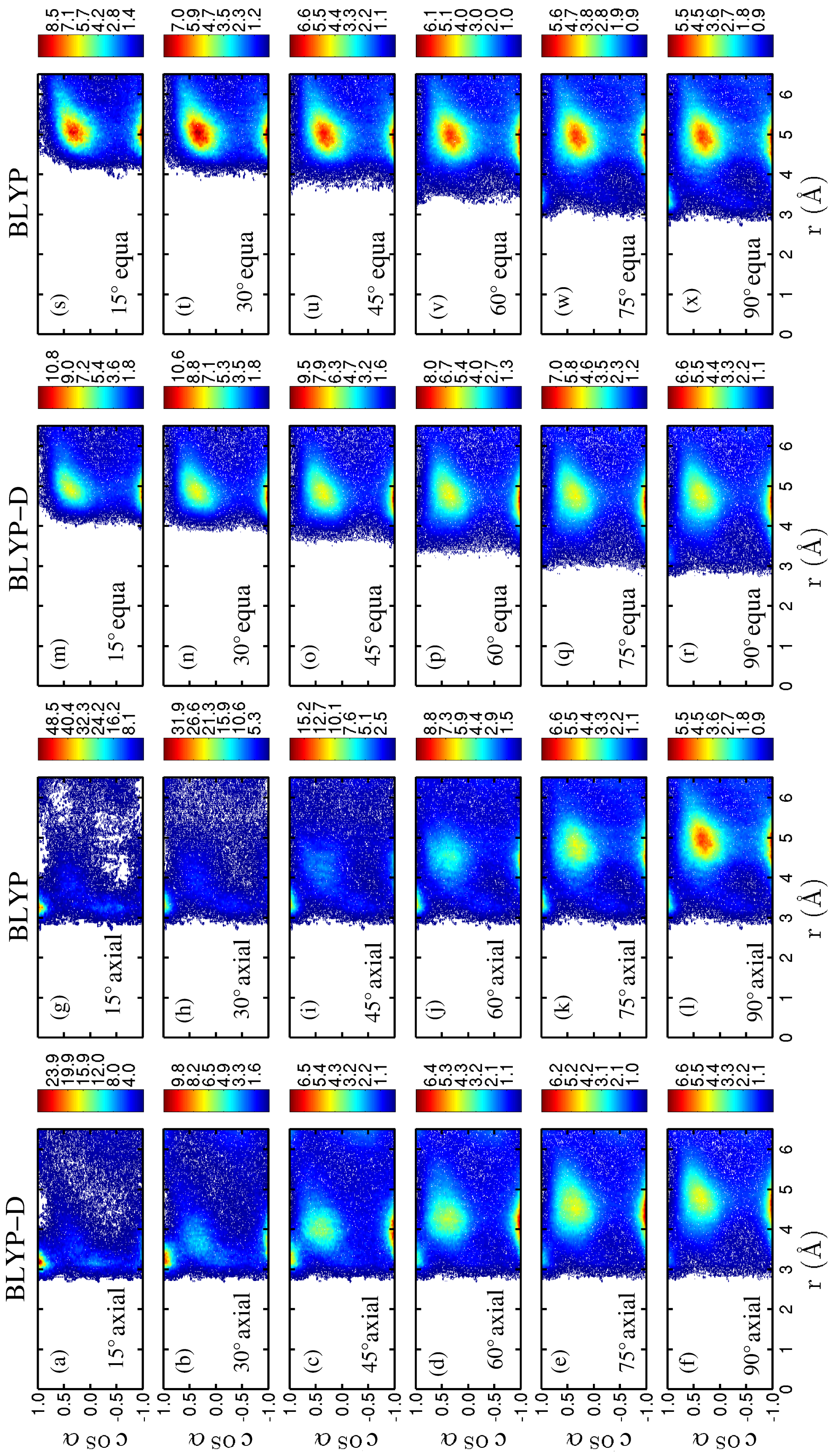

Fig.S5. Radial/Angular distribution functions of water, $g_{\mathrm{Bz-O}}(\mathrm{r}, \cos\,\alpha)$, in the axial and equatorial conical regions of the benzene solvation shell where α refers to the OD vector tilt angle as defined in Fig.S3. Results are shown for both the BLYP-D and BLYP functionals.

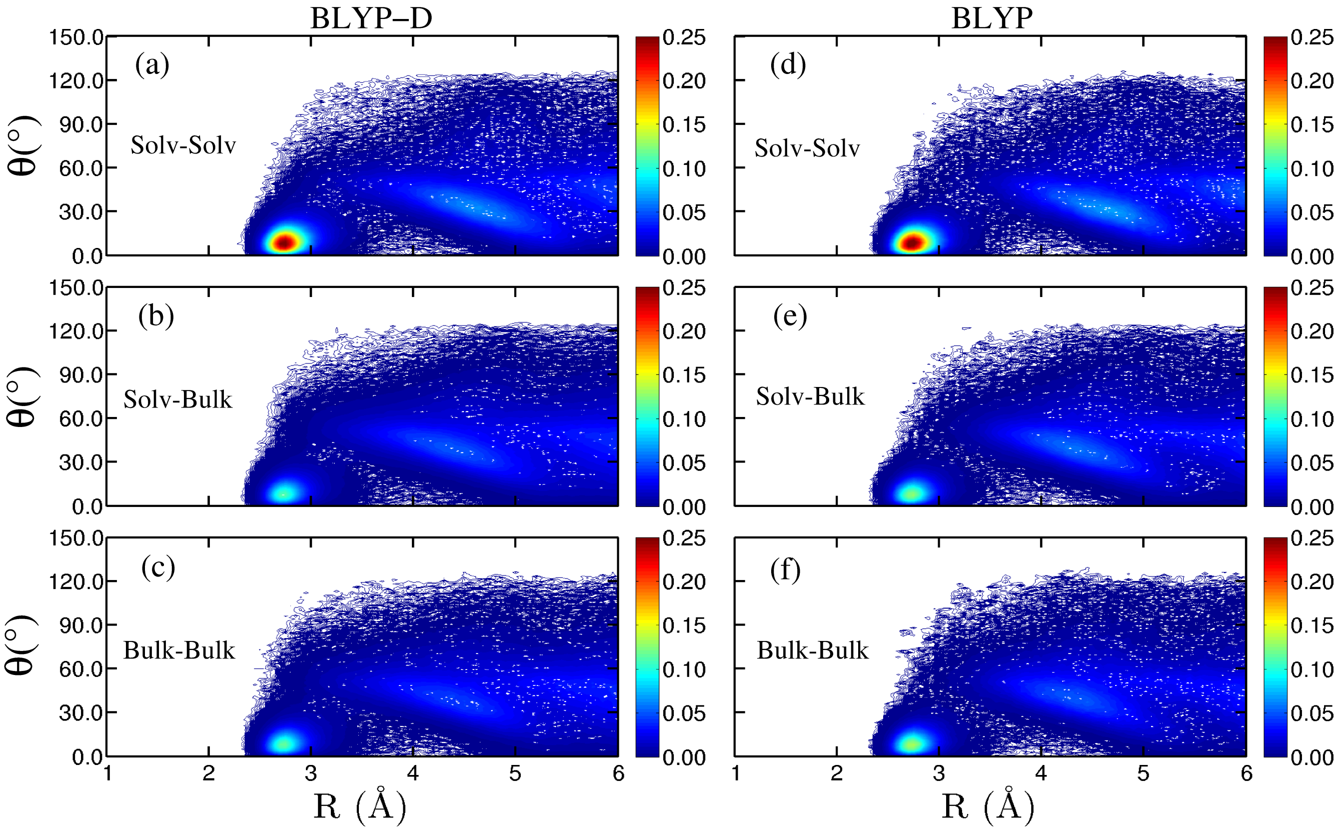

Fig.S6. Water-water interparticle distance/angle distributions in the benzene solvation shell (solv-solv), between solvation shell and bulk (solv-bulk), and in the bulk region (bulk-bulk). Figs.(a)-(c) are for BLYP-D functional and Figs.(d)-(f) are for the BLYP functional.