Supporting Information for

Large Amplitude Angular Jump Motions Connect Temporal Heterogeneity in Aqueous Solutions

Debasish Das Mahanta[*], Rajib Kumar Mitra[*]

Chemical, Biological and Macromolecular Sciences
S. N. Bose National Centre for Basic Sciences
Block-JD, Sector-III, Salt Lake, Kolkata, 700106, India
Phone: 91-33-23355706, Fax: +91-33-23353477

* Email: snbdebasish@gmail.com (DDM), rajib@bose.res.in (RKM)

Functional form of force field for DME

We used the unified atom models for DME molecules. The interaction potential energy function (V) among the molecules is in general represented as follows,

$$V(r_1, r_2, r_3 ...., r_n)$$
$$= \sum_{bond} \frac{1}{2} K_b (b - b_0)^2 + \sum_{angles} \frac{1}{2} K_\theta (\theta - \theta_0)^2 + \sum_{dihedral} K_\varphi [1 + \cos(n\varphi - \delta)] + \sum_i \sum_{j>}$$

(S1)

The above equation (equation S1) consists of two types of interactions, bonded and non-bonded interactions. The first four terms in the equation represent the bonded interactions and the last two terms represent the non-bonded interactions. K_b is the bond force constant associated with the equilibrium bond distance (b_0), K_θ is the angle force constant with the equilibrium angle (θ_0). K_φ is the dihedral constant with periodicity n, dihedral angle φ and phase shift δ. r_{ij} is the distance between the i-th and the j-th atoms with partial charges q_i and q_j, respectively. $A = 4\epsilon\sigma_{ij}^{12}$ and $B = 4\epsilon\sigma_{ij}^6$ are the Lennard-Jones constant with ϵ is the depth of the potential well, and σ is the distance where the potential vanishes to zero. Further details about the force parameters are given in the table S1.

Radial distribution function

To compute the spatial distributions of the atoms of the molecules as a function of distance (r) in all those binary mixtures, we compute the radial distribution functions (RDF) of various possible pairs of oxygen following the equation as given below,

$$RDF_{ij}(r) = \left\langle \sum_{ij} \delta(r - r_{ij}) \right\rangle$$

(S2)

where r_{ij} is the distance between any i-th and j-th oxygen atoms.

Average Number of Rotational Jumps:

According to Poissonian probability distribution function,

$$P(N,t) = \frac{1}{N!}(t/\tau)^N e^{-(t/\tau)}$$

where N can take values as 0, 1, 2, 3,….. The average number of events in an interval t can be written as,

$$\langle N(t) \rangle = \sum_{N=0}^{\infty} N(t)P(N,t)$$

$$\langle N(t) \rangle = e^{-(t/\tau)}[\,(t/\tau) + \frac{1}{2!}(t/\tau)^2 + \frac{1}{3!}(t/\tau)^3 + ...]$$

$$\langle N(t) \rangle = e^{-(t/\tau)}(e^{t/\tau} - 1)$$

$$\langle N(t) \rangle = [1 - e^{-(t/\tau)}]$$

Neglecting the higher order terms of (t/τ),

$$\langle N(t) \rangle = t/\tau \tag{S3}$$

This shows that the average number of events in a certain time interval is proportional to the time (increase linearly with t).

Table S1. DME force field parameters.

Lennadr-Jones parameters				
Atom types	C_6 (kJ mol^{-1})	C_{12} (kJ mol^{-1}nm^{12})	Charge (e)	Mass (uma)
C(H3)	9.3547×10^{-3}	3.6075×10^{-3}	0.225	15.035
C(H2)	5.9491×10^{-3}	1.7912×10^{-3}	0.225	14.027
O	2.0751×10^{-6}	1.5127×10^{-3}	-0.450	15.999
Modified atom pairs				
Atom pair type		C_6 (kJ mol^{-1})		C_{12} (kJ mol^{-1}nm^{12})
O_{DME}-O_W		0.6082×10^{-2}		0.5475×10^{-5}
Bonds Distance (in nm)				
C-C			C-O	
0.153			0.141	
Bond angles				
Angles		Φ (deg)		K_Φ (kJ mol^{-1} rad^{-2})
C-C-O		109.5		418.68
C-O-C		109.5		501..22
Proper dihedrals				

Dihedrals	C_0 (kJ mol^{-1})	C_1 (kJ mol^{-1})	C_2 (kJ mol^{-1})	C_3 (kJ mol^{-1})	C_4 (kJ mol^{-1})
O-C-C-O	-3.10	-0.74	-4.69	-6.87	15.4
C-O-C-C	1.12	-3.51	-2.54	0.03	4.90

Table S2. Composition of the simulation box at different X_w.

X_w	Water	DME
0.06	800	50
0.25	600	200
0.45	500	393
0.60	200	300
0.70	200	500
0.85	200	1133
0.90	100	900

Table S3. Waiting time of the jump events (as calculated from the linear fit of n. vs t) at different X_w.

X_w	Waiting time (ps)
0.06	2.89
0.25	3.68
0.45	3.91
0.60	4.00
0.70	4.12
0.85	4.21
0.90	4.20
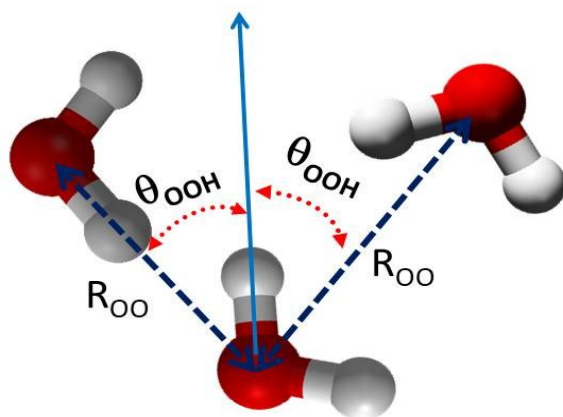
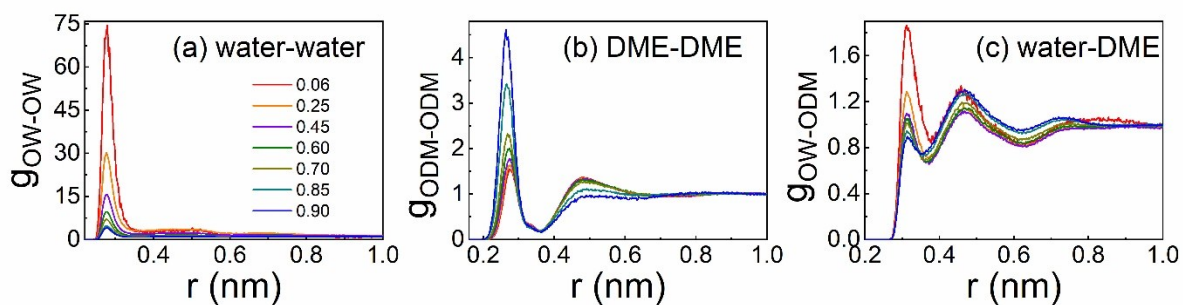**Scheme S1.** Geometrical definition (both distance and angle criteria) of hydrogen bond among water molecules.

Figure S1. Radial distribution functions (RDF) in between (a) water oxygen-oxygen atoms (OW-OW), (b) DME oxygen-oxygen atoms (ODM-ODM) and (c) water oxygen-DME oxygen atoms (OW-ODM) for all the mixtures.
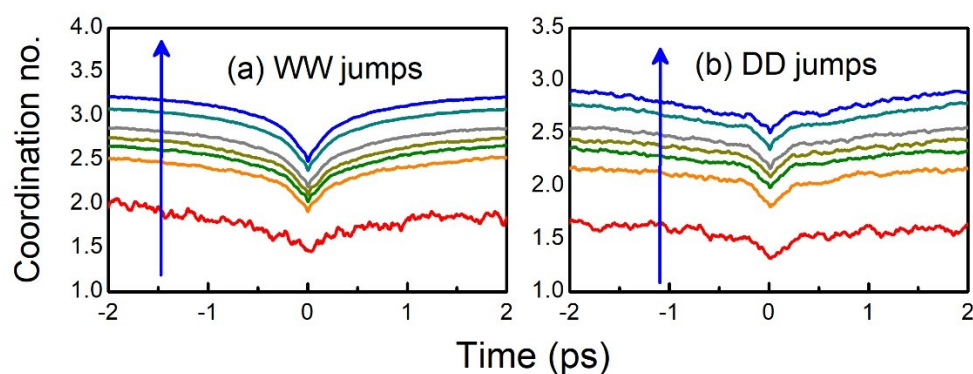
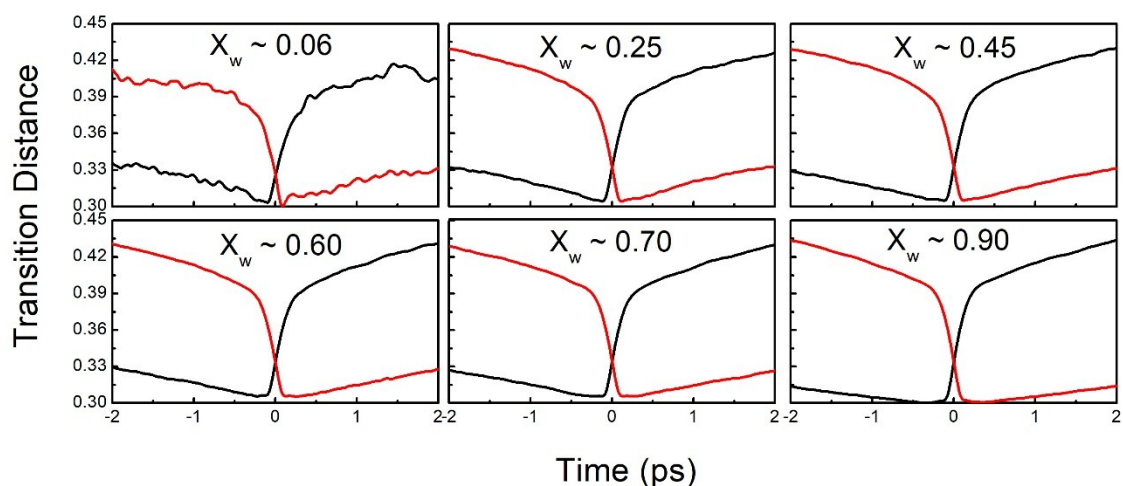**Figure S2.** Coordination number of the rotating water molecule average over (a) water-water jumps and (b) DME-DME jumps. Arrow indicates the increasing of water concentration.

Figure S3. Average transition distance (average over only water-water jump events) from the central rotating water molecule to the initial (black lines) and the final (red lines) H-bond partner at the instant of H-bond switch (transition state; t=0) at various X_w.
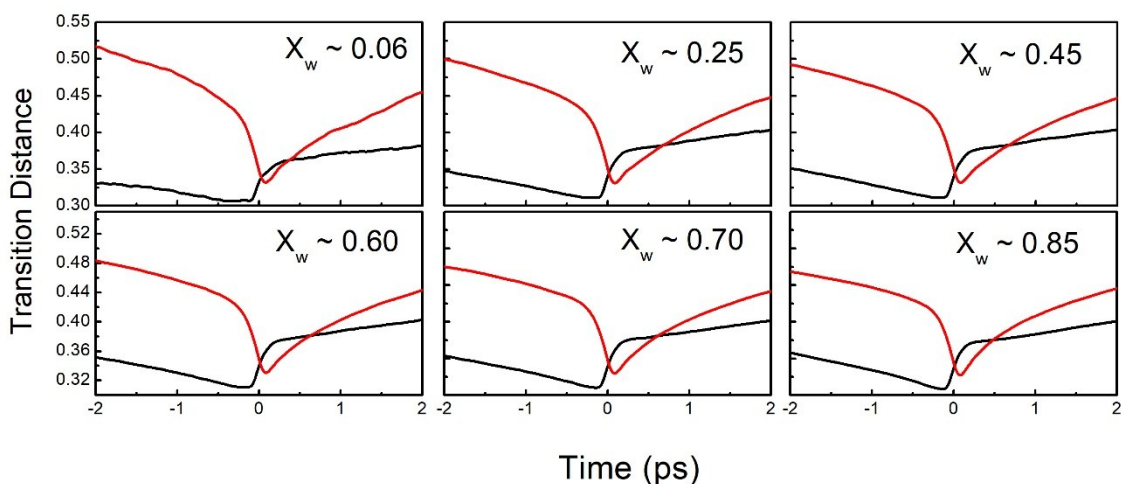
Figure S4. Progress of the average transition distance (average over only water-DME jump events) from the central rotating water molecule to the initial (black lines) and the final (red lines) H-bond partner around H-bond switching (transition state; t=0) at various X_w.
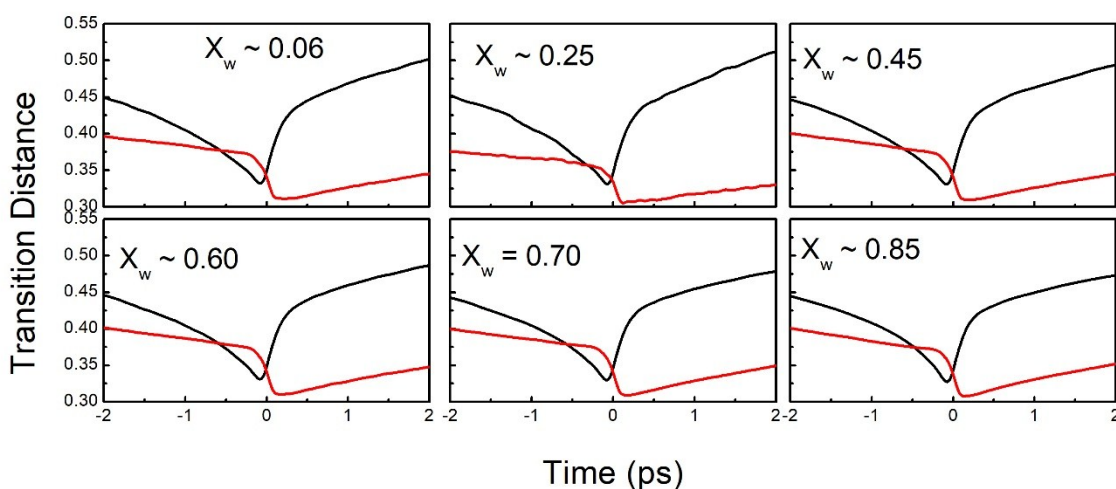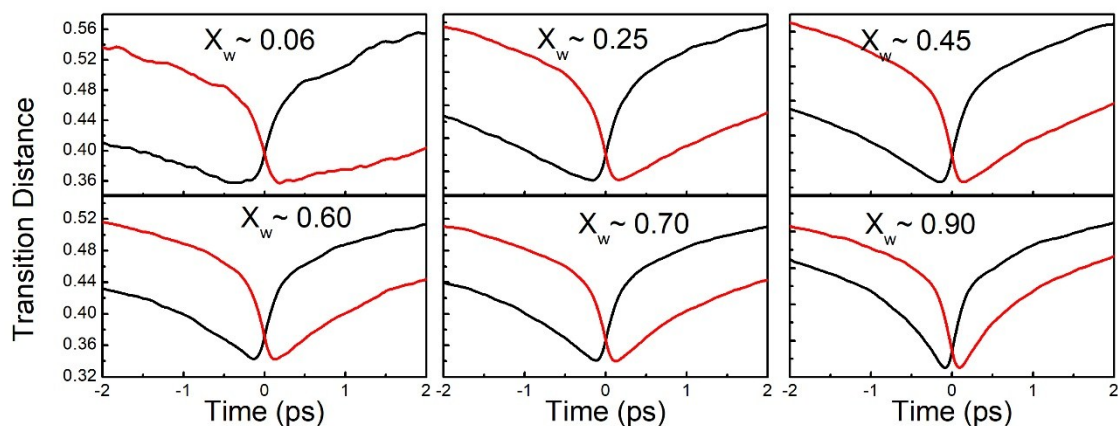

Figure S5. Progress of the average transition distance (average over only DME-water jump events) from the central rotating water molecule to the initial (black lines) and the final (red lines) H-bond partner around H-bond switch event (transition state; t=0) at various X_w.

Figure S6. Progress of the average transition distance (average over only DME-DME jump events) from the central rotating water molecule to the initial (black lines) and the final (red lines) H-bond partner around H-bond jump (transition state; t=0) at various X_w.
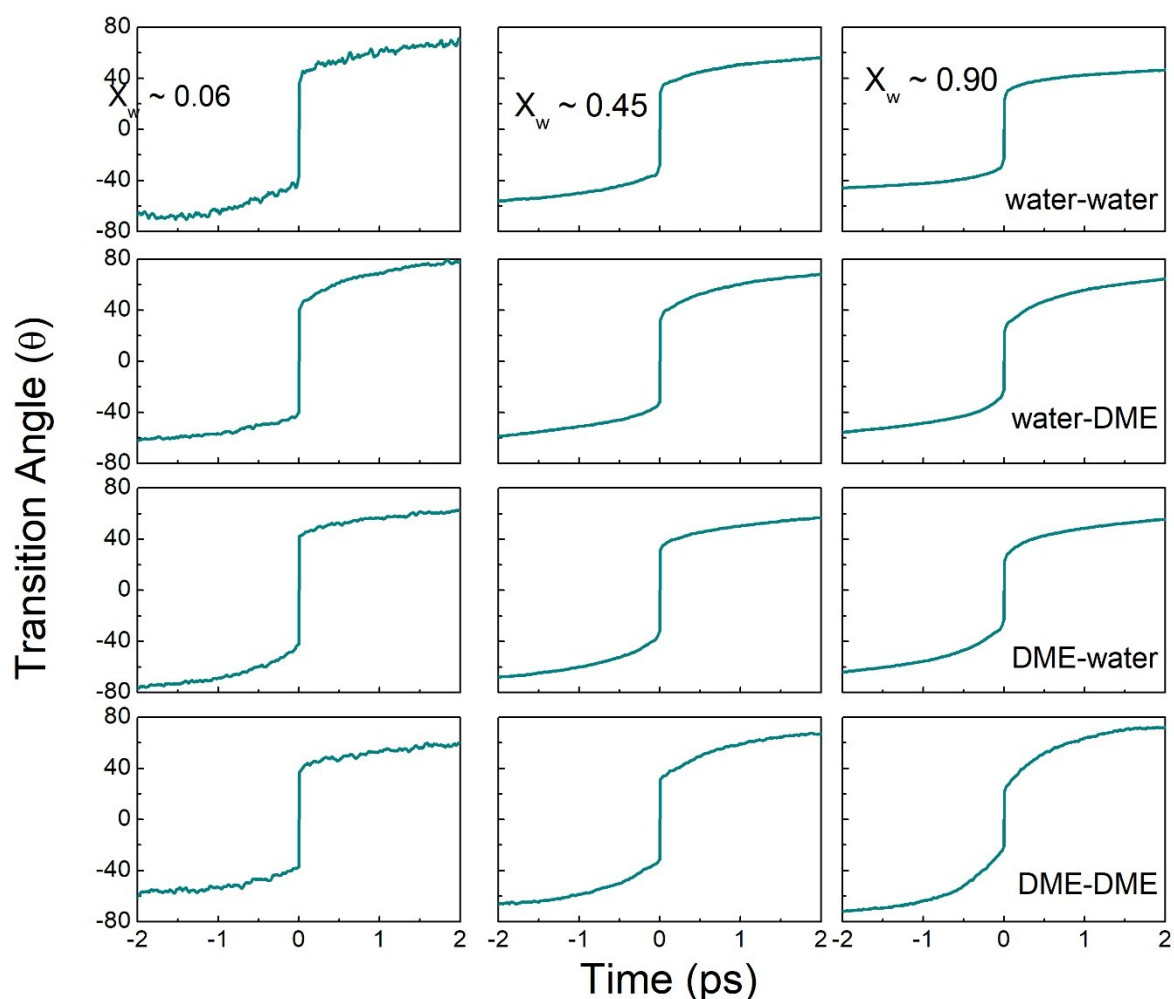

Figure S7. Time evolution of the average transition angle for various individual types of H-bond partner exchange events for three different X_w.
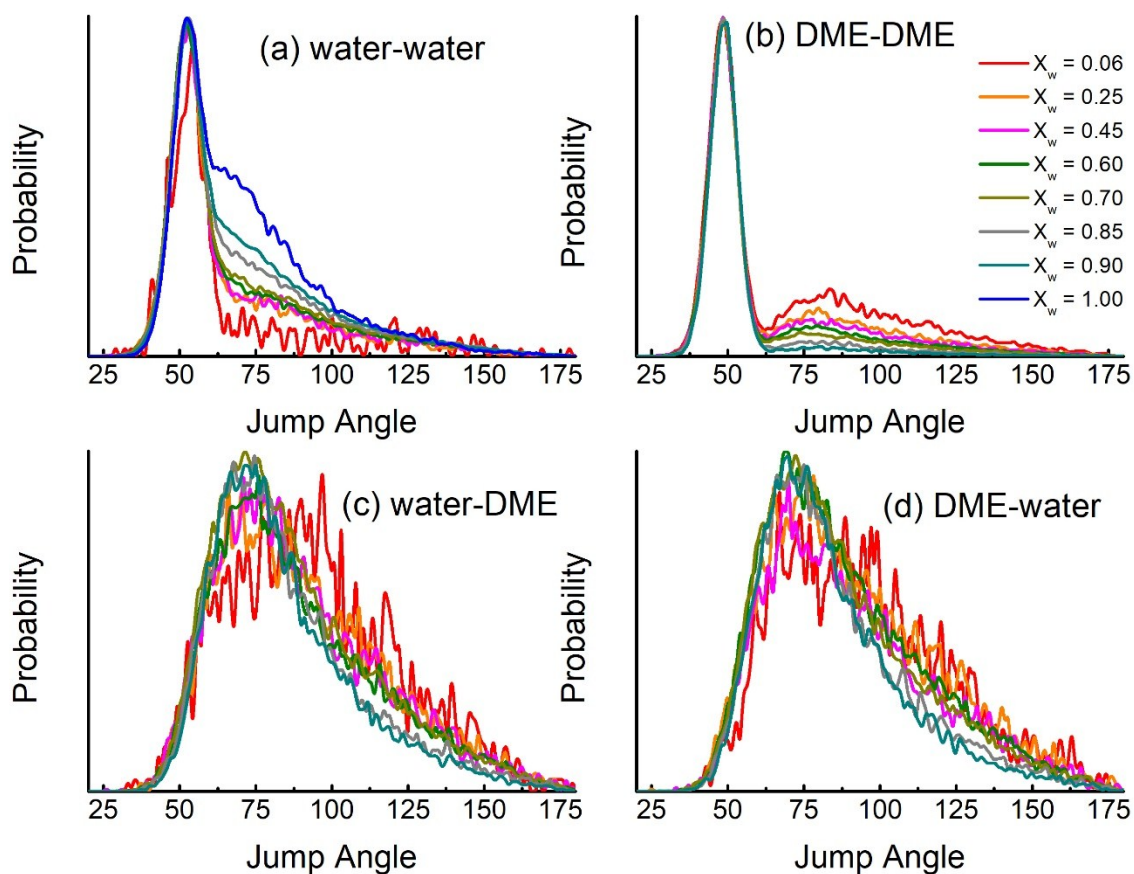
Figure S8. The jump angle distributions of any rotating central water molecule for various type of jump events (a) water-water, (b) DME-DME, (c) water-DME and (d) DME-water at each simulated concentrations.