

Supplementary Information

Rotational Motion of a Single Water Molecule in Bucky ball

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S.1-Scaling factor for M06-2X/6-311G(2d,p) frequencies

DFT calculations can be used to compute internal vibrational frequencies of molecules assuming that the potential energy close to the minimum varies quadratically with respect to the position of the nuclei. Since the anharmonicity of the potential is neglected, this leads to an over-estimate of the vibrational frequencies¹. Hence, the computed frequencies are usually scaled by a factor calibrated using the F38/10 database¹. The scaling factor is optimized by minimizing the root mean-squared deviation between the frequencies computed by the DFT method and by experimental measurements. The frequencies are summarized in Table S.1.1.

Table S.1.1. Experimental and DFT frequencies for F38/10 database

Molecule	mode	Frequency (cm^{-1})		
		Experiments*	M06-2X/6-311G(2d,p)	
			With anharmonicity correction	Without anharmonicity correction
HF	1	3959	3980	4216
H2	1	4159	4224	4474
N2	1	2330	2367	2507
F2	1	894	1088	1153
CO	1	2143	2146	2273
OH	1	3568	3554	3765
Cl2	1	554	544	576
CO2	1	1333	1330	1409
	2	2349	2326	2463
	3	667	659	698
H2O	1	3657	3669	3886
	2	1595	1556	1648
	3	3756	3761	3984
N2O	1	2224	2275	2409
	2	1285	1281	1357
	3	589	617	653
HCN	1	3312	3267	3461
	2	2089	2123	2249
	3	712	740	784
C2H2	1	3374	3334	3531
	2	1974	1995	2113
	3	3289	3231	3423
	4	612	654	693
	5	730	743	787
H2CO	1	2782	2811	2978
	2	1746	1779	1885
	3	1500	1465	1552
	4	1167	1148	1215
	5	2843	2854	3023
	6	1249	1213	1285
NH3	1	3337	3306	3502
	2	950	1045	1107
	3	3444	3418	3620
	4	1627	1592	1686
CH4	1	2917	2886	3057
	2	1534	1481	1569
	3	3019	2996	3174
	4	1306	1269	1344

* Experimental data are originally summarized in Table 1 of Alecu *et al.*¹

S.2-Description of water orientation in DFT

Water orientation is described using one arbitrarily chosen hexagonal ring of C₆₀ as the reference plane. α is the angle formed between the C₆ axis of the hexagonal ring of C₆₀ (as indicated by orange dash line) and one O-H bond of water molecule. ψ represents the rotation of the water plane along the O-H bond.

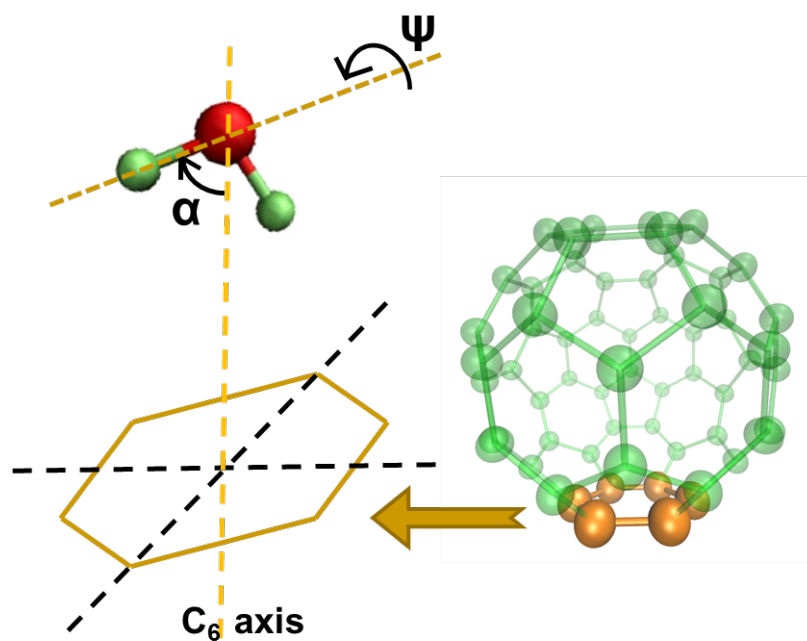


Figure S.2.1. The description of water orientation using one arbitrarily chosen hexagonal ring of C₆₀ as the reference.

S.3- Frequency calculation in MD

The trajectories of the hydrogen atoms of the water molecule are collected during MD simulations. The velocity autocorrelation of the hydrogen atoms, $C_H(t)$ is computed by:

$$C_H(t) = \frac{\langle v_H(t)v_H(0) \rangle}{\langle v_H^2(0) \rangle}$$

where $v_H(0)$ and $v_H(t)$ are the velocity of hydrogen atoms at time 0 and at time t . $\langle \rangle$ denotes average over 200 runs with different initial velocity. For each run, the system is equilibrated for 500ps and then the simulation is run for 200ps for data production. The coordinates of the atoms are stored every 1fs. Fourier transformation of the velocity autocorrelation $C_H(t)$ gives the power spectra density, $S(\omega)$,

$$S(\omega) = \int_0^\infty dt C_H(t) \cos \omega t$$

The vibrational frequencies correspond to the peak positions in the power spectra density².

Since finite temperature tends to spread the peaks in the spectra, MD simulations are done at a temperature of 10 K.

S.4 Gas-phase vibrational frequencies of water

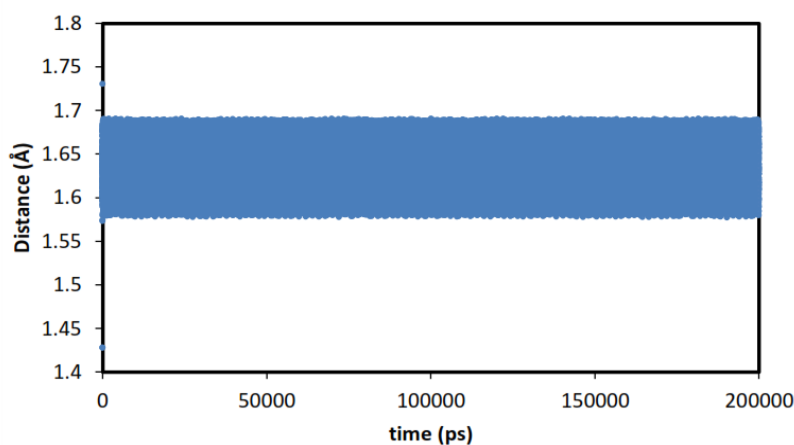
The accuracy of the water model is tested by comparing it to the experimental gas-phase vibrational frequency³. The vibrational frequencies predicted by Ferguson water model⁴ compare well with experimental data. The frequencies obtained using the SPC/E, SPC, and TIP3P flexible water models⁵ deviate from experimental data. The frequencies of stretching mode predicted by density functional theory calculation with M06-2X functional also agree well with experiments.

Table S.4.1. The gas-phase vibrational frequencies of water.

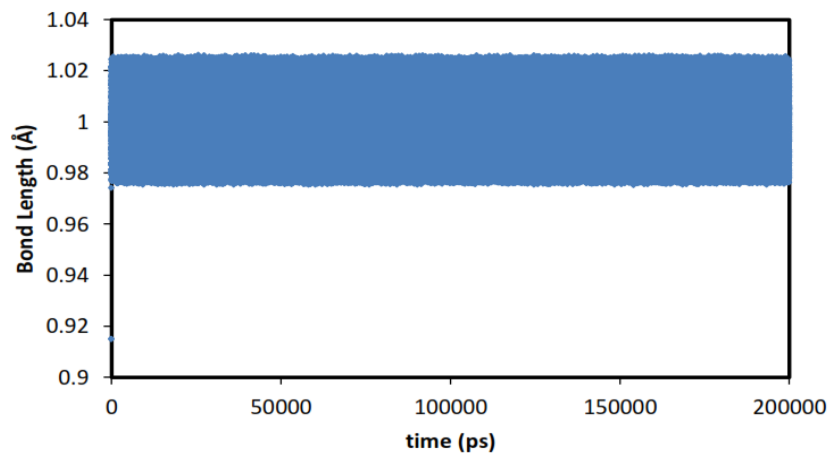
	Experiment	DFT	Ferguson	SPC/E	TIP3P	SPC
Asymmetrical stretching	3755	3761	3725	3234	3901	3234
Symmetrical stretching	3656	3669	3651	3171	3831	3171
Bending	1594	1556	1588	1522	2105	1522

S.5-Water angle and bond lengths

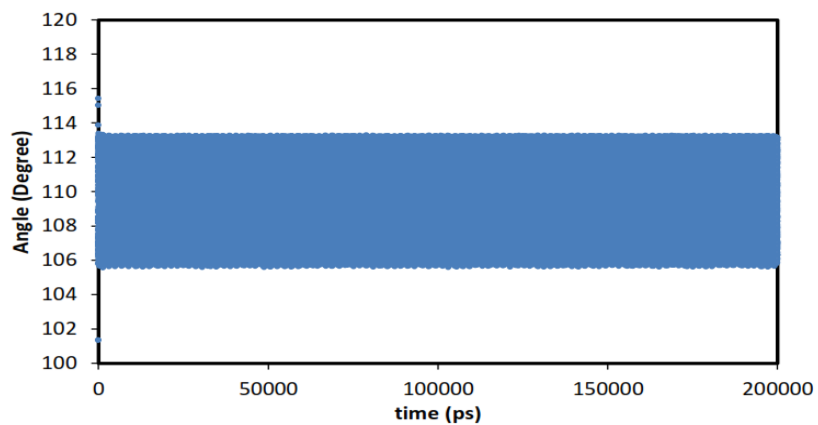
We have computed the bond length vibration (stretching of O...H bond), the variation of hydrogen – hydrogen distance, and water (H---O---H) angle. The positions of atoms were stored and the position changes and angles were tracked. Figures S.5.1-S.5.3 show the range of bond lengths and angles.



Figures S.5.1. H...H distance versus time (range 1.58-1.68 Å), Average= 1.6352 Å.



Figures S.5.2. O...H bond stretching versus time (range 0.977-1.02 Å), Average= 1.0002 Å.



Figures S.5.3. \angle HOH distribution versus time (range 105.91° - 113.75°), Average= 109.64° .

S.6. Rotational diffusion and entropy

S.6.1. Rotational diffusion

We have computed the rotational mean squared displacement (RMSD) of bulk water and a single water molecule in C60. The total rotational angular displacement, $[\phi_i(t) - \phi_i(0)]$, is described by the following equation:

$$\phi_i(t) - \phi_i(0) = \sum_{n=0}^{k-1} \delta\phi_i(n\delta t, \delta t) \quad (\text{S.6.1})$$

where $k=t/\delta t$ (t is the whole simulation time, and δt is the time step). We used the dipole vector $\mathbf{p}_i(t)$, which is fixed to the water molecule at each time instance. $|\delta\phi_i(t, \delta t)|$, is computed by using the cross product of $\mathbf{p}_i(t)$ and $\mathbf{p}_i(t + \delta t)$:

$$|\delta\phi_i(t, \delta t)| = \cos^{-1}[\mathbf{p}_i(t) \cdot \mathbf{p}_i(t + \delta t)] \quad (\text{S.6.2})$$

The rotational mean squared angular displacement is calculated (averaged over all molecules for the case of bulk water) based on equation S.6.3. To have the best resolution for computation of RMSD, the time interval is taken to be $\delta t = 0.5$ fs. The RMSD is given by⁶:

$$\langle \Delta\phi^2(t) \rangle = \frac{1}{N} \sum_i \langle |\phi_i(t) - \phi_i(0)|^2 \rangle \quad (\text{S.6.3})$$

where $\langle \rangle$ denotes the averaging over time. The rotational diffusion coefficient can be computed for the limit of long time as given by:

$$D_{rot} = \lim_{t \rightarrow \infty} \frac{1}{4t} \langle \Delta\phi^2(t) \rangle \quad (\text{S.6.4})$$

By plotting RMSD versus time, the best linear fit to the RMSD curve is found and the slope of this fit represents the rotational diffusion.

S.6.2. Rotational entropy

The configuration (rotational) entropy can be estimated using the Boltzmann entropy law. By knowing the angular distribution of dipole in θ and φ directions (see Fig.S.6.1), it is possible to estimate the rotational entropy by integrating the Boltzmann entropy law over all angular distributions of the dipole. The rotational entropy⁷ can be estimated using the equation:

$$S_{rot} = -k_B \int \int (p(\varphi) \log(p(\varphi)) \cdot (p(\theta) \log(p(\theta)))) d\varphi d\theta \quad (\text{S.6.5})$$

The angles θ and φ , are the water molecule's angles in spherical coordinates (Fig.S.6.1), $p(\theta)$ (PDF of the angle distribution in θ), and $p(\varphi)$ (PDF of the angle distribution in φ). For water in C60, these two PDFs are estimated and the rotational entropy is computed based on Equation S.6.5. For bulk water, the average angular distribution of water molecules in θ and φ are considered.

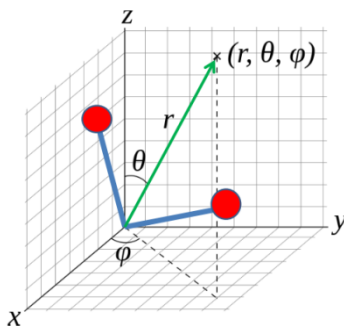


Fig.S.6.1. Demonstration of water molecule's angles in spherical coordinate (φ , θ)

References

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