

# **Nuclear Quantum Effects in the Reorientation of Water**

Francesco Paesani,<sup>1,a</sup> Soohaeng Yoo,<sup>2</sup> Huib J. Bakker,<sup>3,a</sup> and Sotiris S. Xantheas<sup>2,a</sup>

<sup>1</sup> *Department of Chemistry and Biochemistry, University of California, San Diego,  
9500 Gilman Drive, La Jolla, CA 92093*

<sup>2</sup> *Chemical and Materials Sciences Division, Pacific Northwest National Laboratory,  
902 Battelle Boulevard, P.O. Box 999, MS K1-83, Richland, WA 99352*

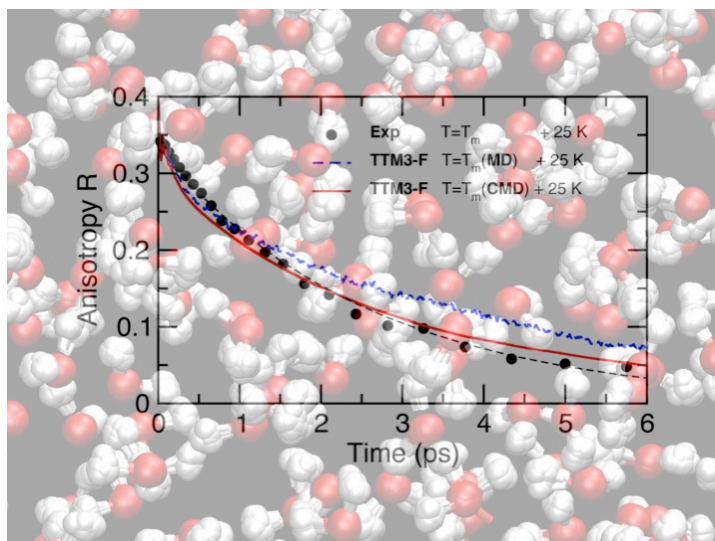
<sup>3</sup> *FOM Institute for Atomic and Molecular Physics, Science Park 104, 1098 XG,  
Amsterdam, The Netherlands*

<sup>a)</sup> Authors to whom correspondence should be addressed:

Electronic mail: fpaesani@ucsd.edu, h.bakker@amolf.nl, sotiris.xantheas@pnl.gov

## Abstract

The molecular reorientation associated with the dynamics of the hydrogen-bond network in liquid water is investigated using quantum molecular dynamics simulations performed with the *ab-initio* based TTM3-F interaction potential. The reorientation dynamics calculated at different temperatures are found to be in excellent agreement with the corresponding experimental results obtained from polarization-resolved, femtosecond mid-infrared, pump-probe spectroscopic measurements. A comparison with analogous results obtained from classical molecular dynamics simulations with the same interaction potential clearly indicates that the explicit inclusion of nuclear quantum effects is critical for reproducing the measured time-dependence of the anisotropic signal.



Keywords: water, anisotropy, spectroscopy, interaction potential, molecular dynamics, nuclear quantum effects

Water plays a fundamental role in many processes of relevance to various areas of science, including physics, chemistry, biology, geology, and climate research<sup>1</sup>. Although the anomalous properties of water have been the subject of intense experimental and theoretical investigations, a molecular-level description of liquid water (H<sub>2</sub>O) under different thermodynamic conditions (e.g., pressure and temperature) and environments (e.g., in the presence of ions and/or hydrophobic/hydrophilic species) still remains elusive. The local structure of liquid water is directly connected to the ability of the H<sub>2</sub>O molecules to establish a dynamic hydrogen-bond (HB) network in which both the number and the strength of the hydrogen bonds continuously fluctuate. Such dynamical behavior plays a central role in a wide range of processes occurring in aqueous environments (e.g., proton transfer and transport, and molecular hydration). To a large extent, the continuous rearrangement of the HB network involves the reorientational dynamics of individual water molecules.

Measurements and calculations of the H<sub>2</sub>O reorientational dynamics have provided a molecular description of the rearrangement of the water hydrogen bond network leading to reorientation<sup>2-9</sup>. Experimentally, the water dynamics has been inferred from the analysis of the orientational time correlation functions obtained from femtosecond, mid-infrared pump-probe spectroscopic measurements<sup>2-4,10</sup>. Theoretically, classical molecular dynamics (MD) simulations with simple point charge water force fields, have proposed a molecular jumping mechanism for the reorientation of liquid water<sup>5-8</sup>. In these earlier studies it was proposed that the mechanism of the reorientation proceeds through a transition state in which the rotating hydroxyl group of the water molecule forms a bifurcated hydrogen bond with two other water molecules.

Nuclear quantum effects have a significant impact on the properties of water. For example, the melting point of deuterated water ( $D_2O$ ) is 3.82 K higher than that of  $H_2O$  water and this difference becomes even larger (4.5 K) for tritiated water ( $T_2O$ )<sup>11</sup>. The structural differences between liquid  $H_2O$  and  $D_2O$  display an appreciable variation over the temperature range of the liquid state<sup>12,13</sup>, and recent deep inelastic neutron scattering measurements have reported an excess of proton kinetic energy associated with a significant proton delocalization in supercooled  $H_2O$ <sup>14</sup>. It has also been shown that small, nonpolar molecules appear to be more stable in  $D_2O$  than in  $H_2O$ , and that polypeptides tend to reduce the surface area in contact with the  $D_2O$  by adopting more compact shapes. Finally, it is well known that only primitive organisms can develop some form of life when immersed in heavy water ( $D_2O$ )<sup>15</sup>. In spite of all these observations, a thorough understanding of the origin of the differences in properties of  $D_2O$  and  $H_2O$  is still missing<sup>16,17</sup>.

In this study we provide a quantitative assessment of the nuclear quantum effects on the water reorientational dynamics as a function of temperature through a detailed comparison of quantum and classical molecular dynamics simulations using the *ab initio*-based TTM3-F force field<sup>18-20</sup>. Since the TTM3-F water model was parameterized using the results of high-level *ab initio* calculations of the water dimer potential energy surface<sup>21</sup> and validated from the analysis of the energetics of small water clusters<sup>22-26</sup>, it provides an accurate representation of the full multidimensional Born-Oppenheimer potential energy surface. Furthermore, since polarization effects are explicitly included in the parameterization, the atomic charges of each water molecule vary instantaneously in response to any structural modification of the local environment<sup>19,27</sup>. Consequently, the

TTM3-F model does not assume any *a priori* structure of the liquid but is instead capable of capturing the occurrence of possible asymmetries in the hydrogen bond network. When combined with quantum dynamical simulations, the TTM3-F model has been shown to provide a quantitative account of the quantum effects on the structural and thermodynamics properties of liquid water,<sup>28-30</sup> and to enable an accurate description of linear and nonlinear infrared spectra of liquid water.<sup>31</sup> We note here that previous quantum simulations of the water properties as a function of temperature were carried out either with empirical force fields<sup>32</sup> or on an absolute temperature scale with an ab-initio based force field,<sup>29</sup> which precluded a quantitative assessment of nuclear quantum effects in the water reorientation.

Quantum dynamical simulations with the TTM3-F force field were performed using centroid molecular dynamics (CMD) with the centroid forces computed “on the fly” according to the adiabatic time scale separation scheme (ACMD scheme).<sup>33-35</sup> Briefly, the CMD formalism draws upon the prescription of distribution functions in which the exact quantum expressions are cast into a phase space representation leading to a classical-like interpretation of the variables of interest. It has been demonstrated that CMD quantitatively accounts for the most important nuclear quantum effects in different condensed phase systems (e.g., see Ref. <sup>30</sup>). The ACMD simulations were carried out at several different temperatures for a system consisting of 128 H<sub>2</sub>O molecules in a cubic box with periodic boundary conditions. The actual density at each temperature was obtained from path-integral molecular dynamics simulations (PIMD) carried out in the isobaric-isothermal ensemble.<sup>30</sup> The results described in this study were obtained by averaging over 10 independent ACMD trajectories of 25 ps each. In all calculations the

path-integral ring-polymers corresponding to each quantum particle were discretized using  $P = 32$  quasi-particles (“beads”). The ACMD adiabaticity parameter was set to  $\gamma = 0.4$ , which was found to be small enough to guarantee a sufficiently large separation in time scales between the centroid and noncentroid motions.<sup>30</sup> The ACMD equations of motion were propagated according to the velocity-Verlet algorithm with a time step  $\Delta t = 0.02$  fs, while a time step  $\Delta t = 1$  fs was used in the corresponding classical MD simulations.<sup>36</sup> In the latter case, a larger system containing 1000 water molecules in a periodic cubic box was used. The Ewald summation technique was used for the long-range electrostatic interactions in both quantum CMD and classical MD simulations.

The results of the calculations are compared with experimental data obtained from polarization-resolved pump-probe experiments. In these experiments the [OD stretch vibrations of HDO molecules dissolved in H<sub>2</sub>O](#) are excited with an intense linearly polarized light pulse (pump) [at 4  \$\mu\text{m}\$  \(2500  \$\text{cm}^{-1}\$ \)](#) with a pulse duration of 150 femtoseconds.<sup>2-4</sup> This excitation results in an anisotropic transmission change of which the time dependence is measured with 150 femtosecond probe pulses that are polarized parallel and perpendicular to the pump polarization. [The probe signals measured for the two polarizations at frequencies between 2475  \$\text{cm}^{-1}\$  and 2525  \$\text{cm}^{-1}\$  are spectrally integrated yielding the absorption changes  \$\Delta\alpha\_{\parallel}\$  and  \$\Delta\alpha\_{\perp}\$ . These absorption changes are](#) used to construct the anisotropy parameter that reflects the reorientation dynamics only:

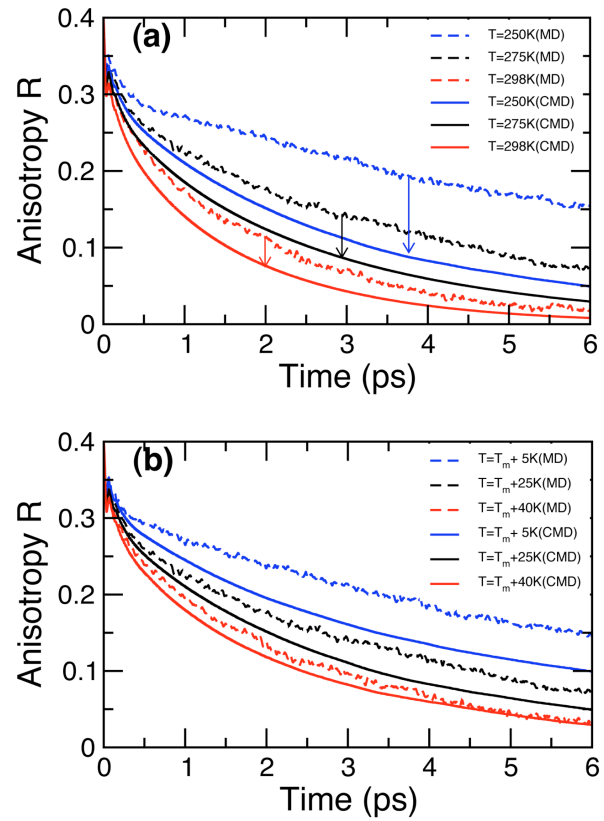
$$R = \frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp}} = \frac{2}{5} C_2(t). \quad (1)$$

In Eq. (1),  $C_2(t) = \langle P_2[\mathbf{e}(0) \cdot \mathbf{e}(t)] \rangle$  is the time autocorrelation function of the second order Legendre polynomial  $P_2[\mathbf{e}(0) \cdot \mathbf{e}(t)]$ , where  $\mathbf{e}(t)$  is a unit vector along a specific direction

in the body-fixed reference frame of each water molecule. Both in the pump-probe experiments and in the quantum and classical calculations  $\mathbf{e}(t)$  is a vector along one of the OH bonds of a water molecule. In connection to Eq. (1), it is important to note that it has been recently shown that the term  $\frac{2}{5}C_2(t)$  is only an approximation to the anisotropy parameter, although the differences with the exact expression are small.<sup>8</sup>

Since a smaller system consisting of 128 water molecules was used for the quantum CMD simulations, the system size effects on the water dynamics were first assessed. For this purpose, classical MD simulations (see Figure S1 of the Supporting Information) were performed using two different periodic cubic boxes with 128 and 1000 water molecules, respectively. No noticeable size effects on the anisotropic signal were found at three different temperatures ( $T=250$  K, 275 K and 298 K), a result that further justifies the use of a smaller cubic box with 128 molecules for the quantum CMD simulations.

The magnitude of nuclear quantum effects on the reorientational dynamics of liquid water was then quantitatively assessed as a function of temperature. Figure 1(a)



**Figure 1.** Results of classical (MD, dashed lines) and centroid (CMD, solid lines) molecular dynamics simulations at various temperatures with the TTM3-F interaction potential. The arrows are indicative of the magnitude of the quantum corrections at each temperature. The comparison is performed on: (a) the absolute, and (b) the relative to the melting point ( $T_m$ ) temperature scale.

shows the comparison between the results from quantum (CMD, solid lines) and classical (MD, dashed lines) simulations for the same set of temperatures (250 K, 275 K and 298 K) for which the size effects were previously examined. In all cases the CMD results show a faster overall decay of the anisotropy than the classical MD results. The difference between classical and quantum results (indicated by an arrow in Figure 1(a) for each temperature) clearly increases when the temperature decreases. This observation is consistent with previous results, which showed that quantum effects in water become significantly more important at lower temperatures.<sup>14,37</sup> Moreover, this difference also suggests that molecular simulations with explicit inclusion of nuclear quantum effects describe significantly faster water dynamics than classical MD simulations carried out at the same temperature. Since the water dynamics is controlled by the underlying PES of the system and considering that the TTM3-F potential has been parameterized to reproduce the Born-Oppenheimer PES, the observed differences can be easily attributed to the explicit inclusion in the CMD simulations of zero-point energies and possibly tunneling contributions, which are absent in the corresponding classical calculations.

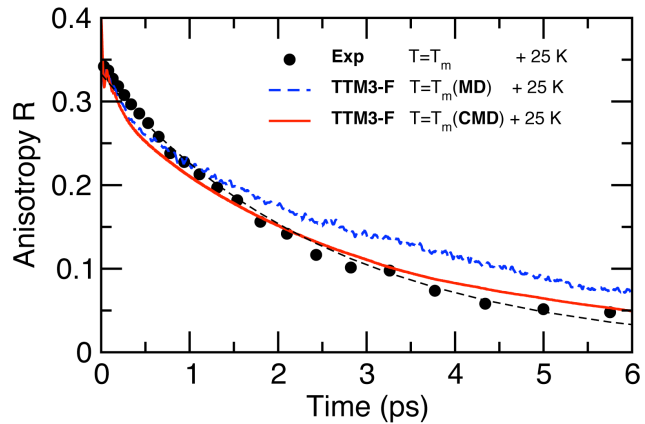
It is to be expected that the water phase diagrams obtained from quantum and classical simulations are shifted relative to each other. Indeed, it was previously shown that quantum simulations predict a lower melting temperature ( $T_m$ ) than their classical counterparts.<sup>29,38</sup> For the TTM3-F potential the melting point calculated from quantum simulations is  $T_m = 225$  K while the classical counterpart is  $T_m = 250$  K.<sup>39</sup> This suggests that the phase diagram of water obtained from quantum CMD simulations is slightly shifted towards lower temperatures when compared to the classical one, and both phase



diagrams are shifted to lower temperatures relative to the experimental data. This naturally introduces the notion that equivalent thermodynamic conditions of quantum CMD and classical MD simulations may be found at different temperatures due to the difference in melting temperatures, which can be considered as the reference point.

Although there is no rigorous justification in assuming *a priori* that the temperature scaling is either linear or even the same across different models and simulation protocols, the behavior of the properties of liquid water above the melting point is likely “universal” in character as  $T_m$  is approached and, more importantly, should depend only on the relative temperature difference  $T - T_m$ .<sup>40</sup> Therefore, in order to quantitatively assess the effects of nuclear quantization on the reorientational dynamics of liquid water and to make a consistent comparison with the experimental data, the nominal temperature in both CMD and MD simulations was “rigidly” shifted relative to the corresponding  $T_m$  values in order to reproduce the experimental thermodynamic conditions.

Figure 1(b) shows the comparison between quantum CMD and classical MD results for the anisotropic signal calculated at three different temperatures relative to  $T_m$ . Although the differences between the quantum and classical on the relative-to- $T_m$  temperature scale are smaller than on the absolute temperature scale, they are nevertheless still significant,



**Figure 2.** Comparison of the anisotropic signal at  $T = T_m + 25$  K of the experiments (black filled circles) and the results calculated with the TTM3-F interaction potential (MD: blue dashed line, CMD: red dotted line). The thin black dashed line corresponds to an exponential fit of the experimental data.

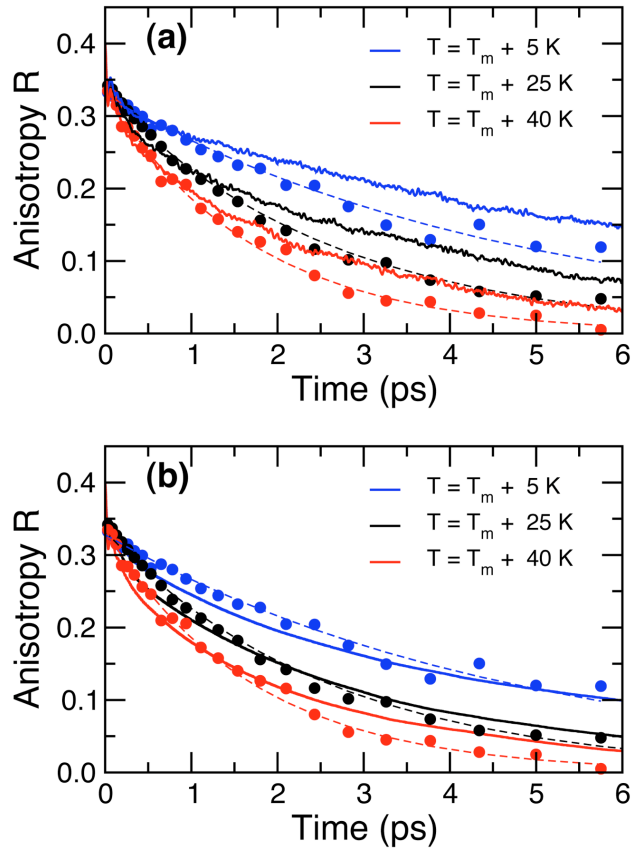
especially when the temperature decreases, which is in line with recent experimental measurements of isotope effects in liquid water.<sup>13</sup>

The comparison between the experimental results for the anisotropic signal at  $T = 298$  K ( $T_m^{\text{exp.}} + 25$  K), the classical MD at  $T = 275$  K ( $T_m^{\text{TTM3-F(MD)}} + 25$  K) and the quantum CMD at  $T = 250$  K ( $T_m^{\text{TTM3-F(CMD)}} + 25$  K) is shown in Figure 2. To enable this comparison we performed an accurate determination of the delay time zero of the pump-probe experiments by monitoring the

phase modulation induced by the pump pulse on the probe pulse (Kerr effect). The frequency change of the probe resulting from this phase modulation changes sign at perfect temporal overlap, thus allowing an accurate determination of delay time zero.

Excellent agreement is found between the experimental data and the results obtained from quantum CMD simulations. In contrast, the classical MD results predict a slower decay,

corresponding to significantly slower HB dynamics. The results of the classical and quantum CMD simulations at three different



**Figure 3.** Comparison of the temperature dependence of the [experimental anisotropy](#) (filled circles) and the [anisotropy](#) (a) calculated from classical MD simulations with the TTM3-F interaction potential (solid lines), (b) calculated from quantum CMD simulations with the TTM3-F potential (solid lines). The comparison is shown on the temperature scale relative to  $T_m$ . In both panels (a) and (b), the thin dashed lines correspond to exponential fits of the experimental data.

temperatures, viz.  $T_m + 5$  K,  $T_m + 25$  K and  $T_m + 40$  K, are compared with the corresponding experimental values in Figure 3. Clearly, the quantum CMD results obtained with TTM3-F closely reproduce the temperature dependence measured in the pump-probe experiments. The previously observed deviation of the classical MD results from the experimental anisotropy at  $T = T_m + 25$  K (cf. Fig. 2) is also observed at the other two temperatures examined in the present study ( $T = T_m + 5$  K and  $T = T_m + 40$  K) (Fig. 3a). The anisotropy decays were fitted to a single-exponential function ( $f \propto e^{-t/\tau}$ ). The orientational relaxation times ( $\tau$ ) obtained from the fit of the quantum and classical anisotropy decays are compared in Table 1 with the corresponding experimental values at all three temperatures. Clearly, the quantum CMD results are in significantly better agreement with the experimental values than their classical counterparts at all three temperatures. Interestingly, the agreement is essentially quantitative at the lowest temperature examined in this study ( $T = T_m + 5$  K) and becomes somewhat less good as the temperature increases.

T (K)	MD	CMD	Exp.
$T_m + 5$	7.5	4.9	$4.7 \pm 0.3$
$T_m + 25$	4.0	3.1	$2.6 \pm 0.2$
$T_m + 40$	2.5	2.4	$1.7 \pm 0.1$

**Table 1.** Comparison of the orientational relaxation time (in ps) calculated from the fit of the experimental, quantum (CMD) and classical (MD) anisotropic signals at three different temperatures:  $T = T_m + 5$  K,  $T = T_m + 25$  K, and  $T = T_m + 40$  K.

This confirms that, as mentioned above, a constant temperature scaling relative to the calculated melting point is expected to provide the best approximation at temperatures near  $T_m$ . Importantly, the present results show that classical simulations predict significantly slower HB dynamics at all temperatures with the

calculated  $\tau$  being 60% larger than the corresponding experimental value at  $T = T_m + 5$  K.

The (large) differences between quantum and classical results (especially at the lowest

temperature examined in this study) strongly suggest that nuclear quantum effects play a non-trivial role in the water reorientation and, consequently, in the HB dynamics. It is also worth noting that the quantum and classical results show the smallest differences at  $T = T_m + 40$  K, which indicates that nuclear quantum effects become less important as the temperature increases as expected from the analysis of the De Broglie thermal wavelength. The fact that the magnitude of the nuclear quantum effects is not constant but depends on the temperature, further reinforces the notion that nuclear quantum effects cannot be simply taken into account using classical MD with a constant temperature scaling but should always be explicitly included in simulations with *ab initio* PESs. In this regard, it is important to mention that classical simulations with empirical force fields were also shown to provide an accurate description of the water reorientation at room temperature (e.g. see Ref. <sup>8</sup>). An increasing deviation from the experimental values was instead found in classical MD simulations when the temperature difference with room temperature increased,<sup>9</sup> which are possibly due to the fact that empirical water models are generally parameterized to reproduce water properties at ambient conditions. A preliminary analysis of the underlying mechanism responsible for the cleavage and formation of hydrogen bonds indicates the existence of a large number of possible pathways that also include the “jump mechanism”, {Laage, 2006 #290; Laage, 2006 #522; Laage, 2007 #252} which, however, does not appear to be more probable than other alternative pathways (or to be the dominant pathway ???). A more quantitative analysis of the impact of nuclear quantum effects on the molecular mechanisms that govern the H-bond dynamics in water will be the subject of a forthcoming publication.<sup>41</sup>

In summary, we have calculated the temperature dependence of the anisotropic signal in liquid water using quantum dynamical simulations with the *ab-initio* based TTM3-F interaction potential. A very good agreement (which is quantitative at lower temperatures) with the corresponding experimental results is found when a relative-to-the-corresponding- $T_m$  temperature scale is adopted. By contrast, analogous classical molecular dynamics simulations predict a significantly slower water reorientational dynamics over the temperature range examined in this study. These results thus demonstrate the importance of explicitly accounting for nuclear quantum effects and ensuring a comparison of equivalent thermodynamic conditions when simulating the molecular properties of liquid water.

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**Supporting Information Available:** Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>



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## Supporting Information

### Nuclear Quantum Effects in the Reorientation of Water

Francesco Paesani<sup>1,a</sup>, Soohaeng Yoo<sup>2</sup>, Huib J. Bakker<sup>3,a</sup>, and Sotiris S. Xantheas<sup>2,a</sup>

<sup>1</sup> Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093

<sup>2</sup> Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MS K1-83, Richland, WA 99352

<sup>3</sup> FOM Institute for Atomic and Molecular Physics, Science Park 104, 1098 XG, Amsterdam, The Netherlands

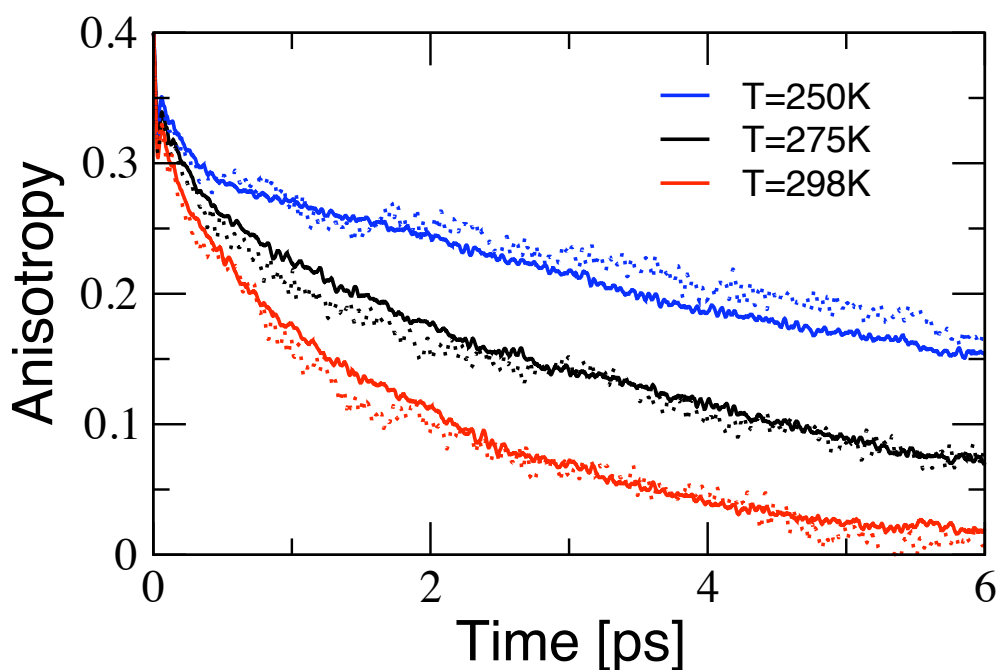


Figure S1. System size effect in the water dynamics at different temperatures. Anisotropy for two different periodic cubic boxes with 1000 (solid line) and 128 (dotted line) water molecules, respectively.