Nuclear quantum effects and hydrogen bond fluctuations in water
Supplementary Information

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DISTRIBUTION OF ν FOR DIFFERENT MODELS AND STATE POINTS

As discussed in the main text, a hydrogen bond involves three atoms: the hydrogen H, the oxygen atom O it is covalently bound to and the acceptor oxygen O′. The proton transfer coordinate $\nu = d(\mathrm{O{-}H}) - d(\mathrm{O'{-}H})$ provides a convenient structural parameter to characterise the hydrogen bond. When nuclear quantum effects are accounted for, the hydrogen H is strongly delocalised, with a small but not-negligible fraction of protons reaching positive values of ν – a situation one could classify as a transient autoprotolysis event.

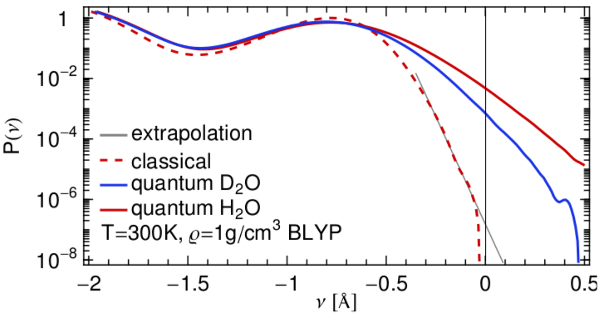

FIG. 1. Comparison between the probability of finding a hydrogen bond with a given value of the proton transfer coordinate ν in a simulation based on classical MD and in one that includes nuclear quantum effects. Both were performed at temperature $T = 300$ K and density $\rho = 1.0$ g/cm^3, using the BLYP functional. The simulation with quantum nuclei is plotted as a continuous line (red: H_2O, blue: D_2O, experimental density), and the one with classical nuclei is plotted as a dashed line. The grey line extrapolates the classical distribution assuming a linear potential of mean force in the range $-0.3 < \nu < -0.1$, so as to obtain an upper bound to the probability of finding $\nu > 0$ – which is beyond the statistics we can collect.

Figure 1 shows the probability distribution as a function of ν for liquid water at ambient conditions. The probability of finding $\nu > 0$ is 1/1000th of the probability of finding a "well-formed" HB with $\nu > -1.25$, if one includes nuclear quantum effects in the simulation. In a classical simulation we could not detect a single configuration with $\nu > 0$. However, extrapolating the potential of mean force one can estimate that the fraction of transient autoprotolysis in a classical simulation is smaller than 10^{-7}.

It is clear from the analysis we have performed that the nature of these fluctuations is inherently quantum mechanical, and that they are strongly coupled to the compression of the O–O′ bond – which in turn depends on the density much more strongly than on the temperature. Figure 2 compares the distribution of ν at different thermodynamic state points, with and without nuclear quantum effects.

In the text and for most thermodynamic state points we used the BLYP functional and a supercell containing 64 water molecules. We have also examined the sensitivity of our results to the choice of the exchange-correlation functional by performing test calculations with a smaller simulation cell containing 32 water molecules under ambient conditions. Figure 2 shows the results from a simulation using the higher-quality TZV2P basis set, one using the PBE [1] functional, one using the B3LYP [2] and one using the PBE0 hybrid functional [3] together with D3 empirical Van der Waals corrections [4], as implemented in CP2K [5, 6]. We also show a simulation using the q-TIP4P/F empirical model of water [7], and several simulations performed with our basic computational setup, but different thermodynamic state points. One sees that the choice of the functional or the basis set affect only slightly the quantitative conclusions of our study, whereas the use of an empirical model that does not allow for dissociation of water molecules alters significantly the tail behaviour of the distribution of ν.

We can rationalise why the DFT results are relatively insensitive to the choice of functional as follows. The proton transfer coordinate can be thought as a combination of the O–O′ compression coordinate and of the O-H covalent bond stretch. The former basically controls the position of the maximum of the distribution of values of ν, and it is relatively insensitive to the choice of functional as it is mostly controlled by the density. The fluctuations of the O-H covalent bond stretch are strongly quantized, with a large zero-point energy that corresponds to an effective temperature in excess of 2000 K. While DFT struggles to reach quantitative accuracy on the energy scale that is relevant at 300 K, it is sufficiently reliable to capture quite accurately effects on the energy scale of this zero-point energy. Indeed the fact that the extreme fluctuations of the proton transfer coordinate in our quantum simulations are seen with different density functionals and at different thermodynamic state points makes us confident that these fluctuations are real, and not merely an artefact of our modelling.

However things do change when the computational model becomes *qualitatively* different, as in the case of the non-dissociable q-TIP4P/F empirical forcefield. While this empirical water model contains anharmonic terms

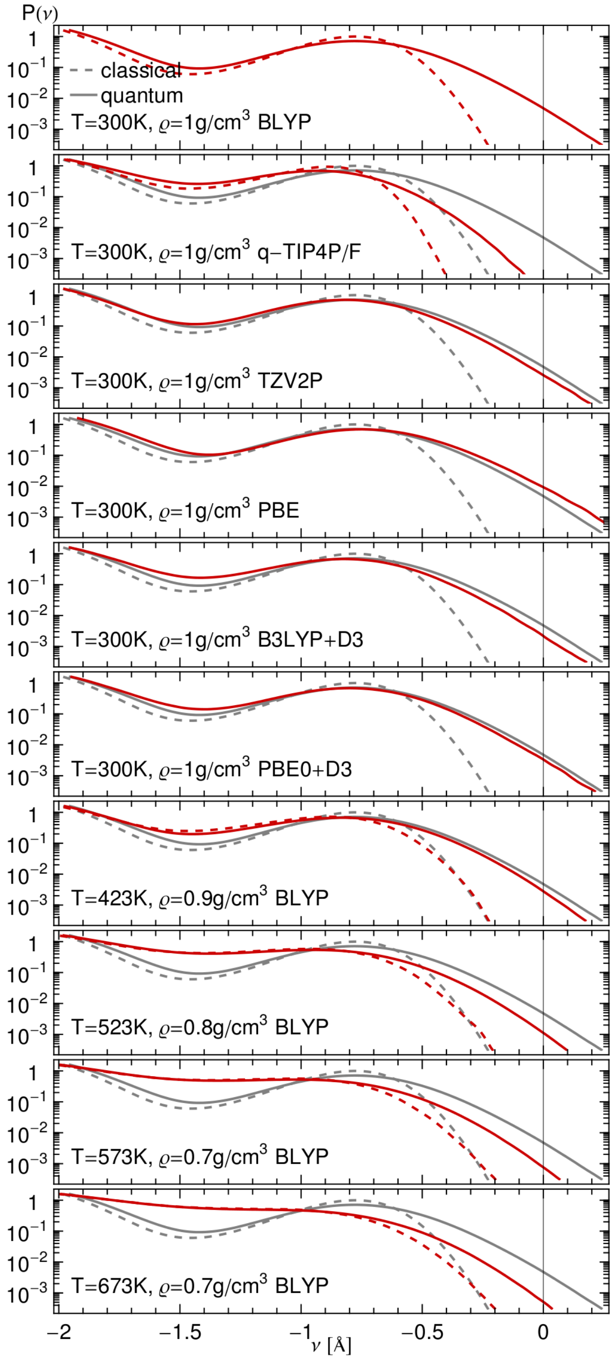

FIG. 2. The top panel shows the distribution of ν for an *ab initio* simulation of liquid water, at temperature $T = 300$ K and density $\rho = 1.0$ g/cm^3, using the BLYP functional. The simulation with quantum nuclei is plotted as a continuous line, and one with classical nuclei is plotted as a dashed line. Other panels report the same curves as a reference, in gray, along with the results obtained with different computational methods and at other thermodynamic state points, in red.

and can therefore describe the softening of the O-H covalent bond in the presence of a hydrogen bond – for example reproducing the experimentally observed red-shift in the stretching frequency upon condensation – it does not contain the explicit treatment of the electronic structure that is necessary to account for the charge transfer associated with transient autoprotolysis events. Nuclear *and* electronic quantum effects both seem to be essential to fully capture the nature of fluctuations of the hydrogen bond.

EFFECTS OF THE FUNCTIONAL ON THE DISTRIBUTION OF WANNIER CENTRES

Figure 2 demonstrates that the distribution of ν changes only slightly when one uses a hybrid functional and dispersion corrections. However, one might wonder whether there is a qualitative change in the correlation between ionic and electronic fluctuations when a fraction of exact exchange and dispersion corrections are included in the density functional. Figure 3 demonstrates that this is not the case. The fluctuations of the Wannier centres are still correlated with ν when a hybrid functional is used, even if there is a small reduction in the fraction of fluctuations reaching out to $\nu > 0$.

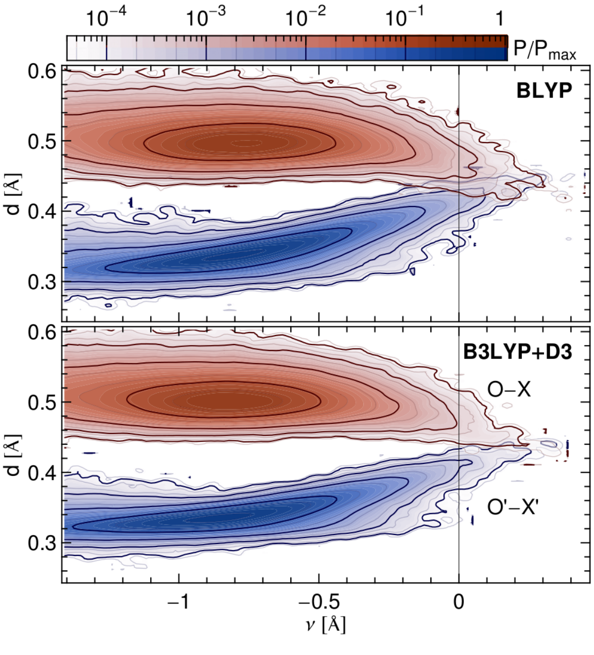

FIG. 3. Given a tagged H atom, the oxygen atom O it is covalently bound to and the acceptor atom O′, X and X′ are the Wannier centres of the two oxygens that are closest to H. The plots report the joint probability distribution of ν and of the distances d of the Wannier centres to the corresponding oxygen. The upper panel comes from a quantum simulation of BLYP water, and the lower panel from a simulation using B3LYP with D3 dispersion corrections.

SORTING AND COUNTING: FLUCTUATIONS AND ASYMMETRY IN LIQUID WATER

A very recent study by Kühne and Khaliullin [8] suggests that “asymmetric” water molecules, characterized by one strong and one weak hydrogen bond, exhibit a characteristic signature in x-ray absorption spectroscopy (XAS). This observation could help to reconcile conflicting interpretations of XAS experiments in water[9, 10].

It is however important to clarify that the asymmetry that is observed does not have a profound origin, but is merely a consequence of the breadth of fluctuations, and of the analysis performed in Ref. [8]. There is just one kind of hydrogen bond, and for the majority of water molecules there is no significant correlation between the geometric (and presumably energetic) configurations of the hydrogen bonds in which each water molecule is involved.

If one takes the two donated HBs for a given water molecule, sorts them and then computes separately the distribution of the “stronger” and “weaker” bonds, it is inevitable that the two distributions will be different, as a consequence of the preliminary sorting of the pair of bonds. Given the joint probability of un-sorted bonds $P^{(2)}(\nu,\nu')$, one finds that the distribution of the stronger and weaker HB read, respectively

$$\begin{aligned}\frac{P_s(\nu)}{2} &= \int\limits_{\nu'<\nu} P^{(2)}(\nu,\nu')\mathrm{d}\nu' \approx P^{(1)}(\nu)\int\limits_{\nu'<\nu} P^{(1)}(\nu')\mathrm{d}\nu' \\ \frac{P_w(\nu)}{2} &= \int\limits_{\nu'>\nu} P^{(2)}(\nu,\nu')\mathrm{d}\nu' \approx P^{(1)}(\nu)\int\limits_{\nu'>\nu} P^{(1)}(\nu')\mathrm{d}\nu'\end{aligned} \tag{1}$$

where the approximate equality becomes exact in the absence of correlations. As is often the case, it is instructive to consider the Gaussian limit of (1). If $P^{(1)}(\nu)$ is a Gaussian with mean $\langle\nu\rangle$ and variance $\sigma^2(\nu)$, the two resulting “sorted” distributions will have means $\langle\nu\rangle \pm \sigma(\nu)/\sqrt{\pi}$. In other words, the broader the initial distribution, the farther apart the distributions of the “strong” and the “weak” components.

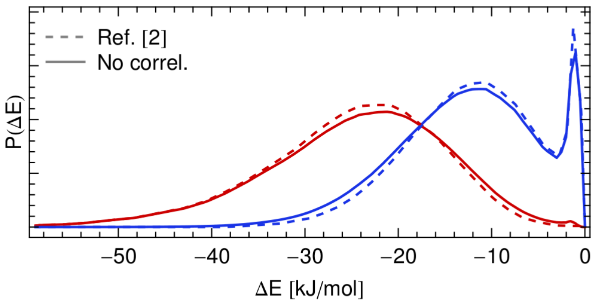

FIG. 4. Comparison between the distribution of the first (red) and second (blue) donor interactions in liquid water, adapted from Fig. 3a of Ref. [8] (dashed line), and the distributions obtained applying Eq. (1) to the average of the two distributions (full line).

We do not have access to the joint probability distribution of the hydrogen bond energies ΔE that underlies the work of reference [8], but we can easily verify that correlations between the two donor interactions are very small. Figure 4 compares the probability distribution of the strongest and second-strongest HB as reported in Ref. [8], with the distributions that we have reconstructed by first computing the marginal distribution $P^{(1)}(\Delta E) = [P_s(\Delta E) + P_w(\Delta E)]/2$ – hence removing any information on the asymmetry – and then applying Eqs. (1). The difference between the two distributions P_s and P_w is clearly just a consequence of the sorting procedure, and does not imply the existence of large correlations between the two hydrogen bonds formed by each water molecule.

CORRELATIONS BETWEEN EXTREME H-BOND FLUCTUATIONS

Even though the typical fluctuations of the hydrogen bonds around a water molecule show very little correlation, as we have just discussed, this is not true for the extreme excursions we have focussed on in the text, which are rare events. Among “well-formed” HB configurations, with $\nu > -1.25$, just one in a thousand has $\nu > 0$. It is therefore interesting to ask whether these extreme fluctuations – which modulate the electronic structure of the hydrogen bond concerned – have more significant repercussions on the other hydrogen bonds the water molecule is involved in.

Consider the joint probability distribution between one of the hydrogen bonds donated by a tagged water molecule (characterised by a PT coordinate ν_a), and the hydrogen bond donated by the second H atom of the same molecule (PT coordinate equal to ν_b). We can characterise the correlation between these two coordinates by the ratio

$$\frac{P^{(2)}(\nu_a,\nu_b)}{P^{(1)}(\nu_a)P^{(1)}(\nu_b)} = \frac{P^{(2)}(\nu_b|\nu_a)}{P^{(1)}(\nu_b)}, \tag{2}$$

which quantifies the extent to which knowing the value ν_a affects the probability of finding the second HB with a PT coordinate ν_b, relative to the case where no knowledge of ν_a is assumed.

Figure 5a demonstrates quantitatively that the correlation is negligible for the clear-cut, well-formed HB configurations with $-1.2 < \nu < -0.4$. For these “normal” HBs, the ratio in Eq. (2) is very close to one. There is however significant correlation for more borderline configurations: if one of the hydrogen atoms is stretching out towards the neighbouring water molecule, approaching a transient autoprotolysis event ($\nu > -0.4$), the probability that the second HB is also involved in an extreme fluc-

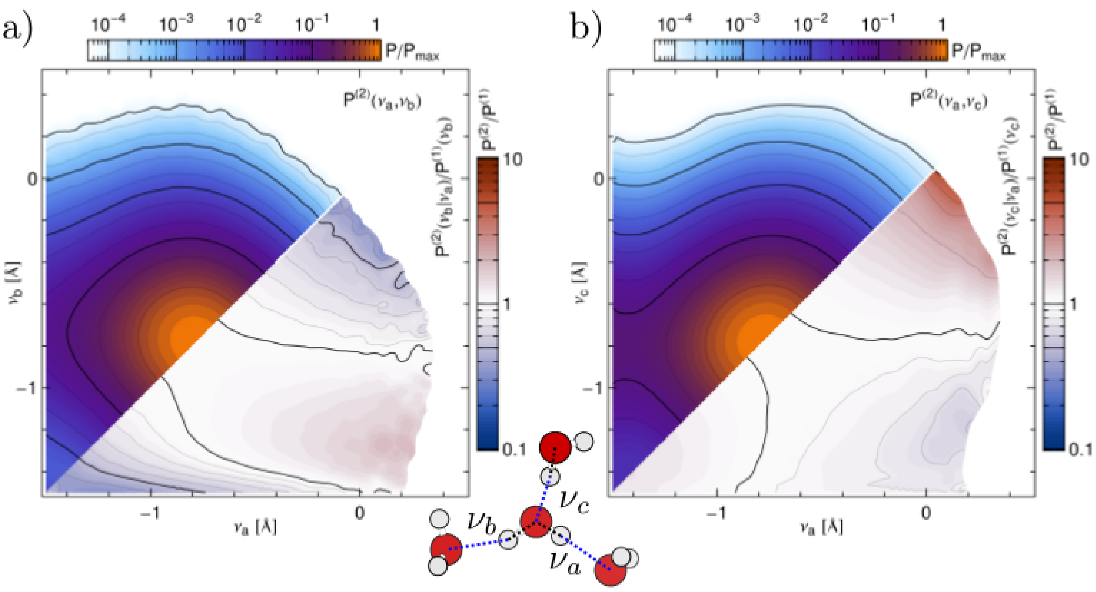

FIG. 5. a) The joint probability distribution of the PT coordinate for the two hydrogen bonds donated by a tagged water molecule, $P^{(2)}(\nu_a, \nu_b)$. The lower-right corner shows the relative conditional probability as defined in Eq. (2). b) The joint probability distribution $P^{(2)}(\nu_a, \nu_c)$ of the PT coordinate for one accepted and one donated HB for a given water molecule. The lower-right corner shows the value of Eq. (2).

tuation is significantly reduced. If the two events were uncorrelated, there would be one chance in a million of observing the simultaneous fluctuation of both HBs to $\nu > 0$, while the actual probability is smaller than 10^{-7}. On the other hand, if one of the HBs is weak, or broken, with $\nu < -1.2$, there is a slight enhancement of the probability that the second donated HB will be involved in a transient autoprotolysis event.

It is even more interesting to consider the correlation between one donated HB (ν_a) and one of the hydrogen bonds *accepted* by the same water molecule (whose PT coordinate is denoted ν_c). In this case, we observe an opposite trend to that discussed above. Figure 5b shows that if a molecule donates a weak hydrogen bond it is less likely to be the recipient of a fluctuating proton from a neighbouring molecule. On the other hand, if the donated H-bond is experiencing an extreme fluctuation, it is more likely that a neighbouring H will fluctuate towards the tagged molecule. Again, if the events were uncorrelated, there would be a probability of one in a million of observing two simultaneous autoprotolysis events; instead we find that these concerted jumps are enhanced by a factor of five relative to the uncorrelated case. These correlations are especially interesting: one molecule that is simultaneously accepting and donating a fluctuating proton is the elementary constituent of proton motion along a *water wire*, an important element in our understanding of proton transport and of genuine, persistent autoprotolysis.

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