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 $\nu = d(\text{O–H}) - d(\text{O′–H})$ 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 negative values of ν – a situation one could classify as a transient autoprotolysis event.

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 1 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 1 shows the results from a simulation using B3LYP [1], a simulation using the PBE0 hybrid functional [2] together with D3 empirical Van der Waals corrections [3], as implemented in CP2K [4, 5], and a simulation using the q-TIP4P/F empirical model of water [6]. One can explain why DFT results are relatively insensitive to the functional and to computational details by the following argument. The proton transfer coordinate can be thought as a combination of the O–O′ compression coordinate and of the O-H covalent bond. The former basically controls the position of the maximum of the distribution of values of ν, but is relatively insensitive to computational details as it is mostly controlled by the density. The fluctuations of the O-H covalent bond are strongly quantized, and the large zero-point energy can be thought to be equivalent to an effective temperature in excess of 2000K for the stretching mode. While DFT struggles to reach quantitative accuracy on the energy scale that is relevant at 300K, it is sufficiently reliable to capture quite accurately the fluctuation behaviour on the energy scale of the zero-point energy of the O-H stretch. The fact that the qualitative observation of these extreme fluctuations is shared amongst different functionals and thermodynamic state points makes us confident that the effect is real, and not merely an artefact of our modelling.

This argument breaks down when the model becomes *qualitatively* different, as it is the case of the non-dissociable q-TIP4P/F empirical forcefield. While the empirical water model we used contains anharmonic terms 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 – an explicit treatment of the electronic structure is necessary to account for the charge transfer that is associated with transient autoprotolysis events. Quantum effects and an explicit treatment of the electronic structure seem to be both essential ingredients to fully capture the nature of fluctuations of the hydrogen bond.

SORTING AND COUNTING: FLUCTUATIONS AND ASYMMETRY IN LIQUID WATER

A very recent study by Kühne and Khaliullin [7] 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[8, 9].

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. [7]. 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
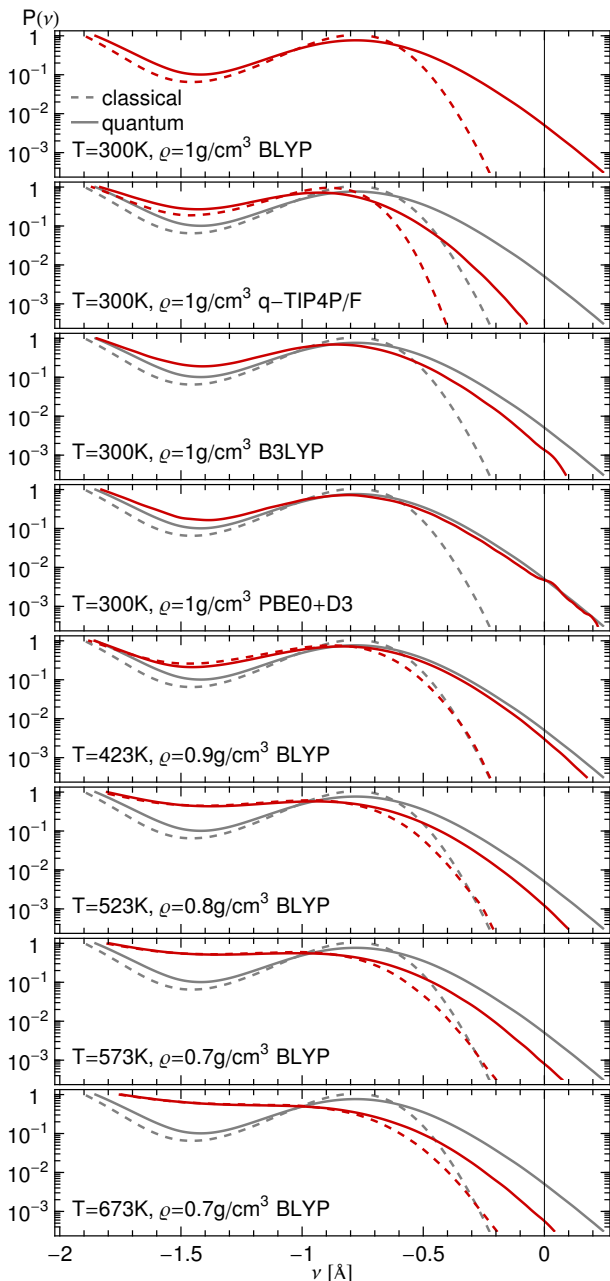
FIG. 1. The top panel shows the distribution of ν for an *ab initio* simulation of liquid water, at temperature $T = 300$ K and density $\rho = 1.0$ g/cm^3, using the BLYP functional. The simulation with quantum nuclei is plotted as a continuous line, and one with classical nuclei is plotted as a dashed 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 weaker HB read, respectively

$$\frac{P_s(\nu)}{2} = \int\limits_{\nu' < \nu} P^{(2)}(\nu,\nu')\mathrm{d}\nu' \approx P^{(1)}(\nu) \int\limits_{\nu' < \nu} P^{(1)}(\nu')\mathrm{d}\nu'$$

$$\frac{P_w(\nu)}{2} = \int\limits_{\nu' > \nu} P^{(2)}(\nu,\nu')\mathrm{d}\nu' \approx P^{(1)}(\nu) \int\limits_{\nu' > \nu} P^{(1)}(\nu')\mathrm{d}\nu'$$

(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.

We do not have access to the joint probability distribution of the hydrogen bond energies ΔE that underlies the work of reference [7], but we can easily verify that correlations between the two donor interactions are very small. Figure 2 compares the probability distribution of the strongest and second-strongest HB as reported in Ref. [7], 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.

However, the extreme excursion along the PT coordinate that we discuss in the main text are rare events. Amongst "well-formed" HB configurations, with $\nu > -1.25$, just one in a thousand has $\nu > 0$. It is interesting to assess whether fluctuations that change so much the electronic nature of a hydrogen bond have more significant repercussions on the other hydrogen bonds one water molecule is involved in. To this aim, we consid-
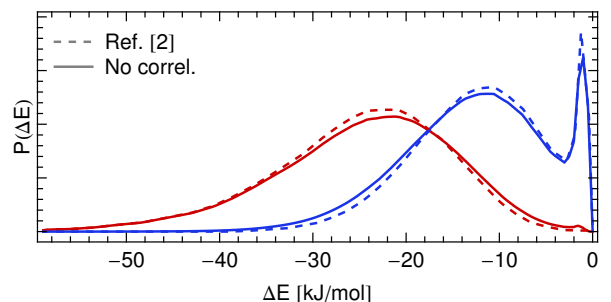

FIG. 2. Comparison between the distribution of the first (red) and second (blue) donor interactions in liquid water, adapted from Fig. 3a of Ref. [7] (dashed line), and the distributions obtained applying Eq. (1) to the average of the two distributions (full line).
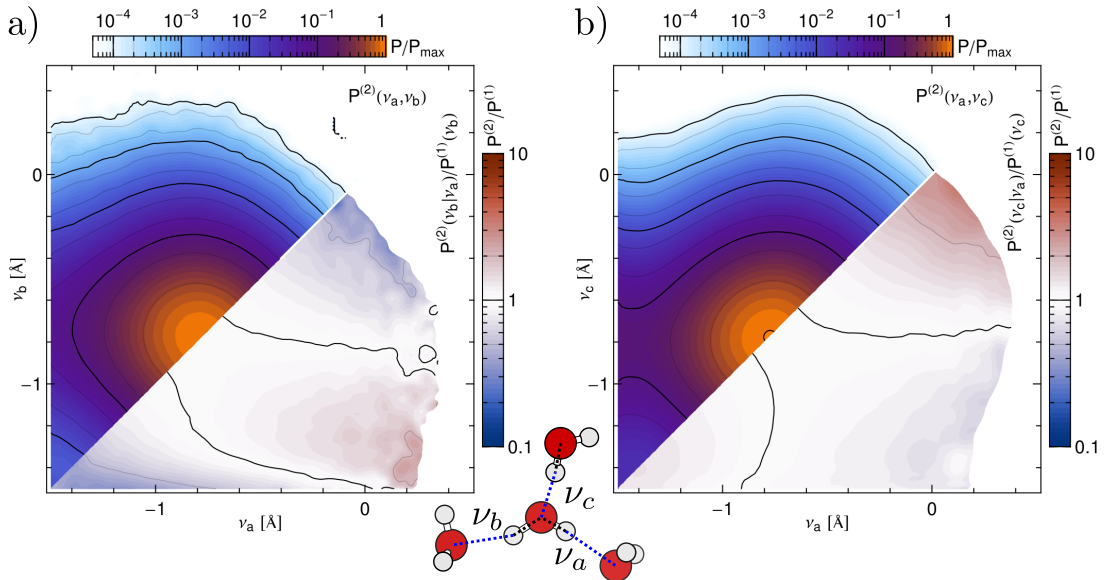
FIG. 3. a) The joint probability distribution of the PT coordinate for the two hydrogen bonds donated by a tagged water molecule, $P^{(2)}(\nu_a, \nu_b)$. The lower-right corner shows the relative conditional probability as defined in Eq. (2). b) The joint probability distribution $P^{(2)}(\nu_a, \nu_c)$ 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).

ered the joint probability distribution between the one of the hydrogen bonds donated by a tagged water molecule (characterized 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 describe the correlation by the ratio

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

which quantifies to what extent knowing the value ν_a of the PT coordinate for one of the HBs modifies 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 3a demonstrates quantitatively that such correlation is negligible for the clear-cut, well-formed HB configurations with $-1.2 < \nu < -0.4$. For these "normal" HBs, the value of Eq. (2) is very close to one. There is however significant correlation for what concerns more borderline configurations: if one of the hydrogen atoms is stretching out towards the neighbouring water molecule, experiencing a transient autoprotolysis event ($\nu > -0.4$), the probability that the second HB is also involved in an extreme fluctuation is greatly reduced with respect to what one would expect. If the two events were uncorrelated, there should be one chance in a million to observe 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 is involved in a transient autoprotolysis event.

It is possibly even more interesting to considere the

correlation between one donated HB (ν_a) and one of the hydrogen bonds *accepted* by the tagged water molecule (whose PT coordinate is indicated as ν_c). In this case, we observe an opposite trend as what we discussed above. Figure 3b shows that if a molecule donates a weak hydrogen bond it is less likely to be the recipient of a flucutating proton from a neighboring molecule. Vice versa, if one H is experiencing an extreme fluctuation, it is more likely that a neighbouring HB will fluctuate towards the tagged molecule. Again, if the events were uncorrelated we would expect a probability in a million to observe two simultaneous autoprotolysis; here, instead, we observe that these concerted jumps are enhanced by a factor of five relative to the uncorrelated case. This kind of correlations are extremely important: one molecule that is simultaneously accepting and donating a fluctuating proton is the building block of so-called *water wires*, an important element in our understanding of proton transport and of genuine, persistent autoprotolysis. Finding that quantum effects can generate traces of such wires even in neat water is a sign of the important role they will play in determining the extent of delocalisation of charged species in water.

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