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Insights on Hydrogen-Bond Lifetimes in Liquid and Supercooled Water

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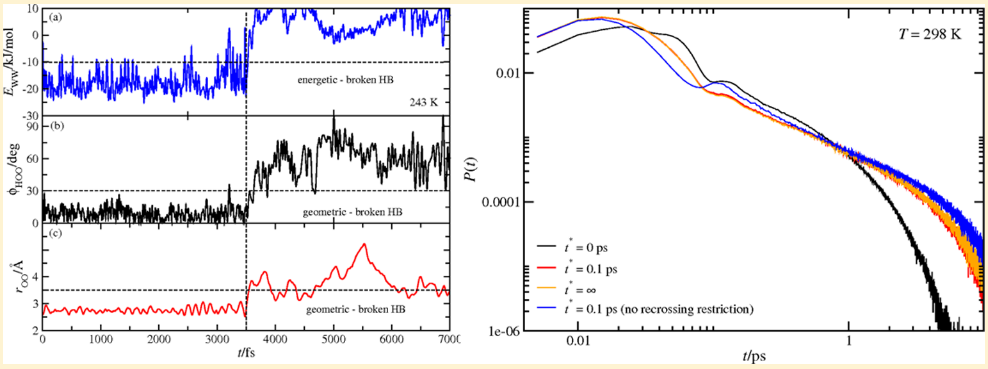

ABSTRACT: We study the temperature dependence of the lifetime of geometric and geometric/energetic water hydrogen-bonds (H-bonds), down to supercooled water, through molecular dynamics. The probability and lifetime of H-bonds that break either by translational or librational motions and those of energetic broken H-bonds, along with the effects of transient broken H-bonds and transient H-bonds, are considered. We show that the fraction of transiently broken energetic H-bonds increases at low temperatures and that this energetic breakdown is caused by oxygen−oxygen electrostatic repulsions upon too small amplitude librations to disrupt geometric H-bonds. Hence, differences between geometric and energetic continuous H-bond lifetimes are associated with large H-bond energy fluctuations, in opposition to moderate geometric fluctuations, within common energetic and geometric H-bond definition thresholds. Exclusion of transient broken H-bonds and transient H-bonds leads to H-bond definition-independent mean lifetimes and activation energies, ∼11 kJ/mol, consistent with the reactive flux method and experimental scattering results. Further, we show that power law decay of specific temporal H-bond lifetime probability distributions is associated with librational and translational motions that occur on the time scale (∼0.1 ps) of H-bond breaking /re-forming dynamics. While our analysis is diffusion-free, the effect of diffusion on H-bond probability distributions where H-bonds are allowed to break and re-form, switching acceptors in between, is shown to result in neither exponential nor power law decay, similar to the reactive flux correlation function.

1. INTRODUCTION

The dynamics of the hydrogen-bond (H-bond) network of water is believed to play a key role in many processes in physics, chemistry, and biology.[1] Further, the anomalous properties of water,[2−6] in particular, at low temperatures, are closely associated with this dynamics. H-bonds break and form on fast time scales, from tens of femtoseconds to picoseconds, and this dynamics can be indirectly probed through distinct experimental techniques[7−20] or through molecular simulations.[21−38] H-bond lifetimes are sensitive to temperature and pressure and to the chemical environment, and these have often been studied through molecular dynamics[21−32] (MD) or Monte Carlo[38] simulations. For this end, different approaches and H-bond definitions have been adopted in simulation studies.[25,27−29,39] The former include the calculation of probability distributions of H-bond lifetimes,[24,28,29] continuous and intermittent H-bond correlation functions,[21,27,29] or the reactive flux method introduced by Luzar and Chandler.[32] Luzar[25] established analytical relationships between different approaches followed to compute the H-bond lifetimes from MD and critically evaluated their dependence on stricter and less strict geometric (g) H-bond definitions, concluding that the reactive flux method is the most consistent approach to estimate H-bond lifetimes. The lifetimes of SPC/E water computed from distributions of H-bond lifetimes, $P(t)$, were shown by Starr et al.[29,30] to depend on the H-bond definition, for g and energetic (e) definitions. H-bond definition-dependent "lifetimes" for g and e definitions have also been found from continuous H-bond correlation functions for SPC/E water at room T for a similar e definition and for a more restrictive g criteria;[23] the latter are not, however, exactly average H-bond lifetimes but rather H-bond mean persistence times[25] and are larger (∼0.5 ps) than the mean continuous H-bond lifetimes (∼0.20 ps) found from $P(t)$ and lower than the mean H-bond lifetimes obtained from the reactive flux method and the transience analysis performed here (∼1.5 ps).

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Experimental depolarized Rayleigh scattering relaxation times follow the Arrhenius law with an activation energy of ~10 kJ/mol, and the latter has been interpreted as the energy required to break a H-bond in liquid water.[8,9,13] This behavior is reproduced by the lifetimes obtained from $P(t)$, despite the lower lifetimes observed, and the activation energies for the SPC/E water model,[29,30] respectively 8.8 ± 0.8 and 9.3 ± 1.2 kJ/mol for e and g definitions, are in reasonable agreement with that from depolarized light scattering experiments (10.8 ± 1.0 kJ/mol).[9] The origin of the dependence of the H-bond lifetimes and the activation energy on the H-bond definition is not, nevertheless, clear. Furthermore, g and e H-bond lifetime differences are temperature-dependent, significantly increasing at low T. The fact that H-bond lifetimes computed through $P(t)$ depend on the H-bond definition provides a path to understand this dependence. This is one of the objectives of the present study, specifically, to understand the origin of the differences between "e" and "g" H-bond lifetimes and the temperature dependence. Further, the nature of the long-time decay of $P(t)$ is considered, in particular, the observation of a power law,[28] exponential,[25,38] or neither[29] depending on the H-bond definition (see discussion by Luzar[25]). The observation of a nonexponential decay has been connected to the introduction of a temporal resolution on the H-bond definition because of diffusion, which occurs on every time scale including the time scale of bond breaking/re-forming;[25,29] following Luzar,[25] "a bond can be broken for a time longer than the librational period and still has a greater than random probability of reforming". This point is important because observation of a long-time power law decay of $P(t)$ has also been associated with the existence of a liquid−liquid critical point of water at low temperatures.[5,28,29] Here, we show that the probability of a H-bond to break and re-form on a time longer than the librational period (~0.1 ps) is actually very low, and therefore, diffusion makes a minor contribution to the nonexponential decay of $P(t)$. Thus, instead, we find that the origin of the appearance of a power law decay region are essentially librational and translational motions that take place during H-bond breaking/re-forming processes on a time scale of ~0.1 ps. We study the dynamics of the nonpolarizable rigid water model, TIP4P-EW,[40] for g and geometric/energetic (g/e) H-bond definitions and deconvolute H-bonds that break due to distance, angle, or e breakdown at temperatures extending from 85 down to −30 °C. The effect of transient broken H-bonds and transient H-bonds in the g and g/e H-bond lifetimes is analyzed, and the results are compared with depolarized Rayleigh scattering and quasi-elastic incoherent neutron scattering (QENS) relaxation times. Further, the activation energies associated with the different H-bond lifetime definitions are compared with the energetics of the H-bond network of water from distinct experimental techniques.

2. METHODS

MD simulations of the TIP4P-EW[40] model of water for 256 molecules in the (N,P,T) ensemble were carried out with the program GROMACS.[41] TIP4P-EW has been parametrized with recourse to experimental density and enthalpies of vaporization at a number of temperatures, including at the supercooled regime; because we are interested in the H-bond dynamics in ambient and supercooled water, this is particularly important. Furthermore, it is interesting to compare its performance with that of the SPC and SPC/E potentials, which have been extensively used in the past to probe the H-bond dynamics of water.[23,25,29,30,32] The T and P were controlled with the thermostat of Bussi et al.[42] and the Parrinello-Rahman[43] barostat. The water molecules were kept rigid with recourse to the SETTLE algorithm,[44] and electrostatic interactions were computed with the particle-mesh Ewald method.[45] The equations of motion were solved with the Verlet leapfrog algorithm with a 1 fs time step, and the systems were equilibrated for 2 ns followed by another 2 ns for analysis purposes.

The H-bond dynamics was studied for a g H-bond definition, where a pair of water molecules is considered H-bonded[29,36] when $r_{OO} < 3.5$ Å and $\phi_{HOO} < 30°$, where r_{OO} is the distance between the donor and acceptor oxygen atoms and ϕ_{HOO} is the angle between the intramolecular O−H bond and r_{OO}, and a g/e H-bond definition, where the g part is conserved and the e component requires the water pair interaction energy, E_{WW}, to be lower than some threshold value, E_{HB}. This is a more restrictive g/e definition than that used by other authors[23,29,30] where the angle criterion is relaxed; however, as shown here, similar conclusions would be found with both g/e definitions because the e restriction overrides the H-bond angular condition. We considered g/e H-bond definitions for both $E_{HB} = 0$ and −10 kJ/mol for comparison purposes; the former definition nonetheless led to results similar to those for the g definition, and these are omitted here. H-bond lifetime distribution functions for water were calculated from[24,29] $P(t) = N_{HB}(t,\Delta t)/\sum_t N_{HB}(t,\Delta t)$, where $N_{HB}(t,\Delta t)$ is the number of donor (or acceptor) H-bonds that (i) remained unbroken at all times up to $t \pm \Delta t/2$ and (ii) got broken at $t \pm \Delta t/2$. $N_{HB}(t,\Delta t)$ was calculated through sampling of every time origin, Δt was set to 2.5 fs, and the mean H-bond lifetime was calculated through the ensemble average, $\tau_{HB} = \sum_t tP(t)$; $P(t)$ is also called the first passage time probability density of H-bonds, and the mean H-bond lifetime is the mean first passage time.[25,39] Probability distribution functions, where $N_{HB}(t,\Delta t)$ is the number of donor H-bonds that remained continuously unbroken up to $t \pm \Delta t/2$ and got broken at $t \pm \Delta t/2$ because (i) $r_{OO} > 3.5$ Å, (ii) $\phi_{HOO} > 30°$, or (iii) $E_{WW} > E_{HB}$ kJ/mol, were also computed. Further, conditional probability distribution functions where transient broken H-bonds and transient H-bonds are accounted for, were computed the following way:[24] if a H-bond between water molecules i (donor) and j (acceptor) break and re-form within t^*, the H-bond is considered unbroken during this tolerance (transience) time, t^*. A further restriction, called hereafter recrossing restriction, is imposed, namely, that during the tolerance time, the proton of the water donor i does not form a H-bond with a third water acceptor k; because this condition is more difficult to ascertain for acceptors, the H-bond probability distributions and lifetimes reported here are for H-bond donor (HBD) water molecules. The nonconditional probability distribution functions are, naturally, equal for acceptors and donors. Transient H-bonds were accounted for by excluding H-bonds that form and break in less than t^{**} (i.e., H-bonds with $\tau_{HB} < t^{**} = t^*$), without later re-forming within a similar time interval ($<t^*$). We note that previous works[46−48] dealt with the problem of exclusion of fast librations at the origin of transient H-bond breaking; although some temporal resolution, t^*, was also defined in these works, distinct approaches have been followed. In a recent MD study,[24] one of us showed for the polarizable model of water, AMOEBA, that when both transient broken H-bonds and transient H-bonds are neglected, g H-bond lifetimes found from $P(t)$ are comparable to those from depolarized light

scattering experiments,[9] while the Arrhenius behavior is conserved. Nevertheless, during the calculations of the present work, the author found an error in the original program, which resulted in wrong (lower) H-bond lifetimes when transient broken H-bonds are neglected; unfortunately, the H-bond lifetimes reported on a following correction[49] are also incorrect (and even lower) because of a first deficient correction of this problem. Here, although we report H-bond lifetimes for a different model, we found these to be very similar to the correct lifetimes for AMOEBA water.

3. RESULTS AND DISCUSSION

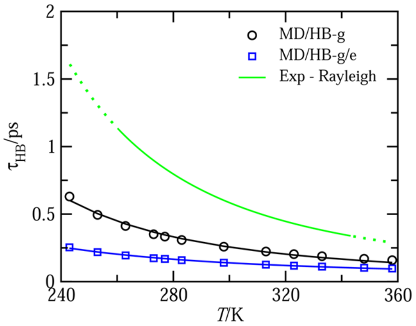

Figure 1. Mean H-bond lifetimes for the g and the g/e H-bond definitions. The lines are the respective fitted Arrhenius curves; the pre-exponential factor and activation energies $[A; E_a]$ are, respectively, $[0.0066\text{ ps}; 9.1\text{ kJ/mol}]_g$ and $[0.012\text{ ps}; 6.1\text{ kJ/mol}]_{g/e}$. The Arrhenius curve fitted to Rayleigh depolarized scattering relaxation times is shown [0.0077 ps; 10.8 kJ/mol]; the dots are low- and high-temperature extrapolations to the T interval of the experiments.

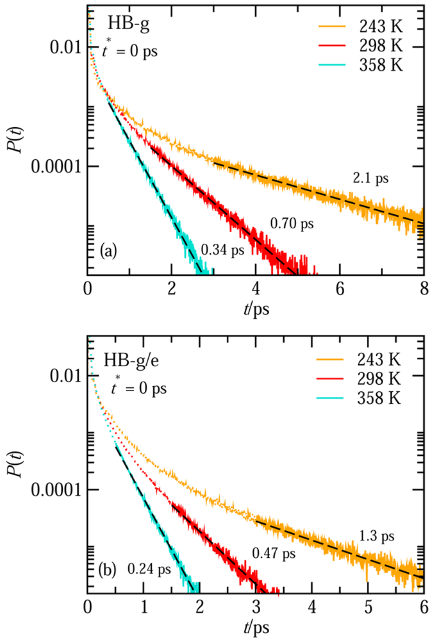

Figure 2. H-bond lifetime probability distributions at the lowest and highest T studied and at room T for the g and g/e H-bond definitions; the dashed lines are exponential fits to the long-time tails of $P(t)$.

Figure 1 compares the g and g/e mean H-bond lifetimes, τ_{HB}, with the depolarized Rayleigh scattering Arrhenius fitted curve of Conde and Teixeira.[9] The τ_{HB} for the g/e definition are noticeably lower, especially at low temperatures; a similar observation led Starr et al.[29] to suggest that $P(t)$ "may not be the best function for studying HB dynamics", in contrast with the intermittent H-bond (see also the discussion in ref 25) and the reactive flux correlation functions, which include bond re-formation. Furthermore, the activation energy for the g/e definition, 6.1 kJ/mol, is 3 kJ/mol lower than that found for the g H-bond definition, 9.1 kJ/mol. Concerning the long-time decay of $P(t)$, we find that after a T-dependent transient period, the probability distributions exhibit a monoexponential (Figure 2) decay. Following Luzar, this is consistent with the fact that $P(t)$ probes an elementary process, that is, H-bond breaking,[25] although other decays have been reported for distinct water potentials and H-bond definitions (this is further discussed below). On the other hand, the relaxation times for the g/e definition are lower than those for the g definition, as expected, and this difference increases at low T, similar to τ_{HB} (Figure 1). The large differences between the g and the g/e H-bond lifetimes and the depolarized Rayleigh scattering results observed in Figure 1 will be discussed below. First, however, we address the observed differences between the τ_{HB} and the activation energy, E_a, for the g and the g/e H-bond definitions. Figure 3a shows the mean number of donor H-bonds for the g and g/e definitions and the fraction of donor H-bonds that break because the g, r_{OO} or ϕ_{HOO}, or the e H-bond definition components have been violated. Here, we do not concern with the future of the broken bond, in particular, if a broken H-bond will re-form with the same acceptor after some transient time or the HBD will form a new bond with a different acceptor; this problem will be considered later on. For the g/e definition, a lower number of H-bonds is observed, relative to the g definition, although this difference decreases at low temperatures. The fraction of g broken donor H-bonds due to molecular translations and librations is nearly constant with T, and the latter is, not surprisingly, ~95%. For the g/e definition, e broken H-bonds are dominant and increase by almost 15%, from water at 358 K to supercooled water at 243 K. Notice that if a more restrictive g H-bond definition had been used[33] (for instance, by restricting the H···O distance to 2.45 Å,[23,25] the distance of the first minimum of the OH partial radial distribution function), the difference between the g and the g/e number of H-bonds and H-bond lifetimes would be smaller, and eventually, a g definition[50] that nearly reproduces the g/e could be found. However, that was not our approach here; rather, we will show that the seemingly different H-bond lifetimes can be reconciled if H-bond breaking/formation transient events are excluded, indicating that the H-bond definitions are effectively equivalent (without the requirement of any additional g criteria) within a kinetic[25,32] description, in line with Luzar's conclusions.[25] Figure 3b shows the respective H-bond lifetimes for the components of the g and the g/e H-bond definitions and supports the previous discussion, that is, g H-bond lifetimes are controlled by librational motions, while for g/e H-bonds, energy assumes the most important role. In particular, it can be seen that the large difference between the g and the g/e H-bond lifetimes at low temperatures is associated with the low lifetime of e H-bonds. The g, r_{OO} and ϕ_{HOO}, broken H-bonds for the g/e definition also have lower lifetimes, especially at low T, than their equivalents in the g definition. We show below that this difference is due to large energy fluctuations that cause g/e H-bonds to break transiently, and therefore, only low lifetime g H-bonds contribute to the mean lifetime of r_{OO} and ϕ_{HOO} broken H-bonds. To gain further insight into the origin of these e broken H-bonds, we computed the distance, r_{OO}, and angle, ϕ_{HOO}, distributions of g/e H-

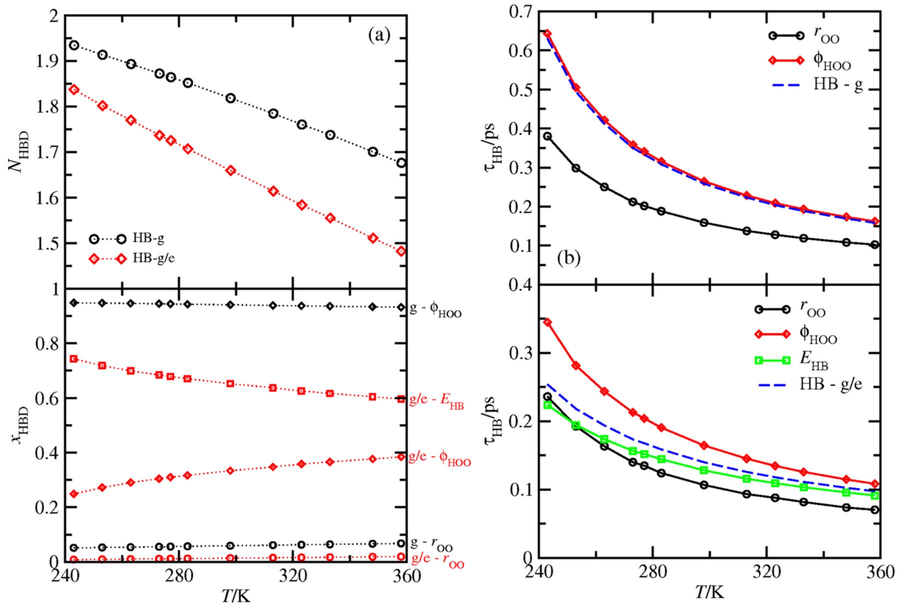

Figure 3. (a) Mean number of HBDs at the different temperatures for the g and the g/e H-bond definitions (upper panel) and fraction, x, of H-bonds that broke due to molecular translations, librations, or energy (lower panel). (b) Mean H-bond lifetimes of H-bonds that broke due to the distance, angle, or energy H-bond component and the lifetimes for the full g (upper panel) and g/e (lower panel) definitions.

bonds at the instant that the e definition breaks down (see Figure 4); note that at this instant, H-bonds are still geometrically intact. Further, we analyzed the van der Waals (O−O) and the nine (O(M)−O(M), O(M)−H, and H−H) electrostatic interactions involved between the O(M) and H atoms of the H-bonded pairs; M stands for the fictitious electrostatic interaction site in the TIP4P-EW[40] model, put 0.125 Å away from the O atom on the HOH angle bisector. The main cause for e H-bond disruption is the O−O repulsion between H-bonded pairs, which, upon a libration that increases ϕ_{HOO} and stretches the H-bond length (H···O distance), weakens the (electrostatic) H-bond. Furthermore, it can be seen from the distribution of ϕ_{HOO} that a smaller angle is needed for the e component to break at low temperatures (see Figure 4) because of the shorter mean O−O distance (larger O−O repulsion). The largest and second largest electrostatic contributions to the water pair interaction energy are the O−O repulsion and the H···O attraction, respectively. Thus, at low temperatures, the O−O distances are small enough that a relatively small amplitude libration is enough to at least transiently break down the e component of the H-bond definition. Notice that this could not be inferred from the mean number of H-bonds, which in fact is closer at lower T for the g and g/e H-bond definitions. Thus, at low temperatures, water is more tetrahedral,[24] O−O distances are smaller,[24] and H-bonds are stronger, increasing the number of g H-bonds that also conform to the e component of the g/e definition.

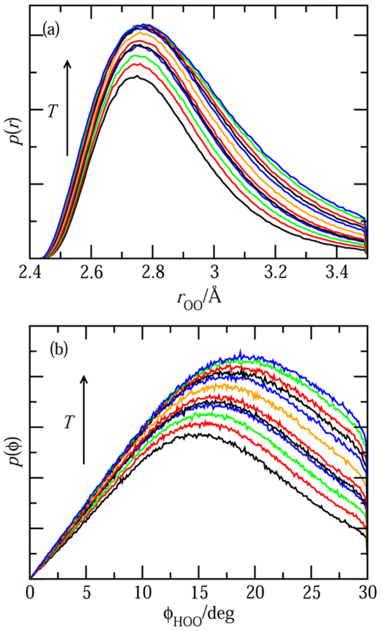

Figure 4. (a) Oxygen−oxygen distance, r_{OO}, and (b) H-bond angle, ϕ_{HOO}, distributions, computed at the instant a g/e H-bond violates the e definition ($E_{WW} > -10$ kJ/mol).

We now address the reasons behind the large differences observed in Figure 1 between the depolarized scattering and MD H-bond lifetimes. The H-bond lifetimes computed from the H-bond probability functions, $P(t)$, are in fact expected to be lower than the scattering lifetimes because the latter have a limited resolution and should not be sensitive to transient broken H-bonds and transient H-bonds. $P(t)$ does not take into account possible recrossings, neither from broken (B) to unbroken (U) in U → B “reactions” nor from unbroken to broken in B → U “reactions”, and probes instead continuous H-bond lifetimes. Hence, to compare MD H-bond lifetimes computed through $P(t)$ with depolarized light scattering relaxation times, these transient occurrences should be neglected. Figure 5 shows these transient broken H-bonds for a pair of water molecules H-bonded at 243 K for ~3.5 ps and for a similar period after the H-bond is permanently broken. The time evolution of E_{WW} shows that although the time average of E_{WW} is lower than −10 kJ/mol for the period that the water molecules are H-bonded, significant energy fluctuations take place that result in frequent transient H-bond breaking. These energy fluctuations are much larger than those observed for the g components, relative to the respective

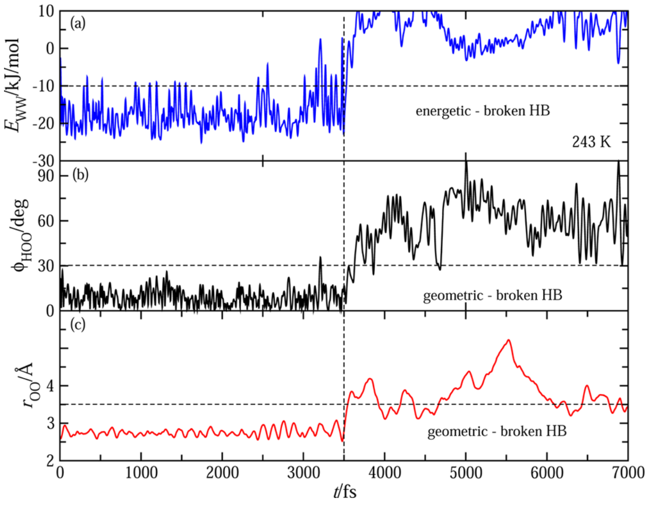

Figure 5. Time evolution of a H-bond in water at 243 K, before and after the H-bond breaks, showing g and e transient broken periods.

H-bond definition boundaries, and are at the origin of the lower H-bond lifetimes for the g/e definition relative to the g H-bond definition, discussed before. On the other hand, although at high temperatures energy fluctuations also take place, because H-bond lifetimes are lower the difference between the g and g/e H-bond lifetimes is also smaller (see Figure 1). From Figure 5, it is clear that the H-bond lifetime is independent of the H-bond definition, as expected, and only depends on the calculation approach. Hence, we now consider exclusion of transient broken H-bonds and transient H-bonds. Although the transience times $t^* = t^{**}$ (see the Methods section) are somewhat arbitrary, the introduction of the recrossing restriction eliminates this arbitrariness for reasons discussed below. We choose a value of $t^* = 0.1$ ps, which is approximately the time window corresponding to the 0−50 cm^{-1} region of the depolarized Rayleigh scattering spectra. Thus, even though some H-bonds may re-form after periods longer than t^*, experimental relaxation times obtained from the depolarized spectra are probably sensitive to these transient broken H-bonds. Figure 6 shows the mean H-bond lifetimes found when neither transient broken H-bonds nor transient H-bonds are neglected ($t^* = 0$ ps and $t^{**} = 0$ ps, the same as Figure 1), when only transient broken H-bonds are neglected ($t^* = 0.1$ ps and $t^{**} = 0$ ps), and when both transient broken H-bonds and transient H-bonds are neglected ($t^* = 0.1$ ps and $t^{**} = 0.1$ ps). The exclusion of transient broken H-bonds leads to a significant increase of τ_{HB}, both for the g and g/e H-bond definitions, but larger lifetimes are observed for the latter definition. These lifetimes are already higher than those from depolarized Rayeligh scattering relaxation times, although following Teixeira et al.,[51] depolarized Rayleigh scattering lifetimes are somewhat arbitrary. When we exclude transient H-bonds, we observe a larger increase of τ_{HB} for the g definition, and the g and g/e lifetimes become similar. This behavior reflects the fact that g/e H-bonds are easier to break and more difficult to form because of the additional e component. The τ_{HB} for both H-bond definitions are approximately Arrhenian, and a similar E_a is found for both definitions, ~11 kJ/mol, consistent with the E_a found through depolarized Rayleigh scattering experiments. This E_a is also similar to that found through Raman scattering,[52] 11 kJ/mol, and is within the range between 8 and 11 kJ/mol found through coherent QENS,[20] incoherent QENS,[51] and IR transient hole burning,[12] although the exact relationship between the H-bond dynamics characteristic times measured through these techniques and the H-bond lifetimes calculated here is difficult to establish.[20] On the other hand, E_a is larger and smaller, respectively, than the values reported from the total electron yield near-edge X-ray absorption fine structure[19] (TEY-NEXAFS), 6.3 kJ/mol, and 2D IR,[14] 14 kJ/mol. Interestingly the TEY-NEXAFS value, which should be more sensitive to an e H-bond criterion,[19] is very similar to that found from continuous H-bond lifetimes for the g/e definition, 6.1 kJ/mol. Concerning the magnitude of the H-bond lifetimes, we also compare in Figure 6 the MD H-bond lifetimes with QENS relaxation times;[51] QENS relaxation times have recently been the object of different reinterpretations.[16,53] These are longer and shorter, respectively, than the H-bond lifetimes computed excluding only transient broken H-bonds and excluding both transient broken and transient H-bonds. The latter are, however, very similar to those obtained by Teixeira et al.[20] through the reactive flux method for the SPC water model (see Figure 7 of ref 20); at room temperature, Luzar[25] found a τ_{HB} of 1.6 ps for two distinct g H-bond definitions for SPC water; a value of 1.4 ps had previously been reported[32] for the same g H-bond definition used here. Here, we obtained 1.5 and 1.6 ps for the g and g/e H-bond definitions, respectively. Thus, our analysis shows that H-bond lifetime differences are due to g−e fluctuations, and this should also be true for any other reasonable g or g/e H-bond definition[33] for a given water model. For instance, a more restrictive g definition based on the inclusion of a H···O cutoff[23,25] will result in lower (continuous)

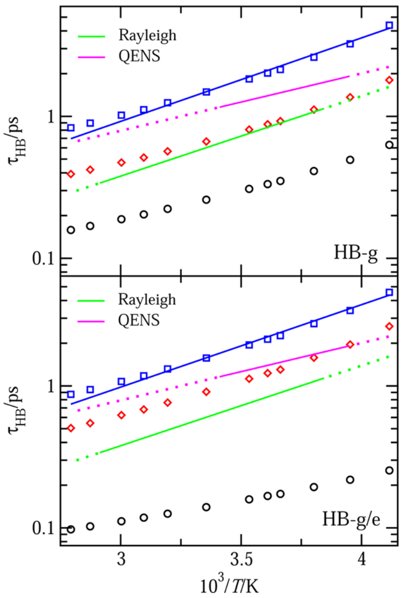

Figure 6. MD H-bond lifetimes for the g, and g/e H-bond definitions calculated for $t^* = 0$ ps (circles), $t^* = 0.1$ ps and $t^{**} = 0$ ps (diamonds), and $t^* = 0.1$ ps and $t^{**} = 0.1$ ps (squares). The Arrhenius fitted curves to experimental Rayleigh depolarized scattering and QENS relaxation times are also shown; the dots are low and high T extrapolations. The experimental pre-exponential factor and activation energy are $[0.0077 \text{ ps}; 10.8 \text{ kJ/mol}]_{\text{Rayleigh}}$ and $[0.0485 \text{ ps}; 7.7 \text{ kJ/mol}]_{\text{QENS}}$. The respective values from $P(t)$ for $t^* = 0.1$ ps and $t^{**} = 0.1$ ps are $[0.016 \text{ ps}; 11.3 \text{ kJ/mol}]_{\text{g}}$ and $[0.018 \text{ ps}; 11.1 \text{ kJ/mol}]_{\text{g/e}}$. Deviations from Arrhenius behavior can be observed at $T < 273$ K; Arrhenius fits to τ_{HB} in the T range $T < 273$ K and $T \geq 273$ K give, respectively, E_a = 14 and 9 kJ/mol for both g and g/e H-bond definitions.

H-bond lifetimes because this criterion will often be violated. However, this violation will only be transient; otherwise, e breakdown would not be transient either as O−O electrostatic repulsions would remain unbalanced and $E_{WW} > E_{HB}$. Thus, while continuous H-bond lifetime differences are inherent to a discrete H-bond definition, the introduction of a transience time reduces their discrete nature as H-bonds are no longer broken or intact based only on a single (or multiple) distance, angle, or energy cutoff; during the transience time, H-bonds can have a continuum of distances, angles, and energies beyond these cutoffs (Figure 5) and still be considered unbroken (or broken). Our analysis is further supported by the conclusions of a recent MD study,[54] which showed significantly different (continuous) H-bond lifetimes for g and topological H-bond definitions and is also in line with the conclusions from 2D IR spectroscopy and MD simulations on the (in)stability of broken H-bonds.[10]

We now analyze the long-time decay of the conditional $P(t)$ distributions. Figure 7 shows the distributions for water at room temperature calculated for the g H-bond definition, for $t^* = 0$ and 0.1 ps and for infinite t^*; $t^{**} = 0$ ps for every $P(t)$ in Figure 7. Further, the distribution computed by relaxing the recrossing restriction is shown for $t^* = 0.1$ ps. Except for $t^* = 0$ ps, we observe a power law decay region similar to that reported by Sciortino et al.[28] (see also the discussion in ref 29), although for a distinct "bond"[47] definition ($r_{OO} < 3.5$ Å and $E_{WW} < 0$ kJ/mol), this power law region significantly increases at low temperatures (not shown here), also consistent with Sciortino et al. observations. A power law decay of $P(t)$ and of specific H-bond correlation functions has also been associated[5,28,29] with the possibility of the existence of a second, liquid−liquid critical point[5,55,56] in water. Here, however, we can see that this is related to molecular motions that take place on the time scale of H-bond breaking/re-forming, ∼0.1 ps. Note that $P(t)$ is very similar for $t^* = 0.1$ ps and ∞, which means that most H-bonds break and re-form in less than 0.1 ps, in good accord with 2D IR spectroscopy and MD results.[10] The respective τ_{HB} are 0.67 and 0.70 ps, largely eliminating, therefore, the arbitrariness of the choice of t^* for $t^* \geq 0.1$ ps. If the recrossing restriction is relaxed, however, longer τ_{HB} are found; at 298 K, for $t^* = 0.1$ ps, we find $\tau_{HB} = 1.1$ ps, compared to $\tau_{HB} = 0.67$ ps when the recrossing restriction is imposed. This means that some newly formed H-bonds (transient H-bonds excluded through t^{**}), involving the switch of the H-bond acceptor, rapidly break, having the donor returning to its original acceptor; notice that this also leads to a slight increase of the power law region (see the discussion below). The recrossing restriction, in fact, should not be very different from that of the reactive flux method[32,36] where the H-bond breaking product is limited to "non-bonded pairs that were initially bonded and whose molecules remain within the first coordination shell of each other" used to decouple H-bond population and diffusion contributions to the reactive flux time correlation function relaxation.[25,32] We followed a similar approach here and computed $P(t)$, allowing only for those transient breaking/re-forming events where the pair did not diffuse apart more than 3.5 Å. The results show that only a minor fraction of water pairs diffuse apart more than 3.5 Å, as expected, during t^*, and $P(t)$ (not shown here) is indistinguishable from those shown in Figure 7 for $t^* = 0.1$ ps or $t^* = \infty$ ps; the mean τ_{HB} decreases from 0.67 to 0.64 ps for $t^* = 0.1$ ps. Thus, on the time scale of 0.1 ps, diffusion is not significant (as expected), and the appearance of a power law decay region is associated instead with librational and translational motions that occur on this time scale, increasing the probability of finding a H-bond with $\tau_{HB} > \sim 1$ ps (see Figure 7). Notice further that only by relaxing the recrossing restriction and for transience times $t^* > 0.1$ ps does diffusion contribute to the decay of $P(t)$ (see Figure 8) as "non-elementary" H-bond breaking/re-forming events, where a donor i may H-bond to one or more acceptor k during t^* and still re-form with the original acceptor j, are considered. Figure 8 shows the appearance of a region in the time window ($t < t^*$) where diffusion intervenes, which is neither exponential

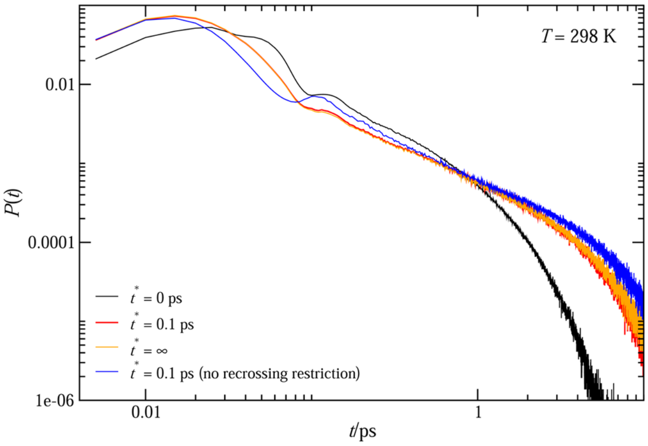

Figure 7. H-bond (g) lifetime probability distributions, $P(t)$, for $t^* = 0$ and 0.1 ps and ∞ at 298 K; $P(t)$ for $t^* = 0.1$ ps and ∞ are similar, and the corresponding τ_{HB} are 0.67 and 0.70 ps, respectively. The effect of eliminating the recrossing restriction is shown for $t^* = 0.1$ ps; the respective τ_{HB} is 1.1 ps. A power law region can be observed for $t^* = 0.1$ ps and ∞ associated with librational and translational motions of water during H-bond breaking/re-forming; the extent of this region increases at lower T.

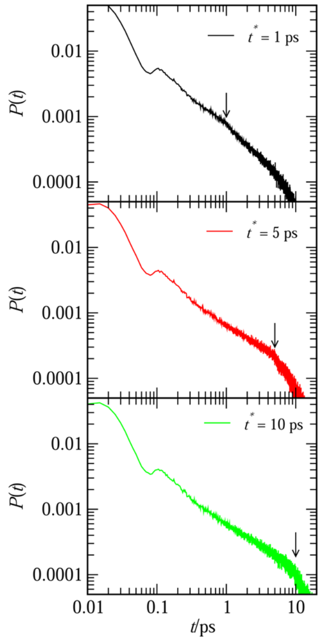

Figure 8. H-bond (g) lifetime probability distributions, $P(t)$, for $t^* = 1$, 5, and 10 ps at 298 K when the recrossing restriction is relaxed. The arrows mark t^*, corresponding to the end of the time windows where diffusion intervenes.

nor power law, resembling that observed by Luzar and Chandler[32] for the reactive flux time correlation function.

4. CONCLUDING REMARKS

We studied the H-bond lifetimes of neat water at a number of temperatures down to supercooled water for g and g/e H-bond definitions. Our results show that when a −10 kJ/mol threshold e condition is defined along with a g definition, the continuous H-bond lifetimes are lower by a factor of ∼2 at low temperatures, relative to the g definition alone. The reason is two-fold; first, the fraction of transient e broken H-bonds increases at low temperatures because of the short O−O distances resulting in strong electrostatic O−O repulsions and weaker O···H attractions upon small-amplitude librations, and second, because the effect of transient broken H-bonds is larger at low temperatures, where H-bond lifetimes are longer. We showed that through exclusion of transient broken H-bonds and transient H-bonds, coupled with a recrossing restriction, we obtain H-bond definition-independent lifetimes similar to those computed through the reactive flux method. We find approximate Arrhenius dependence for the temperatures studied and an activation energy consistent with that found through different experimental techniques. Further, the long-time power law decay regions of H-bond probability distribution functions, previously found by other authors, were shown to be related to molecular motions of water on a subpicosecond (∼0.1 ps) time scale where H-bond breaking/re-forming dynamics occurs.

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Notes

The authors declare no competing financial interest.

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