The kinetics of forming and breaking water-water hydrogen bonds in neat water, an aqueous solution of ethane, and an aqueous solution of NaCl are studied by molecular dynamics simulations. We compare nonpolarizable and polarizable water models to elucidate the effect of water’s polarizability on hydrogen bonds. We find that polarizability strengthens the hydrogen bonds and slows down the kinetics by a factor of between 50% and 100%. The Gibbs energy of activation for breaking hydrogen bonds is $\sim 0.2 \text{kcal mol}^{-1}$ higher for the polarizable water model. Polarizability also causes the rate of forming and breaking hydrogen bonds to be more dependent on the local environment.

The unique properties of water depend fundamentally on its ability to form hydrogen bonds. [1,2] The elementary process of forming and breaking water-water hydrogen bonds plays a crucial role in the dynamic behavior of liquid water. [3] Consequently, water-water hydrogen bond kinetics has been the subject of intensive study. [4–9] Molecular dynamics simulations, which are able to provide atomistic resolution of the dynamic process, have contributed greatly to the understanding of water-water hydrogen bond kinetics. [7,9–14] The water models so far used in these studies, however, are fixed charge models and thus do not incorporate explicit polarizability. Such nonpolarizable water models are unable to describe the response of the electronic structure to a varying environment. Experimentally, water has a non-zero and nearly isotropic polarizability ($\alpha_{xx}, \alpha_{yy}, \alpha_{zz} = (1.47 \text{Å}^3, 1.53 \text{Å}^3, 1.42 \text{Å}^3)$). [15] In general dynamic processes, such as translational and rotational diffusion as well as dielectric relaxation, tend to be slower in polarizable water, and more in agreement with experiment, than in fixed charge water. [16] The coordination number of hydrated anions is sensitive to polarizability. In nonpolarizable water the coordination number of the Cl$^-$ ion is approximately seven whereas in polarizable water it is six. [17,18] Polarizable models also predict fine details like translational rattling effects observed in dielectric relaxation experiments which are absent in nonpolarizable models. [16]

The presence of polarizability gives rise to many-body interactions as a consequence of which the water-water interaction will not only depend on the pair’s mutual position and orientation but also on its environment. The electric field from nearest neighbors induces changes in the electronic configuration of the water molecules, which in turn affect their interaction with other water molecules. This will give rise to cooperativity in the behavior of water. In particular, when a water molecule forms a hydrogen bond, it undergoes an internal rearrangement of charge density which generally strengthens other hydrogen bonds formed by the same water. Therefore we expect to see mutual enhancement of hydrogen bond strength due to water polarizability. This should produce cooperative behavior in hydrogen bond kinetics, which has not been observed in other studies using nonpolarizable water models. [11] We explore such cooperativity in this article.

We performed molecular dynamics simulations for neat water, an aqueous solution of ethane, and an aqueous solution of NaCl, using both polarizable and nonpolarizable water models. For simulations with nonpolarizable water we used the TIP4P model of Jorgensen et al. [19] For simulations with polarizable water we used the TIP4P/FQ model of Rick, Stuart, and Berne. [16] The TIP4P/FQ model shares the same geometry as the TIP4P model but it allows the partial charges on the molecule to dynamically fluctuate in response to changes in the electrostatic environment. As in the original paper, we treated the fluctuating charges as dynamic variables and used the extended Lagrangian method [16,20–22] to propagate them. The OPLS/AA force field [23] (a nonpolarizable force field) was used for the solute molecules. Standard OPLS combining rules were used for the Lennard-Jones interaction ($\sigma_{ab} = \sqrt{\sigma_a \sigma_b}$, $\epsilon_{ab} = \sqrt{\epsilon_a \epsilon_b}$) between the solute atoms and the water oxygen. All molecular dynamics runs were performed with 512 water molecules, and in the case of the ethane and NaCl solutions, five solute molecules or pairs of solute counterions for an approximate solute concentration of 0.5 M. For each system, data was taken from five 100-picosecond (ps) trajectories run in the $NVE$ ensemble with the velocity Verlet integrator. Every 20 femtosecond (fs) a configuration is used in the following analysis. Each trajectory was started from a configuration sampled from a well-equilibrated $NPT$ simulation using Nosé-Hoover chain (NHC) thermostats [24] and an Andersen-Hoover-type barostat. [25] All runs used cubic periodic boundary conditions and Ewald summation for the electrostatics. [26] In terms of the box length $L (\approx 25 \text{Å})$, the real-space cutoff for the Ewald sum was $0.35 L$, the reciprocal-space cutoff was $7/2 \pi L$, and the screening parameter was set to $7.9 / L$. The Lennard-Jones pair potential was truncated at $L/2$.

Autocorrelation analysis is used to characterize the structural relaxation of hydrogen bonds. The autocorrelation function $c(t)$ [9,27] is defined as

$$c(t) = \frac{\langle h(0) h(t) \rangle}{\langle h \rangle} \tag{1}$$

where $h(t) = 1$ if a tagged water pair is hydrogen bonded at time $t$, and $h(t) = 0$ otherwise. Water-water hydrogen bonds are identified by a geometric criterion: a water pair is
considered to be hydrogen bonded if the oxygen-oxygen distance is no greater than 3.5 Å and simultaneously the bonded O—H···O angles is no greater than 30°. [11] We note that the liquid structures of TIP4P and TIP4P/FQ water models are similar enough that the same hydrogen bond definition should be valid for both models. Using this definition, the distributions of the number of hydrogen bonds formed by a water molecule are only slightly different for the two models (Fig. 1). A TIP4P water molecule forms an average of 3.54 hydrogen bonds, while a TIP4P/FQ water molecule forms an average of 3.62 hydrogen bonds. TIP4P/FQ water thus shows a slightly stronger propensity for forming hydrogen bonds.

The polarizable model exhibits a much slower structural relaxation of hydrogen bonds than the nonpolarizable model (Fig. 2). The relaxation times \( \tau_{\text{nonp}} \), defined as \( c(\tau_{\text{nonp}}) = e^{-t} \), are \( \tau_{\text{nonp,IP}} = 5.26 \text{ps} \) for the polarizable model and \( \tau_{\text{nonp,IP}} = 3.32 \text{ps} \) for the nonpolarizable model. It is interesting to relate hydrogen bond kinetics with self-diffusion of liquid water. [9] Hydrogen bonds hinder the self-diffusion of water, and faster hydrogen bond kinetics will result in faster diffusion. Conversely, broken hydrogen bonds can form again if the two water molecules haven’t diffused away from each other; therefore slower diffusion will result in slower hydrogen bond relaxation. To eliminate the contribution of pair diffusion, we computed the following correlation function: [9]

\[
d(t) = \frac{\langle h(0)(1-h(t))H(t) \rangle}{\langle h \rangle}
\]  

(2)

where \( H(t) = 1 \) if the pair of water molecules are closer than 3.5 Å at time \( t \) and \( H(t) = 0 \) otherwise. \( d(t) \) is the time-dependent probability that the hydrogen bond is broken at time \( t \) but the pair of water molecules haven’t diffused away. At long time, the behavior of \( d(t) \) is dominated by the rotational diffusion of water molecules. Therefore the relaxation time scale for \( d(t) \) is proportional to the rotational time constant \( \tau_{\text{rot}} \), defined by the long time behavior of the rotational correlation function. [28] \( \tau_{\text{rot}}^{\text{IP}} = 1.4 \text{ps} \) and \( \tau_{\text{rot}}^{\text{IP}} = 2.1 \text{ps} \). [16] Figure 2 (bottom plate) shows the close agreement between \( d_{\text{nonp}}(t) \) and \( d_{\text{IP}}(t) \), where we scaled the time by \( \alpha = \tau_{\text{rot}}^{\text{IP}} / \tau_{\text{rot}}^{\text{IP}} \) for the \( d(t) \) of the TIP4P model.

To explore the cooperativity in bond hydrogen kinetics due to water polarizability and concomitant many-body interactions, we calculated the autocorrelation function for hydrogen bonds in different environment, distinguished by the number of hydrogen bonds each water of the concerned hydrogen bond forms. Specifically, we computed the following conditional correlation function: [11]

\[
c_{mn}(t) = \frac{\langle p_{mn}(0)h(0)h(t) \rangle}{\langle p_{mn}h \rangle}
\]

(3)

where \( p_{mn}(t) = 1 \) if at time \( t \) one water molecule of the tagged pair forms \( m \) hydrogen bonds, and the other forms \( n \) hydrogen bonds; \( p_{mn}(t) = 0 \) otherwise. \( c_{mn}(t) \) describes the structural relaxation of the subset of hydrogen bonds whose water molecules are initially in the bonding states \((m, n)\). For the nonpolarizable model, \( c_{mn}(t) \) shows little difference for typical initial bonding states \( m = 3, 4; n = 3, 4 \) (Fig. 3), in agreement with the findings of Luzar et al. [11] The relaxation times for the hydrogen bonds in the typical initial bonding states are \( \tau_{\text{nonp}}^{\text{IP}} = 3.22 \text{ps} \), \( \tau_{\text{nonp}}^{\text{IP}} = 3.36 \text{ps} \) and \( \tau_{\text{nonp}}^{\text{IP}} = 3.54 \text{ps} \), which are only slightly different from each other. When water polarizability is included, however, \( c_{mn}(t) \) splits for different \((m, n)\) (Fig. 3). The relaxation times for the hydrogen bonds are \( \tau_{\text{nonp}}^{\text{IP}} = 4.71 \text{ps} \), \( \tau_{\text{nonp}}^{\text{IP}} = 5.18 \text{ps} \) and \( \tau_{\text{nonp}}^{\text{IP}} = 5.76 \text{ps} \). The differences between the hydrogen bonds with different initial bonding states are very pronounced. When a water molecule forms the ideal number of 4 hydrogen bonds, the near tetrahedral structure in the vicinity induces the most favorable electronic configuration for strong hydrogen bonds, and the involved hydrogen bonds relax particularly slowly. Interestingly, a water molecule can occasionally form more than 4 hydrogen bonds by the geometric definition. Such situation usually corresponds to the transition state where one hydrogen bond is being replaced by another. In the nonpolarizable model, \( c_{45}(t) \) decays slightly faster than \( c_{33}(t) \), suggesting that in absence of polarizability, the tetrahedral structure of one water does not stabilize the hydrogen bond enough to compensate the disturbance of the intruding 5th water, which readily replaces the existing hydrogen bond. In the polarizable model, in contrast, \( c_{45}(t) \) decays slower than \( c_{33}(t) \). The tetrahedral structure induces a very favorable electronic configuration that stabilizes the hydrogen bond and it more than compensates the disturbance introduced by the 5th water. Thus hydrogen bonds are apparently cooperative in their kinetic behavior when water polarizability is taken into account. Note that the difference in \( c_{mn}(t) \) vanishes at time \( t > 10 \text{ps} \), because the hydrogen bonds have sufficiently relaxed that the memory of the initial bonding states is lost.

In another study, using a nonpolarizable water model, we have found the kinetic behavior of water-water hydrogen bonds to differ significantly in the solvation shells of various residues of a polypeptide and its counterions. [29] Near hydrophobic groups, the breaking of water-water hydrogen bonds is much slower than in bulk water. Around solvated cations such as Na\(^+\), hydrogen bonds break more rapidly than in bulk. Here we investigate the effect of water polarizability on hydrogen bond kinetics in solvation shells. Ethane is chosen as a representative hydrophobic molecule, while NaCl is used to represent ionic solutions.

The relaxation of hydrogen bonds is found to be slower in ethane’s solvation shell, for both the nonpolarizable and polarizable models (Fig. 4). This is in agreement with our previous findings. Moreover, hydrogen bond kinetics near the hydrophobic group is found to slow down to a larger degree for the polarizable water model than for the nonpolarizable model. The dimer energy between hydrogen bonded water pairs is well defined for the nonpolarizable model. The distribution of such dimer energies for different environment shows that hydrogen bonds between two water molecules both in the solvation shell of ethane tend to be slightly stronger than hydrogen bonds in bulk (inset, Fig. 4). We expect the same for...
the polarizable model, even though the dimer energy is not well-defined for polarizable models because of the many-body interactions. Polarizability causes the hydrogen bonds to mutually strengthen each other. Therefore the stronger hydrogen bonds in the solvation shell in turn strengthen the hydrogen bonds between the water in the solvation shell and the water in bulk. We speculate that for the polarizable model such indirect enhancement of hydrogen bond strength contributes partly to the slowdown in the kinetics of hydrogen bonds between bulk and solvation shell water.

The effect of polarizability increases with the electric field of the environment. In an ionic NaCl solution as dilute as 0.5M, polarizability makes a pronounced difference in both ionic coordination numbers [30] and hydrogen bond kinetics between TIP4P/FQ and TIP4P models (Fig. 5). For the nonpolarizable TIP4P model, the dilute ions have very little effect on the kinetics of the water-water hydrogen bonds and the hydrogen bond autocorrelation functions are almost identical for neat water and 0.5M NaCl solution. For the polarizable TIP4P/FQ model, in contrast, hydrogen bonds relax more slowly in the dilute ionic solution than in neat water. This, again, can be attributed to the induced dipole in polarizable water that strengthens the hydrogen bonds. Around the cations, the water dipoles point away from the cation, and the electrons are drawn toward the cation by the electric field. This results in an intramolecular charge transfer that increases the water dipoles. Around the anions, the dipoles point toward the anion, while the electrons are pushed away from the anion, resulting in a charge transfer that also increases the water dipoles. Therefore polarizability always augments the water dipole and strengthens the hydrogen bonds around solvated ions. For the nonpolarizable model, the hydrogen bonds between a water molecule in the solvation shell of Na⁺ and another one in bulk (denoted simply as bulk-⁻Na⁺ below) relax slightly more rapidly than the bulk-bulk hydrogen bonds for time < 5 ps (inset, Fig. 5). The relaxation times for the nonpolarizable model are \( \tau_{\text{rel}}^{\text{bulk-bulk}} = 3.24 \text{ ps} \) and \( \tau_{\text{rel}}^{\text{bulk-}\text{Na}⁺} = 3.1 \text{ ps} \), respectively (Table I), showing that the hydrogen bonds break more rapidly near the positive Na⁺ ions. This is because the water dipoles are aligned with the strong radial electric field arising from the small ions, thereby distorting the hydrogen bond geometries. [29] In contrast, for the polarizable model the bulk-⁻Na⁺ hydrogen bonds relax more slowly than the bulk-bulk ones. The respective relaxation times are \( \tau_{\text{rel}}^{\text{bulk-bulk}} = 5.77 \text{ ps} \) and \( \tau_{\text{rel}}^{\text{bulk-}\text{Na}⁺} = 6.83 \text{ ps} \). Hydrogen bonds break more slowly near the Na⁺ ions. The strong electric field around small Na⁺ ions gives rise to a large induced dipole in surrounding water. This enhances the hydrogen bond strength near the ions which more than offsets the distortion of the hydrogen bonds. Near the larger Cl⁻ ions, the electric field is weaker, and consequently the effect of polarizability is less pronounced. Hydrogen bond breaking slows down to a lesser degree around Cl⁻ ions than around Na⁺. (See Fig. 5, inset of the TIP4P/FQ model.)

The transition state theory rate constant for breaking a hydrogen bond is given by

\[
k_{\text{TST}} = -\frac{d}{dt} c(t)|_{t \to \alpha +} \tag{4}
\]

For the conditional autocorrelation function dependent on the environment \( c_{mn}(t) \), we have

\[
\frac{d}{dt} c_{mn}(t) = \langle p_{mn}(0) \hat{h}(0)(1 - h(t))\rangle / \langle p_{mn}h \rangle + \langle \dot{p}_{mn}(0) \hat{h}(0)(1 - h(t))\rangle / \langle p_{mn}h \rangle \tag{5}
\]

where we used the equilibrium condition \( \langle p_{mn}(0) \hat{h}(0)\rangle + \langle \dot{p}_{mn}(0) \hat{h}(0)\rangle = \frac{d}{d\tau} \langle p_{mn}(t) \hat{h}(t)\rangle |_{\tau = 0} = 0 \). Since on average the first passage time of hydrogen bonds is on the order \( \sim 0.3 \text{ ps} \), we have \( \langle \dot{p}_{mn}(0) \hat{h}(0)(1 - h(t))\rangle \approx 0 \) for small \( t \). Therefore we can define the conditional transition state theory rate constant by

\[
k_{\text{TST}}^{(\text{cond})} = -\frac{d}{dt} c_{mn}(t)|_{t \to \alpha +} = -\frac{\langle p_{mn}(0) \hat{h}(0)(1 - h(t))\rangle}{\langle p_{mn}h \rangle} |_{t \to \alpha +} \tag{6}
\]

We assume that \( k_{\text{TST}} \) obeys the Arrhenius relation:

\[
k_{\text{TST}} = A e^{-\Delta G^1 / RT} \tag{7}
\]

where \( \Delta G^1 \) is the activation Gibbs energy for breaking hydrogen bonds. Prefactor \( A \) depends on the transition state, which is identical for both models. We can therefore estimate the effect of polarizability on \( \Delta G^1 \) in different environment. To that end, we computed

\[
\Delta \Delta G^1 = \Delta G^1_{(\text{TIP4P/FQ})} - \Delta G^1_{(\text{TIP4P})} = RT \ln \left( \frac{k_{\text{TST}}^{(\text{TIP4P/FQ})}}{k_{\text{TST}}^{(\text{TIP4P})}} \right) \tag{8}
\]

As shown in Table I, we see that polarizability invariably elevates the activation Gibbs energy for breaking hydrogen bonds. In neat water, \( \Delta \Delta G^1 \) generally increases with the number of hydrogen bonds the two water molecules form, supporting our speculation that in presence of polarizability, hydrogen bonds mutually strengthen each other. (We point out the exception when a water forms 5 hydrogen bonds. This usually corresponds to transition states where the hydrogen bonds are distorted and the mutual stabilization effect disappears.) In ethane solution, the increase in \( \Delta \Delta G^1 \) caused by polarizability is 0.1 kcal-mol⁻¹ more for the hydrogen bonds between two water molecules both in the solvation shell than for those in bulk. Polarizability also increases \( \Delta G^1 \) for hydrogen bonds between bulk water and solvation shell water, partly due to the indirect enhancement of hydrogen bond strength as mentioned before. The elevation of \( \Delta G^1 \) is very pronounced in NaCl solutions, since the polarization effect increases with the electric field due to the ions. The elevation of \( \Delta G^1 \) by polarizability in different environment lies in the order:

\[
tetrahedral bonding structure > Na⁺ > Cl⁻ > other bonding structures \tag{9}
\]
where tetrahedral bonding structure corresponds to the situation when the water molecule forms 4 hydrogen bonds with other water molecules. Other bonding structures refers to situations in which the water molecule forms other than 4 hydrogen bonds.

It is important to note that there are rapid recrossings in hydrogen bond kinetics, so that the TST rate constant, $k_{\text{TST}}$, is considerably larger than the inverse relaxation time of the hydrogen bonds, $\tau_{\text{rel}}$. This can be inferred from the time-dependent reactive flux of hydrogen bond breaking. (See, for example, Ref. [9, 11].)

We conclude that water polarizability causes hydrogen bonds to mutually strengthen each other. It significantly slows down hydrogen bond kinetics. It makes hydrogen bond kinetics cooperative and more dependent on the local environment.

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[30] The first minimum in the oxygen-Na$^+$ radial distribution function is at 3.25 Å. The corresponding coordination numbers are 6.1 for the TIP4P model and 6.0 for the TIP4P/FQ model. The first minimum in the oxygen-Cl$^-$ radial distribution function is at 3.80 Å. The corresponding coordination numbers are 7.3 for the TIP4P model and 6.4 for the TIP4P/FQ model.

---

**TABLE I.** The difference in the relaxation time of hydrogen bonds $\tau_{\text{rel}}$, the transition state theory rate constant $k_{\text{TST}}$, and the activation Gibbs energy of breaking hydrogen bonds between the nonpolarizable and the polarizable models. “Total” stands for all the hydrogen bonds in the system. Bulk is abbreviated as B and solvation shell as SS. The unit for the relaxation time is ps, the unit for the rate constants $k_{\text{TST}}^{\text{TIP4P}}$ and $k_{\text{TST}}^{\text{TIP4P/FQ}}$ is ps$^{-1}$, and the unit for the difference in activation Gibbs energy $\Delta \Delta G^i$ is kcal mol$^{-1}$.

<table>
<thead>
<tr>
<th>System Environment</th>
<th>$\tau_{\text{rel}}$</th>
<th>$k_{\text{TST}}^{\text{TIP4P}}$</th>
<th>$k_{\text{TST}}^{\text{TIP4P/FQ}}$</th>
<th>$\Delta \Delta G^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>3.32</td>
<td>2.56</td>
<td>2.00</td>
<td>0.146</td>
</tr>
<tr>
<td>water</td>
<td>3.22</td>
<td>2.51</td>
<td>1.92</td>
<td>0.111</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.54</td>
<td>2.00</td>
<td>1.32</td>
<td>0.248</td>
</tr>
<tr>
<td>C$_2$H$_6$ soln.</td>
<td>3.11</td>
<td>2.24</td>
<td>2.24</td>
<td>0.252</td>
</tr>
<tr>
<td>SS</td>
<td>4.41</td>
<td>2.42</td>
<td>1.88</td>
<td>0.151</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.24</td>
<td>2.64</td>
<td>1.98</td>
<td>0.171</td>
</tr>
<tr>
<td>C$_2$H$_6$ soln.</td>
<td>3.11</td>
<td>2.10</td>
<td>2.10</td>
<td>0.226</td>
</tr>
<tr>
<td>B••SS(Na$^+$)</td>
<td>3.39</td>
<td>2.54</td>
<td>1.80</td>
<td>0.203</td>
</tr>
<tr>
<td>B••SS(Cl$^-$)</td>
<td>3.39</td>
<td>2.54</td>
<td>1.80</td>
<td>0.203</td>
</tr>
</tbody>
</table>
FIG. 1. The distribution of the number of hydrogen bonds, as defined by the geometric criterion, a water molecule forms in liquid water. There is only a slight difference between the polarizable and nonpolarizable model. The polarizable water model shows a stronger propensity to form hydrogen bonds.

FIG. 2. The hydrogen bond autocorrelation function $c(t)$ for TIP4P and TIP4P/FQ water models. The hydrogen bonds relax much slower for the polarizable TIP4P/FQ model. The relaxation time $\tau_{\text{rel}}$, defined as $\tau_{\text{rel}} = e^{-\gamma}$, for the polarizable TIP4P/FQ model is 1.56 times longer than for the nonpolarizable TIP4P model. The time dependent probability that a hydrogen bond is broken but the water pair remains closer than 3.5\AA, $d(t)$, is shown in the bottom plate. Also shown is $d(t)$ for TIP4P model with time $t$ scaled by $\alpha = \tau_{\text{rel}}^{\text{TIP4P/FQ}} / \tau_{\text{rel}}^{\text{TIP4P}}$, the ratio of the rotational time constant. The close agreement between $d^{\text{TIP4P}}(\alpha t)$ and $d^{\text{TIP4P/FQ}}(t)$ supports the hypothesis that the long time behavior of $d(t)$ is determined by the rotational diffusion of water molecules.
FIG. 3. The conditional hydrogen bond autocorrelation functions for hydrogen bonds with different initial bonding states \((m, n)\). For the nonpolarizable TIP4P model, hydrogen bond kinetics is uncorrelated with the bonding states of the involved water molecules. For the polarizable TIP4P/FQ model, however, hydrogen bond kinetics differ for different initial bonding states of the involved water molecules, suggesting cooperativity in the dynamic behavior of hydrogen bonds.

FIG. 4. The autocorrelation function of hydrogen bonds in the solvation shell (SS) of ethane and in bulk water. Bulk-bulk represents the hydrogen bonds between two water molecules in bulk, bulk-SS represents the hydrogen bonds between a water molecule in bulk and another in the solvation shell of ethane, and SS-SS those between two water molecules both in the solvation shell of ethane. A water molecule is considered to be in the solvation shell of hydrophobic groups if its oxygen atom is within 4.0 Å from a carbon in ethane. [31,32] The hydrogen bonds relax slower in the solvation shell of hydrophobic groups. The distribution of the dimer energy of hydrogen bonded water pairs in the solvation shell (inset, for TIP4P model) shifts slightly to the lower end. The average dimer energy of hydrogen bonded water pairs in the solvation shell is \(E_{\text{w-w}}^{\text{ss}} = -4.12\text{kcal-mol}^{-1}\), slightly lower than the bulk value \(E_{\text{w-w}}^{\text{bulk}} = -4.00\text{kcal-mol}^{-1}\). (Unfortunately, in polarizable model, the many-body nature of the interaction prevents us from making a similar analysis.) There’s a wider spread between \(c(t)\) in different environment for the polarizable model than for the nonpolarizable model.
FIG. 5. The hydrogen bond autocorrelation function in neat water and 0.5M NaCl solution. There’s little difference between the two for the nonpolarizable TIP4P model. For the polarizable TIP4P/FQ model, $c(t)$ decays slower in 0.5M NaCl than in neat water. The autocorrelation functions for hydrogen bonds between a water molecule in bulk and another water molecule in the solvation shell of an ion are shown in the inset. (bulk-$\text{Na}^+$ and bulk-$\text{Cl}^-$). We consider a water molecule to be in the solvation shell of Na$^+$ if the oxygen-Na$^+$ distance is no greater than 3.25 Å, and of Cl$^-$ if the oxygen-Cl$^-$ distance is no greater than 3.80 Å. [30]) For the polarizable model, the bulk-$\text{Na}^+$ hydrogen bonds relax slower than the bulk-bulk hydrogen bonds, whereas for the nonpolarizable model, the bulk-$\text{Na}^+$ hydrogen bonds relax slightly faster than the bulk-bulk ones for time $< 5$ ps.