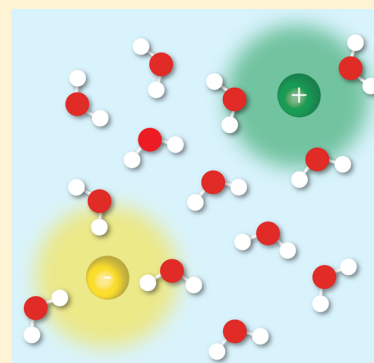


## Mechanisms of Acceleration and Retardation of Water Dynamics by Ions

Guillaume Stirnemann,<sup>†,¶</sup> Erik Wernersson,<sup>‡,§</sup> Pavel Jungwirth,<sup>\*,‡</sup> and Damien Laage<sup>\*,†</sup><sup>†</sup>Department of Chemistry, Ecole Normale Supérieure, UMR ENS-CNRS-UPMC 8640, 24 rue Lhomond, 75005 Paris, France<sup>‡</sup>Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

## S Supporting Information

**ABSTRACT:** There are fundamental and not yet fully resolved questions concerning the impact of solutes, ions in particular, on the structure and dynamics of water, which can be formulated as follows: Are the effects of ions local or long-ranged? Is the action of cations and anions on water cooperative or not? Here, we investigate how the reorientation and hydrogen-bond dynamics of water are affected by ions in dilute and concentrated aqueous salt solutions. By combining simulations and analytic modeling, we first show that ions have a short-ranged influence on the reorientation of individual water molecules and that depending on their interaction strength with water, they may accelerate or slow down water dynamics. A simple additive picture combining the effects of the cations and anions is found to provide a good description in dilute solutions. In concentrated solutions, we show that the average water reorientation time ceases to scale linearly with salt concentration due to overlapping hydration shells and structural rearrangements which reduce the translational displacements induced by hydrogen-bond switches and increase the solution viscosity. This effect is not ion-specific and explains why all concentrated salt solutions slow down water dynamics. Our picture, which is demonstrated to be robust vis-a-vis a change in the force-field, reconciles the seemingly contradictory experimental results obtained by ultrafast infrared and NMR spectroscopies, and suggests that there are no long-ranged cooperative ion effects on the dynamics of individual water molecules in dilute solutions.



## ■ INTRODUCTION

Water in our environment is never found as the pure substance but always contains dissolved salts that affect its molecular properties and play a key role in a wide range of contexts. Examples include ions in seawater which participate in corrosion processes,<sup>1</sup> ions in atmospheric aerosols involved in environmentally relevant reactions,<sup>2</sup> and ions in the cellular medium affecting the stability of proteins<sup>3,4</sup> and nucleic acids.<sup>3</sup> In addition to the dramatic impact that ions can have both on the structure and dynamics of the surrounding water molecules, it was further observed that these effects are strongly ion-specific. Different ions can have radically different effects, as shown for example by their varying abilities to precipitate proteins from aqueous solutions, expressed in Hofmeister's empirical classification.<sup>3,4</sup>

Despite the fact that it is crucial to understand and characterize the action of ions on water, there is still no consistent molecular picture to describe the impact of ions on water dynamics, and several essential aspects are still unclear. A first fundamental but unresolved question is whether ions retard or accelerate water dynamics. All recent time-resolved experiments<sup>5–9</sup> have observed that water dynamics in salt solutions is slower than in neat water, but viscosity, dielectric relaxation, and NMR measurements<sup>10–14</sup> have suggested that some salts can increase the water lability. A related unexplained and intriguing result is the finding by these latter experiments<sup>12</sup>

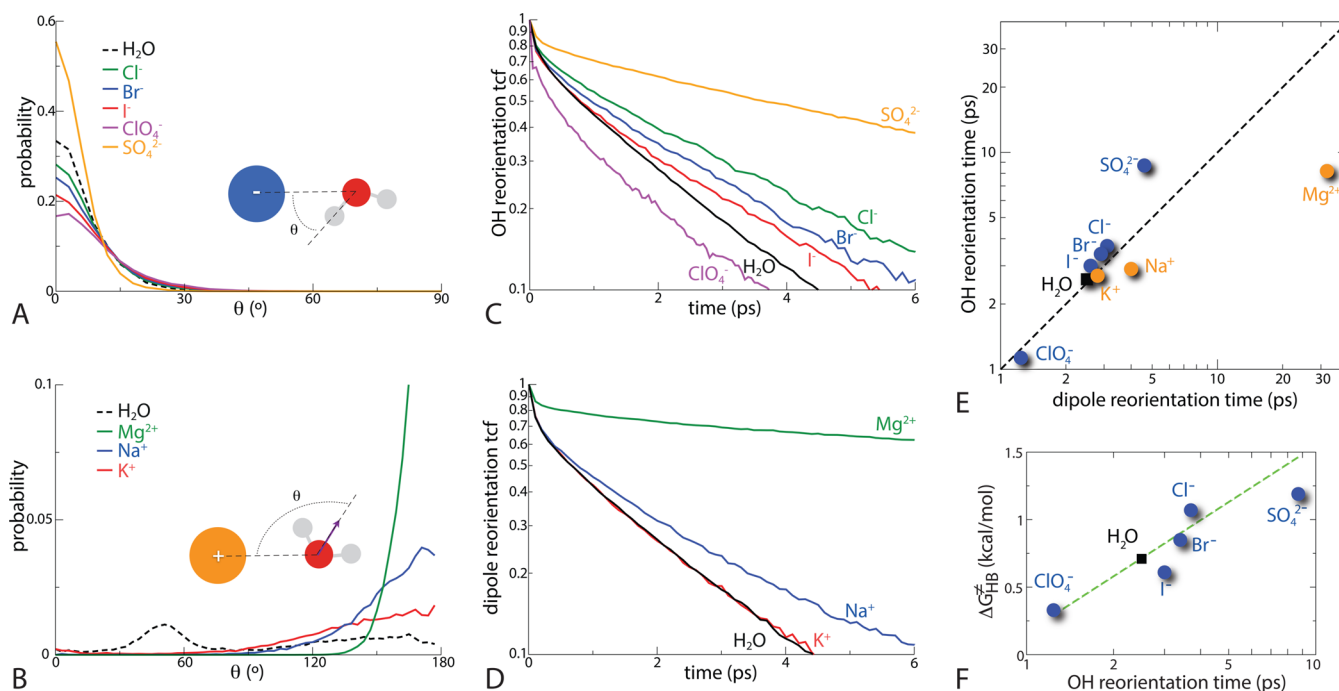
that all ions slow down water dynamics at high salt concentrations, including those which accelerate water in dilute conditions.

A second essential question pertains to the range of influence of an ion on the water molecular properties. Numerous experimental and theoretical<sup>15,19</sup> studies have suggested that a single ion typically perturbs only its first hydration layer, except for species with a high charge density, that is, very small (e.g.,  $F^-$ ,  $Li^+$ ) or multiply charged (e.g.,  $Mg^{2+}$ ,  $Ca^{2+}$ ) ions, whose influence can extend to the second or third shells. A consequence is that, as found in several studies,<sup>10–12,18</sup> in dilute solutions the influence of a given ion should be independent of its counterion. However, for salts like  $MgSO_4$  and  $Na_2SO_4$ , this standard additive picture was recently challenged by experiments<sup>5</sup> which suggest instead that due to some long-ranged cooperative effects the nature of the counterion can markedly change the influence of a given ion on the surrounding water molecules even in dilute salt solutions. However, these conclusions seem to contrast with those from an earlier ultrafast spectroscopy study<sup>15</sup> on a series of salt solutions (including  $Na_2SO_4$ ) which found that the

Received: April 4, 2013

Revised: May 23, 2013

Published: July 18, 2013



**Figure 1.** Effect of isolated ions on water structural and dynamical properties: angular probability distribution for (A) a water OH bond lying within an anion first shell and (B) for the water dipole within a cation first shell; orientation tcf eq 1 (C) for a water OH initially bonded to an anion and (D) for the dipole of a water initially in a cation hydration shell; (E) correlation between the OH and dipole reorientation times, where the dotted line corresponds to an isotropic reorientation; (F) correlation between the OH reorientation time and the free energy cost  $\Delta G_{\text{HB}}^{\ddagger}$  to stretch the water–anion HB from its equilibrium distance to the elongation at the first maximum in the radial distribution function (dots). Within the extended jump model,<sup>27</sup>  $\rho_{\text{HB}} \approx \exp[-\Delta\Delta G_{\text{HB}}^{\ddagger}/(k_{\text{B}}T)]$  (dashes).

addition of ions had no influence on the rotational dynamics of water molecules outside the ions' first solvation shells.

Here, we combine analytic modeling and molecular dynamics (MD) simulations to study and characterize the ion-specific effects on water dynamics. Classical MD simulations appear as an exquisite tool here because they provide a molecular picture of the reorientation dynamics while giving results that can be compared with available experimental measurements, including ultrafast infrared anisotropy decays<sup>5,6</sup> and NMR orientational relaxation times.<sup>10,11</sup> Because of the presence of highly localized charges in ionic systems we employ polarizable force fields to account for the polarization of the surrounding waters by the ionic charges and its impact on the dynamics.<sup>20</sup> We have carefully verified that these force fields yield a description of the solution structure and of water dynamics in good agreement with the available experimental data, both at low and high salt concentration and we have also checked that our conclusions are robust vis-a-vis a change of force field. We first consider the influence of a series of single ions on water reorientational dynamics and determine why some ions accelerate the dynamics of water while others induce a slowdown with respect to the bulk situation. We then study the effect of multiple ions in concentrated aqueous salt solutions and choose two paradigm systems ( $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$ ) simulated at different concentrations. We investigate the potential presence of cooperative effects, whereby the impact of a given ion on the dynamics of individual water molecules changes with the nature of the counterion. We eventually identify the reason why the same salt can have totally opposite effects on water dynamics when its concentration is changed.

## RESULTS AND DISCUSSION

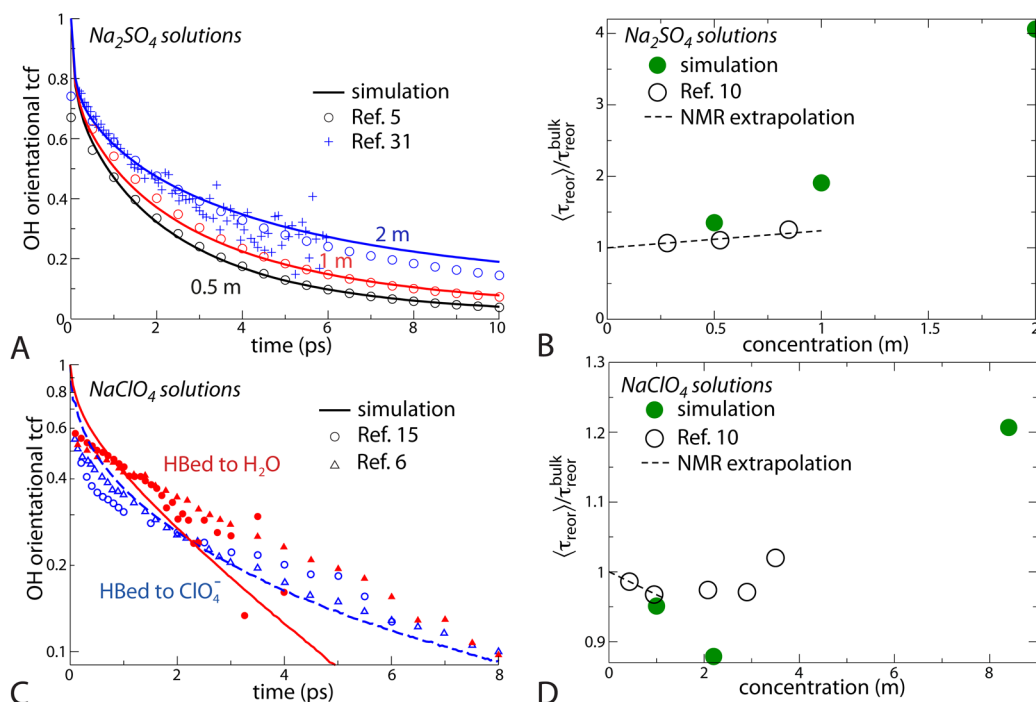
**Influence of a Single Ion. Hydration Shell Structure and Dynamics.** We start by characterizing the impact of isolated anions and cations on the surrounding water molecules. As already well established,<sup>16,21–23</sup> a water molecule tends to point one of its OH bonds toward an anion while its dipole points away from a cation. However, these hydration structures are not rigid and the amplitude of the water fluctuations around these average configurations increases with decreasing ionic charge densities (Figure 1A,B and Supporting Information).

While a classification of ions based on their impact on water structure was shown to be ill-defined,<sup>22,23</sup> considering the effect of ions on the surrounding water dynamics provides a less ambiguous alternative.<sup>10–12</sup> This can be measured via the water orientation time correlation functions (tcf)

$$C_2(t) = \langle P_2[\mathbf{u}(\mathbf{0}) \cdot \mathbf{u}(\mathbf{t})] \rangle \quad (1)$$

where  $P_2$  is the second-order Legendre polynomial and  $\mathbf{u}$  is the orientation of a molecular body-fixed vector such as the water OH bond or dipole direction.  $C_2(t)$  is accessible from time-resolved ultrafast IR spectroscopy and from MD simulations, while NMR provides the value of the time-integrated tcf for several water molecular axes or tensors, determined by the chosen isotope.<sup>24</sup>

Both for water molecules in the aqueous bulk and those initially in an ion's first shell, the OH and dipole orientational tcfs exhibit a fast, sub-0.2 picosecond (ps), partial decay due to librations, followed by a picosecond decay leading to a full decorrelation (Figure 1C,D). This slower decay is approximately exponential, and its characteristic reorientation time  $\tau_{\text{reor}}$  is reported in Figure 1E. For both anions and cations, the reorientation time is observed to increase with growing ionic



**Figure 2.** Experimental and simulated water reorientation dynamics in two salt solutions. (A) Orientation tcf eq 1 in Na<sub>2</sub>SO<sub>4</sub> solutions from our simulations and from ultrafast anisotropy decays<sup>5,31</sup> (crosses correspond to ref 31 and circles were reconstructed from the fits given in ref 5; both are shifted to compare the long-time decays). (B) Ratio between the average reorientation time in the salt solution and the bulk value for increasing Na<sub>2</sub>SO<sub>4</sub> concentrations from our simulations and from NMR;<sup>10</sup> dashes represent the additive picture prediction. (C) Same as panel A for 6 M NaClO<sub>4</sub> with anisotropy decays from refs 6 and 15. The simulated tcf values have been corrected for vibrational lifetime effects as explained in ref 28 using the lifetimes from ref 6. (D) The same as panel B for NaClO<sub>4</sub> solutions.

charge densities, in agreement with prior NMR measurements.<sup>10,11</sup> However, even with Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> which induce the largest retardation factors in our study, the OH reorientation time remains short enough so that at dilute conditions water molecules in the ions' hydration layers cannot be considered as immobilized.

To rationalize how ions affect water dynamics, it might be tempting to suggest a simplified model where anions would only affect the water OH dynamics while cations would only act on the water dipoles.<sup>5</sup> To assess the validity of this description, we have determined the degree of anisotropy in water reorientation dynamics, estimated through the comparison of the reorientation times associated with these two water molecular vectors. In the bulk, water reorientation was suggested to be only slightly anisotropic.<sup>25</sup> Next to ions, Figure 1E shows that only strongly interacting ions like Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> induce a significant anisotropy between the OH and dipole reorientations. This is in agreement with NMR measurements probing the reorientation of different molecular axes,<sup>24</sup> and results from the similar interaction energies experienced by a water molecule in the hydration shell with the ion and with the other surrounding water molecules. No strong decoupling can be seen in the dipole and OH librational amplitudes either (see Supporting Information). Our simulations thus show that cations do not exclusively affect the water dipole dynamics, and similarly anions do not exclusively affect water OH bonds.

We have also examined the size of the dynamically perturbed shell of water molecules around an ion. For water molecules initially in the second shell, the reorientation dynamics is already bulk-like for all ions except those with a very high

charge density, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, for which a moderate residual slowdown is observed (see Supporting Information). No effect could be detected in the third layer. This reinforces prior conclusions obtained with various techniques<sup>15–19</sup> about the local and short-ranged nature of the perturbation by a single ion.

**Origin of Slowdown and Acceleration.** Another key point in Figure 1C,D is that compared to the bulk, some ions accelerate the reorientation dynamics of water molecules within their shell while others slow it down, in agreement with NMR results<sup>12</sup> (see Supporting Information). We now identify the physical mechanism causing these opposite effects.

We analyze the reorientation time within the recently suggested extended jump model framework.<sup>26,27</sup> Beyond the librational decay, water molecules were shown<sup>26,27</sup> to reorient both via large amplitude angular jumps when a water OH group trades hydrogen-bond (HB) acceptors and by a diffusive frame reorientation of an intact HB axis between successive jump events (see Figure 4E). The resulting reorientation time is<sup>26,27</sup>

$$\tau_{\text{reor}}^{-1} = (\tau_{\text{reor}}^{\text{jump}})^{-1} + (\tau_{\text{reor}}^{\text{frame}})^{-1} \quad (2)$$

where  $\tau_{\text{reor}}^{\text{jump,frame}}$  are, respectively, the jump and frame contributions to the reorientation time.  $\tau_{\text{reor}}^{\text{jump}}$  is determined by the time  $\tau_{\text{jump}}$  between successive jumps and by the jump amplitude.<sup>26,27</sup> This model was successfully applied to water dynamics next to several anions.<sup>28,29</sup> Studies of water reorientation next to a wide range of dilute solutes have revealed that the changes in the water reorientation dynamics mainly result from a change in the jump time.<sup>27</sup> For a water molecule lying at the interface between a solute and the bulk, the jump time depends on two factors, the local topology and

the strength of the HB to be broken,<sup>27</sup> that we now discuss in the specific context of salt solutions.

The topological effect is induced by any type of ion and results from the partial hindrance of a new water HB partner's approach. Compared to that of the bulk situation, the volume occupied by the ion reduces the number of accessible transition state configurations for the jump exchange and leads to a slowdown  $\rho_V > 1$  (where  $\rho_V$  is the excluded volume factor) in the jump rate constant.<sup>27</sup> The HB strength factor arises from the free energy cost to stretch the initial HB to reach the jump transition state configuration. This  $\rho_{HB}$  factor differs from 1 only when the initial HB acceptor is an anion which either accelerates the jump rate because it accepts an initial bond weaker than a water–water HB (leading to an HB strength factor  $\rho_{HB} < 1$ ), or slows it down if the bond is stronger ( $\rho_{HB} > 1$ ).<sup>27</sup> The jump time results from the combination of the excluded volume and HB strength factors,  $\tau_{\text{jump}} = \rho_V \rho_{HB} \tau_{\text{jump}}^{\text{bulk}}$ .

Anions affect water dynamics through both  $\rho_V$  and  $\rho_{HB}$ . For very weak HB acceptors, such as,  $\text{ClO}_4^-$ , the  $\rho_V$  slowdown can be more than compensated by the  $\rho_{HB}$  acceleration, leading to an overall acceleration relative to the bulk situation ( $\rho_V \rho_{HB} < 1$ , as illustrated in Figure 1C by the faster tcf decay for OHs initially bonded to the anion). All other investigated anions whose HB strength with water is comparable to or greater than that of the water–water HB induce a slowdown ( $\rho_V \rho_{HB} > 1$ ).<sup>29</sup> Since the  $\rho_V$  factor changes little between anions, a good correlation is found between the water reorientation time next to an anion and the free energy cost to stretch the anion–water HB (Figure 1F). A qualitative guideline can thus be determined: anions for which the HB elongation cost is greater than that in bulk water (approximately 0.8 kcal/mol) tend to slow down water dynamics. While our model is not fully quantitative and still requires to be extended, for example, to comprehensively describe all cations (see Supporting Information), we underline that the simple  $\rho_V$  and  $\rho_{HB}$  considerations can already semiquantitatively rationalize the effects of both cations and anions on water reorientation dynamics and identify the HB strength effect as the key factor to discriminate between water-accelerating and retarding ions.

**Concentrated Salt Solutions.** We now apply the understanding gained about the influence of a single ion on water dynamics to study concentrated aqueous salt solutions including several anions and cations. In particular, we establish why some techniques like ultrafast spectroscopy experiments systematically observe a slowdown while others see an acceleration in some cases.

**Paradigm Salts.** To investigate the impact of an increasing ionic concentration on water reorientation dynamics, we focus on two salts,  $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$ , which exhibit qualitatively different behaviors and for which femtosecond infrared and NMR spectroscopy results are available. For each salt, we have performed simulations at several concentrations (see Supporting Information). Figure 2 shows that for the two salts the results of our simulations are in good agreement with both the time-resolved anisotropy decays<sup>3,6,30,31</sup> and with the average water reorientation time measured by NMR<sup>10</sup> for increasing salt concentration. While water dynamics is retarded at any  $\text{Na}_2\text{SO}_4$  concentration (Figure 2A,B), it is accelerated at low  $\text{NaClO}_4$  concentration and slowed down at higher concentration (Figure 2D), as observed in NMR.<sup>10</sup> We now establish the molecular factors which explain why a change in concentration can dramatically modify the effect of a given salt on water dynamics.

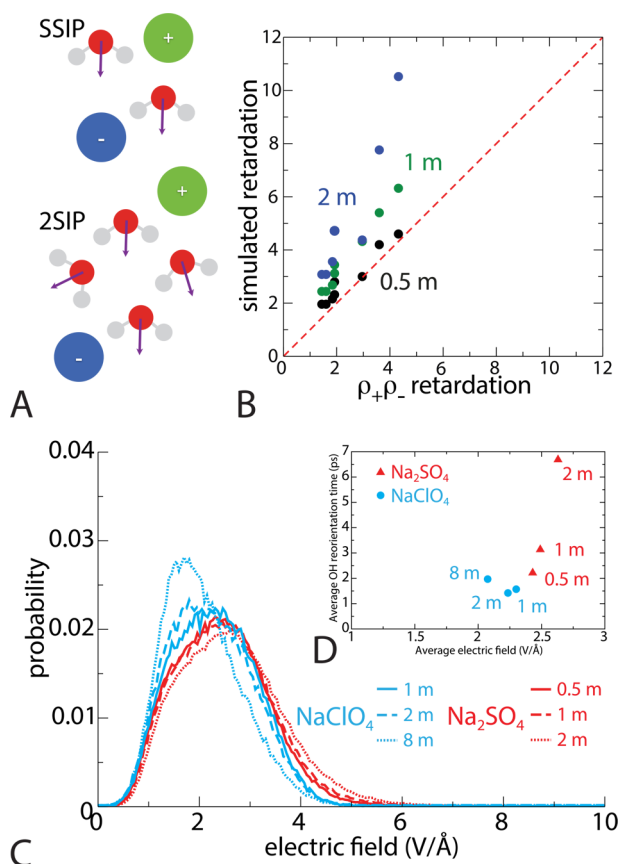
**Test of the Additive Picture.** We first test the standard additive picture suggested by viscosity and NMR measurements.<sup>10,11</sup> In dilute solutions, the average water reorientation time  $\langle \tau_{\text{reor}} \rangle$  is a weighted average of the water bulk, cationic, and anionic hydration shell reorientation times, which are assumed to be independent of the salt concentration. As previously recognized in experimental measurements,<sup>10,11,32</sup> our simulations (Figure 2 and Supporting Information) confirm that this additive picture holds at lower concentrations (typically below 1 m). The  $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$  salts are respectively a retardant and an accelerant, and the average water dynamics changes linearly with the salt concentration. However, when the salt concentration exceeds a threshold value (which decreases with the ion–water interaction strength), water reorientation slows down more rapidly than predicted by the simple additive model (Figure 2 and Supporting Information). This is observed for both salts, including  $\text{NaClO}_4$  for which there is a dramatic qualitative change from acceleration to retardation. Deviations from the linear behavior imply that the reorientation times of each population change with concentration and are usually explained by the combined influences of cations and anions on some water molecules, either because the cationic and anionic hydration shells overlap at high concentration or because of ion pairing whose probability may be higher than expected from a simple homogeneous distribution, especially for multivalent ions.

**Ion Pairs.** To understand how the dynamics of a water molecule is affected by the concomitant presence of several ions, we focus on water molecules between ions involved in two types of pairing:<sup>33</sup> solvent-shared ion pairs (SSIP) where the cation and anion share a fraction of their hydration layers, and solvent-separated ion pairs (2SIP) where the two ions are separated by two hydration layers (see Figure 3A). For the OH bond and dipole dynamics of different types of water molecules engaged in those ion pairs in  $\text{Na}_2\text{SO}_4$  solutions at several concentrations, Figure 3B compares the slowdown directly measured in our simulations  $\rho_{\pm}$  and the slowdown predicted by combining the perturbations induced by isolated ions as  $\rho_+ \rho_-$ , that is, assuming that the changes in the reorientation free energy barrier induced by the two ions can be simply added. In the dilute 0.5 m solution, a high correlation is found between  $\rho_{\pm}$  and  $\rho_+ \rho_-$ , showing that the collective effect of the two ions is simply a combination of their respective effects taken separately.

However, for growing salt concentration, the slowdown experienced by water molecules in ion pairs increasingly exceeds the simple  $\rho_+ \rho_-$  combination (Figure 3), which shows that the retardation at high concentration is caused by more than the combined actions of two ions only. We now provide additional arguments suggesting that the increasing slowdown observed for the entire solution at high concentration cannot be explained by an increasing fraction of slow water molecules engaged in ion pairs. First, even though dielectric relaxation spectroscopy may underestimate the number of ion pairs since it is mostly sensitive to long-lived pairs, measurements suggested that in dilute  $\text{Na}_2\text{SO}_4$  solutions less than 20% of the ions are engaged in ion pairs and that this fraction decreases with concentration above 0.2 m.<sup>34</sup> Second, the retardation induced by these ion pairs cannot exceed their lifetime, which was found to be usually shorter than 10 ps in our simulations.

**Local Electric Field.** Since ion pairs cannot explain the deviation from the additive behavior at high concentration, we then consider more collective effects and whether the





**Figure 3.** Cooperativity and electric fields in salt solutions: (A) schematic representations of the SSIP and 2SIP configurations; (B) correlation plot between the retardation factor for the OH and dipole orientations of the different types of water molecules depicted in panel A, obtained from our simulations and from the combination of the individual slowdowns  $\rho_+\rho_-$  in  $\text{Na}_2\text{SO}_4$  solutions, respectively; (C) probability distributions of the electric field modulus experienced by a water H; (D) correlation diagram between the electric field and the average water reorientation time in solution.

slowdown could be due to an increase in the local electric field generated by all ions and water molecules. In our simulations we compute the electric field experienced by water hydrogen atoms (Figure 3C). While in  $\text{Na}_2\text{SO}_4$  solutions the field is very little affected by an increasing salt concentration, in  $\text{NaClO}_4$  solutions the field decreases markedly with increasing concentration. Both observations are consistent with experimental infrared spectral shifts.<sup>6,31</sup>

While in  $\text{Na}_2\text{SO}_4$  solutions the average water OH reorientation time in the solution increases approximately in proportion to the average electric field, it is almost the opposite in  $\text{NaClO}_4$  solutions where the reorientation time decreases for growing local electric field values (Figure 3D and Supporting Information). This thus clearly shows that the slowdown in water dynamics observed at high salt concentration cannot be understood by electrostatic considerations.

**Extended Jump Analysis.** We now use the framework of the extended jump model described above to identify the origin of the changes in water dynamics with salt concentration. In these ionic solutions, a water OH can be either hydrogen-bonded to another water oxygen, or bonded to an anion, or non-hydrogen-bonded. We neglect the initial fast (librational) decay since the dangling situation is unstable and transient, and we do not explicitly consider the influence of the cation which is  $\text{Na}^+$

in both salts and which only weakly perturbs water dynamics (Figure 1). The average water OH reorientation time in solution  $\langle\tau_{\text{reor}}\rangle$  can then be expressed as

$$\langle\tau_{\text{reor}}\rangle \simeq p_w \tau_{\text{reor}}^W + (1 - p_w) \tau_{\text{reor}}^A \quad (3)$$

where  $p_w$  is the fraction donating an HB to a water and  $\tau_{\text{reor}}^{W,A}$  are the reorientation times when the HB acceptor is respectively a water oxygen or an anion oxygen. Within the extended jump model, the reorientation time in each state is given by the jump and frame contributions (eq 2). At a given salt concentration  $c$ , the difference between  $\langle\tau_{\text{reor}}\rangle$  and the pure water reorientation time can then be decomposed into distinct contributions,

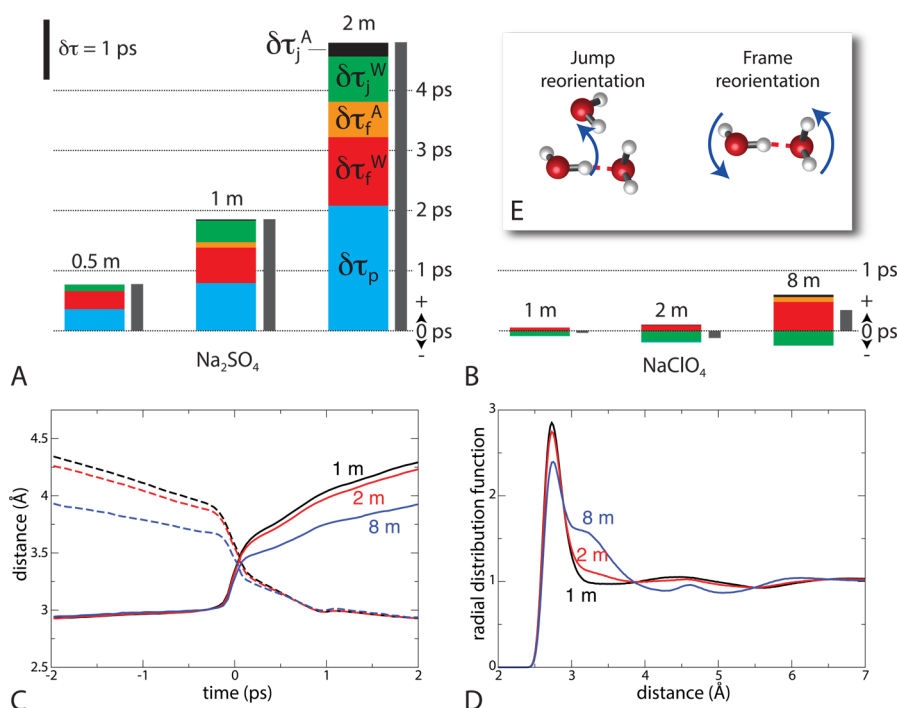
$$\langle\tau_{\text{reor}}(c)\rangle - \tau_{\text{reor}}^{\text{bulk}} = \delta\tau_p(c) + \delta\tau_f^W(c) + \delta\tau_f^A(c) + \delta\tau_j^W(c) + \delta\tau_j^A(c) \quad (4)$$

where  $\delta\tau_p$ ,  $\delta\tau_j^{W,A}$ ,  $\delta\tau_f^{W,A}$  arise respectively from the change in the  $p_w$  fraction, and changes in the  $\tau_{\text{reor}}^{\text{jump},W/A}$  and  $\tau_{\text{reor}}^{\text{frame},W/A}$  reorientation times. The  $\delta\tau_p$  change corresponds to the prediction of the additive picture, where the reorientation times within each population are constant.

At every concentration, each of these contributions can be estimated from our simulations (Supporting Information) in order to establish the main factors causing the slowdown in the salt solutions (Figure 4A,B). For  $\text{Na}_2\text{SO}_4$ , both the cation and the anion slow the dynamics of water when taken separately. It is thus not surprising that the dominant contribution to the growing slowdown with concentration arises from the increase in the population of water OH donating a HB to a sulfate ion, which is a strong retardant<sup>12</sup> ( $\delta\tau_p$ ). The next biggest contributions come from the slowdown in the frame reorientation times of waters donating a HB to another water or to an anion ( $\delta\tau_f^{W,A}$ ).

In  $\text{NaClO}_4$  solutions, the change in water dynamics with concentration is not monotonic. In dilute solutions the acceleration of  $\langle\tau_{\text{reor}}\rangle$  with salt concentration results from the acceleration of  $\tau_{\text{reor}}^{\text{jump},W}$  (Figure 4B), due to the introduction of  $\text{ClO}_4^-$  ions which bring a high density of labile HB acceptors in the solution, while at high concentration, the slowdown is clearly due to the increase in  $\tau_{\text{reor}}^{\text{frame},W}$ . We note that in the concentrated solutions studied in the experiments of refs 6 and 15 water reorientation thus proceeds almost exclusively through jumps.

Figure 4 reveals how all concentrated salt solutions can retard water dynamics, independently of the ions' nature and effect on water in dilute conditions. For both  $\text{NaClO}_4$  and  $\text{Na}_2\text{SO}_4$ , a key contribution to the water reorientation slowdown at high concentrations arises from the frame retardation. A qualitative interpretation of the latter slowdown can be obtained by first noticing that the diffusive<sup>35</sup> frame reorientation time scales with the solution viscosity (see Supporting Information) and second by applying Eyring's description of viscosity. Although this model is certainly not quantitative, it provides an insightful description in terms of microscopic jumps<sup>36</sup> which suggests that the frame reorientation time is proportional to  $\tau_{\text{jump}}/L^2$ , where  $L$  is the translational displacement induced by an HB jump (see Supporting Information). This can be used to provide a molecular interpretation of the frame slowdown in  $\text{NaClO}_4$  solutions, where  $\tau_{\text{jump}}$  decreases slightly with increasing salt concentration (Figure 4B) while  $L$  decreases markedly, as shown in the average jump mechanism (Figure 4C). While in dilute solutions the new HB acceptor most frequently



**Figure 4.** Contributions to the change in the average water reorientation time arising from the different terms in eq 4 at different concentrations for (A)  $\text{Na}_2\text{SO}_4$  and (B)  $\text{NaClO}_4$ . (C) Average distances between the rotating water oxygen and the initial (solid lines) and final (dashes) water HB acceptors during a jump event and (D) radial distribution functions between water oxygens in  $\text{NaClO}_4$  solutions of increasing concentration. (E) Schematic representation of the jump and frame reorientation motions.

originates from the second shell, in concentrated solutions salt-induced structural changes enhance the probability to find water HB acceptors in an interstitial position between the first and second shells, as shown by the radial distribution function Figure 4D. These structural changes have also been observed for many salt solutions by neutron scattering<sup>37</sup> (see Supporting Information). They lead to a decrease in the jump-induced translational displacement with increasing concentration and thus to a viscosity increase and to a frame reorientation slowdown. This partial decoupling between angular jumps and translational displacements could provide an interpretation for the absence of correlation between the collective reorientation and translation dynamics of water, measured by dielectric relaxation and optical Kerr effect spectroscopy in salt solutions of increasing concentration, respectively.<sup>38</sup> Similar arguments could also explain why a solute like urea slightly accelerates water dynamics at low concentration<sup>39</sup> but retards it at high concentration.<sup>40</sup> This important and sometimes dominant viscosity contribution which arises at high concentration regardless of the nature of the ions is clearly distinct from ion-specific contributions such as electrostatic or ion-pair effects. We underline that test calculations run with a different force field where polarization is described in an effective manner lead to the same conclusions (see Supporting Information), which strongly suggests that these results are robust.

**Interpretation of Experiments.** We now use our description to resolve the apparent contradiction between NMR and IR/THz experimental results and test some recent suggestions about the presence of cooperative effects in ionic solutions.

First, our results explain why NMR finds<sup>10–12</sup> that in dilute conditions some salts accelerate water reorientation dynamics while others slow it down. Our model suggests that the key

factor is the anion–water HB strength. The growing slowdown due to structural rearrangements and increasing viscosity at high concentration explains why a slowdown is measured by all techniques in concentrated salt solutions. Ultrafast infrared spectroscopy requires a high salt concentration (and a clear difference in reorientation times) to distinguish the dynamics of the water molecules affected by ions from that of the bulk, which explains why all of these studies so far<sup>5–7</sup> have observed a slowdown.

Our simulations, which were verified to satisfactorily reproduce the ultrafast anisotropy decays in several salt solutions (Figure 2), clearly show that both the semirigid propeller-like description and the cooperative immobilization of water molecules by special combinations of anions and cations that were recently suggested<sup>5</sup> to interpret those experiments are not valid, even qualitatively. First, regarding the propeller picture, our simulations show that, in agreement with other prior experiments,<sup>10–12</sup> water molecules are far from being systematically locked by ions since they are even accelerated by some ions, and their motion remains quite isotropic (Figure 1). Second, our work provides a test of the cooperative picture which had suggested<sup>5</sup> that for certain salts like  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$ , ions act cooperatively through long-ranged electrostatic interactions to lock individual water molecules and dramatically retard their reorientation dynamics. Our results on  $\text{Na}_2\text{SO}_4$  solutions (one of the salts studied in ref 5) unambiguously show that there is no such cooperative effect (Figure 3). In contrast, they support a picture where ions have a short-ranged influence on water,<sup>15–19</sup> and where the deviation from the additive behavior is strongly concentration-dependent and arises from the overlap of hydration shells and, more importantly, from the dramatic slowdown of the frame reorientation between HB jumps due to structural rearrangements. While this latter effect is collective, it is neither

electrostatic nor ion-specific. The different ultrafast anisotropy decays measured<sup>5</sup> for various salts can be rationalized within our picture and are suggested to arise from two effects. First some salts combine ions with similar effects on water dynamics (e.g., Na<sub>2</sub>SO<sub>4</sub> which leads to a strong slowdown) while others associate ions with opposite effects (e.g., Cs<sub>2</sub>SO<sub>4</sub> which induces a moderate slowdown). Second, vibrational lifetime effects were shown<sup>28</sup> to induce large differences between the measured anisotropy and the orientation tcf eq 1; for example the short OH stretch vibration lifetime next to Mg<sup>2+</sup> might explain the similar anisotropy decays for MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>, while Mg<sup>2+</sup> is a much stronger retardant than Na<sup>+</sup>.<sup>33</sup> We finally note that the THz dielectric relaxation results<sup>5</sup> which had also been interpreted by cooperative effects were recently explained<sup>18</sup> with only short-ranged additive ion effects, while the counterion influence observed<sup>9</sup> in Raman spectra was attributed<sup>9</sup> to the nonideality of the studied concentrated salt solution.

## CONCLUDING REMARKS

We have identified how ions in dilute and concentrated salt solutions alter the dynamics of water. Through a combination of simulations in agreement with experimental data and obtained with different force fields, together with a simple but potent extended jump model, we have shown that ions induce a strong but short-ranged static and dynamic water response. At low concentration, the impact of a salt on water dynamics is ion-specific and follows the simple additive picture. Depending on the interaction strength, dilute ions may retard or accelerate water dynamics relative to the bulk. In contrast, in concentrated solutions, the slowdown is observed for all salts and has an important contribution which is nonspecific and arises from an increase in viscosity due to a reduction in the translational displacements induced by HB jumps, also found in concentrated nonionic solutions. For weakly hydrated ions, this contribution is dominant, while for strongly hydrated ions it reinforces the ion-specific slowdown. Seemingly contradictory experimental results have thus been rationalized. While no cooperative effect due to the locking of water by some ion pairs could be found, our study highlights the key role played by the salt concentration. Further work is underway on the implications for enzyme catalysis focusing on explaining how different salt conditions affect the protein hydration layer lability and how ions may enhance the enzymatic activity.<sup>41</sup>

## ASSOCIATED CONTENT

### Supporting Information

Simulation methodology, force-field assessment, and electric field calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

pavel.jungwirth@uochb.cas.cz; damien.laage@ens.fr

### Present Addresses

<sup>¶</sup>(G.S.) Department of Chemistry, Columbia University, New York, USA

<sup>§</sup>(E.W.) Department of Chemistry, Lund University, Sweden

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank C.H. Giammanco and M.D. Fayer for providing the data in Figure 2A, and O. Marsalek for providing the ab initio molecular dynamics simulation described in the Supporting Information. P.J. thanks the Czech Science Foundation (Grant P208/12/G016) for support and the Academy of Sciences for the Praemium Academie award. Part of this work was accomplished while P.J. was a Visiting Professor at ENS. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Program (FP7/2007-2013)/ERC Grant Agreement No. 279977.

## REFERENCES

- (1) Kritzer, P. J. *Supercrit. Fluids* **2004**, *29*, 1–29.
- (2) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301–6.
- (3) Record, M. T.; Zhang, W.; Anderson, C. F. *Adv. Protein Chem.* **1998**, *51*, 281–353.
- (4) Lo Nostro, P.; Ninham, B. W. *Chem. Rev.* **2012**, *112*, 2286–322.
- (5) Tielrooij, K. J.; Garcia-Araez, N.; Bonn, M.; Bakker, H. J. *Science* **2010**, *328*, 1006–9.
- (6) Park, S.; Odelius, M.; Gaffney, K. J. *J. Phys. Chem. B* **2009**, *113*, 7825–35.
- (7) Park, S.; Fayer, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 16731–8.
- (8) Moilanen, D. E.; Wong, D.; Rosenfeld, D. E.; Fenn, E. E.; Fayer, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 375–80.
- (9) Heisler, I. A.; Mazur, K.; Meech, S. R. *J. Phys. Chem. B* **2011**, *115*, 1863–73.
- (10) Engel, G.; Hertz, H. G. *Ber. Bunsen.-Ges. Phys. Chem.* **1968**, *72*, 808–34.
- (11) Endom, L.; Hertz, H. G.; Thül, B.; Zeidler, M. D. *Ber. Bunsen. Phys. Chem.* **1967**, *71*, 1008–31.
- (12) Marcus, Y. *Chem. Rev.* **2009**, *109*, 1346–70.
- (13) Wachter, W.; Kunz, W.; Buchner, R.; Heftner, G. *J. Phys. Chem. A* **2005**, *109*, 8675–83.
- (14) Kim, J. S.; Wu, Z.; Morrow, A. R.; Yethiraj, A.; Yethiraj, A. *J. Phys. Chem. B* **2012**, *116*, 12007–13.
- (15) Omta, A. W.; Kropman, M. F.; Woutersen, S.; Bakker, H. J. *Science* **2003**, *301*, 347–9.
- (16) Soper, A. K.; Weckström, K. *Biophys. Chem.* **2006**, *124*, 180–91.
- (17) Smith, J. D.; Saykally, R. J.; Geissler, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 13847–56.
- (18) Funkner, S.; Niehues, G.; Schmidt, D. A.; Heyden, M.; Schwaab, G.; Callahan, K. M.; Tobias, D. J.; Havenith, M. *J. Am. Chem. Soc.* **2012**, *134*, 1030–5.
- (19) Lin, Y.-S. S.; Auer, B. M.; Skinner, J. L. *J. Chem. Phys.* **2009**, *131*, 144511.
- (20) Wernersson, E.; Jungwirth, P. *J. Chem. Theory Comput.* **2010**, *6*, 3233–40.
- (21) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157–1204.
- (22) Mancinelli, R.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. *J. Phys. Chem. B* **2007**, *111*, 13570–17.
- (23) Galamba, N. *J. Phys. Chem. B* **2012**, *116*, 5242–50.
- (24) Van der Maarel, J. R. C.; Lankhorst, D.; De Bleijser, J.; Leyte, J. C. *J. Phys. Chem.* **1986**, *90*, 1470–8.
- (25) Ropp, J.; Lawrence, C.; Farrar, T. C.; Skinner, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 8047–52.
- (26) Laage, D.; Hynes, J. T. *Science* **2006**, *311*, 832–5.
- (27) Laage, D.; Stirnemann, G.; Sterpone, F.; Rey, R.; Hynes, J. T. *Annu. Rev. Phys. Chem.* **2011**, *62*, 395–416.
- (28) Laage, D.; Hynes, J. T. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 11167–72.
- (29) Boisson, J.; Stirnemann, G.; Laage, D.; Hynes, J. T. *J. Phys. Chem. Chem. Phys.* **2011**, *13*, 19895–901.

- (30) Omta, A. W.; Kropman, M. F.; Woutersen, S.; Bakker, H. J. *J. Chem. Phys.* **2003**, *119*, 12457–61.
- (31) Giammanco, C. H.; Wong, D. B.; Fayer, M. D. *J. Phys. Chem. B* **2012**, *116*, 13781–92.
- (32) Jenkins, H. D. B.; Marcus, Y. *Chem. Rev.* **1995**, *95*, 2695–724.
- (33) Marcus, Y.; Hefter, G. *Chem. Rev.* **2006**, *106*, 4585–621.
- (34) Buchner, R.; Capewell, S. G.; Hefter, G.; May, P. M. *J. Phys. Chem. B* **1999**, *103*, 1185–92.
- (35) Laage, D.; Hynes, J. T. *J. Phys. Chem. B* **2008**, *112*, 14230–42.
- (36) Kincaid, J. F.; Eyring, H.; Stearn, A. E. *Chem. Rev.* **1941**, *28*, 301–65.
- (37) Leberman, R.; Soper, A. K. *Nature* **1995**, *378*, 364–6.
- (38) Turton, D. A.; Hunger, J.; Hefter, G.; Buchner, R.; Wynne, K. J. *Chem. Phys.* **2008**, *128*, 161102.
- (39) Bagno, A.; Lovato, G.; Scorrano, G.; Wijnen, J. W. *J. Phys. Chem.* **1993**, *97*, 4601–7.
- (40) Shimizu, A.; Fumino, K.; Yukiya, K.; Taniguchi, Y. *J. Mol. Liq.* **2000**, *85*, 269–78.
- (41) Eppler, R. K.; Komor, R. S.; Huynh, J.; Dordick, J. S.; Reimer, J. A.; Clark, D. S. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 5706–10.