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2005 J. Phys.: Condens. Matter 17 S3215

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Effect of ions on the structure and dynamics of liquid water

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Received 28 September 2005

Published 28 October 2005

Online at stacks.iop.org/JPhysCM/17/S3215

Abstract

We use femtosecond two-colour mid-infrared spectroscopy to study the dynamics of aqueous solutions of salts in HDO:D₂O. We find that the lifetime of the O–H stretch vibration of HDO molecules in the solvation shell of the halogenic anions Cl[−], Br[−], and I[−] is much longer than the lifetime of the O–H stretch vibration of the HDO molecule in bulk D₂O solution. This difference in lifetime allows for a clear separation of the response of the solvation shell from that of the bulk liquid. We observe that the solvating HDO molecules show much slower hydrogen-bond and reorientation dynamics than bulk water molecules. In contrast, the dynamics of the water molecules outside the first ionic hydration shell are observed to be negligibly affected by the ions.

1. Introduction

An important problem in the experimental study of the properties of aqueous solvation interactions is the distinction of the response of the solvating water molecules from that of the other (bulk) water molecules. This problem can be solved by studying small clusters of a molecule or ion surrounded by a few water molecules in the gas phase [1, 2]. However, in studies of this kind on clusters of ions and water the solvation structure was observed to depend strongly on the number of water ligands [3]. For small numbers of ligands, the water molecules tend to cluster at one side of the ion (surface structures) [3], and only at large numbers of liquid water molecules does the ion get truly encaged by the water molecules (internal structures).

The structure of the solvation shells of ions in bulk aqueous solutions has also been investigated with NMR [4], x-ray and neutron diffraction [5, 6]. Unfortunately, these techniques do not give information on the dynamics of aqueous solvation shells, because the timescales involved in these techniques are much longer than the typical lifetimes of the solvation structures. Hence, the present knowledge of these dynamics mainly originates from molecular dynamics simulations [7, 8].

Recently, it was shown that molecular-scale information on the hydrogen-bond dynamics and energy relaxation dynamics of liquid water can be obtained with femtosecond mid-infrared spectroscopy [9–14]. Here we report on the use of this technique to study the effects of ions on the hydrogen-bond structure and dynamics of liquid water.

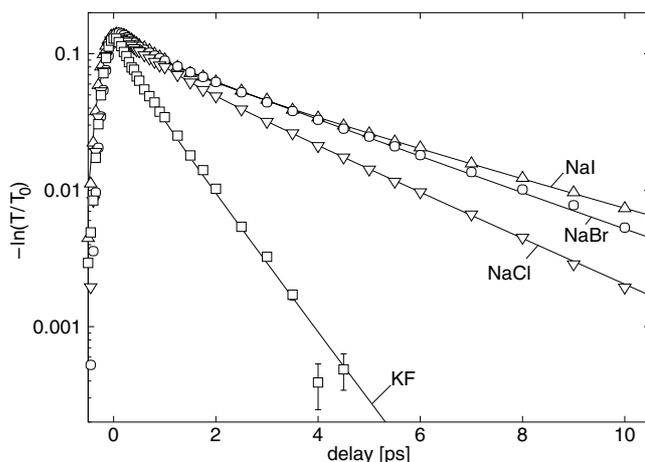


Figure 1. Pump–probe transients measured for aqueous solutions of different salts in HDO:D₂O. The transients were measured using a pump frequency of 3450 cm⁻¹ and a probe frequency of 3200 cm⁻¹.

2. Experimental details

We performed two-colour femtosecond mid-infrared pump–probe experiments on a dilute (0.1 M) solution of HDO dissolved in D₂O that contains a high concentration (0.5–6 M) of salt (KF, NaCl, NaBr, NaI, NaClO₄, Mg(ClO₄)₂). The pump pulse excites the O–H stretch vibration of approximately 5% of the HDO molecules to the first excited state ($v = 1$). This excitation leads to a bleaching of the linear absorption spectrum ($\ln(T/T_0) > 0$, with T the transmission of the probe and T_0 the transmission of the probe in absence of the pump), due to the depletion of $v = 0$ and stimulated emission out of $v = 1$, and to an induced absorption ($\ln(T/T_0) < 0$) at lower frequencies due to the $1 \rightarrow 2$ transition. The latter absorption is redshifted by approximately 270 cm⁻¹ with respect to the $0 \rightarrow 1$ transition, due to the anharmonicity of the O–H stretch vibration.

The wavelength of the pump and probe pulses can be varied between 2.7 and 4 μm . The pulses have a typical energy of 20/0.1 μJ (pump/probe) and a duration of approximately 200 fs [11]. The pump and probe pulses are independently tunable, and have a bandwidth of 80 and 60 cm⁻¹, respectively.

3. Vibrational relaxation of aqueous salt solutions

In figure 1 pump–probe transients are shown that are measured for four different salt solutions. For the solution of KF, the relaxation can be modelled with a single exponential decay with a time constant of 0.7 ± 0.2 ps. For the solutions of NaCl, NaBr, and NaI, the observed transients can be modelled as a sum of two exponential components, of which the first has a time constant of 0.8 ± 0.2 ps, and the second a time constant that depends on the dissolved salt. For NaCl, NaBr, and NaI we find time constants of 2.6 ± 0.3 , 3.4 ± 0.3 , and 3.9 ± 0.3 ps, respectively. The amplitude of the second component increases with increasing concentration of dissolved salt. Interestingly, changing the nature of the cation has little effect on the experimental observations: solutions of KCl and NaCl of equal molarity give similar results. In view of these observations, the second component is assigned to HDO molecules that solvate the halogenic anion via the

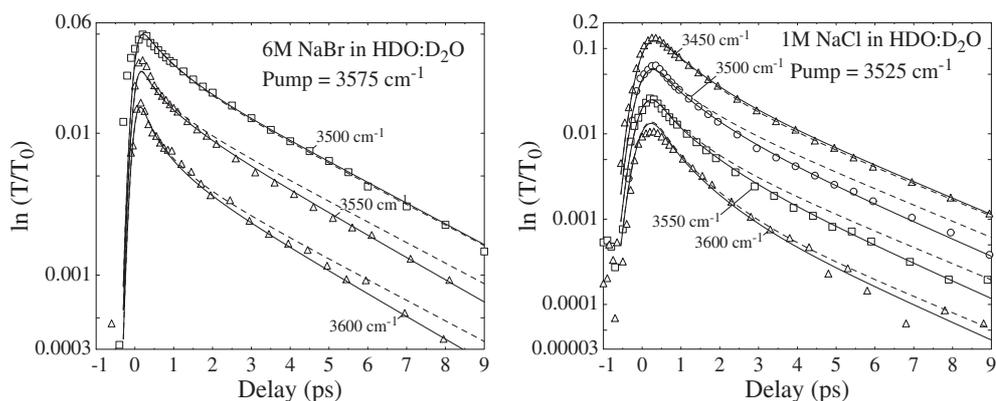


Figure 2. Pump-probe transients for solutions of 6 M NaBr and 1 M NaCl in HDO:D₂O. The solid curves are calculated with a Brownian oscillator model using a time constant τ_c of 25 ps for the O-H \cdots Br $^-$ hydrogen bond and of 12 ps for the O-H \cdots Cl $^-$ hydrogen bond. The dashed curves are calculated with the same model using $\tau_c = \infty$.

formation of an O-H \cdots X $^-$ hydrogen bond (with X $^-$ = Cl $^-$, Br $^-$, I $^-$). This means that the time constant of the second component corresponds to the lifetime T_1 of the O-H vibration of HDO molecules that are hydrogen bonded with their O-H group to the anion. For solutions containing F $^-$, we do not observe a slow second component, which shows that the vibrational relaxation of O-H groups that are hydrogen bonded to F $^-$ is not slower than the vibrational relaxation of the O-H stretch vibration of bulk HDO:D₂O. The latter relaxation has a time constant of 0.8 ps [9].

The differences in vibrational lifetimes can be employed to distinguish the dynamics of the anionic hydration shells from the rest of the liquid. After excitation with a pump pulse with a frequency near 3400 cm $^{-1}$, the bulk vibrational excitations decay with a time constant of \sim 0.8 ps. Hence, for solutions containing Cl $^-$, Br $^-$, or I $^-$ ions, the signals observed after a few picoseconds only represent the response of water molecules that form O-H \cdots X $^-$ hydrogen bonds (X = Cl, Br, I), thus allowing a very selective study of the dynamics of the solvation shells of these ions. Unfortunately, because the vibrational relaxation of water molecules forming O-H \cdots F $^-$ hydrogen bonds is too fast, this method cannot be used to study the dynamics of the solvation shell of the F $^-$ ion.

4. Hydrogen-bond structure and dynamics of the anionic hydration shell

In figure 2 pump-probe transients of solutions of 6 M NaBr and 1 M NaCl in HDO:D₂O are presented. The time constant of the second relaxation component shows a small but significant dependence on the probe frequency. To illustrate this more clearly, figure 2 contains dashed curves that run parallel at large delay times (>3 ps). The decay time constant is observed to increase with increasing frequency difference between pump and probe. If the pump is at 3575 cm $^{-1}$, the fastest decay is observed at 3600 cm $^{-1}$ and the slowest decay at 3500 cm $^{-1}$. If the pump is at 3525 cm $^{-1}$, the fastest decay is observed at 3500 cm $^{-1}$ and the slowest decay at 3600 cm $^{-1}$. This frequency dependence of the decay time results from the spectral diffusion of the excitation frequency. Due to this spectral diffusion process, excited molecules diffuse (spectrally) away from the excitation frequency, which leads to a faster decay at probe frequencies close to the pump frequency and a slower decay at probe frequencies that

Table 1. The central frequency ω_{eg} , width $\Delta\omega$, vibrational lifetime T_1 and spectral diffusion time τ_c of the O–H stretch vibration of different hydrogen-bonded O–H groups, obtained by fitting the time-resolved measurements to a two-component Brownian oscillator model.

	ω_{eg} (cm ⁻¹)	$\Delta\omega$ (cm ⁻¹)	T_1 (ps)	τ_c (ps)
O–H...O	3420 ± 10	280 ± 20	0.8 ± 0.1	0.5 ± 0.2
O–H...Cl ⁻	3440 ± 15	160 ± 15	2.6 ± 0.3	12 ± 3
O–H...Br ⁻	3470 ± 15	130 ± 15	3.0 ± 0.3	25 ± 5
O–H...I ⁻	3490 ± 15	105 ± 15	3.7 ± 0.3	18 ± 5

significantly differ from the pump frequency. The spectral diffusion reflects the fluctuations in the length of the hydrogen bond between the ion and the solvating HDO molecule [15]. In order to determine the correlation time constant τ_c of the spectral diffusion, we modelled the data of figure 2 with a Brownian oscillator model. All transients can be well fitted with two Brownian oscillators that represent the O–H...O and O–H...X⁻ components. In table 1, the resulting parameters are presented. For all solutions, we obtain the same set of parameters for the O–H...O component. These parameters are quite similar to those found for a pure solution of HDO dissolved in D₂O [10, 11].

It follows from table 1 that the central frequency of the absorption band of the O–H...X⁻ component increases in the halogenic series Cl⁻, Br⁻, and I⁻, and that the width of the absorption band decreases. Both trends reflect a decrease of the strength of the hydrogen-bond interaction between the solvating HDO molecule and the anion. From the width of the absorption component, a width of the distribution of hydrogen-bond lengths can be deduced by using the relation between the O–H stretch vibrational frequency and the length of the hydrogen bond [15]. This relation has been measured for many hydrogen-bond acceptors including the halogenic anions. For the O–H...Cl⁻, O–H...Br⁻, and O–H...I⁻ hydrogen bonds, widths of the length distribution are obtained of 20 ± 5 pm (=10⁻¹² m), 21 ± 5 pm, and 12 ± 4 pm, respectively (the mean lengths of these hydrogen bonds are 320, 340, and 360 pm, respectively). These widths of the distributions of O–H...X⁻ hydrogen-bond lengths are relatively small compared to the width of 36 ± 2 pm of the distribution of O–H...O hydrogen-bond lengths of HDO:D₂O. The narrow width and long τ_c of the O–H...X⁻ absorption component imply that the water molecules in the first solvation shell of the X⁻ halogenic anion form a relatively stable and well-defined structure.

The values of τ_c of the hydration shells of Cl⁻, Br⁻, and I⁻ will be similar to (but not exactly the same as) the residence time of the water molecule in the solvation shell. The residence times of water in the solvation shell of the halogenic ions have been calculated with MD simulations. For Cl⁻, a residence time in the first hydration shell of 12 ps was calculated [16], for Br⁻ a residence time of 19 ps [17], and for I⁻ a residence time of 7.4 ps, [18]. These values are all in quite good agreement with the values of τ_c .

The value of τ_c of the hydration shells of Cl⁻, Br⁻, and I⁻ is 20–50 times longer than for bulk liquid water. This large difference in τ_c likely results from differences in local structure. Bulk liquid water possesses a disordered three-dimensional structure for which the energy cost of a local lengthening of a hydrogen bond can be largely compensated for by a shortening of hydrogen bonds at other positions. Hence, the energy barriers for reorganizing bulk liquid water are relatively small (much smaller than the hydrogen-bond binding energy), resulting in fast hydrogen-bond dynamics. Probably the energy required for deforming the solvation shell cannot as easily be compensated by strengthening other hydrogen bonds to the ion. Therefore, the energy barrier for changing the length of the hydrogen bond to the solvation shell is relatively high, resulting in relatively slow dynamics.

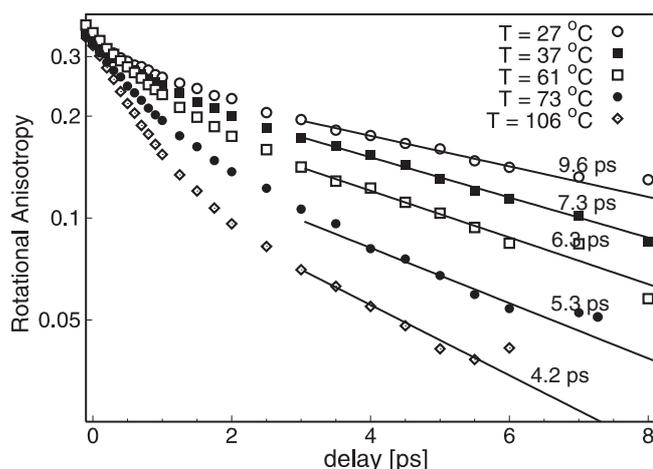


Figure 3. R as a function of delay τ for a solution of 3 M NaCl in HDO:D₂O at five different temperatures. The pump frequency is 3450 cm⁻¹ and the probe frequency is 3200 cm⁻¹.

Further information on the hydrogen-bond dynamics of the hydration shells can be obtained by measuring the time dependence of the anisotropy of the excitation of the O–H stretch vibration. The excitation is anisotropic, because HDO molecules that have their O–H stretch vibration oriented along the polarization of the excitation pulse are excited preferentially. Due to this anisotropic population of excited molecules, the absorption change $\Delta\alpha_{\parallel}$ for the case where the probe polarization is parallel to the pump polarization will be larger than the absorption change $\Delta\alpha_{\perp}$ for the case where the probe polarization is perpendicular to the pump polarization. From $\Delta\alpha_{\parallel}$ and $\Delta\alpha_{\perp}$, the rotational anisotropy can be calculated:

$$R = \frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp}}. \quad (1)$$

The denominator of equation (1) represents the isotropic signal that is not affected by the reorientation. Hence, the delay dependence of R directly represents the orientational dynamics of the water molecules, because isotropic effects like vibrational relaxation and spectral diffusion are divided out.

In figure 3, the anisotropy parameter R is presented as a function of delay for a solution of 3 M NaCl in HDO:D₂O at different temperatures. All signals show a non-exponential decay, but this becomes single exponential for delays >3 ps. After this delay time, the signals only represent the orientational dynamics of the HDO molecules in the first solvation shell of the Cl⁻ ion, due to the difference in vibrational lifetime of the O–H···O and the O–H···Cl⁻ groups. Also shown in figure 3 are fits to the data in the delay-time window from 3 to 8 ps. At 27 °C, τ_{or} of these HDO molecules is 9.6 ± 0.6 ps, which is long in comparison with the value of τ_{or} of 2.6 ps of HDO molecules in a solution of HDO in D₂O [19]. With increasing temperature, the orientational relaxation becomes faster: τ_{or} decreases to 4.2 ± 0.4 ps at 106 °C.

From the observation that τ_{or} is shorter than τ_{c} , it follows that the orientational dynamics of the HDO molecules in the first solvation shell of the Cl⁻ ion must result from motions that do not contribute to the spectral diffusion, i.e. that do not affect the length of the O–H···Cl⁻ hydrogen bond. Hence, the observed reorientation represents the orientational diffusion of the *complete solvation structure*. This result suggests that the dynamics of the anisotropy R can be modelled with the following equation that is derived from the Stokes–Einstein relation for

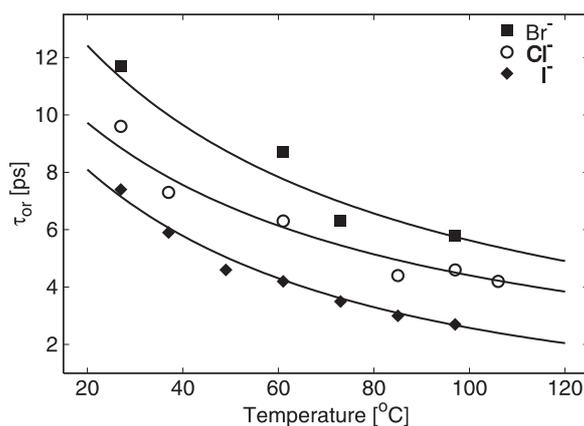


Figure 4. τ_{or} of the solvation shells of Cl^- , Br^- , and I^- as a function of temperature. The solid curves represent fits of the data using equation (2).

orientational diffusion:

$$\tau_{or}(T) = \frac{4\pi\eta(T)r_{h,solv}^3}{3kT} \quad (2)$$

with $\eta(T)$ the temperature-dependent viscosity, $r_{h,solv}$ the hydrodynamic radius of the solvation structure, and k Boltzmann's constant. In figure 4, the orientational diffusion time constants τ_{or} of the first solvation shell of the halogenic anions Cl^- , Br^- , and I^- are presented as a function of temperature. Also shown in figure 4 are fits to the data using equation (2). The temperature-dependent viscosities were obtained from the literature [20], leaving the radius $r_{h,solv}$ as the only parameter. For the hydrodynamic radii we find $r_{h,solv}(\text{Cl}^-) = 213$ pm, $r_{h,solv}(\text{Br}^-) = 237$ pm, and $r_{h,solv}(\text{I}^-) = 205$ pm.

The values of $r_{h,solv}$ are much smaller than expected. The value of $r_{h,solv}$ is expected to be comparable to the anion–water hydrogen-bond length: $r_{HB}(\text{Cl}^-) = 323$ pm, $r_{HB}(\text{Br}^-) = 340$ pm, and $r_{HB}(\text{I}^-) = 360$ pm [15]. This deviation illustrates that the Stokes–Einstein relation is only valid for macroscopic objects, as was to be expected. In the present case the diffusing objects are of about equal size as the molecules of the viscous liquid. In this regime the orientational mobility is governed by the specific interactions between the solvation shell and its surroundings. If these molecular interactions were to have led to the same friction as the macroscopic viscosity, the reorientation would have been 5–10 times slower than observed.

5. Hydrogen-bond structure outside the anionic hydration shell

An interesting question is how the water *outside* the first solvation shell compares to bulk water. The hydrogen-bond dynamics of this water can best be studied using aqueous salt solutions for which the water molecules solvating the anion are spectrally separated from the spectral response of the other water molecules. For solutions containing perchlorate (ClO_4^-) salts, the $\text{OH}\cdots\text{ClO}_4^-$ absorption band of the hydration shell of the anion is quite well spectrally separated from the $\text{OH}\cdots\text{O}$ absorption band of bulk water molecules. The $\text{OH}\cdots\text{ClO}_4^-$ absorption band has its maximum at 3575 cm^{-1} [21], while the absorption band of O–H groups hydrogen bonded to D_2O molecules peaks at 3400 cm^{-1} .

In figure 5 it is shown that the anisotropy decay is non-exponential when the pump and probe pulses are resonant with the $\text{OH}\cdots\text{ClO}_4^-$ absorption band. After ~ 3 ps the decay becomes single exponential, and only represents the orientational dynamics of OH groups

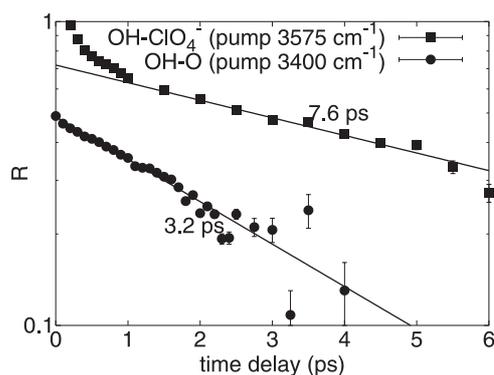


Figure 5. R as a function of delay τ for a solution of 6 M NaClO_4 in $\text{HDO}:\text{D}_2\text{O}$.

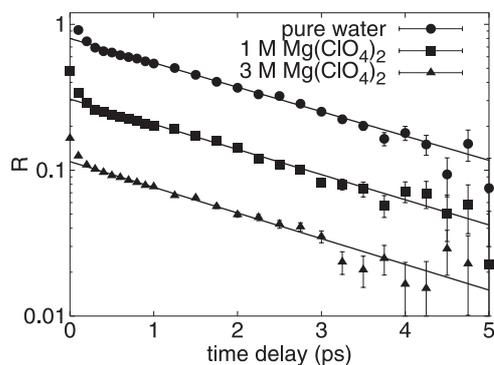


Figure 6. Delay dependence of R for solutions of 0, 1, and 3 M $\text{Mg}(\text{ClO}_4)_2$ in $\text{HDO}:\text{H}_2\text{O}$.

bonded to ClO_4^- , because of the difference in vibrational lifetime between the anion-bonded (2.2 ps), and the water-bonded O–H vibrations (0.8 ps). When the pump and probe are resonant with the O–H \cdots O band, the observed anisotropy decay is single exponential over the whole delay-time range, and only represents the orientational relaxation of HDO molecules hydrogen bonded to D_2O molecules.

To measure the effect of ions on the dynamics outside the first hydration shell, we studied aqueous solutions of $\text{Mg}(\text{ClO}_4)_2$. We chose $\text{Mg}(\text{ClO}_4)_2$, because Mg^{2+} is considered to be a strong structure-making ion: the viscosity of 1 M $\text{Mg}(\text{ClO}_4)_2$ is about 30% higher than the viscosity of pure water. If the higher viscosity of a $\text{Mg}(\text{ClO}_4)_2$ solution were caused by a homogeneous change in the stiffness of the hydrogen-bond network, the reorientation time of individual water molecules solution should be much larger in a concentrated $\text{Mg}(\text{ClO}_4)_2$ solution than in pure liquid water.

In figure 6, the measured decay of R for solutions of 0, 1, and 3 M $\text{Mg}(\text{ClO}_4)_2$ in $\text{HDO}:\text{H}_2\text{O}$ is shown. In these measurements, the OD \cdots O band was pumped and probed at the $0 \rightarrow 1$ transition using pump and probe pulses at 2500 cm^{-1} . We used the O–D vibration to probe the bulk water orientational dynamics, because, due to its long vibrational lifetime of 1.7 ps [22], this vibration allows us to measure the anisotropy decay over a much longer delay time interval than when the O–H vibration is probed.

Surprisingly, figure 6 shows that the decay of R is independent of the salt concentration, which means that the orientational correlation time τ_{or} for the water-bonded O–D groups is not affected by the presence of Mg^{2+} and ClO_4^- ions. These water-bonded O–D groups represent

both bulk HDO molecules and HDO molecules in the solvation shell of the cation (with their O–H groups pointing away from the cation). From fits of the data to a single exponential, we found the same value for τ_{or} of 2.5 ± 0.1 ps at all concentrations. This value agrees well with the orientational correlation time of pure liquid water that was measured with femtosecond mid-infrared spectroscopy [19], NMR [23] and terahertz spectroscopy [24].

6. Viscosity effects of ions on water

Although the results of the previous section show that ions have a small effect on the hydrogen bonds outside the anionic solvation shell, it is well known that ions can make liquid water much more viscous. This increase in viscosity has been considered to be one of the prime indications for the strong structure-making effect of ions like Mg^{2+} . However, it should be realized that viscosity is a macroscopic property that represents the average behaviour of a large number of water molecules in an aqueous solution. Clearly, this average behaviour is only a good measure for the behaviour of individual molecules in the aqueous solutions if all molecules were to show similar molecular dynamics. However, the findings in the previous sections show that the effects of ions on the orientational mobility are in fact extremely inhomogeneous. In the first hydration shell, the orientational dynamics are observed to be slower by a factor 3–5 and the translational dynamics by a factor 20–50 than the corresponding dynamics of pure liquid water. Beyond this shell, there is no measurable difference with pure liquid water. This means that an aqueous salt solution should not be viewed as a homogeneous liquid with a modified but uniform intermolecular interaction, but rather as a colloidal suspension of inert particles in pure liquid water, with the particles formed by the ions and their first hydration shells. In this picture, the viscosity at low concentration can be described by the Einstein equation [25]:

$$\frac{\eta - \eta_0}{\eta_0} \approx 2.5\phi$$

with ϕ the volume fraction of the spheres.

It follows from this equation that a 30% increase of the viscosity, as observed for a 1 M $\text{Mg}(\text{ClO}_4)_2$ solution, can be obtained with a solution of 3 M suspended spheres that have a radius of about 250 pm. This colloidal radius compares quite well with the typical radius of an ion and its first hydration shell of water molecules. Hence, the increase in viscosity upon adding ions to liquid water can indeed be explained from the rigid nature of the solvation structure formed by the ion and its first hydration shell. The thus determined colloidal radius forms an average of the colloidal radii of the cations and the anions. From a comparison of the viscosities of different solutions it should be possible to determine the colloidal radius of each of the separate ions.

7. Conclusions

We studied the effects of ions on the hydrogen-bond structure and dynamics of liquid water (HDO:D₂O). We find that the O–H stretch vibration of HDO has a much longer vibrational lifetime in the solvation shells of Cl^- ($T_1 = 2.6$ ps), Br^- ($T_1 = 3.0$ ps), and I^- ($T_1 = 3.7$ ps) than in the bulk ($T_1 = 0.8$ ps). As a result, the spectral and orientational dynamics of the solvating HDO molecules can be measured with great selectivity. The results of these measurements are summarized in figure 7. This figure illustrates that the water molecules in the hydration shell of an I^- ion show much slower translational and orientational dynamics than the water molecules in the bulk liquid.

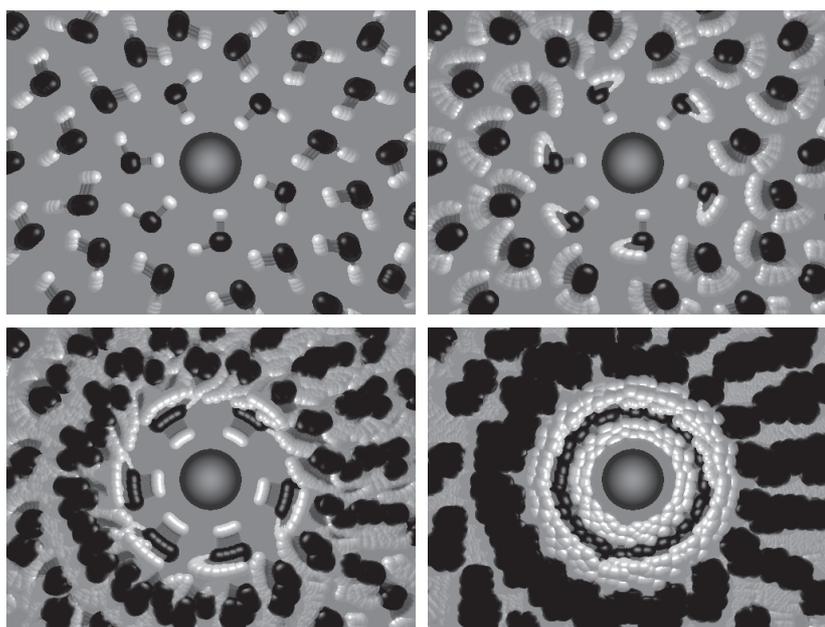


Figure 7. An I^- ion solvated by water in liquid solution. The water molecules in the hydration shell show translational (hydrogen-bond stretching) and orientational dynamics with characteristic time constants of 18 and 10 ps. Outside the shell these dynamics have time constants of 0.5 and 2.6 ps, respectively. The figure is an artist's impression showing four pictures of the liquid taken with shutter times of 1 ps (top left) 4 ps (top right), 10 ps (lower left), and 30 ps (lower right).

Outside the first hydration shell, the ion is observed to have surprisingly little effect on the strength of the hydrogen-bond interactions between the water molecules. Therefore the influence of ions on the viscosity of water should not be explained from their ability to enhance or weaken the hydrogen-bonded network, but rather from the rigidity of their first hydration shells.

Acknowledgments

The research presented in this paper is part of the research program of the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)', which is financially supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)'.

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