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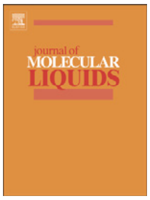

# Femtosecond study of the effects of ions on the reorientation dynamics of water

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ABSTRACT

We study the effects of ions on the reorientation dynamics of liquid water with polarization-resolved femtosecond mid-infrared spectroscopy. We probe the anisotropy of the excitation of the O–D stretch vibration of HDO molecules in solutions of NaCl, NaI and $N(alkyl)_4Br$ (tetra-alkylammoniumbromide) salts in 8% HDO:$H_2O$. We find that the reorientation of the O–D groups of HDO molecules hydrating the $Cl^-$ and $I^-$ anions occurs on two different time scales with time constants of $2 \pm 0.3$ ps and $9 \pm 2$ ps. The fast component is due to a wobbling motion of the O–D group that keeps the hydrogen bond with the halogenic anion intact. For solutions of $N(alkyl)_4Br$ salts we observe a very strong slowing down of the reorientation of water that is associated with the hydration of the hydrophobic alkyl groups of the $N(alkyl)_4^+$ ions.

## 1. Introduction

Water plays an essential role in the determination of the spatial structure of (bio)molecules and (bio)molecular ions. Examples of this role of water are the hydrophobic collapse in the folding of proteins and the self-organized formation of cell membranes [1]. However, the interactions between water and a solute not only determine the properties of the solute, these interactions also change the structure and dynamics of water itself.

Water molecules close to a solute or interface tend to show slower orientational dynamics than in bulk liquid water. For hydrophylic solutes and surfaces the slowing down can be explained from the specific interactions between the water molecules and the solute/surface. These interactions can take the form of a hydrogen-bond or can be purely electrostatic.

The electric fields exerted by ionic charges lead to a strong ordering of the surrounding water. In earlier times it was thought that the effects of ions on water structure were quite long range and would extend well beyond the first hydration layer [2]. Some ions were thus referred to as structure makers, others as structure breakers. However, recent experimental and theoretical work showed that for most ions the effect on the structure and dynamics of water is limited to only one or two hydration layers [3–7]. Only for specific combinations of ions, like $Mg^{2+}$ and $SO_4^{2-}$, it was found that the water dynamics can be impeded over relatively long ranges [8].

Hydrophobic surfaces also influence the structure and dynamics of water due to the fact that hydrophobic molecular groups take up space in the hydrogen-bond network of the water liquid. This occupation of space has profound effects on the free energy of the solute and its hydration shell. These effects depend on the size of the hydrophobe [9]. Small hydrophobes (<1 nm) can be accommodated in the hydrogen-bond network of water without significantly breaking the hydrogen bonds, similar as one may create a hole in loosely woven fabric by distorting the pattern of the threads without needing to break them [10]. The water molecules form tangential hydrogen bonds to each other along the hydrophobic surface, and the water density near this surface is larger than in the bulk [9]. For large hydrophobic structures (>1 nm), the water hydrogen-bond network is truncated near the hydrophobic surface. In this case, the water density is lower near the surface than in the bulk. If two hydrophobes merge, the solvation free energy is reduced, which forms the driving force of the hydrophobic collapse. The occupation of space in the hydrogen-bond network of water also explains the slowing down of the dynamics of nearby water molecule. The reorientation of a water molecule in bulk water involves the collective repositioning of several water molecules, and these collective dynamics are hindered by the presence of the hydrophobe [11–13].

In this paper we study the effects of different ions on the orientational mobility of water molecules. We probe these dynamics with polarization-resolved femtosecond mid-infrared spectroscopy. We study the combined effects of electrostatic and hydrophobic interactions on the dynamics of water by measuring the dynamics of water in the hydration shells of different $N(alkyl)_4^+$ (tetraalkylammonium) ions.

## 2. Experiment

We study the dynamics of water molecules in salt solutions by monitoring the reorientation of HDO molecules in isotopically diluted water (4% $D_2O$ in $H_2O = 8\%$ HDO:$H_2O$). These orientational dynamics

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are measured by probing the anisotropy dynamics of excited O–D vibrations with polarization-resolved femtosecond mid-infrared (fs-IR) pump-probe spectroscopy. This technique requires intense femtosecond light pulses at a wavelength of 4 μm (2500 $\text{cm}^{-1}$). These pulses are obtained via parametric amplification processes that are pumped by the pulses of a regeneratively amplified Ti:sapphire laser system (Spectraphysics Hurricane).

The Ti:sapphire laser system generates pulses at a wavelength of 800 nm with a pulse energy of ~900 μJ at a repetition rate of 1 kHz. The output of the laser is split into two parts. The first part is used to pump a white-light seeded Optical Parametric Amplifier (OPA) based on a $\beta$-bariumborate (BBO) crystal (Spectra Physics). The BBO crystal is angle tuned to generate light at 1.3 μm (signal) and 2 μm (idler). The idler is frequency doubled in a second BBO crystal to a wavelength of 1 μm. This 1 μm pulse is used as a seed in a parametric amplification process in a potassium niobate crystal (KNB) crystal that is pumped with the remaining part of the 800 nm beam. In this latter process pulses are generated with a central wavelength of 4 μm, a pulse energy of 5 μJ, and a pulse duration of 120 fs.

The 4 μm pulses are sent onto a wedged $CaF_2$ plate. The transmitted part (~90%) serves as the pump in the polarization-resolved pump-probe experiment. The reflection from the front side is sent into a variable delay stage with a resolution of 3 fs. This fraction forms the probe. With the delay stage we vary the time delay $t$ between pump and probe. The reflection from the back side of the wedged $CaF_2$ plate serves as a reference. The pump is transmitted through a λ/2 plate to rotate its polarization at 45° with respect to the probe. The pump, probe and reference are all focused in the sample using a gold-coated parabolic mirror, but only the pump and the probe are in spatial overlap. After the sample, the probe and the reference are dispersed with an Oriel monochromator and detected with the two lines of an Infrared Associates 2 × 32 MCT (mercury–cadmium–telluride) detector array. The measurement of the reference thus allows for a frequency-resolved correction for shot-to-shot fluctuations of the probe-pulse energy.

The pump promotes population from the equilibrium ground state $v=0$ to the first excited state $v=1$. This excitation leads to a bleaching signal and stimulated emission at frequencies matching the $v=0\rightarrow1$ transition, and to an induced absorption at frequencies matching the $v=1\rightarrow2$ transition. The pump pulse will preferentially excite the O–D groups of which the transition dipole moment is oriented parallel to the polarization of the pump pulse. Hence, the excitation will be anisotropic. After the sample, the polarization components of the probe parallel and perpendicular to the polarization of the pump are selected with a polarizer mounted on a rotation stage. Thereby we obtain the pump-induced transient absorption changes for both polarization directions: $\Delta\alpha_{\parallel}(\omega,t)$ and $\Delta\alpha_{\perp}(\omega,t)$. These absorption changes are used to determine the anisotropy of the O–D excitation:

$$R(\omega,t)=\frac{\Delta\alpha_{\parallel}(\omega,t)-\Delta\alpha_{\perp}(\omega,t)}{\Delta\alpha_{\parallel}(\omega,t)+2\Delta\alpha_{\perp}(\omega,t)}, \tag{1}$$

with $R(\omega,t)$ the anisotropy of the excitation that depends on the probe frequency $\omega$ and the delay time $t$ between pump and probe. The denominator of the above expression represents the so-called isotropic signal and serves to divide out the decay of $\Delta\alpha_{\parallel}(\omega,t)$ and $\Delta\alpha_{\perp}(\omega,t)$ due to the vibrational relaxation of the O–D excitation. As a result, $R(\omega,t)$ only reflects the orientational dynamics of excited O–D vibrations. In the case of isotopically diluted samples, the dynamics of $R(\omega,t)$ only represents the molecular reorientation of the O–D groups of the HDO molecules.

We use the above described technique to study the anisotropy dynamics of HDO molecules in solutions of NaCl, NaI and different $N(alkyl)_4Br$ salts in 8% $HDO:H_2O$. All salts were of ≥99.5% purity and were purchased from Sigma Aldrich. $D_2O$ was also purchased from Sigma Aldrich and has a purity of ≥99.99%. The sample cell consisted of two 4 mm calcium fluoride windows which were pressed against each other with a teflon spacer in between. To keep the infrared transmission around 10% we used spacers of 25 μm for the samples with low salt concentrations and 50 μm for the samples with high salt concentrations. All concentrations in this paper are denoted in moles of solute per kilogram of solvent (molality).

## 3. Results and discussion

Fig. 1 shows transient absorption spectra of the O–D stretch vibration of HDO molecules at different delay times $t$ measured for a solution of 4 m NaI in 8% $HDO:H_2O$. These transient spectra are difference spectra between the absorption spectrum measured at a particular delay time after the excitation, and the original ground state absorption spectrum (no excitation pulse). At early delays the transient spectra are characterized by a negative (bleach) contribution at high frequencies (>~2450 $\text{cm}^{-1}$) representing the bleached absorption and stimulated emission of the $v=0\rightarrow1$ transition, and a positive signal at lower frequencies (<~2450 $\text{cm}^{-1}$), representing the induced $v=0\rightarrow1$ absorption. The bleaching signal and the induced absorption both decay with a time constant of ~2 ps.

After ~10 ps the transient spectrum does not change any further with increasing delay time. After this time the excited O–D vibrations have completely relaxed and the transient spectrum represents the spectral response resulting from the heating of the sample by a few Kelvin. An increase in temperature induces a decrease in the cross-section and a small blueshift of the O–D stretch vibrations. The difference spectrum of the absorption spectrum at long delay times and the original absorption spectrum thus shows a persistent bleaching in the main part of the O–D stretch absorption spectrum and a small induced absorption in the blue wing of this spectrum.

We find that the vibrational relaxation of the O–D vibrations does not immediately lead to a rise in temperature. A similar delayed rise of the thermal response was observed in a study of the vibrational dynamics of neat 8% $HDO:H_2O$ [17]. This delayed thermal response can be due to the transient population of a particular non-thermal state in the vibrational relaxation of the O–D stretch vibration. Such a non-thermal state may involve the H–O–D bending mode and/or the librational modes. However, the intermediate state was observed to have no spectral signature [17], which means that its absorption spectrum is identical to that of the O–D stretch vibration before the excitation by the pump. Therefore, the delayed rise of the thermal response is likely not due to the transient excitation of a specific mode like the H–O–D bending vibration, because such an excitation would lead to an anharmonic frequency shift of the absorption spectrum of

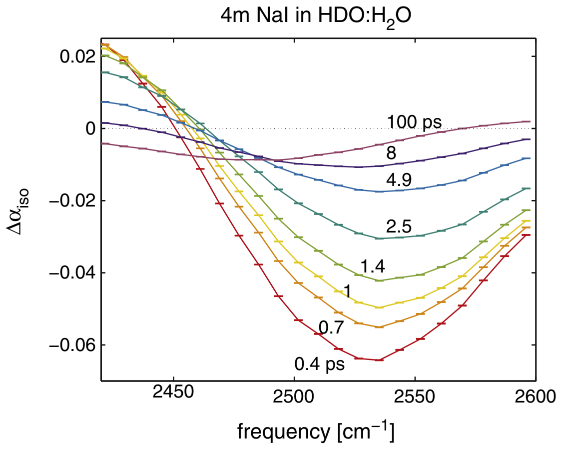

**Fig. 1.** Transient isotropic spectra at different delay times after excitation of the O–D stretch vibration of HDO molecules for a solution of 4 m NaI in 8% $HDO:H_2O$.