

# Reorientation dynamics of water molecules in the presence of hydroxide ions

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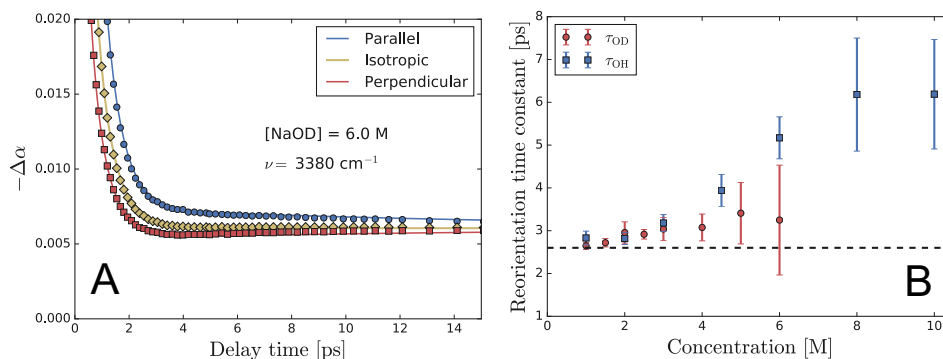
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Protons ( $H^+$ ) and hydroxide ions ( $OH^-$ ) play important roles in many chemical and biophysical processes. In liquid water both ions form special hydration complexes in which the excess positive or negative charge is delocalized. Rearrangement of the hydrogen bonds of these complexes leads to transfer of the charge: the so-called Grotthuss mechanism. Both the properties of aqueous protons and aqueous hydroxide ions have been intensely studied with femtosecond mid-infrared spectroscopy [1-4]. However, up to now there has been very little experimental work on the structural dynamics of the water solvent in aqueous hydroxide solutions. Here, we use polarization-resolved pump-probe infrared spectroscopy to study the reorientation of water molecules in the presence of hydroxide ions. We study isotopically diluted solutions, i.e. the dynamics of the OD vibration of HDO molecules in  $H_2O/OH^-$  solutions, and the dynamics of the OH vibration of HDO molecules in  $D_2O/OD^-$  solutions.

We measure the reorientation dynamics of OD/OH groups of HDO molecules directly interacting with  $OH^-/OD^-$  ions and of HDO molecules at a larger distance from the hydroxide ions. For solutions with  $OH^-/OD^-$  concentrations up to  $\sim 4$  M, we find that HDO molecules that are not directly interacting with the ions, have a reorientation time constant of  $\sim 2.6$  ps, similar to pure liquid water. When the concentration of  $OH^-/OD^-$  ions is increased, the reorientation time constant increases, indicating a slowing down of the structural dynamics of the solution.



A) Parallel (blue), isotropic (yellow) and perpendicular (red) absorption change  $-\Delta\alpha$  as a function of delay time following the excitation of the OH vibration of HDO in a 6 M [NaOD]:D<sub>2</sub>O solution. The solid lines are fits following a two HDO species model that rapidly relax ( $< 2$  ps) and form a thermally heated ground state. B) Reorientation time constant as a function of the concentration of  $OH^-/OD^-$ . The red circles represent the dynamics of HDO molecules in  $H_2O/OH^-$  solutions, and the blue squares the dynamics of HDO molecules in  $D_2O/OD^-$  solutions. The dashed line shows the molecular reorientation time constant of the pure liquid water.

## References

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