191
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Title:Vibrational and orientational dynamics of water in aqueous hydroxide solutions
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Abstract:We report the vibrational and orientational dynamics of water molecules in isotopically diluted NaOH and NaOD solutions using polarization-resolved femtosecond vibrational spectroscopy and terahertz time-domain dielectric relaxation measurements. We observe a speed-up of the vibrational relaxation of the O-D stretching vibration of HDO molecules outside the first hydration shell of OH- from 1.7±0.2ps for neat water to 1.0±0.2ps for a solution of 5M NaOH in HDO:H2O. For the O-H vibration of HDO molecules outside the first hydration shell of OD-, we observe a similar speed-up from 750±50fs to 600±50fs for a solution of 6M NaOD in HDO:D2O. The acceleration of the decay is assigned to fluctuations in the energy levels of the HDO molecules due to charge transfer events and charge fluctuations. The reorientation dynamics of water molecules outside the first hydration shell are observed to show the same time constant of 2.5±0.2ps as in bulk liquid water, indicating that there is no long range effect of the hydroxide ion on the hydrogen-bond structure of liquid water. The terahertz dielectric relaxation experiments show that the transfer of the hydroxide ion through liquid water involves the simultaneous motion of ~7 surrounding water molecules, considerably less than previously reported for the proton.
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