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Accession number:20114414474371
Title:Anisotropic water reorientation around ions
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Source title:Journal of Physical Chemistry B
Abbreviated source title:J Phys Chem B
Volume:115
Issue:43
Issue date:November 3, 2011
Publication year:2011
Pages:12638-12647
Language:English
ISSN:15206106
E-ISSN:15205207
CODEN:JPCBFK
Document type:Journal article (JA)
Publisher:American Chemical Society, 2540 Olentangy River Road, P.O. Box 3337, Columbus, OH 43210-3337, United States
Abstract:We study the reorientation dynamics of water molecules around ions using terahertz dielectric relaxation spectroscopy and polarization-resolved femtosecond infrared pump-probe spectroscopy. The results are discussed in relation to the ion-specific Hofmeister series and the concomitant "structure-making" and "structure-breaking" effects of ions on water. We show that when a dissolved salt consists of a strongly hydrated ion with a weakly hydrated counterion the reorientation of water molecules around the strongly hydrated ion is anisotropic, in the sense that differently charged ions affect reorientation along different molecular axes: cations mainly slow the reorientation dynamics of the water dipole vectors, and anions mainly slow down the reorientation dynamics of the hydroxyl group that points toward the anion. In both cases, motion along only one molecular axis is impeded, so that the hydration shell is best described as semirigid. In this semirigid hydration picture, water molecules in the first hydration shell show anisotropic reorientation, whereas water molecules outside the first hydration shell remain unaffected. The inferred anisotropy in molecular motion explains why terahertz dielectric relaxation spectroscopy, which probes dipolar relaxation, is more sensitive to cation hydration effects while femtosecond infrared pump-probe spectroscopy, which is sensitive to reorientation of hydroxyl groups, is more sensitive to anion hydration effects. We also show that dissolution of CsI - a salt for which both cation and anion are weakly hydrated - has little effect on water reorientation dynamics, with hydration water displaying dynamics that are similar to those in bulk water.
Number of references:49