IONS AS PROBES OF SUB-PS WATER NETWORK DYNAMICS.

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We present THz measurements of salt solutions which shed new light on the controversy of salts as kosmotropes (structure makers) or chaotropes (structure breakers). We performed concentration dependent narrow-band THz-absorption spectroscopy on fifteen alkali-halide salt solutions around 85 cm^{-1} (2.5 THz) and wide-band (30-300 cm^{-1}) THz Fourier transform measurements on six alkali halide salt solutions. All solutions show an increased THz-absorption compared to pure water with a linear concentration dependence. Our comprehensive data set is well-described by a model including damped harmonic oscillations (rattling modes) of both anions and cations within the water network. This model well-predicts key features of THz spectra for a variety of salt solutions. Complementary molecular dynamics simulations using the TIP3P water model support experiments and show that the fast sub-ps ionic motions and their surroundings are almost decoupled. These findings provide a complete description of the solute-induced changes in the THz solvation dynamics for the investigated salts and suggests a treatment of the ions as simple defects in an H-bond network. Our results show that THz spectroscopy is a powerful experimental tool to establish a new insights on contributions to the structuring of water by anions and cations.

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