

Structural and Dynamic Correlations of Alkali Halide Salts in Water/Alcohol Mixtures: a Combined Optical Kerr Effect (OKE) Spectroscopy and Molecular Dynamics Investigation

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Experiments to measure the electromagnetic response of liquids in the terahertz (THz) frequency range, either by dielectric spectroscopy or related non-linear methods like the optical Kerr effect (OKE) can provide valuable insight into the dynamics of intermolecular interactions in aqueous solutions and in particular hydrogen bonding. While aqueous electrolyte solutions have been much studied with these and other methods, salts in mixtures of polar solvents are much less well understood. Water/alcohol mixtures feature non-ideal behavior characterized by strong anomalies in the thermodynamic properties and by the formation of nano-scale water clusters. The changes undergone in the hydrogen bond structure of water and the modification of the dielectric constant provide an interesting medium for ion cluster formation. Improving understanding of these ternary mixtures is especially relevant to electrospray ionization (ESI), where water/methanol mixtures are commonly used as solvents. In this contribution we will discuss the THz response of a system of alkali halide salts in water/alcohol mixtures. This technique in conjunction with molecular dynamics simulations enables a detailed analysis of correlations in mixtures and through the theoretical modelling of the experimental measurements. Our study represents a stepping stone towards using THz spectroscopy to measure the thermo-molecular orientation (TMO) effect, which heretofore has only been observed in computer simulations.