MAR14-2013-001480

Abstract for an Invited Paper
for the MAR14 Meeting of
the American Physical Society

Water in Room Temperature Ionic Liquids

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Room temperature ionic liquids (or RTILs, salts with a melting point below 25 °C) have become a subject of intense study over the last several decades. Currently, RTIL application research includes synthesis, batteries, solar cells, crystallization, drug delivery, and optics. RTILs are often composed of an inorganic anion paired with an asymmetric organic cation which contains one or more pendant alkyl chains. The asymmetry of the cation frustrates crystallization, causing the salt's melting point to drop significantly. In general, RTILs are very hygroscopic, and therefore, it is of interest to examine the influence of water on RTIL structure and dynamics. In addition, in contrast to normal aqueous salt solutions, which crystallize at low water concentration, in an RTIL it is possible to examine isolated water molecules interacting with ions but not with other water molecules. Here, optical heterodyne-detected optical Kerr effect (OHD-OKE) measurements of orientational relaxation on a series of 1-alkyl-3-methylimidazolium tetrafluoroborate RTILs as a function of chain length and water concentration are presented. The addition of water to the longer alkyl chain RTILs causes the emergence of a long time bi-exponential orientational anisotropy decay. Such decays have not been seen previously in OHD-OKE experiments on any type of liquid and are analyzed here using a wobbling-in-a-cone model. The orientational relaxation is not hydrodynamic, with the slowest relaxation component becoming *slower* as the viscosity *decreases* for the longest chain, highest water content samples. The dynamics of isolated D_2O molecules in 1-butyl-3-methylimidazolium hexafluorophosphate ($BmImPF_6$) were examined using two dimensional infrared (2D IR) vibrational echo spectroscopy. Spectral diffusion and incoherent and coherent transfer of excitation between the symmetric and antisymmetric modes are examined. The coherent transfer experiments are used to address the nature of inhomogeneous broadening by observing $\sim$ 100 fs time scale oscillations in the shape of the 2D IR spectra.