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Solvation dynamics in room temperature ionic liquids studied by ultrafast vibrational spectroscopy SEAN GARRETT-ROE, ZHE REN, DUANE COUCHOT-VORE, THOMAS BRINZER, Department of Chemistry, University of Pittsburgh — Room temperature ionic liquids are a challenging new area for understanding solvation dynamics. These solvent systems are liquids with a delicate balance of electrostatic, dispersion, and hydrogen-bonding forces which lead to complex structure and dynamics on many time- and length-scales. Here we probe the dynamics of thiocyanate ions in several imidazolium bis(trifluoromethylsulfonyl)amide ionic liquids from femtoseconds to 100 ps using ultrafast vibrational spectroscopy. Two-dimensional infrared (2D-IR) spectroscopy of thiocyanate ions detects both intertial motion (on the hundreds of femtosecond timescale) as well as slower, diffusive motions (on the tens of picosecond timescale). The 2D-IR experiments show that the rate of fluctuation of the electrostatic environment around the thiocyanate is sensitive to hydrogen bonding at the 2-position of the imidazolium ring, depends mildly on water concentration, changes with counter-ion, and is roughly independent of the thiocyanate concentration (up to 30 mM). The results are compared to ab initio simulations which predicted a 10 – 15 picosecond hydrogen bond lifetime. The implications for topics such as the concept of ionicity, the effect of hydrogen bonding on viscosity, and structural and dynamical heterogeneity will be discussed.

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