Ultrafast vibrational spectroscopy of ionic liquids

Thomas Brinzer[1], Zhe Ren[1], Clyde A. Daly[2], Eric J. Berquist[1], Steven A. Corcelli[2], Daniel S. Lambrecht[1], and Sean Garrett-Roe[1]*

[1]Department of Chemistry, University of Pittsburgh, 219 Parkman Ave, Pittsburgh, PA, 15260, USA
[2]Department of Chemistry and Biochemistry, Univeristy of Notre Dame, Notre Dame, IN, 46556, USA
*sgr@pitt.edu

Ultrafast dynamics in ionic liquids are studied with 2D-IR spectroscopy. Quantum chemistry and molecular dynamics simulations unravel the experimentally observed vibrational frequency fluctuation correlation functions of CO_2. Thiocyanate ionic liquids in reverse micelles respond to confinement depending on micelle size and surfactant.

Ionic liquids are complex solvents. Due to their tunable properties they are being explored for applications as carbon capture absorbents, electrolytes, and energy storage media. From a fundamental perspective, ionic liquids are at the forefront of research because of their structural and dynamical heterogeneity.

Here, we use ultrafast 2D-IR spectroscopy to reveal the dynamics of CO_2 [1] and thiocyanate [2] in ionic liquids. Temperature dependence shows that the dynamics of CO_2 and SCN^- are due to different relaxation mechanisms, though the timescales at room temperature are similar. Quantum chemistry combined with molecular dynamics simulations reveal the nature of the forces experienced by a CO_2 molecule that cause the observed frequency fluctuations [3]. Finally, the effects of confinement on ionic liquid dynamics will be discussed (Fig.1).

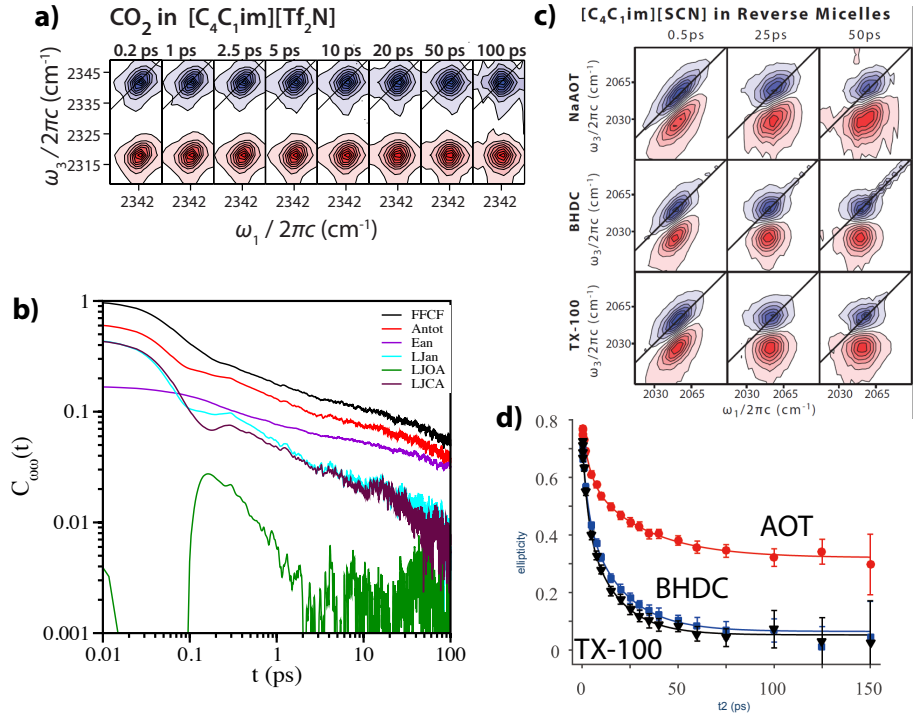

Fig.1 (a) 2D-IR spectra of CO_2 in ionic liquids change on a tens of picosecond timescale. (b) Simulations identify the molecular origin of the frequency fluctuations. (c) SCN^- in reverse micelles has very different dynamics based on surfactant and micelle size.

[1] T. Brinzer *et al.*, J. Chem Phys. **142,** 212425 (2015).
[2] Z. Ren *et al.*, J. Phys. Chem. B **119,** 4699 (2015).
[3] C. A. Daly *et al.* JPCB **in preparation**.