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**Solvent Influenced Fluxionality Studied by Ultrafast Chemical Exchange Spectroscopy** MATTHEW ROSS, Program in Applied Physics, University of Michigan, KEVIN KUBARYCH, Department of Chemistry, University of Michigan — Two-dimensional infrared spectroscopy (2DIR) allows unprecedentedly detailed understanding of the dynamics of chemical systems in the condensed phase. Carbonyl vibrations of small transition metal complexes report intramolecular dynamics and solvent-solute interactions due to their strong oscillator strengths and moderate environmental sensitivity. We studied the fluxional dynamics of iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ), which is unique in that it contains nearly perfectly uncoupled vibrational modes. We seek to probe the “molecularity” of condensed phase activated barrier crossings beyond the continuum Kramers theory picture. Using 2DIR chemical exchange spectroscopy, we show how the dynamics of Berry pseudorotation, the only significant mechanism for vibrational mode mixing on our experimental timescale, is sensitive to interactions with the environment. In a wide range of solvents, we have investigated the effects of hydrogen bonding with alcohols and friction from high viscosity alkanes. In addition, we have monitored vibrational energy redistribution as a solvation shell probe. Moreover, recently implemented mid-infrared pulse shaper based methods allow increased flexibility in experimental design, enabling experimental techniques that are not possible using passive optics.

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