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Ultrafast dynamic exchange of hydrogen bonds ROBIN HOCHSTRASSER, University of Pennsylvania

Measurements of H-bond dynamics in solutions aim to obtain energetics and equilibrium dynamics of making and breaking these bonds. Two dimensional IR with fs pulses can follow both the vibrational kinetics associated with H-bonds and the dynamic effects of exchange on vibrational coherence. The principles are analogous to those from 2D-NMR chemical exchange but the 2D IR measures dynamics on the fs to ps time scales and exchange is coupled to ultrafast spectral diffusion. Therefore distinctive types of reactions can be accessed by 2D IR. Results will be presented for CN vibrators in liquid methanol and carbonyl and NH groups of peptides in water and methanol. In all examples the solute modes act as probes of the dynamics of the surrounding liquid structures. As a consequence the exchange coupling between different vibrators that results in energy transport along the chains of peptides is also seen. This research was supported by NSF-CHE, NIH-GM and by an NIH Resource Grant all to RMH.