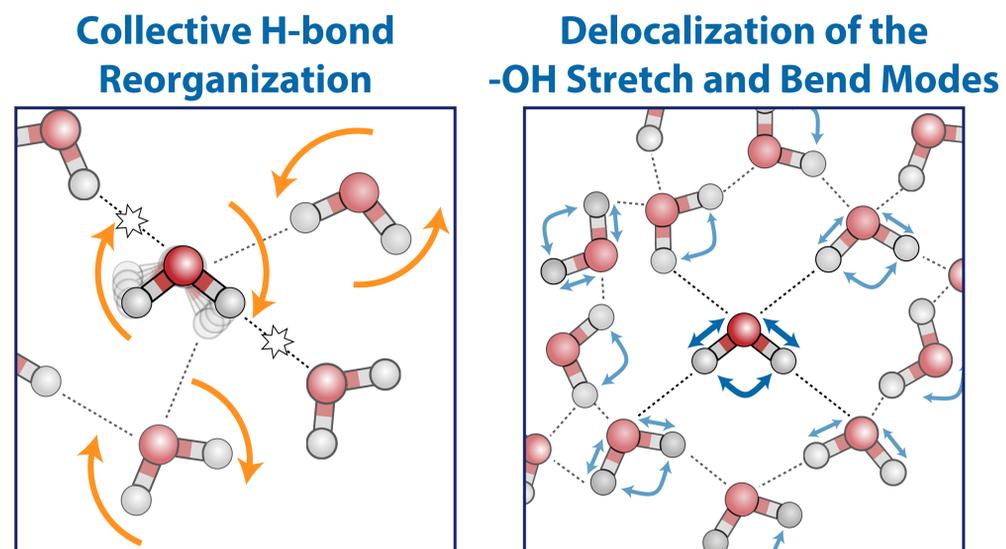


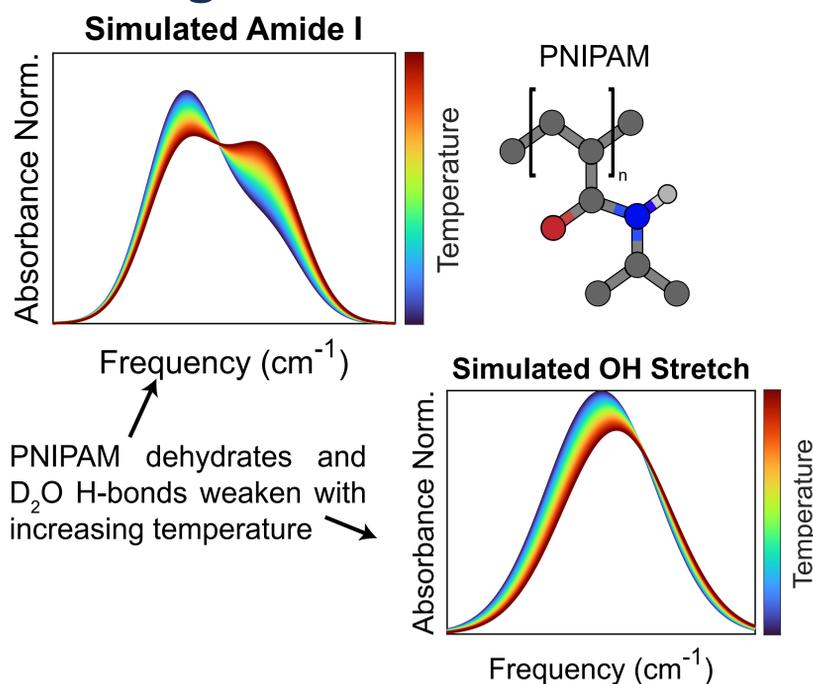
Hydrogen Bonding Couples the Motion of Individual Waters

Water forms a complex hydrogen-bonding network which fluctuates and rearranges on the fs-ps timescale. A consequence of such strong and highly directional intermolecular interactions is that the individual motions of water molecules are coupled to one another. The dynamics in the condensed phase are therefore concerted -- a signature of water's molecular scale behavior and the origin of many of water's unique capabilities as a solvent. As such, cooperative phenomena manifest regularly in the dynamics of water and is the focus of our current research.



Hydration dynamics such as hydrogen bond switching, occurring every ~ 1.5 ps, are collective in nature, requiring the subsequent rearrangement of many nearest-neighboring waters for even a single exchange to occur.⁽¹⁾ Even elementary motions such as water's stretching and bending vibrations deviate from the typical gas phase perspective due to the hydrogen bonding network. Where the common perspective is of localized modes on single bonds/molecules. Rather, due to the highly anharmonic nature of hydrogen bonding, the two vibrational modes are instead delocalized both intra- and intermolecularly across ~ 8 -10 water molecules.⁽²⁾ The two canonical modes being excitonic in character.

Isolating a Solute's Solvation Environment with 2D IR Cross Peaks



IR spectroscopy is uniquely suited for studying the structural dynamics of water and the hydrogen bonding network due to its structural sensitivity on the length scale of a molecular bond and capabilities for time-resolved measurements. A prerequisite for resolving cooperative dynamics is the ability to monitor the relative motions of two molecules. Given that IR spectroscopy is an ensemble technique where each water molecule contributes to an average absorption signal, this requires that we add a distinct solute to contrast the dynamics of water with. We've chosen to study aqueous thermoresponsive polymers which when at an increased temperature undergo a demixing phase transition with water that's intrinsically cooperative

Beyond basic linear IR measurements, nonlinear 2D IR is a powerful tool to monitor the structural dynamics of water. In particular 2D IR cross peaks which uniquely measure correlations between distinct yet coupled vibrations allow us to isolate the solvent environment of a solute due to the short ranged nature vibrational coupling. By exciting the -OH stretch of water and detecting the amide I mode of a model system we can isolate the immediate solvent environment. By varying the delay between our laser pulses we can resolve the structural dynamics of water directly solvating the solute which can then be contrasted with the bulk water dynamics.

