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Title: State-resolved THz spectroscopy and dynamics of crystalline peptide-water systems

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Abstract: Vibrationally state-resolved THz spectra are obtained at cryogenic temperatures for three crystalline peptide-water systems that represent different structural motifs. The systems include two types of secondary structures and a hydrophobic peptide nanopore structure. Almost all of these systems are shown to undergo exchange with water at room temperature that alters the hydrogen bonding network in ways easily detectable in the THz region at cryogenic temperatures. Stark differences are observed in the spectra of model alpha-helical and beta-sheet structures upon water removal at hydrophilic binding sites. However, within the confined pore of a hydrophobic nanotube, water in the form of helical wires has a subtle but significant impact on the phonon modes of the tube. The THz spectra are shown to easily distinguish between the different hydration states of the system that have been independently characterized by mass change measurements. Spectral comparisons with quantum chemical predictions of fully relaxed crystal structures confirm the hydration states and give detailed information about the free energies associated with dehydration. The vibrational free energies are shown to make significant contributions to the overall energy balance of the dehydration processes.