Decoding the Spectroscopic Features and Timescales of Solvated Proton Defects

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Abstract:
Proton defects in solution exhibit a variety of complex structural and dynamical features. However, disentangling the transient structural motifs of proton defects in hydrogen bonded liquids and the mechanisms for their interconversion remains a formidable challenge. In this talk I will discuss our recent developments that allow for the treatment of nuclear and electronic quantum effects 100 fold faster than was previously possible. I will then discuss how these advances can be used to elucidate the observed spectroscopic features and relaxation time scales of aqueous protons using a physically transparent coordinate that encodes the overall asymmetry of the solvation environment of the proton defect. This coordinate can be used both to discriminate the extremities of the features observed in the linear vibrational spectrum and to explain the molecular motions that give rise to the interconversion time scales observed in recent nonlinear experiments. I will also demonstrate how this analysis provides a unified condensed-phase picture of the proton structure and dynamics in water that, at its extrema, encompasses proton sharing and spectroscopic features resembling the limiting Eigen $[H_3O(H2O)_3]^+$ and Zundel $[H(H2O)_2]^+$ gas-phase structures, while also describing the rich variety of interconverting environments in the liquid phase.