Condensed phase vibrational spectroscopy: from quantum decoherence to ion channels.

Vibrational spectroscopy is a powerful tool for investigating the structure and dynamics of condensed-phase systems. The usefulness of vibrational line shape experiments derives from the high sensitivity of vibrational frequencies to local molecular environments. Infrared (IR and 2DIR) and Raman spectroscopies are often used to study many condensed-phase systems including water, aqueous solutions, and proteins in various environments. Theoretical methods have become an indispensable tool for interpreting experimental spectroscopic results. Because full quantum-mechanical calculation of optical response functions and corresponding spectral line shapes is computationally prohibitively expensive for realistic condensed-phase systems, methods based on classical molecular dynamics simulations and ab initio parametrized spectroscopic maps are often the only feasible strategy. I will present one such approach as well as our recent methodological developments including machine learning parameterized spectroscopic maps and multivariate curve resolution spectroscopy. I will also present several recent applications of this approach to study vibrational couplings in liquid water and transport of ions across cell membranes. Additionally, I will present new general developments in the analytical theory of absorption and emission line shapes emphasizing the interplay between vibrational dephasing and quantum decoherence.