Investigating the dynamics of interfacial ester carbonyls in lipid bilayers

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We present a general approach for parameterizing vibrational maps using input from experimental FTIR and 2D IR spectra. We develop an electrostatic map to model IR linear and nonlinear spectra of ester C=O vibrations in lipids, and we apply it to simulate spectra of lipid bilayers under different hydration conditions.

Carbonyl vibrations are useful probes of protein structure and dynamics. Multidimensional spectroscopy combined with molecular modeling and electrostatic maps have turned amide I IR spectroscopy into a powerful tool to investigate protein dynamics and folding. Despite being ubiquitous in biology, similar C=O probes, such as lipid ester carbonyls, have received relatively little attention from the ultrafast community. Here we develop a general method to parameterize an electrostatic model for ester C=O vibrations using empirical input from FTIR and 2D IR spectroscopy. In short, the method involves fitting a set of electrostatic parameters to carbonyl frequencies that best reproduce IR absorption spectra. The electrostatic environments are sampled from molecular dynamics trajectories in a variety of polar and non-polar solvents. Fig. 1, shows a comparison between simulated and experimental spectra of ethyl acetate in different solvents. The excellent agreement between simulations and experiment suggests that this approach will be useful for parameterizing multiple IR probes. We apply the map to simulate linear and non-linear spectra of lipid bilayers under different hydration conditions, and compare our results to IR spectra of bilayers consisting of pure and mixed lipids to understand the water-lipid interface and the specific lipid-lipid interactions that induce phase separation in biological membranes.

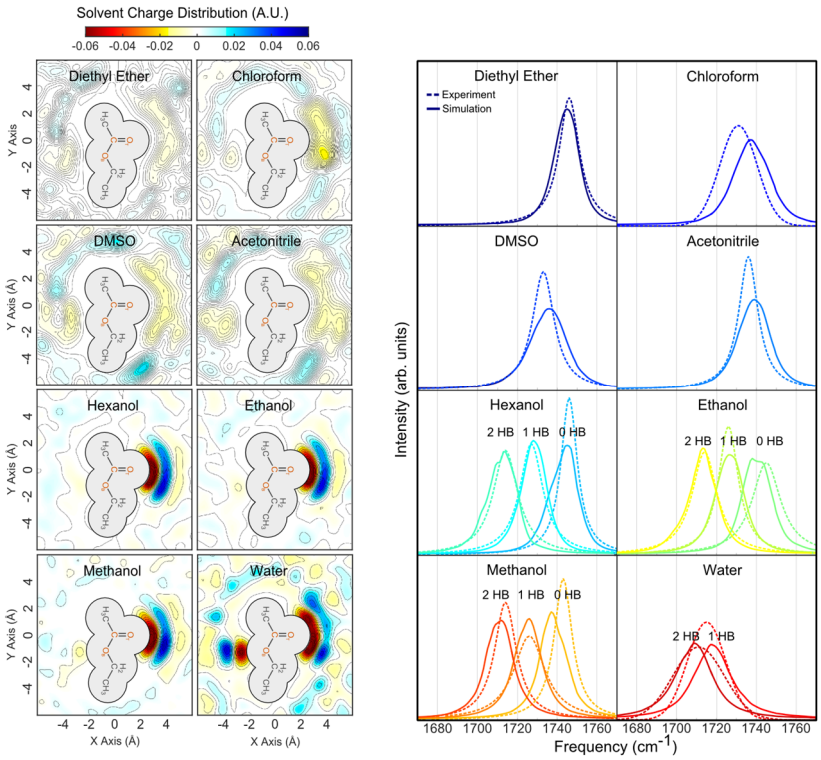

Fig 1. (left) Spatial maps showing solvent charge distributions surrounding an ethyl acetate molecule. The maps are obtained from MD simulations. Charge localization induced by hydrogen bonding in alcohols and water is evident in these plots (right) Experimental (dashed) and simulated (solid) IR absorption spectra of ethyl acetate in eight common solvents. Dashed curves represent Gaussian/Lorentzian fits to the experimental absorption spectra. Separating the hydrogen bonding environments (0HB, 1HB, 2HB) enables us to sidestep sampling issues in MD.