

Energy transfer in water underneath oppositely charged surfactants

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Energy transfer in water underneath both negatively and positively charged surfactants is studied with two-dimensional vibrational sum frequency generation spectroscopy. For the negatively charged surfactant, two distinct water sub-ensembles are identified with sub-picosecond energy transfer between them. In contrast, water underneath a positively charged surfactant behaves like bulk water.

Hydrated lipids and surfactants are model systems for cell membranes. Moreover, surfactants are also used as detergents for both domestic and industrial applications. Surfactants form a self-assembled monolayer at the water-air interface. Using vibrational sum frequency generation (SFG) spectroscopy, we selectively study the water molecules in the few Å neighborhood of the surfactant. Time resolved two dimensional SFG provides information on coupling between water molecules and on vibrational energy transfer pathways in the system.

Two distinct sub-ensembles of water underneath the negatively charged surfactant sodium dodecyl sulfate (SDS) have been identified. One ensemble reflects more isolated water molecules close the SDS headgroup, while the other ensemble has bulk-like character. Between these two sub-ensembles energy transfer occurs within 250 fs [1].

Water underneath the positively charged lipid 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP) behaves indistinguishable from bulk water. The lifetime of the stretch vibration depends on the excitation frequency and efficient energy transfer occurs between the interfacial water molecules. A model of vibrational energy transfer between water stretch vibrations and vibrational relaxation through the bend overtone can describe both the frequency dependent lifetime and the spectral diffusion obtained from the slope of 2D SFG spectra [2]. As bulk and surface water can be described with exactly the same model [3], we conclude that water underneath a positively charged lipid behaves like bulk water.

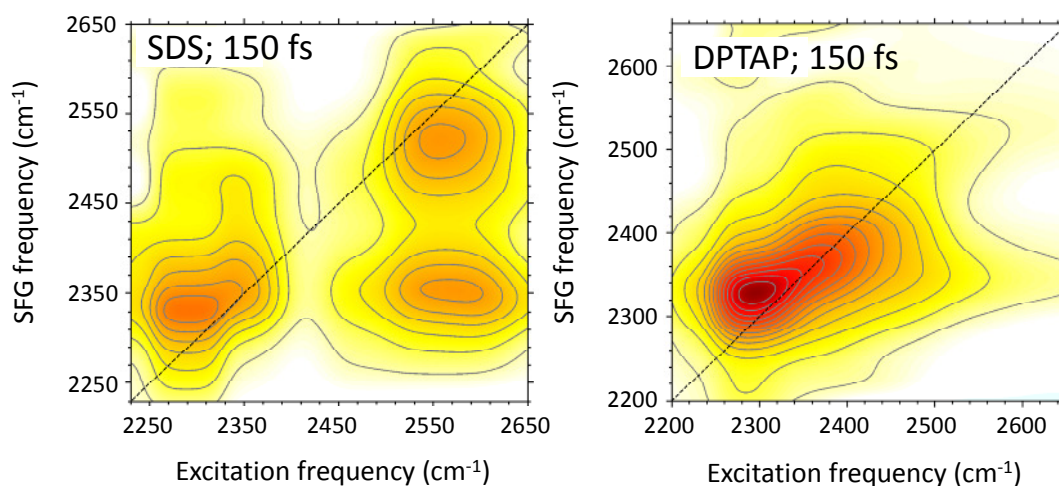


Fig.1 2D-SFG spectrum of water underneath SDS and DPTAP.

[1] R. A. Livingstone *et al.*, JACS **137**, 14912 (2015).

[2] R. A. Livingstone *et al.*, JPCB submitted (2016).

[3] S. T. v. d. Post *et al.*, Nat. Comm. **6**, 8384 (2015)