Structure, composition and dynamics of interfacial water studied with surface specific vibrational spectroscopy

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The molecular organization of aqueous solutions at the water-air interface is important, in particular for atmospheric chemistry. A key question regards the local, interfacial composition, as compositional variations, e.g. ions enrichment or depletion, affect the local structure, and thereby the reactivity of water. Interfacial enrichment of anions has in fact been theoretically predicted, but is notoriously hard to quantify. We used the recently developed method of femtosecond two-dimensional surface sum-frequency generation [1, 2] to quantify the ion concentrations in the first molecular layer at the interface of sodium chloride and sodium iodide solutions. Femtosecond two-dimensional surface sum-frequency generation allows one to determine, in a non-invasive manner, the rate of vibrational energy transfer between interfacial water molecules. The presence of ions at the interface results in a reduction of energy transfer rates between water molecules resulting from the lowered effective interfacial density of water molecules. Our results reveal remarkably high surface propensities for the anions, even higher for iodide than for chloride ions, resulting in surface concentrations several (3 to 5) times that of the bulk [3].

Using the 2-dimensional sum frequency generation spectroscopy we also explored, the structure and dynamics of water in contact with a model lipid membrane (a DPTAP monolayer) [4]. We monitored the time-dependent frequency fluctuations of the O–H stretch vibration, which sheds light on the structural dynamics of the water hydrogen-bonding network. We found that the lifetime of the stretch vibration varies with the excitation frequency and that efficient energy transfer occurs between the water molecules. Both, spectral diffusion and vibrational relaxation of the stretch vibration are explained in terms of the Förster energy transfer between stretch vibrations and vibrational relaxation via the bend overtone. These conclusions are consistent with those made for bulk water and as such lead us to conclude that water at a positively charged lipid interface behaves similarly to bulk water.

Keywords: water; interface; energy transfer; lipid membrane; sfg

References