

## Understanding Water Interfacial Structures via Sum-Frequency Vibrational Spectroscopy

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Physical and chemical properties of water interfaces are generally dictated by the interfacial molecular structures, information about which can be deduced from their vibrational spectra. Measurement of interfacial vibrational spectra of water is however rather challenging, and so far, surface-specific sum-frequency vibrational spectroscopy (SFVS) has appeared to be the only viable technique. It has been employed by many research groups to study water interfaces in recent years. The spectra are characterized by water-like and ice-like features as well as dangling OH bonds if the interface is hydrophobic. Thus, water interfaces appear to have the structure of a heavily disordered, dynamically varying, hydrogen-bonding network. Attempts to extract more detailed structural information from the spectra, however, have led to confusion and controversy as the results depend on analysis and interpretation of the spectra that are different from different groups. The difficulties lie in the following fact: The measured spectrum represents  $I_{\text{SF}}(\omega) \propto \text{Im}[\chi_{\text{SF}}(\omega)]$ , where  $\chi_{\text{SF}}(\omega)$  is the SF surface response coefficient that carries spectral information through resonance enhancement when  $\omega$  approaches vibrational resonances. But in analogy to absorption or emission spectroscopy, one needs to know  $\text{Re}[\chi_{\text{SF}}(\omega)]$  in order to characterize the resonances. Unfortunately, it cannot be deduced from analysis of the  $I_{\text{SF}}(\omega)$  spectrum. It must be obtained directly from measurement.

We have developed phase-sensitive SFVS to measure directly  $\text{Re}[\chi_{\text{SF}}(\omega)]$  for water interfaces. The observed spectra are clearly different from those reported in the literature by others. They allow us to construct more detailed physical pictures of the interfaces: The vapor/water interface appears as a randomly distorted ice surface, with rapidly decreasing order moving into the bulk. The topmost layer is occupied by H-bonded DAA and DDA molecules, which are also H-bonded to the DDAA molecules underneath. (D and A refer to donor and acceptor bonds, respectively.) A small fraction of such DDAA molecules has symmetric tetrahedral H-bonding geometry resembling that of ice and gives rise to the ice-like feature in the spectrum. Large ions in aqueous solution can approach the surface. They do not significantly disturb the topmost layer structure, but can create a surface field that reorients the DDAA molecules in the subphase. Phase-sensitive SFVS spectroscopic studies of other water interfaces will also be discussed if time allows.

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