Abstract

In recent years, sum-frequency generation (SFG) has been used to investigate numerous interfaces including aqueous interfaces. A longstanding challenge to interpretation of the SFG results, along with the related aqueous-solution infrared and Raman spectra, is a lack of connection between features in the broad hydrogen-bonded region and molecular-level interactions or configurations. This paper reports results of a newly developed polarization analysis of the generated sum-frequency signal as a function of wavelength both to deconvolute spectral resonances and to characterize the dynamic polarization associated with the resonances. Operationally, the polarization angle of the generated sum frequency is determined by identifying the null angle. The technique is hence termed polarization-angle null analysis or PAN. PAN applied to ice is very powerful; it reveals that the hydrogen-bonded region of the basal face of ice \textit{Ih} contains at least five oscillators, each with a distinct polarization. The dynamic polarizability of the longest wavelength oscillator is nearly entirely transverse (perpendicular to the surface normal, i.e., in the surface plane); in contrast, the shortest wavelength oscillator is almost entirely longitudinal (along the surface normal).