LINE SHAPES AND DYNAMICS OF DANGLING OD-STRETCH AT THE AIR/WATER INTERFACE STUDIED BY THE HETERODYNE DETECTED SUM FREQUENCY GENERATION (HD-SFG) SPECTROSCOPY

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True vibrational line shapes of the dangling OD-stretch at the air/water interface contain information on both vibrational dephasing and orientational dynamics of the outer layer of water, which reflect the nature and properties of the hydrogen bonding network near the surface. We will describe our efforts to obtain the true vibrational line shapes of the dangling OD-stretch mode at the vapor/water interface from heterodyne-detected sum frequency generation spectroscopy (HD-SFG) measurements. D_2O/HOD/H_2O mixtures in the range from 100% D_2O to few percent HOD in H_2O are being investigated to address the isotopic effects on the H-bond dynamics as well as the intermolecular vibrational energy transfer affecting the line shape. Phase information in HD-SFG measurements is used for subtraction of the nonresonant background to reveal the resonant OD-stretch line shape. Extraction of the reorientation time scales of the dangling OD at the air/water interface from the line shapes of SSP, PPP and SPS spectra will be discussed, and compared with the bulk water isotopic mixtures.