BROADBAND SUM-FREQUENCY GENERATION SPECTROSCOPY OF HIGH-FREQUENCY VIBRATIONS OF WATER MOLECULES AT SILICA SURFACES

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Building on our discovery of a method to extend noncollinear optical parametric amplification to a broad class of materials, we developed one of the first sources generating ultrabroadband infrared pulses with bandwidths $\Delta\nu > 2500$ cm^{-1} in the near-IR (λ = 1.1-1.6 μm)[a] and $\Delta\nu > 1000$ cm^{-1} in the mid-IR (λ = 1.7-3.5 μm; ν = 2800-6000 cm^{-1})[b]. The ultra-broadband IR source enabled surface-sensitive sum-frequency generation (SFG) vibrational spectroscopy of mineral-water interfaces crucial in many natural and man-made processes such as ion exchange in geochemical environments and oil extraction from tar sands. This novel ultrabroadband IR source allowed the acquisition of SFG spectra of water OH stretch (spanning 3000-3800 cm^{-1}) from mineral surfaces without tuning the IR frequency, in 60 sec or less.

The high signal-to-noise ratio of the broadband-IR SFG setup allowed the extension of SFG spectroscopy of interfacial hydroxyls at mineral/water surfaces to the low cross-section vibrational modes found in the high frequency range (4000-7000 cm^{-1}). We performed, what we believe to be, the first surface-specific vibrational SFG spectroscopic measurements of the stretch+bend combination band, ν_{comb} = ν_{OH}+δ_{HOH} of liquid water at silica surfaces near 5200 cm^{-1} [c]. SFG of the ν_{comb} mode allows in-situ probing of surface-bound, e.g., SiOH, and H-OH hydroxyls separately. This provides access to the interfacial water bending mode δ (near 1600 cm^{-1}), which has not been observed directly in SFG.

[a] O. Isaienko and E. Borguet *Opt. Express* **16**(6), 3949-3954 March 2008.
[b] O. Isaienko and E. Borguet *Opt. Express* **20**(1), 547-561 January 2012.
[c] O. Isaienko, S. Nihonyanagi, D. Sil and E. Borguet (*in preparation*).