Supporting Information for: Multimodal Broadband Vibrational Sum Frequency Generation (MM-BB-V-SFG) Spectrometer and Microscope

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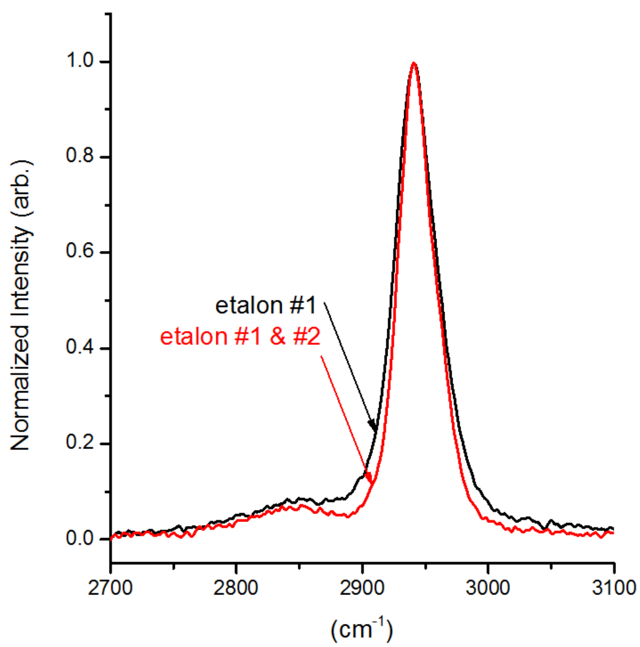

Figure S1. Effect of the spectral bandwidth of the 800 nm pulse on the SFG peak width of the CH vibration region of crystalline cellulose (Avicel®). The spectra were taken with one etalon

(Δλ = 0.96 nm; shown in black) and two etalons (Δλ = 0.78 nm; shown in red). The polarization combination of the SF, Vis, and IR pulses was *ssp*.

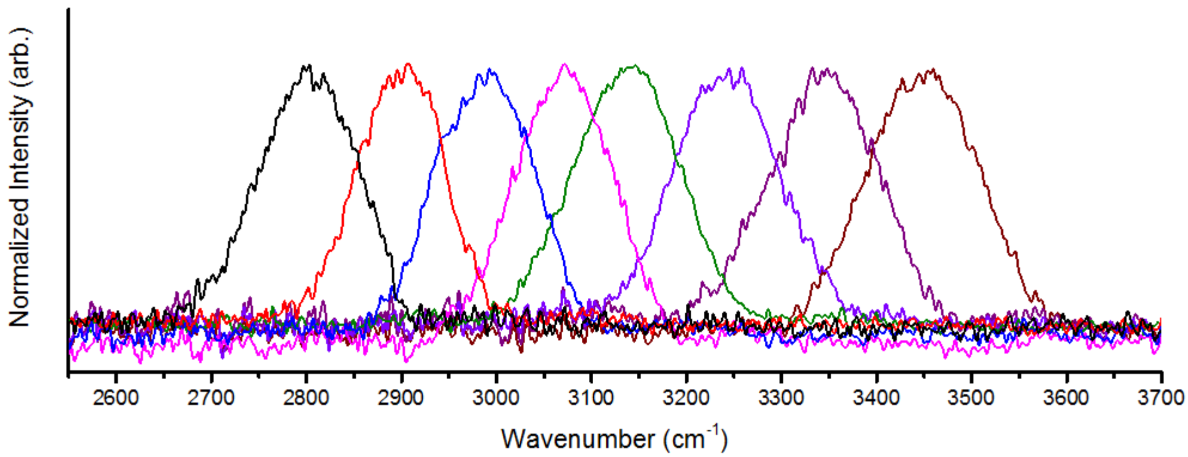

Figure S2. Normalized SFG signals from α-quartz surface obtained with broadband IR pulses generated using 40 fs pulses for OPA pumping. The 40 fs 800 nm pump beam was produced by reconfiguration of the Libra® amplifier. The conversion of the 40 fs broadband 800 nm pulse to the narrowband pulse for SFG experiment was made using a series of two etalons as shown in Figure 2 of the main paper. The full width at half max (FWHM) was ~100–140 cm^{-1}. The data suggested that the pulse width of the 800 nm pump beam (40 fs versus 85 fs) for the OPA does not affect the bandwidth of the IR pulse produced by the OPA; the IR bandwidth seemed to be more sensitive to the phase mismatch of the signal and idler beams of OPA at the NDFG crystal.

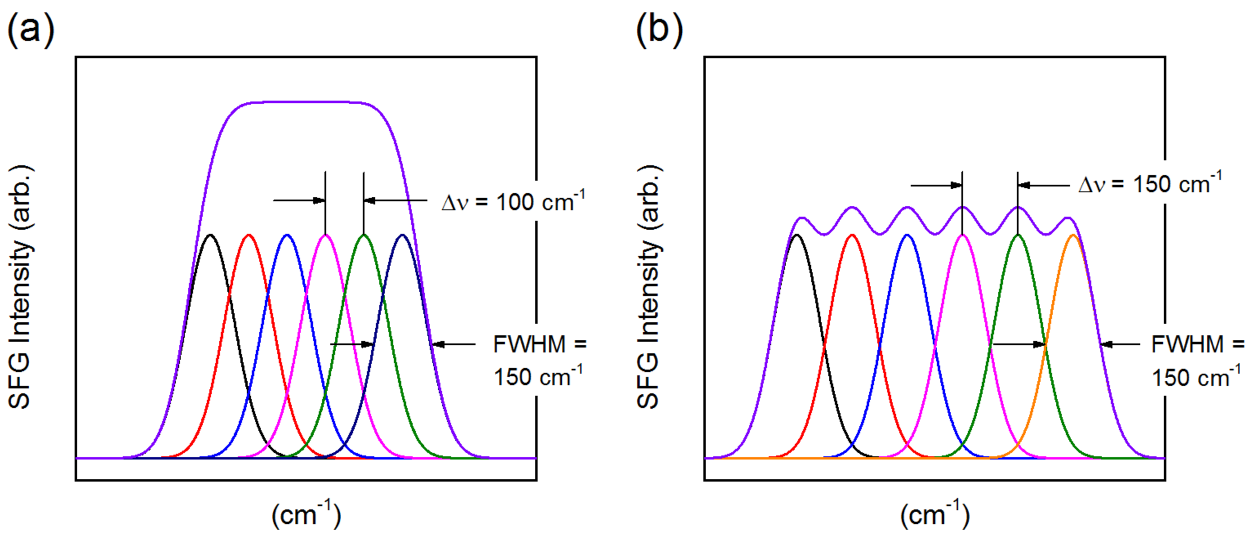

Figure S3. Simulations of the NDFG step-scan setting (Δν) on the IR power spectrum (purple curve) delivered to the sample. For simplification, a Gaussian profile with a 150 cm^{-1} FWHM was used for the spectral shape of the broadband IR pulse. The step size is (a) smaller than and (b) equal to the FWHM of the IR pulse. The simulation indicates that if the step-scan of NDFG is smaller than the measured bandwidth (FWHM) of the IR pulse, then the SFG spectral segments obtained at a constant NSFG step-scan setting can be summed and then normalized with the average IR power spectrum recorded using a pyroelectric power meter upon step-scanning of the NDFG crystal over the same spectral region (for example, continuous line obtained by polynomial fit of the black circle data in Figure 4 of the main paper). The normalized SFG spectrum obtained in this way would be identical with the one obtained by normalizing individual SFG spectra with the non-resonance background spectra obtained at the same NDFG crystal setting (for example, individual spectra shown in Figure 4 and Figure S2) and then summing the normalized segments.

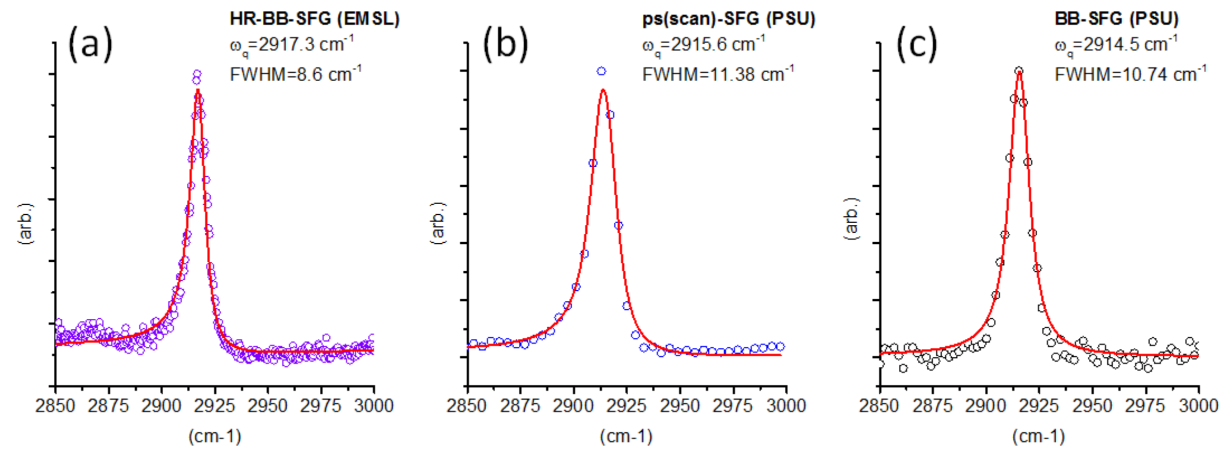

Figure S4. Comparison of the SFG spectral resolutions of the CH_3 stretch signal of the air/DMSO interface (in *ssp* polarization) obtained using (a) HR-BB-SFG system, (b) ps-scanning SFG system, and (c) MM-BB-SFG system. The HR-BB-SFG spectrum was collected using the system constructed by Dr. Hongfei Wang (EMSL User Program 47913). The data in (a) shows the true lineshape of the CH_3 group of DMSO at the air/liquid interface.[1] The ps-scanning system was the one constructed by EKSPLA (using ~27 ps pulses) available in our lab at PSU. The data in (c) was collected with two etalons in series (Figure 2 of the main paper). Using the lineshape of the spectrum shown in (a), the resolutions were calculated to be ~6 cm^{-1} for ps-scanning system and ~5.5 cm^{-1} for the MM-BB-SFG system (with two etalons).[1]

REFERENCES

1. Velarde, L.; Zhang, X.Y.; Lu, Z.; Joly, A. G.; Wang, Z.; Wang, H.F. Communication: Spectroscopic Phase and Lineshapes in High-Resolution Broadband Sum Frequency Vibrational Spectroscopy: Resolving Interfacial Inhomogeneities of “Identical” Molecular Groups. *J. Chem. Phys.* **2011**, *135*, 241102.