Supporting Information for

Molecular Ordering of Layer-by-Layer Polyelectrolyte Films Studied by Sum-Frequency Vibrational Spectroscopy

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We have performed a curve fitting analysis of the SFG spectra in Figure 1(a-d). The spectra were fitted to the SFG equation $I_{SF} \propto \left|\chi^{(2)}_{eff}\right| = \left|\chi^{(2)}_{NR} + \chi^{(2)}_{R}\right|^2 = \left|\chi^{(2)}_{NR} + N_s \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q}\right|^2$, where $\chi^{(2)}_{NR}$, $\chi^{(2)}_{R}$, N_s, A_q, ω_q, Γ_q are the nonresonant and resonant contributions to $\chi^{(2)}_{eff}$, the surface density of molecules and the oscillator strength, resonant frequency and linewidth of the q-th vibrational mode, respectively. Table 1 below shows our best fitting parameters found considering water resonances near to ~3200, ~3400 and ~3600 cm^{-1} and using a real (and positive) nonresonant background. All five spectra (we do not include here the spectra in contact with the rinsing solution) were simultaneously fitted assuming the same resonance frequencies and linewidths.

Table 1: Fitting parameters of SFG spectra for Figure 1.

	Water	**PAH**	**PAH/PSS**	**(PAH/PSS)/ PAH**	**$(PAH/PSS)_2$**
$\mathbf{A_1}$	-69.59439±8.05111	86.57088±8.77512	-45.99965±6.68875	94.33543±10.1315	-63.49851±6.84157
$\mathbf{A_2}$	-55.81816±10.64714	41.22975±9.68808	-44.84953±8.4395	51.63396±10.97394	-41.71648±8.55861
$\mathbf{A_3}$	5.61627±1.89581	-18.44414±4.61432	4.67245±2.45415	-20.3567±4.92769	5.13022±1.6813
$\boldsymbol{\omega_1}$	3198.31271±4.19541				
$\boldsymbol{\omega_2}$	3403.18679±4.62389				
$\boldsymbol{\omega_3}$	3607.7283±4.57903				
$\boldsymbol{\Gamma_1}$	118.48654±7.61205				
$\boldsymbol{\Gamma_2}$	120.47499±12.63874				
$\boldsymbol{\Gamma_3}$	50±9.39962				
$\boldsymbol{\chi^{(2)}_{NR}}$	0.11815±0.02108	0.02944±0.01956	0.05194±0.02093	0.05084±0.02114	0.08932±0.02011

Our best fit shows the alternation of sign for the oscillator strengths A_q, as confirmed by direct phase-measurements shown in Figure 1(e). Fitting performed considering only two resonances around 3200 and 3400 cm^{-1} did not resulted in a good agreement with experimental data.

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