Molecular Interactions of Organic Molecules at the Air/Water Interface Investigated by Sum Frequency Generation Vibrational Spectroscopy

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1. Spectral fitting of SFG-VS Signal

The intensity of the sum-frequency radiation is proportional to the square of the effective second-order susceptibility, which has been introduced in plenty of studies.1-3

\[ I(\omega_{SFG}) \propto \left| \chi_{\text{eff}}^{(2)} \right|^2 I_1(\omega_A) I_2(\omega_R) \]  

(S1)

\( \chi_{\text{eff}}^{(2)} \) can be expressed as the sum of resonant and nonresonant components, \( \chi_R^{(2)} \) and \( \chi_{NR}^{(2)} \). And the frequency dependence of \( \chi_{\text{eff}}^{(2)} \) is described by eq. (S2).

\[ \chi_{\text{eff}}^{(2)}(\omega) = \chi_{NR}^{(2)} + \sum_{\nu} \frac{A_{\nu}}{\omega - \omega_{\nu} + i\Gamma_{\nu}} \]  

(S2)

A_{\nu}, \omega_{\nu}, and \Gamma_{\nu} are the amplitude of the SFG transition moment, frequency, and the line width of the transition, respectively. A_{\nu} could be either positive or negative depending on the phase of the vibrational mode. A_{\nu}, \omega_{\nu}, and \Gamma_{\nu} can be extracted by fitting the spectrum.

2. The ssp and ppp spectra of four dibutyl ester molecules at the air/water interface at SP=5 and 10 mN/m
3. The calculated intensity ratio of $\chi_{ppp}^{(2)}(CH_3_{as})/\chi_{ssp}^{(2)}(CH_3_{ss})$ as a function of the tilt angle.
Figure S3. The calculated intensity ratio of $\chi_{ppp}^{(2)}(CH_3, as) / \chi_{ssp}^{(2)}(CH_3, ss)$ as a function of the tilt angle.

4. The 45°–76°P spectra of four dibutyl ester molecules at the air/water interface at SP=5 & 10 mN/m
Figure S4. 45°76°P spectra of four dibutyl ester molecules at the air/water interface. A) at SP=5 mN/m; B) at SP=10 mN/m

4. SFG ssp spectra of DBP/PVC (a) and DEP/PVC (b) samples taken from reference 4.

Figure S5. SFG ssp spectra of DBP/PVC (a) and DEP/PVC (b) samples with different phthalate bulk concentrations. (Figure S5 reproduced with permission from Langmuir, 2013,29 (12), 4008-4018, Copyright 2013, Am. Chem. Soc.)

5. SFG ssp spectra of pure PVC, TBAC, and PVC-TBAC hybrid films with various bulk TBAC concentrations taken from reference 5.
Figure S6. SFG ssp spectra of pure PVC, TBAC, and PVC-TBAC hybrid films with various bulk TBAC concentrations before (a) and after (b) water contact. (Figure S6 reproduced with permission from *Phys. Chem. Chem. Phys.*, 2015, 17(6), 4472-4482, Copyright 2015, Roy. Soc. Chem.)

References