Supporting Information

Incorporation and Exclusion of Long Chain Alkyl Halides in Fatty Acid Monolayers at the Air-Water Interface

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Analysis of Orientation Angle

Weidemann et al[1] determined by X-ray diffraction that the chains of PA at a pH of 2 were tilted by 25° at 10 mN/m, by 16° at 18 mN/m, and by 0° at 25 mN/m. In a different study[2] at 30 °C, a tilt angle of 21.4° at 15 mN/m and 5.3° at 30 mN/m were determined for PA. Since the dPA orientation changes in the TC phase to the UC phase[1,2], the square root of the intensity will slightly overestimate the number density. To determine the overestimation, orientational angle of the terminal methyl group (CD_3) plots at different polarizations are used (Figure S-1). The orientation angle (Θ) of the CD_3 can be estimated from the relationship $\alpha = 35.5^\circ - \Theta$.[3,4], where α is the chain tilt angle. At 18 mN/m, Weidemann et al[1] determined α to be 16° (and therefore Θ is 19.5°). With this information a theoretical ssp/ppp ratio for the CD_3 ss was estimated from Figure S-4 and compared to the experimental ssp/ppp ratio obtained from our SFG spectra. The theoretical ssp/ppp ratio obtained is of 11.5, whereas the experimental ratio was 12. This yields an overestimate of number density of 4%.

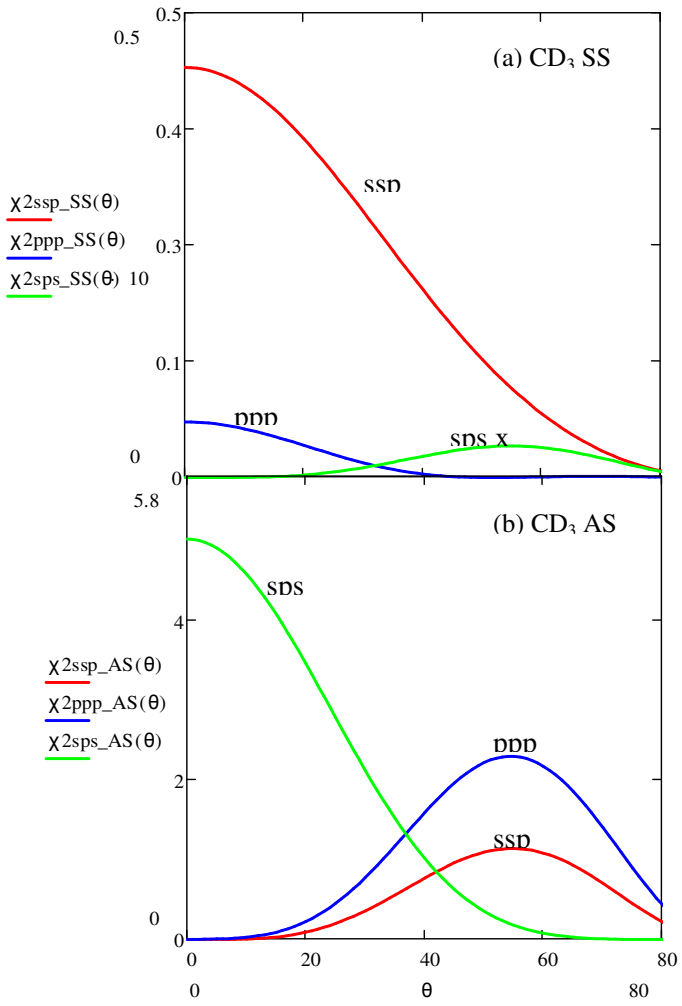

Figure S-1. Orientational angle (θ) at ssp, ppp, and sps polarizations for the (a) CD_3 symmetric stretch (SS) group and (b) CD_3 asymmetric stretch (AS) group.

References

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(2) Lee, K. Y. C.; Gopal, A.; von Nahmen, A.; Zasadzinski, J. A.; Majewski, J.; Smith, G. S.; Howes, P. B.; Kjaer, K. *J. Chem. Phys.* **2002**, *116*, 774.

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