Supporting Information

The Cambridge nanosecond sum frequency spectrometer employs a frequency doubled Nd:YAG laser to provide the visible pulse (532 nm). The infrared pulse is generated through stimulated Raman Scattering (in 34 atmospheres H_2) of the output of a pumped dye laser. For the experiments described in this work the visible and infrared beams impinged on the surface at 60 and 65° respectively in a counter-propagating geometry. At the sample each beam had an energy of approximately 1 mJ and overlapped to give a SF spectrum that was a 2 mm^2 surface average. To prevent film degradation through localised laser heating the sample was constantly rotated by mounting it on a motorised stage. The SF signal was detected by a photomultiplier tube and up to 70 complete scans were averaged to achieve a spectrum. Spectra were typically recorded in four combinations of sum frequency, visible and infrared beam polarisation, PPP, SSP, SPS and PSS. The best signal to noise ratio was obtained for the PPP polarisation combination and it is these spectra which are presented in the article.

The spectra are fitted with a mathematical model for sum frequency generation. The model applies Lorentzian line shapes to approximate the second order non-linear susceptibilities of the interface. Phase effects which occur between resonant signals and the non-resonant signal are incorporated. A Levenberg-Marquardt minimisation method is applied to optimise the theoretical fit to the experimental data.

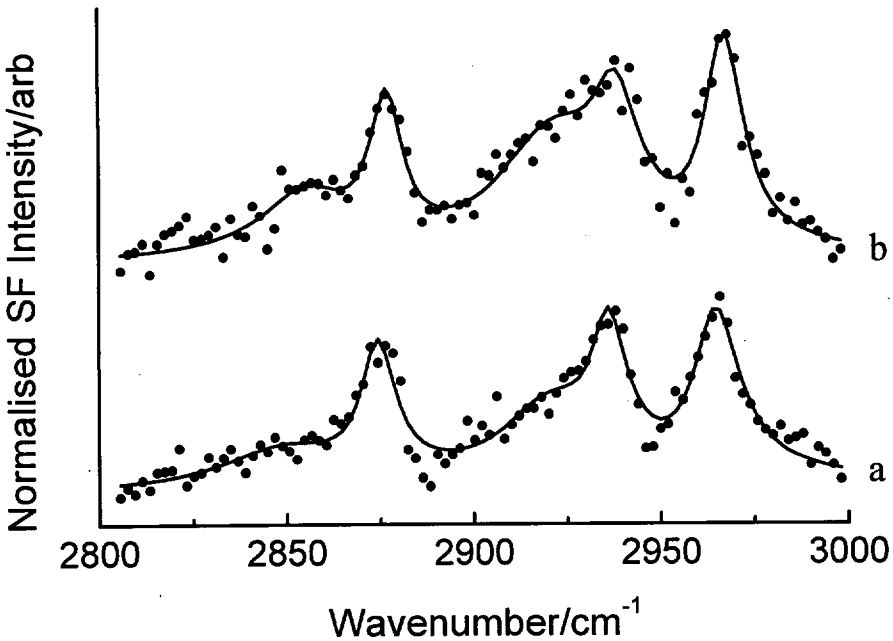

Figure 1. Sum frequency spectrum of a) composite gold nanoparticle/DODAC film formed at the air/water interface (0.40 nm^2/DODAC molecule) and deposited on an evaporated gold substrate, and b) DODAC monolayer deposited on an evaporated gold substrate from a 0.40 nm^2/DODAC molecule layer at the air/water interface. The spectra are reproduced at the same scale as each other and are approximately 180 times more intense than those given in Figure 2 of the article.