

Sum Frequency Spectroscopy of Langmuir–Blodgett Fatty Acid Films on Hydrophobic Gold

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Received: September 5, 2003; In Final Form: November 6, 2003

Langmuir–Blodgett (LB) multilayer films of the cadmium salts of five long chain fatty acids ($C_n\text{COOH}$, $n = 14, 16, 18, 20$, and 22) deposited onto hydrophobic gold have been investigated in the C–H stretching region by sum frequency vibrational spectroscopy (SFS). The highly ordered multilayer films were found to be strongly SF active, although the spectra were complicated by the presence of an interference effect dependent upon the number of layers deposited. This interference effect was evident in the phase of the measured asymmetric methyl stretching mode (r^-). Conversely, the phases of the symmetric stretching modes (r^+ and Γ_{FR}^+) were largely unaffected. The measured SF spectra were shown to arise from the summation of spectra from the uppermost and lowermost fatty acid layers. The SF spectrum of the uppermost fatty acid layer has a characteristic interference behavior arising from interaction of its resonant signal with the nonresonant signal from the substrate. Quantification of this interference effect gives a value in satisfactory agreement with previous theoretical predictions. The SF spectrum of the lowermost fatty acid is, as expected, independent of the multilayer thickness. Summation of individual SF spectra of the uppermost and lowermost fatty acid layers of multilayer films (achieved via selective deuteration) has been shown to accurately reproduce experimental spectra of fully monoisotopic multilayers. These findings imply that interpretation of SF spectra of LB multilayer films deposited on metal substrates must be performed with care and that deconvolution of spectra in terms of contributing layers is imperative.

Introduction

Ultrathin organic films are an essential component of many important nanotechnologies including molecular electronics, biomimetics, and photovoltaic devices.^{1–3} Due to the ease and inexpensive nature of their preparation such films are expected to prove useful for high volume, low-cost applications. A large class of thin films are those constructed via Langmuir–Blodgett (LB) deposition of fatty acids. To fully control and exploit the properties of these organic films it is first necessary to understand their organization and packing on a molecular level.

LB multilayer films composed of fatty acids have been studied by a variety of techniques such as optical absorbance,⁴ grazing incidence X-ray diffraction (GIXD),^{5–7} electron diffraction,^{4,8–10} neutron diffraction,¹¹ atomic force microscopy (AFM),^{12–15} and most recently by the nonlinear optical technique of sum frequency vibrational spectroscopy (SFS).¹⁶ The consensus of such studies is that LB films of the cadmium salts of fatty acids consist of very highly ordered domains of alkyl chains in near complete trans conformers and further that the alkyl chains of the fatty acids are oriented in a plane perpendicular to that of the film. Provided the subphase pH at deposition is greater than 6.5, the bulk of the acidic protons are exchanged for cadmium ions^{10,17,18} resulting in occlusion of cadmium ions between fatty acid layers in the film in a monoclinic structure. Deposition of fatty acid films onto solid substrates (pH 7) results in almost exclusively the Y-type

morphology, that is, head-to-head and tail-to-tail perpendicular to the surface. Fatty acid salt multilayers deposited onto hydrophilic substrates and exposed to air have been shown to be stable only if odd numbers of layers are employed.^{19,20} Even numbers of layers, which necessarily consist of charged headgroups exposed to air in the uppermost layer, subsequently rearrange to expose hydrophobic methyl groups to air. Conversely, fatty acid LB films consisting of an even number of layers are stable on hydrophobic substrates since the uppermost layer is methyl terminated. The stability of these films is reversed if the multilayers are exposed to aqueous solution rather than air.¹⁶

The pulsed laser technique of sum frequency vibrational spectroscopy (SFS) is an attractive tool for investigating LB multilayer films due to the detailed molecular level orientational and conformational information it may potentially provide.^{21,22} Typically a fixed frequency visible laser beam and a tuneable frequency infrared laser beam are spatially and temporally overlapped on an interface resulting in light at a frequency equal to the sum of the incident frequencies being emitted. Measuring the intensity of the emitted light while scanning the infrared frequency over, for example, the 2800–3000 cm^{-1} range produces a vibrational spectrum of SF active interfacial aliphatic species in the C–H stretching region. Since SF is highly interface specific, detailed conformational information of the interfacial region may be obtained. The use of a metal such as gold as a substrate results in nonresonant enhancement of the SF signal due to the increased polarizability of the interface and the large surface electric fields created through its high reflectivity. Moreover, the presence of a nonresonant SF signal

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arising from the substrate, in addition to the resonant signal arising from the interfacial species, allows the determination of the absolute polar orientation of the interfacial species through investigation of the phase of the resulting resonances.²³

Theoretical descriptions of sum frequency generation (SFG) from vibrationally active monolayers adsorbed on dielectric and metal surfaces are well established and are described in detail elsewhere.^{21,24,25} However, SFG from a multilayer adsorbed on a metal surface is a more complicated phenomenon, which has to date not been fully addressed. The complications arise from the fact that SFG may originate from multiple sources: First, unlike SFG from monolayers, multilayer films may potentially generate a nonlinear optical response from within the film itself. Second, interference effects may potentially occur between SFG originating at the metal/film and at the film/air interfaces. These two effects have been discussed separately in the literature by Hirose et al.²⁶ and Lambert et al.²⁷ Hirose and co-workers devised a model for simulating the SF signal produced during the growth of multiple formic acid layers on a reconstructed Pt(110) surface. Multiple reflections of both the excitation and the generated SF beams were used to predict the intensity of the measured signal. It was predicted and verified experimentally that the intensity of the SF signal oscillated with varying thickness of the formic acid layer. It should be noted that nonresonant SFG was not considered due to the use of platinum as a substrate.

The work of Lambert et al. was aimed at simulating SF light generated from a hydrocarbon monolayer adsorbed onto varying thickness inorganic substrates backed with gold. The Lambert et al. model was based solely on distance-dependent interference effects between the SF signal generated at the gold/substrate interface and that generated at the substrate/hydrocarbon interface; the effects of multiple reflections within the substrate were not included. The modeling considered each of the three methyl resonances in the 2800 and 3000 cm^{-1} C–H stretching region (symmetric, r^+ and r_{FR}^+ , and asymmetric, r^-) separately. The principal result was that the symmetric and asymmetric stretching modes were shown to behave differently as a function of substrate thickness. It was predicted that the phase (and hence peak shape) of the symmetric stretching modes (r^+ and r_{FR}^+) would vary regularly with substrate thickness with a periodicity of 3.01 μm . Superimposed upon this periodic phase variation was a lower intensity phase variation with a faster periodicity of 162 nm. The asymmetric stretching mode (r^-) was calculated to have a strong 162 nm periodicity component and a weaker component of 3.01 μm . These predictions were tested by using octadecyltrichlorosilane (ODS) monolayers self-assembled onto mica substrates backed with a gold film. By varying the thickness of the mica layer, Lambert et al. were able to confirm the micrometer scale periodicity of the symmetric stretching modes, and a good correlation between simulation and experiment was found. However, due to experimental limitations involved in cleaving mica, testing the predicted 162 nm periodicity of the asymmetric stretching modes was not possible.

In the present work, sum frequency spectra of multilayers of the cadmium salts of myristic (C_{13}COOH), palmitic (C_{15}COOH), stearic (C_{17}COOH), arachidic (C_{19}COOH), and behenic (C_{21}COOH) acids deposited onto perdeuterated octadecanethiol (*d*-ODT)-coated gold substrates have been recorded in the C–H stretching region. In addition, SF spectra of mixed perprotonated and perdeuterated multilayers of cadmium arachidate have also been measured. The precise control over the layer thickness that is possible with the LB technique and the highly stable and ordered structure of the fatty acid multilayers produced make

them an ideal candidate for testing the validity of the nanoscale interference effect predicted by Lambert et al. for the asymmetric stretching mode, r^- , of interfacial hydrocarbon layers on varying thickness substrates backed with gold. Furthermore the findings establish the limitations and means by which spectra of such systems may be meaningfully analyzed.

Experimental Section

Monolayers of the cadmium salts of myristic, palmitic, stearic, arachidic, and behenic acid were prepared at the subphase/air interface by spreading chloroform solutions of the acids (1.00 mg/mL) onto a PTFE LB trough (Nima 611) containing a subphase of cadmium sulfate (5×10^{-4} M in 18.2 M Ω cm Milli-Q water, pH \approx 7). Surface pressures were measured using Wilhelmy plates of Whatman Chr1 paper. Following chloroform evaporation, films were compressed to a surface pressure of 25 mN/m and allowed to equilibrate for 30 min. LB layers were deposited by sequential dipping onto a silicon wafer coated with a hydrophobic gold layer. Films incorporating combinations of perdeuterated and perprotonated fatty acid layers were formed by the procedure outlined above with the exception that the spread film was changed from perprotonated to perdeuterated fatty acid, or vice-versa, at the requisite time. Complete removal of the old film from the subphase/air interface was verified by the recording of a flat Π –A isotherm prior to the spreading of the new layer. Transfer ratios were, within error, unity for all deposited layers. The hydrophobic substrates employed were formed by self-assembly of perdeuterated octadecanethiol (*d*-ODT) films from methanolic (HPLC grade) solutions onto 150 nm thick gold layers thermally evaporated onto chromium-primed polished silicon wafers.²⁸ Solubilization of *d*-ODT in methanol was achieved by sonication of a needle tip quantity at 40 $^\circ\text{C}$ for 30 min. The gold-coated silicon wafers were subsequently immersed in the methanolic *d*-ODT solution for 12 h at ambient temperature to facilitate self-assembly of a *d*-ODT monolayer. Spectra were recorded in the C–H stretching region (2780–3020 cm^{-1}) at a resolution of 2 cm^{-1} in the PPP (sum frequency, visible, infrared) laser beam polarization combination. Details of the nanosecond spectrometer have been given elsewhere.²³ Generally as few as six scans were necessary to achieve good signal-to-noise ratios. The spectra were fitted using a Levenberg–Marquardt least-squares fitting routine with Lorentzian line profiles.²⁹ All chemicals used were obtained from Aldrich apart from the deuterated fatty acids, which were obtained from CDN Isotopes.

Results

SF spectra of perprotonated cadmium arachidate multilayers (2, 10, 20, 30, 40, and 50 layers) deposited on *d*-ODT-functionalized gold substrates were recorded in the PPP beam polarization combination over the C–H stretching region and are presented in Figure 1. The spectra of Figure 1 contain resonances attributable solely to the terminal methyl groups of arachidate, namely, the symmetric stretching mode, r^+ (2878 cm^{-1}), a Fermi-resonance of the symmetric stretching mode, r_{FR}^+ (2940 cm^{-1}), and the asymmetric methyl stretching mode, r^- (2966 cm^{-1}). No resonances attributable to the methylene groups of arachidic acid such as the symmetric stretching mode, d^+ , the Fermi-resonance of the symmetric stretching mode, d_{FR}^+ , or the asymmetric stretching mode, d^- , are observed. The absence of methylene resonances in the SF spectra implies that the methylene groups are in a locally centrosymmetric environment consistent with a fully trans conformation of the alkyl chain

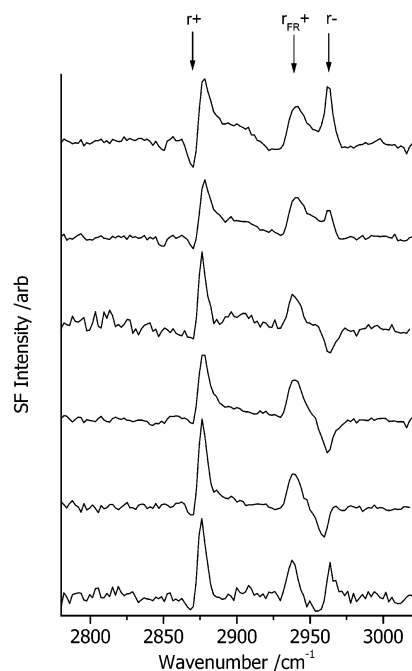


Figure 1. Sum frequency spectra of multilayer films of perprotonated cadmium arachidate deposited onto *d*-ODT-hydrophobed gold substrates recorded in the PPP laser beam polarization combination over the C–H stretching region. The spectra correspond from lower to upper to 2, 10, 20, 30, 40, and 50 fatty acid layer films. Spectra have been displaced vertically for clarity.

of the fatty acid. Three other features of the spectra of Figure 1 are noteworthy. First, for a bilayer of arachidic acid (lowest spectrum), all three methyl resonances occur as peaks indicating that the terminal methyl groups, which are dominantly SF active, point away from the surface and into air.³⁰ Second, as the number of fatty acid layers increases the r^+ and r_{FR}^+ resonances remain as peaks, (and are of approximately constant intensity regardless of the number of layers), while the r^- resonance changes monotonically from a peak to a dip and back to a peak again. Third, when the r^- resonance occurs as a dip, it occurs at lower wavenumber than when it occurs as a peak, that is, approximately at 2955 cm^{-1} compared with 2966 cm^{-1} .

The effect on SF spectra of constructing LB films of varying chain length fatty acids is shown in Figure 2 for films comprising a fixed number of layers, eight, constructed of myristic ($C_{13}\text{COOH}$), palmitic ($C_{15}\text{COOH}$), stearic ($C_{17}\text{COOH}$), arachidic ($C_{19}\text{COOH}$), and behenic ($C_{21}\text{COOH}$) acid. In common with the SF spectra of Figure 1, solely methyl resonances are observed, implying that the alkyl chains of the SF active fatty acids are highly ordered in a fully trans conformation. Further it is noted that, as observed for increasing numbers of layers of arachidic acid in Figure 1, no change in the phase of the r^+ and r_{FR}^+ resonances is observed as a function of the chain length of the fatty acid employed to create the eight layer films. The phase of the r^- asymmetric methyl stretching mode however is observed to change monotonically from a peak to a differential dip as the chain length of the fatty acid employed is increased progressively from 14 to 22, in common with the trend observed in Figure 1 for increasing numbers of deposited layers of a fixed chain length fatty acid.

The spectral trends observed in Figures 1 and 2 imply that the phase of the r^- resonance has a dependence upon the thickness of the multilayer film, which is absent or much less pronounced for the r^+ and r_{FR}^+ resonances. This finding suggests that a single fatty acid layer, the uppermost with its methyl

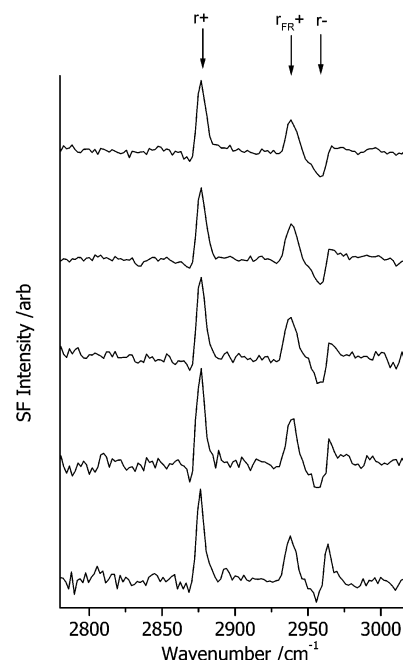


Figure 2. Sum frequency spectra of eight layer fatty acid films comprising perprotonated cadmium salts of myristic ($C_{13}\text{COOH}$), palmitic ($C_{15}\text{COOH}$), stearic ($C_{17}\text{COOH}$), arachidic ($C_{19}\text{COOH}$), and behenic ($C_{21}\text{COOH}$) acid from the lowermost to the uppermost spectrum, respectively.

groups oriented into air and away from the surface, is dominant in the production of the resonant SF signal. The spectral inactivity of the fatty acid layers comprising the bulk of the multilayer structure may be understood in terms of the requirement of asymmetry for SF activity. Specifically, with the exception of the lowermost and uppermost fatty acid layers, each layer within the multilayer structure has an interface with an adjacent layer in the opposite polar orientation. A plane of symmetry therefore exists between the two buried fatty acid layers and they are consequently SF inactive. It may be postulated that the phase change of the r^- resonance arises from a thickness-dependent interference effect such as that observed and modeled by Lambert et al.^{27,31} The number of fatty acid layers required for the r^- resonance to change from a symmetric dip (estimated as layer 20, third spectra from the lowest, Figure 1) to a symmetric peak (estimated as layer 50, upper spectrum, Figure 1), that is, 30 layers or 60 layers for a full period, may, in conjunction with layer thickness data, be used to estimate a length scale over which the interference effect operates. The most accurate data for the thickness of cadmium salt fatty acid films comes from GIXD measurements such as those by Vitta et al.³² For arachidic acid, Vitta et al. determined a bilayer thickness of $5.55 \pm 0.01\text{ nm}$. Multiplication of this thickness value for a bilayer by 30 gives an estimated thickness of 60 layers and hence a value for the periodicity of the interference effect of approximately 167 nm. It is noted that although this is only an estimated value (due to the inaccuracy of determining the precise number of layers corresponding to symmetric peaks and dips), it is in remarkably good agreement with the periodicity predicted by Lambert et al. of 162 nm.

Confirmation of the origin of the dominant resonant SF signal as the uppermost fatty acid layer of the multilayer films was obtained by using selective deuteration of specific fatty acid layers. Layers constructed of perdeuterated fatty acid are inherently SF inactive in the C–H stretching region, and consequently resonances in the $2800\text{--}3000\text{ cm}^{-1}$ vibrational region can be assigned to perprotonated fatty acid layers of

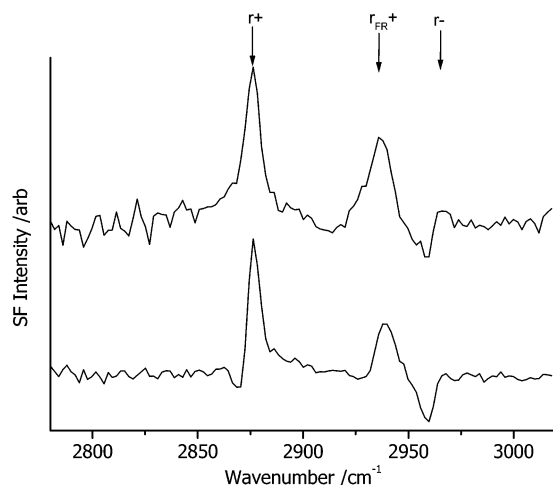


Figure 3. Sum frequency spectra of (upper spectrum) a 10 layer cadmium arachidate multilayer film composed of nine perdeuterated fatty acid layers and with the uppermost layer perprotonated and (lower spectrum) a 10 layer cadmium arachidate multilayer film comprising solely perprotonated fatty acid. The spectra have been displaced for clarity.

known locations within the film. Figure 3 presents the SF spectrum of a multilayer film consisting of 10 layers of arachidic acid with the first nine layers perdeuterated and the uppermost layer perprotonated (upper spectrum). The spectrum is comparable in intensity and phase to that of a fully perprotonated 10 layer film (lower spectrum of Figure 3, reproduced from Figure 1). This finding strongly supports the hypothesis that it is the uppermost fatty acid layer in contact with air that is dominant in giving rise to the SF signal from a multilayer film constructed from a single isotopic species.

Detailed comparison of the two spectra of Figure 3 however reveals that although they are closely similar, minor differences do exist. The peak shapes for the symmetric stretching modes in the perprotonated multilayer spectrum (lower) are narrower, are nonsymmetric, and unlike those of the upper spectrum, are preceded by small dips at lower wavenumbers. Perusal of the spectra of Figures 1 and 2 shows that these observations of perprotonated fatty acid multilayers are not artifacts of a single spectrum but are reproducible. The origin of the difference in line shape of the SF spectrum obtained from a fully perprotonated and a partially perdeuterated/partially perprotonated multilayer film can be shown to lie in the fact that while the SF signal from the uppermost fatty acid layer dominates the spectrum, there is nevertheless a significant contribution from the lowermost fatty acid layer in contact with the hydrophobic gold substrate.

Figure 4 presents SF spectra obtained in the C–H stretching region of cadmium arachidate multilayers composed of two fatty acid layers deposited onto *d*-ODT-treated gold substrates. The upper spectrum is that measured from a film composed of a perdeuterated lowermost layer and a perprotonated uppermost layer. The lower spectrum is that obtained from a film comprising a perprotonated lowermost layer and a perdeuterated uppermost layer. Clearly when the uppermost layer is perprotonated the resonances appear as peaks while when the lowermost layer is protonated the resonances occur as dips. This observation derives from the sign dependence of the second-order nonlinear susceptibility, $\chi^{(2)}$, upon the polar orientation of the species being probed and hence reflects the opposing polar orientations of the perprotonated fatty acids in the two multilayer films investigated. It is also noted that the resonance intensity of the upper spectrum, that with the perprotonated fatty

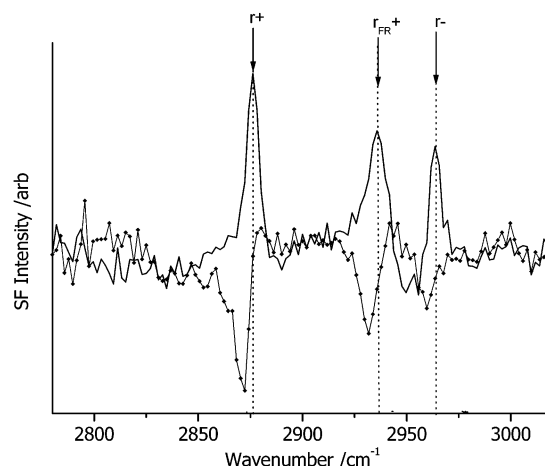


Figure 4. Sum frequency spectra of two layer cadmium arachidate films where (lower spectrum) the lower layer of the film is perprotonated and the upper layer is perdeuterated and (upper spectrum) the lower layer of the film is perdeuterated and the upper layer is perprotonated. Spectra are presented on the same SF intensity scale.

acid layer uppermost and orientated into air, is significantly stronger than that of the lower spectrum corresponding to the perprotonated layer orientated toward the substrate. Comparable observations, that is, dependence of SF intensity upon interfacial separation, are commonly made in SF spectra and are attributable to local field effects.²¹ A potential additional contributing factor to the smaller resonance intensity of the lower spectrum relative to the upper spectrum of Figure 4 is that the corresponding fatty acid layer may be conformationally less well ordered due to interaction with the underlying *d*-ODT layer rather than air. It is noted however that this contribution is expected to be minimal since the lack of methylene resonances in the spectra of Figure 4 indicated that both fatty acid layers lack a significant number of gauche defects and consequently that they are highly conformationally ordered. Finally, the resonance wavenumbers of the lower spectrum are significantly offset to lower values in comparison with those of the upper spectrum. These observed frequency shifts originate from the difference in the local environment of the methyl groups terminating the fatty acid alkyl chains in the two films (air versus a condensed phase). Specifically, it is well-known that vibrational frequencies decrease when a molecule is transferred from a gaseous phase to a liquid phase.³³ Indeed a comparable red shift to that observed in the current work has been reported previously by Ward³⁴ in SF spectra of ODT adsorbed on gold in air and under several organic and aqueous solvents. Methyl stretching resonances were red-shifted by approximately 4–5 cm^{-1} under liquids. Ong et al. observed similar effects in the SF spectra of alkoxy-terminated alkane thiols in air and under various liquids.³⁵

Numerical summation of the two spectra of Figure 4 yields a prediction of the sum frequency spectrum of a two layer film comprising solely perprotonated cadmium arachidate based on the individual contributions of the uppermost and lowermost layers. The result of such a summation is given as the upper spectrum of Figure 5. Comparison of the simulated spectrum with an experimental spectrum of a two layer film of perprotonated fatty acid, lower spectrum of Figure 5 (reproduced from Figure 1), reveals that the spectra are identical to within noise and that the salient features are reproduced. It may be concluded therefore that while the dominant SF signal from a multilayer fatty acid film derives from the uppermost layer, there is a sizable detectable contribution from the lowermost layer, which acts to modify the observed line shapes and spectral intensity.

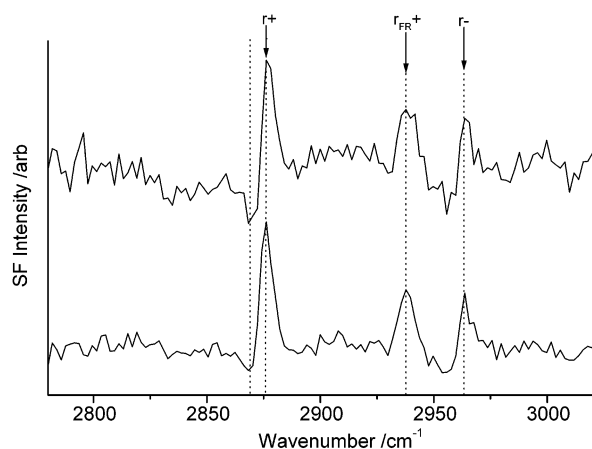


Figure 5. Sum Frequency spectrum (lower spectrum) of a fully perprotonated two layer cadmium arachidate multilayer film, reproduced from Figure 1 and (upper spectrum) a simulated SF spectrum obtained by numerical addition of the two spectra of Figure 4. Spectra displaced for clarity.

It may be shown via creation of multilayer films with perprotonated fatty acid layers buried within otherwise perdeuterated layers that the nanoscale periodicity interference effect observed for the r^- resonance in Figures 1 and 2 is truly distance-dependent and is not a function of the SF active layer necessarily being uppermost in the multilayer film. Specifically, Figure 6a presents spectra of 10 layer arachidic acid multilayer films, which are fully perdeuterated with the exception of layers 2, 4, 6, 8, and 10, respectively, from the lowermost to the uppermost spectra. It is noted that in a comparable manner to that observed in Figure 1, no significant change in r^+ or r_{FR}^+ phase is observed through the spectral series to 10 layers; however, the r^- resonance undergoes a significant phase change. As expected, the fact that the lowermost fatty acid layer (perdeuterated) does not contribute to the spectra is evident in the observation that, unlike Figure 1, the resonance line shapes are symmetrical. Figure 6b presents spectra from comparable 10 layer predominantly perdeuterated arachidic acid films where a single perprotonated fatty acid layer is buried as layer 1, 3, 5, 7, and 9, respectively, from the lower to upper spectra. It is noted that the phase of the resonances of the spectra in Figure 6b are opposite those of the spectra of Figure 6a due to the reversed polar orientation of the fatty acid and the sign dependence of $\chi^{(2)}$. In a manner similar to the spectra of Figure 6a little if any change in the r^+ and r_{FR}^+ phases is observed as a function of the separation of the SF active layer from the substrate; however, in a comparable manner to Figure 6a, the r^- resonance undergoes a significant change in phase. One further noteworthy feature of the spectra comprising Figure 6a,b concerns the red shift of all of the spectra with respect to the uppermost spectrum of Figure 6a. The latter is the only spectrum of a layer exposed to air rather than to another hydrocarbon layer. This observation supports the hypothesis advanced earlier with regard to the origin of the red shift in the spectrum of the lower layer of a two layer film, Figure 4, being due to a change in the local environment of the terminal methyl groups of the fatty acids chains.

To quantify the periodicity of the interference effect of the r^- phase in systems where only one layer is SF active, multilayers comprising an uppermost perprotonated layer on otherwise fully perdeuterated films were prepared for 20, 30, 40, and 50 layer films. The SF spectra recorded of these multilayer films are presented in Figure 7 as the upper four spectra. The lower two spectra of Figure 7 are those of comparable 2 layer

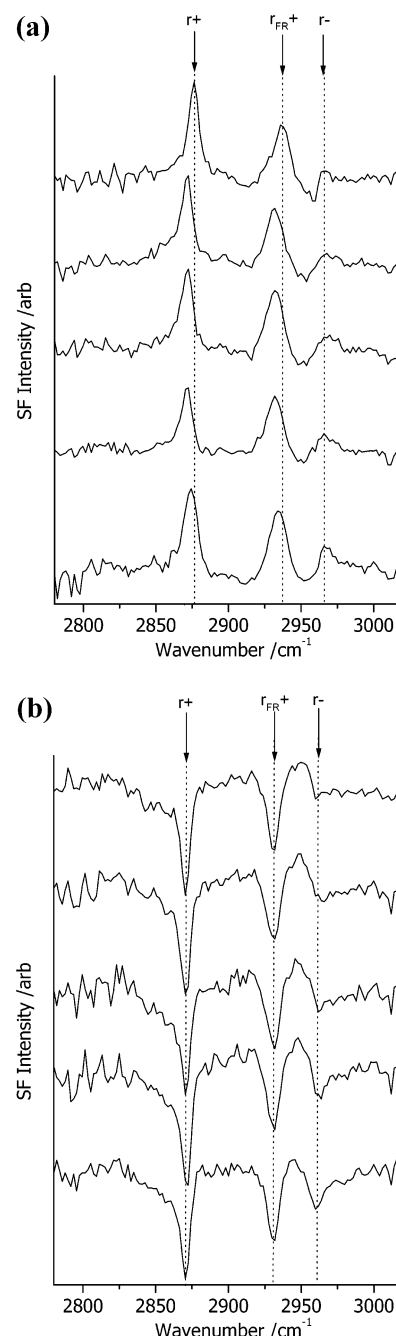


Figure 6. Sum frequency spectra of 10 layer perdeuterated cadmium arachidate multilayer films containing a single perprotonated fatty acid layer (a) at (from lower to upper) layer 2, 4, 6, 8, and 10, respectively, and (b) at (from lower to upper) layer 1, 3, 5, 7, and 9, respectively.

and 10 layer films (lowest and next lowest, respectively) reproduced from Figures 4 and 6a. Investigation of Figure 7 reveals that that the spectra correspond to a little over half of the full periodicity of the r^- interference effect. Specifically, the r^- resonance commences at two layers as a differential peak shape, which by 20 layers has converted to a full dip. Between layers 30 and 40, the r^- resonance converts from a differential dip to a differential peak before finally becoming a full peak at 50 layers. The thickness of the 30 layers between the full dip (layer 20) and the full peak (layer 50) may therefore be considered to represent approximately half of the full periodicity of the r^- interference effect. Employing the GIXD data of Vitta et al.³² allows the observed periodicity to be quantified at approximately 167 nm. Clearly this number matches that determined experimentally for fully perprotonated fatty acid

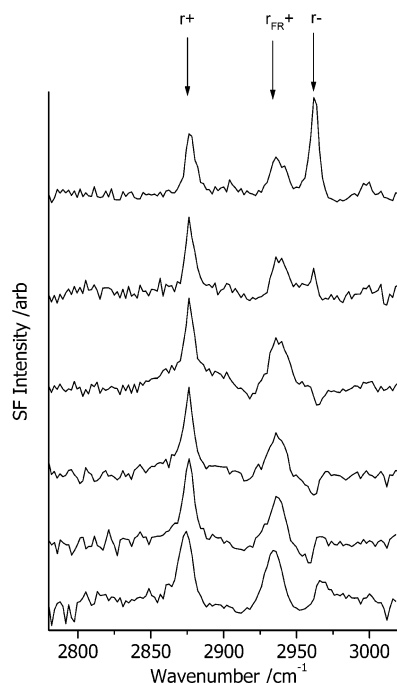


Figure 7. Sum frequency spectra of cadmium arachidate multilayer films where the uppermost layer of each film is perprotonated and all of the lower layers are perdeuterated: from lower to upper, 2, 10, 20, 30, 40, and 50 layers (2 layer spectrum reproduced from Figure 4; 10 layer spectrum reproduced from Figure 6a).

films (167 nm) and correlates well with that predicted theoretically by Lambert et al. (162 nm).²⁷ Again it must be stressed that this number is however an approximation only and is subject to the uncertainty arising from the determination of the appropriate layers corresponding to symmetric peaks and dips.

Discussion

The intensity of SF signals arising from potentially resonant species (such as adsorbed fatty acids) at monolayer or sub-monolayer coverage on substrates with nonresonant SF activity (such as gold) may be described in terms of a resonant susceptibility from the resonant species ($\chi_R^{(2)}$) and a nonresonant susceptibility from the substrate ($\chi_{NR}^{(2)}$):

$$I_{SF} \propto |\chi_R^{(2)} + \chi_{NR}^{(2)}|^2 \quad (1)$$

which may be expanded further in terms of the resonant (δ) and nonresonant (ϵ) phases:

$$\begin{aligned} I_{SF} &\propto |\chi_{R,ijk}^{(2)}| e^{i\delta} + |\chi_{NR,ijk}^{(2)}| e^{i\epsilon}|^2 \\ &\propto |\chi_{R,ijk}^{(2)}| e^{i\delta} + |\chi_{NR,ijk}^{(2)}| e^{i\epsilon} ||\chi_{R,ijk}^{(2)}| e^{-i\delta} + |\chi_{NR,ijk}^{(2)}| e^{-i\epsilon}| \\ &\propto |\chi_{R,ijk}^{(2)}|^2 + |\chi_{NR,ijk}^{(2)}|^2 + 2|\chi_{R,ijk}^{(2)}||\chi_{NR,ijk}^{(2)}| \cos[\epsilon - \delta] \end{aligned} \quad (2)$$

$\chi_{NR}^{(2)}$ is typically orders of magnitude greater than $\chi_R^{(2)}$. Consequently, the first term (resonant) on the right-hand side (RHS) of eq 2 is typically insignificant in relation to the second term (nonresonant), which provides a more or less frequency-independent background SF signal. The third term on the RHS of eq 2, a cross term of $\chi_R^{(2)}$ and $\chi_{NR}^{(2)}$, is of moderate magnitude and provides the measured resonant SF signal. The line shape observed in SF spectra is determined by the phase relation between δ and ϵ . The nonresonant phase ϵ may be considered to be frequency-independent and equal to 90° on a gold

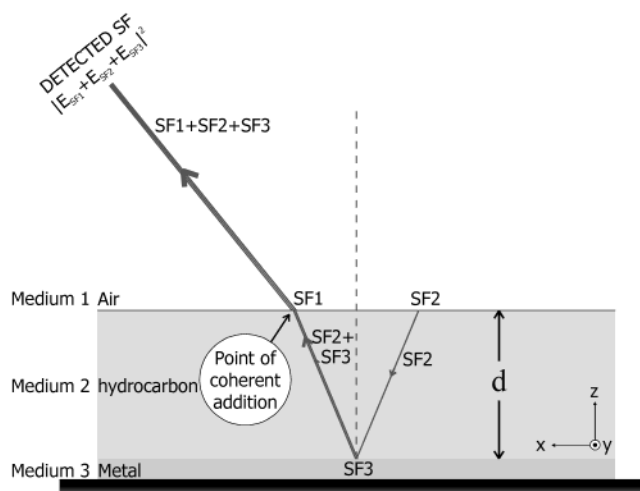


Figure 8. Schematic diagram showing sum frequency generation from the air/hydrocarbon (multilayer)/gold interface system. The incident visible and infrared laser beams are omitted for clarity. SF1 and SF2, the two resonant sum frequency beams generated at the air/hydrocarbon interface, are depicted, as is SF3, the nonresonant sum frequency beam generated at the gold surface. The diagram does not include the resonant sum frequency signal generated at the hydrocarbon/hydrophobic gold interface. The d -ODT layer coating on the gold has been omitted from the diagram for clarity.

substrate, while the resonant phase δ changes as the infrared frequency is scanned through the resonance frequency of the mode under investigation. For resonant groups pointing away from a surface with a strong nonresonant susceptibility such as ODT on gold, the SF spectra can be modeled with $\delta = 90^\circ$. Hence there is constructive interference between the resonant and nonresonant polarizations ($\cos(\epsilon - \delta) = 1$) giving rise to peaks in the spectrum. Conversely, destructive interference ($\delta = -90^\circ$ for a resonant group pointing toward the surface) produces a resonant dip.³⁶ The orientation of a resonant mode in relation to the surface consequently defines the phase of the resonant SF signal generated. Specifically, a terminal methyl group of a fatty acid layer oriented away from a gold surface results in a spectral peak, while a terminal methyl group of a fatty acid layer oriented toward a gold surface results in a spectral dip.

Spatially displacing the sources of resonant and nonresonant SF activity (for example by construction of a multilayer fatty acid film on gold with an SF active uppermost layer) results in interference effects in SF spectra due to changes in phase of individual signals as they traverse the displaced space. As discussed earlier, such interference effects may potentially affect both the intensity and line shape of SF resonances. The intensity component of the interference effect has been exploited in various SF studies of polymer films on nonresonant substrates where through appropriate choice of angles of incidence and film thickness the selective investigation of buried as well as exposed interfaces has been possible.^{37–39}

The modeling and experimental work of Lambert et al.^{27,31} dealt with SFG from a composite system comprising a micrometer thick mica substrate functionalized on one face with an alkyl silane and on the opposite face with gold. Such a system may be considered analogous to the present LB multilayer system in which all but the uppermost fatty acid layer are perdeuterated (Figure 7) and the perdeuterated fatty acid layers are treated as a non-SF-active continuum comparable to mica. In accordance with Lambert et al., the detected SF signal may then be considered as a superposition of three different SF sources as shown in Figure 8. The SF signal labeled SF1 is a

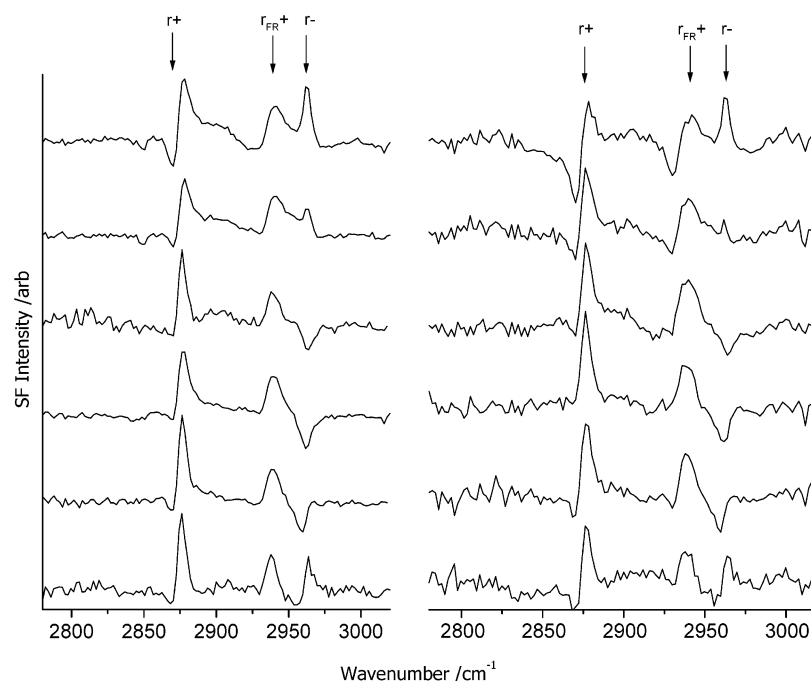


Figure 9. Sum frequency spectra (left) of fully perprotonated cadmium arachidate multilayer films comprising, from lower to upper, 2, 10, 20, 30, 40, and 50 layers, reproduced from Figure 1, and (right) simulated SF spectra of, from lower to upper, 2, 10, 20, 30, 40, and 50 layers, calculated through numerical addition of the lowest spectrum of Figure 6b with each spectrum of Figure 7. Spectra displaced for clarity.

resonant signal originating from the uppermost perprotonated fatty acid layer and radiating into air. The SF signal labeled SF2 arises from the same resonant source but radiates into the perdeuterated multilayer structure, reflects off the gold surface, and emerges into air. The SF signal labeled SF3 is a nonresonant signal arising from the gold surface, which radiates through the perdeuterated fatty acid layer before passing into air. The experimentally measured signal is a coherent summation of SF1, SF2, and SF3. It is evident that interference effects between the three SF beams will occur and be manifest in experimental spectra. Where relevant, the resonant signal from the hydrocarbon/gold interface must also be included (not shown in Figure 8). While this signal does not contribute to the interference effect observed for the uppermost layer, the line shape and intensity of this signal is nevertheless important in interpreting observed SF spectra in systems where the lowermost layer is SF active.

The modeling work of Lambert et al.²⁷ showed that in the PPP laser beam polarization combination there are two dominant interference effects between the three emitted SF beams. The relative contribution of each interference effect to the observed SF spectrum varies with the resonance investigated. Specifically, interference between SF2 and SF3, with a characteristic periodicity on a micrometer scale, is the dominant effect for the r^+ resonance. A weaker nanometer scale periodicity, attributable to interference between SF1 and SF3, is observed concurrently. The r^- resonance conversely is dominated by the nanometer scale periodicity SF1/SF3 interaction but is modulated by the micrometer scale periodicity SF2/SF3 interaction. This apparently disparate behavior is attributed to the relative phases and intensities of the x and z components of the SF E-fields generated in the PPP laser beam polarization combination. Specifically, Lambert et al.²⁷ demonstrated that for the r^+ resonance the x and z components are in phase for the SF2/SF3 interaction but out of phase for the SF1/SF3 interaction. Since the relative intensities of the x and z components are comparable, the former interaction dominates the SF spectrum, while the latter is apparent only as a weak perturbation. Conversely for the r^- resonance, the x and z components are out of phase for

the SF2/SF3 interaction but in phase for the SF1/SF3 interaction. Both interactions are evident in an SF spectrum however since the x and z components are of significantly different intensity.

The mica-based experimental system employed by Lambert et al.³¹ facilitated the quantification of the periodicity of the micrometer scale interference effect as $3.3 \mu\text{m}$ for the r^+ and r_{FR}^+ resonance, in excellent agreement with the modeling prediction. As expected no experimental evidence for a nanometer scale interference effect for the r^+ and r_{FR}^+ resonances was obtained. The micrometer scale interference effect for the r^- resonance was experimentally confirmed and quantified at approximately $3.1 \mu\text{m}$. Superposition of the predicted more intense nanometer length scale interference periodicity effect on the micrometer scale periodicity effect led however to less precision in this value. Quantification of the periodicity of the nanometer scale periodicity for both the r^+ and r^- resonances was not possible due to experimental limitations associated with cleaving mica.

Employing the model of Lambert et al. and substituting literature values for the optical properties of the hydrocarbon layers ($n = 1.45$)⁴⁰ leads to a prediction of the nanometer scale and micrometer scale periodicities for the r resonances of 185 nm and $3.2 \mu\text{m}$, respectively. Clearly the fatty acid multilayer system of the present study is unsuitable for testing periodicities on micrometer length scales (although it is noted that the near invariance of the phase of the r^+ and r_{FR}^+ resonances in the spectra of the present study concurs with the model predictions). However the fatty acid multilayer system is ideally suited to confirming the predictions of the periodicity of the nanometer scale interference effect of the r^- mode (the intensity of the nanometer periodicity in the r^+ mode is predicted to be, and has been experimentally verified to be, very weak). Specifically, the periodicity determined from the spectra of Figure 7 and the GIXD data of Vitta et al.³² of approximately 167 nm is in satisfactory agreement with the theoretical prediction of the nanometer scale r^- interference effect produced by coherent interaction between the resonant SF signal originating at the

fatty acid/air interface and radiating into air and the nonresonant SF signal originating at the gold surface.

Confirmation of the origin and nature of the r^- interference effect, which occurs in systems containing a single SF active layer, facilitates the full interpretation of SF spectra of multilayer films comprising multiple SF active layers. Specifically, SF spectra of multilayer films comprising fully perprotonated fatty acids may be interpreted as comprising two summed SF spectra: that arising from the lowermost fatty acid layer in contact with the hydrophobic substrate, which is invariant with film thickness (Figure 6b, lowest spectrum), and that arising from the uppermost layer, which exhibits an r^- phase dependence upon film thickness with a periodicity of approximately 167 nm (spectra of Figure 7). For example, the left spectral series of Figure 9 reproduces the spectra of Figure 1 for LB multilayer films of fully perprotonated cadmium arachidate. The right spectral series of Figure 9 comprises spectra simulated by numerical summation of the lowest spectrum of Figure 6b and each spectrum of Figure 7 (corresponding to, in ascending order 2, 10, 20, 30, 40, and 50 layers). Clearly the spectra for multilayer films comprising the same number of layers are closely similar, with very good agreement in terms of phase and relative peak intensities. Furthermore such a procedure elucidates the origin of subtle features in SF spectra such as the broad shoulder centered at 2900 cm^{-1} in several of the spectra of Figure 1. This spectral feature does not arise from a methylene d resonance as may be expected from a cursory investigation (it is absent in the uppermost spectrum of Figure 7) but rather is the expected convolution of spectra from the lowermost and uppermost layers in a fully perprotonated multilayer film.

It is evident from these findings that care must be taken in interpreting SF spectra of fully isotopic multilayer films on metal substrates. First, it must be recognized that spectra exhibit an interference effect, which complicates the interpretation of resonant phase with respect to polar orientation. Second, although the dominant resonant signal originates from the uppermost layer, a significant contribution arises from the lowermost layer, which acts to modify spectral line shapes, particularly of the asymmetric methyl stretching mode. As such, SF spectra of such systems require deconvolution to facilitate meaningful interpretation.

Conclusions

Langmuir–Blodgett multilayer films of cadmium salts of fatty acids deposited onto hydrophobic gold surfaces have been found to be sum frequency active in the C–H stretching region. Solely methyl resonances (r) are observed in the SF spectra indicating that the hydrocarbon chains of the fatty acids are highly ordered in fully trans conformations. Through judicious incorporation of perdeuterated fatty acid layers, it has been shown that in fully isotopic films SF signals arise from both the lowermost and uppermost fatty acid layers but not from intermediate layers. The uppermost layer gives rise to an SF spectrum with near invariant r^+ and r_{FR}^+ phases as a function of film thickness but an r^- phase that exhibits a periodicity of approximately 167 nm. The experimentally determined r^- periodicity is in satisfactory agreement with previous theoretical predictions. The lowermost layer gives rise to an SF spectrum with negative phases for all three r^+ , r_{FR}^+ , and r^- resonances that are invariant with film thickness. Experimentally measured SF spectra of fully perprotonated multilayer films are consequently complex summations of multiple SF contributions. Meaningful interpretation of such spectra may only be made via deconvolution.

Acknowledgment. This work was conducted under the auspices of a Leverhulme Trust Research Grant (F/09/650/A). We thank the Oppenheimer Fund of Cambridge University for a studentship for J.H. Samples of perdeuterated arachidic acid were kindly supplied by Unilever Research and Development, Port Sunlight Laboratory.

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