Nonlinear optical studies of monomolecular films under pressure

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Nonlinear optical techniques (second-harmonic and sum-frequency generation) have been used to study the structure of organic molecules that are confined and compressed between a lens and a flat surface. The molecules studied include self-assembled monolayers of *n*-octadecyltriethoxysilane and Langmuir-Blodgett films of stearic acid, octadecylalcohol, octadecylamine, and a liquid-crystal molecule 4'-*n*-octyl-4-cyanobiphenyl (8CB). The contact area created by elastic deformation of the flat surface and lens under pressure was large enough to contain the entire laser beam ($> 100 \mu\text{m}$ radius at $\approx 10 \text{ MPa}$ for $R = 15 \text{ cm}$). Under these conditions, the sum-frequency generation (from CH_3 and OH stretch modes) and second-harmonic generation (8CB) signals were found to decrease by a factor between 100 and 1000 times the original signal. This indicates vanishing of the second-order monolayer susceptibility due to disorder of the head groups and/or flattening of the molecular axis so that they lie parallel to the surface. The phenomenon was reversible and the nonlinear signals recovered completely upon removal of the pressure.

I. INTRODUCTION

Self-organized ultrathin organic films, such as Langmuir-Blodgett (LB) films or solution self-assembled monolayers (SAM's), are attractive systems for fundamental and practical studies of lubrication. While their thickness is only a few nanometers, these films can dramatically alter the tribological properties of the underlying substrate.¹ Because the development of high-performance lubricants calls for a detailed understanding of friction and wear at the molecular level,^{2,3} these ultrathin films are ideal model systems. They have been characterized using a variety of techniques, including diffraction methods,⁴ infrared (IR) and Raman spectroscopy,⁵ atomic-force microscopy (AFM) and scanning tunnel microscope,⁶ and nonlinear optics.⁷

Structural studies by various diffraction and nonlinear-optics methods have been performed only under zero-pressure conditions. Although monolayer structures under pressure and shear have been studied using the AFM (Refs. 8–10) and the surface force apparatus,¹¹ the molecular conformation and orientation within the monolayers under conditions that are closer to real lubricating conditions, i.e., under pressure, is largely beyond their capability. It requires spectroscopic methods to derive such information. Currently, spectroscopic methods, such as infrared and Raman, can readily fingerprint particular chemical functionalities subjected to controlled wear;^{12,13} however, these methods cannot be used to monitor ultrathin lubricant films, *in situ*, with an applied pressure or shear due to their limited sensitivities.

It has recently been demonstrated that second-harmonic generation (SHG) and sum-frequency generation (SFG) are ideal tools to study buried interfaces.^{14,15} These techniques can be readily adopted to study molecular films under static pressure to provide molecular orientation or conformation information. In this paper, we report results obtained using these nonlinear optical tech-

niques to study orientation, conformation, and molecular vibrations of a variety of Langmuir-Blodgett and SAM films under applied pressure. The results indicate that the end groups of the previously oriented molecules lose their polar ordering under pressure, but recover the polar orientation as soon as the pressure is released.

We complete this introduction with a brief review of some of the theoretical aspects of compression of surfaces in the elastic regime and of the basic principles of nonlinear optics as applied to the present study.

A. Elastic contact between surfaces

The elastic deformation and stress distribution in the contact area between a flat and a sphere can be described by the standard Hertzian theory.¹⁶ The contact radius a can be determined from the following expression:

$$a = \left[\frac{3FR}{4E} \right]^{1/3}, \quad (1)$$

where F is the total force exerted on the surface, R is the radius of curvature of the sphere, E is the reduced Young's modulus of the substrates given by $1/E = (1 - \sigma_1^2)/E_1 + (1 - \sigma_2^2)/E_2$, with σ_n the corresponding Poisson ratios of the sphere and flat. The pressure P at position r inside the contact area can then be expressed as

$$P(r) = P(0)\sqrt{a^2 - r^2}$$

and the average pressure is

$$\bar{P} = \frac{F}{\pi a^2} = \frac{1}{\pi} \left[\frac{16FE^2}{9R^2} \right]^{1/3}. \quad (2)$$

The pressure is only dependent on the $\frac{1}{3}$ power of the force. In order to vary the pressure by a factor of 10, for example, the force has to be changed by a factor of 1000. A more efficient way of varying P is by changing the ra-

dus of curvature R . Combining (1) and (2), we have

$$\bar{P} = \frac{4Ea}{3\pi R}. \quad (3)$$

Here $E = 35$ GPa,¹⁷ when both substrates are fused silica, as in the present experiments. The contact radius a is readily measurable with a microscope and, since R is known, we can easily calculate the average pressure. A typical example is $a = 0.5$ mm and $R = 15$ cm, yielding $P = 50$ MPa.

B. Nonlinear optics

SHG or SFG as a probe to study monomolecular films has been described in previous publications.^{18,19} Within the electric dipole approximation, the process is forbidden in a centrosymmetric medium, but allowed at the surface where the inversion symmetry is broken. In our case, the amorphous fused-quartz substrate does not contribute significantly to the signal; therefore, the second-order nonlinear optical response of the system is generated essentially all from the monolayer under study. The SHG and SFG signal S is then proportional to the square of the effective surface nonlinear polarization

$$P_s^{(2)}(\omega_s) = \chi_s^{(2)}(\omega_s = \omega_1 + \omega_2) : E(\omega_1) E(\omega_2) \quad (4)$$

and can be further written as

$$S \propto [L(\omega_3) \cdot \chi_s^{(2)}(\omega_3 = \omega_1 + \omega_2) : L(\omega_1) L(\omega_2)]^2 \times I(\omega_1) I(\omega_2), \quad (5)$$

with $\omega_1 = \omega_2$ for SHG. $E(\omega_i)$ is the electric field at the monolayer and $I(\omega_i)$ the corresponding light intensity at the respective frequencies. $L(\omega_i)$ is the local-field tensor defined as the ratio of the local field at the monolayer to the incident field. The surface susceptibility $\chi_s^{(2)}$ can be related to the molecular polarizability $\alpha^{(2)}$ by a coordinate transformation averaged over the molecular orientation distribution, denoted by the angular brackets:

$$\chi_{s,ijk}^{(2)} = N_s \sum_{l,m,n} \langle (\hat{i} \cdot \hat{l})(\hat{j} \cdot \hat{m})(\hat{k} \cdot \hat{n}) \rangle \alpha_{lmn}^{(2)}, \quad (6)$$

where N_s is the number of molecules per unit area, ijk the unit vectors for the laboratory frame, and lmn for the molecular reference frame. With information of N_s and

$\alpha_{lmn}^{(2)}$ available, the measured $\chi_s^{(2)}$ can be directly related to the molecular orientation. In the case of sum-frequency generation (infrared + visible), the nonlinear polarizability near vibrational resonances can be written as the sum of a resonant and nonresonant part:

$$\alpha^{(2)} = \alpha^{(2)R} + \alpha^{(2)NR} \quad (7)$$

with

$$\alpha^{(2)} = \sum_q \frac{A_q}{(\omega_q - \omega_{IR} - i\Gamma_q)}.$$

Here A_q , ω_q , and Γ_q are the strength, frequency, and damping constants of the q th vibrational mode of the molecules, respectively. For the organic films with azimuthal symmetry studied in this paper, the nonvanishing elements are $\chi_{zzz}^{(2)}$, $\chi_{zii}^{(2)}$, $\chi_{izi}^{(2)}$, and $\chi_{iiz}^{(2)}$ ($i = x, y$). In the case of 8 CB used in our SHG study, only one dominant polarizability element $\alpha_{\xi\xi\xi}^{(2)}$ needs to be considered;²⁰ therefore, the effective surface-susceptibility elements $\chi_{s,ijk}^{(2)}$ are

$$\begin{aligned} \chi_{zzz}^{(2)} &= N_s \alpha_{\xi\xi\xi}^{(2)} \langle \cos^3 \theta \rangle, \\ \chi_{zii}^{(2)} &= \chi_{izi}^{(2)} = \chi_{iiz}^{(2)} = \frac{1}{2} N_s \alpha_{\xi\xi\xi}^{(2)} \langle \cos \theta \sin^2 \theta \rangle, \end{aligned} \quad (8)$$

where $i = x$ or y , θ is the polar angle between the direction of the molecular head axis and the surface normal, z is the surface normal, and x and y are the coordinates in the surface plane.

For CH_3 , we assume a C_{3v} symmetry and a second-order polarizability of each CH bond characterized by a single component $\alpha_{\xi\xi\xi}^{(2)}$ along the bond.²¹ Therefore, the yyz component of the second-order nonlinear susceptibility can be expressed as

$$\chi_{yyz}^{(2)R} = N_s \alpha_{\xi\xi\xi}^{(2)} (0.275 \langle \cos \theta \rangle + 0.165 \langle \cos^3 \theta \rangle), \quad (9)$$

where θ is the angle between the symmetry axis of the CH_3 and the surface normal z .

With the above, the SHG signal is further given by

$$S(s_{\text{out}}, m_{\text{in}}) \propto [L_{yy}(2\omega) \chi_{yyz}^{(2)} L_{yy}(\omega) L_{zz}(\omega) \sin \alpha]^2 \quad (10)$$

for mixed polarization input (45° between s and p) and s polarization output; and

$$\begin{aligned} S(p_{\text{out}}, m_{\text{in}}) &\propto [\frac{1}{2} L_{zz}(2\omega) \chi_{zzz}^{(2)} L_{zz}^2(\omega) \sin^3 \alpha + \frac{1}{2} L_{zz}(2\omega) \chi_{zxx}^{(2)} L_{xx}^{(2)}(\omega) \sin \alpha \cos^2 \alpha \\ &\quad + \frac{1}{2} L_{zz}(2\omega) \chi_{zyy}^{(2)} L_{yy}^2(\omega) \sin \alpha - L_{xx}(2\omega) \chi_{zxx}^{(2)} L_{zz}(\omega) L_{xx}(\omega) \sin \alpha \cos^2 \alpha]^2 \end{aligned} \quad (11)$$

for mixed polarization input and p polarization output. Here α is the incident angle of the laser beam. For our geometry, with a monolayer confined between two solid substrates, it has been proven by Feller, Chen, and Shen²² that $L_{ii}(\omega)$ can be calculated by considering the multiple interference of the field between the two substrates, which can be expressed in terms of ordinary Fresnel factors. For example, if we scan the sample across the contact area boundary, the distance between the two surfaces varies and the local-field factor $L_{ii}(\omega)$ is then an oscillat-

ing function of separation. For SFG, the signal can be similarly expressed.

II. EXPERIMENTAL

A. Optical setup

A frequency-doubled output of Q -switched mode-locked Nd:YAG (yttrium aluminum garnet) laser was

used for SHG study. The laser beam was focused to a spot of $\sim 100\ \mu\text{m}$ at the sample surface. The SHG signal at 266 nm from the monolayer was detected by a photomultiplier. The typical laser power used was $\sim 50\ \text{mJ/pulse}$ with a pulse duration of 10 ns.

The experimental setup for SFG has been described elsewhere.¹⁹ Briefly, the laser system produced a 0.5-mJ visible pulse at 532 nm (diameter = $500\ \mu\text{m}$) and 0.2-mJ tunable infrared pulses (diameter = $300\ \mu\text{m}$) from 2700 to $3900\ \text{cm}^{-1}$. The bandwidth of the infrared beam varied from about $8\ \text{cm}^{-1}$ to about $45\ \text{cm}^{-1}$ at $3700\ \text{cm}^{-1}$. The infrared and visible beams were incident at an angle around 47° from the side of the fused-quartz flat window and overlapped at the quartz and/or monolayer interface. All SFG spectra were normalized to the SFG from a quartz crystal to offset the laser fluctuation and change of overlap due to the tuning of the infrared laser. Absorption of IR light ($\sim 10\%$) due to the fused-quartz window was also normalized out. The polarization for the sum-frequency output, visible input, and infrared input were *s*, *s*, and *p*, respectively.

An optical system was also designed and constructed for fluorescence studies of a compressed monolayer of molecules with Rhodamine 6G attached as the end group. The beam from an argon laser was directed through a $400\text{-}\mu\text{m}$ optical fiber, and focused to a spot of $300\ \mu\text{m}$ diameter on the contacting surfaces of the quartz substrates. Fluorescent emission from this spot was collected by a lens, filtered to pass a 10-nm fluorescence band of Rhodamine 6G at 600-nm wavelength, and detected by a photomultiplier. The excitation beam and detection optics, mounted off-axis to avoid glare, were oriented at an angle of 10° from the surface normal.

B. Pressure cell

The pressure cell used in this study consisted of an optical flat and a planoconvex lens, which were polished to $\lambda/10$. The nanometer scale topography of these optical surfaces was examined by AFM. On the scale of the contact diameter, the surfaces were observed to have large ($200\ \text{\AA}$ deep, 0.3 to $1\ \mu\text{m}$ wide) polishing scratches crisscrossing the surface with an average separation of $5\ \mu\text{m}$. The smaller scale roughness in the flat areas between scratches consisted of smaller scratches and bumps with an rms height of $\sim 0.5\ \mu\text{m}$. At the pressures that created an optical contact area of 0.5-mm radius ($\sim 50\ \text{MPa}$), these small asperities would have deformed to contact diameters of about $0.5\ \mu\text{m}$, which is the length scale of their separation. Therefore, we are confident that the monolayer molecules between the two surfaces in the contact area were under nearly the same pressure in our optical measurements with pressure, except for those adsorbed in the deep scratches, which accounted for a negligible fraction of the total amount.

Only the flat window was coated by the monolayer. The radius of curvature of the lens was chosen according to the desired pressure range, typically between 0.5 and $50\ \text{cm}$. This sphere-on-plane geometry ensured that the concentrated stress at the contact point produced sufficient physical contact between the two surfaces and

allowed the pressure to be applied to the monolayer. The geometry was also simple enough to allow the laser beams to enter and exit without complicated alignment procedures. The entire cell was mounted on an *X, Y, Z* translation stage with a tilt adjustment to allow the SHG or SFG signal generated at the interface to enter the detection system and the sample to be scanned. The size of the contact area could be adjusted between $600\text{--}1000\ \mu\text{m}$ by the loading spring from the lens side. The contact area was readily observed by the disappearance of the light reflection since both the lens and the flat window were made of the same material. If the contact area was smaller than the laser-beam spot, a doughnut-shaped laser reflection was observed. If the contact area was larger than the laser beam, no linear reflection was observed. This disappearance of light reflection also assured that the contact area was of good optical quality. The nonlinear optical signal was by arrangement only generated by the monolayer in the contact area and could radiate in both forward and reflected directions. The experiments were carried out in two ways. One was to measure the signal generated from the monolayer at the flat optical surface first with the lens far away and subsequently with the lens in contact with the flat. The size of the contact area was increased as the pressure was increased and eventually reached a size significantly larger than the laser-beam spot. The other was to measure variation of the SHG or SFG signal by scanning the laser spot over the contact area. Reversibility of the characteristic molecular spectrum under pressure was studied by removal of the pressure.

C. Materials

A variety of films of different molecules were prepared for these experiments. They formed either self-assembled monolayers [*n*-octadecyltriethoxysilane (OTE)] or Langmuir-Blodgett films [stearic acid, octadecylalcohol, octadecylamine, and 4'-*n*-octyl-4-cyanobiphenyl (8CB)]. OTE was purchased from Hols America, Piscataway, NJ. It was vacuum distilled and filtered through $0.2\ \text{mM}$ polytetrafluoroethylene (PTFE) membranes immediately prior to preparation of prehydrolysis solutions. Stearic acid, octadecylalcohol, and octadecylamine were purchased from Sigma and recrystallized from ethanol. 8CB was purchased from Merck and used as received. For our control experiments, we used a fluorescent dye molecule, octadecylrhodamine *B* chloride salt (C_{18}Rh), which was purchased from Molecular Probes and used as received.

House-distilled water was passed through a four-cartridge Millipore μQF purification train, producing a resistivity of $18.2\ \text{M}\ \Omega\ \text{cm}$. Tetrahydrofuran (THF) and cyclohexane were spectral quality. Glassware for preparation for prehydrolysis solutions and for self-assembly of OTE were cleaned with nochromix reagent immediately prior to use.

D. Film preparation methods

IR quartz disks were cleaned in fresh chromic-acid solution (ca, 1:5 saturated sodium dichromate: sulfuric

acid), followed by extensive rinsing with Millipore water. The self-assembled OTE films were prepared by hydrolysis of the triethoxy groups to alcohol.²³ Prehydrolysis solutions were prepared by dissolving 0.2-g OTE (19 mM) in 25-ml THF containing 0.2 g of 1-N HCl. The solution was stirred at room temperature for 2–3 days. The prehydrolysis solution was filtered through a 0.2- μ m nylon or PTFE membranes followed by dilution with 25-ml cyclohexane. This solution was joined with the freshly cleaned quartz disks. Following self-assembly, the samples were briefly rinsed with fresh cyclohexane, dried under a stream of argon or nitrogen, and stored under cyclohexane until used.

Langmuir-Blodgett deposition was carried out using a standard trough deposition system (KSV, Finland) filled with pure deionized water. All monolayers were compressed at 10 mm/min to the desired pressure and transferred to the quartz support using an upstroke transfer speed of 5 mm/min. The 8CB monolayers were deposited at 10 mN/m, with a transfer ratio of 0.93. Stearic acid monolayers were transferred at 25 mN/m, with a transfer ratio of 1.0. For fluorescence studies, stearic acid monolayers were mixed with 0.2-mole % octadecylrhodamine. No changes were observed in the pressure-area isotherm after addition of the fluorescent lipid. Octadecylamine monolayers were transferred at 15 mN/m, with a transfer ratio of 1.0. Octadecylalcohol monolayers were transferred at 25 mN/m, with a transfer ratio of 1.0.

III. RESULTS

A. Control experiments

Control experiments were carried out to ascertain that reductions in the SHG and SFG signals arise from genuine changes in the monolayer and are not due to artifacts like optical distortions caused by the applied pressure, or to the molecules being displaced out of the contact area. Optical distortions could be caused, for example, by inhomogeneous changes in the refractive index of the flat surface and lens across the contact, due to the elastic deformation of asperities and protrusions. This could distort the wave front of the incident light (loss of spatial coherence) and cause the surface oscillators to radiate randomly out of phase, leading to a decrease of the detected signal.

To determine if the nonlinear optical signal is affected by optical effects resulting from the formation of the contact, we performed an experiment with crystalline quartz pressed between the lens and the flat surface. In this experiment, the laser beam was incident from the lens side to avoid bulk contribution to SHG from the crystalline quartz. The second-order nonlinear susceptibility of the crystalline quartz should not change under pressure. In the reflection geometry, the SHG signal only came from the very thin layer near the surface due to the short coherence length for this particular geometry. Therefore, it resembled the geometry of the trapped monolayers in the contact area as in both cases, the SFG arose from the contact surface region. Since crystalline quartz has a

nonvanishing component $\chi_{xxx}^{(2)}$, we used an *s*-in, *s*-out polarization geometry and aligned *s* parallel to the crystal *x* axis. The SHG signal arising from the contact area was found to be ~ 3 times larger than before contact. A theoretical calculation using the formulas shown in Sec. I indicates that changes in the local-field factor alone can explain our observation. A factor of 5 is expected from $S \propto [L_{yy}(2\omega)\chi_{xxx}^{(2)}L_{yy}^{(2)}(\omega)]^2$ for a gap width $d=0$ compared to $d=\infty$. The slight disagreement between the experimental data and the calculation may be due to alignment of the outgoing beam, which was rendered difficult by the curvature of the lens. This result indicates that pressure-induced phase variations across the contact are negligible and the theory to treat such a contact geometry described in the introduction is valid.

The second control experiment was aimed at ascertaining that the monolayer molecules remain trapped in the contact area during compression and are not displaced outside. For this purpose, we performed a fluorescence microscopy experiment with a Langmuir-Blodgett film of stearic acid mixed with 0.2% octadecylrhodamine. Since the Rhodamine was attached to the end of an alkyl chain similar to that of the host (stearic acid), the binding of both molecules to the substrate and to the rest of the film was similar. The apparatus, described in Sec. II A, provided illumination at a wavelength of 480 nm. This is suitable for excitation of Rhodamine whose spectrum peaks at 540 nm, but has a broad tail that extends to shorter wavelength. The emitted light was filtered to pass the fluorescence band of Rhodamine at 600 nm and detected by a photomultiplier. Background fluorescence was determined in the absence of the monolayer, and later subtracted from the measured signal. Using a beam size of 300 μ m, and a contact area of 500 μ m, no fluorescence signal loss was detected by scanning from outside to inside the contact area during compression. This clearly indicates that no molecules were excluded by pressure from the contact area.

B. 8CB monolayers under pressure

We used second-harmonic generation to study the behavior of a Langmuir-Blodgett monolayer of the liquid crystal 8CB under pressure. This rodlike molecule consists of a cyanobiphenyl head and an alkyl chain of eight carbon atoms. Previous studies²⁰ have shown that the molecular polarizability responsible for SHG comes mainly from the polar head of the molecule (i.e., the cyanobiphenyl group) and has only one dominant element. Furthermore, the monolayer has azimuthal symmetry.

Figure 1 shows the intensity of the SHG signal generated at various positions inside and outside the contact area probed by the laser beam with a 100- μ m spot size. The average pressure in the contact was about 20 MPa ($a \sim 300 \mu$ m, $R \sim 20$ cm). The oscillation outside the contact was caused by the interference effect on the fundamental input and can be well accounted for by the local-field factors as a function of gap separation between the surfaces of the lens and the flat surface, as shown by the solid line. For the *m* (mixed polarization, 45° between *s*

and p -in/ p -out polarization combination, the nearly vanishing signal (taking into account the limited signal-to-noise ratio) in the contact area can be well explained by the vanishing local-field factors [Fig. 1(a)]. For the m -in/ s -out polarization combination, the local-field factors predict only a factor of ~ 2.5 decrease of signal in the contact spot. As shown in Fig. 1(b), a much larger decrease in signal (at least a factor of 100) was observed. With a larger laser-beam spot filling almost the entire contact area, a better signal-to-noise ratio was obtained, which allows us to establish the decrease of the signal to at least a factor 1000. Such a significant change must result from vanishing of the nonlinear susceptibility.

Retraction of the lower lens after these measurements to reduce the pressure caused the SHG signal to reappear with only a slight decrease of the intensity.

FIG. 1. Second-harmonic generation (SHG) signal from a 8CB film subjected to an average compressive pressure of 20 MPa, as a function of the beam position across the contact area (radius $\sim 300 \mu\text{m}$). (a) M (mixed) polarization is used for the incident beam (ω) and S polarization for the outgoing beam (2ω). The signal is near the noise level inside the contact and oscillates outside. (b) Same for M polarization in and S polarization out. In both cases, the predicted signal due to changes from the local field (see text) alone are shown by the continuous line.

C. Sum-frequency generation experiments

The spectral region of the CH stretching modes of LB monolayers of stearic acid, octadecylalcohol, octadecylamine, and of a SAM of OTE before contact were found to be identical. Figure 2 shows the SFG spectrum in the CH stretch region for a LB monolayer of octadecylalcohol on the fused-quartz surface before contact. It arises solely from the polar-ordered end group CH_3 , and contribution from the CH_2 groups cancels out because of pairing in opposite directions. This suggests that these monolayers are closely packed and with the hydrocarbon chains in an all-trans configuration. The peaks at 2875 and 2940 cm^{-1} have been assigned to the symmetric CH_3 stretching mode and a Fermi resonance between the stretch and an overtone of the bending vibrations of CH_3 , respectively.⁷

For an octadecylalcohol monolayer, it was found that when the normal force was slowly increased, the SFG signal decreased continuously as the radius of the contact area was increased. When it equaled that of the laser-beam size, the signal fell below our detection limit, set by the scattered background light of the visible laser. The change of SFG signal was observed to be almost completely reversible as the pressure was varied and could be repeated for many cycles of increasing and decreasing pressure. At the end of ~ 10 cycles, a small permanent reduction in the signal occurred, indicating perhaps material loss due to unwanted shearing during pressure loading and unloading despite the attempts in designing the cell to avoid such lateral motions. In Fig. 3(a) we show the SFG signal of the CH_3 peak at 2875 cm^{-1} as a function of sample position across the contact area with a size

FIG. 2. Sum-frequency generation (SFG) signal vs IR frequency in the C-H stretch region for a Langmuir-Blodgett film of octadecylalcohol on a flat quartz surface. The peak around 2875 cm^{-1} is due to the symmetric C-H stretch of the terminal CH_3 group. The peak at approximately 2940 cm^{-1} is a Fermi resonance between CH_3 symmetric stretching and overtone of its bending modes.

of ~ 1 mm. The average pressure in the contact area was about 50 MPa. Similar to the 8CB case in the SHG study, the SFG signal in the contact area drops by about a factor of 1000 to below the noise level. Outside the contact area, the SFG signal oscillates due to interference as discussed in the previous section. The SFG signal from OH at 3250 cm^{-1} for the same monolayer was also found to drop below the noise level inside the contact area as shown by Fig. 3(b). It should be noted that there might be a contribution to the OH stretch signal from H_2O molecules that might have been transferred with the

FIG. 3. (a) SFG signal of the CH_3 symmetric stretch mode of an octadecylalcohol Langmuir-Blodgett monolayer on a flat fused-quartz vs laser spot position in the contact area. (b) Same experiment for the OH stretch mode. Inside the contact, the SFG decreases by a factor of 1000 into the noise level. Oscillations in the outer region are due to interferences. Average pressure ~ 50 MPa.

FIG. 4. SFG signal of the CH_3 symmetric stretch mode of a self-assembled monolayer of OTE adsorbed on the flat quartz (fused) window vs laser-beam position across the contact area. At 50-MPa pressure, the intensity inside the contact area decreases by a factor of approximately 15. At the higher pressure of 80 MPa, the decrease is at least a factor 1000, to within the noise level.

LB film. If this were the case, our experiment suggests that these water molecules must have been displaced out of the contact area or randomized by pressure. Although qualitatively similar observations were obtained for the CH_3 stretch peak of SAM OTE films, a significant difference is that a finite SFG signal inside the contact area remained under the same load as shown in Fig. 4. At even higher loads (~ 80 MPa), the CH_3 signal disappeared as in the previous cases.

The consistent result from all these experiments is that the monolayer was unable to generate an SFG signal under high enough pressure. These results imply that like the case of SHG, the loss of SFG signal arises from the vanishing of the nonlinear susceptibility of the film.

IV. DISCUSSION

A. Confinement and compression of molecules

The fluorescence experiment described above proves very clearly that the molecules confined between the lens and the flat surface are not displaced outside of the contact area. In this experiment, Langmuir-Blodgett films were used that are bound to the substrate by only weak van der Waals forces. In other experiments where self-assembled monolayers were used, the binding to the substrate was covalent and displacement of the molecules was even more unlikely, as it would require higher energy.

The response of organic monolayers to local pressure, as exerted by the sharp tip of an AFM, has been studied

recently in our laboratory. Using alkylthiols on Au(111), we have shown that sharp asperities (tip radii < 1000 Å) could reversibly displace the thiols, i.e., the thiols would refill the contact area upon release of the tip pressure.²⁴ The critical load for the displacement was found to be around 300 nN for tips of 700–1000-Å radii, and 10 nN for radii of ≈ 200 Å. This corresponds to pressures of the order of 1 GPa, which is higher than that applied in the present experiments. The displacement or nondisplacement is the result of competition between lateral compression (molecule-molecule repulsion) and molecular deformation induced by the tip pressure.²⁵ If tip radii larger than 1000 Å were used, no displacement of the thiols occurred. In fact, the gold substrate was found to yield plastically before the organic layers could be displaced.²⁶ Similar studies performed on self-assembled monolayers of OTE on mica showed that displacement of the covalently cross-linked alkyl chains was much more difficult. For example, while the threshold load for thiol displacement was about 5 nN for ≈ 100 -Å tips, a load of 10 nN was required for the OTE films using the same tips.²⁷

B. Vanishing of second-order monolayer susceptibility

The decrease of the intensity of the SFG and SHG signals was found to be much more significant than predicted by changes in the local field (Eq. 5). We can calculate the changes due to the local-field factors to predict how they would affect the SFG and SHG signals outside and inside the contact area. This is shown in Fig. 1 for SGH from 8CB. The solid curves are the result of calculations using Eq. (5), assuming that no change in the 8CB monolayer susceptibility has occurred. Inhomogeneities in the film cause a signal imbalance between the left and right side of the contact. The oscillation of the signal outside the contact region fits well with the calculation. It arises from the dependence of $L_{ii}(\omega)$ on the distance between the surfaces of the lens and the flat surface, averaged over the laser-beam size of 100 μm . A sizable signal is predicted from the calculation for the *m*-in/*s*-out polarization combination inside the contact area. The fact that the experimental value for this polarization combination drops to zero in the contact area indicates that the second-order susceptibility $\chi_s^{(2)}$ of the monolayer must have been reduced to zero by the pressure used in the experiment. This leads us to conclude that the biphenyl core groups of the 8CB molecules must lie flat on the substrate as a result of the pressure ($\theta = 90^\circ$) in Eq. (9). This is possible because the 8CB monolayer is not too densely packed (~ 35 Å per molecule), which allows such a reorientation of the molecules.

In the case of SFG from CH_3 , the second-order nonlinear susceptibility is given by Eq. (9). If we assume that the axis of CH_3 group is reoriented under the applied pressure, such that both $\langle \cos\theta \rangle$ and $\langle \cos^3\theta \rangle$ vanish, then the disappearance of the CH_3 spectrum in SFG from

molecules with long alkyl chain under pressure can be explained. A similar reasoning can be used to understand the disappearance of the OH stretch mode of the octadecylalcohol monolayer under pressure. Since these changes occur at the ends of the long hydrocarbon chain, they could recover relatively easily. This elastic recovery of molecular films subjected to moderate pressure has been observed with the surface force apparatus²⁸ and also in many AFM experiments with tip pressures up to 1 GPa.^{8,9,24–26} Since our pressures were well below this value, our assumption of molecular distortions at the head and/or tail groups that recover upon release of the pressure, appears well justified.

A recent Monte Carlo simulation²⁹ of self-assembled thiol monolayers suggests that the molecular deformation is in the form of gauche defects, in addition to an increase of the molecular tilt. This study also concludes that the gauche defects are essentially concentrated at the molecular ends. With increasing pressure during compression, a dramatic increase (from 6% to 38%) of the number of molecules with such end gauche defects is observed. These results agree with our observations and the picture presented. We note that a chain oriented close to the surface normal with one single gauche defect at the terminal C-C bond will have the end group oriented with its θ close to 90° ; therefore, it will not contribute to the surface nonlinear susceptibility.

If the hydrocarbon chains contain considerable conformational defects, peaks corresponding to CH_2 stretches might be observable due to the breakdown of inversion symmetry. Such is the case for an uncompressed monolayer of fatty acid on the water surface.⁷ However, in our experiments, the CH_2 stretch was not observed even when the pressure was ~ 0.2 GPa. One explanation is that suggested by the Monte Carlo simulation study,²⁸ where the actual density of internal conformational (gauche) defects is very low.

In conclusion, we have shown that SHG and SFG can be used to provide orientational information for monolayers of molecules under high static pressure. We have shown that for Langmuir-Blodgett and self-assembled monolayers relatively low pressure is needed to alter the end configuration of the chains and that this change is completely reversible. For monolayers like 8CB that are less densely packed, it is possible that the molecules are pressed flat on the surface.

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