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Citation: *Journal of Applied Physics* **90**, 5070 (2001); doi: 10.1063/1.1407850

View online: <http://dx.doi.org/10.1063/1.1407850>

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Effects of mechanical compression on the vibrational spectrum of a self-assembled monolayer

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(Received 23 March 2001; accepted for publication 6 August 2001)

A molecular monolayer (octadecanethiol on gold) is compressed between a bronze ball and a sapphire prism. Vibrational spectra are obtained by optical sum-frequency generation before, during, and after a pressure cycle to 660 MPa (6.6 kbar). Both reversible and permanent effects are observed on the frequency, intensity, and shape of methyl C–H stretching resonances in the monolayer. Spectral broadening indicates the heterogeneity of chemical environments in the contact, while a pressure-dependent loss of orientational order attenuates the resonant signals. These results from a model system demonstrate that contact-modifying molecular films can be investigated spectroscopically. © 2001 American Institute of Physics. [DOI: 10.1063/1.1407850]

I. INTRODUCTION

Contact between solid surfaces can be highly sensitive to the structure of their interface. Particularly when surfaces are in relative motion, or resisting shear, does the chemical nature of a contact area have macroscopic consequences. Even a monomolecular intervening layer can reduce coefficients of friction by an order of magnitude.¹ Although the phenomenology of such “boundary lubrication” constitutes a large body of research, only recently have the microscopic details become accessible. With the development of various proximal force techniques, the mechanical properties of adsorbed molecular layers can be measured directly;² in some cases, frictional forces correlate with structural changes on the atomic scale.^{3–5} Because processes occurring at a solid–solid contact can be explicitly chemical (reactions, phase changes, molecular reorientation) it is desirable to investigate these phenomena by spectroscopic means. However, standard methods are hampered by the small sample size (picomoles per mm²) and its necessarily internal location.

These difficulties can be overcome by exploiting the reduced symmetry of an interfacial region. Within the electric dipole approximation, second-order optical nonlinearities only occur in noncentrosymmetric media. Thus when an interface between two isotropic solids is illuminated by a laser, and light corresponding to the addition of two photons is detected, only the interface can generate a signal. This can be detected sensitively because it is present against a zero background. Optical second-harmonic generation has recently been applied by Eisert *et al.* to the study of films compressed between glass surfaces.⁶ Angular anisotropy of the signal from an adsorbed molecular film was used to detect alignment induced by rolling.

Since this nonlinear mixing is enhanced by molecular resonances, a tunable laser can be used to record surface-selective spectra with monolayer sensitivity. By driving the sample with two lasers, one of which is scanned through the

infrared, vibrational spectra can be obtained. The first application of sum-frequency generation (SFG) to the study of solid–solid contacts was by Du *et al.*;⁷ subsequently Bain and co-workers published sum-frequency and Raman spectra of Langmuir–Blodgett films compressed between sapphire and silica.^{8,9} In each case the principal effect of contact pressure was a large loss of resonant sum-frequency intensity.

Here we report sum-frequency spectra from a contact between a bronze ball and a sapphire prism, with an intervening self-assembled monolayer of octadecanethiol molecules. The experiment differs from previous ones on several points. First, the monolayer is chemically bound to a metal substrate and spontaneously ordered. Second, the metallic contact partner is significantly softer than the prism, hence mechanical failure (on the microscopic scale) occurs by ductile flow. And, finally, the pressure range investigated is an order of magnitude greater.

II. METHODS

A. Contact mechanics

Figure 1 is a schematic cross section of the contact pressure cell. The monolayer is grown on a spherically terminated bronze rod, referred to as the “ball.” Contact is formed by pneumatically loading it against a sapphire prism. Mechanical equilibrium is reached when elastic distortion of the contact counteracts the forces acting on it. In the present experiment, the externally applied force is two to three orders of magnitude greater than typical adhesive forces.³ The latter will have a negligible effect on the stress distribution, which is therefore described by the Hertz theory of contact between smooth elastic spheres.¹⁰ The contact is limited by a circle of radius a . The pressure distribution as a function of radial distance $p(r)$ is an ellipsoid:

$$p(r) = p_0 \sqrt{1 - (r/a)^2}. \quad (1)$$

The maximum, central pressure $p(0)$ is denoted by p_0 . The average pressure, which is necessarily equal to the applied force divided by the contact area, is $(2/3)p_0$. The contact

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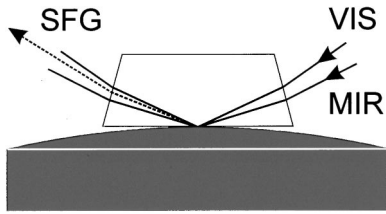


FIG. 1. Schematic cross section of the contact pressure sample (not to scale). The cylindrical bronze rod (shown in gray) is 15 mm in diameter. It terminates in a spherical surface of radius 26 mm centered on the cylindrical axis. The rod is in contact with a sapphire prism, 2 mm thick and 4 mm across the contacting face. These elements are held in position by a brass cell, and forced together by a pneumatic piston. Also shown are the paths of the visible (VIS), midinfrared (MIR), and sum-frequency (SFG) beams. The pump beams enter and emerge p polarized.

radius is determined by the applied force F , the ball's radius of curvature R , and the Young's moduli of the contact partners E_1 and E_2 as follows:

$$a = \left\{ \frac{3FR}{4} \left[\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right] \right\}^{1/3}. \quad (2)$$

The term in square brackets is a (reciprocal) contact modulus, which includes the Poisson ratios of each material (ν_1 and ν_2). In the present case $E_1 = 120$ GPa and $\nu_1 = 0.34$ (bronze)¹¹ and $E_2 = 400$ GPa and $\nu_2 = 0.24$ (sapphire).¹² By a suitable choice of ball radius and pneumatic force, maximum pressures in the range of 0.2–1 GPa (2–10 kbar) are possible. Diameters of the corresponding contacts range from 200 to 600 μm , and are measured by means of a microscope and a graticule. The ball's radius of curvature is determined by measuring Newton's rings when it is in contact with an optical flat and is suitably illuminated by a He–Ne laser.¹³

B. Sample preparation

The phosphor bronze ball is polished on felt with a series of diamond abrasives (Kemet), washed with detergent, then rinsed with de-ionized water and ethanol. A polycrystalline gold layer 200–300 nm thick is evaporated onto the bronze at a base pressure of less than 10^{-5} mbar. Upon removal from the evaporator, the contact spot is compressed briefly to 700 MPa in the pressure cell. The ball is then immersed in fresh 0.3 mM octadecylmercaptan (ODT) (Aldrich, 98% purity) in absolute ethanol (Hayman, Analytical Reagent grade). After 10–15 h the sample is rinsed and moved to a bath of pure ethanol for 48 h. Thereafter it is dried with nitrogen gas and stored in air.

The sapphire prism was manufactured from a synthetic single crystal (Crystran). Its contacting face is perpendicular to the c axis, with a $\lambda/2$ optical polish. Before formation of a contact, the prism is cleaned in a reacting aqueous solution of hydrogen peroxide and ammonia, then rinsed with de-ionized water.

C. Optical system

The light source is a mode-locked, cavity-dumped Nd:YAG laser with a single-pass amplifier (Continuum YG601) that produces 30 ps pulses at 20 Hz. Its frequency-

doubled output drives optical parametric generation and amplification in $\beta\text{-BaB}_2\text{O}_4$ crystals, as developed by Shen,¹⁴ to give tunable near-infrared light. This is subsequently mixed with the Nd:YAG fundamental in a LiNbO_3 crystal; difference-frequency generation yields midinfrared frequencies tunable from 2500 to 4000 cm^{-1} , of 8 cm^{-1} bandwidth. The system is described in detail elsewhere.¹⁵

Also shown in Fig. 1 are the paths of the pumping and sum-frequency beams, all of which are p polarized. A suitably delayed and attenuated fraction of the frequency-doubled Nd:YAG output (532 nm, ~ 20 μJ per pulse) provides the fixed-frequency pump beam. This visible light approaches the contact at a 63° angle of incidence, and is anamorphically focused to yield a round spot of approximately 50 μm in diameter that defines the probed area. While translating the cell on a micrometer-driven stage, scatter of the visible beam from the contact edges is used to locate its center to within ± 50 μm . Infrared light copropagates at a 7° greater angle of incidence and is focused with a spherical lens. The angles of incidence in air are matched to those in contact by an appropriate rotation of the cell, but alignment error and the frequency-dependent refractive index of sapphire limit the reproducibility to $\pm 2^\circ$. A few percent of the available infrared power is used to record a transmission spectrum of polystyrene during each scan; this provides several markers for frequency calibration, which is accurate to ± 2 cm^{-1} . The rest of the infrared light (~ 100 μJ per pulse) is directed toward the sample. Light emerging from the cell is collimated, filtered, dispersed, and detected on a gated photodiode array. At each infrared frequency the peak corresponding to visible-infrared SFG is accumulated for approximately 1 min, integrated, then plotted as a function of infrared pump frequency.

D. Sum-frequency line shape (Ref. 16)

The amplitude of the sum-frequency field at infrared frequency ν has contributions from the complex second-order susceptibility of gold, $\chi_{\text{NR}}^{(2)}$, and from j different resonances, $\chi_{R_j}^{(2)}$. The detected intensity I is proportional to the square of their sum: $I \propto |\chi_{\text{NR}}^{(2)} + \sum \chi_{R_j}^{(2)}|^2$. Each resonance is assigned an amplitude factor B_j , a center frequency ν_j , and phenomenological damping constant ($L_j/2$):

$$I \propto \left| Ae^{i\epsilon} + \sum_j \frac{B_j}{\nu_j - \nu + i(L_j/2)} \right|^2 \quad (3)$$

The phase ϵ of the nonresonant (NR) response is independent of frequency, and its amplitude factor A is set to unity by normalization. A linear background correction is used to remove instrumentally sloped baselines from the raw spectra. Fitting Eq. (3) to the result yields the nonresonant phase, and for each resonance an amplitude, center frequency, and full width at half maximum L_j for the resulting Lorentzian band. The smooth curves in Fig. 2 are best fits that yield the parameters in Table I.

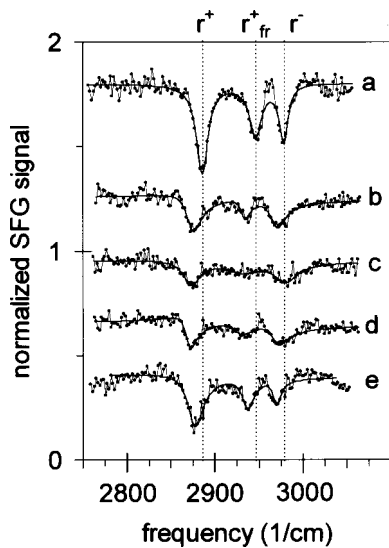


FIG. 2. Spectra of an ODT monolayer on a gold-coated bronze ball (a) in air; (b) in contact at 320 MPa; (c) with pressure raised to 660 MPa; (d) upon returning to 320 MPa; (e) in air, after removal of the prism. The data points are experimental SFG intensities, and the smooth lines are fits to the composite line shape. The spectra were vertically displaced after normalization to background=1. The vertical dashed lines indicate the center frequencies of the three methyl resonances in (a), from Table I.

III. RESULTS

We first consider the mechanical properties of the contact area. The pressure distribution [Eq. (10)] can be expressed independently in terms of applied force or contact radius, both of which were measured. A ball of 26 mm radius of curvature was observed at two pressures, as characterized below:

	Figs. 2(b), and 2(d)	Fig. 2(c)
Applied force, F (N)	7	95
Observed contact radius, a (μm)	129	265
Calculated maximum pressure, p_0 (MPa)	320	660
Calculated p ($r = 50 \mu\text{m}$) (MPa)	290	650

Here the contact radius, being more directly observed, was used to compute the pressure distribution. Values obtained from the applied force differ by 20% at low pressure, but converge to within 6% at high pressure, confirming Hertzian behavior. Over the central $100 \mu\text{m}$ diameter the distribution

is relatively flat. Although the laser footprint averages over a range of pressures, these are within 10% of p_0 , so the maximum pressure is cited in the text.

Plastic deformations will be limited to the bronze, since its hardness (780 MPa) is ~ 25 times less than that of sapphire.^{11,12} Asperities must deform until their cumulative contact area equals applied force/hardness, or $\Delta A = F/H$. With 95 N applied, $\Delta A = 0.12 \text{ mm}^2$, while an apparent area of 0.22 mm^2 was measured. Therefore at least 55% of the ODT layer is in intimate contact with the prism. Bulk plastic flow occurs when $p_0 > \sim 0.6H$, or 470 GPa.¹⁰ Prestressing the contact to 700 GPa produces a visible round spot of enhanced reflectivity $350 \mu\text{m}$ in diameter, but does not flatten the ball macroscopically. Scanning electron microscopy shows that the polishing texture on the metal is removed by this procedure. Therefore we are confident that the metal surface is smooth enough for subsequent compressions to be elastic.

Figure 2(a) is a spectrum obtained from within the prestressed spot on a thiolated ball in air. The frequency-independent signal is due to nonresonant SFG by the gold surface. Since this is separated from the adsorbed layer by less than the coherence length of the optical fields, their separate contributions to the SFG amplitude add coherently. When the ODT/Au system is pumped with collinear beams, methyl resonances appear as dips in the nonresonant background.^{15,17} The smooth line through the data is a fit to the composite SFG line shape, which yields the resonant frequencies and bandwidths in Table I. No methyl C–H stretching vibrations are observed in the SFG spectra of freshly cleaned prisms, or in contacts formed without thiol treatment.

Figure 2(b) represents the same spot as Fig. 2(a), but with it in contact with the sapphire prism at a pressure of 320 MPa. The resonant signals have weakened in comparison to the background, particularly that of r_{FR}^+ ; they have shifted toward lower frequency by approximately 12 cm^{-1} ; they have also broadened asymmetrically. These changes immediately confirm that the resonances arise from stressed molecules: neither the shift, the broadening, nor the asymmetry can be purely optical phenomena. Not apparent in the normalized spectra is an increase in nonresonant SFG intensity—by a factor of typically between 3 and 4—that accompanies the formation of a contact. Increasing the pressure to 660 MPa weakens the resonant bands further, as shown in Fig. 2(c), but has no effect on the nonresonant

TABLE I. Parameters from the best-fit line shapes in Fig. 2.

	Fig. 2	(a)	(b)	(c)	(d)	(e)
Band center ν_j (cm^{-1})	r^+	2885	2873	2872	2870	2876
	r_{FR}^+	2946	2933	...	2927	2936
	r^-	2979	2969	2979	2970	2970
Bandwidth L_j (cm^{-1})	r^+	16	20	23	15	21
	r_{FR}^+	16	13	...	26	16
	r^-	12	20	31	22	11
ϵ (rad)		-1.6	-1.1	-1.4	-0.9	-1.5

signal. The resonances recover when contact pressure is released. Returning to 320 MPa yields the spectrum seen in Fig. 2(d), which is similar to that in Fig. 2(b). Upon removing the prism entirely, we see in Fig. 2(e) the spectrum obtained in air. The widths and relative intensities of the resonances have returned to the precontact values of Fig. 2(a), but an overall redshift, broadening, and a loss of resonant intensity persist. Subsequent pressure cycles have a diminishing effect on the resonant signal level.

IV. DISCUSSION

In a saturated, annealed ODT layer on gold the hydrocarbon tails extend straight from the surface, tilted by 30° , together forming a crystalline, close-packed array.¹⁸ The only C–H bonds that are not in locally centrosymmetric environments are the terminal methyl groups. Accordingly, the SFG spectrum of an ODT monolayer in air contains the three resonances characteristic of methyl groups: the symmetric stretch (r^+ , 2878 cm^{-1}), the antisymmetric stretch (r^- , 2966 cm^{-1}), and a Fermi resonance (FR) between stretching and bending modes (r_{FR}^+ , 2939 cm^{-1}).¹⁹ The bands in Fig. 2(a) are broader than the 2 cm^{-1} achieved by Bain and co-workers, sample heterogeneity may add to the lower instrumental resolution of the present experiment. The peak frequencies are also 7 cm^{-1} higher than expected for this system in air.

The effects of hydrostatic pressure on C–H stretching vibrations have been well documented for bulk materials. The cross sections of dipole- and Raman-allowed modes are not significantly altered over several GPa of external pressure, and shifts of only $+8\text{ cm}^{-1}$ per GPa are observed.²⁰ Even if there are microscopic deviations from Hertzian behavior in the contact cell, all stresses are limited to $<1\text{ GPa}$ by the mechanical strength of gold and bronze. On these grounds, no effects are expected at the sensitivity, resolution, and pressure range of Fig. 2. Similarly, although the presence of a prism modifies the optical properties of the interface, its effects should be similar to those of a solvent. Increased transmission into the metal is expected to generate a larger nonresonant signal, as observed, but the presence of a dielectric overlayer does not affect the relative intensity or phase of resonances measured in Au/ODT.¹⁹ To account for the contact pressure experiment, three of its unusual aspects must be considered.

First, SFG spectroscopy is sensitive to intermolecular order. Given that most molecules are not destroyed or removed from the contact area, the reversible loss of the SFG signal with increasing pressure must indicate a loss of intermolecular order. If the hydrocarbon chains were to become disordered, CH_2 resonances would appear at 2850 and 2930 cm^{-1} .^{21,22} These modes are not detected at any point in the contact pressure cycle, which suggests that disordering under pressure is limited to the terminal methyl groups. The latter response has actually been observed in a Monte Carlo simulation of a compressed hexadecanethiol/Au layer: with increasing force a progressive, reversible “orientational disordering of the terminal C–C bonds” occurred, while crystallinity within the layer improved and the tilt

increased.²³ These changes would be sufficient to account for the SFG observations.

Nevertheless, sufficiently high stress is known to disrupt this system more severely. A critical load has been observed beyond which the “frictional force” image of an ODT/Au layer vanishes.⁴ The load corresponds to an approximate local pressure of 800 MPa (comparable to that in the present experiment). An ordered image returns when the load is reduced. It appears that ODT molecules can move laterally across the gold when a critical level of stress is reached.^{4,23} Subsequent disarray or local reorganization into multilayers would certainly weaken resonant SFG signals. Molecular displacement within contacts may also explain differences between the present SFG results and those published by other groups. Du *et al.*,⁷ Fraenkel *et al.*,⁸ and Beattie *et al.*,⁹ while working at lower pressure (60 MPa), found resonant SFG attenuated by factors ranging from 7 to 300. While the chromophore in these studies was again a methyl-terminated hydrocarbon layer, it was attached to the substrate by relatively weak physical bonds, and hence could be more easily displaced.

A second reason to expect pressure-dependent intensities is the contribution of Fermi resonance to the methyl band shape. Pressure tuning of the unperturbed levels can produce large changes in the infrared and Raman cross sections of Fermi-mixed resonances. In the case of liquid methanol, Raman intensity ratios of the methyl resonances change measurably with less than 1 GPa of pressure applied.²⁴ Since SFG intensity scales as the product of the dipolar and Raman cross sections,¹⁶ the intensity of r_{FR}^+ relative to r^+ is expected to be particularly pressure sensitive.

Third, the stress experienced by the ODT layer is not hydrostatic. The molecules are tethered between different solids, laterally close packed and resisting shear. Since the range of pressures in the contact is insufficient to shift C–H stretch frequencies on the observed scale, the spectral broadening observed under pressure is probably due to the heterogeneity of the chemical environment. Simply immersing the ODT/Au system into water shifts r^+ by -5 cm^{-1} , apparently by dispersive interactions, and broadens r^- .¹⁹ In the present experiment, forcing the monolayer against a hydrated solid surface has similar, exaggerated effects. The conspicuous asymmetry of the resonances at 320 MPa may therefore reflect a range of interactions with the sapphire surface. Alternatively, since the observed asymmetry can be modeled as a phase shift in the nonresonant signal (Table I), it may indicate a change in the electronic structure of ODT/Au under pressure.

Finally, we consider the irreversible effects of a pressure cycle. Figure 2(e) shows that the layer after compression recovers its ordered state, and with some residual heterogeneity. More interesting is the persistent 10 cm^{-1} redshift. Although this is evidence of a physically modified layer, it is the spectrum *before* compression that is anomalous. We have observed a tendency of fresh samples to have blueshifted spectra. With extended exposure to solvent, or contact with the prism, the features shift to their accepted positions. Contact apparently hastens an annealing or aging step in the formation of a canonical ODT layer. These poorly understood

processes are thought to involve expulsion of solvent, removal of *gauche* conformers, and annealing of rotational domains.²⁵

For the sake of experimental clarity, the model contact described here was constructed from esoteric materials. Its physical properties are nevertheless characteristic of mechanical contacts generally. We have found that the vibrational spectrum of a typical boundary layer responds to applied force, and reveals changes in its own structure and physical environment. The molecular basis of these effects can now be explored further by comparing the pressure-sensitive features of chemically different monolayers under similar conditions.

ACKNOWLEDGMENT

This work was funded by the Ernest Oppenheimer Memorial Trust.

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