

Communications to the Editor

In Situ Vibrational Spectroscopy of an Organic Monolayer at the Sapphire–Quartz Interface

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Thin films of surfactants play an important role in lubrication technology. Fatty acids, in particular, are used as additives in liquid lubricants where they dramatically reduce friction and wear between shearing elements.¹ In many applications, such as micromotors, hard disk drives, and fabric conditioners, wet lubrication is undesirable. Here, ultrathin organic films can act as dry boundary-layer lubricants. Although it is well-known that boundary lubricants can reduce the coefficient of friction by a factor of 10 and wear by several orders of magnitude,² we know little about how they function at a molecular level. A knowledge of how the structure of these films changes under pressure and shear would be a major step forward. Here we present the first vibrational spectra of organic monolayers sandwiched between two hard solids.

Modern FTIR spectrometers can readily detect monolayers of organic molecules on large flat substrates, including metals and dielectrics. However, the loss of sensitivity incurred when the signal is confined to the small contact region between two hard solids makes absorption spectroscopy of monolayers in the contact region extremely difficult. Lasers, unlike the incoherent sources in an FTIR spectrometer, can readily be focused into a contact region only a few hundred microns across. Using a technique pioneered by Shen in the late 1980s,³ we have obtained sum-frequency (SF) vibrational spectra of monolayers of a fatty acid compressed between a fused silica lens and a sapphire prism (Figure 1).⁴ In a SF experiment, a pulsed visible laser and a tunable infrared laser are overlapped in the contact region and the light emitted at the sum of the two input frequencies is detected. The SF signal is enhanced when the IR laser is in resonance with a molecular vibration that is both infrared and Raman active. Scanning the IR laser yields a vibrational spectrum of molecules at the interface. Sum-frequency spectroscopy is especially sensitive to conformational disorder in long hydrocarbon chains.⁵ An all-trans chain is locally centrosymmetric and hence, by the rule of mutual exclusion, the methylene modes are sum-frequency inactive. Gauche defects may break the local symmetry and give rise to CH₂ bands in the SF spectra.

In the first experiment of its kind, Du *et al.*⁶ reported the disappearance of the sum-frequency signal from a variety of

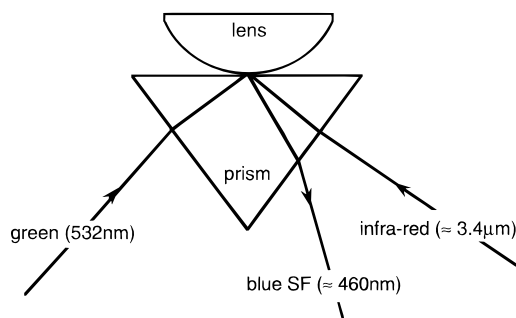


Figure 1. A scheme of the experimental setup. A fused quartz lens (Ealing, 25 mm diameter, 308 mm focal length) was pressed against an equilateral sapphire prism (Graseby-Specac, 15 × 15 × 15 mm). The diameter of the contact area was ~0.7 mm and the average pressure in the contact region was 60 MPa, based on Hertzian theory.¹² A LB monolayer of zinc arachidate was deposited on the prism face. A green beam (0.8 mJ) and an IR beam (0.1 mJ) were directed into the contact region in a counter-propagating geometry and were focused to be contained within the contact area. The angle of incidence of both beams at the prism–lens interface was 55°.

organic monolayers confined between a quartz plate and a quartz lens. We reproduced this surprising result: the SF signal from a monolayer of zinc arachidate was at least 200 times weaker at the quartz–quartz interface than at the quartz–air interface. The absence of the signal might appear to limit the usefulness of SF spectroscopy in the study of lubricants. However, by choosing a different substrate and an optical geometry that gives much larger electric fields in the contact region, we were able to obtain high-quality spectra of a fatty acid monolayer confined between sapphire and quartz.⁷ The door to direct structure measurements on monolayers at the solid–solid interface is now open.

Figure 2 shows SF spectra of a Langmuir–Blodgett (LB) monolayer of zinc arachidate ([CH₃(CH₂)₁₈CO₂]₂Zn) on a sapphire prism in contact with a fused quartz lens. The angles of incidence of the two laser beams were just below the critical angle for the sapphire–quartz interface. This geometry increases the electric fields in the monolayer while still permitting easy alignment of the two beams within the contact region. Spectra are presented for all three independent combinations of polarizations of the laser beams. These spectra are characteristic of a densely packed, well-ordered monolayer. All the major features in the spectra are assignable to the terminal methyl group.⁸ The methylene modes at 2850 and 2890–2930 cm⁻¹ are very weak and arise from the small population of gauche defects that is found even in dense monolayer phases. Spectra could also be obtained from the contact region if the monolayer was initially deposited on the lens rather than the prism.

A comparison of SF spectra of a zinc arachidate monolayer before, during, and after contact with a quartz lens is shown in Figure 3 for one polarization combination. The spectrum in contact has been renormalized to account for the different local electric fields at the interface.⁷ The spectra before, during, and after contact are qualitatively similar. In particular, the relative intensity of the methylene and methyl modes remains low in all spectra: we see no evidence of an increase in gauche defects in

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(2) Rabinowicz, E.; Tabor, D. *Proc. R. Soc. London, Ser. A* **1951**, 208, 455.

(3) Zhu, X. D.; Shur, H.; Shen, Y. R. *Phys. Rev. B* **1987**, 133, 189.

(4) The optical contact area is established from the reflection of the light from the surface of the prism. It is more difficult to determine experimentally what fraction of this area is in actual mechanical contact with the lens. Du *et al.* (see ref 6) have argued, based on Hertzian theory, that under the pressure used in this work, small asperities would deform so that the larger majority of the molecules deposited on the prism are in mechanical contact.

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(6) Du, Q.; Xiao, X.-d.; Charych, D.; Wolf, F.; Frantz, P.; Shen, Y. R.; Salmeron, M. *Phys. Rev. B* **1995**, 51, 7456.

(7) See Supporting Information for a comparison of the relative intensities predicted for the various interfaces.

(8) MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1984**, 88, 334.

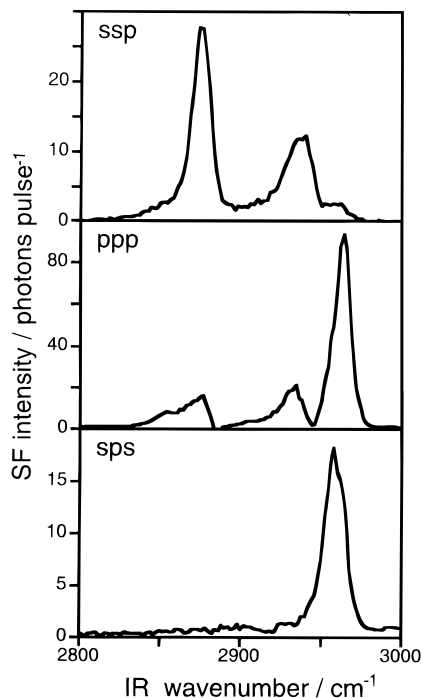


Figure 2. SF spectra of an LB monolayer of zinc arachidate at the sapphire–quartz interface. Spectra for three independent combinations of polarizations of the laser beams are shown. The letters ssp, ppp, and sps refer to the polarizations of the sum-frequency, green, and IR beams, respectively.¹³ Spectra were acquired at 2-cm^{-1} intervals with an acquisition time of 15 s per point. The monolayers were deposited on the prism with an LB trough (Nima Technology). A 1 g dm^{-3} solution of arachidic acid in chloroform was spread over a subphase of $10^{-4}\text{ mol dm}^{-3}$ of ZnSO_4 in ultrahigh purity water. The transfer pressure was 30 mN m^{-1} .

the molecules under pressure or after contact.⁹ Quantitatively, the spectrum after contact is much weaker¹⁰ than the spectrum before contact. Material appears to be transferred from the prism to the lens during contact, but the material that remains behind is structurally little changed.¹¹ We suggest that the contact between the solids results in the removal of patches of material from the prism. The spectrum in contact is much weaker than the spectrum

(9) Differences in the relative intensities of the methyl modes in and out of contact are observed, which may reflect a change in the tilt of the molecules in the contact region.

(10) This observation differs from that reported by Du et al. (ref 6), who saw no difference in the intensity of the SF spectra before and after contact. We observed a significant decrease after the first contact followed by a more gradual decrease after repeated contacts. The extent of decrease varies among experiments.

(11) We note that, due to the dissimilar materials employed in the experiment, microslip will occur at the interface when the contact is made.

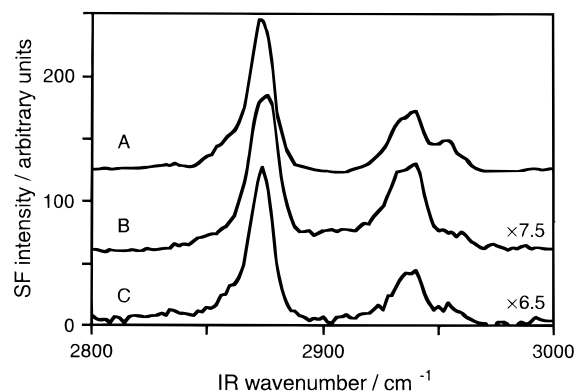


Figure 3. SF spectra of zinc arachidate before contact (A), in contact with a quartz lens (B), and after contact (C). Spectra A and B were offset by 120 and 60 intensity units, respectively. The spectrum in contact was normalized by the relevant Fresnel factors^{14,7} to account for the differences in the local electric fields at the sapphire–air (out-of-contact) and the sapphire–quartz (in-contact) interfaces. Polarization: ssp. For clarity of presentation, spectra B and C were scaled by 7.5 and 6.5, respectively.

before contact, even after correction for the different local fields. Transfer of material in an ordered manner could also explain this decrease, at least in part. The sum-frequency field from material transferred to the lens would have the opposite phase from the monolayer on the prism, resulting in partial cancellation of the sum-frequency signals. Detailed studies of transfer between the two surfaces will be published elsewhere.

In conclusion, we have demonstrated that in situ sum-frequency vibrational spectra can be obtained from boundary lubricants in a tribological contact. At the modest pressures (60 MPa) employed in this experiment, no major structural changes were observed in a densely packed monolayer of a fatty acid. There was evidence of transfer of material between the two surfaces forming the contact while retaining a high degree of conformational order in the monolayer left behind.

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Supporting Information Available: Predicted signal strengths for monolayers on quartz and sapphire prisms in and out of contact with a quartz lens for the experimental geometry of Figure 1 (2 pages). See any current masthead page for ordering and Internet access instructions.

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(13) See ref 5 for a detailed description of the sum frequency spectrometer.

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