

The Adsorption of Synovene on ZDDP Wear Tracks: A Sum Frequency Generation (SFG) Vibrational Spectroscopy Study

Michael T. L. Casford¹ · Paul B. Davies¹ · Tony D. Smith² · Gareth L. Bracchi²

Received: 6 October 2015 / Accepted: 19 February 2016 / Published online: 11 March 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

Abstract The adsorption of the lubricant additive Synovene on steel and on ZDDP/steel wear tracks from base oil has been investigated by sum frequency generation (SFG) vibrational spectroscopy, an interface specific technique. SFG spectra (resonances) were investigated in the C–H stretching region and arise from the aliphatic chains of the palm oil constituent of Synovene. The observation of SFG spectra means that Synovene is adsorbed at the oil/metal and at the oil/ZDDP/metal interfaces and that the aliphatic chains of Synovene have a net polarisation order with respect to the surface. The intense spectrum observed when the film is first formed decreases in intensity with increasing temperature. It is proposed that this is due to a decrease in film thickness as the film tends towards monolayer thickness. A dependence of the intensity and shape of SFG resonances on film thickness due to a thickness-dependent interference effect has been observed in other thin film systems, most notably lipid films on gold. Supporting evidence for the film thickness hypothesis comes from examining the spectra of different thickness films of palmitic acid on steel, one of the constituents of Synovene. The spectra on the wear track are less intense and less reproducible than on the bare metal. After periods of several days at room temperature the spectra on both

surfaces gain in intensity implying a return to thicker layers of Synovene under cold conditions.

Keywords Sum frequency generation · Steel · ZDDP · Lubrication

1 Introduction

Oil additives play a vital role in mitigating the effects of wear in tribological contacts. Metal dialkyl dithiophosphonates are amongst the most widely used additives for reducing wear and friction by tribofilm formation, as well as inhibiting corrosion and oxidation, under boundary layer conditions. Although a wide range of different metal dithiophosphates have been investigated, the zinc dialkyl dithiophosphates (ZDDP) are the most commonly used [1]. The application of surface science analytical techniques in determining the structure of the protective layer formed from wear additives in base oil containing ZDDP under thermal and tribological conditions is an important objective for gaining a better understanding of and improving lubricant performance [2, 3]. For this purpose a range of in situ and ex situ surface science techniques have been applied to ZDDP-coated surfaces, with and without the presence of base oil. These include near edge X-ray absorption spectroscopy (XANES) [4], X-ray photoelectron spectroscopy (XPS) [5] and Auger electron spectroscopy [6] to probe the chemical composition of the surface. Attenuated total internal reflection (ATR) infrared spectroscopy has been used to determine the molecular structure of the surface layer or layers [7]. Investigating changes in the surface topography with increased rubbing time (as a model for tribological action) has been undertaken with atomic force microscopy (AFM) [8].

Electronic supplementary material The online version of this article (doi:10.1007/s11249-016-0662-2) contains supplementary material, which is available to authorized users.

✉ Michael T. L. Casford
mtlc2@cam.ac.uk

¹ Department of Chemistry, University of Cambridge,
Lensfield Road, Cambridge CB2 1EW, UK

² Technology Centre, Castrol Ltd.,
Pangbourne, Reading RG8 7QR, UK

The present investigation sets out to answer a complementary question, namely what differences are there, if any, in the surface orientation and conformation of lubricant surfactants added to base oil off and on ZDDP wear tracks? The specific additive we have investigated is Synovene, an additive patented and developed for use in lubricant compositions by Castrol. Synovene is a natural product consisting of a diester formed from glycerol, citric acid and natural fatty acids comprising mainly palmitic (C16) and oleic (C18) acids. However, as a natural product it has a relatively large chain length distribution. It may also contain additional surface active components. We use the nonlinear optical technique of sum frequency generation (SFG) vibrational spectroscopy to examine the adsorption of Synovene onto the wear track formed by rubbing ZDDP in base oil on steel under tribological conditions.

SFG is an interface specific nonlinear optical technique in which a fixed-frequency visible laser beam and a tunable infrared laser beam are combined spatially and temporally at the surface or interface to generate photons at the sum of the two input frequencies [9–11]. The sum frequency light is monitored as the infrared laser frequency is tuned and changes in intensity when the infrared frequency coincides with a vibrational mode in molecules at the interface. This generates a vibrational spectrum of the interface that yields information on the polar orientation and conformational order of the molecules in the interfacial film. SFG is interface specific with sub monolayer sensitivity and unaffected by the bulk phases either side of the interface. However, it requires the molecules comprising the surface film to have a net polar orientation. In addition vibrational bands are only SFG active if the vibrational mode has nonzero infrared and Raman transition moments.

The SFG vibrational resonances of interest in this work arise from the C–H stretching vibrations of the aliphatic chains of the additive. The recorded SFG spectra are spatial averages of the interface extending over hundreds of microns in the surface plane. To confirm the presence of a ZDDP derived film in the region of interest prior to SFG spectroscopy, the wear track and adjacent bare metal were examined with a scanning electron microscope (SEM) and complementary energy dispersive X-ray analysis (EDXA).

2 Experimental Details

Wear tracks were formed on diamond-polished (0.1 μm) EN1A bright mild steel plates using a bespoke reciprocating plate on static ball rig based on the Cameron Plint design. The plate was thermostated at 95 $^{\circ}\text{C}$ with a contact pressure of circa 1.5 GPa and surface speed of 0.1 m s^{-1} . The \varnothing 20 mm bearing steel balls had a hardness of 65

HRC. ZDDP (Castrol T206 additive) and Synovene were made up in 30 % ZDDP and 0.5 % by weight Synovene solutions, respectively, in a base oil of per deuterated hexadecane (QMX isotopes, 98.5 % isotopic purity). The wear tracks were \sim 500 μm wide and of different thicknesses depending on the rubbing time. Most of the work reported here was carried out on ZDDP layer thicknesses of order 70 nm by comparison with the results of Naveira-Suarez et al. [8]. Following formation of the layer the plate was sonicated in acetone and washed in Decon solution, then UV ozone cleaned for 40 min to remove hydrocarbon contamination from the atmosphere and oxidise the methyl groups intrinsically present in ZDDP. The plate was then covered with a fresh Synovene in base oil layer before recording SFG spectra with a picosecond spectrometer (EKSPLA), described in detail elsewhere [12]. Briefly, co-propagating visible (532 nm) and infrared laser beams (\sim 29 ps, 50 Hz) were incident on the substrate, comprising bare steel and adjacent wear track, through a hemicylindrical CaF_2 prism which was used to sandwich a thin film of oil on top of the metal substrate. Both S and P polarisations with respect to the surface normal could be selected for visible, infrared and sum frequency beams. Although unlikely to occur, in order to identify any contribution from the prism/oil interface prior to each run the laser infrared frequency was set to 2940 cm^{-1} and the SFG intensity recorded before advancing the sample up to the face of the prism. In no case was significant intensity observed in the SFG signal, indicating that any contribution from the prism is likely to be negligible.

SEM images were obtained using a JEOL model JSM-5510LV microscope with concurrent Oxford Instruments Inca EDX analysis package using an acceleration voltage of 20 kV at a working distance of 20 mm.

3 Results and Discussion

Figure 1 shows SEM images and EDX analysis of the bare steel surface and of the adjacent wear track after ozone cleaning. The SEM images confirm the formation of the wear track whilst the presence of elemental sulphur, phosphorus and zinc in the EDX analysis suggests that a phosphate glass is present in the wear track.

Figures 2 and 3 show the SFG spectra of Synovene under base oil in the C–H stretching region recorded on and off the wear track in two polarisation combinations of the input and sum frequency beams, namely SSP (Fig. 2) and PPP (Fig. 3) (beam polarisation sequence: sum frequency, visible, infrared). Although ZDDP also has methyl groups and small, detectable C–H SFG resonances, these were not observed here following cleaning and UV ozone treatment. Hence the SFG C–H resonances shown in Figs. 2 and 3 can

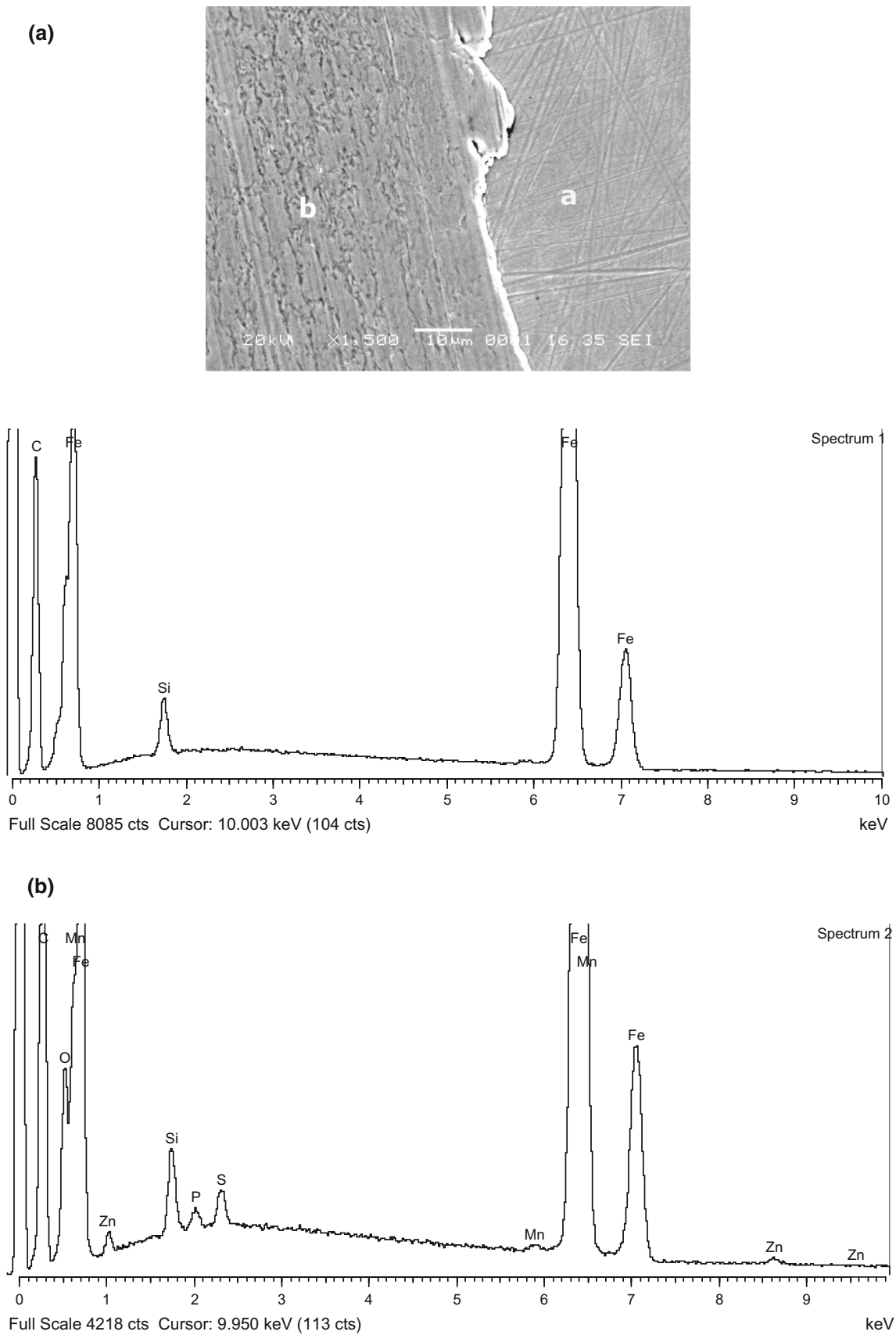


Fig. 1 SEM images (1500× magnification, 10 μm scale bar shown) and EDX analysis of **a** the steel surface and **b** the ZDDP wear track

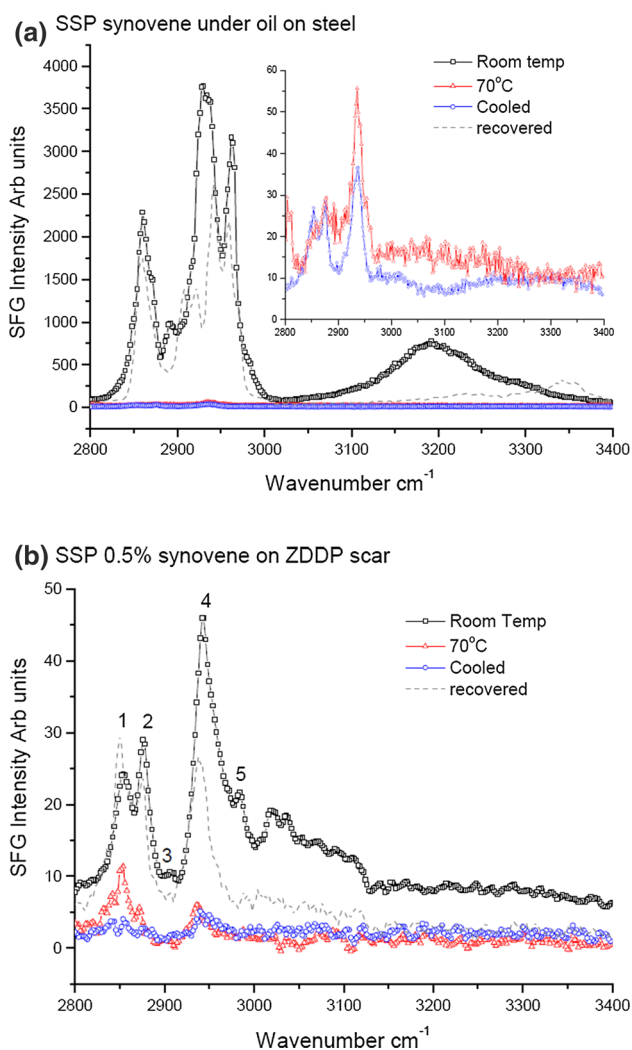


Fig. 2 SFG spectra in the SSP polarisation combination of Synovene under oil recorded at different temperatures and times after the initial film was formed on **a** the steel surface and **b** the ZDDP wear track. The *inset* spectra in **a** are magnifications of the much smaller signals recorded at 70 °C and immediately on cooling. The numbers on the peaks in **b** correspond to the assignments given in the text

be attributed to adsorbed Synovene itself and specifically to the long aliphatic hydrocarbon chains of the palm oil moiety in Synovene. SFG spectra from the long aliphatic chains of surfactants adsorbed at solid/liquid and air/liquid interfaces have been widely reported in the literature [13, 14].

Some qualitative comments about the intensities of the spectra shown in Figs. 2 and 3 can be made regardless of the assignment of individual resonances. Firstly the presence of SFG resonances indicates a net polar orientational ordering of the Synovene molecules at both steel/oil and ZDDP/oil interfaces. Secondly the high intensity of the SFG spectra recorded immediately after the Synovene in oil layer has been formed decreases as the sample is slowly

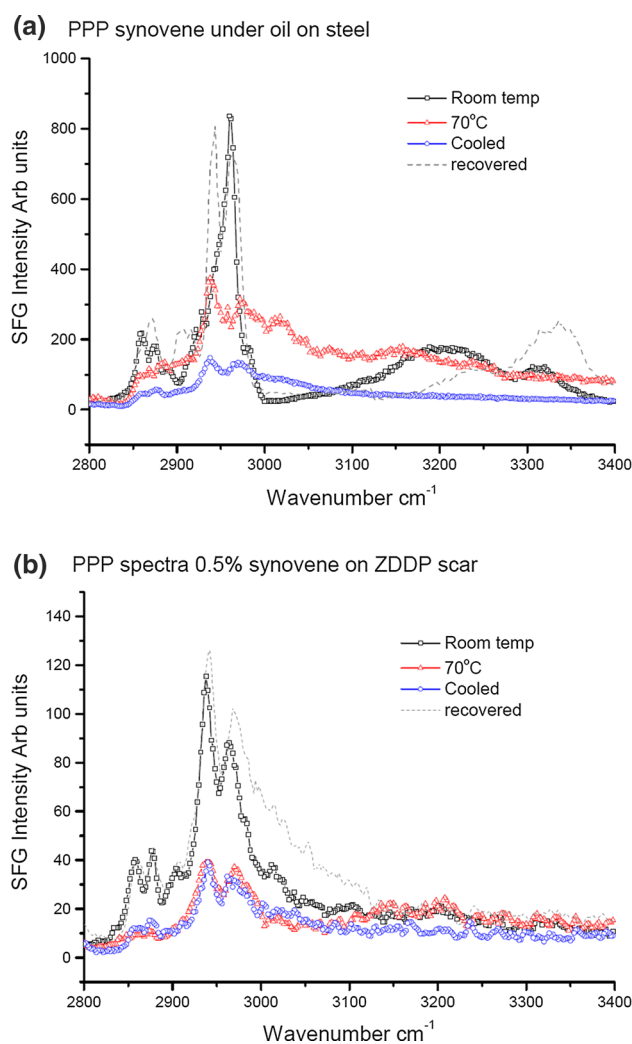


Fig. 3 SFG spectra in the PPP polarisation combination of Synovene under oil on **a** the steel surface and **b** the ZDDP wear track recorded under the same conditions as given in Fig. 2

warmed above the melting point of bulk Synovene (~ 17 – 27 °C). (Because Synovene consists of several fatty acids it melts over an extended temperature range, as demonstrated by the thermogram shown in the supporting information Fig S1.) Thirdly the SSP spectrum is much more intense than the PPP spectrum on steel but more nearly equal to the intensity of the PPP spectrum on ZDDP. Lastly the difference in the relative intensities of the features in the spectra indicates the presence of different structural forms of Synovene, i.e. order and conformation, at the different interfaces.

Given the increased surface roughness of the ZDDP wear track compared with the bare polished metal surface it was a surprise that such a strong SFG spectrum was detected. SFG is a coherent laser technique in which the principle of conservation of momentum dictates that the SFG output angle is rigidly defined. A high surface

roughness therefore causes significant scattering of the emitted SFG beam and consequently a loss of signal intensity. This may be partly responsible for the different intensities observed between the steel and ZDDP interfaces observed at 70 °C. Nevertheless the observation of a SFG spectrum from the wear track indicates the potential of the technique for probing molecular structure at rough as well as smooth surfaces in tribology.

For detailed spectral assignment of the C–H resonances from the Synovene hydrocarbon chains we select the cold spectra from the wear track shown in Figs. 2b (SSP) and 3b (PPP); these are more clearly resolved than the spectra from the bare steel. It should be noted that whilst the initial spectra at room temperature from the bare metal and from the ZDDP wear track are different in absolute intensity (and in the relative intensities of the features within the spectra), the positions of the resonances are the same. From Fig. 2b they can be assigned as follows: (1) symmetric methylene (CH₂) stretch, d^+ , 2855 cm⁻¹; (2) symmetric methyl (CH₃) stretch, r^+ , 2878 cm⁻¹; (3) symmetric methylene stretch Fermi resonance, d_{FR}^+ , ~2900 cm⁻¹; (4) symmetric methyl stretch Fermi resonance, r_{FR}^+ , 2942 cm⁻¹; and (5) asymmetric methyl stretch, r^- , 2966 cm⁻¹.

Due to the SFG symmetry selection rules the methylene resonances from the aliphatic chains do not necessarily dominate the SFG spectrum in the way that they do in linear IR spectroscopy. Any methylene (d) resonances appearing in the spectra indicate the presence of gauche defects in the hydrocarbon chains; that is, the CH₂ groups are not all *trans* to each other. This results in the loss of the centro-symmetry of neighbouring CH₂ groups so that they become both infrared and Raman active and therefore, as mentioned earlier, SFG active. The d^+/r^+ ratio may be used as a qualitative measure of conformational disorder in hydrocarbon chains.

Several differences in the spectra from the two surfaces can be readily identified. For example, in the spectra from the initially adsorbed layer in the SSP polarisation (Fig. 2a, b) the d^+ and r^+ C–H resonances on steel are poorly resolved whilst they are well resolved in the spectra of the ZDDP track. On the other hand the r^- resonance is much more intense on the steel substrate. Generally the r_{FR}^+ resonance seems to be the most intense resonance in all the spectra. This may be due to the effect of an underlying iron oxide layer as postulated by Zhang et al. [15] in their SFG study of alkanethiols on mild steel surfaces where the r_{FR}^+ resonance was prominent. Also evident in the initial room temperature spectra from the wear track (Figs. 2b, 3b) is a weak C–H stretching resonance at 3010 cm⁻¹ presumably arising either from the single C–H bond in the glycol component of Synovene or from a small olefinic component of the Synovene which is clearly absent in the spectra on bare steel. In the former case the implication is that the glycerol backbone is ordered with a net orientation of the

unique glycerol CH bond in the film formed on ZDDP but not in that formed directly on steel. In the latter case the olefinic component is present as an ordered constituent on the ZDDP film but not on the film on steel. Whilst this feature is particularly weak and close to the level of the noise, it is consistently reproducible and therefore has been included in our analysis for this reason.

Additionally two broad resonances observed in the spectra from bare steel in both polarisations (Figs. 2a, 3a) at 3200 and 3300 cm⁻¹ are due to O–H stretching modes. These arise either from residual water at the interface or from the numerous hydroxyl groups present in Synovene. These are not detectable in the spectra from the wear track. The absence of these features in the wear track indicates a significant difference in the film composition and structure between that on ZDDP and that on steel, and correlates with the presence of the isolated C–H band at 3010 cm⁻¹. Further work is required to determine whether these features are due to surface water or OH bonds within the Synovene film structure.

A plausible hypothesis for the high intensity spectra observed when the cold Synovene in oil layer is first laid down, particularly on the bare metal, is that a multilayer of Synovene is formed. As only the topmost layer is strongly SFG active and this layer is displaced from the metal (or ZDDP) surface by several tens of nm or more due to the remaining bulk Synovene which is SFG inactive, a thickness-dependent interference effect on the intensity and line shape of SFG C–H resonances can occur. Phase thickness effects have been thoroughly studied and quantified for well-ordered multilayer lipid films formed on metals, particularly on gold. In these examples the layers are comprised of close-packed alkyl chains orientated perpendicular to the surface that remain conformationally well ordered, i.e. no gauche defects, in the multilayer. It has been shown that the thickness-dependent effect is due to optical interference between the nonresonant susceptibility of the metal substrate and the resonant susceptibility of the SFG active layer or layers [16–18], in particular the topmost layer of the film. Furthermore the effect is different for the SSP and PPP polarisations. Although they are structurally more complex than ordered lipid multilayers, similar thickness-dependent effects have been observed in the SFG spectra of polymer films [19].

Because of their different structures the layers or aggregates of Synovene must pack differently on the surface in comparison with well-ordered lipid multilayers. This view is supported by the presence of the d resonances from the methylene groups in the chain due to gauche defects, for example in Fig. 2b. These resonances are absent for symmetry reasons in the spectra of well-packed lipid multilayers. Nevertheless the presence of the SFG resonances and the variation in their intensity suggests that there are layers of Synovene of different thicknesses on the

surface and with net polarisation order in their hydrocarbon chains.

To test this hypothesis we have examined the SFG spectra of different thickness palmitic acid layers on mild steel (spectra shown in Supporting Information S2). Ordered multilayers of palmitic acid (a constituent of Synovene) were formed by Langmuir–Blodgett deposition to prepare films up to 70 layers thick on steel. This was sufficient to demonstrate the existence of a thickness-dependent effect on the SFG spectrum. Figure 4 shows how the intensity of the resonances varies with thickness in both polarisation combinations. It is noted that the r^+ (i.e. r^+ , r_{FR}^+) and r^- resonances reach a maximum at about 50 layers in the SSP polarisation with the intensity of the SSP polarisation resonances much higher than the PPP resonances. The variation in the PPP polarisation is similar to earlier PPP measurements on gold, namely varying slowly over a μm length scale. The r^- intensity in the PPP

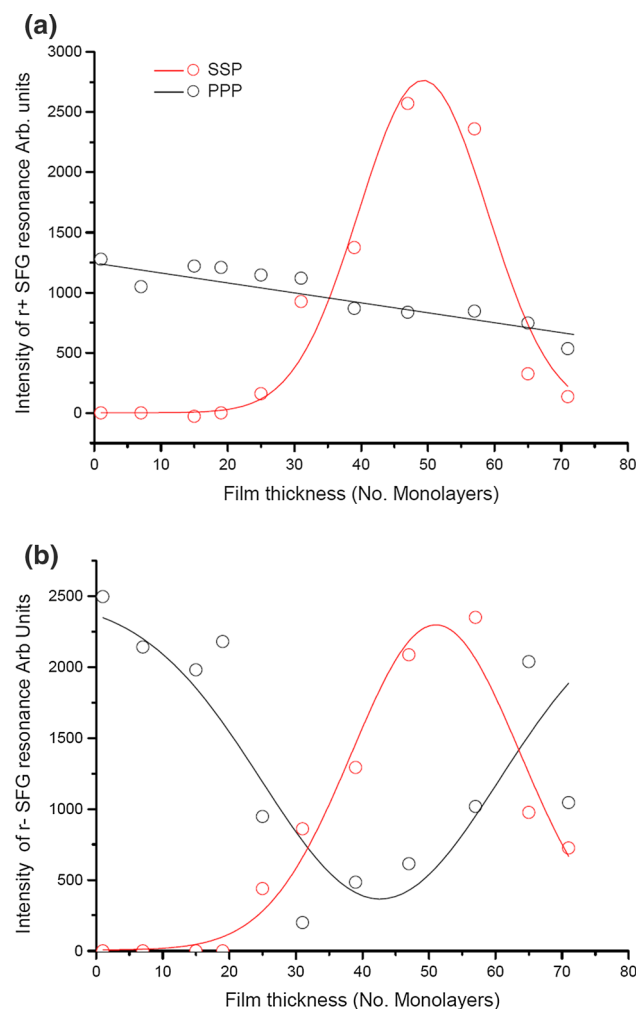


Fig. 4 Integrated intensities of the r SFG resonances from different thickness layers of palmitic acid formed by Langmuir–Blodgett deposition on steel. Upper figure r^- resonances, lower figure r^+ resonance: SSP (red) and PPP (black) polarisations (Color figure online)

polarisation is already intense at just a monolayer thick film and goes through a minimum before rising again at about 60 monolayer thicknesses. It is essential to emphasise that only a qualitative comparison between lipid multilayers on gold and on steel can be made from these results because of the different optical properties of the two metals, particularly the much smaller susceptibility of steel compared with gold. In addition the more complex nature of the Synovene molecule, namely the presence of both saturated and unsaturated hydrocarbon chains, makes accurate modelling of any thickness variation in Synovene layers difficult. Notwithstanding it seems reasonable to conclude that the high intensity signals observed initially, compared with the signal intensity post-heating, is caused by the initial presence of multilayer films of Synovene.

In both polarisation combinations the spectra on bare steel are more intense than on the ZDDP-coated wear track by an order of magnitude or more. A possible explanation for the less intense spectra on the wear tracks compared with the bare metal is the different SFG responses from metal and dielectric substrates. This includes different SFG selection rules. However, the ZDDP layer is less than 100 nm thick and does not in itself constitute a solid dielectric substrate, and therefore, a more plausible explanation has been sought. It has been shown that when a monolayer alkyl film is deposited on thin mica sheets supported on a gold substrate, i.e. analogous to the Synovene film separated from the steel surface by the ZDDP layer as investigated here, the spectrum arises from an interference effect between the metal substrate and the surfactant film as described above [20, 21]. A more likely explanation then is that although the actual Synovene layer may be the same thickness as on the steel surface, the combined thickness of the Synovene layer and the ZDDP layer is greater than the Synovene layer alone giving rise to a different SFG response, i.e. corresponding to different parts of the intensity versus thickness curve shown in Fig. 4. It seems therefore unlikely that the differences in intensity arise simply from differences in the SFG responses of steel and ZDDP-coated steel.

As the sample is slowly heated to just above the melting point the intensity of the corresponding SFG spectra both on the bare metal and on the wear track begins to decrease. This can be explained by the thinning of the adsorbed material corresponding to fewer layers in the film. Figures 2 and 3 show the spectra obtained before, during and after heating the samples at 70 °C. The initially large signal intensity decreases significantly on heating and remains small on subsequent cooling. Nevertheless the presence of the spectra at both low and high temperatures means that significant polarisation order is maintained in the SFG active layer. The intensity of the spectra recorded on the cooled sample gradually increases again with time and

after a period of several hours to days has returned to approximately the same intensity as in the cold starting sample. These spectra are represented by the dotted traces in Figs. 2 and 3. To summarise, the SFG spectra in either polarisation are largest when the Synovene in oil solution is first deposited on the steel- or ZDDP-coated substrates and decreases substantially on heating and recovers to the higher intensity of the initial ‘cold’ spectra after prolonged cooling. From the discussion above this implies that the Synovene multilayers or aggregates decrease in thickness as heat is applied, probably thinning to monolayer thickness at higher temperatures.

4 Conclusion

The adsorption of Synovene on steel and on ZDDP wear tracks on steel from solutions in base oil has been confirmed using the interface specific technique of SFG spectroscopy. The SFG spectra in the C–H stretching region arise predominantly from the aliphatic chains intrinsic to Synovene. The appearance of the spectra means that the SFG active Synovene layer or layers have a net polarisation order with respect to the surface. The high intensity of the spectra when the Synovene is first adsorbed is most likely due to the formation of multilayers or aggregates. The intensity of these spectra decreases when the sample is warmed, which can be accounted for by a change in the separation of the SFG active layer from the metal surface. This hypothesis of thickness-dependent SFG intensity is supported qualitatively by complementary experiments in which the intensity of spectra of multilayers of palmitic acid of different thicknesses is measured. The spectra on the ZDDP wear track are less intense than on the bare metal both initially and on heating. This can be explained qualitatively by the different thickness of the Synovene plus ZDDP layer which is thicker overall in comparison to the Synovene film on steel. The presence of OH resonances in the spectra on steel but not on the ZDDP and the absence of the 3010 cm^{-1} band on steel confirm that different film structures are present at the steel and ZDDP interfaces.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Nicholls, M.A., Do, T., Norton, P.R., Kasrai, M., Bancroft, G.M.: Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates. *Tribol. Intern.* **38**, 15–39 (2005)
- McFadden, C., Soto, C., Spencer, N.D.: Adsorption and surface chemistry in tribology. *Tribol. Intern.* **30**, 881–888 (1997)
- Studt, P.: Boundary lubrication: adsorption of oil additives on steel and ceramic surfaces and its influence on friction and wear. *Tribol. Intern.* **22**, 111–119 (1989)
- Souminen Fuller, M.L., Rodriguez Fernandez, L., Massoumi, G.R., Lennard, W.N., Kasrai, M., Bancroft, G.M.: The use of X-ray absorption spectroscopy for monitoring the thickness of antiwear films from ZDDP. *Tribol. Lett.* **8**, 187–192 (2000)
- Piras, F.M., Rossi, A., Spencer, N.D.: Combined in situ (ATR FT-IR) and ex situ (XPS) study of the ZnDTP–iron surface interaction. *Tribol. Lett.* **15**, 181–191 (2003)
- Barros, M.I.D., Bouchet, J., Raoult, I., Mogne, T.L., Martin, J.M., Kasrai, M., Yamada, Y.: Friction reduction by metal sulfides in boundary lubrication studied by XPS and XANES analyses. *Wear* **254**, 863–870 (2003)
- Mangolini, F., Rossi, A., Spencer, N.D.: In situ attenuated total reflection (ATR/FT-IR) tribometry: a powerful tool for investigating tribochemistry at the lubricant-substrate interface. *Tribol. Lett.* **45**, 207–218 (2012)
- Naveira-Suarez, A., Tomala, A., Pasaribu, R., Larsson, R., Gebeshuber, I.C.: Evolution of ZDDP-derived reaction layer morphology with rubbing time. *Scanning* **32**, 294–303 (2010)
- Shen, Y.R.: *The Principles of Non Linear Optics*. Wiley, New York (1984)
- Bain, C.D.: Sum-frequency vibrational spectroscopy of the solid/liquid interface. *J. Chem. Soc. Faraday Trans.* **91**, 1281–1296 (1995)
- Lambert, A.G., Davies, P.B., Neivandt, D.J.: Implementing the theory of sum frequency generation vibrational spectroscopy: a tutorial review. *Appl. Spectroscop. Rev.* **40**, 103–145 (2005)
- Wang, J., Chen, C.Y., Buck, S.M., Chen, Z.: Molecular chemical structure on poly(methyl methacrylate) (PMMA) surface studied by sum frequency generation (SFG) vibrational spectroscopy. *J. Phys. Chem. B* **105**, 12118–12125 (2001)
- Casford, M.T.L., Davies, P.B.: Adsorption of SDS and PEG on calcium fluoride studied by sum frequency generation vibrational spectroscopy. *J. Phys. Chem. B* **112**, 2616–2621 (2008)
- Tyrode, E., Johnson, C.M., Kumpulainen, A., Rutland, M.W., Claesson, P.M.: Hydration State of nonionic surfactant monolayers at the liquid/vapor interface: structure determination by vibrational sum frequency spectroscopy. *J. Am. Chem. Soc.* **127**, 16848–16859 (2005)
- Zhang, H., Romero, C., Baldelli, S.: Preparation of alkanethiol monolayers on mild steel surfaces studied with sum frequency generation and electrochemistry. *J. Phys. Chem. B* **109**, 15220–15530 (2005)
- Holman, J., Neivandt, D.J., Davies, P.B.: Nanoscale interference effect in sum frequency generation from Langmuir–Blodgett fatty acid films on hydrophobic gold. *Chem. Phys. Lett.* **386**, 60–64 (2004)
- Holman, J., Neivandt, D.J., Davies, P.B.: Sum frequency spectroscopy of Langmuir–Blodgett fatty acid films on hydrophobic gold. *J. Phys. Chem. B* **108**, 1396–1404 (2004)
- Holman, J., Nishida, T., Ye, S., Neivandt, D.J., Davies, P.B.: Sum frequency generation from Langmuir–Blodgett multilayer films on metal and dielectric substrates. *J. Phys. Chem. B* **109**, 18723–18732 (2005)
- McGall, S.J., Neivandt, D.J., Davies, P.B.: Interference effects in sum frequency vibrational spectra of thin polymer films: an experimental and modeling investigation. *J. Phys. Chem. B* **108**, 16030–16039 (2004)
- Lambert, A.G., Neivandt, D.J., Briggs, A.M., Usadi, E.W., Davies, P.B.: Interference effects in sum frequency spectra from monolayers on composite dielectric/metal substrates. *J. Phys. Chem. B* **106**, 5461–5469 (2002)
- Lambert, A.G., Neivandt, D.J., Briggs, A.M., Usadi, E.W., Davies, P.B.: Enhanced sum frequency generation from a monolayer adsorbed on a composite dielectric/metal substrate. *J. Phys. Chem. B* **106**, 10693–10700 (2002)