Optical Analysis of Surfaces by Second-Harmonic Generation: Possible Applications to Tribology

L. Marrucci, D. Paparo, G. Cerrone, and S. Solimeno
Istituto Nazionale Fisica della Materia and Dipartimento di Scienze Fisiche,
Napoli, Italy
R. Russo
Dipartimento di Ingegneria Meccanica per l'Energetica, Universita 'Federico II'
di Napoli, Napoli, Italy
T.L. Lenza
Dipartimento di Ingegneria Meccanica, Universita di Salerno, Salerno, Italy
and P. Siano
RILUB SpA, Napoli, Italy

Abstract

Optical second-harmonic generation is a recently developed technique in surface science, the range of applications of which has been steadily broadening. It allows, among other things, the direct probing of molecular adsorption on to a solid substrate from a liquid or gaseous environment. This paper reports on the possibility of applying it to tribological studies. A set of possible experiments that could offer information, in particular, on the working principle of those oil additives, commonly used in the lubricant industry, whose effect derives from surface adsorption, are discussed briefly. In addition, the preliminary results of a first experiment are described.

Keywords

INTRODUCTION

Over the past few years the study of friction and lubrication by the physics community has been experiencing renewed interest associated with the application of novel methods and experimental tools developed in the broader field of surface science.[1-3] In particular, the surface force apparatus,[1-3] the atomic friction force microscope,[2-4] and the crystal microbalance[1-3] have allowed a shift from a purely macroscopic traditional approach, to a microscopic one, focusing on the relevant molecular and nanoscale phenomena.[1-5]

Another recently developed technique of surface science is optical second-harmonic generation (SHG),[6,7] which offers considerable potential, particularly in the study of interfaces between condensed phases. The basic concept of this technique is that, with second-order nonlinear optical processes, SHG is symmetry forbidden in the bulk of centrosymmetric materials. At the interface between two media, however, the inversion symmetry is broken in a region that typically has a molecular-scale thickness. Therefore, SHG provides background-free molecular-scale information about this interface. SHG retains all the advantages of optical techniques, namely of not requiring a vacuum, of being non-destructive, and of being applicable *in situ* to any interface accessible by light. It can have the transverse spatial resolution of optical microscopy (micrometres) and, exploiting pump-and-probe approaches, it allows time-resolved measurements with sub-picosecond resolution.

Since its first implementation in the mid-1980s,[6] the number of applications of SHG has been growing slowly but steadily, as evidenced, for example, by the literature in reference 8. It is well established that SHG allows one to probe monolayers of adsorbed polar molecules on solid substrates, even when the substrate is coated with a liquid solution of the same molecules.[6-8] Studies have already been made, by means of SHG, of the adsorption of monolayers of polar molecules on anisotropic substrates, in connection with the problem of liquid crystal anchoring.[9,10] These applications suggest that SHG could also be applied to the study of lubrication, and more specifically to the subject of boundary lubrication, where monolayers of adsorbed molecules play a critical role. The idea of applying SHG to this field of tribology is not completely new, but hitherto there have been very few studies related to this reported in the literature.[11-15]

The aim of the present paper is to describe the SHG apparatus used at the laboratories of the Dipartimento di Scienze Fisiche of the University 'Federico II' (within the framework of the project 'Centro Metodologie Ottiche' – Istituto Nazionale per la Fisica della Materia) and to report the preliminary results of first experiments concerning the problem of detecting the adsorption on a metal substrate of polar additives dissolved in a base oil. A survey of the possibilities offered by the SHG technique in the tribological field is also presented.

OPTICAL SHG FROM SURFACES

Optical SHG is a nonlinear optical process, in which the response of a material, characterised by the electric polarisation vector P, acquires a component that is quadratic in the electric field E of the input wave. This component is described by a third-order tensor $\chi^{(2)}$, called the second-order nonlinear optical susceptibility, characterising the material, and is defined by the relationship

$$P_i(2\omega) = \sum_{jh} \chi_{ijh}^{(2)} E_j(\omega) E_h(\omega) \qquad (1)$$

where ω is the optical frequency.[16,17] The polarisation at the second-harmonic frequency 2ω is then the source of an outgoing optical wave at the same frequency. By measuring the intensity, polarisation, and phase of this outgoing wave, one can determine all the elements of $\chi^{(2)}$ and obtain the information about the material contained in this tensor. The elements of $\chi^{(2)}$ are, in general, complex numbers to represent both the amplitude and phase of the wave. The intensity of the generated second-harmonic wave is proportional to the absolute square of the polarisation vector. Omitting all details, which can be found elsewhere,[6,7] one can then write the following relationship between the input wave intensity $I(\omega)$ and the SHG intensity $I(2\omega)$:

$$I(2\omega) \propto \left|\chi_{\text{eff}}^{(2)}\right|^2 I^2(\omega) \qquad (2)$$

where $\chi_{\text{eff}}^{(2)}$ is a linear combination of $\chi^{(2)}$ elements, with coefficients depending on the experimental geometry only (i.e., on the selected input and output polarisations and on the incidence angle).

What turns SHG measurement into a surface-specific technique is the fact that $\chi^{(2)}$ must vanish in centrosymmetric media, being a third-order tensor. Therefore, with the notable exception of non-centrosymmetric crystals and of chiral substances, $\chi^{(2)}$ will completely vanish in the bulk of all materials. However, in the proximity of an interface between two centrosymmetric media, the inversion symmetry is perturbed and a non-zero $\chi^{(2)}$ may appear. In most cases, this perturbation is significant only within a molecular distance of the interface. Therefore, by measuring the second-harmonic wave generated at an interface, one acquires information about it on a scale of only one or two molecular layers across the interface. This can be compared with ordinary linear optical techniques that usually provide information on an interfacial layer having a thickness of the order of the wavelength, i.e., several hundreds of molecular layers.

The interface-generated second-harmonic component can be traced in both the transmitted and the reflected beams emerging from the interface, usually with comparable magnitudes. The choice of which component to measure is then mainly a question of experimental convenience. Clearly, if one of the two media is optically non-transparent, as in the case of a metal, one is forced to measure the SHG in reflection through the other material. **Figure 1** (overleaf) shows a schematic representation of the SHG phenomenon.

The measurement of SHG is probably the only existing technique that allows a real-time, non-destructive, *in situ* monitoring of the adsorption of molecules on to a solid substrate from a liquid solution. This possibility arises from the variations induced by the adsorbed molecules in the $\chi^{(2)}$ tensor. In the case of physical adsorption, where the substrate–adsorbate interactions are weak,

Figure 1 Schematic view of SHG at an interface between two centrosymmetric media
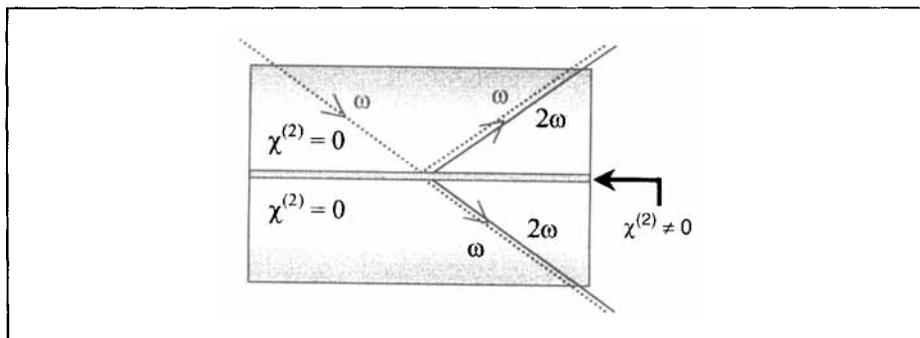
one can usually just assume that the overall surface tensor $\chi^{(2)}$ is a superposition of two contributions, one due to the 'bare' substrate–solvent interface, $\chi_b^{(2)}$, and the other due to the adsorbed molecules, $\chi_m^{(2)}$. If the monolayer of adsorbed molecules does not change its organisation or condensation phase for increasing surface density, then the second contribution will be simply proportional to the surface density N_s of adsorbed molecules. Therefore one can write

$$\chi^{(2)} = \chi_b^{(2)} + \Lambda N_s \tag{3}$$

where $\Lambda = d\chi_m^{(2)}/dN_s$ is a constant tensor characterising a single adsorbed molecule. The measured SHG intensity $I(2\omega)$ will depend on the surface density N_s as follows:

$$I(2\omega) \propto \left|\chi_{b,\mathrm{eff}}^{(2)}\right|^2 + 2\,\mathrm{Re}(\chi_{b,\mathrm{eff}}^{(2)}\Lambda_{\mathrm{eff}}^*)N_s + \left|\Lambda_{\mathrm{eff}}\right|^2 N_s^2 \tag{4}$$

where Re( ) denotes the real part of its argument. Note that the second term in Eq. (4) can be positive or negative, so that the SHG signal can increase or decrease as the adsorption process takes place, depending on the relative phase of the two complex numbers $\chi_{b,\mathrm{eff}}^{(2)}$ and Λ_{eff}. Moreover, the relative importance of the second term, giving rise to a signal that is linear in N_s, and the third one, corresponding to a signal quadratic in N_s, depends on the relative size of $\chi_{b,\mathrm{eff}}^{(2)}$ and Λ_{eff}.

Being a nonlinear optical technique, SHG requires very high input intensities, which can be achieved only by means of laser sources. In particular, it is usually necessary to employ pulsed lasers that concentrate all the light energy in extremely short pulses (nanosecond, picosecond, or even femtosecond lasers are now commercially available) of very high peak power. As a consequence, laser-induced damage of the probed surface usually sets the limit to the maximum SHG signal that can be obtained.

**Figure 2 Schematic representation of the experiment**
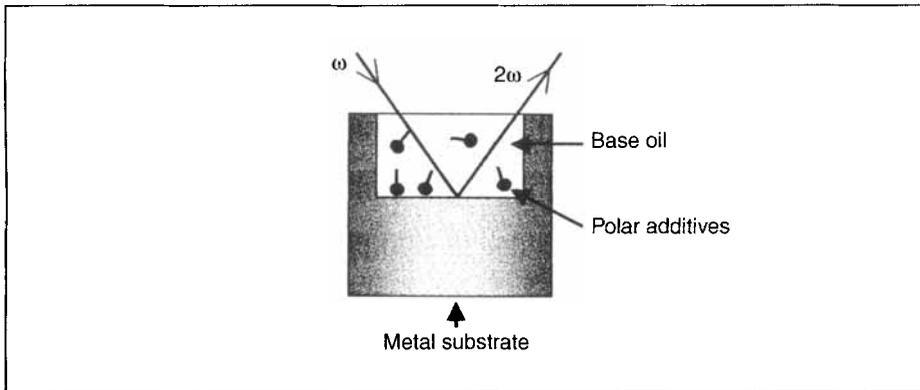
A FIRST EXPERIMENT: PRELIMINARY RESULTS

As a first test of the applicability of SHG to practical problems in the lubricant industry, it was decided to apply this technique directly to the detection of the surface modifications induced in a metal surface coated by a thin film of a lubricant base oil in which a small amount of additive is dissolved. The additive is of a type (antiwear, extreme pressure) that is designed to increase the boundary-lubrication performance of the lubricant, which is a commercial mixture, Lubrizol Anglamol 6085, of confidential composition, based mainly on sulphur–phosphorus compounds. A schematic representation of the experiment is shown in **Figure 2**. The depth of the oil layer of about 2 mm is determined by the size of a small disc-shaped cavity drilled in the metal surface.

The experimental set-up is shown in **Figure 3** (overleaf). The laser source is a titanium–sapphire amplified femtosecond (fs) laser, generating pulses of about 1 mJ of energy with a duration of 120 fs at a repetition rate of 1 kHz. The wavelength is about 800 nm. Only 10% of the total energy was used, while the remaining part was utilised by another simultaneous experiment. Polarising optics were used to set the input beam to either s (electric field orthogonal to the incidence plane) or p (electric field in the incidence plane) linear polarisation. A lens was used to focus the input beam on the sample surface. A low-pass filter placed just before the sample was used to eliminate any second-harmonic component that might be generated by the optics before reaching the sample. The reflected beam first encounters a high-pass dielectric filter that removes most of the fundamental reflected beam (i.e., at frequency ω), letting through the second-harmonic component. A second lens is then used to recollimate the beam, and a half-wave plate and a polariser are used to select the measured output polarisation (s or p). A third lens is used to focus the beam at the entrance

Figure 3 Experimental set-up
BS, beam splitter; λ/2, half-wave plate; P, polariser; L, lens; F, filter;
MC, monochromator; PMT, photomultiplier tube; GI, gated integrator;
DA, data acquisition
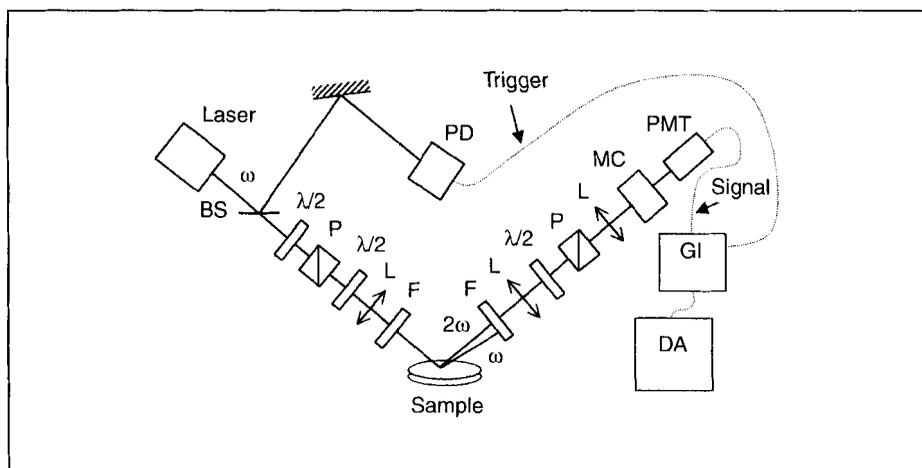
slit of a monochromator that selects the measured wavelength (set to 400 nm during these experiments, to measure the second harmonic at 2ω). The output of the monochromator is then sent to a photomultiplier tube used for the final detection.

Despite the high power of the input laser, the signal collected was extremely weak and consisted of only a few photons of second-harmonic signal detected per input laser pulse. Therefore, the detection scheme required the use of the so-called 'photon counting' approach. In fact, this is a standard situation for SHG experiments when the source is a layer of single-molecule thickness. The approach to the extraction of signal from noise was based on gated-integrator amplifying electronics, allowing the detection of only those photons reaching the photomultiplier within a time 'window' of only 30 ns opened synchronously with the arrival of the input laser pulse. In this way a background noise was achieved of about five photons in 30,000 laser pulses.

To obtain an immediate indication of the ability of the apparatus to detect the surface effects of the lubricant additive, the following trials were performed. First the SHG signal produced by the bare metal without any oil film was measured. With aluminium substrates, no significant SHG (above background) was observed for all possible input–output polarisation combinations (s–s, s–p, p–p, p–s). For steel, a small signal of 60 ± 7 second-harmonic photons in 30,000 laser pulses was detected for the input–output polarisation combination p–p. All other polarisations gave a vanishing signal (actually, for an azimuthally

isotropic surface, such as those considered here, all s-polarised SHG output is expected to vanish by symmetry). Next the SHG for the same metal coated with a thin film of the base oil was measured. The number of photons observed was still 60 ± 7 photons in 30,000 laser pulses, i.e., no significant variation of SHG. This indicates that the main contribution to the signal comes from the metal surface and not from the oil surface in contact with it. The base oil film was then replaced with a film of base oil that had been enriched with 2% (volume ratio) of the commercial additive. This change gave rise to a significant variation of SHG. Indeed, 30 ± 6 photons were observed for the same number of pulses. This decrease by about 50% is not commensurate with the bulk concentration of the additive (2%), indicating that the additive is acting preferentially at the surface, most likely by means of molecular adsorption. Finally, the SHG yield was measured with the base oil film replaced entirely by the additive (which is a liquid solution itself). In this case 40 ± 6 photons were obtained. This signal is close to the signal obtained with the 2% solution of additive in base oil, showing that at 2% the adsorption effects are probably already saturated. When using aluminium, no SHG was observed in all cases.

These results are only preliminary. Some trials are planned using an increasing concentration of additive dissolved in the base oil, looking for the adsorption isotherm of the additive. It is evident that to obtain more significant results all these trials have to be repeated on well-characterised pure materials rather than on commercial mixtures of unknown composition. However, it is reassuring to find that when applied directly to commercial materials of industrial interest, chosen at random without any particular selection criteria, the SHG technique is already capable of providing direct information.

DISCUSSION

Over the past few decades there has been a continuous evolution in the chemical formulation of additives for lubricants and in products with ever-improving performances. This expansion has been favoured, among other things, by the use of more sophisticated instruments of investigation that have allowed a steady growth in our knowledge of the physico-chemical properties and working principles of the molecules making up the additives.

In this context, the SHG technique could make a useful contribution to the investigation of the working mechanism of those classes of additives whose effectiveness relies on being physi- or chemisorbed on to tribological surfaces. These classes include friction modifiers, antiwear agents, extreme pressure (EP) agents, rust inhibitors, and anti-corrosives. A large literature exists concerning the mechanisms of action of these additives,[18,19] and several experiments have been conducted to determine the protection level achieved for various operating conditions and for different physico-chemical compositions of the base oils,

the additives themselves, and the tribological surfaces. In particular, the efficacy of the above-mentioned additives is based on the ability of their molecules to anchor to the metal (or to its oxide) of the tribological surfaces and, according to the need, facilitating relative motion or preventing their oxidation or corrosion. With the exception, perhaps, of those EP additives that start being effective under the action of large loads and very high temperatures, all other additives tend to give rise to this anchoring phenomenon under static equilibrium conditions of the kinematic pair. Therefore, a first use in tribology of the SHG technique could be in the formulation of the correct percentages of additive in base oil. This could be achieved, for example, by estimating the additive concentration beyond which any additional molecules would be likely to remain dissolved in the mineral base oil bulk rather than adsorb on to the surfaces. Reducing all additive quantities to a minimum is in any case a fundamental goal both for evident economic reasons and for achieving a lower environmental impact and better work-safety conditions. In fact, almost all the EP and antiwear additives currently available are rich in odorous compounds based on sulphur and phosphorus that are quite difficult to separate from the base oil in the used oil regeneration process.

The type of study represented by the experiments described above requires measurement of the optical second-harmonic intensity for new and clean samples, for samples that have been coated with pure base oil, and for samples that have been coated with base oil–additive mixtures at various percentages, looking for a signal saturation value showing that the surface has been completely covered. In a second phase of our work, we hope to repeat the same measurements on samples that, coated with the same oils and additives, have undergone a certain number of working cycles under predetermined conditions, such as wear cycles on a pin-on-disc machine.

Another application that is currently being planned would be to carry out tests on a working kinematic pair. In this case, of course, one of the two tribological substrates must be transparent to the laser beam. In varying the operating conditions and scanning different zones of the contact area, this kind of experiment could yield evidence as to the role of those additives that tend to act only under the effect of a high load and/or at particular temperatures. Moreover, they could provide direct information on the modifications taking place in the adsorbed molecular monolayer due to the relative motion of the tribological surfaces. However, an experimental difficulty arises here due to the very small size of the actual contact area compared to the laser spot size. The contribution to the SHG signal arising in the contact areas could then be negligible with respect to that generated by the surrounding non-contact regions. A possible solution to this problem would be to employ atomically flat surfaces, such as those made of mica used in the surface force apparatus.

Probably easier to realise would be experiments aimed at assessing the performance of detergent additives. In this case, after treating an oil-coated

sample with the detergent additive under examination, the SHG signal could be simply compared with the corresponding signal of a clean sample.

More uncertain appears to be the use of SHG in the diagnostic field. In fact, this technique does not easily allow one, for example, to obtain clear-cut chemical or morphological information about the surface investigated. However, there is the future possibility of using a still more powerful spectroscopic technique that is a direct generalisation of SHG, namely infrared–visible sum-frequency generation.[6,7] This much more complex technique allows one to distinguish between different chemical components present at a surface.

CONCLUSION

It should be emphasised that the SHG technique discussed provides a new and sophisticated method for investigation in the fields of both surface science and tribology. The applications described here in the tribological field represent only an initial study of the possibilities that are becoming apparent. As a promising technique, this area deserves discussion and development.

References

1. Persson, B.N.J., *Sliding Friction*, Springer Verlag, Berlin, 1998.
2. Krim, J., 'Friction at the atomic scale', *Scientific American*, 48 (1996) October.
3. Bhushan, B., Israelachvili, J.N., and Landman, U., 'Nanotribology: friction, wear and lubrication at the atomic scale', *Nature*, 374 (1995) 607.
4. Carpick, R.W., and Salmeron, M., 'Scratching the surface: fundamental investigations of tribology with atomic force microscopy', *Chem. Rev.*, 97 (1997) 1163.
5. Granick, S., 'Soft matter in a tight spot', *Physics Today*, 52 (1999) July, p. 26.
6. Shen, Y.R., 'Surface properties probed by second-harmonic and sum-frequency generation', *Nature*, 337 (1989) 519.
7. Shen, Y.R., 'Surfaces probed by nonlinear optics', *Surf. Sci.*, 299/300 (1994) 551.
8. All articles in the special issue of *Appl. Phys. B*, 68, 3 (1999) 287–655.
9. Zhuang, X., Marrucci, L., and Shen, Y.R., 'Surface-monolayer-induced bulk alignment of liquid crystals', *Phys. Rev. Lett.*, 73 (1994) 1513.
10. Zhuang, X., Wilk, D., Marrucci, L., and Shen, Y.R., 'Orientation of amphiphilic molecules on polar substrates', *Phys. Rev. Lett.*, 75 (1995) 2144.
11. Du, Q., Xiao, X.-D., Charych, D., Wolf, F., Frantz, P., Shen, Y.R., and Salmeron, M., 'Nonlinear optical studies of monomolecular films under pressure', *Phys. Rev. B*, 51 (1995) 7456.
12. Herman, H., and Klenerman, D., 'Shedding (laser) light on surfaces', *Spectrosc. Eur.*, 5, 5 (1993) 8.
13. Gracias, D.H., Zhang, D., Shen, Y.R., and Somorjai, G.A., 'Surface chemistry–mechanical property relationship of low density polyethylene: an IR+visible sum frequency generation spectroscopy and atomic force microscopy study', *Trib. Lett.*, 4 (1998) 231.
14. Beattie, D.A., Haydock, S., and Bain, C.D., 'A comparative study of confined organic monolayers by Raman scattering and sum-frequency spectroscopy', *Vib. Spectrosc.*, 24 (2000) 109.
15. Salmeron, M., 'Generation of defects in model lubricant monolayers and their contribution to energy dissipation in friction', *Trib. Lett.*, 10 (2001) 69.
16. Shen, Y.R., *The Principles of Nonlinear Optics*, John Wiley, New York, 1984.
17. Boyd, R.W., *Nonlinear Optics*, Academic Press, Boston, 1992.
18. Del Ros, S., *I Lubrificanti*, Etas Libri, Milan, 1977.
19. Kajdas, C., Harvey, S.S.K., and Wilusz, E., *Encyclopedia of Tribology*, Elsevier, Amsterdam, 1990.