

OPTICAL ANALYSIS OF SURFACES BY SECOND HARMONIC GENERATION: POSSIBLE APPLICATIONS TO THE TRIBOLOGICAL FIELD

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ABSTRACT

Optical second harmonic generation is a recently developed technique of surface science, whose range of applications has been steadily broadening in the last years. It allows, among other things, direct probing of molecular adsorption on a solid substrate from a liquid or gaseous environment. Here we discuss the possibility of applying it to tribological studies. We discuss briefly a set of possible experiments that could obtain information, in particular, on the working principle of those oil additives, commonly used in the lubricant industry, whose effect derives from surface adsorption. Moreover, we describe the preliminary results of a first experiment currently in progress.

INTRODUCTION

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

Another recently developed technique of surface science is optical second harmonic generation (SHG) [6,7], that shows considerable potential, particularly in the study of interfaces between condensed phases. The idea at the root of this technique is the following. As all second-order nonlinear optics 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 molecular-scale thickness. Therefore SHG carries background-free molecular-scale information on the interface. On the other hand, SHG has all the advantages of optical techniques, namely of not requiring vacuum, of being nondestructive and applicable "in situ" to any interface accessible by light. It can have optical-microscope transverse spatial resolution (micrometers) and, exploiting pump-and-probe approaches, it allows time-resolved measurements with subpicosecond resolution. Since SHG first implementation, in the mid-eighties [6], the number of applications of SHG has been slowly but steadily growing, as evidenced for example by the papers collected in Ref. [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]. One of the authors of the present paper has already studied, by means of SHG, the adsorption of monolayers of polar molecules on anisotropic substrates, in connection with the problem of liquid crystal anchoring [9,10]. These past applications suggest that SHG could be applied also to the study of lubrication, and more specifically of 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 are very few related works in the literature [11-13].

The aim of the present paper is to describe the SHG apparatus realised 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 our first experiments concerning the problem of detecting the adsorption on a metal substrate of the polar additives dissolved in a base oil. A survey of the possibilities offered by the SHG technique in the tribological field will be also presented.

OPTICAL SECOND HARMONIC GENERATION FROM SURFACES

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

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

where ω is the optical frequency [14,15]. The polarization at second-harmonic frequency 2ω is then source of an outgoing optical wave at the same frequency. By measuring the intensity, polarization and phase of this outgoing wave one can determine all the elements of $\chi^{(2)}$ and obtain the information contained in this tensor about the material. The elements of $\chi^{(2)}$ are, in general, complex numbers in order to represent both amplitude and phase of the wave. The intensity of the generated second harmonic wave is proportional to the absolute square of the polarization vector. Skipping all details, that can be found for example in Refs. [6,7], one can then write the following relationship between the input wave intensity $I(\omega)$ and the SHG intensity $I(2\omega)$:

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

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

What turns the 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 noncentrosymmetric crystals and of chiral substances, $\chi^{(2)}$ will perfectly vanish in the bulk of all materials. However, in proximity of an interface between two centrosymmetric media the inversion symmetry is perturbed and a nonzero $\chi^{(2)}$ may appear. In most cases, this perturbation is significant only within a molecular distance from 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 has to be compared with ordinary linear optics 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 both in the transmitted and 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 provides a schematic picture of the SHG phenomenon.

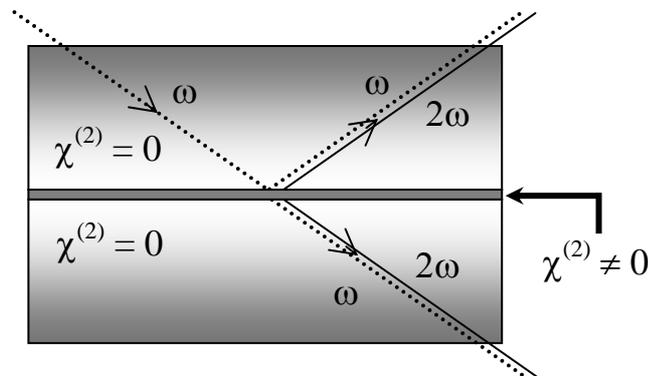


Figure 1. Schematic view of SHG at an interface between two centrosymmetric media.

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 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, 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 - let us denote it as $\chi_b^{(2)}$ - and the other due to the adsorbed molecules - we will denote it as $\chi_m^{(2)}$. If the monolayer of adsorbed molecules does not change its organization 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 has

$$\chi^{(2)} = \chi_b^{(2)} + \mathbf{A}N_s, \quad (3)$$

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

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

where $\text{Re}(\cdot)$ denotes the real part of its argument. Notice that the second term in Eq. (4) can be both positive or negative, so that the SHG signal can both increase or decrease as the adsorption process takes place, depending on the relative phase of the two complex numbers $\chi_{b,eff}^{(2)}$ 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 $\chi_{b,eff}^{(2)}$ and Λ_{eff} .

Being a nonlinear optical technique, SHG requires very high input light intensities, that 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 limits on the maximum SHG signal that can be obtained.

A FIRST EXPERIMENT: PRELIMINARY RESULTS

Looking for a first test of the potential applicability of SHG to real problems in the industry of lubricants, we decided to try 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 small amounts of an additive are dissolved. The additive is of a kind designed for increasing the lubricant boundary-lubrication performances. It is a commercial mixture of different substances of confidential composition. A schematic picture of our experiment is shown in Fig. 2. The thickness of the oil film of about 2 mm is fixed by the size of a small disk-shaped cavity drilled in the metal surface.

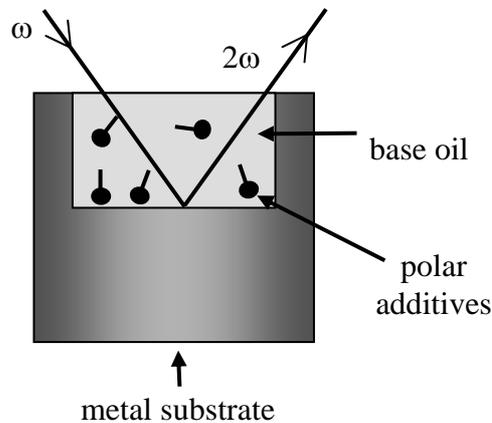


Figure 2. Schematic picture of the experiment

The experimental set-up is shown in Fig. 3. The laser source is a Titanium-Sapphire amplified femtosecond laser, generating pulses of about 1 mJ of energy with a duration of 120 femtosecond at a repetition rate of 1KHz, at a wavelength of about 800 nm. We actually employed only 10% of the total energy, while the remaining part was utilized by another simultaneous experiment. Polarizing optics was 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 polarization. A lens was used to focus the input beam on the sample surface. A low-pass filter placed just before the sample is used to get rid of any second harmonic component that might be generated by the optics before the sample. Then the reflected beam encounters first a high-pass dielectric filter that cuts away most of the fundamental reflected beam (i.e. at frequency

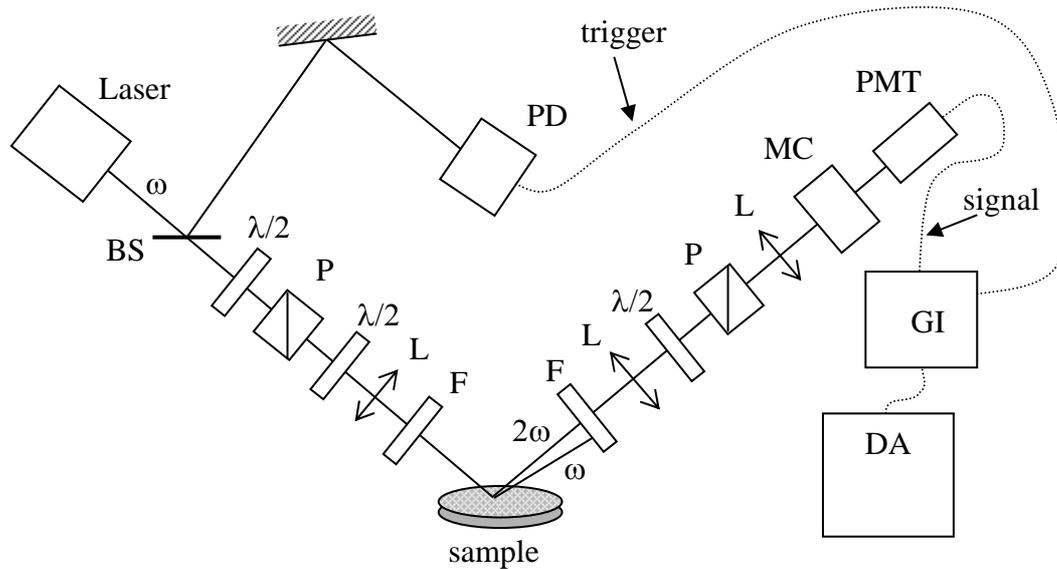


Figure 3. Experimental set-up. Legend: BS - beam splitter; $\lambda/2$ - half-wave plate; P - polarizer; L - lens; F - filter; MC - monochromator; PMT - photomultiplier tube; GI - gated integrator; DA - data acquisition.

ω) letting through the second harmonic component. Then a second lens is used to recollimate the beam, a half-wave plate and a polarizer are used to select the measured output polarization (s or p). Next a third lens is used to focus the beam at the entrance 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 that we collected was extremely weak and consisted of only few photons of second harmonic detected per input laser pulses. Therefore the detection scheme required using the so-called “photon counting” approach. Actually, this is a standard situation for SHG experiments as the source is a single-molecule-thick layer. Our approach to the extraction of signal from noise was based on the 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 we achieved a background noise of about 5 photons in 30000 laser pulses.

To obtain an immediate indication of the ability of our apparatus to detecting the surface effects of the lubricant additive, we performed the following trials. First we measured the SHG signal produced by the bare metal, without any oil film. When using aluminum substrates we observed no significant SHG (above background) for all possible input-output polarization combinations (s-s, s-p, p-p, p-s). For steel, we detected a small signal of 60 ± 7 second harmonic photons in 30000 laser pulses, for the input-output polarization combination p-p. All other polarizations gave a vanishing signal (actually, for an azimuthally isotropic surface such as those considered by us, all s-polarized SHG output is expected to vanish by symmetry). Next we measured the SHG for the same metal coated with a thin film of the base oil. We still observed 60 ± 7 photons in 30000 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. Next, we replaced the base-oil film 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, we observed 30 ± 6 photons 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, we measured the SHG yield with the base-oil film replaced entirely with the additive (which is a liquid solution itself). In this case we obtained 40 ± 6 photons. This signal is close to the signal obtained with the 2%-solution, showing that at 2% the adsorption effects are probably already saturated. When using aluminum, we observed no SHG in all cases.

These results are very preliminary. We are now planning some trials with a slowly increasing concentration of additive dissolved in the base oil, looking for the adsorption isotherm of the additive. Of course, to obtain more definite scientifically-significant results, all these trials will have to be repeated on well characterized pure materials, rather than on commercial mixtures of unknown composition. However, it is reassuring to find out that when applied directly to commercial materials, chosen at random without any particular selection, products of immediate industrial interest, SHG is already capable of providing direct information.

PERSPECTIVES AND CONCLUSIONS

In the last decades, the industry in this sector has given birth to a continuous evolution in the chemical formulation of additives for lubricants and has supplied products granting higher and higher performances. This expansion has been favoured, among other things, by the use of more and more sophisticated instruments of investigation that allowed a steady growth of our knowledge of the physical-chemical properties and working principles of the molecules constituting the additives.

In this context, the SHG technique could provide a useful contribution to investigating the working mechanism of those classes of additives whose effectiveness relies on being physio- or chemi-adsorbed to the tribological surfaces. These classes essentially include the following kinds of additives: Friction Modifiers, Antiwear, Extreme Pressure (EP), Rust Inhibitors and Anticorrosives. About the action mechanisms of these additives a large literature exists [16, 17] and several experiments have been conducted aimed at determining the protection level achieved for varying operating conditions and for different physical-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 anchoring to the metal (or to its oxide) of the tribological surfaces and, according to the case, favouring their relative motion or preventing their oxidation or corrosion. Perhaps with the exception of the EP additives that start being effective under the action of high loads and very high

temperatures, all other additives have a bent to give rise to this anchoring phenomenon also under static equilibrium conditions of the kinematic pair. Therefore, a first yield within the tribological field of the SHG technique could certainly be represented by the help it could provide to the formulator in the process of determining the useful percentages of additive to be included in the base oil. This could be achieved for example by estimating the additive concentration beyond which any additional molecule would likely remain dissolved in the mineral base bulk rather than adsorb to the surfaces. In fact, reducing all additive quantities to a minimum is a fundamental goal both for evident economical reasons and for achieving lower environmental impact and better work-safety conditions. As a matter of fact, almost all EP and antiwear additives currently on the market are rich of compounds based on sulfur-phosphorous that give them a very bad smell, besides being quite hard to be separated from the base-oil in the worn-oil regeneration process, that is compulsory by law.

This kind of study, that represents the part of our experimentation that has already set off, requires the measurement of the optical second harmonic intensity on new and clean samples, on samples that have been coated with pure base oil, and on samples that have been coated with base oil - additive mixtures at increasing percentages, looking for a saturation value of the signal showing that the surface has been completely covered. In a second phase, we expect 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 disk machine.

Another fascinating application that we are currently planning would be to carry out trials 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 operating conditions, scanning different zones of the contact area, this kind of experiments could evidence the role of those additives that tend to act only under the effect of a high load and/or of particular values of the temperature. Moreover, it could provide direct information on the modifications occurring to the adsorbed molecule monolayer due to the motion of the tribological surfaces. However, an experimental difficulty arises here from the very small size of the areas of actual contact compared to the laser spot-size. The contribution to the SHG signal arising in the actual-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 that are used in the surface force apparatus.

Probably easier to be realised would be experiments aimed at assessing the performances of detergent additives: in this case, after treating an oil-wet sample with the detergent additive under examination, the SHG signal should be simply compared with the corresponding one with the clean sample.

More uncertain appears the use of SHG in the diagnostic field. In fact, this technique does not easily allow, for example, to obtain clear-cut chemical or morphological information about the investigated surface. However, we envision here the possibility of using in the future 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.

In conclusion, we wish to emphasize that the illustrated SHG technique provides a new and sophisticated instrument for investigating the field of surface science and more specifically of tribology. The applications we have described in the tribological field represent only an initial partial study of the possibilities that are opening up in this field. All suggestions and advice that should be received on this subject will therefore be quite welcome.

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