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## Probing interfacial properties by optical second-harmonic generation

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### Abstract

Optical second-harmonic generation from surfaces has recently proven to be a very effective and versatile probe for surface studies. It allows, among other things, direct probing of molecular adsorption on a solid substrate from a liquid. In this paper we review the most important features of this new technique. We discuss the possibility of applying it to the study of adsorption of ionic surfactants at solid–liquid interfaces, commonly used in a great number of scientific and technological fields including industrial applications. Moreover, we describe the preliminary results of an experiment currently in progress. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Surfaces; Nonlinear optics; Optical second-harmonic generation; Interfaces

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### 1. Introduction

A good microscopic characterization of surfaces plays a central role in surface science for understanding the complex phenomena occurring at interfaces. This necessity has driven the development of new and sophisticated experimental tools.

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The application of many of the existing techniques is limited to surfaces under vacuum, as they involve emission, absorption, or scattering of charged particles. Optical techniques do not have this limitation, requiring only that one of the two media adjacent to the interface be transparent. Moreover, optical techniques are not destructive and applicable “in situ” to any interface accessible by light. However, ordinary linear optical techniques are not strictly surface-specific as the optical signal is usually sensitive to an interfacial layer having a thickness of the order of the wavelength. Recently, the nonlinear optical phenomenon of second-harmonic generation (SHG) has proven to be suitable to become a very effective technique for probing surface properties with submonolayer sensitivity [1–3]. In particular, this technique has intrinsic surface-specificity, i.e., it is free of background from the bulk. This particular feature of SHG technique is related to the general property that second-order nonlinear optical processes are forbidden in media with inversion symmetry [4,5]. This means that the interaction of a laser beam with such materials cannot give rise to SHG in their bulk. Of course the inversion symmetry is automatically broken at the interface between two different media, even if both are centro-symmetric, due to the strong material gradients. Typically, this symmetry breaking involves regions with molecular- or submolecular-scale thickness, rendering this technique a powerful tool for getting background-free molecular-scale information about the interface. Moreover, SHG can have optical-microscope transverse spatial resolution (micrometers) and, exploiting pump-and-probe approaches, it allows time-resolved measurements with subpicosecond resolution. It is well established that SHG is able to probe monolayers of adsorbed polar molecules on solid substrates, even when the substrate is coated with a liquid solution of the same molecules [6,7]. These and other recent works have suggested the feasibility of using SHG for detecting “in situ” the adsorption of ionic surfactants at solid–liquid interfaces. Often, the molecules of such surfactants have electrons with a high degree of delocalization (presence of aromatic rings with asymmetric substituents groups), whose interaction with external optical fields can induce quite strong dipole moments. As a consequence, these molecules or their substituent can efficiently generate optical second-harmonic light at the interface, which in turn can be used for monitoring directly their adsorption on the substrate. Surfactant adsorption phenomena are extremely important in a great variety of scientific and technological fields including industrial applications. For example, positive organic ions play an important role in mineral flotation (e.g. silicates, clays, etc.), and in enhanced oil recovery, while cationic surfactants are becoming more and more important for road construction and repair [8]. The amphiphilic character of these surfactant molecules reduces the contact angle of bitumen on a mineral surface and lowers the bitumen–water interfacial tension. Other examples of the importance of these materials range from the pigment and ceramic technology to their use as corrosion inhibitors. Despite the relevance of a better understanding of the interfacial properties of these surfactants the methods for investigating the adsorption process still rely on very rough techniques or “ex situ” techniques like X-ray photoelectron spectroscopy. In this context, SHG can be very useful for its “in situ” and “real time” analysis capability.

In this paper, we 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). Moreover, preliminary results of our first experiments concerning the problem of probing the adsorption process of ionic surfactants at solid–liquid interfaces are reported. The paper is structured as follows. Section 2 briefly reviews the physics underlying the phenomenon of optical SHG at interfaces and its most important features. In Section 3 the experimental set-up is described in detail. Section 4 reports the preliminary results of an experiment studying the adsorption of a cationic surfactant at a titanium-dioxide liquid interface. Finally, Section 5 gives the conclusions and briefly discusses the perspectives of these investigations.

## 2. Optical SHG from surfaces

Optical SHG is a second-order nonlinear optical process, occurring when 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  $\omega$  is the optical frequency [4,5]. The polarization at the second-harmonic frequency  $2\omega$  is then the 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 the 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 details, which can be found for example in Refs. [1–3], one can then write the following relationship between the input wave intensity  $I(\omega)$  and the SHG intensity  $I(2\omega)$ :

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

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 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, which 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. Fig. 1 provides a schematic picture of the surface 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 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, which we denote as  $\chi_b^{(2)}$ , and the other due to the adsorbed molecules, denoted 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

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

where  $\mathbf{\Lambda} = d\chi_m^{(2)}/dN_s$  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:

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

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

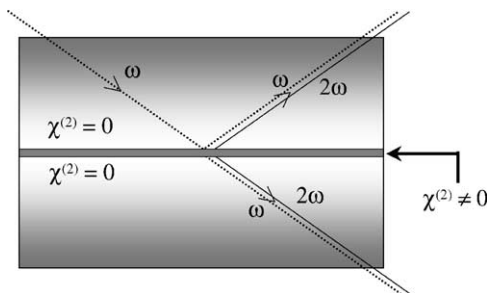


Fig. 1. Schematic view of SHG at an interface between two centrosymmetric media. By symmetry the SHG is forbidden in their bulks and can occur only at the interface.

$A_{\text{eff}}$ . As we will see later, in our case the signal generated from the substrate is low enough that the first two terms in Eq. (4) can be neglected.

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 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.

### 3. The experimental set-up

The SHG experimental apparatus we have set up is based on a commercial titanium-sapphire amplified femtosecond laser. It generates pulses having energy of about 1 mJ and a duration of 120 fs, with a repetition rate of 1 KHz. The wavelength is set to 800 nm, although we may also tune it in the range 750–850 nm with some energy reduction. For our experiment only 10% of the pulse's energy is usually employed, while the remaining part is used by a simultaneous experiment. This beam is directed in the SHG set-up shown in Fig. 2. By using a beam splitter a small fraction of the main beam is directed on a photodiode which serves as reference for taking into account the laser fluctuations during the measurement and for triggering the acquisition electronics. The main beam-line enters a variable attenuator constituted by a half-waveplate and a polarizer. A second half-waveplate beyond the polarizer is used to set the polarization of the beam impinging on the sample to either s (perpendicular to the plane of incidence) or p (parallel to the plane of incidence). The beam is then focused on the sample by a lens of about 10 cm focal length. Due to the intensity of our beam all these optical components can generate

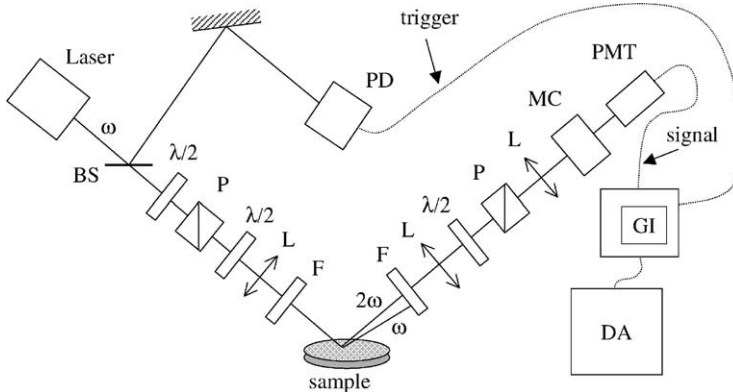


Fig. 2. Experimental set-up. Legend: BS—beam splitter;  $\lambda/2$ —half-wave plate; P—polarizer; L—lens; F—filter; MC—monochromator; PMT—photomultiplier tube; GI—gated integrator; DA—data acquisition.

some second-harmonic light that can influence and even overtake the second-harmonic signal produced by the sample. For this reason a dichroic low-pass filter is placed before the sample in order to block this spurious second-harmonic signal. After the sample one immediately must filter out the reflected fundamental beam in order to avoid further SHG from the other optical components placed beyond the sample. In our set-up, this is achieved by an interferential filter for the 400 nm wavelength which blocks the main part of the fundamental beam. A second lens is then used to recollimate the diverging output beam. Beyond the lens, a polarization analyzer is placed, made of an half-waveplate and a polarizer. We select the analysed polarization (s or p) by rotating the half-wave plate by  $45^\circ$ . The polarizer is kept fixed in order to avoid problems related with polarization-dependent detection efficiency. By changing the input and output polarization we have access to different combinations of the  $\chi^{(2)}$  tensor elements. Next, a third lens focuses the beam on the entrance slit of a monochromator that selects the measured wavelength. The monochromator is used for eliminating the residual fundamental beam and all other spurious signals which contribute to the background noise. Finally, the output of the monochromator is sent on a photomultiplier. It is worth mentioning that, for reducing the background noise as much as possible, the optical path of the outgoing second-harmonic is delimited by several diaphragms and black screens in order to reject all the background radiation that is not coherent and collimated like the second harmonic signal.

Despite the high peak power of the input beam, the collected signal is extremely weak and typically consists of only a few photons of detected second-harmonic per input laser pulse. This is because the second-harmonic signal is generated only from a single monolayer of molecules or less. As a consequence a detection scheme based on a photon counting approach is required. In order to improve our signal-to-noise ratio a gated-integrating electronics is used. Our gated integrator (Stanford Research Systems) sets a detection “window” of 30 ns opened synchronously with the arrival of the input laser pulse. The temporal limit for the gate is set by the time response of the photomultiplier. With this set-up arrangement we have been able to achieve a background of only  $2 \times 10^{-4}$  photons per pulse.

#### **4. An application: probing adsorption of a cationic surfactant at a titanium-dioxide water interface**

The experimental set-up described in the preceding section has been used to study the adsorption of a cationic surfactant dissolved in an aqueous solution at a titanium-dioxide water interface. A schematic picture of the experiment is in Fig. 3. The cationic surfactant used in the experiment is the 1-dodecyl-4-methylquinolinium chloride (see Fig. 4), soon after mentioned in the text as quinolinium, which was synthesized in the laboratories of the Dipartimento di Chimica Generale ed Organica Applicata of the University of Turin. It is an amphiphilic molecule with a hydrophobic chain and a hydrophilic group constituted by a positively charged head ( $N^+$  ion). The latter is always accompanied by a negatively charged  $Cl^-$  ion.

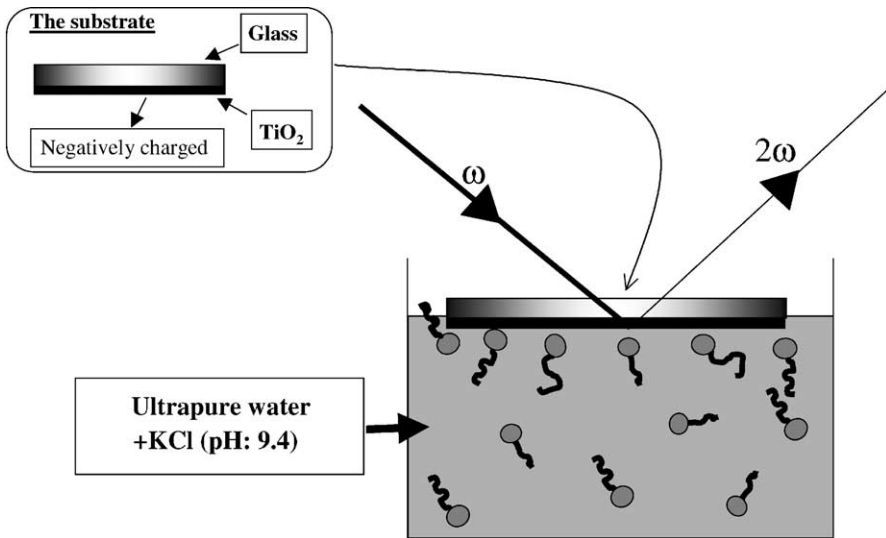


Fig. 3. Schematic picture of the experiment. The surfactant molecules have two distinct parts: the ionic heads are schematically represented by circles, while the hydrophobic chains by segments. In the inset the details of the substrate are described.

The ionic bond between the  $N^+$  and the  $Cl^-$  ions is broken in water so that the  $Cl^-$  ion is not directly involved in the adsorption process. However the presence of these ions in solution affects its ionic force, which in turn can influence the adsorption process. Generally, this process is influenced by several factors related to the different parts of the system such as the nature of the substrate, its charging, the pH of the solution and its ionic force, temperature, the presence of impurities and of course the bulk concentration of quinolinium. In order to fix the ionic force a certain amount of KCl salt is dissolved in the solution so that the ionic force is determined by the salt ions and therefore it is not affected by the small variations induced by changing the concentration of the surfactant. The pH of the solution is fixed at an optimal value of 9.4. A basic solution favours a negative charging substrate and therefore the adsorption of cationic surfactants. The substrate is a glass slide coated with a film of titanium dioxide. Usually on such oxides both acid sites (positively charged) and basic sites (with a negative charge) are present. The first ones can be activated if placed in an acid environment, while a basic pH can activate the basic sites. Since quinolinium has a positive head, its adsorption is enhanced by activating the basic sites by using a solution with an optimal basic pH.

Information about the adsorption efficiency as well as the surfactant–substrate interactions can be obtained by measuring the surface density of the adsorbate at the interface as a function of the surfactant concentration in the solution at a fixed temperature (the so-called “adsorption isotherm”) [9]. As discussed in Section 2, if

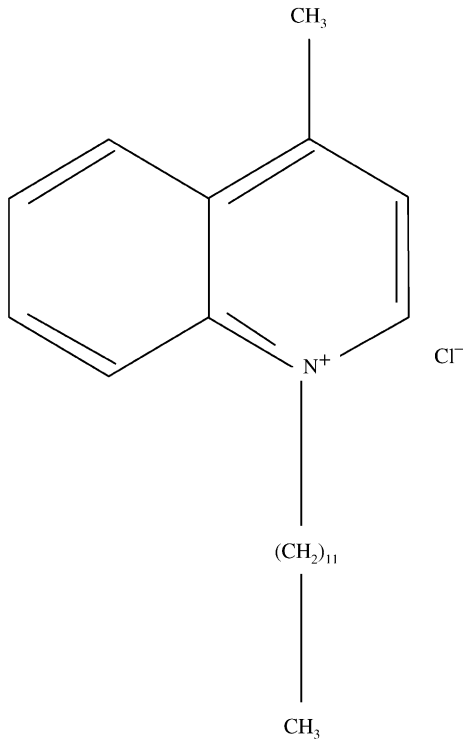


Fig. 4. Molecular structure of the quinolinium.

the signal from the substrate is negligible with respect to the signal due to the surfactant molecules, the first two terms on the right-hand side of Eq. (4) can be neglected and the second harmonic signal is then proportional to the square of the number of molecules adsorbed at the interface. In Ref. [9], the density of the adsorbate at the interface is measured by using two methods which do not permit making an “in situ” analysis and to resolve in time the adsorption dynamics. From this point of view, the SHG technique can provide useful complementary information.

In our experiment, the temperature was kept fixed at about 28°C. We measured SHG for the four independent polarization combinations of the fundamental (input) and second-harmonic (output) beams (p–p, s–p, p–s, s–s) for a variable bulk concentration of surfactant. The signal for the p–s and s–s combinations was negligible in accordance with the prediction for an azimuthally isotropic surface. In the p–p geometry the SHG signal was very low, while the s–p case was found to provide a reasonable signal to noise ratio. These results are reported in Fig. 5, where the square root of the SHG signal, which is proportional to the number of quinolinium molecules adsorbed on the substrate, is plotted versus bulk concentration.

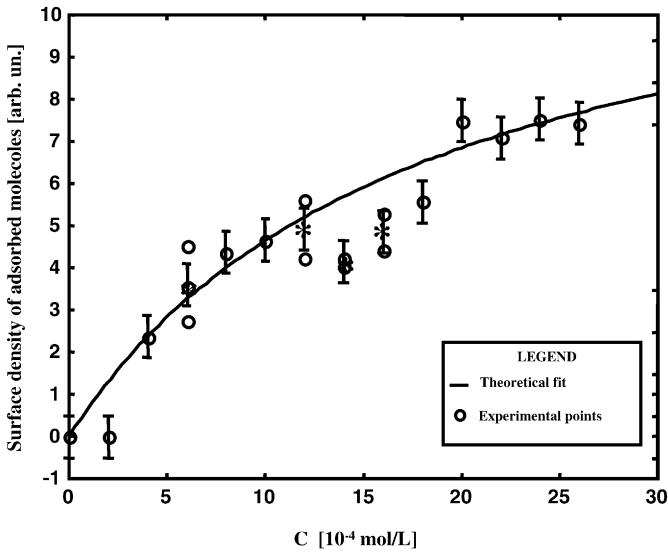


Fig. 5. Surface density of molecules adsorbed at the interface (open circles) vs. the quinolinium concentration. Data refer to a s-p polarizations combination. For some concentrations, the measurements have been repeated. In these cases an asterisk indicates the arithmetic mean of the measured values. The solid line is the result of the fit using the Langmuir relation given by Eq. (5). The obtained fitting parameters are:  $a = 18 \times 10^{-4}$  mol/l and  $n_{\infty} = 13$  in arbitrary units.

The solid line is the result of a best-fit to our data, using an isotherm of the Langmuir type [10,11], having the following expression:

$$n_{\text{ads}}(C) = \frac{n_{\infty} C}{C + a}, \tag{5}$$

where  $n_{\text{ads}}$  is the number of molecules adsorbed at the interface,  $C$  is the quinolinium concentration in solution,  $n_{\infty}$  is the number of adsorbed molecules in the limit of infinitely high concentration and  $a$  is a constant related to the value of the concentration for which  $n_{\text{ads}} = n_{\infty}/2$ . The values of the fit parameters for the curve shown in Fig. 5 are  $a = 18 \times 10^{-4}$  mol/l and  $n_{\infty} = 13$  in arbitrary units. For some concentrations, the measurement was repeated more than one time. This gives an estimate of the errors in our measurement which are larger than the statistical errors given by the Poissonian distribution of the counts. The agreement of our data with the prediction of Eq. (5) is qualitatively good. Work is currently in progress to reduce the measurement fluctuations and the sources of noise, so that the analysis can become more quantitative.

### 5. Conclusions and perspectives

In this paper we have described the SHG apparatus for probing interfacial properties which has been set up in the laboratories of Dipartimento di Scienze

Fisiche of the Università “Federico II” di Napoli. We have also reported the preliminary results of its application to the study of the adsorption of ionic surfactants at solid–liquid interfaces. It has been shown that this technique is certainly suitable for investigating such kinds of interfacial phenomena. To our knowledge, this together with other results reported in Ref. [12] are the first applications of this technique in Italy. They open the way to new perspectives for the community of Italian chemists regarding the possibility of using methods that are suitable for “in situ” and time-resolved analysis of the adsorption process. In this respect an interesting possibility is to study the de-adsorption process. This consists in putting the substrate, after that the absorption is occurred, in touch with ultrapure water and in measuring the temporal decay of the SHG signal. Evidently, SHG gives a unique possibility to carry out such kinds of investigations.

Currently, we plan to apply this technique to recently synthesized surfactants that are more effective than the traditional ones in reducing the surface tension. They are called “twins” since are constituted of two traditional amphiphilic molecules joined together by a hydrophobic chain. We hope that the SHG technique can give access to information that can contribute to understanding the interfacial interactions occurring at the interface and, therefore, the basic reasons for the improved performances of these materials.

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