

**LINEAR AND NONLINEAR  
OPTICS AT  
LIQUID INTERFACES**



**DR PIERRE-FRANÇOIS BREVET**

It is a great honour for me to present the research activities that I have performed during the last years at the Laboratoire d'Electrochimie on linear and nonlinear optical studies of liquid interfaces. On this occasion, I would like to express my deepest thanks to the Latsis Foundation for the honour of being awarded the Prix Latsis Universitaire of the Ecole Polytechnique Fédérale de Lausanne for the year 1997.

## **I. Introduction**

Liquid interfaces, and in particular interfaces between two immiscible liquids, are of great interest in many fields of research, from hydrometallurgy and the science of metal recovery to pharmacology and the design of efficient drugs. Indeed transfer processes, like the transfer of heavy metal ions across membranes in metal recovery or the transfer of ionic drugs across cell membranes in pharmacology, are heavily dependent on the structure and the dynamics of the membrane itself. The latter may indeed act as a blocking barrier thus preventing any transfer or, on the contrary, may selectively favor the transfer of some species. Over the last years, it has been recognized that a true understanding of these transfer processes requires a description of the interface at the molecular level, a refinement that older descriptions based on continuum models were unable to unravel.

At the Laboratoire d'Electrochimie at the Ecole Polytechnique Fédérale de Lausanne, we have developed linear and nonlinear optical techniques to study liquid/liquid interfaces. In particular, the nonlinear optical technique of surface second harmonic generation (SSHG) has been extensively applied to determine the structure and the dynamics of these interfaces. The remainder of this presentation will describe the SSHG technique and some of the most important results obtained. Before concluding, the implications of these results will be discussed for two applied projects in order to

emphasize the close relationships existing between the fundamental and the applied aspects of the research themes studied in the Laboratoire d'Electrochimie.

## **II. Surface Second Harmonic Generation**

When light propagates in media which do not possess the property of inversion, or centrosymmetry, the wavelength may be converted into its harmonics. This process is governed by the laws of nonlinear optics and may be very efficient, with efficiencies up to 40% if the proper media, only 21 classes of crystals out of the 32 are active, and strict conservation rules are followed<sup>1</sup>. The physical properties of this reduced set of classes of nonlinear crystals are widely used in laser physics to manufacture lasers delivering several wavelengths, all harmonics of a fundamental one. On the contrary, in media possessing a center of inversion, like gases or liquids, this conversion phenomenon is forbidden for parity reasons and no light is generated at the harmonic wavelength. This property in liquids is very attractive since the generation process may only occur at interfaces where there is a loss of the inversion property. Hence, any monochromatic light beam impinging at the interface between two liquids may only be converted to its harmonic wavelength at the interface, and the physical properties of the outgoing harmonic light will be defined by the physical properties of the interface where the conversion happened. In particular, no contribution from the bulk of the liquid phase will blend with the interface contribution yielding an extreme surface sensitivity of about a molecular monolayer. As a consequence, the technique allows the study of the structure and the dynamics of the interface without the bulk phase contributions which usually dwarf any interfacial phenomenon in other techniques. The major drawback of the technique lies in the weakness of the signals detected. Nowadays, however, highly sensitive detectors are available to compensate for such low light levels.

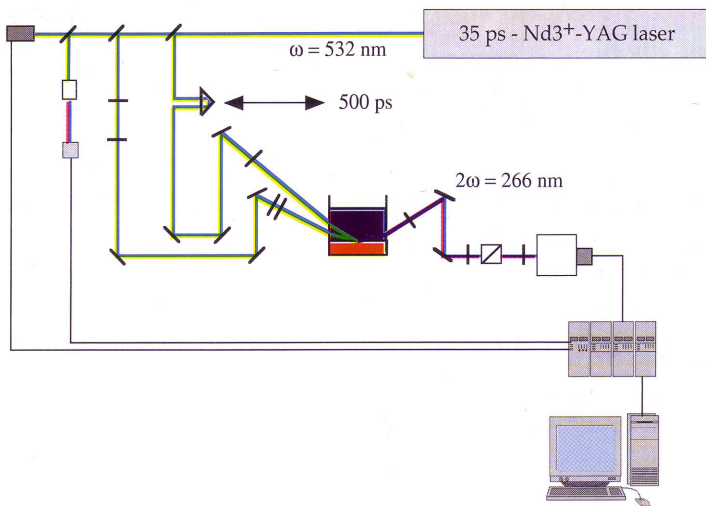


Fig. 1 Experimental Set-Up of the experiment as described in text.

The SSHG signal generated at the interface may be detected either in reflection or transmission but the former geometry is by far the most widely used<sup>2,3</sup>. In a classical experimental set-up, the incoming light at the fundamental wavelength delivered by the pump laser is passed through a half-wave plate to rotate the incoming polarization of the light beam, that is the direction along which the electric field vector of the electromagnetic wave is directed. The output SH signal coming from the sample is passed through a polariser, to select the outgoing polarization, and a set of filters to remove the fundamental light. Detection is finally performed with a photomultiplier tube placed after a monochromator, see Figure 1. The experiments thus consist of monitoring the SH signal as a function of the input and output polarization, as well as the interface modifications. From these measurements, it is possible to retrieve the so-called nonlinear optical susceptibility tensor of the interface which embeds all the microscopic information of the interface<sup>4,5</sup>.

Once the susceptibility tensor of the interface is retrieved through its three different non vanishing elements, the molecular picture of

the interface may be devised. Indeed, each tensor element is the product of four parameters that we shall now enumerate:

- *The number of molecules per unit surface.*

The intensity of the SH signal is indeed proportional to the number of molecules present at the interface and radiating coherently. These molecules are usually surface active and therefore are present in an excess surface concentration. These molecules may be molecular probes of the environment to study the solvent structure at the interface or molecules actively participating in processes under study, like interfacial chemical reactions, for example.

- *The orientation of the molecules.*

The surface activity of the interfacial molecules depends on the affinity of their different sub-groups for the two liquids in contact at the interface. Most surfactants indeed possess an hydrophilic head and an hydrophobic tail enabling a stabilization of the moiety at the interface with the head pointing into the aqueous phase and the tail into the organic phase. However, depending on the presence and the position of other groups on the molecular skeleton, the molecule may be tilted from the interface normal at the interface. This property may readily be retrieved from the measurements and has a great incidence on the surface activity of the compounds.

- *The local fields*

This parameter is often neglected in the studies or more precisely, re-integrated into the molecular hyperpolarizability, see below. Local fields arise from the reaction of any medium to the new electronic configuration of the excited species upon illumination by the incoming electromagnetic field. Hence, depending on the environment of the interfacial molecules, the electromagnetic electric field is screened and the nonlinear activity of the sample is reduced.

- *The molecular hyperpolarizability.*

As expected, the SH signal is also proportional to the SH response of a single molecule. This parameter is very sensitive to the environment of the moiety since it embeds the resonances. At certain wavelengths, the electron of the interfacial molecules are driven at their natural frequencies and large enhancements of the SH response are expected at these wavelengths. The interest in resonances, apart from the enhancements of the signal, lies in the fact that the resonance wavelengths are sensitive to the interactions between the moiety and the solvent.

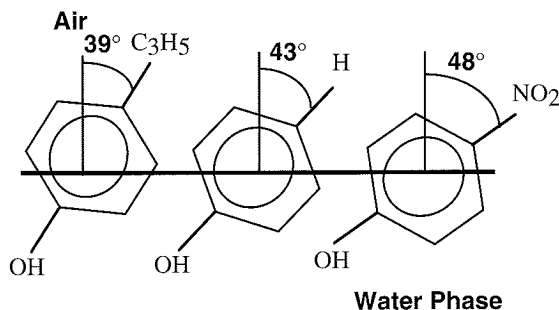
### **III. Structure and Dynamics at Liquid Interfaces.**

The richness of the information one can retrieve from the measurements has allowed one to get a more accurate picture of the liquid/liquid interfaces at a molecular resolution. It has hence been possible to investigate the structure of a monolayer of surface active molecules and to study the dynamics of relaxation of the interface.

In describing the structure of the interface between two liquids, two main aspects may be found: morphology and equilibrium.

On the first hand, describing an interface as built from two solvent phases in contact with a monolayer of surface active molecules, one is compelled to introduce the idea of organization. This idea has been illustrated with a study of monolayers of phenol derivatives. The three compounds used in this study were nitrophenol, phenol and propylphenol. The three compounds differ by their substituents placed in para position, opposite to the hydroxyl -OH group. The hydrophilic character of the substituent group was carefully chosen: the nitro -NO<sub>2</sub> group in nitrophenol is hydrophilic whereas the propyl -C<sub>3</sub>H<sub>5</sub> group of propylphenol is hydrophobic. Phenol presents only a hydrogen atom in the para position and therefore represents an intermediate between nitrophenol and propylphenol. By a care-

ful study of the orientation of the main axis of these compounds with the surface normal, it has been shown that the more hydrophilic the substituent group, the more tilted towards the interface lied the molecules at the air/water interface, see Figure 2. Hence, nitrophenol has an angle of  $48^\circ$  as compared to  $43^\circ$  for the intermediate phenol and  $39^\circ$  for the hydrophobic propylphenol. At the hexane/water interface, an identical angle was measured for all three species indicating that the interaction between the substituent group and the aqueous phase was now screened by the hexane solvent. Further studies on the position of the resonance for nitrophenol at the air/water interface showed that the position of nitrophenol was markedly displaced towards the aqueous phase. The conclusion one may draw from these experiments is therefore that the angle of orientation of the species, as well as their position along the vertical axis perpendicular to the plane of the interface, is determined by the balance between all the hydrophilic-hydrophobic forces acting on the compound<sup>6</sup>. Also, these results show that the interfacial polarity of the solvent is different from the bulk phase polarity, a difference directly connected with the change in structure<sup>7</sup>.



*Fig. 2 Angle of orientation of phenol derivatives at the air/water interface as determined by surface second harmonic generation*

On the second hand, the interface may be described in terms of chemical equilibria and their possible shift towards the reactants or the products. In the case of the acid/base equilibria of the dye molecule Eosin B, it has been shown that the aqueous interfacial region

at the air/water interface was favoring the less charged species. Indeed, the first equilibrium between neutral Eosin B and negatively singly charged Eosin B was displaced towards the neutral form, and the second equilibrium between the negatively singly charged and doubly charged Eosin B was even more displaced towards the singly charged species. These studies shows that the interfacial region of the aqueous phase is less polar than the bulk aqueous phase, thus reducing the stability of charged compounds. This picture is consistent with the solvent structure of water near the interface where it is expected that water molecules tend to form stronger hydrogen bonding networks thus excluding solutes from stabilizing interactions with the solvent<sup>8</sup>. These studies are of great importance in biology, for example, since the transferring species may be determined by the bulk phase pH. Here we show that the interfacial pH may be severely shifted away from the bulk pH, and that therefore this shift should severely affect the properties of the transfer.

Finally, it is possible to study the time evolution of interfacial processes on a time scale only determined by the pulse duration of the pump laser. With a picosecond ( $35 \times 10^{-12}$  s pulse duration) pump laser, we have thus been able to investigate the rotational diffusion time of Eosin B at the air/water interface and show that this time was three times faster than in the bulk of the phase. This has been interpreted in terms of the reduced interaction with the solvent at the interface enabling a faster rotation time owing to a reduced molecular friction. This observation has been shown to be markedly different from what is observed for other compounds where interactions with the solvent lead to an enhanced molecular friction at the interface<sup>9,10</sup>. Hence the mobility of solutes at the interface is not only determined by the structure of the solvent but also by the intermolecular forces between the solute and the solvent.



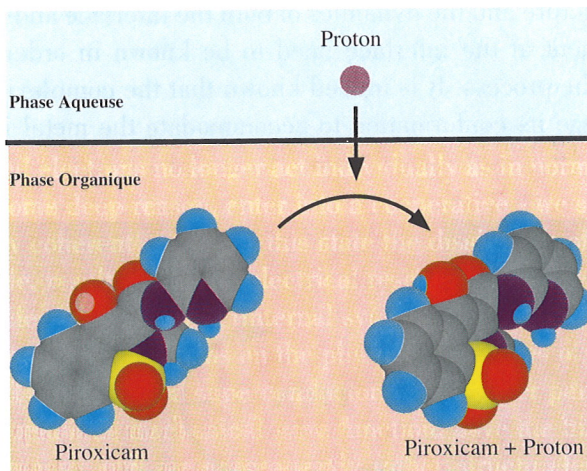
## IV. Applications to Transfer Processes Across Liquid/Liquid Interfaces.

In order to illustrate the use of the wealth of information obtained from the fundamental studies as described above, two examples are now discussed.

### A. Pharmacology

The case of the drug known as piroxicam is an interesting study of the proton transfer. Piroxicam is an anti-inflammatory therapeutic drug, the action of which is to reduce the acidity of the extra cellular medium. It is indeed assumed that an increase of the proton concentration, and therefore an increase of the acidity, is responsible for the inflammation. The action of the drug is thus to facilitate the transfer of protons away from the inflammatory region through a transfer across the membrane, see Figure 3, to reduce the acidity and subsequently the inflammation.

In such a study, it is clear that a careful design of the ionic drug itself determines its efficiency as well as its secondary effects. Proper design will include the optimization of the proton docking site and good encapsulation to prevent undesirable secondary effects. However, a clear knowledge of the transfer mechanism, and subsequently of the structure and dynamics of the membrane across which the transfer occurs, will lower the work required to tailor the drug in order to achieve the proposed goals<sup>11</sup>. In particular, as seen above, the conformational change of the drug molecule in order to facilitate the proton transfer depends on both the structure of the interface and the intermolecular forces of the drug molecule with the solvent.

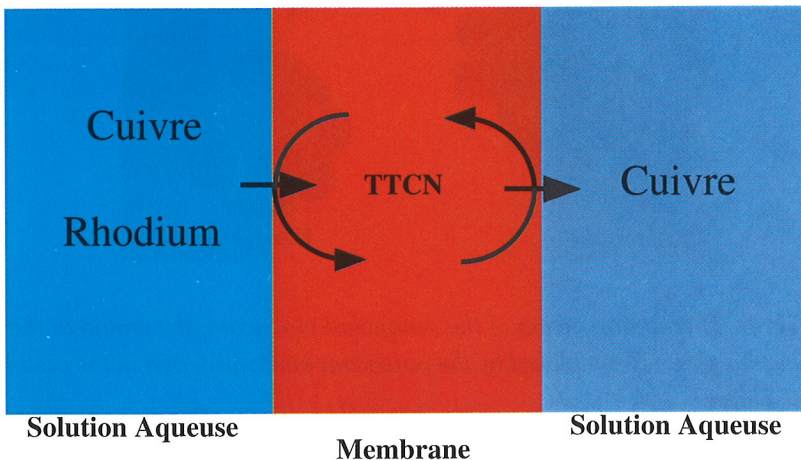


*Fig. 3 Therapeutic action of the compound piroxicam: the proton in the aqueous phase is complexed by the piroxicam and transferred in the organic phase.*

## B. Hydrometallurgy

Another field of application of assisted transfers is the cleaning of aqueous effluents, for example a solution of a precious metal like rhodium, polluted with a less precious metal in weak proportion, in the case presented here copper at a concentration of 5% of the rhodium concentration. In industrial processes, effluents are usually improper to further industrial cycles owing to the presence of undesirable compounds in excess of the levels allowed. One way to get rid of these pollutants is to devise an extraction process through a membrane. This membrane may be a liquid membrane or a gel. With the proper use of a facilitating agent in the organic phase, the undesirable compound may be removed from one compartment and re-concentrated in the other. In this example, copper can be removed from the rhodium solution with the use of the complexing agent 1,4,7-trithiacyclononane (TTCN) in the organic membrane, see Figure 4.

The structure and the dynamics of both the interface and the complexing agent at the interface need to be known in order to fully optimize the process. It is indeed known that the complexing agent must change its conformation to accommodate the metal ion complexation. <sup>12</sup>



*Fig. 4 Copper extraction from a mixed solution of rhodium and 5% copper through a membrane assisted by the ligand TTCN.*

## **V. Conclusions**

In this presentation, it is shown that fundamental and applied science projects are closely connected. The two examples described here in pharmacology and hydrometallurgy have strongly benefited from the knowledge acquired in fundamental spectroscopic studies aiming at the understanding of liquid/liquid interfaces. The organization of monolayers, the intermolecular forces or the dynamics of motions at the interface have all been unraveled by spectroscopic techniques, like surface second harmonic generation, and the physical picture that has emerged from these studies has enabled us to understand the different steps as well as the driving forces of charge transfers across liquid/liquid interfaces.

Through these examples, it is thus shown that state-of-the-art techniques are nowadays required to achieve molecular description levels and detailed understanding of processes, with a direct benefit to the support of on-going research and development efforts in industry.

## **VI. Acknowledgments**

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