Vibrational Sum-Frequency Generation Spectroscopy of Self-Assembled and Langmuir-Blodgett films on surfaces: from monolayers to model lipid membranes

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Investigating the structure and the physico-chemical properties of biomimetic lipid membranes on surfaces is a pre-requisite for a detailed investigation of biological processes occurring within such bio-films, and their selective detection. This also represents a platform to build-up reliable bio-devices mimicking the membrane behaviour. Indeed, the structure and the physico-chemical properties of thin films on surfaces are intrinsically linked. Knowing the organization of organic layers on surfaces is therefore a key element to understand, to control and to tailor their physical, chemical, or biological properties. This requires highly surface/interface sensitive techniques which are able to discriminate interfacial responses from those of the surrounding bulk phases.

The analysis of the physico-chemical properties of bio-interfaces can be achieved by probing their vibrational response. Among the vibrational spectroscopies, sum-frequency generation (SFG) has emerged in the characterization of thin organic layers adsorbed on surfaces [1,2,3]. Indeed, being based on a second order nonlinear optical process, SFG spectroscopy is intrinsically specific to surfaces and interfaces [1,2,3], and therefore it represents an ideal tool to probe organic layers confined at solid surfaces.

In this work, the vibrational signature of (bio)-organic films mimicking the membrane structure has been in order to retrieve information about their structural organization and their molecular orientation. In particular, self-assembled monolayers (SAMs) of thiols (Figure 1a), and solid-supported lipid layers, either in the form of monolayers (Figure 1b), or in that of hybrid bilayers (Figure 1c), have been investigated by SFG spectroscopy (Figure 1, top).

Firstly, we have focused on the analysis of self-assembled monolayers (SAMs) of alkane and of aromatic thiols [4,5], which are models for the interpretation of the vibrational nonlinear optical response of more complex architectures mimicking the lipid membranes. Secondly, we have probed the organization of solid-supported lipid films, prepared either by vesicle fusion or by Langmuir-Blodgett and Langmuir-Schaeffer methods on bare or pre-functionalized substrates. Different lipid molecules have been used to build the model membranes, such as the well-known phosphatidylcholine lipid (PC) or the less-known antigenic 2,4-dinitrophenyl lipid (DNP) [6]. Information about the lipid films order and organization has been obtained, and has indicated that the intimate film organization, which is probed through the analysis of the SFG signature of the lipid hydrophobic chains, strongly depends on the molecular composition and on the surface properties. The SFG responses have been interpreted with the support of DFT calculations, and of experimental measurements of the solid-state IR and Raman activities. This has enabled to predict the SFG active modes of the (bio)-organic films, and therefore to attribute, with high accuracy, the detected signals to vibrational motions.

This analysis is performed in the framework of investigating the structural changes and the physical-chemical interactions induced by recognition processes, which take place within such interfacial layers.

In particular, the high interface/surface sensitivity of SFG spectroscopy may open the way to novel solutions for the detection of biological processes occurring within surface-confined (bio)-organic films.

References

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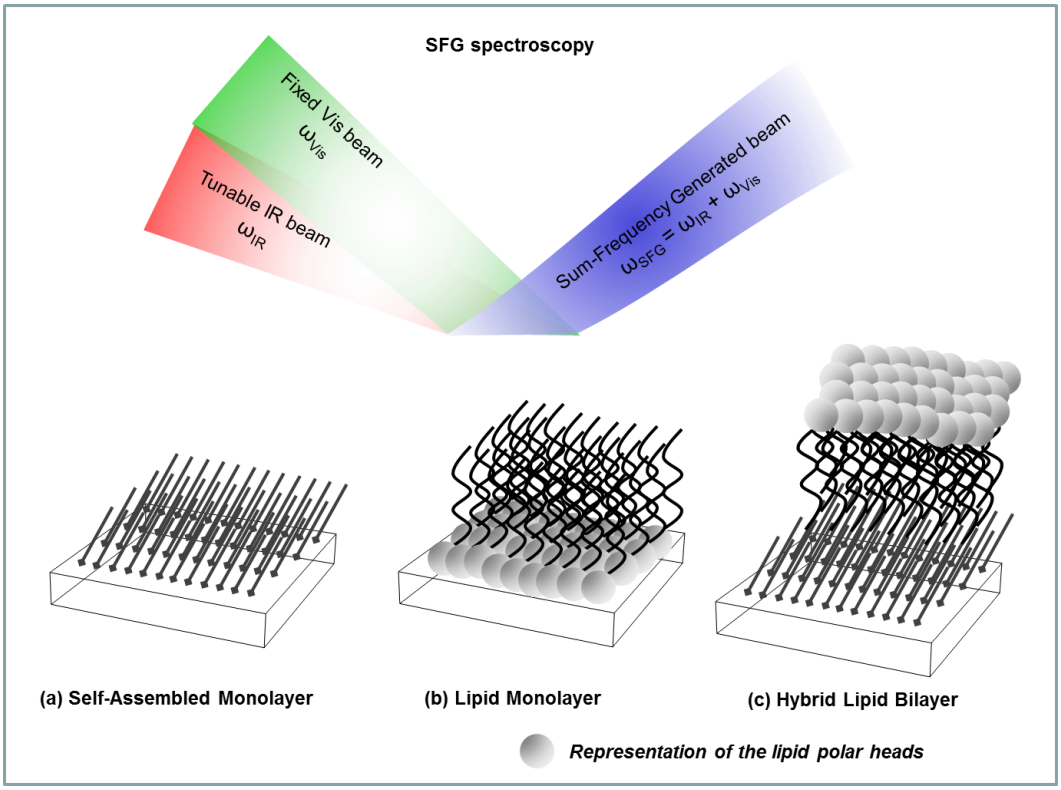

Figure 1. Schematic representation of the SFG spectroscopy (top), and modeling of the (bio)-organic films which are investigated, namely Self-Assembled Monolayers (a), Lipid Monolayers (b), and Hybrid Lipid Bilayers (c).