RETRIEVING THE STRUCTURAL CHARACTERISTICS OF ORGANIC MONOLAYERS BY VIBRATIONAL SUM FREQUENCY GENERATION (SFG) SPECTROSCOPY.

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The structure and the physico-chemical properties of thin films on surfaces are intrinsically linked; therefore, knowing the molecular orientation at surfaces is a key element to understand, to control and to tailor the physical, chemical, or biological properties of such interfacial layers. This requires highly surface/interface sensitive techniques which are able to discriminate interfacial responses from those of the surrounding bulk phases.

In this work, sum frequency generation spectroscopy (SFG), which is intrinsically specific to surfaces and interfaces [1], has been used to investigate the structural organization and the molecular orientation of (bio)-organic monolayers. The SFG response has been interpreted with the support of infrared spectroscopy measurements, and of theoretical modelling based on DFT calculations of the dipole moment and of the Raman tensor derivatives of the vibrational modes, which are involved in the SFG process.

In particular, we have focussed on the investigation of self-assembled monolayers (SAMs) of alkane and of aromatic thiols, which have represented models for the interpretation of the nonlinear vibrational response of more complex architectures based on bioactive lipid films. Indeed, self-assembled monolayers of dodecanethiol (DDT) and of *p*-nitrothiophenol (*p*-NTP) have been investigated regarding their molecular orientation on metal substrates, through polarisation-dependent measurements. Combining the analysis of *ppp* and *ssp* SFG spectra (representing the polarisation of the SFG, vis and IR beams) with theoretical simulations has straightforwardly provided the tilt angle ϑ of the methyl group of DDT (or of the 1,4-axis of *p*-NTP) molecules and the rotation angle ξ of the methyl group of DDT [2]. Then, 2,4-dinitrophenyl lipid films have been investigated regarding their organization and their physical-chemical interactions, and DFT calculations have enabled to attribute the SFG signals measured in the backbone region to vibrational motions localized on the biologically active polar head of the lipid molecules [3]. This result represents the platform to investigate the biological recognition occurring between the surface-confined active lipid film and its complementary antibody.

[1] Shen Y.R., *Nature* **1989**, *337*, 519.

[2] Cecchet F., Lis D., Guthmuller J., Champagne B., Caudano Y., Silien C., Mani A.A., Thiry P.A., Peremans A. *ChemPhysChem* **2010**, *11*, 607.

[3] Lis D., Guthmuller J., Champagne B., Humbert C., Busson B., Tadjeddine A., Peremans A., Cecchet F. *Chem. Phys. Lett.* **2010**, *489*, 12-15.