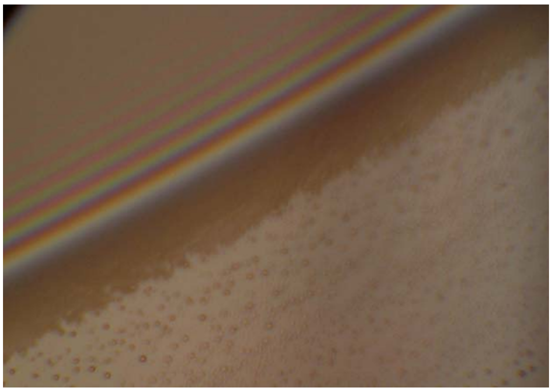
Publishable summary

The aim of this project was to obtain molecular information on the structure of thin liquid films confined between a gas and solid interface, as an effort to relate macroscopic measurable parameters, such us disjoining pressures, to structural properties at the molecular level (Figure 1). The approach consisted in combining an apparatus capable of accurately measuring interfacial forces in wetting films (air/liquid/solid) with state of the art surface specific vibrational spectroscopic techniques.



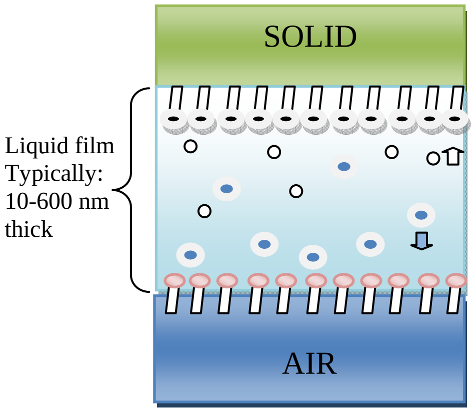


Figure 1. Left: Photograph showing an example of a thin wetting film (evaporating water film on glass). Right: Schematic of the molecular perspective of a thin wetting film.

Wetting films play a crucial role in the understanding of many practical applications, including mineral flotation, surface cleaning processes, and the coagulation of colloidal dispersions. The stability of these films depends on the molecular interactions between the two interfaces which macroscopically manifest themselves as surface forces. The measurement of these forces, in particular using the thin film pressure balance (TFPB) apparatus, has provided valuable insight in the identification of the different types of interactions, which could be of electrostatic, dispersive, steric and/or structural nature, just to mention a few. Nonetheless, the link between the measured forces and the molecular origin of these interactions remains elusive, as force measurements provide no direct chemical, structural or conformation information, which are expected to change significantly in confined geometries. In this sense vibrational spectroscopic techniques, in particular those sensitive to molecules at interfaces can provide an important part of the puzzle: chemical and orientation molecular information.

Recent advances in vibrational spectroscopic techniques allow collection of unprecedented information from molecules at interfaces. In this category Vibrational Sum Frequency Spectroscopy (VSFS) has emerged as an invaluable tool. The intrinsic surface specificity of VSFS distinguishes molecules at the interface from a vast excess of the same molecules present in the bulk, even at a submonolayer coverage. Moreover, current developments in conventional Raman scattering, in particular when using a Total Internal Reflection (TIR) geometry, have demonstrated that submonolayer sensitivity is achievable and that it can also be used to determine the conformation of surface molecules. Diagrams of the spectrometers measuring principles are shown in Figure 2.

The main objective of this project was to combine the two spectroscopic techniques mentioned above (TIR Raman and VSFS) with a thin film pressure balance apparatus to obtain a molecular insight into the order and structure of thin wetting films. The coupling of these advanced techniques had never been successfully attempted before. The project plan was subdivided in three sections:

a) Design, construction and setting up of the instrumental apparatus and measuring cell.
This included setting up the spectrometers (TIR Raman and VSFS) which were only at the design stage at the start of the project, as well, as designing and constructing the measuring cell for force measurements (TFPB), including software development.

b) Validation Phase of the experimental setups.
Systematic evaluation of the individual performances of the newly developed force measuring device (TFBP) and spectrometers. Carrying out the first proof of principle experiments combining the different experimental techniques.

c) Experimental Phase.
Studying the molecular conformational changes along the thinning process of a selected number of systems, with emphasis on phospholipid bilayers and the water structure under confinement.

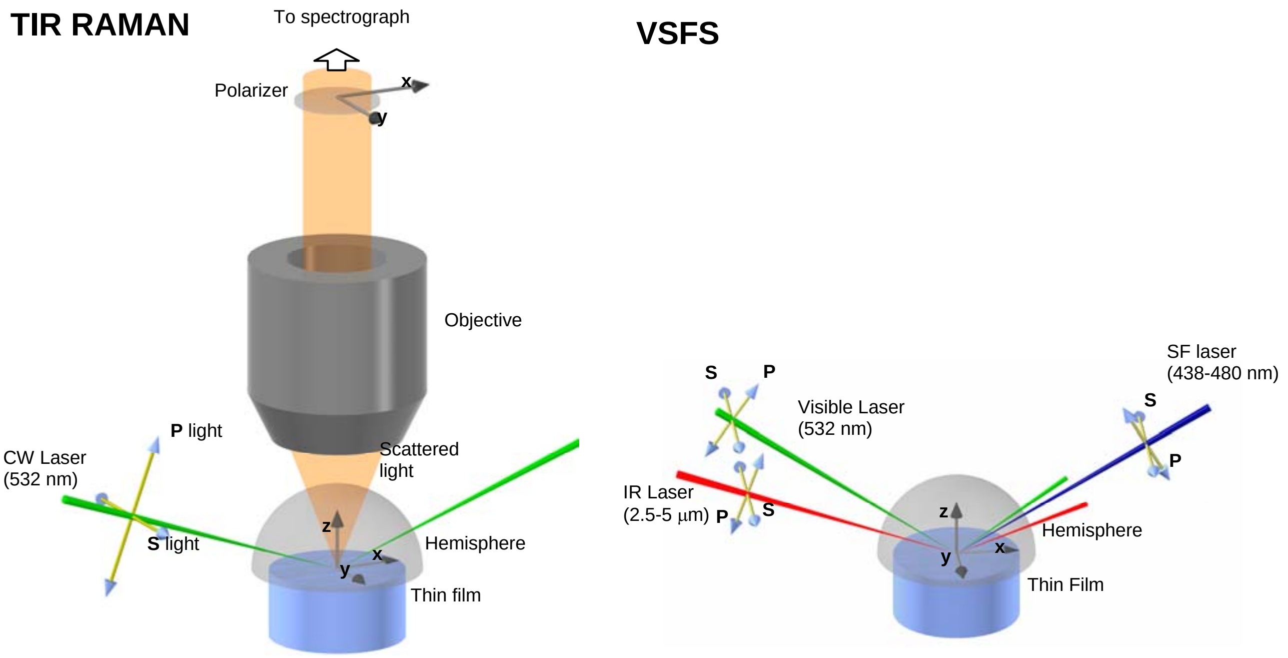


Figure 2. Diagrams of the TIR Raman and VSFS setups. TIR Raman makes use of evanescent waves to detect molecules at interfaces. VSFS is intrinsically surface specific and usually probes closer to the interface. In TIR Raman a laser is sent to the interface at an angle above the critical angle and the scattered light is detected with the help of microscope objective. This same objective is used for measuring the film thickness in the TFPB. In VSFS two laser are directed to the interface and a third one is generated at the surface, carrying the surface information.

Work performed

During the length of the project the main objectives were reached. The VSFS and TIR Raman spectrometers were constructed and validated. Although this EU Reintegration Grant only financially supported a very small fraction of the costs of building these spectrometers, their successful implementation was a key element for the subsequent development of the project. Moreover, the thin film pressure balance adapted for spectroscopy measurements, which in turn was largely financed by this EU grant, was successfully built and implemented. Coupling these techniques was technically challenging and required a number of different skills, which ranged from advanced optics and spectroscopy knowledge, to technical drawing and computer programming. The first development stage consumed more than 2 years of the total project time.

During the last months of the project a successful proof of principle experiment was carried out, where vibrational spectroscopy data was collected during the thinning process of the surfactant aqueous film (i.e. sodium dodecyl sulphate solutions). These positive results are currently being extended and a seminal manuscript which is expected to have a very high scientific impact will be submitted in the coming months. Finally, the experiments proposed in the last stage of the project (Experimental Phase) where only partly completed and expected to be continued after the first paper in this area is published.

It was early recognized that the output in terms of scientific papers for this rather risky project would be slow. As a consequence, an effort was made to exploit the advantages of the methodology and instrumentation developed along the Thin Wetting Films project. In this sense a total of 4 peer reviewed scientific papers (+2 recently submitted) were published, where at least part of the knowledge and instrumentation specifically developed for Thin Wetting films was used. Here it is worth mentioning the fabrication of photonic crystal in fused silica, using butterfly wingscales as bio-templates (see Figure 3). This work specifically benefited from the white light interferometry instrumentation developed to determine the thickness of thin wetting film.

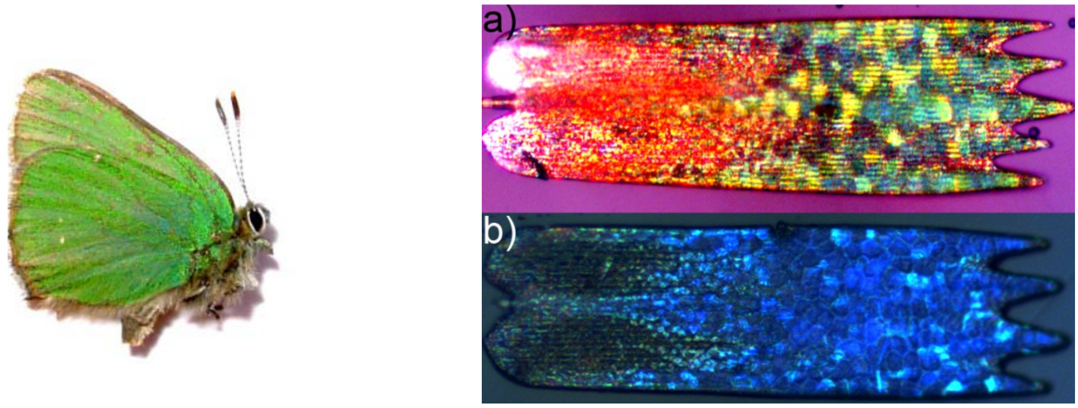


Figure 3. The scales of the *Callophrys rubi* butterfly wings were used as biotemplate to replicate their gryoid photonic crystal properties in fused silica. Left image: The *C. rubi* butterfly with its green coloured wings. Right image: Light microscope of a single butterfly wingscale (a) and its replica in fused silica (b). The change in colour upon replication is mainly due to differences in the refractive index between silica and chitin (main organic constituent of butterfly wingscales).

Potential Impact

It is expected that once published, the outcome of this study will make a significant contribution, not only in the surface chemistry community, but also in the natural science community in general, as for example the studies on confined water films may help resolving the long-standing debate about the origin of long-ranged hydrophobic attractive forces. These hydrophobic interactions are of central importance in protein folding pathways, enzymatic reactions that take place in locked hydrophobic pockets, as well and many other areas of science and technology. Moreover, the project constituted an important step in the researcher’s long term strategy of implementing the use of surface specific vibrational spectroscopic techniques to study surface layers under confinement by one and two interfaces. The work was essentially carried out to a very large extent, exclusively by the researcher (Eric Tyrode). Close collaboration at the European level with leading research groups in the area´(Prof. Colin Bain, Durham University in the UK, and Prof. Regine von Klitzing at the Technische Universität Berlin, in Germany) helped making this project a reality.