Vibrational spectroscopy of molecules on surfaces

Sergio Mauri

Surface Science Research Centre, Department of Chemistry, University of Liverpool

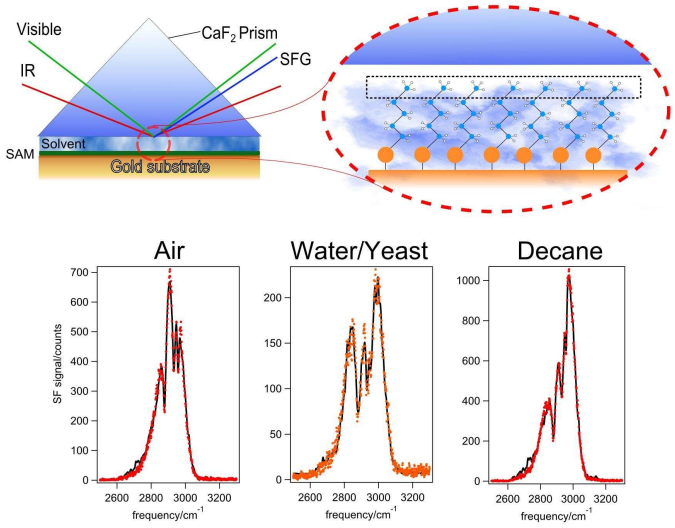

Fig. 1 TOP: schematic of SFS experiment for probing solid/liquid interfaces. BOTTOM: Spectra of Octadecanethiol self-assembled monolayers on Au(111) under different environments. The relative intensity between the methyl vibrations can tell the orientation of the functional group.caption

Self-assembled monolayers (SAMs) are often used as intermediates for adsorbing bigger molecules like proteins, DNA and cells on surfaces and their structure might trigger conformational changes in biomolecules. Characterization of the relevant functional groups in such monolayers is very important in order to understand the interaction between the molecule of interest and the surface. A reliable vibrational method to determine protein secondary structure at interfaces is therefore needed. Common vibrational spectroscopies like Raman and Infrared are not suitable, either because of their low sensitivity or because they detect molecules in the bulk as well as on the surface (even in total internal reflection, the probe depth is of the order of microns!). Sum frequency spectroscopy (SFS) is a surface sensitive nonlinear vibrational technique which can be successfully adopted to solve these problems. SFS works by mixing a femtosecond IR laser beam and a picosecond visible laser beam that are spatially and temporally overlapped on the sample of interest, coherently generating a sum frequency photons. The nonlinear optical selection rules mean that a signal is only generated from molecules at an interface where "up" is different to "down". Suitable interfaces are solid/air, solid/liquid, liquid/liquid and air/liquid. SFS has monolayer sensitivity and can determine the orientation of functional groups and protein different secondary structure pattern like alpha helices and beta sheets [X. Chen et al. 2004, Langmuir 2005, 21,2662-2664] by using different polarisation combinations of the incoming and outgoing beams. SFS can therefore detect conformational changes in the SAM and changes in the adsorbing protein. Here we present a study of hydrophobic SAMs on Au and Si. Orientational information of Trimethoxypropylsilane SAMs on silicon, and Octadecanethiol on gold are obtained under different environments (solvents, yeast cells and air).