Breathing chemistry investigated at NAPP

In October 2013, a friendly users group, formed by Celia Rogero, Jorge Lobo-Checa and Mikel Abadía from the Centro de Física de Materiales (CSIC-UPV/EHU) and Donostia International Physics Center, performed at the Near Ambient Pressure Photoemission branch an experiment of attraction/liberation of dioxygen by phthalocyanine molecules. The main aim was to understand the reactivity of biological molecules in contact with metal surfaces. The experiment was fully performed inside the NAPP UHV chambers (sample cleanness, molecular deposition and surface analysis at different pressures).

The adsorption and self-assembly of biological species on solid surfaces can provide important information to understand basic biological reactions, such as one of the most important reaction in living organisms: breathing. This process consists on the transport and storage of the dioxygen/carbon dioxide molecules thanks to haemoglobin formed by Fe tetrapyrrole molecules. In order to mimic this process at CIRCE beamline we expose Fe-phthalocyanine molecules, which had been previously evaporated in vacuum on a clean Au(111) surface, to different O_2 partial pressures. By means of a combination of XPS and NEXAFS we detect the anchorage of O_2 when pressure in the chamber was changed from UHV to around $1x10^{-2}$ mbar, being this process reversible. Thus, when the O_2 partial pressure was reduced again O_2 liberation takes place

This reversibility was basically detected by analyzing the O 1s core level photoelectron spectra and the Fe 2p adsorption edge of the system under different pressure conditions inside the chamber. When pressure is around 10^{-2} mbar, a new component appears in the O 1s core level region in the XPS spectrum. This new component is completely separated from the O₂ in the gas phase, disappears when the gas is removed and was not observed for the clean Au(111) under the same pressure conditions. Such behaviour indicates that this feature is related with the O₂ molecules bonded to the Fe ions in the FePc molecules. Moreover, Fe 2p adsorption edge reveals that Fe(II) ions change their conformation during O₂ bonding. The central metal core of the phthalocyanine moves from the initial planar configuration to a more tetrahedral structure when the O₂ is temporary bonded to the surface. This change is again reversible, i.e. the system returns to the flat configuration when the gas is removed. Similar conformational changes have been reported in living organisms for the haemoglobin during the breathing process. Thus, with this system we confirm that it is possible to mimic these biological processes at the nanoscale.



Figure: O1s XPS spectra (left) and Fe 2p adsorption edges (right) of FePc/Au(111) measured at a base pressure of $7x10^{-10}$ mbar (blue spectrum), at 10^{-2} mbar O₂ partial pressure (red spectrum) and after removing the O₂, measured at $1x10^{-9}$ mbar (green spectrum). Schemes illustrate the conformation of the molecules due to the bond between Fe ions and O₂ molecules