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## Molecular and Electronic Structure at Electrochemical Interfaces from In Situ Resonant X-Ray Diffraction

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In electrocatalysis, reactivities are crucially affected by the structure at the electrochemical interface, the few Å thick region at the metal-liquid interface. A precise understanding of the charge and molecular distribution is a mandatory step for the comprehension of the underlying mechanisms. Nevertheless, up to now direct experimental methods probing electronic/molecular structure at the atomistic level in the electrochemical interface were lacking.

We recently proposed an original method [1,2] coupling in situ Surface Resonant X-Ray Diffraction (SRXRD) to DFT calculations. Following the Helmholtz description, we modelled the interface as a double layer, where an ionic plane in the liquid phase faces the oppositely charged metal surface.

After a preliminary attempt [3], allowing only a semi-quantitative description of the charge distribution at the interface, we have now introduced a realistic physical model [1] which gives access quantitatively to the molecular and electronic structure both in the crystal surface layers and in the close solution. The ionic layer is here described by chemically defined ions/molecules set in front of the metal. Their occupation rate, charge, position and Debye Waller factor are the parameters we have to solve by comparison with SRXRD spectra, thanks to a confidence factor. Because our system is neutral and our simulations are self-consistent, we also obtain the atomic charge distribution in the crystal surface layers.

We successfully applied our method to the archetypal Pt(111) system in an acidic medium, focusing on the potential region where no adsorbates are present. In situ SRXRD measurements were made at the D2AM beamline (ESRF, Grenoble). The spectra were recorded at several reciprocal space positions and with different orientations of the polarization to probe the chemical bonds in and out of the surface plane.

Contrarily to the typical assumption of zero free charge on the Pt metal surface at this potential, our experimental data clearly reveal the presence of partially ordered water molecules and hydronium ions close to the negatively charged metal surface, signature of a significant interaction between the metal and water.

We believe that our original approach will significantly contribute to bridging the knowledge gaps surrounding electrocatalytic mechanisms comprehension and will be instrumental in enhancing theoretical predictions, which have lacked data from physical characterization techniques.

1. Y. Soldo-Olivier, Y. Joly, M. De Santis, Y. Gründer, N. Blanc and E. Sibert, JACS 147(6), 5106 (2025)
2. Y. Gründer; C. Lucas, P. Thompson, Y. Joly and Y. Soldo-Olivier, J. Phys. Chem C 126, 4612 (2022)
3. Y. Soldo-Olivier, E. Sibert, M. De Santis, Y. Joly and Y. Gründer, ACS Catalysis 12, 2375 (2022)

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