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► **To cite this version:**

Y Gründer, Yves Joly, Yvonne Soldo-Olivier. New tool for simulation of surface resonant x-ray diffraction. 2019. hal-02347160

HAL Id: hal-02347160

<https://hal.science/hal-02347160>

Preprint submitted on 8 Nov 2019

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New tool for simulation of surface resonant x-ray diffraction

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In-situ studies of the chemical bonding at an electrochemical interface are rather difficult due to the presence of the electrolyte and also because standard characterisation techniques which are mostly UHV based cannot be applied.

Surface x-ray diffraction (SXRD) is widely used to solve the atomic structure at the surface of single-crystals. One of its advantages is that it can be performed *in-situ* and even *operando*. On the other hand, x-ray absorption near edge spectroscopy (XANES) as well as resonant x-ray diffraction (RXRD) are highly sensitive to the oxidation states considering the edge energy shift compared to a known reference. Recording spectra across an absorption edge is possible on specific points of the crystal truncation rods (CTR), which are surface sensitive points in reciprocal space. As in 3D anomalous diffraction, spectra exhibit large intensity variations around the edge. The so-called *surface resonant x-ray diffraction* (SRXR) is therefore expected to be sensitive to both the surface structure and the electronic structure around the absorbing elements. The existing fitting tool allows the description of the geometry but no one up to now was able to reproduce the spectra experimentally.

We have successfully employed SRXR to gain site specific information about the charge distribution at a buried interface. Furthermore, the development of a theoretical tool based on an *ab-initio* approach further elucidated the charge transfer and bond formation at a polarised solid-liquid interface [1].

The calculation uses density functional theory to calculate the electronic structure around the resonant atoms. The atomic charges and the bonding with the neighbouring atoms can then be deduced. With this information the modified form factors and thus energy and angular dependent resonant scattering amplitudes around the x-ray absorption edges can be modelled. For SRXR, all contributions from the bulk and from the surface, which includes the substrate topmost atomic layers and the eventual adsorbed layers, are

summed up and finally one obtains the intensity of the diffracted beams. It is the angular dependence of the surface alignment with the incoming x-ray beam, specifically the incoming beam polarisation, which shows that specific chemical bounds are probed.

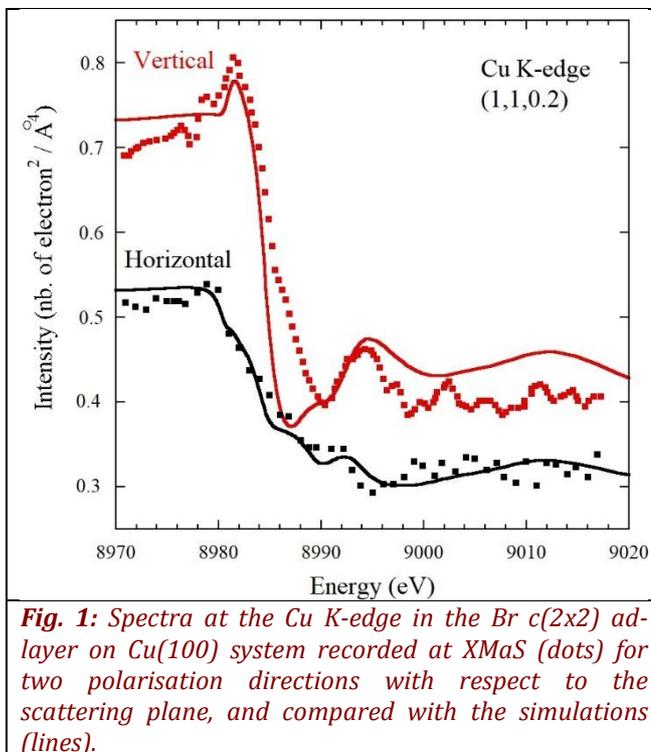


Fig. 1: Spectra at the Cu K-edge in the Br $c(2 \times 2)$ ad-layer on Cu(100) system recorded at XMaS (dots) for two polarisation directions with respect to the scattering plane, and compared with the simulations (lines).

We have demonstrated the validity of our approach studying different systems. As an example, we consider the formation of a bromine ad-layer on copper at an electrochemical interface. We show here the comparison of the simulated spectra with the data recorded at the XMaS beamline, at the Cu K-edge and along two polarisation directions of the incoming light (Fig. 1). The relative shift of these spectra versus references are related to the oxidation state of Cu. Furthermore, most of the features are signature of the bounding with the neighbouring atoms. Because all the Cu atoms from deep in the bulk and at the surface contribute, spectra recorded at different L values in reciprocal space must be analysed. Beyond this peculiar study, this work opens a new root to explore the electronic structure at surfaces and interfaces.

[1] Y. Joly *et al.*, *J. Chem. Theory Comput.* 14, 973 (2018).