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Ions at interfaces: accessing the first nanometers using X-ray standing waves

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Ion-surface interactions are of high practical importance in a wide range of technological, environmental and biological problems [1-4]. In particular, they ultimately control the electric double layer structure, hence the interaction between particles in aqueous solutions. Despite numerous achievements, progress in their understanding is still limited by the lack of experimental determination of the surface composition with appropriate resolution.

In the present work, we have developed a method based on X-ray standing waves coupled to nano-confinement which allows the determination of ion concentrations at a solid-solution interface with a sub-nm resolution.

We have investigated mixtures of KCl/CsCl and KCl/KI in 0.1mM to 10mM concentrations on silica surfaces and obtained quantitative information on the partition of ions between bulk and Stern layer as well as their distribution in the Stern layer [5]. Regarding partition of potassium ions, our results are in agreement with a recent AFM study [6]. We show that in a mixture of KCl and KI, chloride ions exhibit a higher surface propensity than iodide ions, having a higher concentration within the Stern layer and being on average closer to the surface by $\sim 1\text{-}2 \text{ \AA}$, in contrast to the solution water interface. Confronting such data with molecular simulations will lead to a precise understanding of ionic distributions at aqueous interfaces.

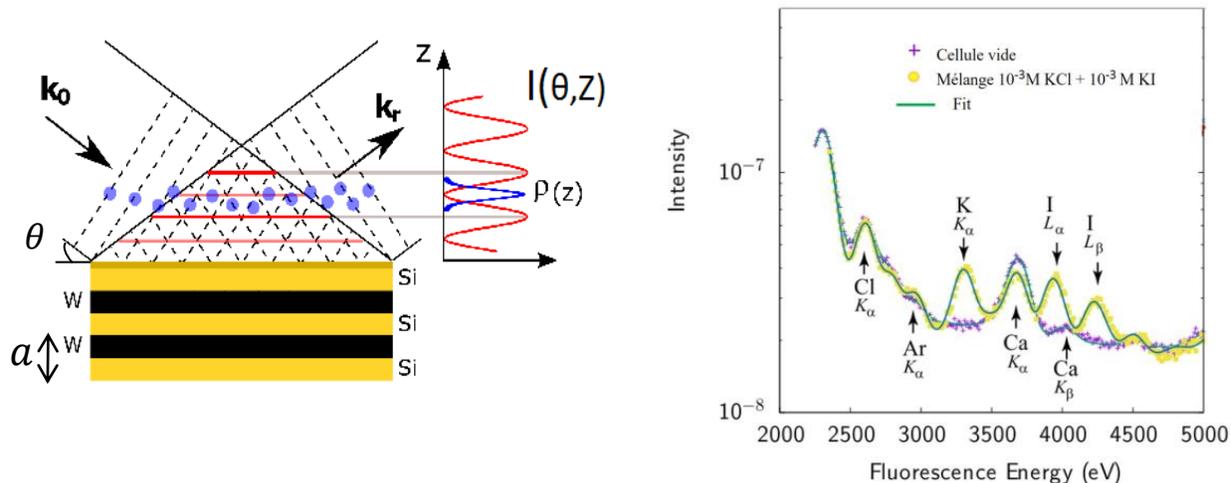


Figure 1. **Left.** Schematics of the standing wave experiment. Incident (wave vector k_{in}) and reflected (wave vector k_r) X-ray waves interfere to create a standing wave field perpendicular to the interface. The species (sketched by blue dots) present in the XSW field are excited and emit secondary fluorescence photons for absorption edges below the incident beam energy. **Right.** Fluorescence intensity (experiments: symbols - fits:solid lines) recorded at 1.95° from an empty cell and a 250nm thick cell filled with a 10mM KCl + 10mM KI solution.

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