Karlsruhe Institute of Technology

Rb^+ at the calcite(104)–water– interface

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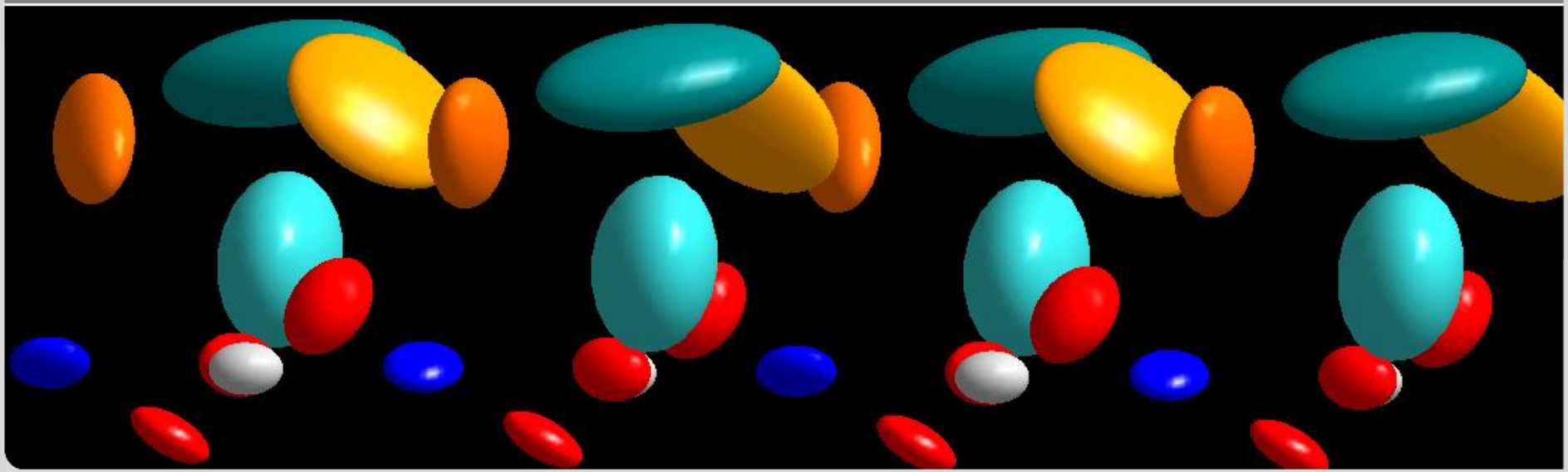
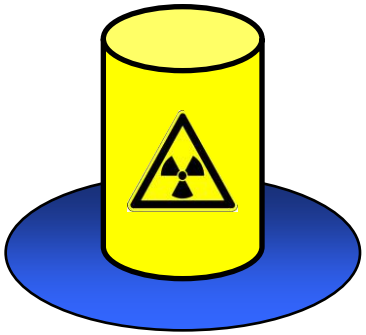
Ions at solid electrolyte interfaces – Lorentz Discussion 2014 – Leiden



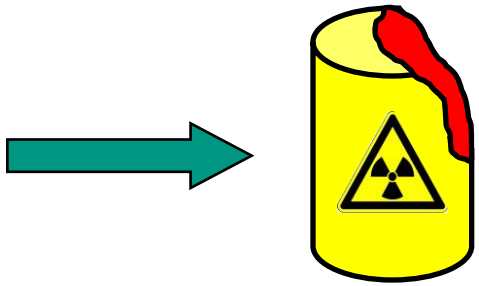
Outline

- Introduction
- Surface diffraction: non-resonant crystal truncation rod (CTR) measurements and resonant interface diffraction (RIDS)
- Rb^+ at the calcite(104)-water-interface

Introduction

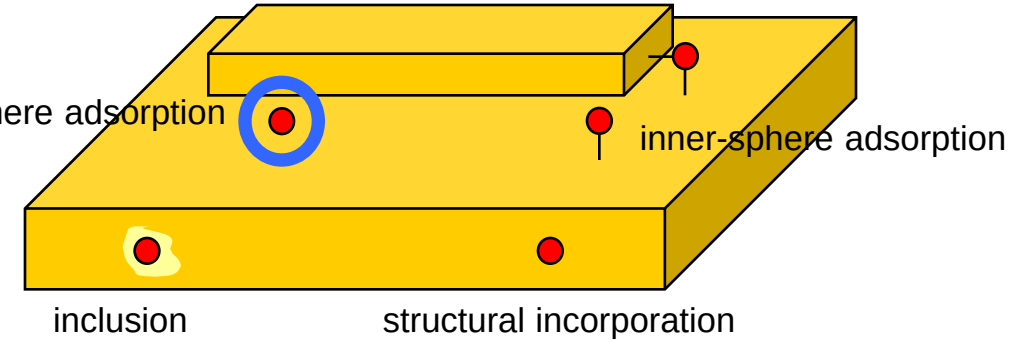


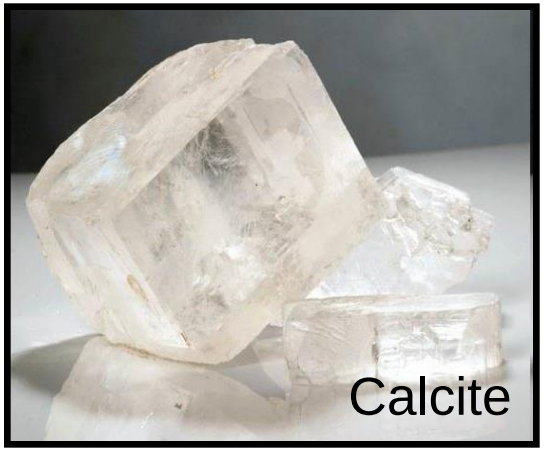
Influx of groundwater
into a waste repository in a deep geological formation



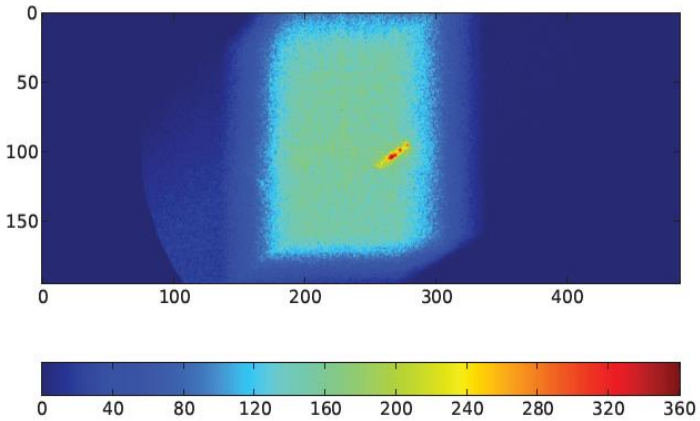
Containers and waste may corrode
→ radionuclides may be released into the groundwater

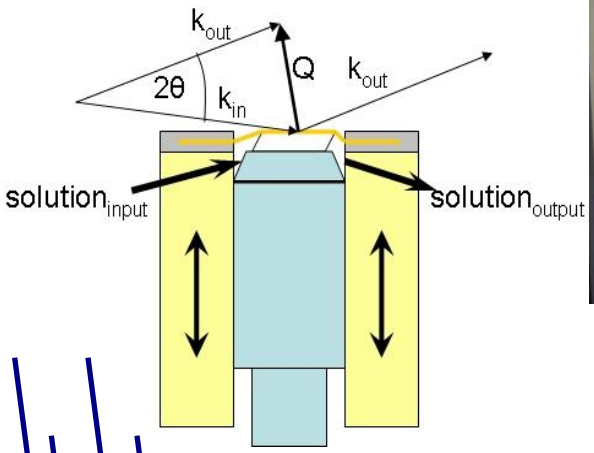
Radionuclides migrate through an aqifer and interact with mineral surfaces:

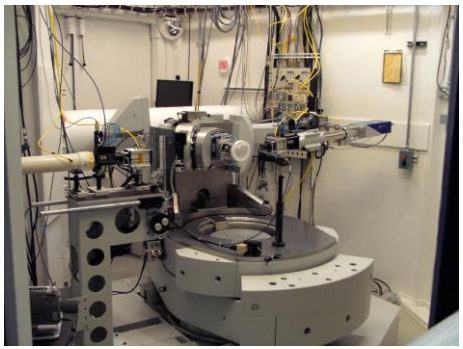




X-ray Surface Diffraction

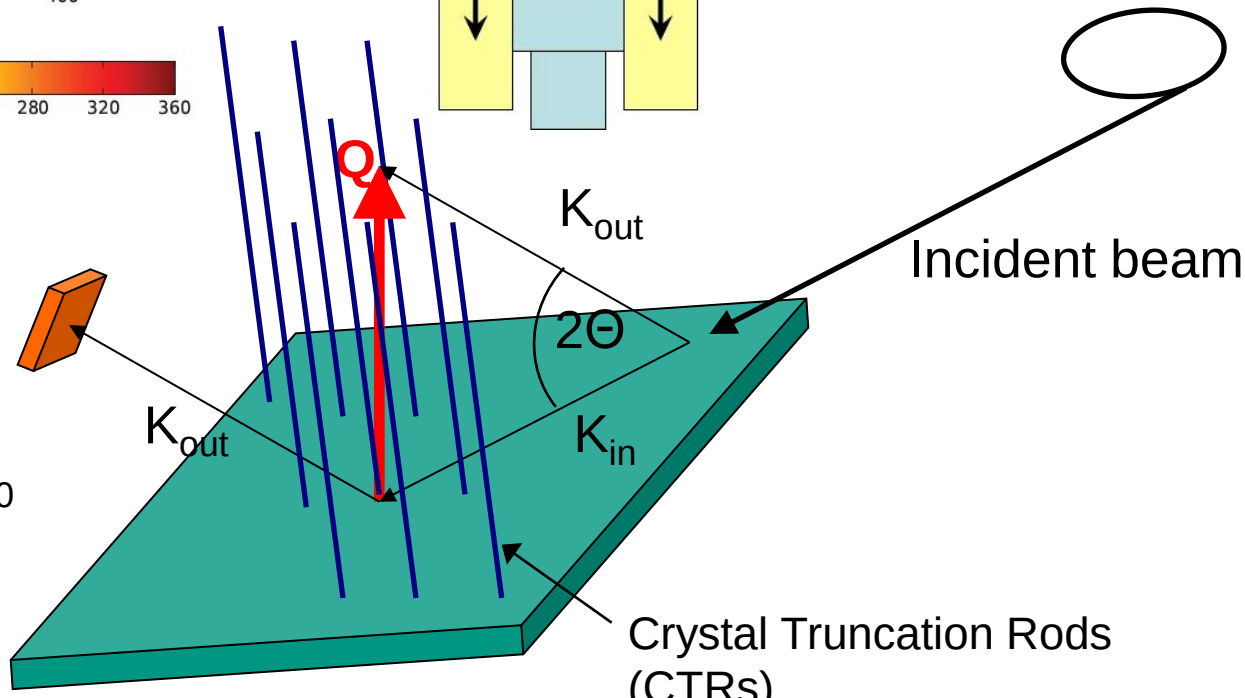




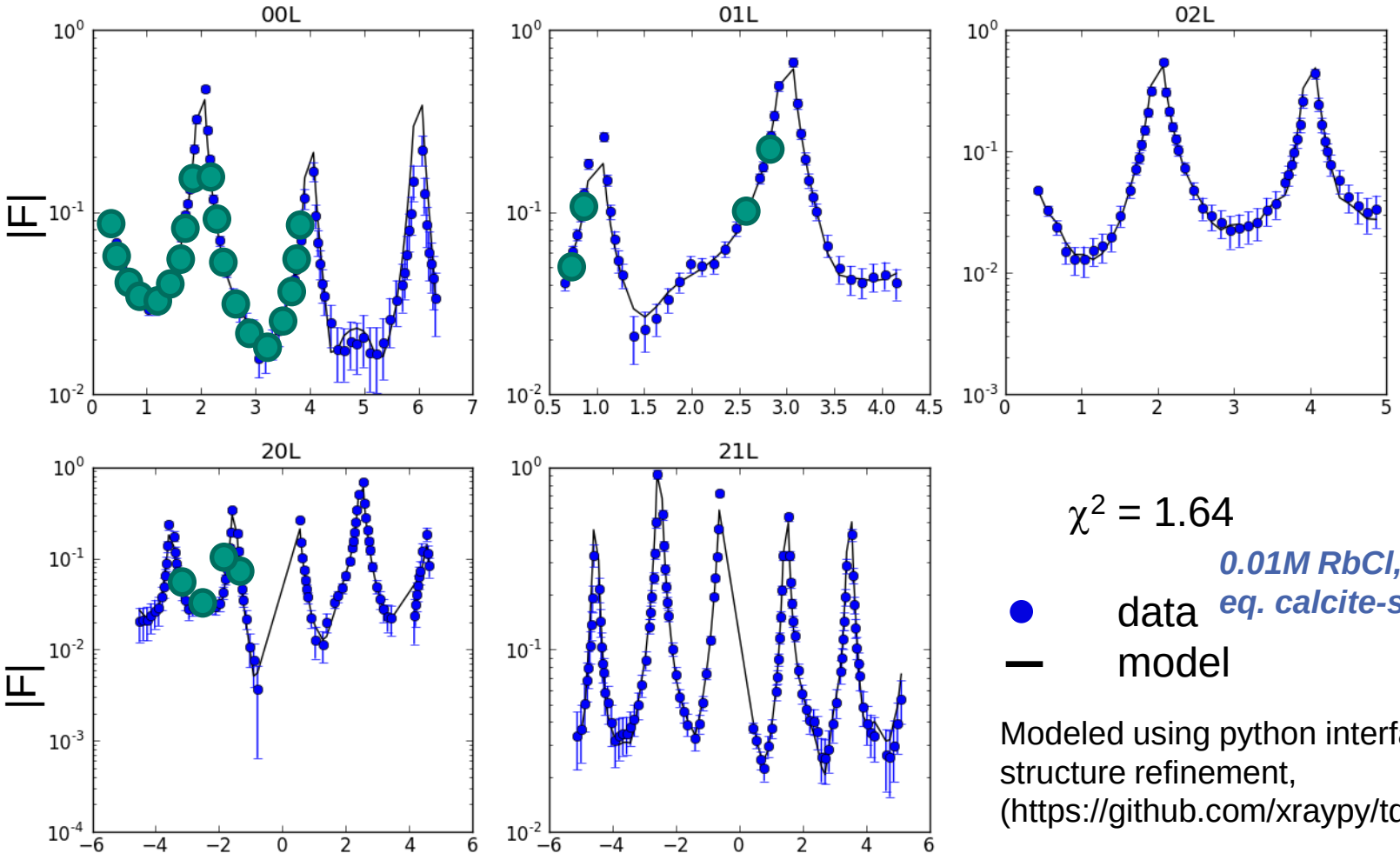


Pilatus
Pixel array
Detector

$I(Q) \approx |F(Q)|^2 C(Q) I_0$



Surface diffraction data for Rb^+ at the calcite(104)–water–interface



$\chi^2 = 1.64$

0.01M RbCl, pH 8.2, eq. calcite-solution-air

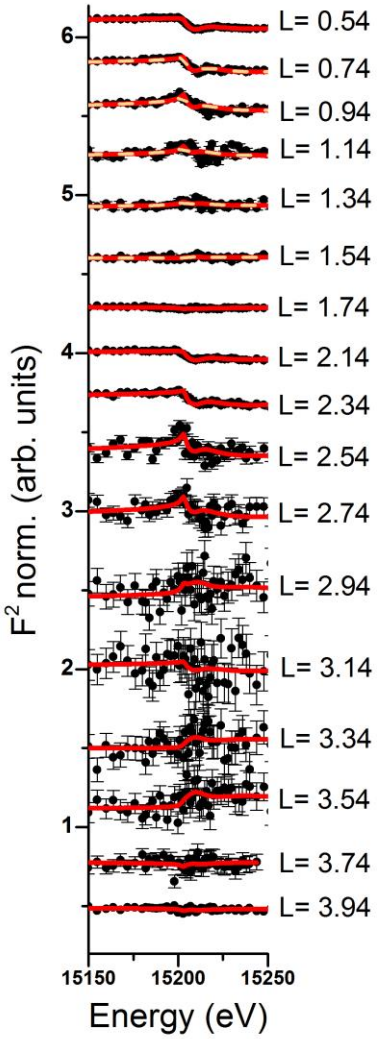
● data

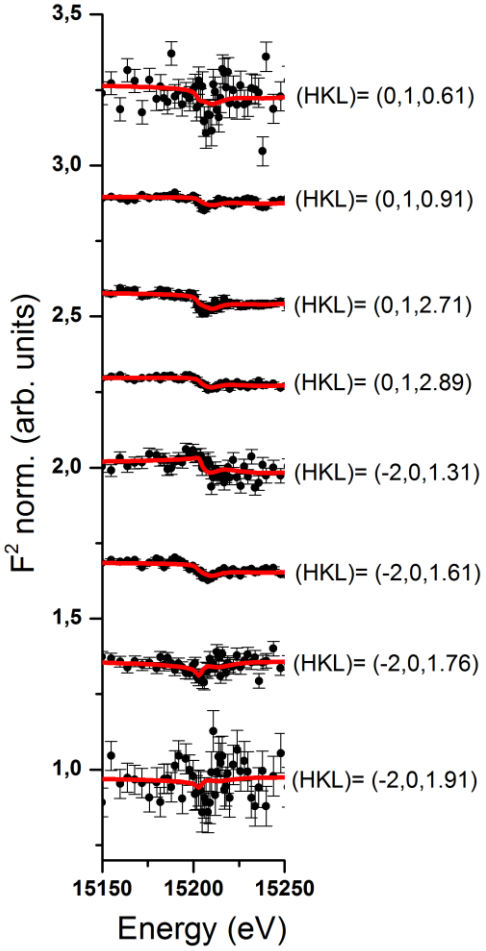
— model

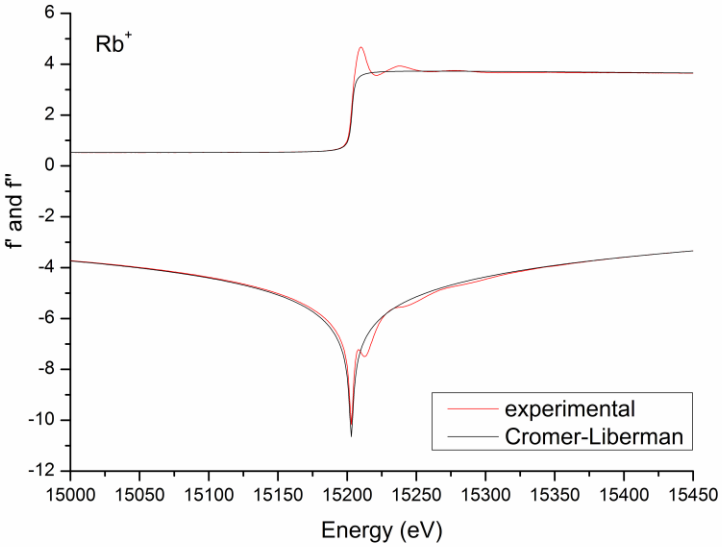
Modeled using python interface structure refinement, (https://github.com/xraypy/tdl)

● 25 resonant datasets: energy scans around Rb K-edge at 15200 eV at fixed points in reciprocal space

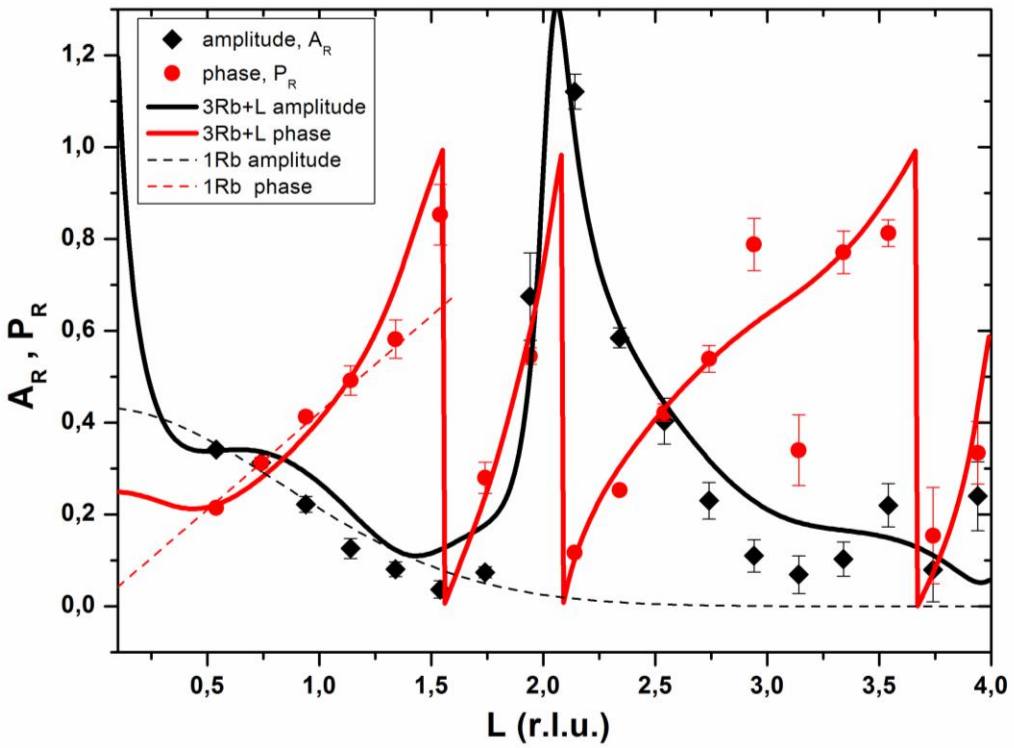
Specular and off-specular resonant surface diffraction data

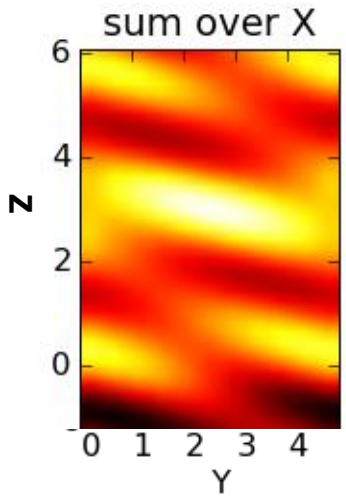






Rb^+ at calcite(104), specular resonant amplitude and phase



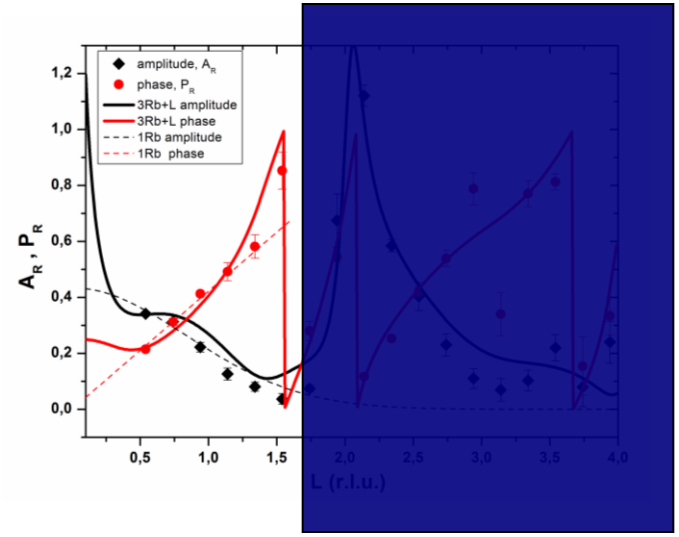


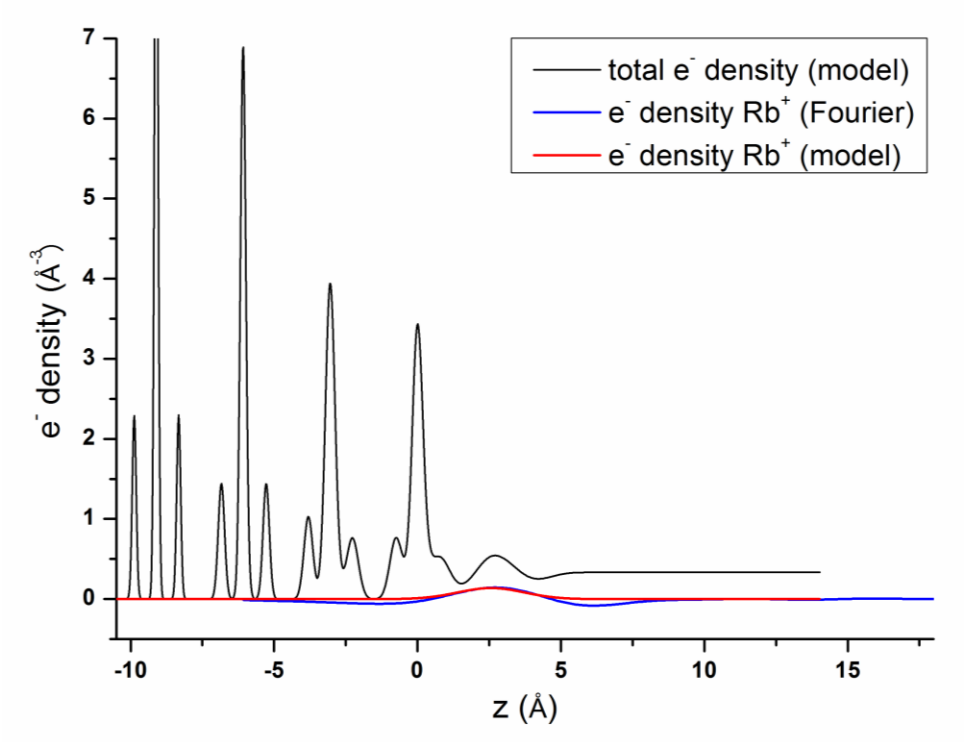
Determination of resonant amplitudes and phases allows straight forward Fourier synthesis of the electron density distribution related to Rb^+.

Capabilities of the method

- Advantages
  - Surfaces can be studies in-situ with molecular scale resolution
  - Element specific information is obtained
  - Multiple species can be structurally characterized and quantified simultaneously.
  - Compared to XSW the method is sensitive to a larger sample volume; usually 1 UC in X and Y and several UCs in z
- Disadvantages
  - Flat and large (at least some mm^2) good quality crystals are required
  - Measurements and data analysis are time consuming / beam time is restricted
  - Average structures are obtained that do not necessarily correctly reflect the local structural environment of adsorbed ions.

Rb^+ at calcite(104), simple model

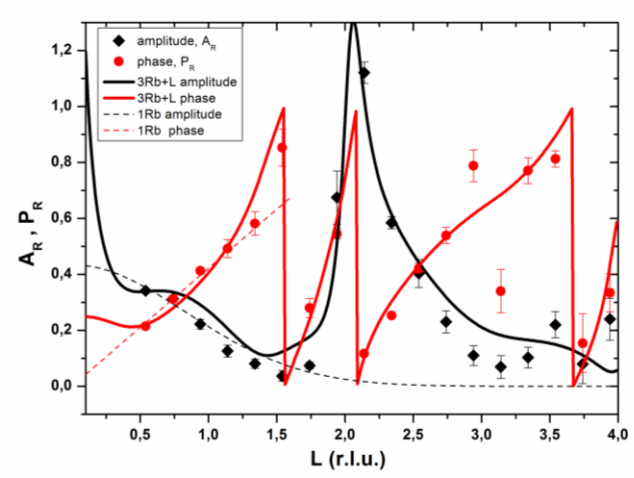


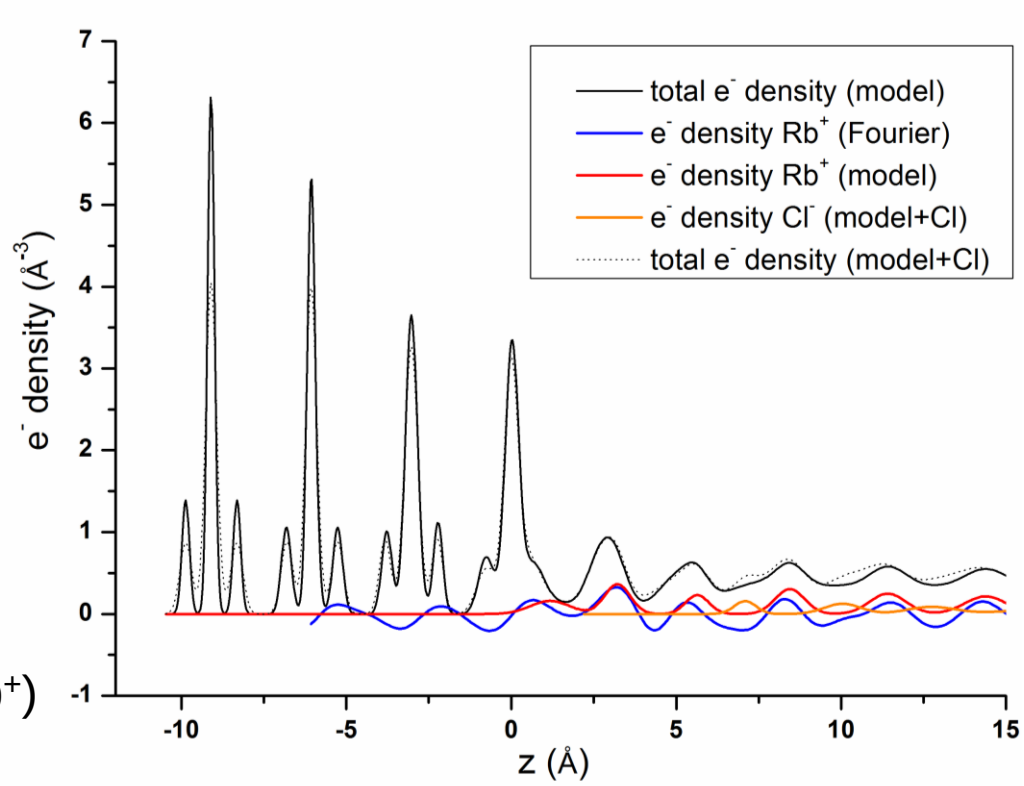


Inner-sphere adsorption

Agrees nicely with recent AFM results by M. Ricci et al. (2013) Langmuir

Rb^+ at calcite(104), full model





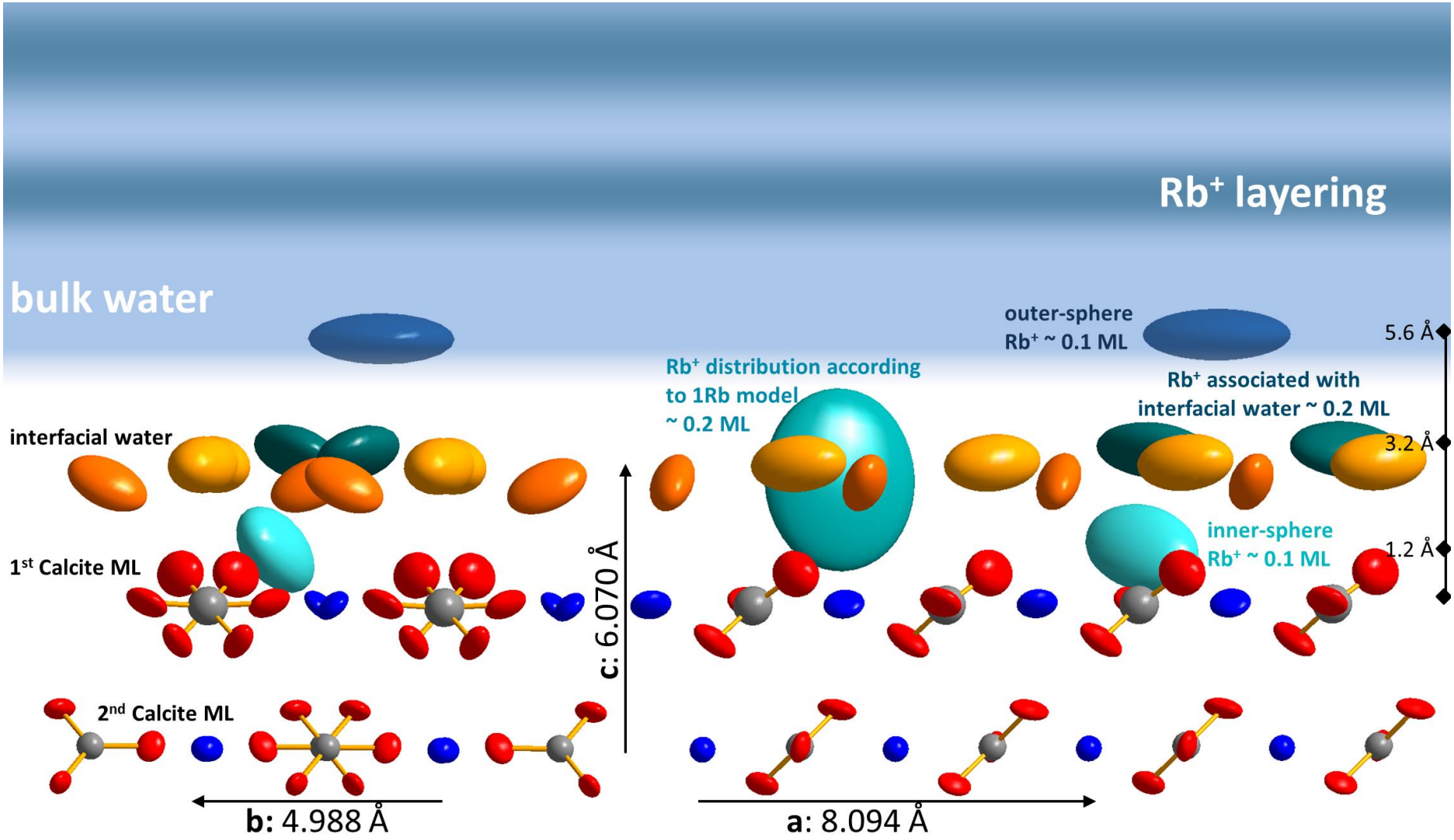
Three distinct adsorption species (confirmed by off-specular data)

Intense layering of the electrolyte (Rb^+)

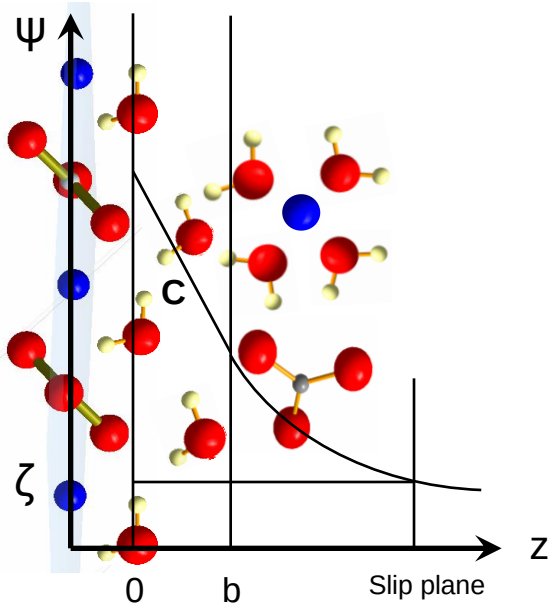
Cl^-?

might be a similar effect as proposed by Shchukarev et al. (2007) for NaCl on hematite (001) based on cryo XPS

Rb^+ at calcite(104)



Calcite Surface Complexation Model?



Basic Stern Model (Heberling et al. (2011) JCIS):

0-plane: between surface and first water layer, highly negative harged due to deprotonation of surface hydration water

b-plane: 0-plane charge screened by outer-sphere adsorbed cations beyond second water layer

Diffuse layer beyond the b-plane

Acknowledgement

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- and thanks for your attention…