Resonant anomalous X-ray reflectivity as a probe of ion adsorption at solid–liquid interfaces ☆

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Abstract

We discuss new opportunities to understand processes at the solid–liquid interface using resonant anomalous X-ray reflectivity (RAXR). This approach is illustrated by determination of element-specific density profiles at mica surfaces in aqueous electrolyte solutions containing Rb^+ and Sr^{2+}. The total interfacial electron density profile is determined by specular reflectivity (i.e., reflected intensity vs. momentum transfer, q, at an energy, E, far from any characteristic absorption edge). RAXR spectra (i.e., intensity vs. E at fixed q) reveal element-specific ion distributions. Key differences in the interaction of Rb^+ and Sr^{2+} with mica are observed using resonant anomalous X-ray reflectivity: Rb^+ adsorbs in a partially hydrated state, but Sr^{2+} adsorbs in both fully and partially hydrated states.
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1. Introduction

The distribution of ions near charged surfaces is fundamental to understanding a broad range of phenomena in which interfacial reactions in electrolyte solutions are central, e.g., transport of aqueous metal ions in natural waters [1], colloidal and macromolecular interactions in physiological environments [2], and electrostatically controlled metal catalyst impregnation on oxide surfaces [3]. Measurements using the surface force apparatus (SFA) showed that there are fundamental differences in the interactions between mica sheets separated by monovalent and divalent cation solutions [4,5], and the derived ion sorption isotherms based on these measured forces (Fig. 1) suggest that the interactions between ions and charged surfaces are not determined solely by electrostatic contributions. In particular, the SFA results were interpreted as strong vs. weak adsorption of monovalent and divalent cations to mica, reflecting their small vs. large ion hydration energies, respectively. However, these phenomena remain poorly understood largely due to lack of direct in-situ observation of the interfacial structures with molecular scale resolution [6]. Clearly, these issues can be understood best when the element-specific distribution is directly measured, reflecting the full complexity of adsorption at the solid–liquid interface. Here we describe the use of resonant anomalous X-ray reflectivity, an X-ray technique combining interface-specificity of high resolution X-ray reflectivity and element specificity of X-ray absorption spectroscopy, for probing both total electron density distributions and element-specific sub-structures at solid–liquid interfaces. The efficacy of this new approach is demonstrated by determination of element-specific density profiles at mica surfaces in aqueous electrolyte solutions containing Rb^+ and Sr^{2+}.

2. Techniques for probing cation adsorption at the solid–liquid interface

At present, there are few experimental probes that are capable of directly observing cation distributions at charged
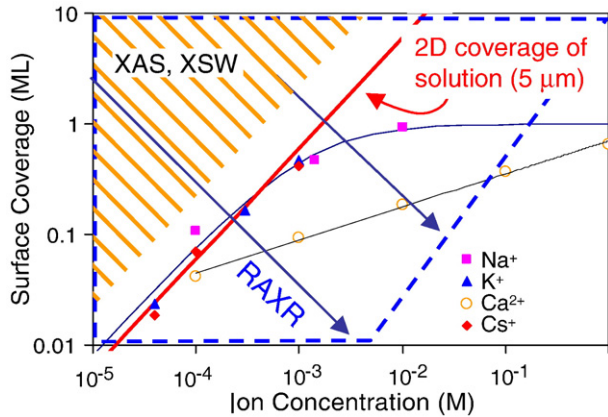
Fig. 1. Data of mono- and divalent ion coverages derived from surface forces apparatus (SFA) measurements [4,5], and the projected two-dimensional coverage of solution ions in monolayer units (ML) assuming a 5 μ-thick solution layer. Also super-imposed on this plot is the range of sensitivity of fluorescence-based probes (hatched region for X-ray absorption spectroscopy, XAS, and X-ray standing waves, XSW) and resonant anomalous X-ray reflectivity (RAXR) as a function of ion concentration and surface coverage. The high solution concentration limits for RAXR are approximate since they depend upon various experimental details including incident angle and sample cell geometry.

mineral-aqueous interfaces. In many cases, specular and non-specular X-ray reflectivity (XR) have been used to probe ion adsorption at solid–liquid interfaces [7–12] making use of their interface-specificity. In the case of specular reflectivity, the measured reflectivity, R (i.e,. the ratio of reflected to incident flux), can be derived from the structure factors of the semi-infinite substrate crystal lattice, the surface and the water [13]:

$$R(q) = (4\pi r_e / A_{uc} q)^2 |F_{UC} F_{CTR} + F_{surf} + F_{water}|^2, \qquad (1)$$

where F_{UC} is the unit cell form factor of the substrate crystal, F_{CTR} is the crystal truncation rod form factor [14], F_{surf} is the form factor of the surface region, F_{water} is the form factor of the semi-infinite water layer above the surface, r_e is the classical radius of the electron, A_{uc} is the unit cell area, and $q = (4\pi / \lambda)\sin(\theta)$ is the momentum transfer for incident angle of θ. However this approach can be substantially limited by the lack of elemental specificity. In particular, it is difficult to know uniquely whether observed changes are due to reorganization of the interfacial hydration structure and/or cation adsorption unless the cation charge and coverage are sufficiently large that a substantial increase in the interfacial electron density is observed.

Elemental specificity in measurements of ion adsorption can be achieved with X-ray fluorescence, through such techniques as X-ray absorption spectroscopy (XAS, including X-ray absorption near-edge structure, XANES and extended X-ray absorption fine-structure, EXAFS) [15–17] and X-ray standing waves (XSW) [18,19]. However, the use of X-ray fluorescence limits the range of systems that can be studied in-situ because the X-ray fluorescence signal is not interface specific. It is therefore only possible to study systems in which coverage of the adsorbed species is significantly greater than the projected two-dimensional density of the same ions present in the solution

or in the substrate as bulk impurities. For typical thin-film cell geometries, with 2–5 μ-thick water films held in place with kapton film [13], measurements can be made only for ions that readily adsorb at concentrations of $\sim 10^{-4}$ M or less, which effectively limits the application of fluorescence-based techniques to strongly adsorbing species. Literature data shows that mono-and divalent ion adsorption at the muscovite-water interface [4,5] is representative of such systems (Fig. 1), and is largely inaccessible to fluorescence-based techniques (hatched area in Fig. 1).

3. Resonant anomalous X-ray reflectivity (RAXR)

The ideal technique for probing cation adsorption is therefore one that provides both element-and interface specificity. These both are attributes of resonant anomalous X-ray reflectivity (Fig. 2). With RAXR, the reflected intensity is measured as a function of energy near the absorption edge of the adsorbing cation at fixed momentum transfer [20–23]. Elemental specificity derives from the full atomic scattering factor of the resonant atom,

$$f(q, E) = f_o(q) + f'(E) + if''(E), \qquad (2)$$

where $f'(E)$ and $f''(E)$ are the anomalous dispersion terms and $f_o(q)$ is the non-resonant atomic scattering factor [24]. Consequently, RAXR spectra are modulated at the characteristic absorption edge of the resonant species, thereby providing element-specific information concerning the ion profile, while retaining the interfacial specificity of surface scattering.

A key conceptual simplification of interpreting RAXR spectra derives from rewriting the relationship between the scattering intensity and the interfacial structure factor. If one considers that the non-resonant reflectivity is determined by the total interfacial electron density profiles with contributions only from $f_o(q)$, all of the resonant terms, $\Delta f(E) \equiv f'(E) + if''(E)$, can be separated out into a resonant structure factor F_R revealing:

$$R(q, E) \sim |F_{NR}(q) + F_R(q, E)|^2, \qquad (3)$$

where $F_R(q, E) = \Sigma_i \theta_i \Delta f_i(E) \exp(iqr_i) \exp[-(q\sigma)^2 / 2]$, and θ_i is the coverage, r_i is the location and σ_i is the rms width of the i'th species. From this relationship, it is evident that once the non-resonant structure factor is known, any RAXR spectra can be explained with information specific to the resonant atom (including its XANES spectrum, coverage, and spatial distribution). Because the reflectivity signal is interface specific, this approach is much more robust for probing the structure of the liquid–solid interface in the presence of non-adsorbed resonant species (e.g., bulk solution concentration or substrate impurities). The main limitation in applying RAXR to the liquid–solid interface is the energy-dependent linear attenuation of the X-ray beam through the solution, which can interfere with the resonant modulation from the surface species. This limitation, however, is less constraining than that from X-ray fluorescence. For example, simulations show that the resonant signal from a monolayer of adsorbed Rb$^+$ is significantly larger than the