Ion distributions at charged aqueous surfaces by near edge x-ray spectra

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Introduction

We have recently reported on the spatial distributions of monovalent ions (Cs^+) at highly charged interfaces within a 3Å resolution by using synchrotron x-ray anomalous reflectivity techniques [1]. We demonstrated that these distributions are exceedingly well described by a Poisson-Boltzmann theory that accounts for proton release and binding (see also [2]). Herein, we briefly report on the extension of these studies by analyzing the spectra obtained from x-ray energy scans at fixed momentum-transfers (Q_z) under specular-reflectivity conditions (for a related study see also [3]). Our analysis yields the energy dependence of the dispersion corrections $f'(E)$ and $f''(E)$ near the Cs^+ L_{III} resonance. This approach provides improved resolution of minute ion accumulations at interfaces and allows spectroscopic studies of ions in aqueous environment.

Methods and Materials

To introduce interfacial charges, monolayers of dihexadecyl hydrogen phosphate (DHDP) were spread at CsI solution/gas interfaces [4]. Detailed procedures of sample preparations and handling were described in Ref. [1]. X-ray studies at the gas/liquid interface were conducted on the Ames Laboratory Liquid Surface Diffractometer at the Advanced Photon Source (APS), beam-line 6ID-B [5]. The highly monochromatic X-ray beam is deflected onto the liquid surface at any desired angle of incidence by a second monochromator (Ge(111) or y-cut quartz single-crystals; *d*-spacings 3.26637 and 4.25601 Å, respectively) mounted on the diffractometer with energy resolution ~0.85 eV at ~5 keV.

Results and Discussion

Figure 1(A) shows normalized reflectivities at fixed Q_z values *versus* incident photon energies (E) measured near the Cs^+ L_{III} resonance. Similar reflectivity measurements performed on the CsI solution without the monolayer did not detect any anomalies as a function of E (triangles). The E-scans exhibit periodic dependence on Q_z with a lineshape resembling a superposition of $f'(E)$ and $f''(E)$. The spectra systematically exhibit opposite characteristic for each two points that are separated by $\Delta Q_z \sim 0.125$ Å^{-1}. To explain these features semi-quantitatively, it can be shown that in the Born approximation, the normalized reflectivity in the presence of Cs^+ is proportional to

$$R(Q_z,E) \propto \rho_{Cs}[f'(E)\sin(Q_z d) - f''(E)\cos(Q_z d)] , \quad (1)$$

where ρ_{Cs} is the electron density of Cs^+ and $d = d_1 + d_2/2$ (d_1 and d_2 are the lengths of the acyl tail and headgroup, respectively). Equation (1) predicts the observed periodicity with the property $\Delta Q_z d = \pi$, yielding $d = 25.1$ Å. Using the literature value for $d_1 \approx 19.7$ Å [4], we obtain $d_2 \approx 10.8$ Å, corresponding to the thickness of the headgroup and hydrated Cs^+ compartment which is much larger than that found for the same monolayer spread on pure water, ~ 3.4 Å[4]. This unequivocally demonstrates that Cs^+ ions accumulate next to but do not bind to the phosphate headgroup forming a diffuse layer, in agreement with previous results [1].

A quantitative account of the E-scans uses a non-linear square fit (NSLF) model of a generalized complex function density profile [1]. To include the energy dependent dispersion corrections near resonance, we construct the absorptive portion,

$f''(E)$ as a sum of one Error function and superimposing on it the minimum number of Lorentzians necessary to obtain the best fit.
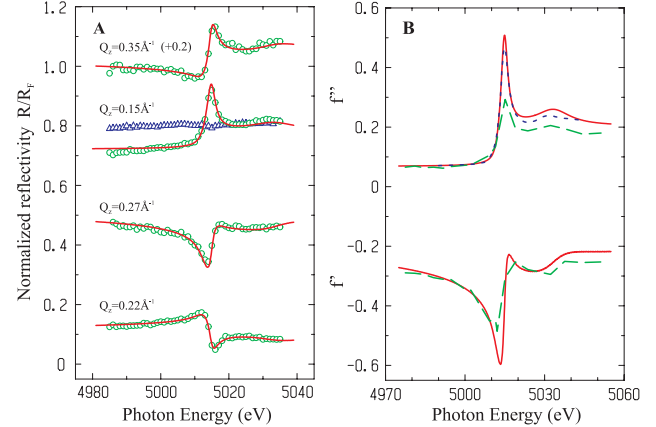

Figure 1: (A) Normalized reflectivity (R_F is the calculated reflectivity of the subphase) versus photon energy at fixed Q_z for DHDP monolayer spread on 10^{-3} M CsI solution (surface-pressure 40 mN/m). Solid lines are obtained from calculation assuming a single structural model to all four scans. No anomalies are observed without the monolayer (triangles). (B) Dispersion corrections for Cs^+ (solid lines) used for fitting the data in (A); dashed- and dotted-lines were obtained for Cs^+ in hydrogen [6] and oxygen surrounding [7], respectively.

The dispersive portion, $f'(E)$, is numerically calculated by the Kramer-Kroning relation. The solid lines in Fig. 1(A) are the best-fit calculated with the dispersion curves shown in Fig. 1(B) using a single parameter set for the refinement of a combined data of all energy-scans at different Q_z values. Ion distributions from the NLSF procedure are in agreement with our previous studies [1]. Comparison of Cs $f''(E)$ in different environments, as shown in Fig. 1(b), is consistent with interfacial Cs^+ ion surrounded by eight oxygen atoms [7]. This technique is currently being applied to discriminate free from bound ions, as predicted [8] for multivalent ions, such as Ba^{2+} or La^{3+}.

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