

# Elemental Profiles of Metal Complexes Adsorbed at Oxide-Water Interfaces by Resonant Anomalous X-ray Reflectivity

C. Park,<sup>1</sup> P. Fenter,<sup>1</sup> J.R.Regalbuto<sup>2</sup>, N. C. Sturchio<sup>2</sup>

<sup>1</sup>Argonne National Laboratory, Argonne, IL U.S.A.

<sup>2</sup>University of Illinois at Chicago, Chicago, IL U.S.A.

## Introduction

Adsorption of the aqueous platinum-tetraammine complex ( $\text{Pt}(\text{NH}_3)_4^{2+}$ , or PTA) on silica surfaces at high pH is a primary step in noble metal catalyst impregnation. Previous studies have found that this process is electrostatically driven and appears comparable to the 'outer-sphere' adsorption. However, the physical structure and the spectroscopic properties of the adsorbed PTA species on a well defined homogenous oxide surface have never been directly probed. High-resolution (non-resonant) specular x-ray reflectivity revealed changes to the total interfacial structure due to adsorption of PTA (at pH~10, 200 ppm PTA concentration) [1], but the Pt sub-profile is not readily resolved from these data due to the small Pt occupancy which is obscured by the electron density profile of the interfacial water. To resolve the Pt-specific interfacial profile, resonant anomalous x-ray reflectivity (RAXR) as a function of incident photon energy near Pt  $L_{\text{III}}$  edge was measured at fixed momentum transfer. The measured RAXR spectra from PTA complexes adsorbed at the quartz (100)-water interface reveal the interfacial structure, plus modifications of the Pt  $L_{\text{III}}$  x-ray absorption near edge structure (XANES) spectrum of the adsorbed PTA.

## Fundamentals

The distribution of a specific element at the solid-liquid interface (i.e., the resonant atom in the upper-left panel of Fig. 1) may be obscured in the total electron density as probed by non-resonant X-ray reflectivity (upper-right panel, Fig. 1). Since the resonant anomalous dispersion of x-rays scattered from a specific element (lower-left panel, Figure 1) is independent of momentum transfer  $q$  [2], the element-specific structure can be revealed by combining two orthogonal measurements: the non-resonant reflectivity  $q$  (upper-right panel, Fig. 1) and the resonant anomalous reflectivity at fixed  $q_0$  vs incident photon energy (lower-right panel, Fig. 1). RAXR utilizes the elastic coherent scattering channel so that the measurement is interface-specific as well as element-

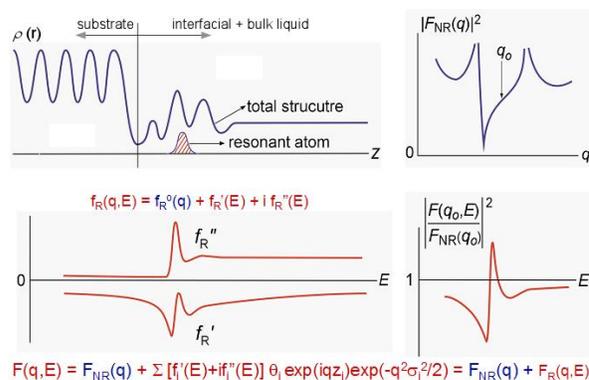


Figure 1: Schematic of resonant anomalous x-ray reflectivity. The energy dependent anomalous dispersion  $[f'(E) + if''(E)]$  of the resonant atom modulates the total scattering intensity as function of photon energy (at a fixed momentum transfer) near a characteristic absorption edge. The RAXR spectra are directly controlled by the distribution of resonant atoms at the solid-liquid interface.

specific. Therefore, the physical and spectroscopic properties of the adsorbed species at the solid-liquid interface can be simultaneously explored without interference from the bulk and/or solution signals.

## Surface Preparation and Measurements

Quartz single crystals used in this study and the sample preparation for x-ray measurements have been described previously [1, 3]. The non-resonant x-ray reflectivity and the resonant anomalous x-ray reflectivity from quartz (100)-PTA solution interface were measured at 12-BM-B, 11-ID-D, and 12-ID-D beamlines (BESSRC-CAT), Advanced Photon Source, Argonne National Laboratory. The incident photon energy for the non-resonant reflectivity was 20.0 keV. Details of measurement techniques and data analysis are described elsewhere [4]. RAXR spectra of the adsorbed PTA (Fig. 2) were measured near the Pt  $L_{\text{III}}$  edge (11.564 keV) at fixed momentum transfer values

( $q_0 = 1.03, 1.62, 2.50, \text{ and } 3.24 \text{ \AA}^{-1}$ ) as indicated. The RAXR spectra are derived solely from elastic coherent scattering and thus are related only to the coherently adsorbed interfacial species.

## Results and Discussion

Figure 2 shows the RAXR spectra measured from quartz (100)-PTA solution interface, which are normalized to the non-resonant scattering intensity. A phase inversion in the resonant modulation is observed between spectra at  $q_0=1.03$  and  $1.62$ , and again between  $q = 1.62$ , and  $2.50 \text{ \AA}^{-1}$ , which is related to the position of the adsorbed Pt. The resonant modulation is apparent even at high  $q$  indicating that the distribution of Pt in the adsorbed PTA species is essentially narrow. In addition, the magnitude of the resonant modulation is much larger than expected, suggesting that the spectroscopic characteristics of the adsorbed PTA are different from that of the PTA in bulk solution. Analysis of the RAXR data through non-linear least-squares fits to model structures (red solid lines in Fig. 2) results in satisfactory agreement only when the Pt distribution contains at least two distinct layers and the interface-specific anomalous dispersion (i.e., the XANES profile) contains a substantial white-line enhancement at the Pt  $L_{III}$  edge. Polarization-dependent RAXR measurements might be needed to resolve whether this difference comes from changes in the oxidation state of the adsorbed PTA or from strong orientational preference of the square-planar structure of PTA complex upon adsorption at the quartz (100)-water interface.

These results demonstrate a powerful element-specific approach for probing ion adsorption at the oxide-water interface and show that adsorption of electrostatically bound aqueous metal complexes at the oxide-water interface can exhibit complexities that can be understood only when both the structural and spectroscopic sub-structures are fully resolved.

## Acknowledgements

This work was supported by the Geosciences Research Program, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (W-31-109-ENG-38), and the National Science Foundation (CTS 99-08181). The X-ray reflectivity measurements were performed at beamlines 12-BM-B, 11-ID-D, and 12-ID-D at the Advanced Photon Source at Argonne National Laboratory. Use of the Advanced Photon Source was supported by the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, under contract W-31-109-ENG-38 at Argonne National Laboratory. .

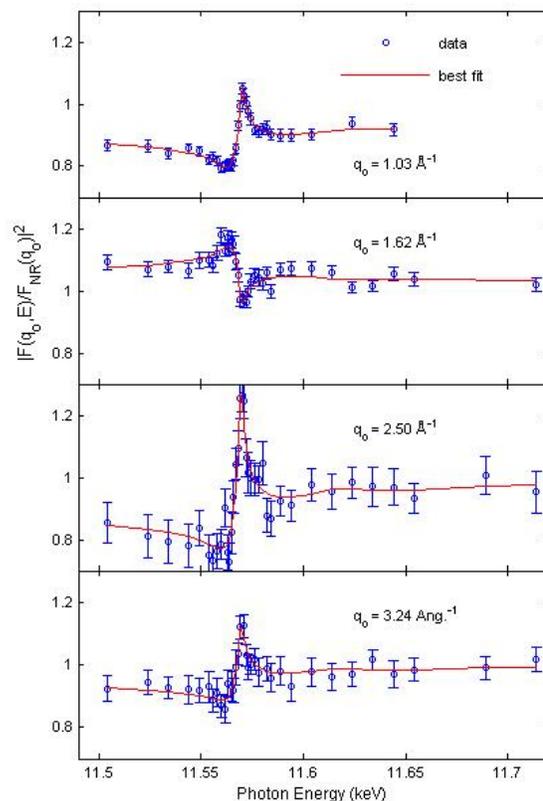


Figure 2: Normalized RAXR spectra from adsorbed PTA at quartz (100)-water interface. The resonant signals are normalized to the non-resonant reflectivity. The red solid lines correspond to the best-fit model.

## References

- [1] C. Park, P.A. Fenter, J.R. Regalbuto and N.C. Sturchio, in *Advanced Photon Source Activity Report 2002*.
- [2] J. Als-Nielsen and D. McMorrow, *Elements of Modern X-ray Physics*, Chap. 7. pp.235-260. (Wiley, Chicester, 2001).
- [3] M.L. Schlegel, K.L. Nagy, P.Fenter, and N.C. Sturchio, *Geochim. Cosmochim. Acta* 66, 3037-3054 (2002).
- [4] P. Fenter, *Reviews in Mineralogy & Geochemistry 2002* (eds., P. Fenter, M.L. Rivers, N.C. Sturchio, and S.R. Sutton), Chap. 3, pp.149-220.