

Surface resonance x-ray scattering

H. You, Y.S. Chu, T.E. Lister, and Z. Nagy

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 USA

A.L. Ankudinov and J.J. Rehr

Department of Physics, University of Washington, Seattle, WA 98195 USA

Introduction

X-ray techniques are practically the only tools for *in situ* investigations of buried electrified interfaces of materials that are important to various technologies such as energy storage and conversion. We have demonstrated the feasibility of the surface resonance x-ray scattering measurements; indeed, this novel technique provides information on the state of oxidation of the interfacial atoms.

Methods and Materials

We have chosen the surface oxidation/reduction of platinum as a model system to prove the principles of this new technique. A Pt(111) surface was mechanically polished and electrochemically prepared to a nearly ideal surface. The energy scans were made at the various points on the specular rod at an oxidation potential where a monolayer of platinum oxide is formed.

Results

The critical question to answer was whether one can measure the core-binding energy shift of the top monolayer under water (something that is easily done in ultrahigh vacuum with photoemission-type measurements) with the surface resonance x-ray scattering. That was the focus of our recent publication in which we unambiguously demonstrated the principle of such measurements. The effect of the core-binding energy shift is largest when the momentum transfer is set so that the scattering from the top layer is out of phase compared to that from the bulk. Under this condition, the normally negative singular behavior of f' near the resonance (as shown in Figure 1A) splits into a negative and a positive singularity (due to the out-of-phase condition) and the position shifts by the core-binding energy shift of the top layer. In addition, the height of the positive singularity exhibits a sensitive dependence on the momentum transfer due to the change in the relative phases between the scattering from the top layer and that from the bulk. The examples shown in Figures 1A and 1B are for momentum transfer vectors of $(0\ 0\ 2.2)$ and $(0\ 0\ 2.6)$, respectively. The solid lines in the Figures show a fit based on the 9 eV shift of the Pt L_{III} edge upon oxidation. In Figure 1A, we can easily see that the negative singularity is followed by the inverted, positive one just above the edge. The positive singularity is significantly smaller in Figure 1B and the detailed discussion of the Q -dependence has been published [1].

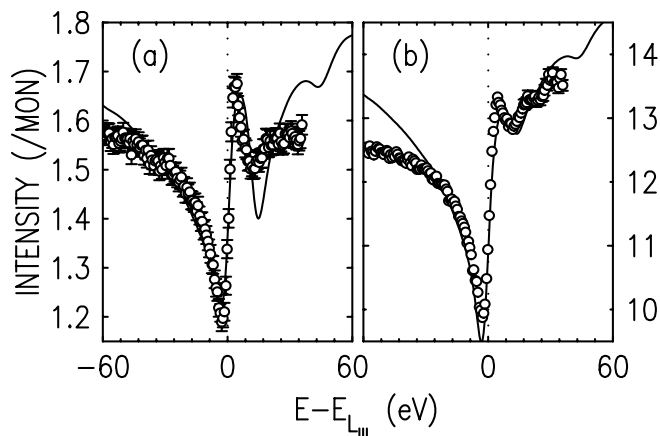


Figure 1: Energy scans (a) near an anti-Bragg position and (b) near a Bragg position.

Discussion

During our data analysis, we have found that resonance surface scattering is the best way to measure f' because we have complete control over the depth sensitivity from a monolayer to many layers where no absorption correction is needed (or at most the small absorption correction can be easily applied). We also found that most of the commonly used x-ray absorption fine structure (XAFS) codes compute a completely incorrect f' near the resonance energy. Therefore, the data analysis was done without any XAFS correction, using only the Cramer-Liberman computation in our publication. We developed a computational scheme including solid-state effects, thereby correctly calculating f' and f'' over a large energy range as well as near the resonance energy.

This new computational scheme (requiring considerably extensive computation) was compared to scattering from the completely clean "unmodified" Pt(111) surface, where an ideal scattering factor of $|f_0 + f' + if''|$ with solid state effects (shown as the open circles in Figure 2A) can be measured with the resonance surface scattering and the corresponding f'' (shown as the open circles in Figure 2B) that can be directly measured with fluorescence or with independent absorption measurements [2]. The computed scattering factors based on the Cramer-Liberman method including solid-state effects are shown as solid lines in Figure 2A and B for comparison. The Cramer-Liberman computer code without the solid-state effect produces only smooth lines without any fine structure.

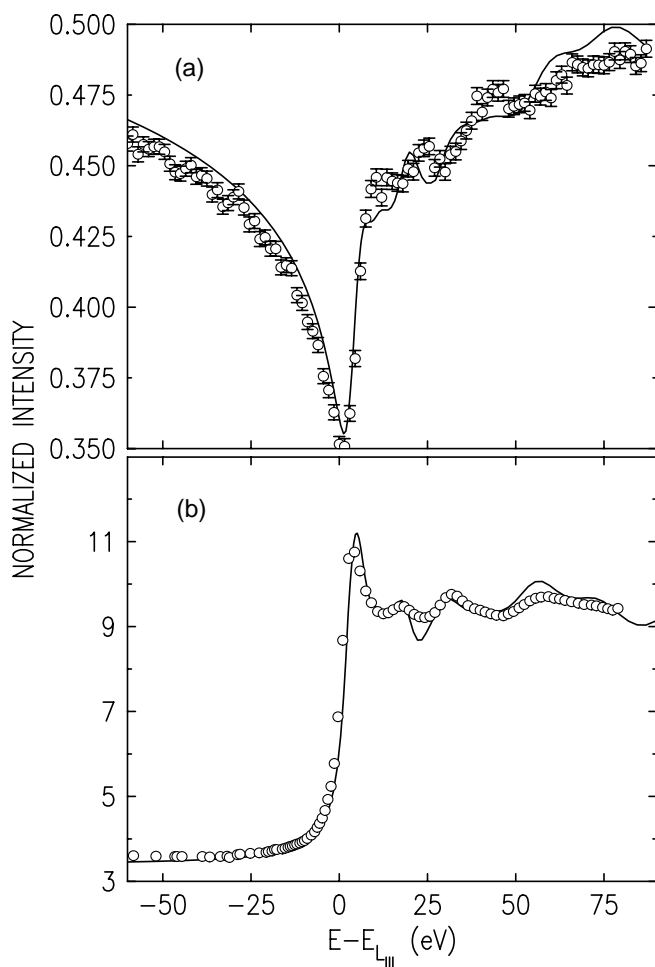


Figure 2: Measured f' (a) and f'' (b) from the unoxidized Pt(111) surface. The solid lines are the calculation.

Acknowledgments

The experiment was performed at 12-ID-B, the Advanced Photon Source (APS). The use of APS was supported by the U.S. Department of Energy (DOE), Basic Energy Sciences (BES), Office of Science, under Contract No. W-31-109-Eng-38. This work was supported by Chemical Science Program of DOE, BES.

References

- [1] Y. S. Chu, H. You, J. A. Tanzer, T. E. Lister, and Z. Nagy, *Phys. Rev. Lett.* **83**, 552 (1999).
- [2] H. You, Y.S. Chu, J.A. Tanzer, T.E. Lister, Z. Nagy, A.L. Andudiniv, and J.J. Rehr, *Physica B* (in press), *Proc. 6th International Conference on Surface X-ray and Neutron Scattering, Netherlands*, (1999).