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Experimental apparatuses for ReflEXAFS studies

Francesco d'Acapito*

CNR–IOM–OGG, 71 Avenue des Martyrs, 38000 Grenoble, France. *Correspondence e-mail: dacapito@esrf.fr

Reflection extended X-ray absorption fine-structure spectroscopy (ReflEXAFS) is a unique tool in the investigation of real surfaces or systems with low surface coverage (monolayers or below). Exploiting the total external reflection phenomenon permits the probe beam to be confined to a few nanometres below the surface. Particular experimental apparatuses are needed for this data-collection mode and a description of some noticeable instruments and data-collection modes is provided in this chapter.

1. Introduction

Reflection extended X-ray absorption fine-structure spectroscopy (ReflEXAFS) is a particular collection mode of X-ray absorption spectroscopy (XAS) data with the probe beam impinging on the sample in total external reflection conditions. The main advantage of total reflection XAS is that the extinction length of the probe beam is greatly reduced with respect to the normal incidence, as shown in Fig. 1.

This makes ReflEXAFS a surface-sensitive technique in the range of a few nanometres, with the considerable advantage that it does not need ultrahigh-vacuum conditions like electron-based techniques. Thus, this method can be applied to a variety of interfaces (gas–solid, liquid–solid, liquid–liquid and solid–solid), realizing *operando* conditions for the materials under study. The drawback is that working in total reflection conditions poses several limitations on the X-ray optics (low beam size and divergence), on the sample (centimetre size along the beam direction) and on the mechanics of the sample manipulator (high stability and accuracy).

2. Data-collection modes

ReflEXAFS is an ideal technique for the study of surface systems, especially when real conditions for the surface are required or when the coverage is below the monolayer level and the scattering from the substrate needs to be minimized. Typical values for critical angles are in the range 0.5–5 mrad (0.03–0.3°), posing severe requirements on the accuracy and stability of the sample-positioning system. In practice, even more stringent mechanical limits are required in order to fully exploit the potentialities of total reflection, and typical resolutions of microradians for rotations and micrometres for translations are required, with a comparable level of vibration amplitude and long-term stability.

Indeed, thanks to the highly polarized beams from synchrotrons, ReflEXAFS can provide a detailed geometrical description of single-crystalline samples. Because the polarization vector can be oriented either parallel or perpendicular to the surface (linear dichroism), this enhances the sensitivity to bonds placed along that vector. This effect is different if $\{K, L_1\}$ or $\{L_2, L_3\}$ edges are considered. In the former case the relation between the amplitude $N_{K\text{edge}}$ of a single bond

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making an angle δ with the polarization vector is $N_K = 3\cos^2(\delta)$, whereas in the latter case it is $N_{L_{2,3}} = 0.7 + 0.9\cos^2(\delta)$ (Iwasawa, 1997). This concept is the basis for the polarization-dependent total reflection XAFS (PTRF-XAFS; Shirai *et al.*, 1995) technique and has been largely exploited by the catalysis community to describe adsorbates on model surfaces. The sample manipulator in this case must allow the orientation of the sample in space on three rotation axes so the polarization vector can be placed parallel to any crystallographic direction of interest in the sample under investigation.

Another aspect that can be exploited using total reflection is the large variation of the extinction length of the probe X-ray beam as a function of the incidence angle, as shown in Fig. 1. This value passes from a few nanometres to a few micrometres by varying the incidence angle by a fraction of a milliradian, thus giving the possibility of studying the surface and the bulk of the sample just by changing the incidence angle from below to above the critical value, as presented in Souchier *et al.* (2015). In this case the manipulator accuracy needs to be largely below the typical critical angle values in order to finely adjust the incidence angle to the sample under investigation.

3. Experimental apparatuses

Several experimental apparatuses for ReflEXAFS data collection have been presented by various groups exploiting this technique, each with a peculiar aspect linked to the class of experiments for which it was designed. In general, these instruments are mounted on wiggler sources (Oyanagi *et al.*, 1995) in order to have a high X-ray flux available for studies at the monolayer (ML) level. Bending-magnet sources are also used, but in this case X-ray focusing optics are mandatory for highly diluted samples (d'Acapito *et al.*, 2003). In all cases the beam size in the reflection plane must typically be of 20–50 μm in order to keep the sample dimensions at acceptable values. Such a size is obtained by focusing and by cutting with slits. A notable instrument is that presented in Shirai *et al.* (1995), Chun *et al.* (1996) and Asakura *et al.* (2000) comprised of a measurement chamber coupled to a sample-preparation stage for *in situ* treatments. The apparatus was installed on the BL-7 beamline at KEK and was dedicated to studies in the fields of chemistry and catalysis (Fig. 2).

The samples could be kept at a variable pressure from ultrahigh vacuum (10^{-9} mbar) to ambient pressure and at temperatures from 100 to 800 K. The sample was conditioned in the preparation chamber and successively transferred into the measurement chamber. Here, it could be oriented with the surface either parallel or perpendicular to the beam polarization vector, thus permitting the collection of PTRF-XAFS data on systems such as dispersed metal particles on oxide monocrystalline surfaces (Koike *et al.*, 2008). Beryllium windows permitted the collection of the reflected and fluorescence beams with ion-chamber or NaI detectors. Subsequently, an evolution of this instrument was presented by the same group (Chun *et al.*, 2001) with a better-performing multi-element solid-state energy-resolving detector and a more complete set of ancillary surface-characterization techniques (Auger, reflection high-energy electron diffraction). A data-

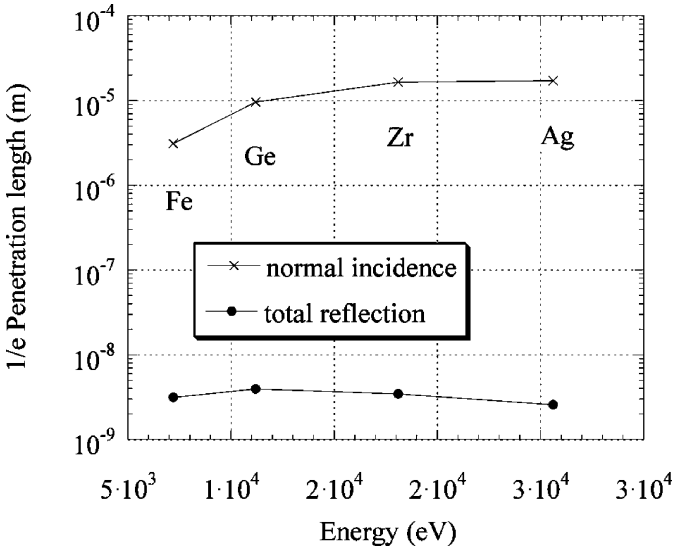

Figure 1
Extinction length of photons above the *K* absorption edges of some elements in their metallic state. A comparison is made between normal incidence (upper curve) and total reflection (lower curve). Reprinted from d'Acapito *et al.* (2003).

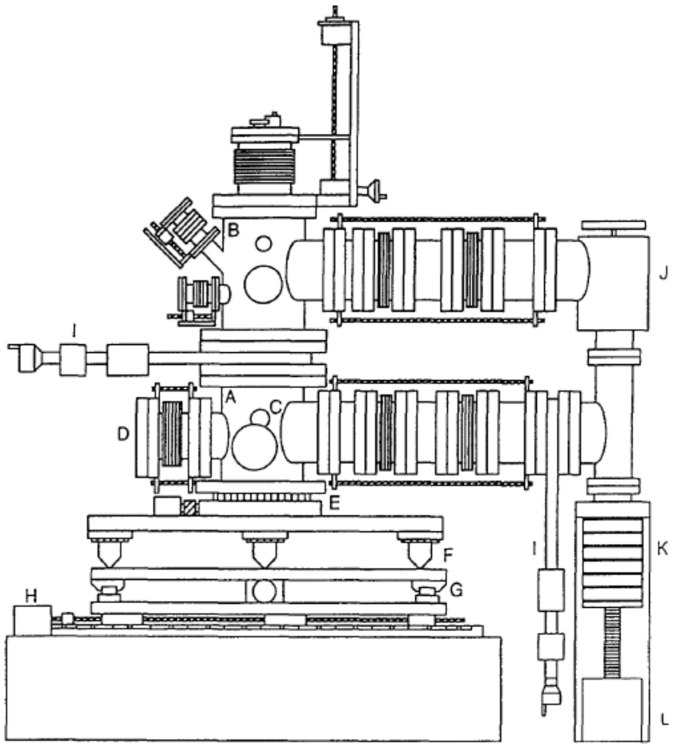

Figure 2
Sketch of the chamber for PTRF-XAFS installed at KEK. The X-ray beam is perpendicular to the plane of the paper, directed towards the reader. A, measurement chamber; B, sample-preparation chamber; C, window for reflected beam; D, window for sample fluorescence; E, rotation table (rotation around *z*); F, kinematical plane (height in *z* and rotation around *x*); G, H, translations in *x* and *y*; I, J, valves; K, L, pumping system. Reprinted from Chun *et al.* (1996) with permission from Elsevier.

collection chamber with analogous capabilities for data collection with different sample orientations was presented by Oyanagi *et al.* (1995, 1998) and installed on the BL13B beamline at the Photon Factory. This apparatus was conceived for experiments in the materials science/surface science field and permitted the collection of data in multiple sample orientations in ultrahigh vacuum and at temperatures between 15 and 300 K. In this case particular care was also taken in the choice of the fluorescence detector: both Si(Li) and HP-Ge multi-element devices were used to reach a sensitivity of about 0.1 monolayer.

Further data-collection apparatuses have been presented in the literature, some of which maintain the sample in an ambient environment (Pizzini *et al.*, 1989; Lützenkirchen-Hecht *et al.*, 2009; López-Flores *et al.*, 2007), whereas in others the sample manipulator is entirely confined to a vacuum chamber to limit the effects of air absorption or scattering (Smith *et al.*, 1995; d'Acapito *et al.*, 2003). ReflEXAFS facilities have been reported for several beamlines (Ciatto *et al.*, 2016; Morina *et al.*, 2014).

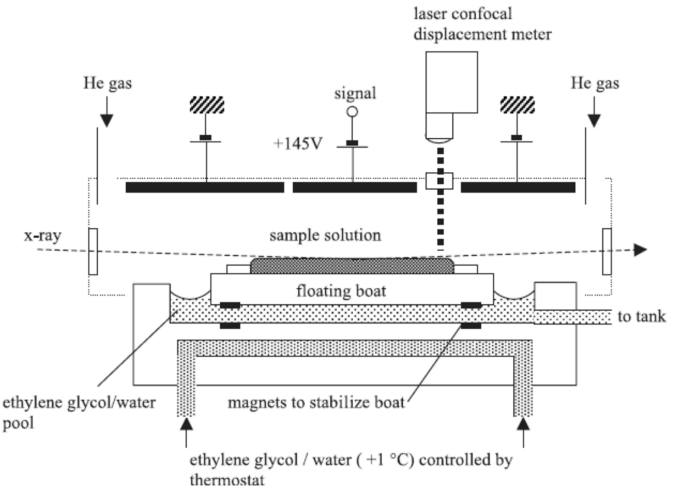

Figure 3
Sketch of a sample holder for ReflEXAFS measurements on a liquid surface with isolation from ambient vibrations. Reprinted from Tanida (2004) with permission from Elsevier.

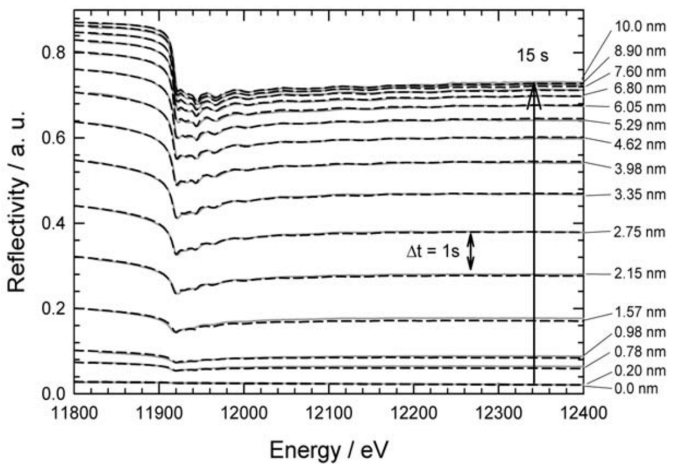

Figure 4
ReflEXAFS spectra collected at the Au L_3 edge during the formation of a gold film over a glass substrate. The film was deposited via DC sputtering and the whole process lasted 15 s. The layer thickness at each step is indicated at the side. Reprinted from Lützenkirchen-Hecht, Stötzel, Müller, Just *et al.* (2013).

ReflEXAFS on liquid surfaces comprises a particularly challenging topic. This class of experiments are of particular interest in the case of surfactants on water or floating Langmuir–Blodgett films. In this case the need to maintain a stable surface free from ripples and other mechanical instabilities led to the realization of particular experimental apparatuses.

The first aspect is that the impinging beam needs to be tilted instead of the sample, so that the sample stage is preceded by a flat mirror that bends the beam at the desired angular value. Angle-variable reflectivity is measured by changing the angle of the mirror and the height of the sample at the same time to keep the beam at its centre. The issue of ripples at liquid surfaces has been solved by using vibration-damping solutions such as a floating sample boat placed in a pool filled with a damping liquid, as described in Watanabe *et al.* (1997) and Tanida (2004) (see Fig. 3). In this case the solution is contained in a boat floating over a pool filled with a water/ethylene glycol solution. The boat is kept in place by pairs of magnets placed in its lower part and in the pool. The system is mounted over a Z-translation stage with high precision (0.5–0.2 μm) and the height is checked over time by a laser diode and, if necessary, adjusted during the data-collection cycle. This system was coupled to a detection system that could be either a total electron yield detector based on a helium chamber or a multi-element solid-state detector (which performs better in the case of highly diluted systems). A further apparatus for liquid surfaces that is operative at the DELTA storage ring and equipped with a Langmuir trough for the *in situ* formation of Langmuir–Blodgett (LB) films is reported in Lützenkirchen-Hecht, Wagner *et al.* (2013).

An activity that has been growing in importance is coupling time-resolved XAS techniques such as Quick-XAS or dispersive XAS with total reflection studies, with the aim of describing the evolution of surfaces with time. Using a typical Quick-XAS scheme (Lützenkirchen-Hecht, Stötzel, Müller & Frahm, 2013; Lützenkirchen-Hecht, Stötzel, Müller, Just *et al.*, 2013) the capability to collect data in below 1 s in a widely extended k-space has been reported. An example of such studies can be found in Lützenkirchen-Hecht, Stötzel, Müller, Just *et al.* (2013), where the formation of a gold film on a glass substrate by sputter deposition was followed *in situ* using this technique (Fig. 4).

Dispersive XAS has also been used for time-resolved studies, as in principle it opens the way to much shorter collection times (4–10 ms), although at the cost of a more limited extension of the spectrum (Abe *et al.*, 2014).

4. Conclusion

ReflEXAFS has been found to be an effective technique for the characterization of surface systems under real conditions. In spite of the severe mechanical requirements in terms of

beam stability and sample-positioning accuracy, several data-collection apparatuses have successfully been realized and operated. Measurement chambers with *in situ* sample-preparation stages, multiple-orientation data collection, holders for liquid samples and time-resolved studies are all achievements that have made this technique a unique tool in surface science.

References

Abe, H., Niwa, Y., Nitani, H. & Nomura, M. (2014). *J. Phys. Conf. Ser.* **502**, 012035.

Asakura, K., Chun, W.-J. & Iwasawa, Y. (2000). *Top. Catal.* **10**, 209–219.

Chun, W.-J., Shirai, M., Tomishige, K., Asakura, K. & Iwasawa, Y. (1996). *J. Mol. Catal. A Chem.* **107**, 55–65.

Chun, W.-J., Tanizawa, Y., Shido, T., Iwasawa, Y., Nomura, M. & Asakura, K. (2001). *J. Synchrotron Rad.* **8**, 168–172.

Ciatto, G., Chu, M. H., Fontaine, P., Aubert, N., Renevier, H. & Deschanvres, J. L. (2016). *Thin Solid Films*, **617**, 48–54.

d'Acapito, F., Davoli, I., Ghigna, P. & Mobilio, S. (2003). *J. Synchrotron Rad.* **10**, 260–264.

Iwasawa, Y. (1997). *Catal. Surv. Jpn*, **1**, 3–16.

Koike, Y., Fujikawa, K., Suzuki, S., Chun, W.-J., Ijima, K., Nomura, M., Iwasawa, Y. & Asakura, K. (2008). *J. Phys. Chem. C*, **112**, 4667–4675.

López-Flores, V., Ansell, S., Bowron, D. T., Díaz-Moreno, S., Ramos, S. & Muñoz-Páez, A. (2007). *Rev. Sci. Instrum.* **78**, 013109.

Lützenkirchen-Hecht, D., Stötzel, J., Müller, O. & Frahm, R. (2013). *J. Phys. Conf. Ser.* **425**, 092001.

Lützenkirchen-Hecht, D., Stötzel, J., Müller, O., Just, J. & Frahm, R. (2013). *J. Phys. Conf. Ser.* **430**, 012124.

Lützenkirchen-Hecht, D., Wagner, R., Bieder, S. & Frahm, R. (2013). *J. Phys. Conf. Ser.* **425**, 132006.

Lützenkirchen-Hecht, D., Wagner, R., Haake, U., Watenphul, A. & Frahm, R. (2009). *J. Synchrotron Rad.* **16**, 264–272.

Morina, A., Zhao, H. & Mosselmans, J. F. W. (2014). *Appl. Surf. Sci.* **297**, 167–175.

Oyanagi, H. (1998). *J. Synchrotron Rad.* **5**, 48–53.

Oyanagi, H., Owen, I., Grimshaw, M., Head, P., Martini, M. & Saito, M. (1995). *Rev. Sci. Instrum.* **66**, 5477–5485.

Pizzini, S., Roberts, K. J., Greaves, G. N., Harris, N., Moore, P., Pantos, E. & Oldman, R. J. (1989). *Rev. Sci. Instrum.* **60**, 2525–2528.

Shirai, M., Nomura, M., Asakura, K. & Iwasawa, Y. (1995). *Rev. Sci. Instrum.* **66**, 5493–5498.

Smith, A. D., Roper, M. D. & Padmore, H. A. (1995). *Nucl. Instrum. Methods Phys. Res. B*, **97**, 579–584.

Souchier, E., D'Acapito, F., Noé, P., Blaise, P., Bernard, M. & Jousseaume, V. (2015). *Phys. Chem. Chem. Phys.* **17**, 23931–23937.

Tanida, H. (2004). *At. Spectrosc.* **59**, 1071–1076.

Watanabe, I., Tanida, H., Kawauchi, S., Harada, M. & Nomura, M. (1997). *Rev. Sci. Instrum.* **68**, 3307–3311.