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The ESRF beamline ID26: X-ray absorption on ultra dilute sample

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The ESRF beamline ID26 is dedicated to X-ray absorption spectroscopy on Ultra dilute samples. Technical characteristics are briefly described : optics, monochromator, detectors and sample environment. Recent results will be reported in order to illustrate present performance of the beamline

Keywords: XAFS spectroscopy, Dilute samples, Instrumentation.

1. Introduction

The ESRF beamline ID26 is dedicated to XAFS studies on Ultra-diluted Samples (XAUS beamline). The spectral range 2.3-30 keV is covered. The aim of the beamline is to extract structural and electronic information on dilute samples for which the concentration of the absorbing element ranges from a few ppm up to 10 000 ppm. A wide range of applications is covered in biology, catalysis, chemistry, environmental sciences, solid state physics, etc. The beamline accepted the first users in November 1997. We give herein a brief description of the beamline and report on recent results.

2. Source Characteristics

The x-ray source consist of three planar undulators. Each of them has a magnetic period of 42 mm and a length of 1.65 meter. The undulators are inserted in high β straight section of the ring. The energy of the fundamental harmonic is 2.35 keV at the minimum gap value (16 mm). The whole energy range is obtained by exploiting different harmonics of the undulators emission spectra. Using a single undulator segment the monochromatic flux on the sample is in excess of 10^{13} photons per second at the maximum of the fundamental harmonic in the energy range 2.3-5 keV. Higher fluxes can be achieved by phasing the three undulator segments : on the fundamental harmonic at a small gap (20 mm) the gain in intensity is 3.12 (see figure 1) using narrow slits (200 µm x 200µm). It should be emphasised that for larger slits openings, the gain is reduced due to the loss of coherency between the undulators emission. The theoretical source size assuming a 1% coupling is 875 x 23 μm^2 (hor. x vert). Since the width of the undulator emission peaks is very narrow (typ. 100-200 eV FWHM), the gap scan technique is used to record XAFS spectra (Rogalev 1998). No distortions in the EXAFS spectra could be observed. This gap scan technique has been extended to the case of phased undulators.

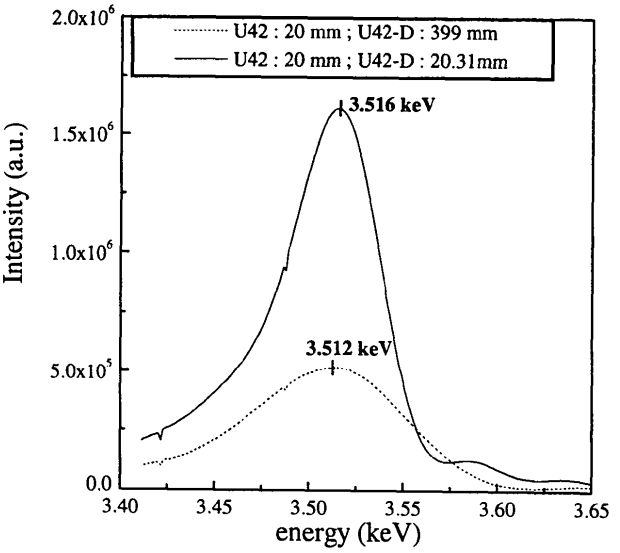

Figure 1
Phasing of two undulators : Dot line : first harmonic intensity *v.s.* energy of one undulator. Plain line : First harmonic intensity *v.s.* energy of two phased undulators. The gain in flux is 3.12.

3. Beamline optics

The design of the beamline optics is optimised in order to reduce background radiation and provide an efficient harmonic rejection. The beamline optics are described in details in these proceedings (Signorato, these proceedings), we summarise herein the optical layout of the beamline

The first component is a flat silicon mirror that deflect laterally the beam apart from the bremsstrahlung emission cone of the ring. This mirror damps the thermal power of the X-ray source and protects the other optical components. The X-ray beam is focused by two segmented piezoelectric bimorph mirrors, in a Kirkpatrick-Baez configuration, located in the monochromatic section of the beamline (Signorato, 1998). The focusing mirrors are made of fused silica. The typical focal spot size at the sample location is 200 µm (horizontal) x 15 µm (vertical). The measured photon flux on the sample is 10^{13} photons per second at 4 keV using the fundamental harmonic of the undulator emission. Smaller spot size can be achieved : 80 µm (hor.) x 7µm (vert.) with a lower flux (10^{12} photons/s). This loss in flux can be compensated by phasing the undulators. Each mirror has three reflective layers : silicon, chromium and platinum. Each of them is selected easily by translating vertically the mirrors without realigning the beamline.

A two crystal fixed exit Kohzu monochromator is inserted after the first horizontally deflecting mirror. The monochromator is equipped with two pairs of crystals Si (111) and Si (220) cooled down to -140 °C. The crystal pairs can be exchanged in less than one hour by a lateral translation of the monochromator. The stability of the fixed exit is 20 µm at a distance of 10 meters after the monochromator when changing the Bragg angle from 8° to 45° for both crystals pairs. For a 1.5 keV energy range the stability of the fixed exit is 1 µm in both directions.

4. Sample environment

At present, two experimental stations are used : a fluorescence chamber operated at room temperature and a fluorescence station equipped with a continuous flow liquid helium cryostat. The temperature range covered is 4.8 K -293 K with an accuracy of 0.05 K. The cryostat is equipped with a very accurate (1 µm) vertical sample translator and a rotary stage with an angular accuracy of 0.13 mrad. The experimental stations are installed on low vibration tables equipped with high accuracy vertical and lateral translation stages (1 µm). Reflectivity measurements are possible using the cryostat facility. A third experimental station will be installed for specific experiments for which the users bring their own sample chamber *e.g.* an electro-chemistry cell, a high pressure cell, etc.

5. Detectors

In the case of dilute samples, X-ray absorption spectra are recorded in the X-ray fluorescence excitation mode (Stern, 1979). To reach very high dilution's various difficulties have to be overcome : **i)** The fluorescence signal is buried into a large radiation background (elastic or inelastic scattering, fluorescence) originating from the sample matrix. One has to get rid of this background which degrades the fluorescence signal statistics. **ii)**. The use of the gap-scan technique may results in sudden changes in the beam intensity. This imposes requirement for a very high detection linearity so that changes due to the gap-scan can be accurately compensated. **iii)** Due to the very high flux delivered by the source, sample radiation damage may be a major source of difficulties, especially in the case of biological samples. **iv)** For a large number of experiments the photon rate is very high and the main noise source is the non-statistical noise originating from the electron beam instabilities and residual mechanical vibrations of the beamline optics. The beam intensity monitor and the fluorescence detector must have an equivalent linearity. In these conditions a careful correlation of the measurement time of the detectors allows to recover statistical noise.

Our beam intensity monitors are based on PIN silicon diodes associated to scattering or fluorescence foils in an optimised geometry in order to achieve the same sensitivity to beam instabilities as for the fluorescence detector.

For moderate dilution's (down to 50 ppm depending on the absorbing element and sample matrix composition), silicon PIN diodes associated with absorption filters are used for the fluorescence signal detection. Silicon PIN diodes are highly linear, fast detectors with a very large saturation level. Another advantage is found in the high internal gain of silicon : a photon of energy 3.6 keV will create 1000 electron-hole pairs. This is about 10 time larger than the electronic signal of ionisation chambers. This allows for the design of fast readout current amplifiers without degrading the signal statistics with electronic noise. This opens the possibility to perform quick-EXAFS or to use beam modulation techniques to improve the long term stability and the signal to noise ratio of the measurement (Gauthier 1995). The performances of these detectors will be illustrated later in this paper.

For very high dilution's. it is mandatory to discriminate in energy the fluorescence from the background radiation. Due to the severe counting rate limitations of energy resolving detectors, the development of large detector arrays (up to 100 channel) is desirable in order to restrict the data acquisition time within realistic limits. Over recent years, we have developed new energy resolving detectors : Silicon Drift Diodes (Moguiline 1997). These detectors have a very small readout anode which capacitance is independent on the detector active area. This results in the possibility of preserving good energy resolution together with high counting rates. These detectors are linked to digital filtering electronics designed at the ESRF (Goujon 1999). A first prototype, 12 channel array is used on the beamline. Figure 2 shows an EXAFS spectrum recorded from a 200 µmol/l (12 ppm) aqueous solution of cobalt acetate during a test experiment. The data acquisition time was 9 hours. It is clear that the signal to noise ratio can be improved with longer data acquisition time. The highest sample dilution which can be achieved is 5-10 ppm depending on the sample. A 35 channel array under production in collaboration with Eurisys Mesures Inc. will allow us to lower this limit.

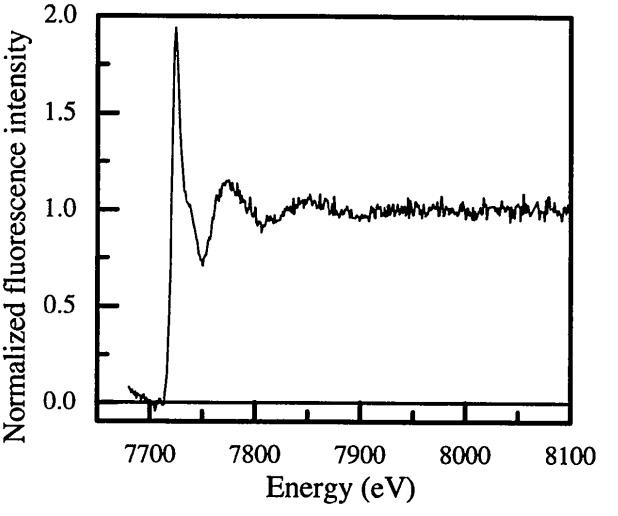

Figure 2
XAS spectrum of an aqueous solution of cobalt acetate recorded at room temperature in air with a 12 channel SDD array. The cobalt concentration is 200 µm/L (12 ppm). Data acquisition time is 9 hours

6. Quick -EXAFS on dilute samples.

The applicability of Quick-EXAFS to dilute systems can be derived from simple statistical considerations (Dobson, 1993 ; Frahm, 1993). The background radiation introduces a degradation of the fluorescence signal statistics which can be modelled by introducing the concept of the effective number of fluorescence photons N_{Fe} (Stern, 1979)

$$N_{Fe} = \frac{N_F}{1+\frac{N_F}{N_B}} \qquad (1)$$

Where :

N_{Fe} is the effective number of fluorescence photons.
N_F is the number of detected fluorescence photons.
N_B is the number of detected background photons.

N_{Fe} is the number of fluorescence photons for which the statistical noise in absence of any background would correspond to the statistical noise of the fluorescence signal in presence of the radiation background.

So, for a total intensity detector, *i.e.* with no energy resolution capability, as long as the scattering processes do not induce baseline distortion, the degradation of the fluorescence signal statistic can be compensated by a very high flux source. On the beamline ID26 the number of fluorescence photons detected by a PIN diode for a sample containing 300 ppm of iron can reach 10^8 - 10^{10} photons per second (depending on the sample matrix and detection geometry) while the background photons represents approximately 80% of the total number of detected photons. The effective number of fluorescence photons is then 2.10^7 - 2.10^9 photons per seconds. For an integration time of 10 ms, the signal to noise ratio derived from Poisson statistics is still *c.a.* 450 - 4500. This noise level can only be preserved if the detector dynamic range is large enough (at least 10^6) and the electronic noise negligible in comparison with statistical noise for short data acquisitions times.

The technical developments needed to perform quick-EXAFS with an undulator source are explained in details in these proceedings (Solé). The monochromator Bragg angle and the undulator gap are scanned simultaneously during the measurement of the EXAFS spectra. In fig 3, we reproduces the XANES spectra of a 7 mMol/l Carbonmonoxy-Myoglobin sample recorded in 3 seconds with the (220) crystal pair of the monochromator at room temperature. The detector was a silicon PIN diode operated in air with no absorption filter.

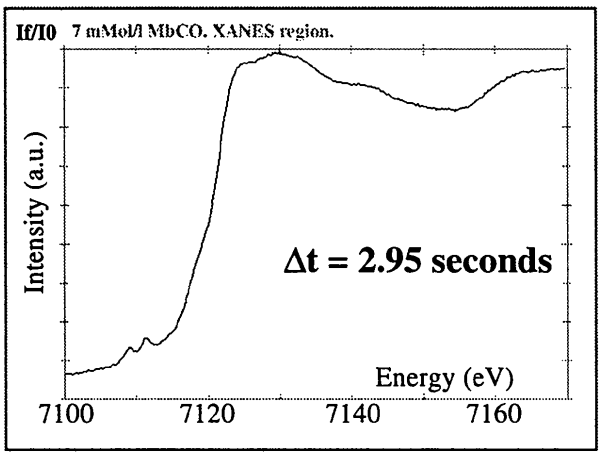

fig 3
XANES spectra of a 7 mMol/l Carbonmonoxy-Myogloby sample at the Iron K-edge recorded at room temperature. The (220) crystal pair of the monochromator was used. The detector is a PIN photodiode operated in air without absorption filter.

The use of the Quick-EXAFS technique in the fluorescence excitation mode opens the possibility to perform time resolved studies on slowly evolving diluted systems. The data acquisition system allows to perform pump and probe experiments in the stroboscopic mode. Furthermore, radiation damage during one scan is minimised due to the short exposure time. It can eventually be monitored with time. Summation of successive spectra allows to improve signal to noise ratio. Thus, XAFS studies on biological samples at room temperature are feasible. Sample dilution can reach 1mMol/l or less depending on the absorption edge and on the availability of efficient absorption filters. Another range of application is the gross mapping of heterogeneous systems using the small focal spot of the beamline optic and the excellent stability of the monochromator fixed exit.

7. Conclusions

The beamline ID26 is opened to users since November 1997. The present dilution limit is 5-10 ppm depending on sample composition. Exploiting the very high flux delivered by our undulator sources (10^{13} photons per seconds) time resolved studies can be performed on dilute samples using the Quick-EXAFS technique in the fluorescence detection mode as well as pump and probe experiments or biological XAFS at room temperature. A major improvement is the extension of the dilution ranges accessible with integrating detectors. Concentration down to 50 ppm (1 mMol/l) can be reached using silicon photodiodes associated to X-ray absorption filters. Good quality EXAFS spectra can be recorded in less than one hour. This would require at least several hours using energy resolving detectors. Due to the excellent performances of the beamline optics, gross mapping of heterogeneous samples is also feasible in a reduced data acquisition time.

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