# Piezo-QEXAFS: advances in time-resolved X-ray absorption spectroscopy

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The Piezo-QEXAFS technique is a novel tool for time-resolved X-ray absorption spectroscopy in the hard X-ray range. Monochromator components consisting of specialized tilt stages to perform fast energy scans, lightweight crystal holders, bending mechanics, and control electronics are being installed and commissioned. It is planned to perform fast EXAFS scans with time resolution in the millisecond range. With Piezo-QEXAFS all typical X-ray absorption experiments will be possible as it retains the standard linear geometry. The achieved time resolution opens interesting insights into the dynamics of phase transitions and chemical reactions. **Keywords: XAFS**; **time resolution**; **Piezo-QEXAFS.**

## 1. Introduction

X-ray absorption spectroscopy in its various forms is a common tool to examine the local structure of novel materials. The time needed for a conventional step-by-step EXAFS scan, i.e. to measure the absorption of a sample as a function of energy within an energy range with a good energy resolution, depends only partly on the data collection time needed to achieve a satisfactory signal-to-noise ratio. A large fraction of that time is spent waiting for the monochromator mechanics to move and for mechanical vibrations to settle after the movement has stopped, as well as for delays by software and the readout time of detectors. This is a rather ineffective approach and also limits the experimental possibilities to the examination of static systems.

During the last twenty years, several improvements in the experimental capabilities have been established in order to reduce the time needed to collect an EXAFS spectrum and to increase time resolution. Utilizing an energy-dispersive method (Matsushita & Kaminga, 1980, Phizackerley *et al.*, 1983, Dartyge *et al.*, 1986, Hagelstein *et al.*, 1989), it has been shown that it is possible to record all data points of an EXAFS spectrum parallel in energy on a sub-second time scale. However, dispersive EXAFS is mostly limited to transmission experiments. With standard setups, it is not possible to use for instance fluorescence mode detection efficiently which is essential for diluted samples. Recent developments, for instance at the ESRF (two publications by Pascarelli *et al.*, 1999), dramatically broadened the possibilities of the energy dispersive XAFS, which has now become a well-established tool for time-resolved investigations.

QEXAFS, developed at HASYLAB by Frahm (1989), utilizes a standard double crystal monochromator with stepper motor driven goniometers. Similar experimental setups were established at the SRS and the ESRF (Murphy *et al.*, 1995, and Als-Nielsen *et al.*, 1995). For this technique, the goniometers accommodating the monochromator crystals are continuously moving to allow for a complete EXAFS scan in less than a second. To further improve this method, we developed new crystal driving mechanics making use of piezo driven tilt tables. By using standard tilt tables, the possibility of fast time resolved XANES spectroscopy has been shown (Bornebusch, 1998 and Bornebusch *et al.*, 1999, Grundmann, 1999, Lützenkirchen-Hecht *et al.*, 1999, and Richwin *et al.*, 1999). These tilt tables are usually installed to fine-tune the Bragg angle or to perform x-ray standing-wave measurements. An improved setup is currently under development, with the actual design goal being to perform full EXAFS scans with a repetition frequency of at least 20 Hz, hence the name 'Piezo-QEXAFS'. As two absorption spectra can be recorded during one period of the monochromator movement, the achieved time resolution is twice the repetition frequency.

## 2. Implementation

### 2.1. Theory of Operation

To achieve for example a full EXAFS scan of about 1 keV at the Cu K-edge, it is necessary to change the Bragg angle of a Si(111) monochromator crystal by at least 1.5°, as can be seen in Table 1.

The standard setup is based on a double-crystal monochromator reflecting vertically. The twice reflected beam is parallel to the incoming beam; its angular direction is always independent of the Bragg angle, however, without any further precautions, it will change its height. To keep the beam offset (the difference in height between the incoming and the outgoing beam) constant during an energy scan, additional linear movements of at least one of the crystals are generally necessary. This applies to all conventional double-crystal monochromators independent of their actual implementation.

In Piezo-QEXAFS, the Bragg angle is changed by piezo driven tilt tables; the movement of the tilt tables is a rotation around a fixed axis. Any additional movement of stepper motors is to be avoided as it is inherently slow and hard to synchronize with the movement of the piezo stacks. This leads to the problem that the required linear translation cannot be performed and the beam offset changes with energy, which has to be avoided. Typical changes in the beam offset during a scan of the Bragg angle are compiled in Table 2. With about 150 mm nominal beam offset, which is the standard value at the BW1 beamline at HASYLAB, Hamburg, a variation in beam height of about 18 mm would be observed when performing the mentioned scan over 1.5° in Bragg angle. However, the change in beam offset is proportional to the absolute value of the beam offset. By minimizing the beam offset in the beamline layout it is possible to achieve a stability of the beam offset of the order of millimeters when changing the Bragg angle by the mentioned amount; this is still not acceptable for most XAFS experiments. The stability of the beam can be further improved by using a vertically focusing mirror behind the monochromator, which largely reduces any changes in the vertical beam offset.

**Table 1**
Change in vertical offset in millimeters as a function of angular range and nominal vertical offset, for scans at the Cu K-edge [12.7° using Si(111)].

| Angular range → | 0.13° | 0.50° | 1.50° |
|---|---|---|---|
| Nominal vertical offset | Change in offset [mm] | | |
| 10 mm | 0.12 | 0.41 | 1.22 |
| 50 mm | 0.41 | 2.04 | 6.12 |
| 100 mm | 0.82 | 4.08 | 12.24 |
| 150 mm | 1.22 | 6.12 | 18.36 |

  

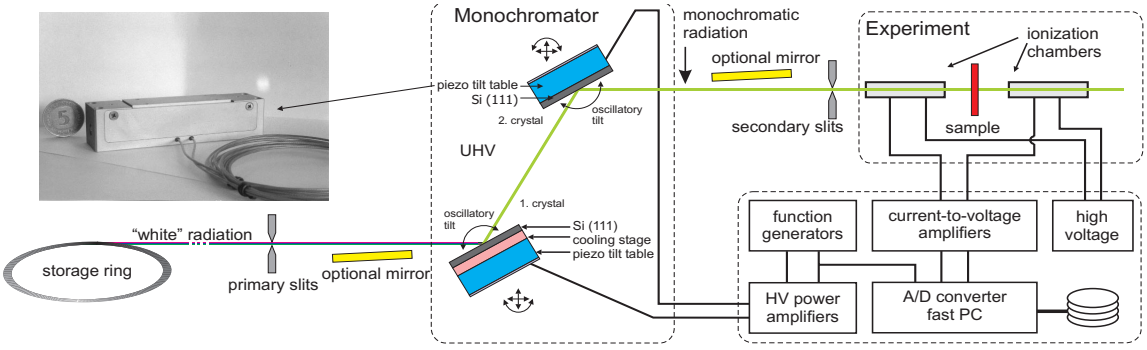


**Figure 1**
This sketch shows the setup at the BW1 beamline at HASYLAB for transmission experiments. The photograph shows the actual realization of a large range tilt table explained in the text. Note that the XAS experiment can also use fluorescence detection or make use of reflection-mode EXAFS.

To perform large angular scans using a piezo driven device, a new design for tilt tables has been employed which is patented for HASYLAB (Brüggmann & Frahm, 1996). It utilizes two piezo stacks working against each other and a lever system to enlarge the mechanical motion. In Figure 1, the realization of such a tilt table is shown in the photograph.

### 2.2. *Mechanical Set-Up and Control Electronics*

Given the considerations of section 2, it is possible to install a Piezo-QEXAFS monochromator at BW1, HASYLAB, using most of the standard equipment. In Figure 1, a schematic layout of the experiment is shown. White radiation from the x-ray undulator BW1 is passing the primary slit system from the left and a beam shutter. It can be reflected upwards by a Au coated Si mirror before it enters the monochromator. Inside the monochromator vacuum vessel, two Si(111) single crystals are attached to piezo driven tilt tables, which themselves are mounted on goniometers. The tilt tables are used to change the desired Bragg angle in an oscillatory manner. To set the center of the available angular scan range, the goniometers are rotated by stepper motors. Both goniometers are mounted on linear stages to achieve a fixed offset during an EXAFS step scan. Afterwards, the outgoing monochromatic beam can be focused on the sample using a bent Au coated Si mirror.

The BW1 standard piezo tilt tables have an angular range of about 0.13°, yielding an energy range of about 90 eV with the center of the energy range set to Cu-K. These can be replaced by special piezo tilt tables with a larger angular range of about 1.5°, which are under development. To achieve a fixed beam offset even with this large angular range, i.e. to stay within the acceptance area of the second mirror, the absolute value of the beam offset has to be as small as possible. This can be achieved by changing the angles of both mirrors to values close to the pink beam operation, where the beam reflected by the first mirror hits the second one directly.

**Table 2**
Energy scan range for a Si(111) monochromator crystal. The scan is to be performed at the Cu K-edge (8980 eV), with a fixed starting point at 8930 eV well below the edge.

| Angular scan range | Energy scan range [eV] | | |
|---|---|---|---|
| | start | end | range |
| 0.13° | 8930 | 9020 | 90 |
| 0.50° | 8930 | 9287 | 357 |
| 1.00° | 8930 | 9675 | 745 |
| 1.50° | 8930 | 10098 | 1168 |

The first crystal is indirectly water cooled and can also be bent to reduce beam divergence due to the thermal bump and therefore improve energy resolution and intensity of the monochromatized beam (Zaeper *et al.*, 2000). Both cooling and bending mechanics are optimized for low weight and high stability. The second crystal is simply a flat crystal.

For each piezo tilt table, a function generator generates a sinusoidal voltage with the desired oscillation frequency for the monochromator crystals. As each tilt table encompasses two piezo stacks working against each other, it is necessary to have two control signals with 180° phase difference. This is established by an inverting amplifier which also allows to fine-tune both signal offset and amplitude. The two control signals are then fed into high-power high-voltage amplifiers (2 x 60 W, i.e. 150 V, 400 mA) which are connected to the piezo stacks. This electronic system is exactly copied for the second monochromator crystal holder mechanics. The two function generators involved are phase-locked; their phase difference can be adjusted to 1/1000° to accommodate for different phase responses of the two mechanical systems which have to be moved synchronously.

As a feedback for the motion of the system, eddy current sensors are being used. Their resolution of about 20 arc seconds is not high enough to measure the positions within the width of the rocking curve (about 7 arc sec for Si(111) at the Cu K-edge), but is accurate enough to serve as a sensor for the total angular range as well as for the phase behavior of the system for the initial adjustment. The complete control and feedback system is controlled via GPIB from a standard PC which also measures the beam intensities during the Piezo-QEXAFS experiment. Beam intensities are measured using ionization chambers and fast current-to-voltage amplifiers with filter time constants of 10 $\mu$s. Their output is directly sampled using a fast A/D converter integrated into the PC. This device is capable of sampling 4 channels simultaneously with 200,000 samples per second at 16 bit resolution (Bornebusch, 1998, Grundmann, 1999).

## 3. Test Experiments

To test the new setup, fluorescence mode detection tests as well as time-resolved examinations of chemical reactions were performed (e.g. Lützenkirchen-Hecht *et al.*, 1999, Richwin *et al.*, 1999). In the latter, near-edge features of the species of interest were evaluated to gain information on the time behavior of the reaction. A nominal time resolution of 30 ms could be reached.

Figure 2 shows spectra of a Pt foil, demonstrating the stability and especially reproducibility of the setup. The comparison between the standard step-scan and the piezo data reveals a linear relation between the energy scale and the piezo control voltage. Furthermore, all characteristic features that are resolved by the step-scan can also be seen in the piezo data. To demonstrate the feasibility of fluorescence mode detection for diluted systems, aqueous solutions of copper sulfate have been investigated (Lützenkirchen-Hecht *et al.*, 2000).

During the test experiments no deterioration of the performance of the piezo crystal stacks has been found so far; however, as the piezo crystals are not cooled, their temperature is being monitored to prevent heat damage.

## 4. Conclusion

Piezo-QEXAFS is a novel technique to perform time-resolved x-ray absorption spectroscopy experiments. The current state allows to perform XANES spectroscopy with time resolution of the order of 30 ms, an improved setup covering a larger energy range is currently under development and being installed at BW1, HASYLAB.

This technique opens new possibilities to gain insight into the kinetics of chemical reactions, without limiting the capabilities on the experimental side. The system is also useful whenever there is a need to perform fast EXAFS scans even on static systems, for instance in combination with focusing optics to achieve high spatial resolution and perform EXAFS or XANES mappings of samples.

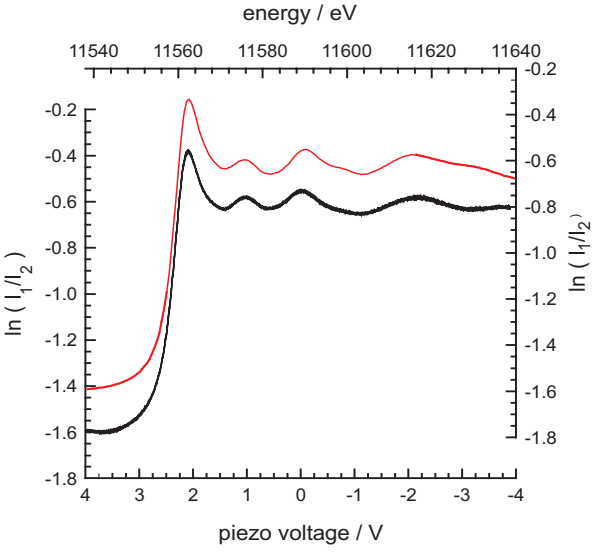


**Figure 2**
Piezo-QEXAFS scan of a Pt foil, at the Pt $L_{III}$-edge (11564 eV), scan range approx. 130 eV, 20 Hz oscillation frequency yielding 40 spectra per second. Sampling rate: 30 kHz. 20 spectra in the same scanning direction are overplotted in the lower diagram. The upper plot shows a standard step scan of the same foil.

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