Physics – Uspekhi **64** (1) 83 – 87 (2021)

INSTRUMENTS AND METHODS OF INVESTIGATION PACS numbers: 07.85.Ne, 07.85.Qe, 61.05.cj

QEXAFS method implementation using adaptive X-ray optical elements

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DOI: https://doi.org/10.3367/UFNe.2020.06.038779

Contents

Abstract. A modification of the of high-speed high-resolution X-ray absorption spectroscopy (Quick Extended X-ray Absorption Fine Structure, QEXAFS) method based on an adaptive bending element of X-ray optics is described. This technique was implemented at the Langmuir station of the Kurchatov Synchrotron Radiation Source (KISI-Kurchatov). The absorption spectrum of a model sample, bromine in a sodium bromide compound, was recorded. A recording speed up to 5 seconds per spectrum was achieved in the continuously recording regime. The method is applicable for obtaining information about both the structure and dynamics of a wide range of objects, ordered and disordered, in any aggregate state.

Keywords: time-resolved research methods, X-ray absorption spectroscopy, QEXAFS

1. Introduction

X-ray absorption spectroscopy (XAS) is employed for investigating a wide range of objects: crystalline and amorphous objects, solutions, including dilute ones, films, and nano- and bioobjects. The main condition for applying XAS is the presence of short-range order in the sample under investigation. XAS has enjoyed especially wide use since the advent of synchrotron radiation (SR) sources due to the high intensity and broad spectral range.

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Received 18 May 2020, revised 5 June 2020
Uspekhi Fizicheskikh Nauk **191** (1) 88 – 92 (2021)
Translated by E N Ragozin

Furthermore, with the development of high-power optical lasers, which were able to produce laser-plasma X-ray sources (in the late 1960s) and of bright and temporally structured synchrotron radiation back in the 1970s, proposals were advanced to investigate the dynamics of processes using X-ray diffraction, emission, and absorption [1, 2]. The processes of current research interest span a broad range of time scales, from 10^2 s for chemical catalytic reactions and electrochemical processes in battery cells to 10^{-15} s for fast transitions of excited electron states.

The time resolution limit of XAS techniques is due to the use of a monochromatic X-ray beam, whose energy is varied in the course of an experiment by adjusting the angular position of the monochromator relative to the incident X-ray beam. The monochromator positioning is traditionally effected with mechanical goniometric systems, the moving parts experiencing repetitive cycles of acceleration-deceleration during monochromator adjustment in the course of measurements. Shortening the time for monochromator adjustment signifies increasing the load on the goniometer structure, which underlies the limitation on the time response of classical methods. The time resolution of classical XAS techniques involving a step-by-step measurement mode amounts to 10^2 s and over.

Moving from the step-by-step spectrum recording mode to continuous scanning with the use of a monochromator became the first stage for XAS techniques [3], which permits achieving a time resolution of the order of 10 ms per spectrum [4]. Further improvement in the speed became possible due to the development of piezoelectric element-based monochromators: continuous vibrations of the monochromator crystal about the Bragg position neutralizes parasitic vibrations and makes it possible to carry out continuous measurements. Sinusoidal monochromator vibrations may be effected with inclined piezoelectric stages mounted on the principal goniometer, which is employed for a 'coarse' angular adjustment and remains immobile in the course of measurements. This system was first implemented at the BW1 experimental station in DESY (Hamburg, Germany) [5]. The highest vibration frequency was 111 Hz, making it possible to measure an XANES spectrum in

4.5 ms [6]. Fast fluorescence measurements were carried out in 55 ms [7], and catalytic reactions were investigated [8]. Subsequent developments were aimed at broadening the scan range, which made it possible to record the EXAFS spectrum of copper in a range of 750 eV using Si(111) monochromator crystals. The main disadvantage of this design is its relative complexity, the inability to change the vibration frequency, the limited scanning amplitude, and the hysteresis of the vibrations of the piezoceramics in use. The presence of hysteresis made it impossible to precisely determine the angular position of the monochromator crystal at any point in time. The solution lay with the use of optical sensors of the rotation angle attached to the piezo actuator. This, in turn, made the mobile part of the structure heavier and limited the vibration frequency to 100 Hz. More recently, systems were developed that were reliant on mechanical vibrational devices, which permitted varying the frequency and the vibration range of the monochromator. At present, such systems are finding wider use and are applied at several synchrotron stations: SLS (SuperXAS [9]), SOLEIL (SAMBA [10], NSLS (X18A, X18B) [11]), Spring-8 (BL33X [12]), PETRA III (P64). The disadvantages of mechanical vibrational devices is their large size and lower speed (under 50 Hz) in comparison with piezoelectric systems.

Proposed recently were methods for the fast control of X-ray beam parameters with the use of special adaptive X-ray optical elements (AXOEs) that employ longitudinal and flexural vibrations. Elements of the first type — ultrasonic longitudinal vibration resonators — have demonstrated the feasibility of fast (over 100 kHz) precision angular and spectral tuning of X-ray beam parameters over a relatively narrow range of about 100 eV [13–16]. A wider tuning range, about 500 eV, is possible to achieve using elements of the second type — hysteresis-free flexural actuators based on bidomain lithium niobate crystals with a resonance frequency of about 200 Hz [17–20]. In comparison with piezoceramic actuators, the absence of hysteresis provides a high vibration stability and makes it possible to precisely determine the angular actuator position at an arbitrary point in time. Lowering the mass of mobile elements to the requisite minimum, i.e., the element itself, improves the Q factor considerably and increases the maximum frequency and amplitude of vibrations.

In this paper, we investigate the feasibility of employing bidomain piezoactuators for a fast spectral beam tuning for the purpose of implementing the method of quick X-ray spectroscopy (QEXAFS). Selected for demonstration was a model sample, sodium bromide (NaBr) powder enclosed in a capsule transparent to X-rays. The reference bromine K-edge spectrum was obtained by traditional step-by-step scanning using the standard monochromator of the experimental station. A similar spectrum was then obtained by quick spectral X-ray beam tuning with the use of an adaptive element.

2. Experimental procedure, description of equipment and samples

Our experiments were carried out at the Langmuir synchrotron station of the Kurchatov synchrotron radiation source. The reference EXAFS spectrum from the sample under investigation was obtained by the standard technique (Fig. 1) by way of mechanical rotation of the slotted Si(111) monochromator crystal with a small gap between the reflecting planes, so that the vertical beam displacements amounted to ten micrometers in the scanning over a narrow energy range. The crystal goniometer was equipped with a feedback system with a positioning accuracy of 0.00003° (0.108 ang s). The mirrors were parallel and retained the initial beam direction at the output. The EXAFS spectrum was measured in the transmission mode. The photon flux was recorded before and after the sample with the use of IC plus FMB Oxford ionization chambers.

The absorption spectrum of the sample was recorded in a range of 700 eV at a constant increment of 1 eV with an exposure time of 1 second, which provided sufficient energy resolution and statistics. The recording mode was selected in view of the subsequent use of the resultant data as a reference for comparison with measurements made employing the adaptive element.

An experiment with the quick adjustment of synchrotron beam characteristics using the adaptive flexural X-ray optical element (Fig. 2) was performed as follows: the beam arriving from the bending magnet was collimated by water-cooled entrance slits to a size of 60×100 μm. The monochromator crystal was removed from the beam. A 100-μm-wide collimating slit was mounted at the output of the vacuum volume of the monochromator unit. Placed immediately after the slit was the beam monitor. The sample under investigation was mounted behind the beam monitor in front of the bendable element to avoid beam displacement across the sample in the course of measurements. To investigate solid samples, a compound adaptive element was mounted on the goniometer head with a special cantilever holder.

The adaptive element was employed as an analyzer crystal. Applying the control signal at the resonance frequency induced periodic actuator vibrations, its angular position varying continuously $\theta = \theta(t)$ according to the harmonic law about angle θ_0 from $\theta_{\min}$ to $\theta_{\max}$. In this case, the scanning range is $\Delta\theta = \theta_{\max} - \theta_{\min}$. As this takes place, the diffracted radiation energy also varies $E = E(t)$ in the range $\Delta E = E_{\max} - E_{\min}$.

The beam transmitted through the absorbing sample and spectrally modulated at the adaptive X-ray optical element was recorded with an X-ray SCSD-4 Radicon single channel scintillation detector. A set of two 0.2-mm-wide, 100-mm-distant slits was mounted in front of the detector. The aperture of the acceptance slits in front of the detector was selected proceeding from the width of the beam diffracted by the active element with the inclusion of its broadening due to vibrations of the flexural element. For time scanning, use was made of an Ortec Easy MCS multichannel pulse counter, which divided the continuous signal flux from the detector into N independent time intervals (channels) of short discrete duration, in which the intensity $I(n)$ was recorded in relation to the channel number n. In this case, to each n there corresponded a certain phase $\varphi(n)$ of active element vibrations and, therefore, deflection angle $\theta(n)$ and transmitted energy $E(n)$. Due to timing to the control signal, the counter could integrate the data for a preset number of repetitions of vibration cycles so as to improve the statistics.

To obtain the energy spectrum, the recorded channel numbers were converted to their corresponding transmitted beam energy values. The phase $\varphi_1 = 2\pi n_1/N$ corresponds to channel n_1. For a harmonic control signal, the phase dependence of the angle is expressed by the formula $\theta(n) = \theta_0 + \Delta\theta \sin\varphi(n)$. In this case, the energy variation of

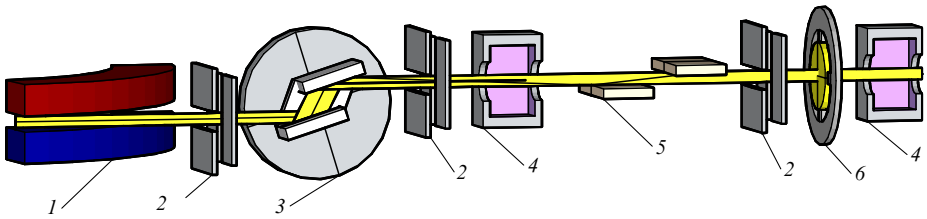

Figure 1. X-ray optical configuration of the experiment to record the EXAFS absorption spectrum with mechanical goniometer rotation: *1* — SR source, *2* — collimating slits, *3* — channel-cut monochromator, *4* — ionization chambers, *5* — total external reflection X-ray mirrors, *6* — NaBr sample.

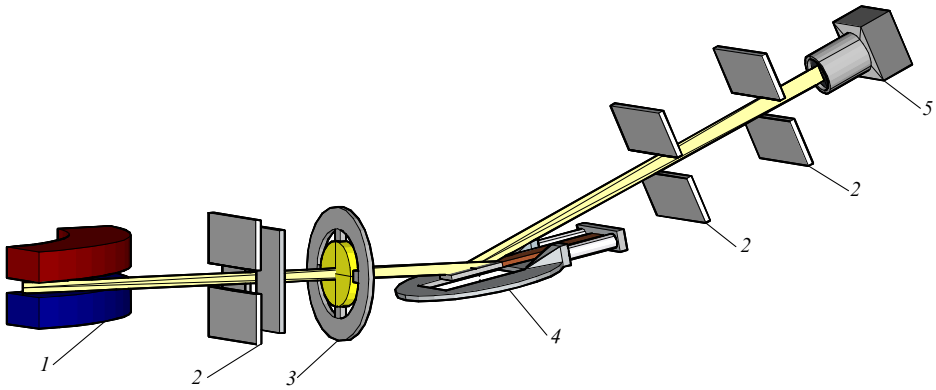

Figure 2. X-ray optical configuration of the experiment to record the EXAFS absorption spectrum by adjusting the adaptive flexural actuator: *1* — SR source, *2* — collimating slits, *3* — NaBr sample, *4* — flexural actuator, *5* — detector.

the diffracted beam is not harmonic, $E(n) = hc/\lambda = hc/2d(\theta_0 + \Delta\theta \sin\varphi(n))$, where h is the Planck constant, c is the speed of light, λ is the radiation wavelength, and d is the interplanar spacing. The energy resolution of the EXAFS spectrum obtained in this way is defined by the number of multichannel analyzer channels (of the time intervals), into which the total cycle of adaptive element vibrations is divided, as well as by the width of the diffraction reflection curve of the X-ray diffraction element (a perfect silicon crystal). The experimental data statistics were acquired using a multipass technique. The resultant energy spectra were summed up by accumulating data from several adaptive element vibration cycles, making it possible, where necessary, to acquire data over a long period of time.

It is noteworthy that the configuration of quick spectral tuning of a synchrotron beam implemented with a special cantilever holder is easily scalable and may be employed at other synchrotron stations or in laboratory instruments.

3. Experimental results

Calibrating the adaptive element yielded the energy tuning range, which was 380 eV. This was sufficient for recording the EXAFS spectrum near the K edge of Br in an NaBr sample, which was located in front of the adaptive element. The energy range may be broadened by increasing the amplitude of the control signal.

The adaptive element was set at the requisite Bragg angle using the Br absorption edge. Next, after precise alignment of the optical configuration, we carried out a series of experiments without using goniometric systems. The adaptive element vibrated at a resonance frequency $f_r = 239$ Hz, providing the recording of one spectrum during one half vibration cycle. The number of channels in the multichannel analyzer $N = 2000$. In this case, the energy increment varied from 0.2 eV at the ends of the range to 0.6 eV at the center, and could be further improved. The difference between increment values is due to the harmonic nature of adaptive element vibrations.

The limiting time required for recording one spectrum is half the actuator vibration cycle, i.e., 2.1 ms. Practically, however, the actual speed is determined by experimental configuration parameters, including the beam intensity, the capabilities of the detection instruments, and the beam collimation setup. To obtain a high-quality spectrum under our conditions, we summed up about 2400 spectra, which corresponds to a 5-second time resolution. Figure 3a shows the time evolution of transmitted radiation spectra, and Fig. 3b depicts the spectra obtained by data summation over 5 s and 500 s, the latter being used for further processing and deriving the final normalized absorption spectra.

Demonstrating the recording of the time evolution of absorption spectra of the samples under investigation, which is a set of separate spectra recorded over 500 s and which consists of 100 separate 5-s-long 'frames', opens up possibilities for investigating the dynamics of relatively slow physical processes and chemical reactions in real time. In the framework of future research, we plan to employ the proposed method for studying the dynamics of self-oscillating chemical reactions. Faster processes may be recorded due to improvement of the time resolution and the number of recorded spectra, which may be achieved by optimizing X-ray optical configurations, using more advanced detectors and a higher-intensity radiation source.

The reference absorption spectrum about the K edge of Br was recorded using the traditional method (by goniometer rotation). The measurements were performed in the range from 13,340 to 14,040 eV with increments of 1 eV. The time taken to measure one spectrum was about 1000 s, considering the hardware features of the equipment. The measured energy

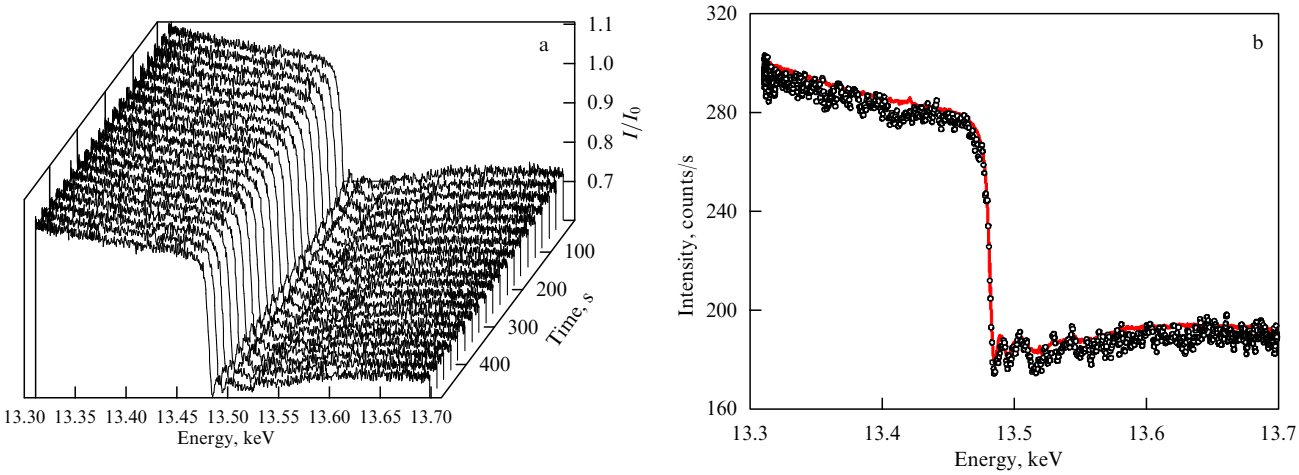

Figure 3. Spectra of transmitted radiation recorded by the QEXAFS technique: (a) evolution over 500 s (acquisition time: 25 s); (b) individual spectrum with an acquisition time of 5 s (points) and the integral spectrum accumulated in 500 s (line).

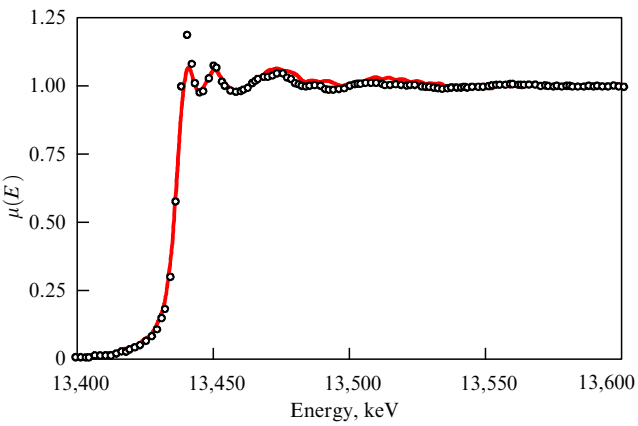

Figure 4. Normalized Br K-edge absorption spectra obtained by mechanical scanning (points) and QEXAFS (curve) techniques.

of the absorption edge $E_K = 13{,}434$ eV (the tabular value $E_K = 13{,}473$ eV).

The reference spectrum obtained with monochromator crystal rotation and the spectrum recorded using the piezoelectric flexural actuator with an acquisition time of 500 s were jointly processed using the Demeter software package. The normalized absorption spectra are plotted in Fig. 4.

Figure 5 shows the functions $k^2\chi(k)$ and the moduli of the Fourier transformants of the considered spectra.

4. Data analysis and conclusions

As is clear from a spectrum comparison (Fig. 5), the positions of the absorption edge agree nicely, as do the main fine structure peaks of the spectrum in some domain behind the absorption edge. The functions $k^2\chi(k)$ also coincide well in the domain $k > 3$. Next, the noise level of the function of the QEXAFS method increases, supposedly due to a shorter scanning range. The moduli of Fourier transformants coincide in the domain of the first coordination sphere. The resultant spectra are characterized by the same feature sets. The position and the profile of the absorption edge coincide for the mechanical and QEXAFS spectra, which also testifies that the energy resolution of the proposed technique is sufficiently high. A signal-to-noise ratio sufficient for the

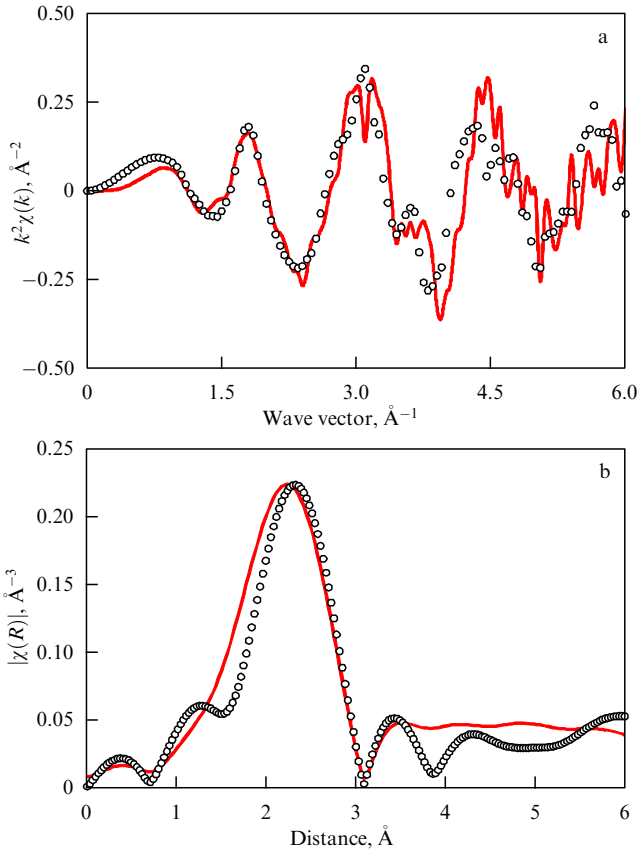

Figure 5. (a) Functions $k^2\chi(k)$ derived from experimental absorption spectra for mechanical (points) and QEXAFS (solid line) methods; (b) corresponding Fourier transformant moduli $|\chi(R)|$ for EXAFS spectra.

analysis of spectral fine structure features was achieved during a 500-s acquisition time. The divergence of the spectra in the domain farther than 100 eV from the absorption edge may be attributed to the QEXAFS spectrum distortion by the higher harmonics of diffracted radiation, which were not rejected in the one-crystal configuration of the QEXAFS method.

Therefore, in this paper, we introduced and successfully tested a method (QEXAFS) for recording absorption spectra

involving adaptive X-ray optical elements, which is characterized by a high speed (down to milliseconds). This method may underlie *in situ* investigations of chemical reactions. A two-fold advantage in speed relative to the traditional method was obtained in the course of testing, the limitations in speed being largely related to the intensity of the beam in use.

We plan to further improve the quality of the resultant spectra and improve the speed up to the time resolution of about 2 ms theoretically possible for this adaptive element. This will be achieved by upgrading the X-ray optical configuration, in particular by using detectors with a faster response and a higher transmission capacity, a double-crystal monochromator based on flexural piezoactuators, and a higher-intensity research beam.

Acknowledgments
This study was supported by the Russian Foundation for Basic Research (grant nos 18-32-20108 mol_a_ved and 19-29-12037 mk) in relation to the development of beam parameter control methods and data processing and by the Ministry of Science and Higher Education of the Russian Federation in the framework of performing work on the State Assignment of the Federal Scientific Research Center Crystallography and Photonics of the Russian Academy of Sciences in relation to testing adaptive flexural elements. The work was performed with the use of equipment from the Center for Collective Use of the Federal Scientific Research Center Crystallography and Photonics with support from the Ministry of Science and Higher Education (Project RFMEFI62119X0035).

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