

# Investigation of the dynamics of the Belousov–Zhabotinsky reaction by time-resolved X-ray absorption spectroscopy using adaptive X-ray optical elements

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We performed an in-situ study of the Belousov–Zhabotinsky self-oscillatory chemical reaction using the developed technique of time-resolved X-ray absorption spectroscopy implemented with the help of adaptive X-ray optical elements (AXOEs). The dynamics of the K-edge absorption of bromine (Br), which is found in various substances during the reaction, were monitored. We carried out sequential recordings of the K-edge absorption spectrum of bromine in the vicinity of 275 eV with a spectral resolution of better than 1.4 eV, an accumulation time of 1 s per spectrum, and a repetition rate of 0.71 Hz. The acquired series of spectra allow us to trace the kinetics of the Belousov–Zhabotinsky reaction, in particular, the kinetics of chemical self-oscillations taking place in it.

**Keywords:** time-resolved X-ray spectroscopy, adaptive X-ray optics, bending actuator

## 1. Introduction

X-ray research methods are a unique tool for obtaining structural information for a wide variety of objects. Even

when working with substances that do not have a crystalline structure—amorphous substances, nano- and biological objects, liquids—there are X-ray methods that make it possible to study the structure of the immediate environment of the sample's atoms. They include X-ray absorption spectroscopy (XAS). The classical implementation of the XAS method is based on sequential energy variation of a monochromatic X-ray beam using goniometric mechanical systems, whose speed is seriously limited, and therefore the classical method is hardly applicable for studying dynamic processes. The development of methods and technical implementations of such studies is still relevant today.

One of the approaches to increase the performance of X-ray spectroscopy methods is the development of X-ray monochromators based on piezoelectric actuators [1]. However, the piezoceramics traditionally used in such monochromators have a low oscillation frequency (less than 50 Hz) and hysteresis, which affects the repeatability of monochromator movements.

As an alternative approach, a method for fast modulation of the spectral characteristics of an X-ray beam using adaptive elements based on bending actuators, so-called adaptive X-ray optical elements (AXOEs), has been proposed and is being actively developed [2–5]. These actuators are manufactured using a special technology [6, 7] involving bidomain LiNbO<sub>3</sub> single crystals. The operating principle of the proposed AXOEs is described in detail in Ref. [8] and is similar to that of X-ray piezo monochromator models. However, an AXOE based on bidomain lithium niobate single crystals (LiNbO<sub>3</sub>) is advantageously characterized by the absence of hysteresis, which is critical for precision studies, and is also characterized by the possibility of easy integration into various X-ray optical configurations.

The fundamental possibility of implementing the proposed method was demonstrated using a laboratory X-ray source [9] and a synchrotron source [10] using a static model NaBr object. The K-edge absorption spectra of bromine were obtained by AXOE-assisted tuning of the energy of a monochromatic beam in the range of 13,319–13,700 eV.

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However, it was not possible to evaluate the achievable time resolution of this method, because the object under study was static.

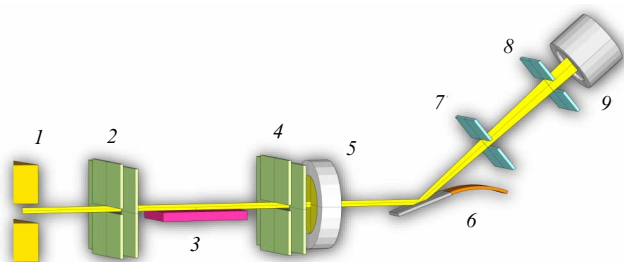
The goal of the next experiment was the practical application of the capabilities of AXOE-assisted time-resolved absorption spectroscopy and the assessment of the achievable time and spectral resolution of the technique. The self-oscillating chemical reaction of Belousov–Zhabotinsky (B–Z) was chosen as a model subject, since self-oscillating processes significantly extend the period of the dynamics of the chemical reaction and are periodic processes, which simplifies the analysis of the results.

The Belousov–Zhabotinsky reaction comprises a whole class of chemical reactions that occur in an oscillatory mode, in which some reaction parameters, such as color, local component concentrations, and temperature, change periodically and make up a complex spatiotemporal structure of the reaction medium. The first such reaction, the oxidation of citric acid with potassium bromate in an acidic medium in the presence of a catalyst — cerium ions  $\text{Ce}^{+3}$  — was discovered by Belousov in 1951 [11] and was the first to demonstrate the self-organization of self-oscillatory processes in an inorganic chemical system. This composition of reagents was also used in the present work.

The B–Z reaction is of scientific interest as a basic model of self-organization processes in inorganic and organic systems. In addition, similar self-oscillatory mechanisms have been found in a variety of media: for example, self-propagating high-temperature synthesis proceeding in solids in the solid state. Many scientific studies, including those using X-rays, have been devoted to the study of the B–Z reaction. In Ref. [12], ultraviolet and X-ray radiation absorption in the reaction volume was shown to depend on the phase of chemical self-oscillations, which indicates the applicability of X-ray methods to the study of the B–Z reaction.

## 2. Methodology of QEXAFS implementation and experimentation

The experiments were carried out at the ‘Langmuir’ beamline station of the Kurchatov Synchrotron Radiation Source (KISI-Kurchatov). The experimental X-ray layout repeated (see Fig. 1) that in Ref. [9], but a number of technical improvements were made. In particular, a new precision optical line of slits and the detector was assembled, and algorithms for processing the resultant experimental data were optimized.



**Figure 1.** X-ray optical configuration of the experiment: 1 — SR source; 2, 4, 7, 8 — collimating slits; 3 — total external reflection mirror; 5 — chemical cell; 6 — AXOE; 9 — detector.

According to the AXOE-assisted technique of recording absorption spectra, which was described in more detail in Ref. [9], the adaptive element was set to the Bragg angle corresponding to the energy for the K absorption edge of Br (13.47 keV). AXOE resonant operating mode was used [13, 14], the frequency of the control signal was 86 Hz, and after calibration the angular tuning range was determined to be 1026 arc s, which corresponds to the spectral range of 275 eV.

To carry out the B–Z reaction, a specialized chemical cell was designed and assembled. A hydraulic system was provided for the remote introduction of reagents into the active volume of the cell, which made it possible to start the reaction *in situ* during sequential recording of absorption spectra. The active volume was limited to 4 mm along the beam axis by Capton windows. In the beamline layout, the cell was placed before the AXOE to minimize the X-ray beam width on its surface.

The B–Z reaction was carried out with the basic composition of reagents, some of which were preliminarily introduced into the reactor volume: an aqueous solution of potassium bromate ( $\text{KBrO}_3$ ), cerium (III) sulfate  $\text{Ce}_2(\text{SO}_4)_3$ , and citric acid  $(\text{HOOC})\text{C}(\text{OH})(\text{CH}_2\text{COOH})_2$ . This combination of reagents remains stable until the introduction of an oxidizing agent — sulfuric acid ( $\text{H}_2\text{SO}_4$ ) — and the onset of the B–Z reaction. Sequential recording of absorption spectra began before the introduction of the oxidizing agent in order to record the initial spectrum of Br. Then, upon adding the oxidizing agent, the dynamics of the Br spectra were recorded *in situ* at the moment of the onset of the chemical reaction, and further, during its self-oscillations.

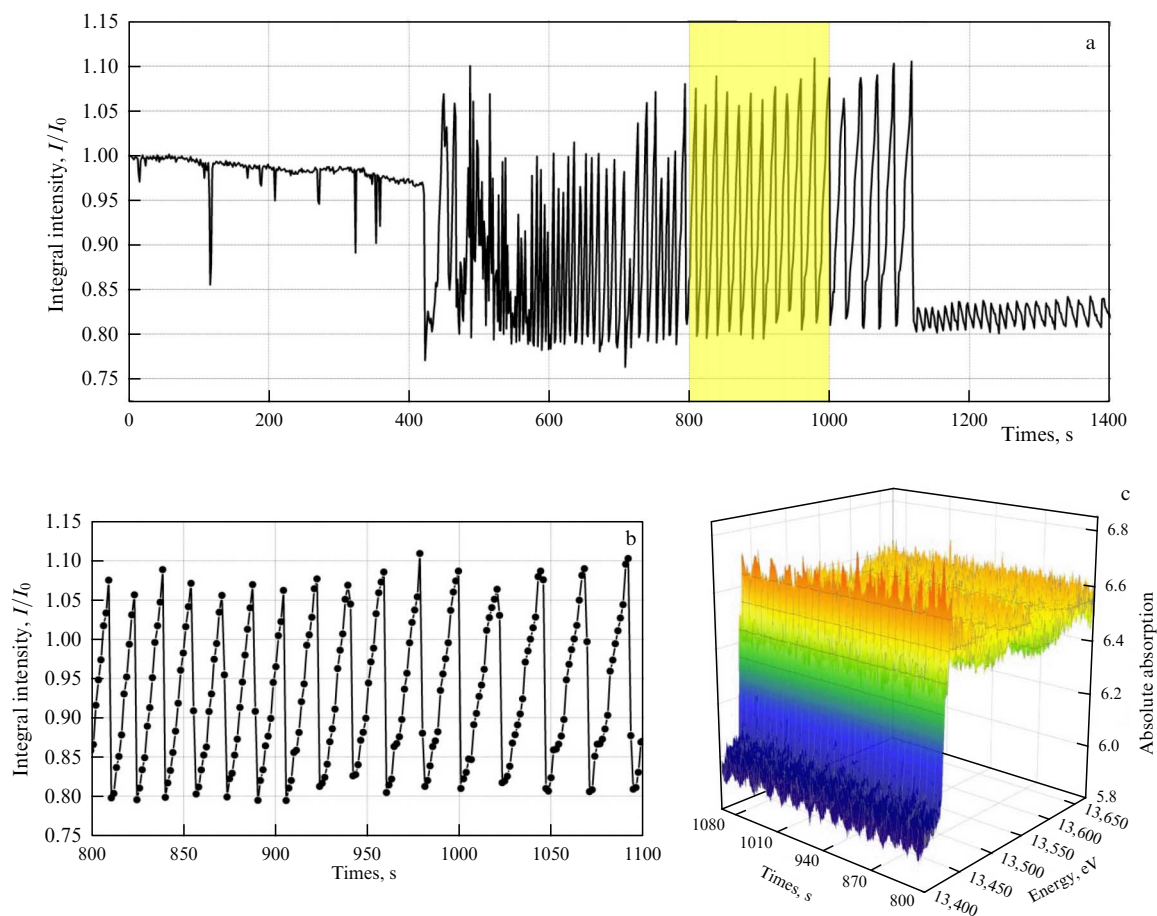
Therefore, a series of B–Z reactions were carried out during the experiment. After setting up the X-ray optical layout and injecting the first part of the reagents into a chemical cell, the bromine K-edge absorption spectra sequential recording was started, similar to the method outlined in Ref. [9]. The optimal recording mode was selected, whereby an acceptable signal-to-noise ratio and energy resolution of the resulting spectra are achieved for a minimum accumulation time. The data accumulation time for one spectrum was 1 s, while the final spectral recording frequency (time resolution) was 0.71 Hz, since  $\sim 0.4$  s was required to restart the multichannel counter. To measure each spectrum, 600 channels of a multichannel counter were used, which is equivalent to an energy resolution of the spectra of less than 1.4 eV.

Each B–Z reaction carried out was monitored *in situ* from the moment the first reagent was injected, some time before the remote initiation of the reaction, and for a long period after its onset. This approach made it possible to monitor the transient process of the onset of the B–Z chemical reaction, as well as the characteristic self-oscillations that arise spontaneously after the onset of the reaction.

## 3. Results and discussion

The initial data of the presented technique are a series of transmission spectra recorded in the range of 13.44–13.71 keV; the accumulation time of an individual spectrum is 1 s at an acquisition frequency of 0.71 Hz.

Based on information about the change in the X-ray radiation absorption in relation to the phase of chemical oscillations in the B–Z reaction, for a quick analysis of the results, we considered the time dependences of the total intensity of transmitted X-ray radiation for a series of B–Z reactions. More precisely, considered was the intensity of a



**Figure 2.** (a) Dynamics of the intensity of transmitted polychromatic (13.44–13.71 keV) radiation for the B–Z reaction. (b) Intensity dynamics over a period of 800–1000 s. (c) Series of absorption spectra of the K-edge of Br in the B–Z reaction over a period of 800–1000 s.

polychromatic X-ray beam passing through the volume of the chemical cell in the spectral range of 13.44–13.71 keV.

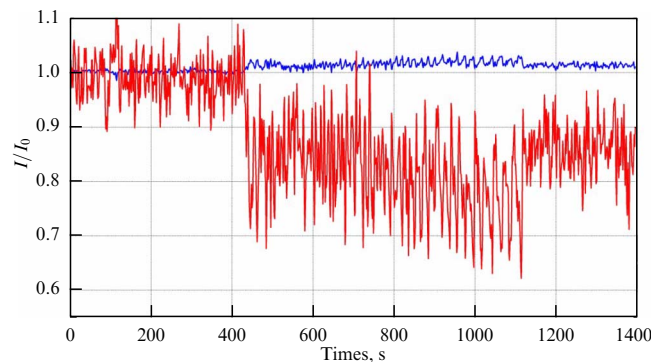
Due to the random nature of the formation of self-oscillation waves and their propagation in the area of exposure to the X-ray beam, the B–Z reactions cannot be considered a reproducible process. Despite the automation of the introduction of reagents into the chemical cell, the dynamics of the B–Z reactions vary greatly; in some cases, no self-oscillations were observed; in others, they occurred aperiodically.

Upon analyzing all of the B–Z reactions performed, the one with the most pronounced periodic self-oscillations was selected. The dynamics of the integral intensity for this reaction are shown in Fig. 2a. Considered in detail is the 800–1000-s period of time with stable periodic self-oscillations. Figure 2b shows the dynamics of the integral intensity over the specified period of time.

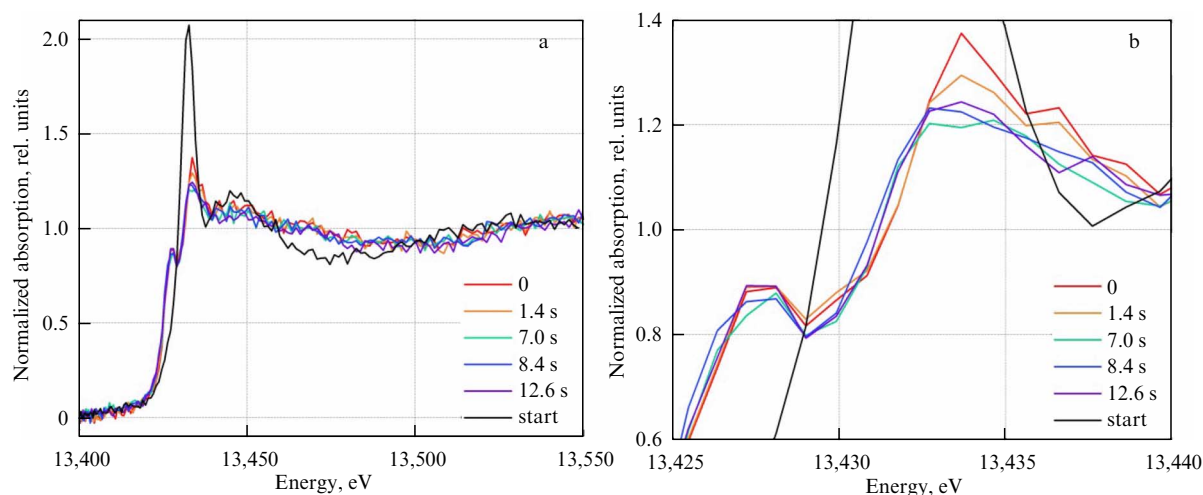
Similar results, i.e., the *in situ* dependence of the intensity of transmitted X-ray radiation during the B–Z reaction, were obtained earlier in Ref. [11]; however, when using the developed X-ray spectroscopy method, each point in Fig. 2a corresponds to the full absorption spectrum of the K-edge of Br. Figure 2c shows the recorded series of absorption spectra over a period of 800–1000 s.

When analyzing the series of Br absorption spectra before their normalization, it was found that the dynamics are present both in the pre-edge ( $E_p = 13.4$  keV) and in the extended region of the spectrum ( $E_d = 13.65$  eV). Since these dynamics will be leveled after normalization of the

absorption spectra, the time dynamics of the pre-edge absorption level  $\mu(E_p)$  and Br absorption step:  $\mu(E_p) - \mu(E_d)$  (Fig. 3) were studied. These dynamics do not relate to the fine structure of the absorption spectrum and do not contain information about the environment of the bromine atom during the reaction, but reflect the course of other chemical processes in the B–Z reaction. Both dependences correlate with the dynamics of the integral intensity of transmitted radiation (Fig. 2a) and demonstrate periodic oscillations in the 800–1100-s range. The amplitude of absorption oscillations in the pre-edge region does not exceed 3%, while the oscillations of the Br absorption step exceed 20%.



**Figure 3.** Dynamics of the intensity of pre-edge absorption (blue curve) and Br absorption step (red curve) during the B–Z reaction.



**Figure 4.** (a) Normalized spectra of the K absorption edge of Br before the onset of the reaction (black curve) and at different instants of the self-oscillation period; (b) dynamics of the main K-edge absorption peak of Br.

The absorption spectra were then normalized to analyze the fine structure dynamics during the B–Z reaction. The state of the system before the onset of the reaction and its dynamics during one period of self-oscillation were examined in detail. To improve the statistics and increase the signal-to-noise ratio, we studied the averaged statistics for five successively recorded spectra before the onset of the reaction, as well as for five successive periods of reaction oscillations. The resultant averaged absorption spectra are shown in Fig. 4.

A noticeable change in the shape of the absorption spectrum of the K-edge of Br is observed after the start of the B–Z reaction. The main peak bifurcates, which corresponds to the presence of Br in the solution in several states simultaneously. The dynamics of the absorption spectra fine structure is also observed during the self-oscillation process: in Fig. 4b it is shown that during one oscillation period the main peak intensity decreases and the peak itself shifts towards lower energies. The maximum shift is achieved at the 7th–8th second of the oscillation period (full period 15 s), and then the peak shifts to its original shape.

#### 4. Conclusions

The practical application of the fast X-ray absorption spectroscopy method using adaptive X-ray optics elements (AXOEs) was demonstrated by the research of the self-oscillatory Belousov–Zhabotinsky chemical reaction. *In situ* absorption spectra of the Br K-edge were obtained in the range of 13.44–13.71 keV with an acquisition time of 1 s per spectrum and a recording frequency of 0.71 Hz. This result allows us to draw conclusions about the dynamics of the close environment of Br atoms during the B–Z reaction.

The implementation of a time-resolved X-ray absorption spectroscopy technique at a synchrotron source required the integration of one AXOE into the beamline optical layout, which indicates the possibility of carrying out comparable measurements at similar or more advanced synchrotron sources.

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