Operation of a bending magnet beamline in large energy bandwidth mode for non-resonant X-ray emission spectroscopy

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A B S T R A C T

Two new operation modes, “pink beam” excitation, which has the energy bandwidth defined by X-ray mirrors and filters, and “broadband beam”, where the energy bandwidth is defined by the reflection from a multilayer monochromator, were implemented at the SuperXAS beamline of the Swiss Light Source (SLS). These setups allow measuring non-resonance X-ray emission spectra (XES) with 2–3 orders of magnitude higher incident flux than non-resonant XES measurements with a monochromatic incident beam. For the broadband beam mode, a Mo/Si multilayer structure was designed, with which the energy can be tuned in the 5–17 keV range. The multilayer demonstrates a relatively large energy bandwidth of 4 ± 0.2% through the whole energy range and a reflectivity of 23–60%, which increases with energy. We show that by using pink beam mode one can investigate the electronic structure of photocatalytic intermediates through time-resolved core-to-core XES experiments of diluted samples with a concentration of the element of interest of ~1 mM. Broadband beam mode is optimal for valence-to-core XES experiments and allow to avoid the excitation of additional KLβ satellites that can complicate the interpretation of spectra.

Introduction

X-ray emission spectroscopy (XES) is a technique that is complementary to X-ray absorption spectroscopy (XAS) and provides valuable information on the local electronic structure of materials and their chemical composition. In contrast to absorption spectroscopy, which probes the empty electronic states, an emission spectrum reflects the density of occupied electronic states. XES is a powerful tool to study the electronic structure of the element of interest in crystals, dissolved compounds, amorphous samples and other non-crystalline forms of materials [1].

There are three regimes in which X-ray emission spectra can be acquired: the resonance, the off-resonance, and the non-resonance XES regime. Resonance XES, also known as RIXS (resonant inelastic X-ray spectroscopy) contains detailed information about the electronic structure of the material. Monochromatic excitation with energies around the X-ray absorption edge is required for these measurements [2–5]. Off-resonance XES also uses monochromatic excitation, but at one incident energy point significantly below the absorption edge. High energy-resolved off-resonant XES spectra (HEROS) reflect the projected empty density of states similar to the X-ray absorption near edge structure (XANES) [6]. Such an approach is promising for applications at X-ray free-electron lasers and for measuring samples in fluorescence mode free of self-absorption effects [7]. Non-resonance XES is the method with the longest history. The main emission lines (Kα\textsubscript{1,2}, Kβ\textsubscript{1,3}) are sensitive to the spin and oxidation state of the studied element. The two orders of magnitude weaker satellites of Kβ emission lines correspond to the transitions from valence states to the core level and are sensitive to the type of ligand surrounding the absorbing atom [8–10]. At synchrotron facilities the main emission lines from concentrated samples are measured routinely, such measurements are even possible with laboratory-based spectrometers [11–13]. Experiments that are more challenging and require high flux are valence-to-core XES and time-resolved (laser pump – X-ray probe) XES experiments for which...
samples are often diluted to achieve appropriate absorption of the laser beam.

Synchrotron radiation facilities covering the hard X-ray range typically have at least one beamline equipped for X-ray emission measurements, often in combination with XAS. The combination of XAS and XES allows performing all types of XES experiments and other photon-in-photon-out techniques, for example, high energy resolution fluorescence detected (HERFD) XAS or X-ray Raman scattering experiments. On the other hand, the flux of the incident radiation is limited by the monochromatic incident beam, which has a bandwidth of ~0.01%. Undulator-based beamlines at high-energy synchrotrons, for example, ID26 (ESRF, Grenoble, France), have a higher monochromatic flux and are therefore more efficient for XES measurements. Nevertheless, in application to non-resonance XES experiments, the bending magnet beamlines can profit from the large energy bandwidth of the source and thus deliver incident X-ray fluxes comparable to those achieved at undulator stations.

At synchrotron facilities, there are 3 types of X-ray emission spectrometers available that are used for XES measurements in the energy range 4–12 keV with Johann [14], Johansson [15] and von Hamos geometry [16]. The Johann-type spectrometer uses a spherically bent crystal, which together with the sample and detector is located on the so-called Rowland circle (typically with a 1 m diameter). The crystal reflects and focuses photons of one emission energy from the sample to the point detector. To scan the emission energy, the crystal and detector need to be moved simultaneously so that both devices remain constantly on the Rowland circle. The sample position is fixed. Spectrometers of this type are available at many synchrotron facilities [17–20]. Unlike the Johann-type geometry, Johansson-type spectrometers are characterized by negligible geometrical contributions to the energy broadening because of the use of diffraction crystals with Bragg planes which are not parallel to the crystal surface. Thanks to this property, Johansson-type spectrometers can be used with larger crystal apertures and they demonstrate high energy resolution at relatively low Bragg angles and thus may efficiently explore Si and Ge crystals especially at tender X-ray energies. At synchrotrons, such a spectrometer was recently introduced at BL22-CLÆSS (ALBA, Barcelona, Spain) [21,22], for tender X-rays at ID26 (ESRF, Grenoble, France) [23] and will be commissioned soon at the BALDER beamline (MAX IV, Lund, Sweden) [24]. Von Hamos-type spectrometers use cylindrically bent crystals that disperse photons emitted by the sample on a position-sensitive detector in the flat direction of the crystal and focus the X-rays in the bending direction. All points of the X-ray emission spectrum are measured simultaneously with such an approach without the need for any mechanical movements. Therefore, von Hamos spectrometers are suitable for time-resolved experiments. At synchrotron facilities this type of spectrometer is implemented at the SuperXAS beamline (SLS, Villigen, Switzerland) [25], P64 (PETRA III, Hamburg, Germany) [26], 7ID (APS, Argonne, IL, USA) [27] among others; and at X-ray free-electron lasers: for example, ID26 (ESRF, Grenoble, France), have higher monochromatic flux and are therefore more efficient for XES measurements. Nevertheless, in application to non-resonance XES experiments, the bending magnet beamlines can profit from the large energy bandwidth of the source and thus deliver incident X-ray fluxes comparable to those achieved at undulator stations.

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We explored the use of larger energy-bandwidth operation mode for the incoming X-ray beam to increase the flux for time-resolved non-resonance XES measurements, with potential applications for i) time-resolved non-resonance XES experiments, in particular for pump–probe spectroscopy, and ii) steady-state valence-to-core XES measurements. The SuperXAS beamline is already equipped with the required infrastructure for pump–probe experiments including lasers that have been used for pump–probe X-ray absorption spectroscopy [32–34]. There are two potential side effects of excitations by radiation with a large energy bandwidth: i) if the spectrum of the incident radiation overlaps with the range of the XES measurements, the elastically scattered incident photons will contribute to the background signal, ii) K-shell ionization by high energy photons can lead to knock-out and shake-off processes resulting in additional ionization of the L-shell of the scattering atom. As a consequence, additional satellite features in the emission spectra, known as KL satellites, can appear in the non-resonant XES spectra [35]. In order to control these effects, we consider two operation modes with “pink” and “broadband” beams. In the pink beam mode, the radiation spectrum is defined by the cutoff of X-ray mirrors (limiting higher energies to ~17 keV by the Rh coating of the collimating and focusing mirrors) and by using additional absorbing filters (limiting low energies). As the lowest limit at the SuperXAS beamline, the reasonable intensity of X-ray starts at around 5 keV. For the broadband beam, we added the reflection from multilayer optics, which defines a narrower energy bandwidth.

We present a modification of the optical scheme at the SuperXAS beamline to enable pink and broadband beam experiments by using a compact experimental Mo/Si multilayer monochromator, which is installed in the experimental hutch of the SuperXAS beamline. Using this setup, we investigated i) the lower concentration limit of acquiring non-resonant Kβ XES spectra of 3d elements (Co in our test) at which Kβ main lines can be efficiently measured and ii) the possible influence of KL satellites on valence-to-core XES spectra.

**Methods**

**Growth parameters of the multilayer**

The Mo/Si multilayer was grown by an ion-beam sputtering deposition setup based on a 12 cm RF Kaufman ion source with RF neutralizer in IK BPU (Kaliningrad, Russia) [36]. As a substrate, we used a 50 × 50 × 3 mm Si(100) commercial plate (STV-Zelenograd, Rms ~1 nm). This substrate was cleaned in an ultrasonic bath for 15 min in a mixture of isopropanol and acetone, then washed for 1 min in deionized water, and dried by flowing nitrogen. The deposition of the multilayer started with a basic pressure in the vacuum chamber of 2 × 10⁻⁷ mBar. Pure Mo (99.95%) and Si (99.99%) targets were sputtered by the direct Ar-beam with an energy of 800 eV maintaining a constant pressure of 1–2 × 10⁻⁴ mBar in the chamber at room temperature. Both targets were mounted on a water-cooled holder, and the Si(100) substrate was fixed on a metallic plate connected to the water cooling system. 200 pairs of Mo and Si layers were deposited using a quartz thickness control system connected to a pneumatic shutter, which cut off samples from the main chamber volume when the programmed thickness of 1.3 nm for Mo (or 2.2 nm for Si) was achieved. Temperature fluctuations on a quartz sensor and delay in shutter actuation can produce uncertainties in the thickness of the deposited layers. After initial tests, we increased the shutter delay to obtain a mean error of 1 Å for 10 Mo/Si pairs which corresponds to optimal Bragg peak widening. The final pressure in the pneumatic system is 2.5 Bar (common pressure is 4 Bar).

**Characterization of the multilayer**

X-ray reflectometry (XRR) of the multilayer optics was performed using a Bruker D8 Discover diffractometer (λ = 0.154 nm), the parameters of period thickness and boundary roughness were evaluated with the Bruker Diffrac.Leptos and IMD software [37]. The energy bandwidth and the reflectivity of the multilayer were measured at the SuperXAS beamline of the SLS by monitoring the X-ray elastic scattering from a Mylar foil placed after the multilayer or from the elastic scattering of air using a silicon drift detector (SDD, Vortex). The polychromatic X-ray beam resulting from a 2.9 Tesla bending magnet was collimated using a Rh coated mirror and focused by a Rh-coated toroidal mirror. The incidence angle for mirrors was 0.22° (3.9 mrad), which resulted in a cut-off energy of ~17 keV. The reduction of the low-energy component of the beam was performed by a 5 mm carbon filter.
For broadband experiments, the Mo/Si multilayer was placed in a vacuum chamber, which was evacuated to $10^{-2}$ mBar, and fixed on a water-cooled Cu block. The alignment of the multilayer was performed using two degrees of freedom: rotation within a few degrees limit and vertical translation. The pink beam was focused to a size of 150 µm vertical and 250 µm horizontal at the sample position. The beam size was measured using a CCD camera that images a YAG crystal (so-called ‘X-ray eye’ setup) protected by a 1 mm Al filter. The same camera was used to find the zero angle of the multilayer and to measure the angle between the pink beam (which can be seen if the multilayer is moved out of the beam path) and the beam reflected from the multilayer. A radiation stability test was performed using the same scheme and by using the maximal achievable incident X-ray flux. The multilayer was fixed at an angle corresponding to an energy of 11.3 keV. The X-ray intensity and energy spectrum of the multilayer were measured before and after 8 h of X-ray exposure.

**XES measurements**

XES spectra were measured at the SuperXAS beamline of the SLS using a von Hamos type spectrometer. Details about the spectrometer were reported previously [25,38]. As an energy dispersing element for measuring Fe Kβ spectra, we used a segmented Si(531) crystal of cylindrical shape with a focusing radius of 25 cm. For Co Kβ spectra we have used a Si(311) crystal. Energy calibration of Fe (Co) XES spectra was performed using the maximum of the K main line at 7059.3 eV (7649 eV) for Fe (Co) foil. A Pilatus 100 K detector (172*172 µm² pixel size) was used as a position-sensitive detector [39].

**Samples**

A [CoBr(tpyOH)]Br catalyst (tpyOH - 2-bis(2-pyridyl)(hydroxy)methyl-6-pyridylpyridine) was synthesized according to the published procedure [40] and dissolved in a water-based buffer solution (HBF₄, pH 8.5) with triethanolamine. The concentration of [CoBr(tpyOH)]Br was 2 mM for the measurements as a reference and 0.8 mM in the multi-component photocatalytic system. Additionally, before adding the catalyst, the photosensitizer [Re(bipyridine)(pyridine)(CO)₃](OTf)₂ 0.25 mM was added to the buffer solution as part of the multi-component photocatalytic system and was sonicated for one hour to be dissolved.

N₅,N₅,N₅,N₅,N₅-(Tetrafluorouridoborate)bis[μ-(2,3-butanedionedi- imato)]cobalt(II) dehydrate (Co(II) cobaloxime) was purchased from Strem Chemicals Inc and was dissolved at a concentration of 2 mM in demineralized water. Meso-Tetraphenylporphyrin-Fe(III)-chloride (FeTPPCl) was acquired from Por-Lab, Porphyrine-Laboratories GmbH. 20 mg of the sample was diluted with cellulose (Sigma Aldrich) in a ratio of 1:2 and prepared in a pellet with a diameter of 1.3 cm.

**Results and discussion**

**X-ray optical scheme**

A vertically focused beam is required to achieve good energy resolution for XES spectra acquired by a vertically oriented von Hamos spectrometer. Therefore, we decided to use a toroidal mirror, which is already available at the beamline for focusing. The optical scheme includes only two mirrors (Fig. 1). The incidence angle for the first mirror was set to 0.22° (3.9 mrad) in order to send the beam bypassing the monochromator. The cutoff energy of the first mirror with Rh coating at 0.22° (3.9 mrad) is ~17 keV and ~10.8 keV for Si.

Two positions for the implementation of multilayer optics at the beamline were considered: i) as a double multilayer monochromator between mirrors or ii) as a single multilayer after the focusing mirror. The first approach has a few advantages: the X-ray beam at this position is collimated and such a parallel beam provides higher energy resolution. Moreover, due to the large spot-size of the beam at the multilayer, the heat load on the multilayer is distributed over a large area. The multilayer also reduces the heat load on the ensuing focusing mirror. The second option for the multilayer position has also some advantages: the reflectivity losses occur only from one reflecting surface, therefore, such an approach can potentially be more efficient. Such a scheme is also easier to realize due to the smaller space required and simpler mechanical design. The lower energy resolution of this scheme, which leads to a broadening of the incident energy resolution, is desirable for non-resonant XES as long as it does not exceed 5% bandwidth. The second scheme with a pink beam defined by two mirrors and subsequently reflected from a single multilayer was selected. The main risk associated with this approach is the possible damage of the multilayer due to the high photon density. This was checked by exposing the multilayer for several hours to the pink X-ray beam. The rejection of X-rays with energies corresponding to higher harmonics can be achieved by selecting the appropriate coatings of collimating and focusing X-ray mirrors for both single and double multilayer options.

**Characterization of the multilayer**

The multilayer structure was designed for operation in a wide X-ray energy range of 5–17 keV and consists of 200 Mo/Si pairs. The optimal period thickness of 3.5 nm allows operating with an incidence angle $\geq 0.6°$. Thus, the spatial dimensions of the reflecting surface can be reasonably limited (to 50*50 mm in our case). A large width of the multilayer provides sufficient space for translation to a fresh area if long-term damage is observed. During thin film deposition, a slight divergence from the mean period thickness (~0.1 nm) was introduced into all layers to increase the energy bandwidth of the multilayer. We used Diffrac.Lepitos and IMD software [37] to evaluate the structure and have found the following parameters: thickness (Mo plus Si) $d = 3.6 \pm 0.1$ nm, the ratio of thicknesses Mo/Si $\Gamma = 0.552$ (see Fig. 2a). In several papers, the formation of a MoSi₂ interlayer is proposed and experimentally proven [41,42], therefore, we have reason to assert that the aperiodicity of fringes in Fig. 2a is caused not only by the direct divergence in period thickness but also by MoSi₂ interlayers with unstable thickness [43]. The energy bandwidth remains practically the same through the energy range of pink beam operation – 4 ± 0.2% (Fig. 2b), but the reflectivity changes from 23% to 60% with increasing energy (Fig. 2d). The reflectivity can be increased if the dispersion of the multilayer period is reduced, but the energy bandwidth decreases in this case and the integrated flux after the multilayer remains almost the same.

At synchrotron beamlines, multilayer structures are usually placed in vacuum chambers. This serves to prevent pollution of the multilayer surface and to avoid the formation of defects that are related to gas ionization. We also learned that at least low vacuum conditions (<10⁻² mBar) are essential. At ambient air pressure, we observed significant damage of the multilayer coating, seen as spherical defects, even with an unfocused (a few mm wide horizontally) X-ray beam. The blisters formation is one of the recently understood problems connected with the operation of multilayer structures in the presence of gas. Blisters are defects, which typically have a spherical shape and are induced by gas condensation at the layer-layer or layer-substrate interfaces. Yurkevich et al. [44] studied thin films grown by atomic layer deposition exposed to pink beam radiation under different environments: vacuum (10⁻⁶ mBar), dry air (1.3 mBar), N₂ (1.1 mBar), He (1.1/1.3 mBar) and Ar (1.3 mBar). In all conditions, except vacuum, the same defects appeared, and the formation of blisters was shown. Though in our case the thin film deposition method is different, the same type of damage might occur in our multilayer. There are several possible mechanisms to form blisters: i) a small amount of Ar atoms is present in the multilayer because an ion beam is used to sputter materials, consequently, Ar can be ionized by the pink beam; ii) the pink beam causes local heating in the structure, therefore, the drift of ions is
Probable; iii) a small amount of hydrogen is present, even in ultra-high vacuum chambers [45], and the formation of blisters in the presence of hydrogen is expected as a multi-step process [46–49]. When the multilayer is operated in air, X-ray beam generates gas ions near its surface, which interact with the multilayer and accelerate the formation of blisters in comparison to vacuum conditions.

As one can see, there are reasons to expect the formation of blisters even when the multilayer is operated in a vacuum chamber, thus we decided to check the performance of our multilayer after a few hours long exposure to the pink beam. We fixed the multilayer at an angle corresponding to 11.3 keV and irradiated it with the pink X-ray beam of full intensity. Spectra of the beam reflected from the multilayer are presented in Fig. 2c: the black line corresponds to the energy spectrum measured before prolonged exposure, colored lines visualize the energy spectrum after 8 h exposure. We have not observed any significant change of reflectivity neither in the center of the irradiated area nor at its periphery. Thus, the Mo/Si structure demonstrated radiation stability under $10^{-2}$ mBar vacuum conditions.

**Kβ main lines of diluted samples**

In order to determine the low concentration limit of elements which we can efficiently study using pink beam excitation, we have performed XES experiments for a typical multi-component photocatalytic system.

![Fig. 1. Main components of the SuperXAS beamline during broadband beam experiments. The SDD detector registers elastic X-ray scattering to measure the incident beam spectrum while the von Hamos-type spectrometer acquires the non-resonance XES spectrum from the sample.](image)

![Fig. 2. (a) The measured reflectivity curve for the Mo/Si multilayer obtained for 8.05 keV radiation. (b) The energy spectra from the Mo/Si multilayer compared with the energy spectrum of the pink beam. (c) The radiation stability test realized at 11.3 keV. The multilayer energy spectrum measured before exposure (black line) is compared with spectra measured after 8 h of exposure with the incident beam impinging at the same point of the multilayer (red line) and translating the multilayer horizontally perpendicular to the beam direction by 0.1 mm (blue line) and 3.2 mm (green line). (d) Absolute reflectivity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
A similar system has been investigated previously by using pump–probe X-ray absorption spectroscopy [34].

As one can see from the spectrum shown as a black line at the bottom panel of Fig. 3, the signal to background ratio is ~0.75 for a 0.8 mM Co sample. For measurements with a two times higher concentration (1.6 mM) the background remains the same while the signal increases proportionally to the concentration. To quantify the noise level of spectra of the low concentrated sample, we have measured the difference between two spectra by switching between the accumulation of them every 50 s for 4 h. Odd and even spectra were summed up separately and these two spectra are shown as solid black and dotted red lines (Fig. 3, bottom). A similar acquisition mode is used for pump–probe experiments with ~100 µs time resolution [50] when we switch the laser irradiation on and off also for seconds. The signal-to-noise ratio \( N_{\text{signal}}/2\sigma \) for the XES spectra shown in Fig. 3 (bottom) is ~66. The level of fluctuations observed in the experiment is in agreement with expectations from the photon counting statistics, which demonstrates that other factors, for example, instabilities of the setup versus time give negligible contributions. This is achieved due to the use of the von Hamos X-ray spectrometer, which has no moving parts to collect a XES spectrum, in combination with the high stability of the synchrotron storage ring. From the comparison of this noise level with the difference spectrum obtained by subtracting the spectrum of low spin Co(II) reference cobaloxime (Fig. 3 top), we see that spin state changes of 10% of Co(II) atoms can be visible with 50 s level at present measurement conditions. For the data presented in Fig. 3 we have used an incident X-ray beam formed by the bare Si collimating mirror that cuts off higher energies at ~10.8 keV, a 2 mm carbon filter and not fully opened front end slits. This provided an increase in the count rate of XES by a factor of 100 in comparison to the monochromatic beam. With a wider slit opening and the same Si mirror, we achieved a count rate increase of 1000 and switching to the Rh-coating on the collimating mirror allowed us to increase the count rate up to 3000, which allows the measurements of weaker transient signals.

Thus, a combination of pump beam excitation with a von Hamos type spectrometer is efficient for XES measurements of samples with a concentration of the element of interest of ~1 mM and higher. Weak transient signals can be measured which opens up possibilities for time-resolved, in particular, pump–probe XES experiments.

Valence-to-core XES

Valence-to-core XES spectra are weak relative to the main emission lines: they are ~800 times weaker than the K\(\alpha_1\) line and ~100 times weaker than the K\(\beta_{1,3}\) line. These satellite peaks are, however, often used to explore the coordination environment of the absorbing atom and contain information complementary to XAS [8–10,51]. In order to compare monochromatic (7170 eV), pink and broadband beam (with maximum at 7450 eV) excitations for valence-to-core XES measurements, we have measured spectra of a Fe foil and a FeTPPCl pellet using monochromatic beam and pink beam for Fe foil and using pink and broadband beam for FeTPPCl (Fig. 4). As one can see, a weak feature at energies higher than the K\(\beta_{2,5}\) peak appears in the case of pink beam excitation, which is the KL\(\beta\) satellite. This peak is not visible neither for monochromatic excitation nor for broadband beam excitation. Similar features for Mn compounds were reported previously [38]. We also observed an additional feature below the K\(\beta_{2,5}\) peak in the case of pink beam excitation, which corresponds to energies of the K\(\beta\) satellite and therefore is easy to misinterpret. Codes that are currently used for calculations of valence-to-core XES [8,52] are based on one-electron excitations and do not include the contributions from KL excitations.

Fig. 3. Bottom panel: Co K\(\beta\) XES spectra of a multi-component system containing a Co(tpyOH) catalyst with a Co concentration of 0.8 mM. Two spectra accumulated for 4 h by adding spectra collected for 50 s (solid black line represents the sum of odd spectra and dotted red line is the sum of even spectra) and the difference between them (blue line) are shown. Top panel: XES spectra of cobaloxime (black line) and Co(tpyOH) (red line) as Co(II) low spin and Co (II) high spin references and the difference between them (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Valence-to-core XES spectra of FeTPPCl, measured with pink beam (blue solid line), and broadband beam (orange dashed line) (bottom) and spectra of metallic Fe (top) measured with pink beam (black solid line) and monochromatic beam (red dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
This is the main reason why measurements of valence-to-core transitions excluding high energies from the incident beam are currently preferred.

We should notice that the intensity of the KL satellite observed with pink beam excitation and with monochromatic beam tuned above the KL edge are generally different. The main reasons are: i) the probability of additional L shell ionization after absorption of a high-energy photon by the K shell is energy-dependent, ii) only part of the pink beam spectrum excites above the KL edge and a significant part of the radiation excites only the K-electron, especially in the case of cut-off of higher energies by using a Si-coated mirror. The bandwidth of the multilayer that we have developed is 4 ± 0.2%. Therefore, it allows us to tune the incident energies so that the whole energy bandwidth of the incident beam is located between K and KL edges for any selected 3d element. With two orders of magnitude increase of flux in comparison to the monochromatic excitation, this broadband beam approach is optimal for valence-to-core XES measurements.

For experiments with such high incident X-ray flux, it is important to monitor the X-ray induced damage of the sample. Due to higher flux, the damage can occur within minutes or seconds (instead of many hours typically observed for monochromatic excitation and a cobalt-based molecular catalysts [50]). A von Hamos-type XES spectrometer is best suited to follow the radiation damage since it allows to measure all energy points of the XES spectrum simultaneously, without the need for scanning. For example, during the accumulation of statistics in the valence-to-core part of the spectrum, the main Kβ line (which is measured simultaneously) can be used to monitor the radiation damage with 10 or even 1 s time resolution. A Johann-type spectrometer does not provide these possibilities since it requires the rotation of crystals and movements of the detector to change the energy and, therefore, the acquisition of a single spectrum with ~100 energy points requires a few minutes, which sets the low limit for the time-resolution for radiation damage monitoring. The possibility of radiation damage monitoring is demonstrated in Fig. 5. The broadband beam induced gradual changes of the XES spectra which are seen in the Kβ main line region in the series of 97 spectra acquired with a 10 s time step. Two components, which represent the beginning and the end of the measurements series are shown in Fig. 5a, the weight of the component 1 is presented in Fig. 5c. The components were extracted from the series of 97 spectra using principal component analysis employing the approach used previously for XAS [53,54]. Partial reduction of the sample induced by the X-ray beam is seen in the Kβ main line region as a shift of the main maximum and as a flattening of the Kβ peak. Also, a small energy shift of the valence-to-core peak is seen (Fig. 5b). With pink beam, the X-ray induced reduction of the sample occurs faster than with the broadband beam, which explains the shift between spectra measured with pink and broadband beams for FeTPPCl (Fig. 4, bottom). For valence-to-core XES, the minimization of the background significantly improves the signal-to-noise ratio. There are two sources of background: i) scattering from air and beamline windows, fluorescence and scattering from the beam-stop and other components of the setup that are spatially separated from the sample, ii) the sample itself scatters X-rays both elastically and inelastically (in particular as the X-ray Raman scattering process) and produces Kα fluorescence. The first type of background can be efficiently blocked by using shielding of the beam path, sample, and detector. Regarding the second type, Kα fluorescence from the sample is 3 orders of magnitude stronger than the fluorescence from valence-to-core transitions, therefore scattering of this radiation from the crystals of the spectrometer (with the same X-ray path as the valence-to-core radiation, but with low efficiency) produces a significant background. X-ray Raman scattering can also contribute to the background because these photons can have the same energy as valence-to-core peaks. The reduction of the background of this type with shielding is not possible because this radiation comes from the same point as the useful signal. This unwanted contribution can only be reduced by using the energy resolution of the detector. Indeed, Kα and valence-to-core emission have sufficient energy differences to be separated by using a silicon drift detector. Elastically scattered radiation can also be separated from valence-to-core emission if we use a broadband beam with an energy a few hundred eV higher than the absorption edge of the studied element. Nevertheless, the contribution from X-ray Raman scattering cannot be removed because these photons have the same energy as valence-to-core photons. In the von Hamos spectrometer setup, we use a 1D (Mythen) or 2D (PILATUS) detectors that do not have the required energy resolution. A better energy resolution of modern pixel detectors, for example, MÖNCH [55] will allow improving significantly the signal to background ratio while keeping the advantage of the parallel acquisition of the whole XES spectrum. Alternatively, a Johann-type spectrometer can be used together with a silicon drift detector because a single element detector is sufficient for such a spectrometer. Therefore, for valence-to-core spectroscopy broadband beam radiation in combination with a spectrometer equipped with an energy-resolving detector is the optimal combination.

Conclusions

In this work, we demonstrate the optimization of a bending magnet beamline for non-resonance XES measurements using pink and broadband beam operation modes. In order to allow broadband beam operation, a Mo/Si multilayer thin film monochromator was produced, characterized, and tested. Due to slight divergence in period thickness (~0.1 nm), the multilayer demonstrates a relatively large energy bandwidth 4 ± 0.2% through the whole pink beam range and
reflectivity of 23–60% which increases with energy. We demonstrate that the signal-to-noise ratio that can be achieved for core-to-core XES measurements of diluted samples with sub-mM concentrations is sufficient to perform time-resolved experiments. Measurements of valence-to-core XES spectra are optimal with broadband beam excitation since their analysis can be difficult in the presence of KL Auger satellites induced by the pink beam.

CRedit authorship contribution statement

Olga Dikaya: Methodology, Formal analysis, Investigation, Writing - original draft. Maarten Nachtegaal: Conceptualization, Methodology. Ksenia Maksimova: Supervision, Funding acquisition. Ksenia Maksimova: Investigation, Resources. Nicola Weder: Investigation, Resources. Benjamin Probst: Investigation, Resources. Roger Alberto: Supervision, Resources. Dmitrii Serebrennikov: Methodology, Formal analysis. Evgeny Clementyev: Supervision, Funding acquisition. Ksenia Maksimova: Conceptualization, Methodology. Alexander Goikhman: Conceptualization, Resources, Supervision. Grigory Smolentsev: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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