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Micro-focused MHz Pink Beam for Time-resolved X-ray Emission  
Spectroscopy

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## ABSTRACT

Micro-focused MHz Pink Beam for Time-resolved X-ray Emission Spectroscopy

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Valence-to-core (vtc) x-ray emission spectra (XES) provides direct information on occupied valence orbitals and is sensitive to chemical environment. Combining with element specificity and high penetration of hard x-rays, it is emerging as an information-rich technique and its applications have been demonstrated in research fields, such as catalysis and metalloenzymes. However, the vtc feature is typically two orders of magnitude weaker than  $K\alpha$  emission lines, making it hard to collect, especially for transient species. To overcome this disadvantage, pink beam excitation capability was demonstrated recently at Sector 7 of the Advanced Photon Source. A water-cooled mirror rejects high harmonics from the undulator, and beryllium compound refractive lenses (CRL) focus the reflected fundamental beam (pink beam) to a  $40\ \mu\text{m} \times 12\ \mu\text{m}$  elliptical spot ( $\sim 10^{15}$  photons/second) at the sample target that matches the laser spot size used for photoexcitation. In combination with an ultrafast laser, the focused pink beam was utilized to probe the photoexcited spin crossover (SCO) process of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  in a liquid jet with

a laser-pump/x-ray-probe scheme. The results successfully demonstrated the application of this pink beam capability for ultrafast charge transfer dynamics in solvated molecules.

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## CHAPTER 1

### Introduction

X-ray emission spectroscopy (XES) involves the excitation of a core electron and the spectral measurement of the fluorescence emitted in the relaxation process to fill the core hole. Among the emission features of XES, the valence to core (vtc) transitions directly provide information on the occupied valence orbitals and are sensitive to chemical environment, such as ligand identification and bonding length. Owing to the availability of its theoretical modeling, vtc XES is emerging as an information-rich technique [1] [2] [3]. It has been utilized to elucidate the dynamics of photoexcited Fe-based complexes [4] and to investigate metalloenzymes [5]. The applicability of vtc XES to rather complex sample environments has also been demonstrated in the study of capture, conversion and transport of small molecules ( $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ) in catalyst systems [6].

In addition, an important advantage of XES for 3d transition metals is that the K-edges range from 4 to 10 keV within the hard x-ray region. Because an ultra-high vacuum condition around the sample is not required with hard x-rays, it is possible to measure XES *in situ/operando*, or in extreme conditions such as high pressure [7] and high temperature [8].

The vtc features are typically two orders of magnitude weaker than  $\text{K}\alpha$  emission lines (please refer to Chapter 3), making them challenging to collect with good statistics, especially for transient species. Although the successful development of high brilliance x-ray sources (x-ray free electron lasers (XFELs) and synchrotron radiation) and advancements

in high-resolution crystal analyzers have profoundly improved the quality of the XES spectra, it presently takes tens of hours of acquisition time to attain high quality vtc XES with a multicrystal von Hamos spectrometer [4]. To overcome this difficulty, here we present a micro-focused pink beam excitation scheme to significantly enhance the XES measurement efficiency. The pink beam is the 1st order harmonic from a synchrotron radiation undulator. In comparison to a monochromatic beam produced with a crystal monochromator, the main advantage of the pink beam is the enormously boosted available flux owing to its much broader bandwidth ( $\sim 1\text{-}2\%$  energy bandwidth). It has been employed for XRD [9] and various imaging systems [10] [11] [12] [13], while here we apply pink beam to time-resolved XES of solvated molecules.

In our scheme, a water-cooled flat mirror was used to reject high harmonics out of the undulator radiation, and beryllium compound refractive lenses (CRL) were utilized to focus the reflected fundamental beam (pink beam) to a  $40\text{ }\mu\text{m} \times 12\text{ }\mu\text{m}$  elliptical spot at a liquid jet sample target, matched by the laser spot size used for photoexcitation (details in Chapter 4). After characterizing the focused pink beam (details in Chapter 5), we could reproduce previous measurements of nonresonant XES spectra of  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  with only a fraction of the acquisition time with the benefit of pink beam's high flux of  $10^{15}$  x-ray photons per second. In combination with an ultrafast high-repetition-rate laser, the focused pink beam was utilized to probe photoexcited  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  in a liquid jet with a laser-pump/x-ray-probe scheme (details in Chapter 7). The results successfully demonstrate the applicability of this recently achieved pink beam capability for ultrafast charge transfer dynamics.

## CHAPTER 2

**X-ray Science and Synchrotron Radiation**

X-rays are electromagnetic radiation having wavelengths roughly within the range from 0.005 to 10 nm [31]. When fast electrons strike target atoms, the radiation spectrum that appears is the superposition of continuous radiation as well as very narrow emission lines in the x-ray range, as shown in the right panel of Fig. 2.1. The continuous radiation comes

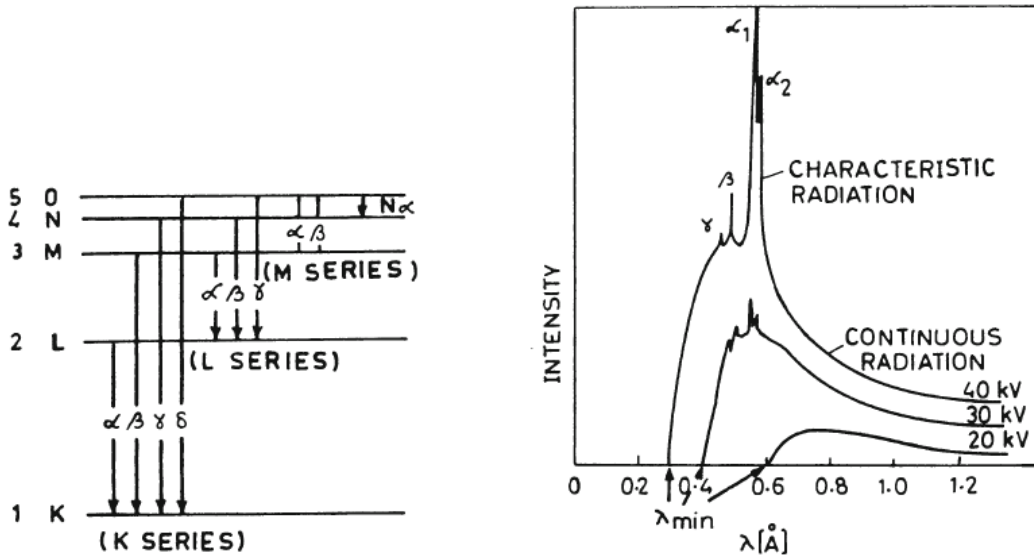


Figure 2.1. Left: the scheme of electron shells in an atom. The electronic transitions correspond to the x-ray emission lines in the quantum theory of Bohr. Right: x-ray spectrum of Ag target at various tube voltages. [32]

from the scattering process of the incident electrons with the target atoms. However, if the incident electron has sufficient energy, it is able to knock out one of the inner bound electrons in the target atom. The emission lines occur in the process as electrons in a



higher energy level fall down to fill the vacancy. The wavelengths of the emission lines reveal the unique energy structure of a specific atom and are also called characteristic x-ray lines of the element. In 1917 the Nobel Prize in Physics was awarded to Charles Glover Barkla owing to his significant work in the discovery of the characteristic x-ray radiation of the elements. The element specificity makes x-ray absorption and emission a powerful tool in science research. In this project, x-ray photon energy is utilized to excite a core electron for XES. Furthermore, the K-edges of 3d transition metals range from 4 to 10 keV lying in the hard x-ray region. An advantage of using hard x-rays is that an ultra-high vacuum condition around the sample is not required, and it is possible to measure XES *in situ/operando* or in extreme conditions. This chapter introduces the unique characteristics of interaction of hard x-ray photons with matter as well as the properties of synchrotron radiation which is employed as the high brilliance x-ray source for this project.

## 2.1. Interaction of X-ray Photon with Matter

Various physical processes might be observed in the interactions of x-ray photons with matter: photoelectric effect (absorption), Rayleigh (coherent) scattering, Compton (incoherent) scattering and pair production. In the photoelectric effect the incident x-ray photon is absorbed and if the photon energy  $\hbar\omega$  exceeds the binding energy  $E_b$  of the electron, an electron is expelled with kinetic energy  $E_k$ .

$$(2.1) \quad E_k = \hbar\omega - E_b$$

The photoelectric effect absorption coefficient  $\tau$  is the summation of cross sections from different absorption edges (K, L, M, etc.) with energy lower than the incident x-ray photon. For instance,

$$(2.2) \quad \tau = \tau_K + (\tau_{L1} + \tau_{L2} + \tau_{L3}) + \dots, \quad \hbar\omega > E_{K-edge}$$

$$(2.3) \quad \tau = (\tau_{L1} + \tau_{L2} + \tau_{L3}) + \dots, \quad E_{K-edge} > \hbar\omega > E_{L-edge}$$

Approximately,

$$(2.4) \quad \tau \simeq CZ^4/(\hbar\omega)^3$$

where the constant  $C$  increases abruptly at each absorption edge of a specific element [32].

From the  $1/\omega^3$  scaling it follows that high energy x-rays are highly penetrating.

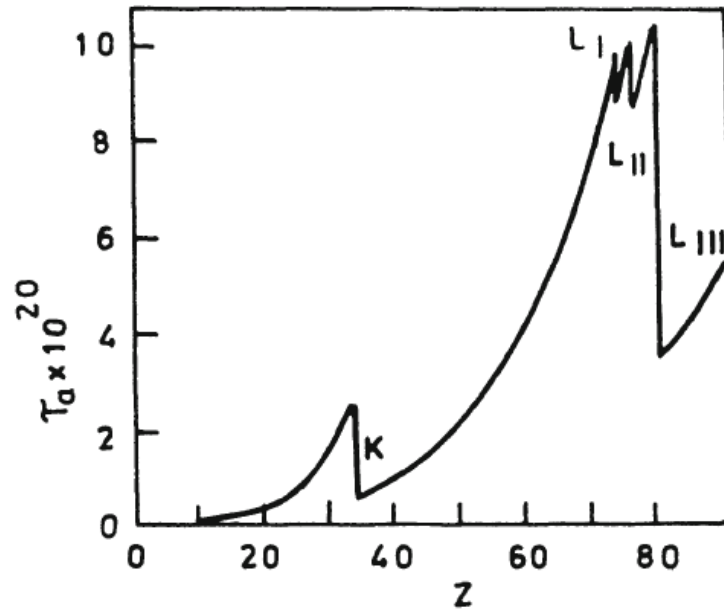


Figure 2.2. Photo absorption coefficient  $\tau$  as a function of  $Z$  for  $\lambda = 1 \text{ \AA}$ . [32]

Figure 2.2 plots  $\tau$  as a function of  $Z$  for a given incident x-ray photon energy. An x-ray of 1 Å wavelength can excite the K-edge electron of light elements and  $\tau$  increase with  $Z$  up to a certain value of  $Z$ , at which  $E_{K-edge}$  is about equal to  $\hbar\omega$  for this element and then  $\tau$  drops abruptly. Therefore, a discontinuity occurs. Then an increase of  $\tau$  with  $Z$  happens again until a new discontinuity is found at another  $Z$  value for  $L_1$ -edge, and so on.

Scattering refers to a process which changes the direction of a incident photon but does not absorb it. It can be elastic or inelastic. The elastic scattering of x-rays by bound atomic electrons is described by Rayleigh scattering with a cross section  $\sigma_R \sim Z^2$ . [31] In Rayleigh scattering the atom is neither ionized nor excited and the incident photons are scattered with unchanged energy and with a definite phase relation between the incoming and scattered waves. The intensity of the radiation scattered by an atom is determined by summing the amplitudes of the radiation coherently scattered by each of the electrons bound in the atom. In x-ray physics, one of the important applications of Rayleigh scattering is Bragg reflection, which occurs in periodic samples with a periodicity on the order of the incident wavelength. Another scattering process is the Compton scattering which is the interaction of a x-ray photon with a free electron that is considered to be at rest. The incident x-ray photon collides with the electron, changing its own wavelength and direction with cross section  $\sigma_C \sim Z$ . [31] The weak binding of electrons to atoms could be neglected, provided the momentum transferred to the electron greatly exceeds the momentum of the electron in the bound state. Therefore, Compton scattering is an inelastic scattering process. Relativistic energy and momentum are conserved in this process and the scattered x-ray photon has less energy and therefore greater wavelength

than the incident x-ray photon. In addition to photoelectric effect and scattering, pair production can occur when the X-ray energy exceeds 1.022 MeV. The process is that a

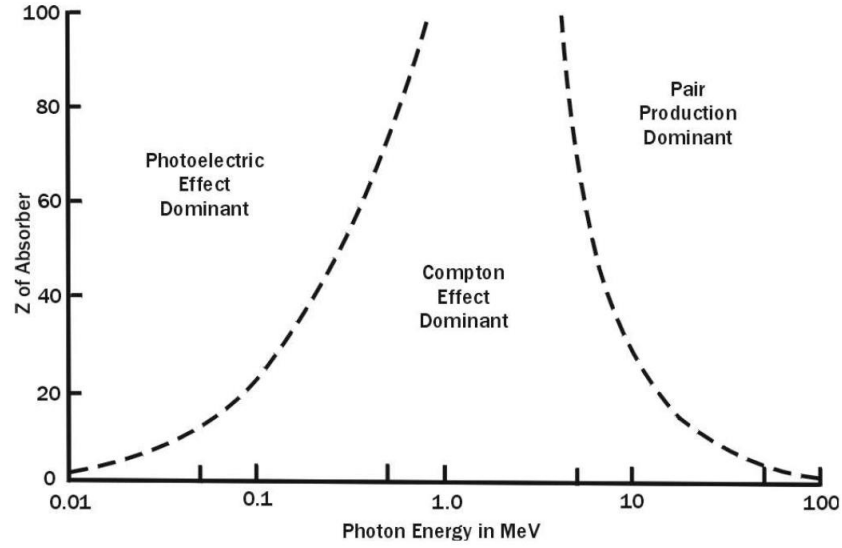


Figure 2.3. Three different physical processes, photoelectric effect, Compton scattering and pair production, dominate different domains of the atomic number  $Z$  and photon energy  $E$ . [33]

photon in a strong electric field, such as near an atom core, can produce an electron-positron pair with the annihilation of the photon, if the photon energy is sufficiently high.

$$(2.5) \quad \hbar\omega \longrightarrow e^- + e^+ + E_{e^-} + E_{e^+}$$

where  $E_{e^-}$  and  $E_{e^+}$  are the kinetic energies of  $e^-$  and  $e^+$ . It is required that  $\hbar\omega > 2m_e c^2 \simeq 1.022 \text{ MeV}$ . Pair production cannot occur in a vacuum but can only take place in the presence of a massive particle such as an atomic nucleus. A massive particle must participate in the process in order that energy and momentum can be conserved

simultaneously. Figure 2.3 shows that different physical processes of the interaction of x-rays and matter dominate at different atomic numbers  $Z$  and photon energies  $E$ . Compton scattering dominates the energies from 500 keV to 5 MeV. The pink beam energy employed in this project is 8 keV. It will be shown in Chapter 4 and Chapter 7 that the important elements involved in this project are rhodium (Rh) for the harmonic rejection mirror, beryllium (Be) for the CRL, and iron (Fe) for XES with atomic numbers of 45, 4 and 26 respectively. It is clear that the photoelectric effect overwhelms Compton scattering and pair production in the interaction of the pink beam with important components in the experiment.

## 2.2. Synchrotron Radiation Facility

Synchrotron radiation is an extremely powerful x-ray source which is generated by high energy electrons circulating in a synchrotron storage ring. The photon emission in a synchrotron is attributed to one physical phenomenon: When a moving electron changes direction, it radiates photons. If the electron is moving fast enough, the emitted energy is at x-ray wavelengths. A synchrotron radiation facility consists of the following components: electron gun (e-gun), linear accelerator (LINAC), booster ring, storage ring, bending magnets, insertion device, radio frequency cavities (RF) and beamline. Figure 2.4 is a common schematic diagram of a modern synchrotron radiation facility and Figure 2.5 is the picture of the Advanced Photon Source (APS) at the U.S. Department of Energys Argonne National Laboratory.

Taking Advanced Photon Source (APS) as an example, the electron gun begins the process by running high voltage electricity through a heated ( $\sim 1000^\circ \text{C}$ ) cathode to repel

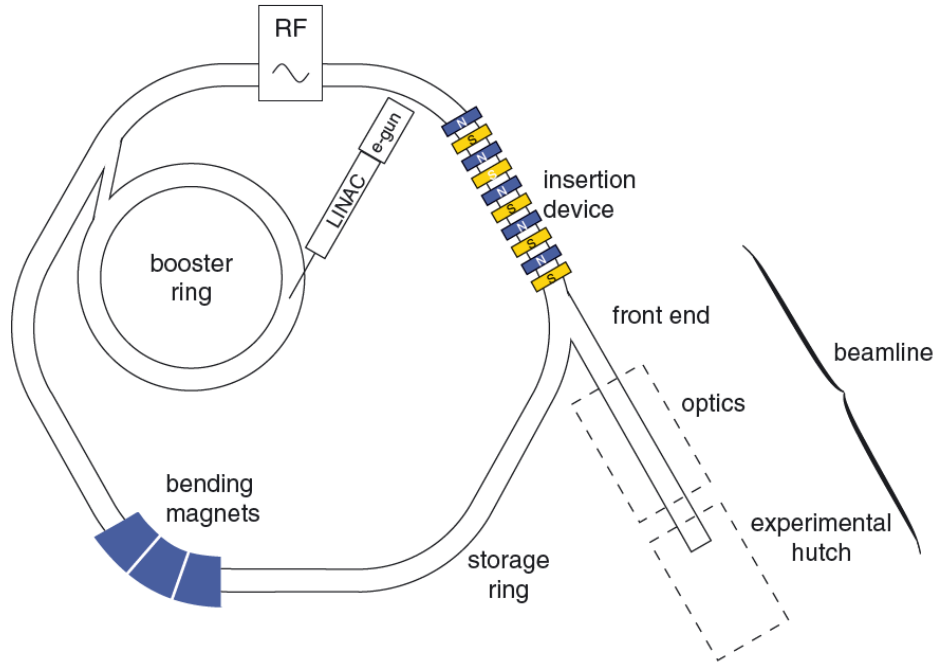


Figure 2.4. A synchrotron radiation facility consists of electron gun (e-gun), linear accelerator (LINAC), booster ring, storage ring, bending magnets, insertion device, radio frequency cavities (RF) and beamline. [34]

the electrons being produced by the cathode and accelerate them towards the LINAC. The LINAC is a series of radio frequency cavities which accelerate the electrons to an energy of 450 MeV. The high energy electrons are then injected from the LINAC into a booster ring and are accelerated from 450 MeV to 7 GeV, traveling near the speed of light. The 7 GeV electrons are then injected into the 1104-m-circumference storage ring. The kinetic energy of the electrons in the storage ring dissipated due to emission of radiation at the bending magnets and insertion devices is replenished by a radio frequency cavity (RF) of 352 MHz [38].



Figure 2.5. Advanced Photon Source (APS) [38]

### 2.2.1. Synchrotron Radiation

There are three categories of synchrotron radiation which are generated by bending magnets, wigglers, and undulators respectively. The main characteristics is introduced here.

The primary purpose of bending magnets is to circulate the electron beam in the storage ring on a closed path, since electrons prefer to travel in a straight line. The emission of bending-magnet radiation is a by-product of the deflection function. Bending magnets have typical magnetic field strengths of around a Tesla. The bending-magnet radiation is in a flattened cone with a fan angle roughly equal to the angular change of the path of the electrons [34], as illustrated in Figure 2.6.

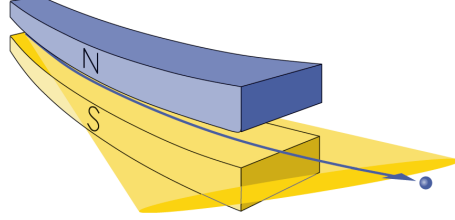


Figure 2.6. An illustration of the radiation generated by a bending magnet. [34]

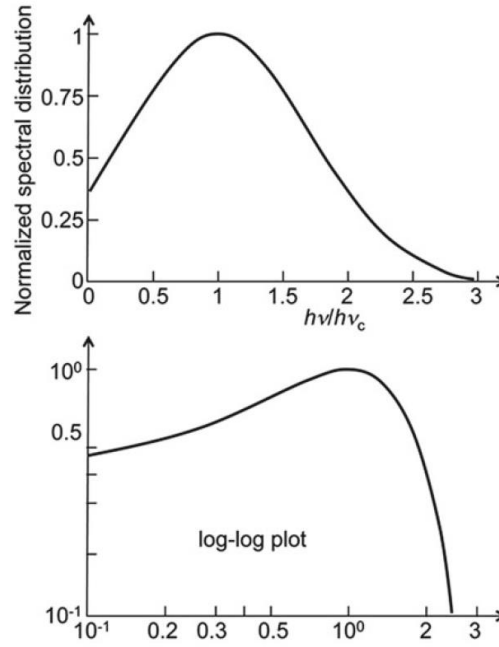


Figure 2.7. A typical spectral lineshape of a broadband bending magnet emission in a linear-linear plot (top) and in a log-log plot (bottom). [35]

The emission spectrum of the bending magnet is peaked at the photon energy

$$(2.6) \quad h\nu_c \approx h\gamma^2 eB/(\pi m_o),$$



with the photon energy bandwidth

$$(2.7) \quad \Delta h\nu \approx h\gamma^2 eB/(\pi m_o)$$

where

$$(2.8) \quad \gamma = \frac{1}{\sqrt{1 - (v/c)^2}}, \quad (v : \text{velocity of electrons}, \quad c : \text{speed of light}).$$

Therefore the ratio between bandwidth and peak energy equals to unity:

$$(2.9) \quad \Delta h\nu/h\nu_c \approx 1.$$

Consequently, the radiation from a bending magnet is a broadband emission. Figure 2.7 represents a typical bell-shaped Gaussian-like spectral lineshape of a bending magnet [35].

The bending magnet radiation is automatically available in all storage rings. However, the peak energy is determined by the magnet lattice characteristics rather than by the research purpose. This stimulated the development of radiation sources dedicated to the emission of light: insertion devices (ID). Insertion devices are installed in straight sections of the polygonal storage ring between the bending magnets. Electrons are forced to execute an oscillatory path in the plane of the storage ring by an insertion device which are composed of a set of magnets by which spatially alternating static magnetic fields are generated, as illustrated in Fig. 2.8.

There are two types of insertion devices: wigglers and undulators. They are distinguished by the degree to which the electrons are forced to deviate from a straight path. For angular excursions larger than the natural opening angle, the radiation cones from

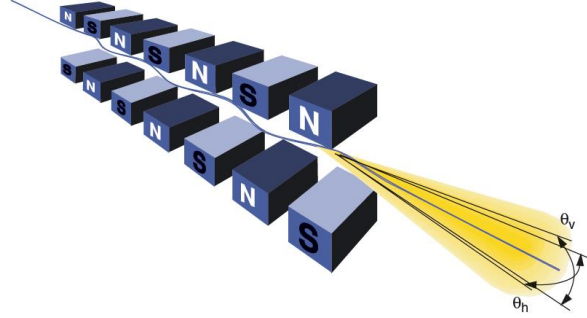


Figure 2.8. An illustration of the radiation generated by a insertion device (ID). [34]

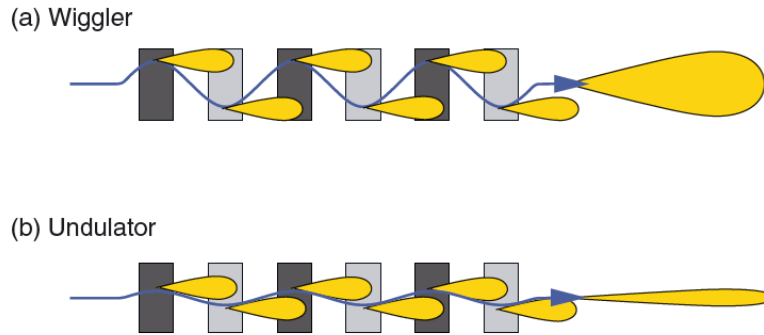


Figure 2.9. Wigglers and undulators in principle differ only in the size of the excursions from a straight path that electrons are forced to execute. The distinction has a fundamental effect on the nature of the radiation. The angular excursions shown here have been greatly exaggerated. [34]

each wiggling turn do not overlap and therefore the intensities are added and the insertion device is designated as a wiggler. In contrast, for gentler excursions, the radiation cones emitted by the electrons as they execute the slalom motion overlap and interfere with one another, and the insertion device is called an undulator. In this case, the field amplitudes are added vectorially (i.e. including the phase difference from each contribution) and the

sum is squared to produce the intensity, which peaks at those wavelengths where interference is constructive. Figure 2.9 illustrates the distinction of wigglers and undulators. A dimensionless parameter  $K$  is utilized to define the distinction:  $K \gg 1$  for a wiggler, while  $K \ll 1$  for an undulator.

$$(2.10) \quad K = \frac{eB\lambda_{ID}}{2\pi m_0 c},$$

where  $B$ : magnetic field,  $\lambda_{ID}$ : period of oscillations,  $m_0$ : electron rest mass.

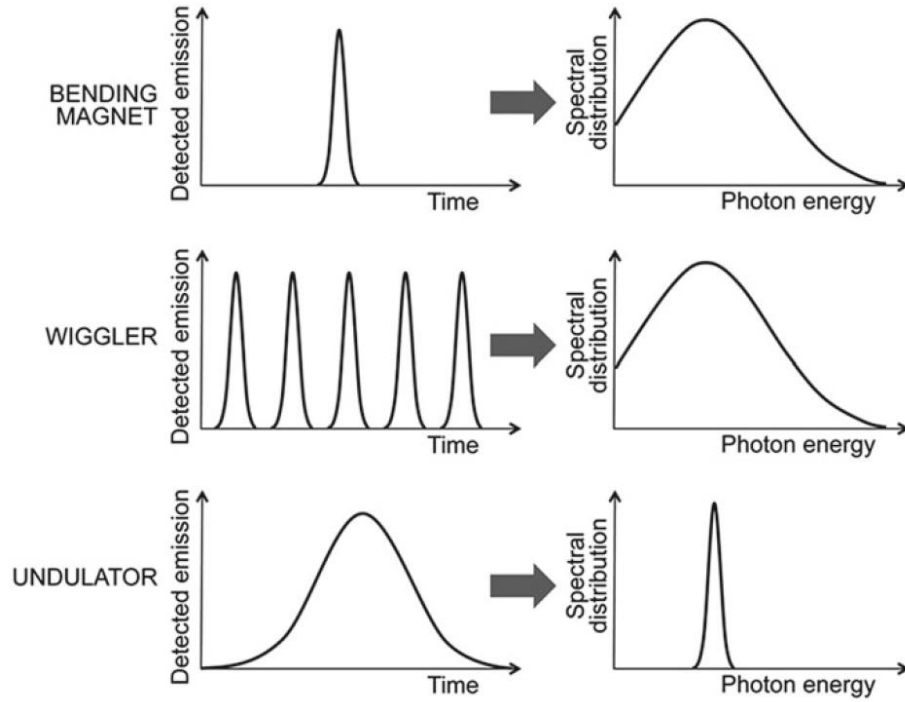


Figure 2.10. Temporal structure and its emission spectrum counterpart for different types of radiation sources. Top: short pulse and broad emission band from a bending magnet. Middle: series of short pulses from a wiggler, again corresponding to a broad emission band. Bottom: longer pulse from an undulator and narrower bandwidth. [35]

A wiggler can be thought of as a series of bending magnets that turn the electrons alternately to the left and to the right. Thus, the emitted light is produced as a series of short pulses, in contrast to the single pulse from a bending magnet, as illustrated in Fig. 2.10. In contrast, an undulator radiates a single, long pulse. The beam size and angular spread of radiation is much lower than that from the bending magnet and wiggler. In addition, the spectral bandwidth is narrow and the sharp resonances happen at regular energy intervals, where the emissions at every magnet of the undulator are in phase. The spectrum can be adjusted via the magnetic field; in practice this is done by changing the undulator gap, the spacing between the poles of each magnet. Figure 2.10 illustrates the time structure and its emission spectrum counterpart for different types of radiation sources. Undulator radiation is unique in its intensity and brilliance, and it can be generated across the range of the electromagnetic spectrum: from infrared to visible light to x-rays.

The emitted peaks of the undulator radiation are:

$$(2.11) \quad \textit{first order} : \quad h\nu_c \approx 2\gamma^2(hc/\lambda_{ID})/(1 + K^2/2),$$

$$(2.12) \quad \textit{nth order} : \quad h\nu_c \approx 2\gamma^2(hnc/\lambda_{ID})/(1 + K^2/2),$$

with bandwidth

$$(2.13) \quad \Delta h\nu/h\nu_c \approx 1/(nN), \quad N : \textit{the number of periods in the undulator}$$

The whole spectrum of the undulator radiation is designated as white beam and the first order harmonic of the undulator radiation is called pink beam.

### 2.3. Sector 7ID Beamline of APS Synchrotron

Beamline 7ID of the Advanced Photon Source (APS) is dedicated to time-resolved x-ray research. In the standard 24-bunch mode of APS, 24 electron bunches evenly spaced by 153 ns circulate the storage ring at a revolution frequency of 272 kHz and with a total current of 102 mA. X-ray pulses are produced at a high repetition rate of 6.52 MHz, as illustrated in Fig. 2.11. By taking advantage of the high repetition rate of

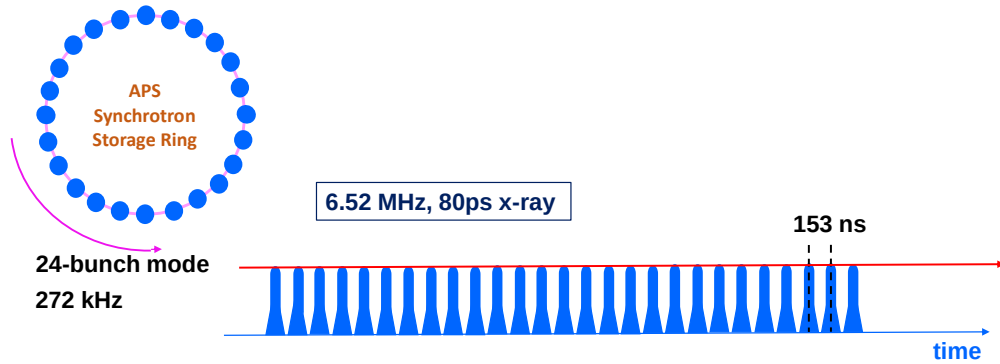


Figure 2.11. Temporal structure of APS synchrotron radiation in the standard 24-bunch mode.

the x-ray pulses in APS, a wide variety of time-resolved measurements are performed

by combining different laser systems in three dedicated experimental stations for time-resolved x-ray diffraction, spectroscopy, unfiltered white beam, and micro- and nano-focus techniques [41]. Figure 2.12 depicts the Sector 7ID beamline layout of APS.

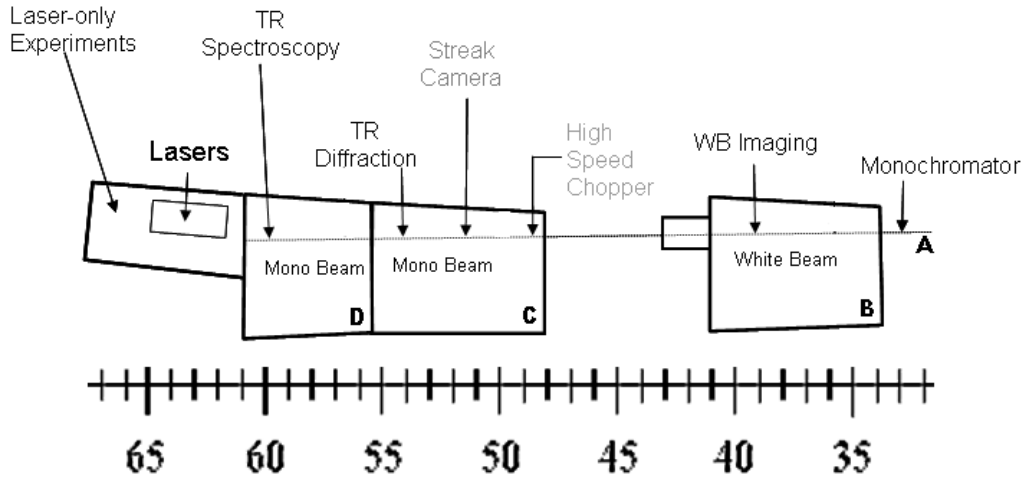


Figure 2.12. Sector 7ID beamline layout of APS. WB stands for white beam; TR for time-resolved capability. [42]

A MOPA (Master Oscillator Power Amplifier) laser system which is a high repetition rate (54 kHz – 6.5 MHz), high power (>10 W) laser source, is built for laser-pump/x-ray-probe studies of optically driven molecular processes. The laser system is employed for the dynamic XES of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  in this project (refer to Section 7.2). Detailed information of this laser system is introduced here.

This high repetition rate laser is a customized commercial master oscillator power amplifier (Time-Bandwidth Products, Duetto) with a central wavelength of 1064 nm and a variable repetition frequency and pulse duration. The oscillator repetition frequency was customized to be 78.2 MHz. The laser is designed to operate at all submultiples of the

oscillator frequency between 54 kHz and 6.52 MHz. The repetition frequency is selected by specifying the rate at which pulses from the oscillator train are picked for amplification. The AOM in Figure 2.13 works as the pulse picker. The system produces 10 W power at 54 kHz, corresponding to  $185 \mu\text{J}/\text{pulse}$ , and 16 W at 6.52 MHz, corresponding to  $2.5 \mu\text{J}/\text{pulse}$ . The laser can produce pulses with durations of either 10 ps FWHM or 130 ps FWHM. The 10 ps duration is useful for experiments requiring optical excitation of molecules [43]. The second and third harmonics of the laser, at 532 nm and 355 nm, are

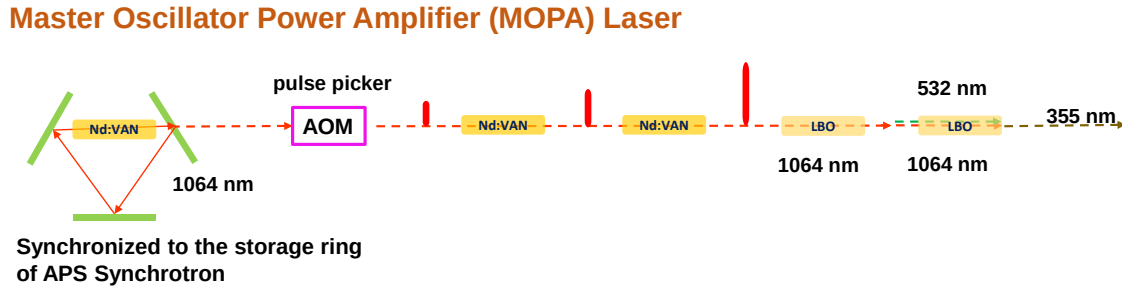


Figure 2.13. Schematic of ultra-fast high-repetition-rate MOPA laser

generated by focusing the output into two lithium triborate nonlinear crystals (Newlight Photonics), as illustrated in Figure 2.13. The second harmonic is produced in a crystal with dimensions  $5 \times 5 \times 15 \text{ mm}^3$  that is cut for Type I mixing and non-critical phase

matching. The third harmonic is produced by mixing the second harmonic light of 532 nm and the residual fundamental light of 1064 nm in another  $5 \times 5 \times 15$  mm<sup>3</sup> crystal that is cut for Type II mixing. Figure 2.14 summarizes the available power and pulse energy at the fundamental, second, and third harmonics in the 10 ps operational mode at different selected repetition rates. It shows that the higher repetition rate, the lower power and pulse energy. To make most use of the x-ray pulses, high repetition rates are preferred and the laser beam should be focused to a small spot size, such as 10  $\mu$ m, at samples to provide high enough intensity.

| Wavelength | 54.3 kHz |         | 135.8 kHz |         | 3.25 MHz |         | 6.52 MHz |         |
|------------|----------|---------|-----------|---------|----------|---------|----------|---------|
|            | W        | $\mu$ J | W         | $\mu$ J | W        | $\mu$ J | W        | $\mu$ J |
| 1064 nm    | 10       | 185     | 11.3      | 83      | 14.5     | 4.4     | 16       | 2.5     |
| 532 nm     | 7.0      | 130     | 8.9       | 66      | 10.6     | 3.3     | 9.5      | 1.5     |
| 355 nm     | 2.5      | 45      | 4.2       | 31      | 4.8      | 1.5     | 3.6      | 0.6     |

Figure 2.14. Duetto MOPA's available power and pulse energy at the fundamental, second, and third harmonics in the 10 ps operational mode at different selected repetition rates. [43]

Synchronization of the laser pulses of the Duetto MOPA with the x-ray pulses and control of the delay between the two is accomplished electronically. The oscillator cavity length is adjusted with a piezo-actuated cavity mirror mount to lock the oscillator pulse train repetition rate to the storage ring rf signal which has been down converted to 78.2 MHz from 352 MHz by an in-house built frequency divider that multiplies by 2 and then



divides by 9. The trigger for the pulse picker (within the laser is also derived from the 352 MHz storage ring rf signal. After downconversion by the 2/9 frequency divider, the signal is sent to another frequency divider with a variable integer divisor value (Pulse Research Lab, PRL-260BNT) which is required to change the laser repetition frequency and does not disrupt the synchronization. Control of the laser delay with respect to the x-ray pulse on target is implemented in two parts. Coarse temporal delay is achieved through the selection of particular laser pulses within the oscillator pulse train for amplification. By adding a delay in the trigger signal using a delay generator (SRS, DG645), later pulses of the oscillator pulse train are selected. Since the oscillator repetition frequency is 78.2 MHz, this effectively leads to control of the laser delay in 12.8 ns steps. Control of the fine delay is achieved by shifting the phase of the rf reference signal. This effectively shifts the oscillator pulse train in time. A programmable delay line (Gigabaudics, PADL3-5-12-15355) shifts the reference signal in steps of 5 ps, with a range of 15 ns [43].

For a fast liquid jet sample with a 25 mL/min flow rate, it takes around 320 ns to pass a 10  $\mu\text{m}$  measurement area. In this case, the temporal spacing between laser pulses should be larger than 320 ns; otherwise, the sample would be contaminated by prior laser pulses. Figure 2.15 depicts the temporal structure of laser-pump/x-ray-probe measurement in this project. One laser pulse appears every five x-ray pulses. An electronic gating system enable users to count and discriminate between consecutive x-ray pulses for data acquisition. The x-ray pulse right before a laser pulse is to probe the laser off condition; the x-ray pulse after the laser off gate is to probe the laser-excited process.

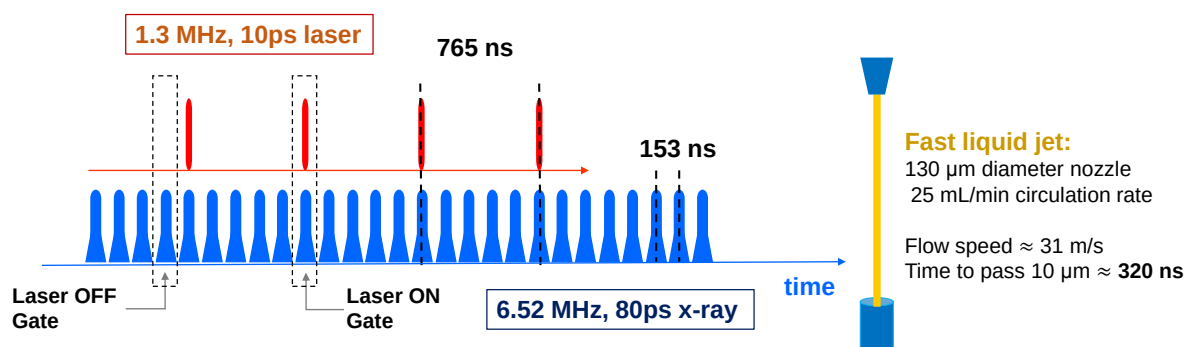


Figure 2.15. Temporal structure for laser-pump/x-ray-probe measurement

## CHAPTER 3

**X-ray Emission Spectroscopy**

X-ray emission spectroscopy (XES) involves the excitation of a core electron and the spectrum measurement of the fluorescence emitted ( $\sim 10^{-15}$  s) in the relaxation process to fill the core hole. The emitted photons in the process have the energy equal to the difference between the original energy level of the relaxation electron and the core hole energy level.

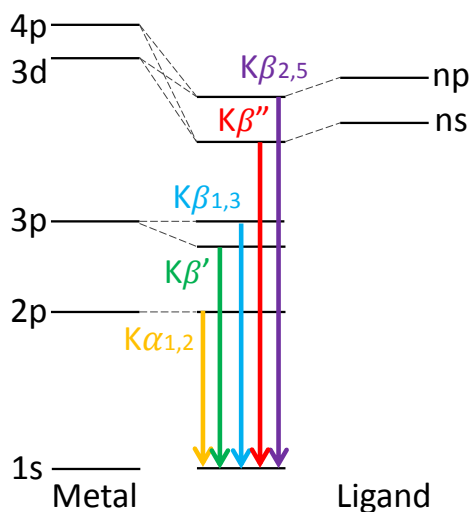


Figure 3.1. XES energy diagram

Among the XES spectra,  $K\alpha$  emission lines ( $K\alpha_1$  and  $K\alpha_2$ ) originate from the refilling of the 1s core hole from a 2p electron. The  $K\beta$  mainline features ( $K\beta_{1,3}$  and  $K\beta'$ ) are from a  $3p \rightarrow 1s$  transition and their intensities are approximately one order of magnitude smaller than  $K\alpha$  emission lines. At the highest energy of the XES spectrum, a valence

electron refilling the 1s core hole gives rise to valence-to-core (vtc) emission features ( $K\beta_{2,5}$  and  $K\beta''$ ) which correspond to transitions from ligand np and ns orbitals to the metal 1s respectively, illustrated in Figure 3.1, and are about two orders of magnitude weaker than  $K\alpha$  emission lines [16]. XES can provide information about occupied orbitals and elucidate the geometric and electronic structure of the probed molecules. The following sections in this chapter will go into detailed characteristics of individual transition features as well as the spectrometer to capture the fluorescence signal.

### 3.1. $K\alpha$ and $K\beta$ Mainlines

Among the XES spectra,  $K\alpha$  ( $2p \rightarrow 1s$ ) spectra are the most intense and split into two features:  $K\alpha_1$  ( $2p_{3/2} \rightarrow 1s$ ) and  $K\alpha_2$  ( $2p_{1/2} \rightarrow 1s$ ), owing to strong 2p core hole spin-orbit coupling [1] [14] [15]. Because of the small overlap of the wave functions of 2p and 3d

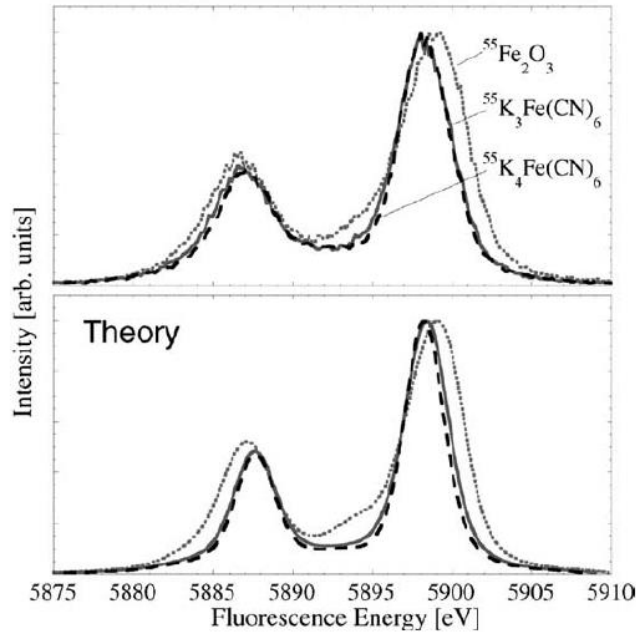


Figure 3.2.  $K\alpha$  emission lines of iron compounds with spin states  $S = 5/2$  (dotted line),  $1/2$  (solid line) and  $0$  (dashed line) respectively [14].

orbitals,  $K\alpha$  emission features are not particularly chemically sensitive [1] [14] [16].

Figure 3.2 presents XES  $K\alpha$  lines of  $^{55}\text{Fe}_2\text{O}_3$ ,  $\text{K}_3 ^{55}\text{Fe}(\text{CN})_6$  and  $\text{K}_4 ^{55}\text{Fe}(\text{CN})_6$ . The nominal spin states of the three compounds are  $S = 5/2$ ,  $1/2$  and  $0$  respectively and the spectral changes are not pronounced. The main advantage of using the  $K\alpha$  emission line in some experiments is its high intensity, which makes it suitable to apply in the study of dilute samples. [14]

The  $3p \rightarrow 1s$  transitions are approximately one order of magnitude smaller than  $K\alpha$  emission lines. The proximity of the  $3p$  orbitals to the  $3d$  manifold imposes a strong influence of  $3p$ - $3d$  exchange interaction on the transitions. The  $3p$ - $3d$  exchange interaction results in a large splitting between final states depending on the unpaired  $3p$  electron with spin parallel or antiparallel to the  $3d$  electrons. Those states of parallel spin compose an intense  $K\beta_{1,3}$  peak while those with antiparallel constitute a less intense  $K\beta'$  peak at a lower energy. Figure 3.3 illustrates the splitting caused by the  $3p$ - $3d$  exchange interaction.

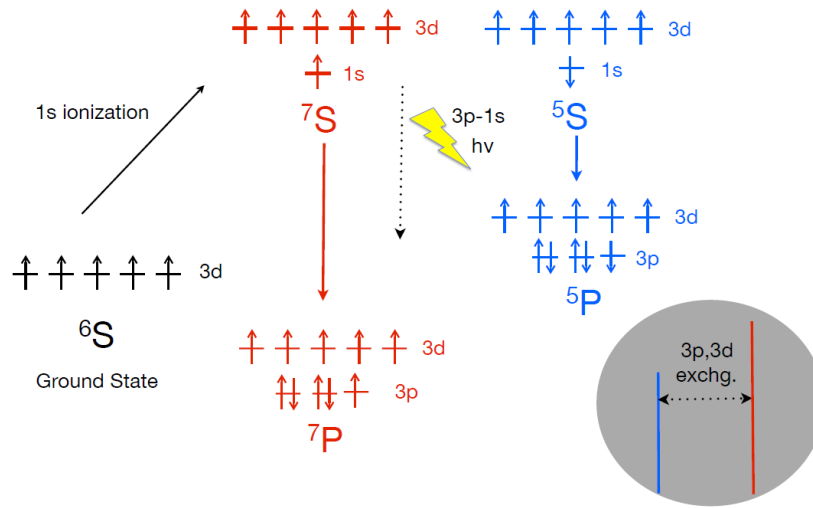


Figure 3.3.  $K\beta$  mainline splitting owing to the  $3p$ - $3d$  exchange interaction [45]

Unlike 2p orbitals, the 3p hole spin-orbit coupling is weak and the splitting between the transitions from  $3p_{3/2}$  ( $K\beta_1$ ) and  $3p_{1/2}$  ( $K\beta_3$ ) is not resolvable to the intrinsic lifetime broadening [14] [15]. The whole  $3p \rightarrow 1s$  emission features are referred to as  $K\beta$  mainlines and are sensitive to the local net spin state of 3d electrons. More exactly as the effective number of unpaired 3d electrons decreases, the energy splitting between the  $K\beta_{1,3}$  peak and the  $K\beta'$  peak becomes smaller, the  $K\beta_{1,3}$  shifts toward lower energy and the  $K\beta'$  reduces in intensity [14] [16] [17].

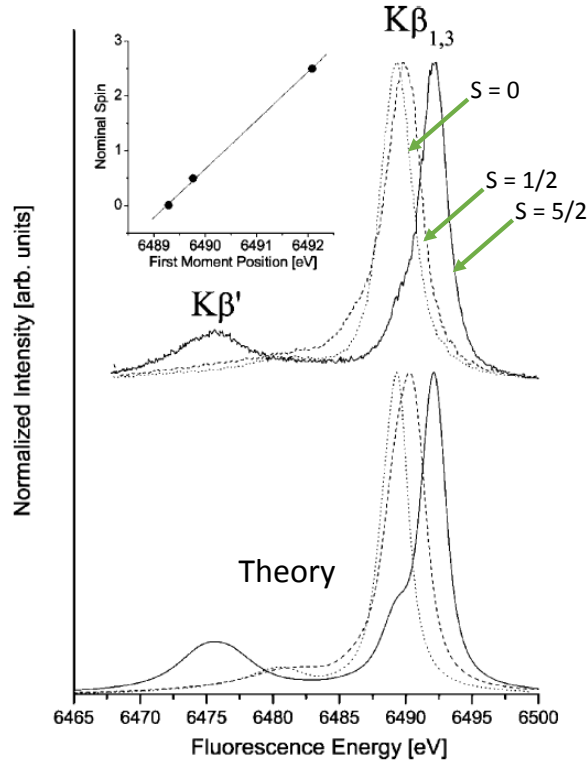


Figure 3.4.  $K\beta$  mainlines of iron compounds with spin states  $S = 5/2$  (solid line),  $1/2$  (dashed line) and  $0$  (dotted line) respectively. The bottom plots are the corresponding simulations. [14]

Figure 3.4 shows XES  $K\beta$  mainlines of three compounds of which the nominal spin states are  $S = 5/2$ ,  $1/2$  and  $0$  respectively. The compound with the highest spin state

exhibits two prominent features in the spectrum of which the strong  $K\beta_{1,3}$  line is at high fluorescence energies. The  $K\beta'$  feature of the compound with the highest spin state at lower fluorescence energies is due to the 3p-3d exchange interaction. The  $K\beta_{1,3}$  and  $K\beta'$  lines move towards each other with decreasing valence spin and thus smaller 3p-3d exchange interaction. For  $S = 0$ , the  $K\beta'$  structure merges into other weak final states on the low energy side of  $K\beta_{1,3}$ . The inset of Fig. 3.4 shows the nominal valence spin state vs. the  $K\beta_{1,3}$  first moment position with a linear fit [14]. In addition, the  $K\beta_{1,3}$  peak is slightly asymmetric with a small shoulder on the low energy side. The shoulder arises

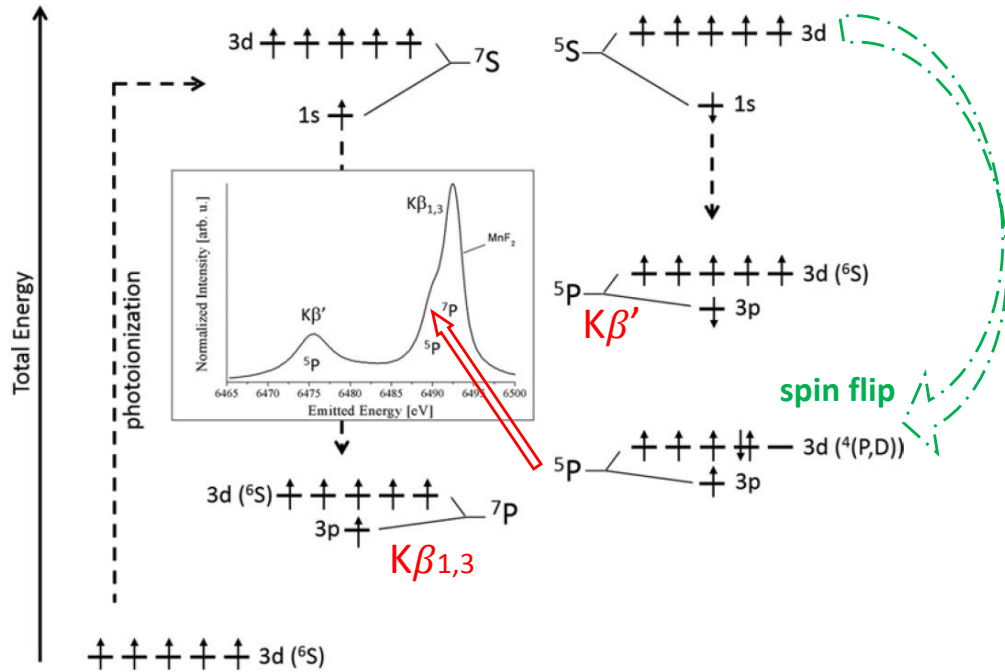


Figure 3.5. The shoulder on the low energy side of  $K\beta_{1,3}$  peak originates from spin flips. The single left  $1s$  electron and one of  $3d$  electrons could flip together in response to the weak  $1s$ - $3d$  exchange interaction in  $5S$  intermediate state. The scenario cannot happen in  $7S$  intermediate state, because it will violate spin selection rules [1].

from spin flips [1] [49] [50], illustrated in Fig. 3.5. As a core hole is created in the  $1s$

orbital, the single left 1s electron and one of 3d electrons could flip together in response to the weak exchange interaction of the 1s electron with 3d electrons.

The characteristics of  $K\beta$  mainlines connected to spin states or oxidation states of various transition metal complexes have been quantitatively investigated [14] [18]. The sensitivity to valence spin and oxidation states has been exploited to study metal-ligand covalency [16] [19], cation site occupation [20] and spin-crossover compounds [21].

### 3.2. Valence-to-Core Features

To the highest energy, slightly below the K-edge, are the valence-to-core (vtc) XES features which are attributed to molecular orbitals that are mainly localized on the ligands but have some metal p-symmetry character. The vtc XES spectrum is about 50 - 100 times weaker than the  $K\beta_{1,3}$  line and can be divided into two regions:  $K\beta_{2,5}$  (metal and ligand p character  $\rightarrow$  metal 1s) and  $K\beta''$  (ligand s  $\rightarrow$  metal 1s) [1] [2] [14] [16]. This  $K\beta_{2,5}$  region is sensitive to changes in the valence orbitals and provides rich information about the nature of the chemical bonds between metal atoms and ligands. The  $K\beta''$  feature originates from molecular orbitals with ligand s type character. The transition energy of the  $K\beta''$  feature is related to the binding energies of the ligand electrons and is valuable for ligand identification. It provides powerful information to distinguish between C, N, O, and F ligands and the degree of ligand protonation, i.e. O vs OH [5] [22] [23] [24] [25] [26] [27]. Furthermore, there is a strong dependence of the  $K\beta''$  intensity on the metal ligand distance.

Figure 3.6 exhibits how  $K\beta''$  is strongly sensitive to both ligand species and the metal ligand distance in particular for N, O and F. The top plots show  $K\beta''$  and  $K\beta_{2,5}$  features



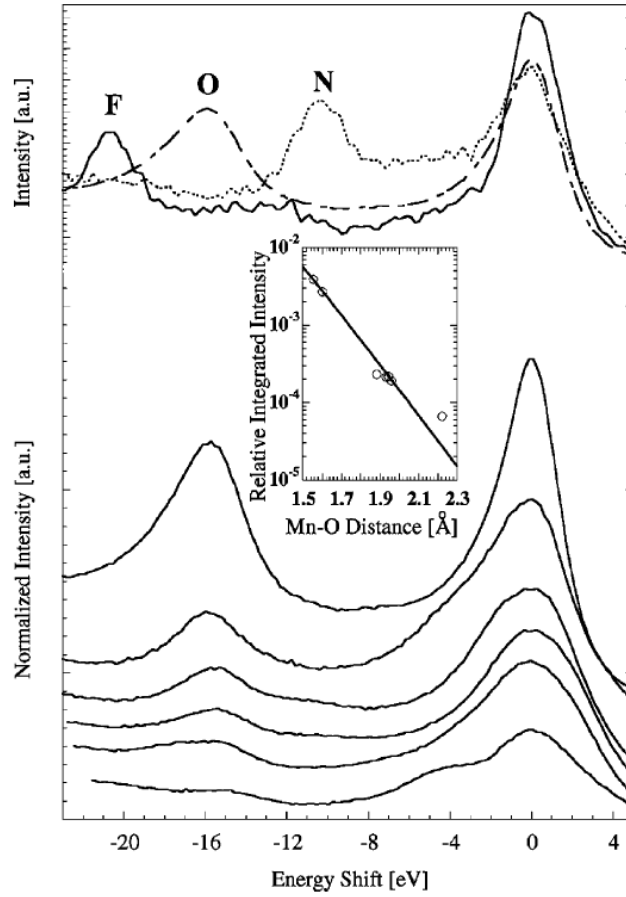


Figure 3.6. XES vtc features distinguish ligand identity and bond length [14] [22].

of Mn complexes with F, O and N ligation. The relative shifts between the  $K\beta''$  and  $K\beta_{2,5}$  fluorescence energies for different ligands correspond mainly to the differences in 2s binding energies of the atomic species. The bottom plots are normalized vtc spectra of manganese oxides with different Mn - O distances. The inset shows normalized intensities of  $K\beta''$  as a function of Mn - O distance and an approximately exponential dependence can be observed over two orders of magnitude [1] [14] [22] [28]. .

If the spectral variation of the bottom or inset plots happens in a single molecule at different time points, it will be an example to exploit time-resolved vtc XES to characterize the evolution of the bond length in a process.

Unlike  $K\alpha$  and  $K\beta$  mainline features, vtc XES spectra offer direct information on occupied valence orbitals and is emerging as a powerful tool for various research fields, such as bioinorganic chemistry [16] [29] and environmental science [2] [30].

### 3.3. Spectrometers for XES

In the hard x-ray regime, high-energy-resolution x-ray detection schemes are based on the diffraction of x-rays over crystallographic planes as expressed with the simple Bragg equation:

$$(3.1) \quad n\lambda = 2d \sin\theta$$

where  $d$  is the lattice constant,  $\theta$  is the Bragg angle,  $n$  is the diffraction order and  $\lambda$  is the wavelength of the x-ray. This formula indicates that an x-ray of a given energy is diffracted at a given angle and vice versa [1].

XES spectrometers usually utilize bent crystals to analyze the fluorescence. Two different approaches are usually employed: scanning Johann spectrometers and dispersive von Hamos spectrometers, depicted in figure 3.7.

In a scanning Johann spectrometer, a point-to-point focus scheme is employed where a spherically bent crystals are placed in a Rowland circle along with the sample and a detector. The fluorescence from the sample impinges on the crystal analyzer and is diffracted by the spherically bent analyzer and focused at the detector. The approach can

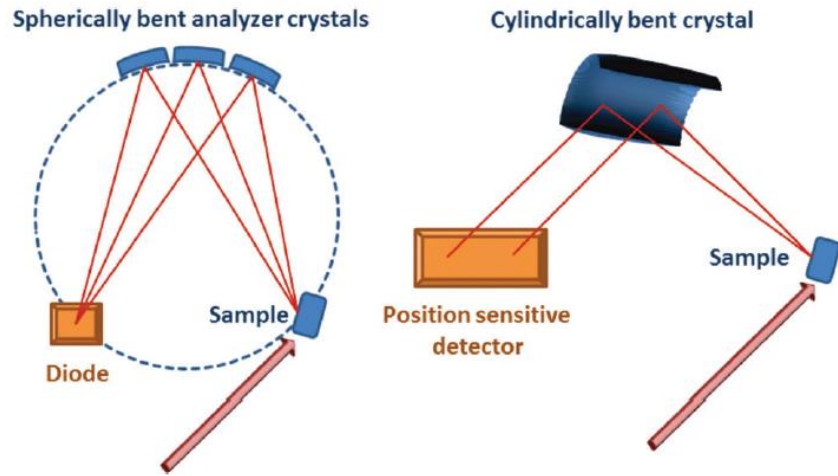


Figure 3.7. Two different approaches are usually employed for high resolution x-ray emission spectrometers: scanning Johann spectrometers (left) and dispersive von Hamos spectrometers (right). [47]

only detect a single emission energy at a time. Therefore, to cover a full emission spectrum, the position and angle of the analyzer, as well as the position and angle of the detector must be synchronously scanned. The primary advantage of scanning spectrometers is its capability to collect a large solid angle at a single emission energy resulting in a higher photon flux per energy unit, or equivalently, a better signal-to-background ratio, compared with the other design.

In von Hamos spectrometers the fluorescence is diffracted by a cylindrically-bent crystal analyzer which focuses the fluorescence in one dimension and spatially separates the different energies in the other. The different x-ray energies are detected by position sensitive detectors, and the spatial dimension can be converted to an emission energy scale by appropriate calibration. This scheme is capable of detecting a large range of fluorescence energies simultaneously, making it particularly applicable in a time-resolved measurement [47].

## CHAPTER 4

### Beamline Layout and X-ray Optical Apparatus

Undulator radiation consists of a series of harmonics (refer to Section 2.2). The full harmonics out of an undulator is designated as white beam of which the first harmonic is described as pink beam. Pink beam has a broader bandwidth ( $\Delta E/E \sim 10^{-2}$ ) than mono beam ( $\Delta E/E \sim 10^{-6}$ ), and therefore provides more flux. As a result, it is desirable to employ pink beam for vacancy creation for nonresonant XES, especially for time-resolved vtc XES, since the line widths and shapes of nonresonant XES are not affected by the large bandwidth of pink beam for ionization.

The 7ID beamline at the APS is equipped with a standard undulator A (3.3 cm period) whose first harmonic radiation can in practice be tuned from about 5 keV to 13 keV. The energy range is desirable to the K-edges of all 3d transition metals as well as the L-edges of lanthanides and 5d transition metals. The white beam power of the undulator radiation can easily go up to 1kW. Therefore, it is necessary to reject high harmonics from the undulator output to reduce the heat load on x-ray optics, as well as avoid any unwanted excitation or process. Here, high harmonics rejection is achieved with a water-cooled flat mirror which is made up of a single-layer 10 nm rhodium deposited on a flat silicon substrate. On the other hand, the pink beam needs to be focused to around 10  $\mu\text{m}$  vertically to fit the refresh rate of samples in a vertical liquid jet (refer to Section 2.3 and Chapter 7). Beryllium compound refractive lenses (CRL) are employed to implement focusing.

Both of the harmonic rejection mirror and the focusing CRL exploit the index of refraction in x-ray regime [54]:

$$(4.1) \quad n = 1 - \delta + i\beta$$

The refractive index decrement  $\delta$  describes the strength of refraction with respect to vacuum and is responsible for dispersion. It has a positive value of the order  $10^{-6}$  owing to the weak interaction of x-ray with matter and the super small value of  $\delta$  indicates that it is non-trivial to bend a x-ray beam by means of refraction. The imaginary part  $\beta$  is linked to absorption and is smaller than  $\delta$  by two or three orders of magnitude. The real part  $(1 - \delta)$  of the index of refraction in material is very close to and smaller than that in vacuum. This property results in the phenomena of total external reflection from material as a x-ray beam grazes the surface at very shallow angles  $\theta$  smaller than the critical angle  $\theta_c$ . From Snell's law,

$$(4.2) \quad \sin \theta_c \approx \sqrt{2\delta}$$

In this project, XES of Fe complexes is demonstrated with the micro-focused pink beam (details in Section 7.2). Accordingly the beamline apparatus is designed to optimize the capability to ionize a 1s core electron of the iron atom of the coordination compounds. The K-edge of iron is around 7.1 keV but the pink beam peak is set at 8 keV for nonresonant XES to make use most of the pink beam flux. Figure 4.1 presents the beamline layout in which the main slit is set to an opening of 0.6mm x 0.6mm and located 26.5 m from the undulator x-ray radiation. The 7-stack beryllium CRL of 200  $\mu\text{m}$  radius of curvature are set 35.5 m from the undulator. The harmonic rejection mirror is 0.65 m

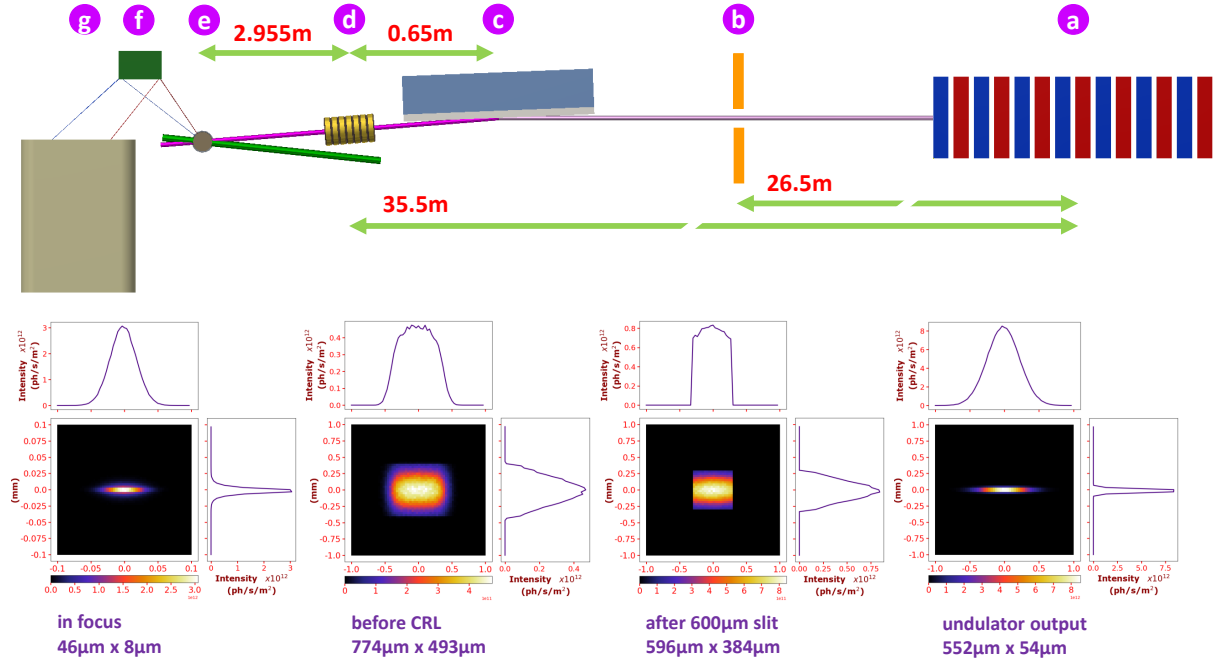


Figure 4.1. The beamline layout for focused pink beam and the beam profile simulation with McXtrace. The apparatus from right to left: (a) APS Undulator A (3.3 cm period), (b) main beam defining slit (0.6 x 0.6 mm), (c) harmonic rejection mirror, (d) CRL, (e) HPLC-backed liquid jet sample, (f) crystal of von Hamos spectrometer, and (g) Pilatus 100K detector. The green line through the sample represents an optical laser beam. The beam profiles are simulations by ray-tracing software McXtrace. (The in focus image size is 0.1 x 0.1 mm; others are 1.0 x 1.0 mm.)

upstream to the CRL. The sample is placed at the focal distance of 2.955 m to the CRL. The mirror is inserted in a horizontal deflection configuration chosen to simplify the technical implementation. Since the CRL are installed on axis, the horizontal deflection keeps the beam at the same height at the focus point, making it easy to position the interaction point. According to the simulations a  $774\mu\text{m} \times 493\mu\text{m}$  FWHM beam profile right before the CRL and a focused  $46\mu\text{m} \times 8\mu\text{m}$  FWHM beam profile at 2.955m focal distance are predicted. Except for the samples, all of the apparatus are connected with long nipples

or soft bellows and are kept in vacuum of better than  $6 \times 10^{-5}$  Torr. A water-cooled 25  $\mu\text{m}$  thick beryllium window is installed 20 cm before the sample to separate the vacuum condition from the liquid jet sample.

In the two sections of this chapter, we discuss the details of the harmonic rejection mirror as well as the focusing CRL.

#### 4.1. Design of Harmonic Rejection Mirror

The harmonic rejection mirror harnesses total external reflection from material to reflect only the selected energy. In addition, the larger grazing angle, the bigger slit opening allowed. And the bigger slit opening, the more flux. As a result, material with a larger critical angle  $\theta_c$  is preferred. In practice, a layer of proper material can be deposited on a substrate for a larger grazing angle and a proper thickness of the deposit is chosen to make destructive interference for high harmonic rejection.

I did a series of simulations, with CXRO online calculation tool, for various thicknesses and materials deposited on a flat silicon (Si) substrate to determine the deposit material, its thickness and the grazing angle. The results show that 10 nm rhodium (Rh) is a good choice. Figure 4.2 presents the reflectivity of the selected 10 nm thickness. The deep dips shown on 2nd and 3rd harmonics (16 keV and 24 keV) and high reflectivity of the fundamental harmonic (8 keV) at 6 mrad grazing angle indicate that the high harmonics can be effectively rejected while more than 80% of the fundamental harmonic is reflected by the mirror at this grazing angle.

Rh has a larger critical angle ( $\theta_c \approx 4.2$  mrad) than Si ( $\theta_c \approx 3.5$  mrad) for 8 keV and therefore the Rh deposit improves the reflectivity of the fundamental harmonic. In

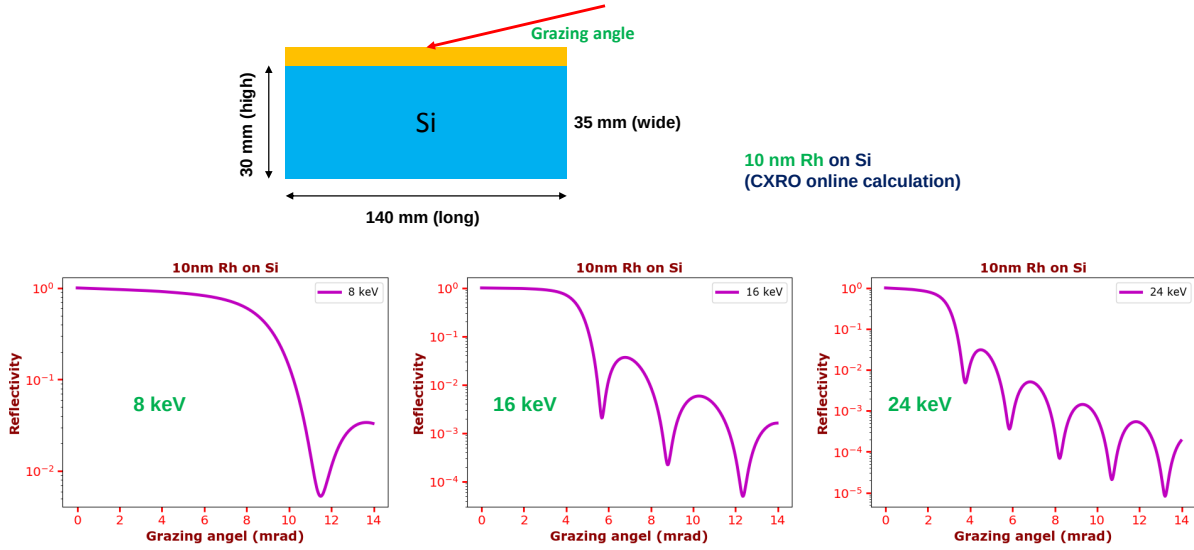


Figure 4.2. The reflectivity of the selected 10 nm Rh deposited on a Si substrate. The 6 mrad grazing angle can reflect 8 keV x-rays and effectively reject 16 keV and 24 keV x-rays.

addition, neither the K-edge ( $\sim 23$  keV) nor the L-edge ( $\sim 3$  keV) of Rh is in the range of K-edges of 3d transition metals (5 keV – 10 keV), and therefore this mirror is applicable to experiments of any 3d transition metal. It is a benefit of Rh.

I made use of a software package XOP [51] [52] to simulate the white beam spectrum of the APS Undulator A out of a  $600 \times 600 \mu\text{m}$  slit, shown in the left panels of Fig. 4.3. The 2nd (16 keV), 3rd (24 keV) harmonics are around one order of amplitude smaller than the first harmonic (8 keV). The mirror's reflective properties are presented in the middle panels of Fig. 4.3. According to the simulation, high reflectivity of 84% for the first harmonic at 8 keV and strong harmonic rejection ( $2.8 \times 10^{-3}$  for the second harmonic at 16 keV and  $5.4 \times 10^{-4}$  for the third harmonic at 24 keV) are expected. Based on our available



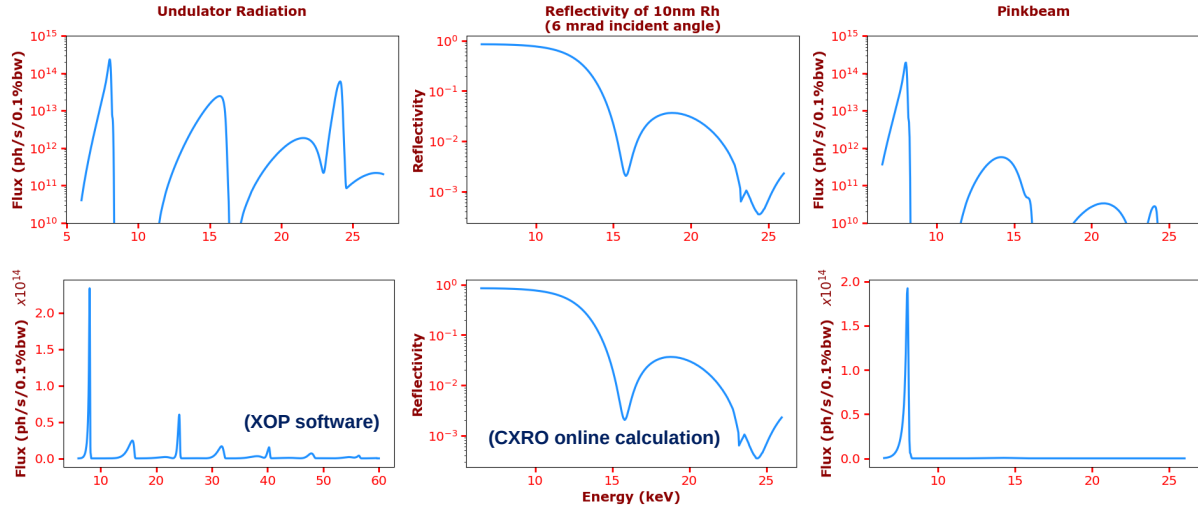


Figure 4.3. Calculations of the the harmonic rejection mirror are shown in logarithmic (upper row) and linear (lower row) scales. Left: Spectrum simulation out of APS Undulator A through a 0.6mm x 0.6mm main slit (1st harmonic peak set at 8 keV); Middle: Reflectivity of a single 10 nm layer of Rh deposited on a silicon substrate with 6 mrad ( $0.34^\circ$ ) grazing angle. Two clear dips occur at 16 keV and 24 keV while high reflectivity of 0.84 at 8 keV is provided. Right: Reflected spectrum by the mirror. The first harmonic retains enormous flux while the high harmonics are 2 or 3 orders of magnitudes smaller than the first harmonic.

silicon substrate (150 mm long, 35 mm wide and 30 mm high), the full beam coming from the white beam slits (set at  $600 \times 600 \mu\text{m}$ ) is easily accommodated with the 6 mrad grazing incidence angle. The right panels of Fig. 4.3 exhibits the calculation results of the undulator radiation spectrum multiplied by the reflectivity of the harmonic rejection mirror, namely the simulation of the radiation spectrum reflected from the harmonic rejection mirror and impinging on the CRL. In the reflected beam the first harmonic

retains enormous flux while high harmonics are 2 or 3 orders of magnitudes smaller than the first harmonic.

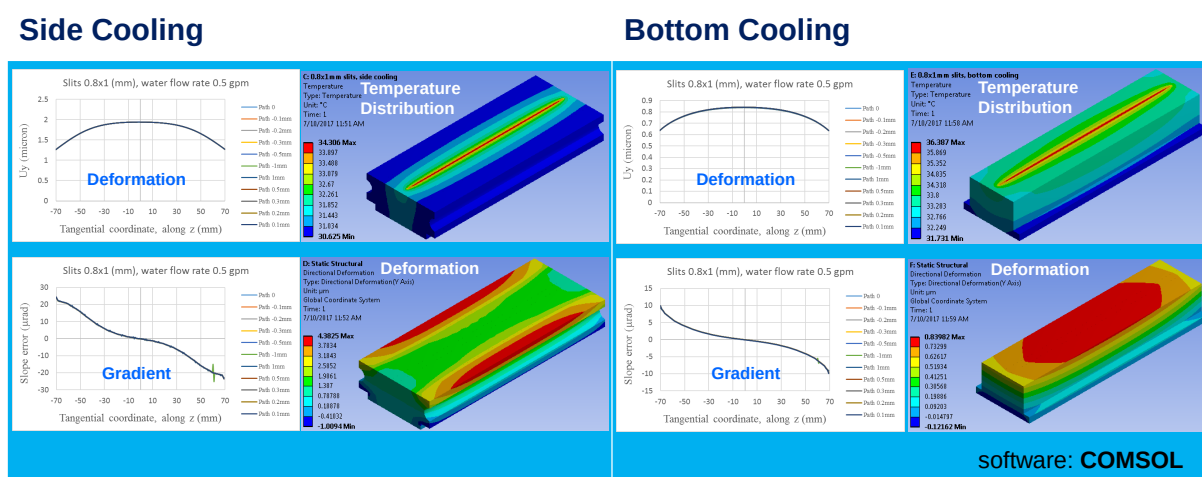


Figure 4.4. Heat load simulation shows that water cooling from the bottom of the substrate is able to maintain a smoother temperature variation and a smaller slope error along the substrate length.

Another concern about the harmonic rejection mirror is the deformation due to heat load. Our simulations of temperature distribution and substrate deformation, with and without water cooling of the substrate, demonstrates the necessity of active cooling. It also shows that water cooling from the bottom is better than from the sides of the substrate in terms of maintaining a smoother temperature variation and a smaller slope error along the substrate length. Figure 4.4 presents the simulation results of water cooling. With the water cooling from the bottom, the maximum height difference is around  $0.2 \mu\text{m}$ .

Slope error is zero around the central area and increases to  $10 \mu\text{rad}$  at the two ends. The temperature could be kept lower than  $36.4^\circ\text{C}$ .

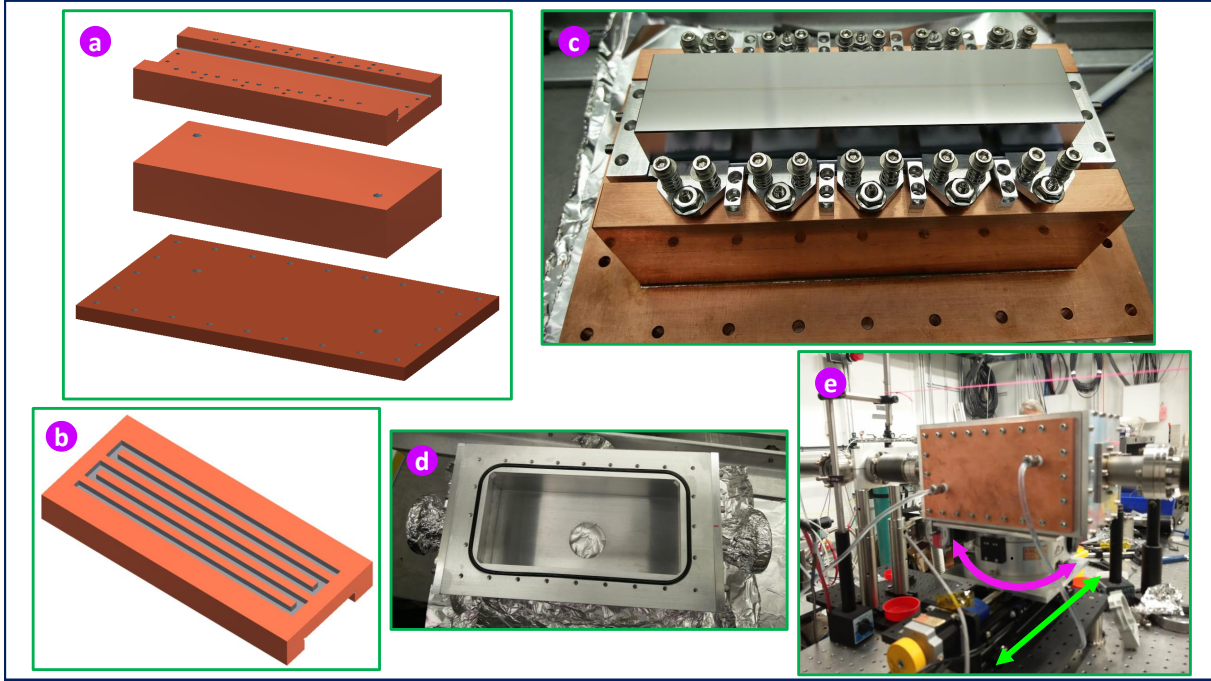


Figure 4.5. The design and pictures of the water-cooled copper heat sink for the harmonic rejection mirror. (a) three copper blocks constitute the heat sink. (dimensions of the whole heat sink assembly:  $184 \text{ mm} \times 80 \text{ mm} \times 65 \text{ mm}$ ) (b) grooves on the bottom side of the top block. (c) mirror mounted on the heat sink. A piece of  $0.1 \text{ mm}$  indium foil was sandwiched between them to improve the thermal conductivity. (d) vacuum chamber for the mirror. The copper heat sink assembly is installed to the chamber and also functions as one of the chamber's walls. (e) the mirror apparatus was installed in the beamline. Two Swagelok connections are installed on through holes connecting hoses to circulate cooling water.

Based on the simulation results, I designed and built a water-cooled copper heat sink for the mirror. The heat sink is assembled with three pieces of copper blocks, as shown in Fig. 4.5. The middle and bottom pieces have only two through holes on each. It is designed to have the mirror substrate mounted on the top surface of the top piece which

has grooves of 5 mm wide and 4.2 mm deep on the other side. The top surface is 8 mm away from the grooves. The three blocks are brazed together. Therefore, the through holes and the grooves constitute a water channel for the cooling water to flow inside the heat sink. The cooling water was circulated by a chiller Thermo Scientific SC100, and the temperature was set at 20 °C. The copper heat sink also functions as one of vacuum chamber's walls. This design facilitates the installation of the whole assembly of the mirror and the heat sink to the vacuum chamber. During the experiment, the vacuum condition was kept better than  $6 \times 10^{-5}$  Torr.

#### **4.2. X-ray Beam Focusing with Compound Refractive Lenses (CRL)**

The characteristics of element specificity and high penetration make hard x-ray unique in electromagnetic wave and able to directly probe and characterize active sites of metalloenzymes. In addition, this advantage combining its extreme short wavelength which benefits spatial resolution inspires the development of x-ray microscopy. Furthermore, the hard x-ray wavelengths of 2 Å to 0.05 Å are in the range of characteristic interatomic distances, such as of condensed matter. It is the foundation of x-ray crystallography. For all of the intriguing x-ray techniques mentioned above, i.e., micro probing, microscopy, and micro diffraction, its development counts on the capability to effectively focus x-ray beams.

For visible light, the most common focusing device is the conventional convex lens by means of refraction of light. In contrast, the design of an instrument to focus x-ray beam is fairly different. It stems from the super small value ( $10^{-6}$ ) of  $\delta$  in the index of refraction  $n = 1 - \delta + i\beta$  in x-ray regime and therefore bending x-ray beam by means of refraction is

not an effective approach. The focal length will be impractical long or most of beam power definitely will be absorbed by a large number of refractive lenses. Therefore, it is typically to employ reflective optics to bend and focus x-ray beams. With a proper curvature design, reflective x-ray optics can effectively focus a x-ray beam. Various x-ray instruments based on reflection have been designed and demonstrated for different applications, such as a Kirkpatrick-Baez mirror (KB mirror) [55] and a Wolter telescope [56]. However, this kind of instrument is typically super expensive, and permanently installed at a beamline, so it is not always applicable to some conditions of experiment.

In recent years with advancement of machining lenses out of light materials (e.g., Li, Be, B, C), refractive lenses for x-ray become feasible. Light materials are beneficial for minimizing power loss due to absorption by lenses because  $\beta$  of index of refraction is  $\sim Z^3/E^3$  where  $Z$  is atomic number and  $E$  is the x-ray energy. The refractive lens for x-ray has a concave shape because the real part of the index of refraction in lenses is smaller than one in x-ray regime (illustrated in the upper right panel of Fig. 4.6), unlike the conventional convex focusing lens in which the index of refraction is larger than one for visible light.

A single piece of refractive lens usually is not capable of effectively focusing a x-ray beam owing to the extreme small value of  $\delta$  in the index of refraction (i.e., weak interaction of x-ray with matter). As a result, stacking a few number of lenses in a row is required to focus x-rays and is designated as Compound Refractive Lenses (CRL), as illustrated in the lower right panel of Fig. 4.6. CRL has focal length

$$(4.3) \quad f \approx R/2\delta N$$

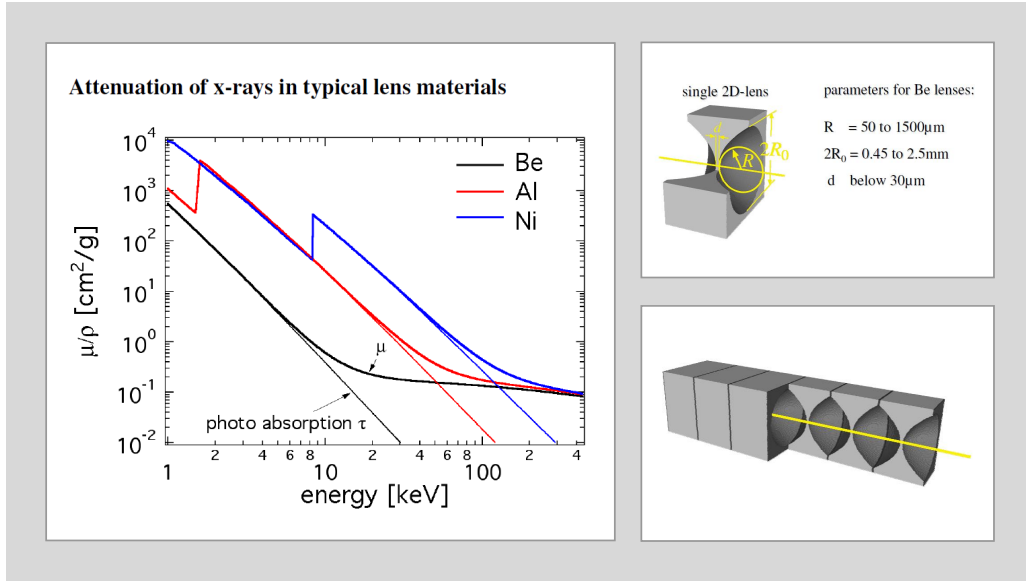


Figure 4.6. Left: Attenuation of X-rays in different lens materials, i.e., Be, Al, and Ni. Upper right: Model of a biconcave refractive lens with a parabolic profile. One quadrant has been removed in order to show the lens profile. Lower right: By stacking many individual lenses in a row to form a compound refractive lens (CRL). [60]

where  $R$  is the radius of curvature,  $N$  is the number of lenses, and  $\delta$  is the index of refraction decrement.

Figure 4.7 summarizes the properties of materials for x-ray lenses. Among light materials, beryllium (Be) is a good choice as far as handling, manufacturing processes and accessibility is concerned. In addition, metal material has the big advantage of avoiding radiation damage and providing good heat conductivity. The left panel in Fig. 4.6 is the attenuation of x-rays in different lens materials [60]. In the plot,  $\mu$  is the total absorption coefficient of the material in Lambert-Beer's law

$$(4.4) \quad I = I_0 e^{-\mu d}$$

| Material       | Z  | Machining and handling                                                      |
|----------------|----|-----------------------------------------------------------------------------|
| Lithium (Li)   | 3  | Kept in an oxygen and water free environment                                |
| Beryllium (Be) | 4  | Toxic. Hard and brittle at room temperature. Pressing possible above 800 °C |
| Boron (B)      | 5  | Very hard for machining                                                     |
| Diamond (C)    | 6  | Expensive                                                                   |
| Sodium (Na)    | 11 | Kept in an oxygen and water free environment                                |
| Magnesium (Mg) | 12 | Brittle at room temperature. Pressing possible around 400 °C                |
| Aluminum (Al)  | 13 | Very good shaping by pressing                                               |

Figure 4.7. Properties of materials for x-ray lenses

where  $I_0$  is the primary intensity and  $I$  is the attenuated intensity behind the material thickness  $d$ . The linear total absorption coefficient  $\mu$  is the sum of the attenuation coefficients for photoelectric absorption  $\tau$ , elastic (Rayleigh) scattering  $\sigma_R$ , inelastic (Compton) scattering  $\sigma_C$ , and pair production  $\sigma_{Pair}$  (for energy exceeds  $2 m_0 C^2 \simeq 1.022$  MeV, refer to Section 2.1)

$$(4.5) \quad \mu = \tau + \sigma_R + \sigma_C + (\sigma_{Pair})$$

The power-law behavior due to photoelectric absorption is limited by Compton scattering which becomes dominant at higher energies and contributes strong background radiation. As a result, lenses should be operated in the energy range to the left of the respective knee. The lenses can be used in a very wide energy range from about 2 keV to about 150

keV. In short, beryllium is the material of choice up to about 40 keV. Roughly from 40 to 80 keV, aluminum is more appropriate. Beyond these energies, nickel is used. In addition, experience has shown that beryllium lenses are able to withstand both the white beam of an undulator and the intense beam of a x-ray free-electron laser.

I did a series of simulations to optimize the design of our experimental setup by means of a Monte Carlo, ray-tracing software — McXtrace [62]. The goal is to reach a compromise between flux, spot size and working distance, considering the available motorized tables in the 7ID-B hutch, while being able to cover the energy range of the first harmonic radiation of APS Undulator A, i.e., from 5 keV to 13 keV. A smaller radius of curvature makes a lens of more focusing power, but it reduces the acceptance as well. However, since I mean to grossly compensate for the chromaticity by adding or removing a number of lenses, lenses with too small radius of curvature do not provide fine enough adjustments. I figured out the best compromise to be given by lenses with 200  $\mu\text{m}$  radius of curvature.

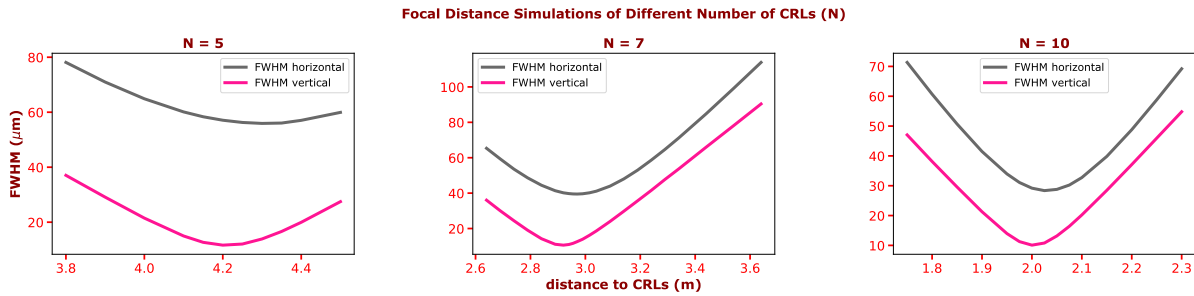


Figure 4.8. Simulations for different numbers of lenses of 200  $\mu\text{m}$  radius of curvature to focus 8 keV pink beam.

Figure 4.8, one of a series of simulations, shows the result of different numbers of lenses with 8 keV pink beam. The x-ray beam out of an undulator has elliptical shape with a



horizontal major axis (refer to Section 2.2). In addition, it has larger beam divergence in horizontal than in vertical. As a result, the focused beam has an elliptical shape and the focal distance of horizontal is longer than that of vertical. The simulations predicted that CRL easily produce a vertical focus of around  $10\text{ }\mu\text{m}$  FWHM, but that adding more lenses does not lead to further decrease in the spot size as chromatic aberration dominates. While adding lenses slightly decreases the horizontal spot size, the increased absorption reduces the available flux.

Based on a series of simulations of different combinations of lens quantities and pink beam energy, I eventually found that a working distance around 3 meters between the lenses and the focus is a good choice in terms of the spatial arrangement of the 7ID-B hutch and the flexibility to focus pink beams of different energy. With a focal distance of around 3 meters, I can use 5 lenses for about 5 keV, 7 lenses for about 8 keV, and 10 lenses for about 10 keV, with very similar focusing properties. For energy between 10 and 13 keV, it is necessary to replace one or two of the lenses of  $200\text{ }\mu\text{m}$  radius of curvature with more-focusing-power  $100\text{ }\mu\text{m}$  radius lenses to keep the same focal distance around 3 meters.

The lenses employed in this project are biconcave with rotationally parabolic profiles [58] [57]. Figure 4.9 exhibits the beryllium CRL of  $200\text{ }\mu\text{m}$  radius of curvature purchased from RXOPTICS [59].

A motorized lens stage from JJ X-Ray [61] was employed for this project, and I designed and built a copper adapter for 2D-focusing parabolic lenses to fit the lens holder of the stage, shown in Fig. 4.10. The adapter fits the CRL and the water-cooled lens holder very well to guarantee good thermal conductivity to dissipate heat out of



Figure 4.9. Beryllium CRL of  $200\ \mu\text{m}$  radius of curvature purchased from RXOPTICS [59]. The two pieces of the right end are Cu-Al-Ni alloy pinholes to reduce scattered radiation.



Figure 4.10. The arrangement in the adapter cube, from right to left (downstream), is 0.8 mm pinhole, two 2 mm thick copper spacers, 7-stack beryllium CRL, 1 mm thick copper spacer, 1.0 mm pinhole, and 1 mm thick copper spacer.



Figure 4.11. The water-cooled holder and the adapter to install round lenses to a rectangular slot. The adapter fits the CRL and the water-cooled lens holder very well to guarantee good thermal conductivity to dissipate heat out of CRL.

CRL, as shown in Figure 4.11. The arrangement in the adapter cube, from right to left (downstream wards), is 0.8 mm pinhole, two 2 mm thick copper spacers, 7-stack beryllium CRL, 1 mm thick copper spacer, 1.0 mm pinhole, and 1 mm thick copper spacer. The pinholes are made of Cu-Al-Ni alloy. The main purpose of installing pinholes at both ends of the lens stack to limit the incoming beam size and to reduce scattered radiation. In addition, the edge of the front pinhole facilitates to center and align the beam with CRL.

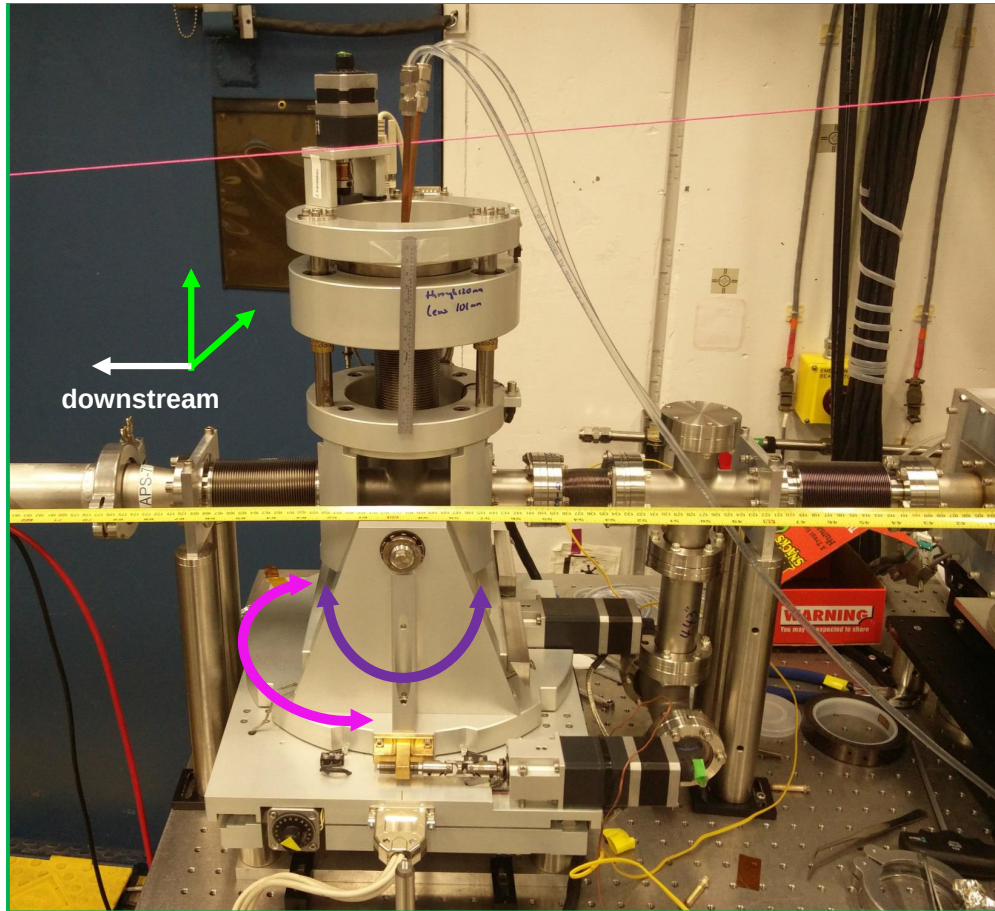


Figure 4.12. The motorized CRL stage.

All of the copper spacers have a 1.4 mm diameter aperture in the middle and are meant to improve the heat dissipation to the water-cooled lens stage.

A quick estimate shows that about half of the pink beam power is going to be absorbed in the lens stack, implying the necessity of water cooling. The water-cooled lens stage can provide two lateral translation movements as well as yaw and pitch rotational movement, shown in Fig. 4.12. The cooling water in the lens stage was circulated by the same chiller model Thermo Scientific SC100, and the temperature was set at 20 °C. The temperature

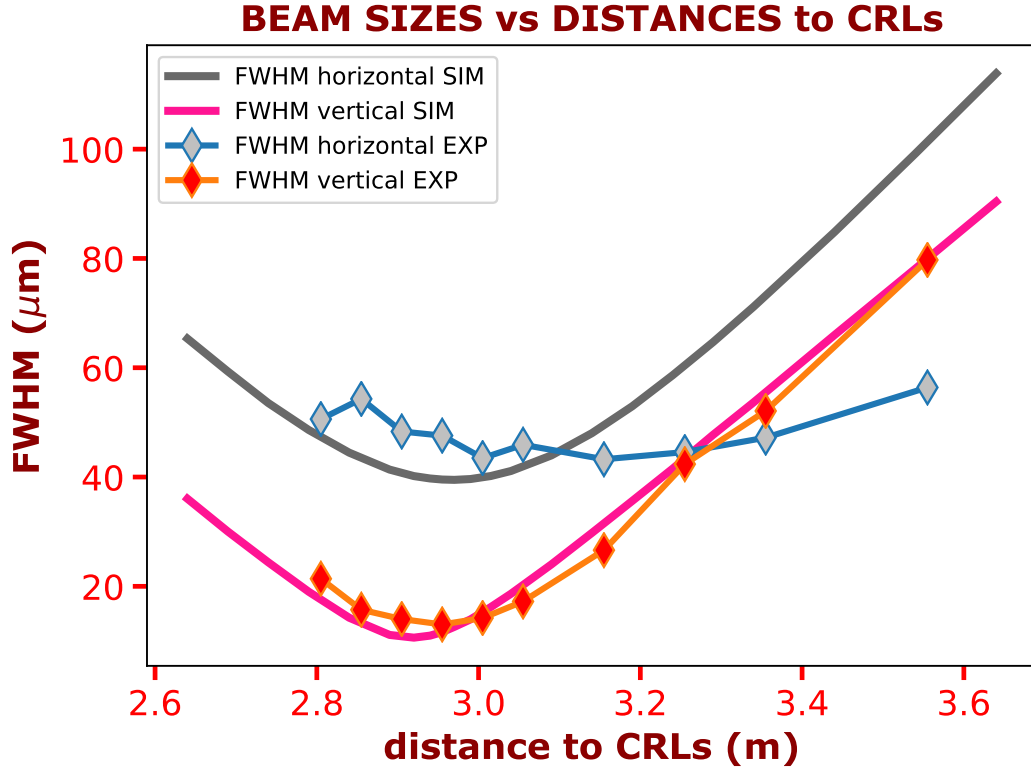


Figure 4.13. 8 keV pink beam sizes at different distances focused by 7-stack CRL of  $200\ \mu\text{m}$  out of a  $600 \times 600\ \mu\text{m}$  main slit. The designed focal distance is  $2.955\ \text{m}$  where the simulated beam size is around  $40\ \mu\text{m} \times 12\ \mu\text{m}$ . The measurement result of the focused beam size at  $2.955\ \text{m}$  is about  $47.5\ \mu\text{m} \times 13\ \mu\text{m}$  by means of scintillator imaging. The vertical simulations are consistent with the measurement results very well.

went up to  $150\ ^\circ\text{C}$  as pink beam struck the CRL. The vacuum pressure of the lens stage went up from  $4.4 \times 10^{-5}$  to  $8.5 \times 10^{-5}$  Torr as the pink beam passed through the CRL.

Figure 4.13 exhibits the direct comparison of the measurement results with the simulations of pink beam sizes of 8 keV plotted versus the distance from the 7-stack CRL. The experimental measurement was accomplished by means of scintillator imaging (details in Section 5.1). The measurement was performed by moving the whole instrument set of scintillator imaging. Overall, the agreement is very satisfactory, especially in the vertical

direction. However, the measurement in horizontal does fit with simulation very well. It is possible that the horizontal beam divergence for the simulation is larger than the reality. As the scintillator imaging set was moved to different places, the height and the alignment in vertical was consistent. However, it is difficult to keep the horizontal alignment consistent to high degree. It is another possibility is that the horizontal measurement did not agree with the simulation well.

Furthermore, the beam size measurements of the energy scan around 8 keV at the designed focal distance of 2.955 m also display a satisfactory result that the minimal focal spots appear around at 8 keV, as shown in Fig. 4.14. The measurement was performed by changing the undulator gap. During the pink beam beamtime, since the bandwidth is much broader than that of mono beam, an energy calibration cannot be performed. Therefore, pink beam energy can only rely on the undulator number, which comes from a table given a certain gap opening of the undulator.

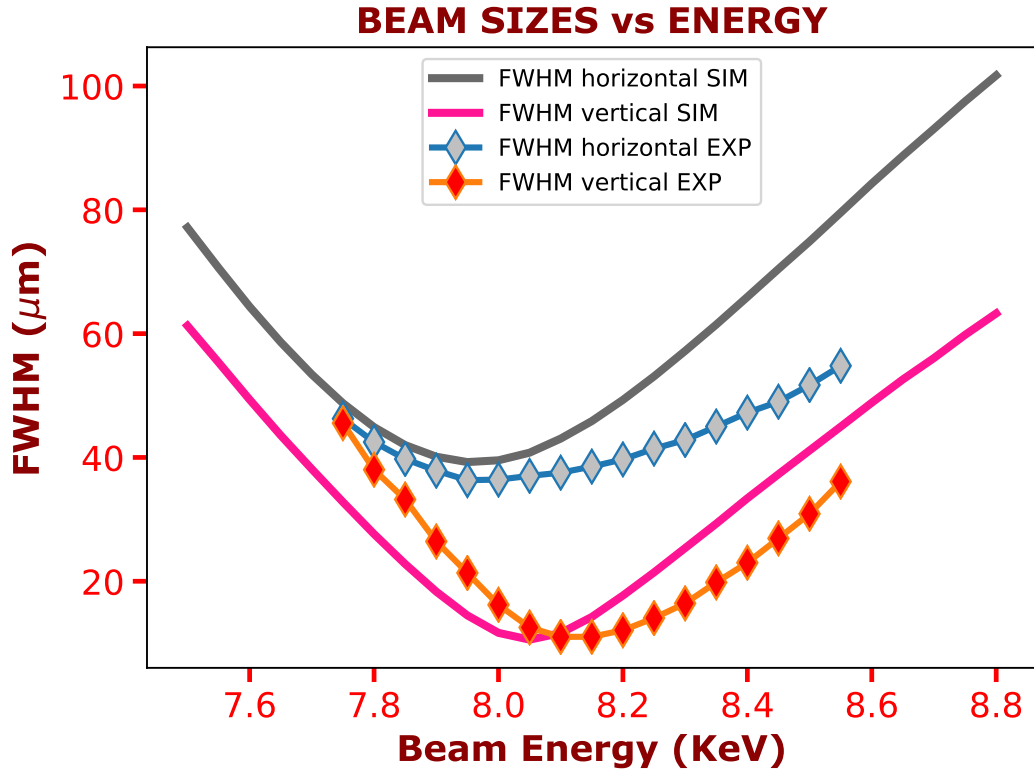


Figure 4.14. The beam sizes of the energy scan around 8 keV at the designed focal distance of 2.955 m focused by 7-stack CLR of  $200\mu\text{m}$  out of a  $600 \times 600 \mu\text{m}$  main slit. The experimental measurements are basically consistent with the simulations in terms of the minimal beam sizes and their energies: the horizontal minimum occurs at 7.95 keV with  $36 \mu\text{m}$  FWHM (simulation: 7.95 keV with  $39 \mu\text{m}$ ) and the vertical minimum is at 8.1 keV with  $10 \mu\text{m}$  FWHM (simulation: 8.05 keV with  $10 \mu\text{m}$ ).

## CHAPTER 5

### **X-ray Beam Profile Measurement**

Although the harmonic rejection mirror, CRL, and beryllium windows were equipped water-cooling systems, in order not to take the risk of any damage by high flux x-ray beam, a high heat load chopper was installed at upstream in the first place to attenuate the power of the incident beam to 1%. With the chopped beam, the harmonic rejection mirror, CRL, and beryllium windows were installed in position and oriented step by step. As all components were set up properly, the chopper was removed and the section was replaced with long nipple vacuum components. As the full x-ray beam started to be employed, a small opening of the main slit was used and gradually increased to assure that the heat dissipation efficiency of each apparatus was good enough to function normally in high x-ray flux.

As for the attenuated beam, in addition to preventing apparatus from any unexpected damage during installation and alignment, it was also a good condition to perform the beam profile measurement of the focused pink beam. We tried three different methods for beam profile measurement, including scintillator imaging, knife edge scan of different materials, and platinum 30- $\mu\text{m}$ -aperture pinhole scan. The scintillator imaging worked best among them in terms of showing fine structures and simplifying analysis process. The following sections present the measurement results of individual methods and their comparisons.



### 5.1. Scintillator Imaging

The scintillator imaging system was composed of a 10mm x 10mm x 0.15mm LYSO:Ce scintillator (Cerium doped Lutetium Yttrium Silicate) [65] [66] [67] [68] [69] from PROTEUS Inc., a mirror, a long working distance objective of X2 magnification (Mitutoyo), and a CCD camera (Prosilica 2450 GC) with 3.45  $\mu\text{m}$  pixels, shown in Fig. 5.1. In this

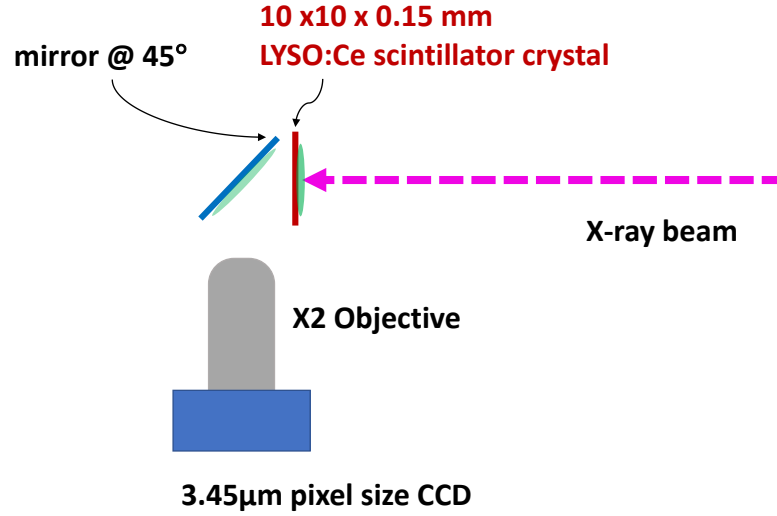


Figure 5.1. Schematic of scintillator imaging system.

imaging configuration, the x-ray beam illuminates the scintillator at normal incidence. The phosphorescent photons formed profile images on the scintillator and then a 45° mirror behind the scintillator reflected the emitted light to the CCD. The phosphorescent images were recorded by the combination of the objective and the CCD camera.

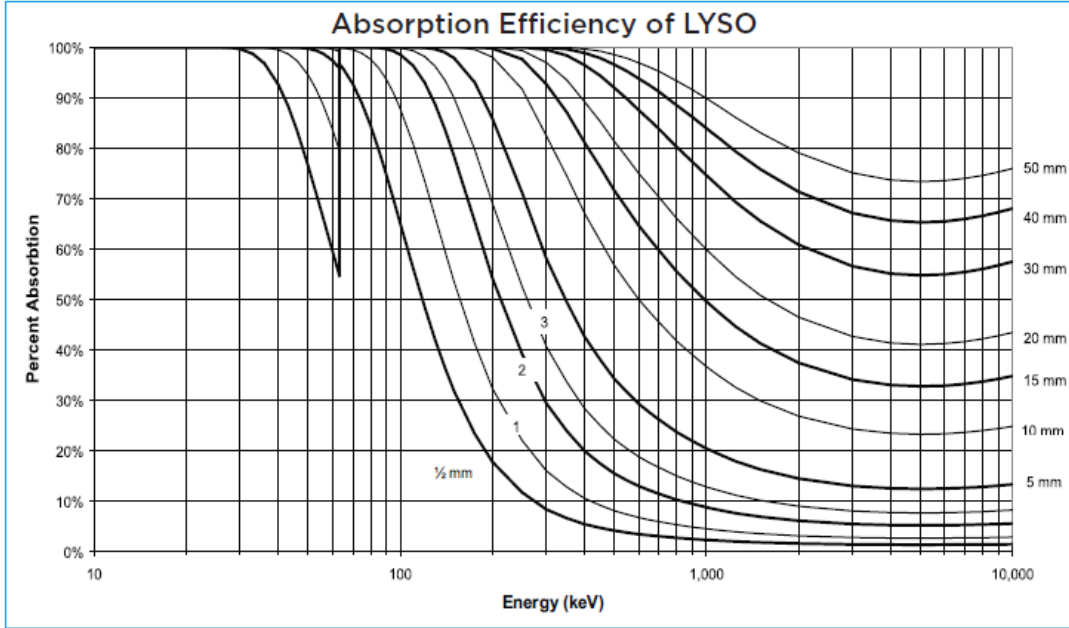


Figure 5.2. Gamma and X-ray absorption efficiency for various thicknesses of LYSO:Ce. [70]

Figure 5.2 presents the absorption efficiency for various thicknesses of LYSO:Ce scintillators. With 0.15 mm thickness, the absorption efficiency is nearly 100% at 8 keV. As excited by the radiation, the LYSO:Ce scintillator emits 420 nm photons [70].

Operation of the scintillator requires some caution regarding the heat load of the radiation that hits it. Much before causing obvious damage in the crystal, temperature rise in the crystal makes it lose scintillation efficiency, which translates into a saturation effect which can easily incorrectly increase the measured beam size.

Using sets of simple metal foil filters positioned before the scintillator imaging can effectively avoid the saturation condition. Aluminum is a good choice to attenuate the

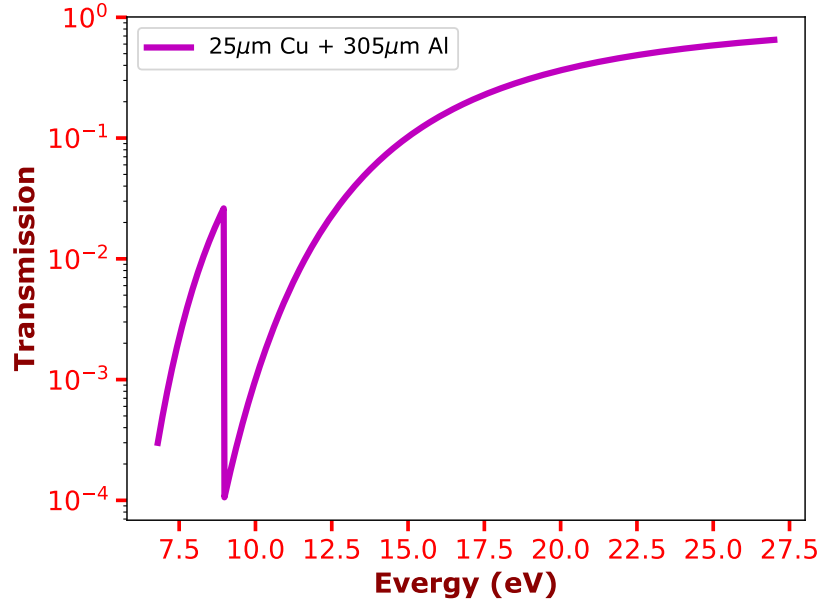


Figure 5.3. Transmission of 25  $\mu\text{m}$  Cu plus 305  $\mu\text{m}$  Al

first harmonic radiation (8 keV) which is dominating the beam after the harmonic rejection mirror. However, there is still a large average flux in the second harmonic (refer to Section 4.1), which can influence any measurements. Therefore, adding another metal filter with a K-edge above the first harmonic makes it possible to study the contribution of the high harmonics. In this case, copper was utilized for high harmonic attenuation.

By combining filters (25  $\mu\text{m}$  thick copper plus 305  $\mu\text{m}$  thick aluminum) to get about 3 orders of magnitude attenuation in the first harmonic and 1 order of magnitude attenuation in the second harmonic (refer to Fig. 5.3), a strongly focused first harmonic spot as well as a loosely focused second harmonic spot can be observed on the scintillator image, as shown in the left image of Fig. 5.4.

Figure 5.4 presents the beam profile comparison before and after being focused by CRL. The left scintillator image shows that CRL focus a pink beam to a 47.5  $\mu\text{m}$  x

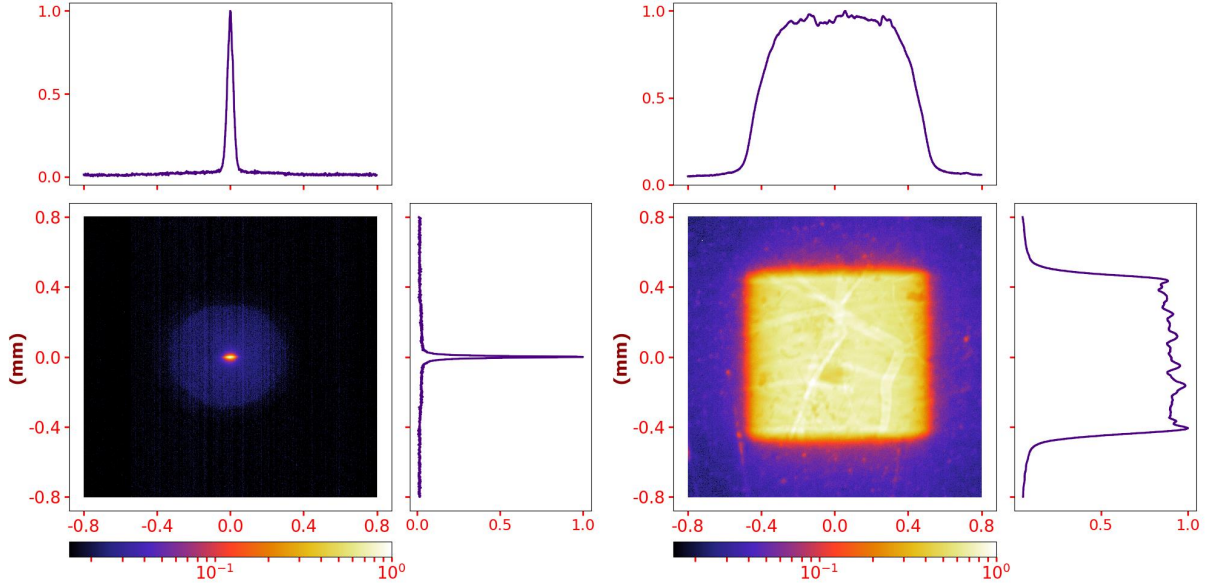


Figure 5.4. Comparison of beam profiles with and without being focused by CRL

13  $\mu\text{m}$  spot. The 600  $\mu\text{m}$  diameter pedestal around the focused spot comes from high harmonics, mainly 2nd and 3rd harmonics, and its intensity is about 2 orders of magnitude smaller than that of the focused pink beam. The beam profile structure demonstrates the chromaticity of CRL. The right scintillator image shows the pink beam profile reflected from the harmonic rejection mirror without being focused by CRL. The 1000  $\mu\text{m}$  wide square profile implies that there is no unwanted deformation on the harmonic rejection mirror and the beam divergence out of the 600  $\mu\text{m}$  x 600  $\mu\text{m}$  main slit. The square This scintillator imaging configuration worked well for beam profile measurement, especially in showing fine structure of a beam profile.

## 5.2. Pinhole Scan

Before the chopper was removed, we demonstrated the pinhole scan for the beam profile measurement. A platinum  $30\text{ }\mu\text{m}$  pinhole (Ted Pella, Inc. [71]) scanned in horizontal or vertical, and x-ray photons passing through the  $30\text{ }\mu\text{m}$  pinhole were detected by an ion chamber.

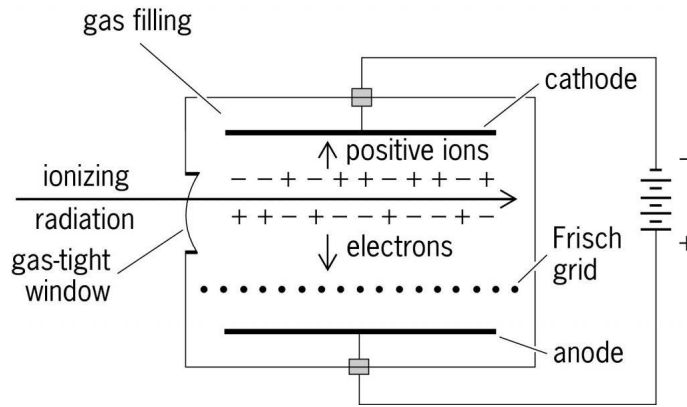


Figure 5.5. Schematic of an ion chamber

The ion chamber employed here consists of two conducting electrodes in a container filled with ambient air. A high voltage electric field between the electrodes is maintained by an external circuit. As a x-ray beam (ionizing radiation) passes through the chamber, it liberates electrons from the gas atoms leaving positively charged ions. The electric field sweeps the electrons going to the anode and the positive ions to the cathode. This generates an ionization current which reflects the relative amount of x-ray beam flux, as illustrated in Fig. 5.5.

Figure 5.6 presents the pinhole scan result compared to the scintillator imaging in the same condition in which the chopped beam was attenuated by  $305\text{ }\mu\text{m}$  Al plus  $25\text{ }\mu\text{m}$  Cu foil (refer to Fig. 5.3). The beam size measured by pinhole scan is  $40\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$  while

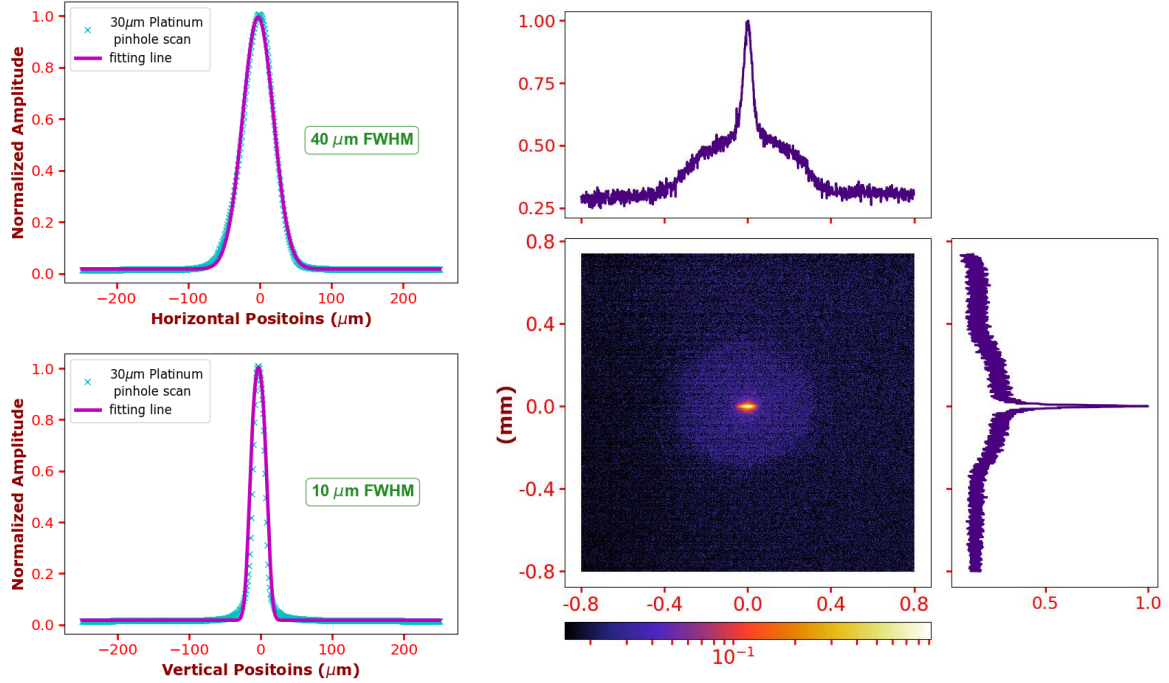


Figure 5.6. 30  $\mu\text{m}$  pinhole scan (left top: horizontal scan; left bottom: vertical scan) in comparison with the scintillator imaging (right) in the same condition.

the scintillator imaging shows a  $47.5 \mu\text{m} \times 13 \mu\text{m}$  focused beam spot with a very dim 600  $\mu\text{m}$  pedestal. The chopped beam exhibits a more clear beam profile structure in a scintillator image than a full beam of Fig. 5.4.

Figure 5.8 presents another comparison in which the chopped beam was attenuated with 230  $\mu\text{m}$  Al foil (refer to Fig. 5.7) and the high harmonics were not further attenuated by Cu or other metal foil. The pinhole scan measured the beam size of  $44 \mu\text{m} \times 26 \mu\text{m}$  while the scintillator imaging shows a  $53 \mu\text{m} \times 90 \mu\text{m}$  focused beam spot with a 600  $\mu\text{m}$  pedestal.

The data analysis of pinhole scan is done with a convolution of a 30  $\mu\text{m}$  circular area with a Gaussian profile whose parameters are to be determined. In other words,

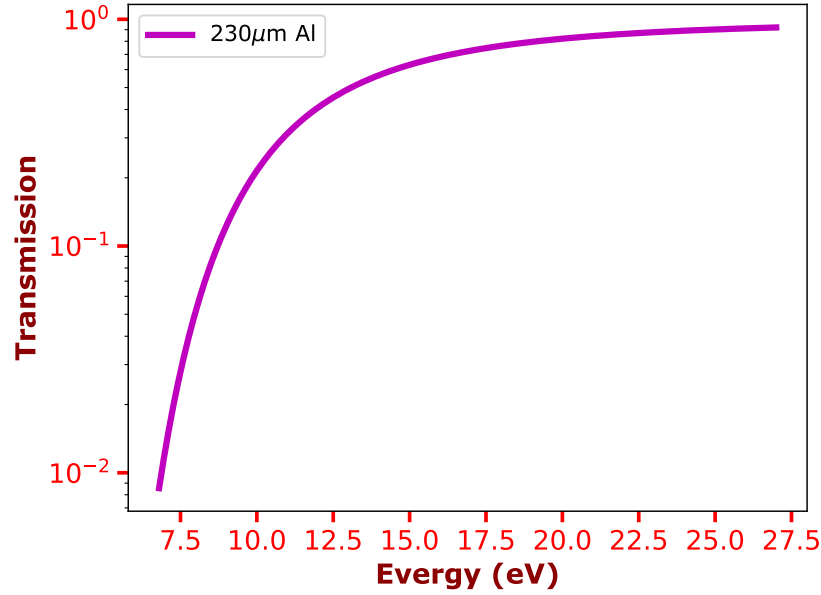


Figure 5.7. Transmission rate of 230  $\mu\text{m}$  Al

this is a simplified model assuming a simple Gaussian profile in scanning direction and a constant distribution in the other direction. The size values from this analysis are definitely smaller than the reality. The real profile is a elliptical shape with a normal distribution in all directions. An advanced analysis with a sophisticated algorithm could approach the real value but it takes time to develop the codes. In addition, this 30  $\mu\text{m}$  pinhole is impracticable to reach high enough spatial resolution to distinguish pedestal structure from the focused peak.

In either condition in which high harmonics are attenuated by Cu foil or not, the scintillator imaging possess advantages over the 30  $\mu\text{m}$  pinhole scan in terms of being able to show fine profile structures and requiring much simpler analysis.

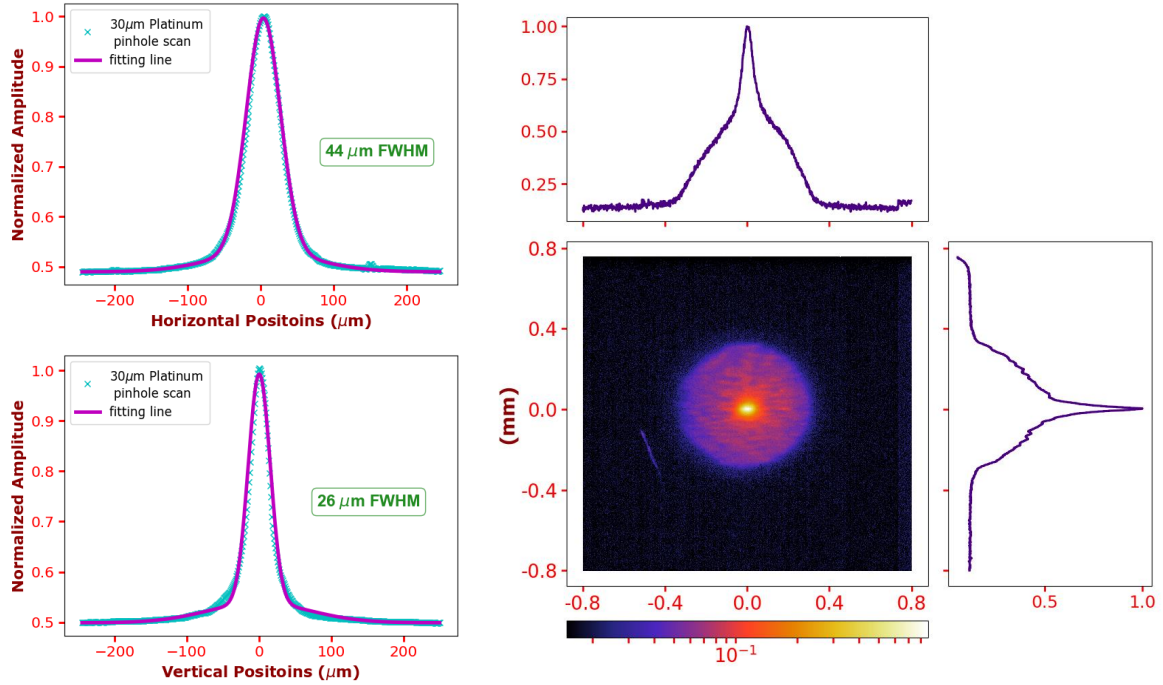


Figure 5.8. Another comparison of 30  $\mu\text{m}$  pinhole scans (left top: horizontal scan; left bottom: vertical scan) with the scintillator imaging (right).

### 5.3. Knife Edge Scan

The knife edge scan was also tested with two different materials, Cu and  $\text{Si}_3\text{N}_4$ , and then compared to scintillator imaging in the same condition in which the chopped beam was attenuated with 230  $\mu\text{m}$  Al foil (refer to Fig. 5.7). Figure 5.9 shows the transmission rates of two different knife materials. The Cu knife blocks over 1st, 2nd and 3rd harmonics; the  $\text{Si}_3\text{N}_4$  knife reduces 1st harmonic by around two orders of magnitude and passes most of high harmonics.

Figure 5.10 presents the measurement and analysis results. The analysis is done with the convolution of a Heaviside step function with a Gaussian profile whose parameters are to be determined. The Cu knife edge got 184  $\mu\text{m}$  in horizontal; the  $\text{Si}_3\text{N}_4$  knife edge scan



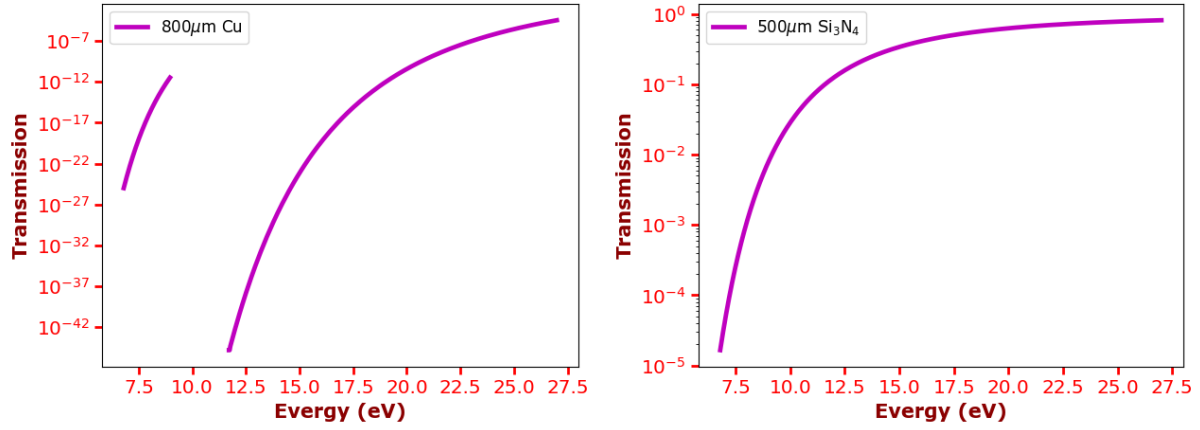


Figure 5.9. Transmission rates of two different materials (Left: Cu. Right: Si<sub>3</sub>N<sub>4</sub>) for knife edge scan

measured  $435 \mu\text{m}$  in horizontal and  $365 \mu\text{m}$  in vertical. Either of them is much larger than the results of scintillator imaging ( $44 \mu\text{m} \times 26 \mu\text{m}$ ). In a knife edge scan, both photons from focused pink beam and high harmonics in pedestal were integrated together. As a result, the fine focused structure cannot be distinguished from the pedestal in a knife scan. However, since Si<sub>3</sub>N<sub>4</sub> attenuated only 1st harmonic by two orders, passing high harmonics, its measurement was close to the pedestal size.

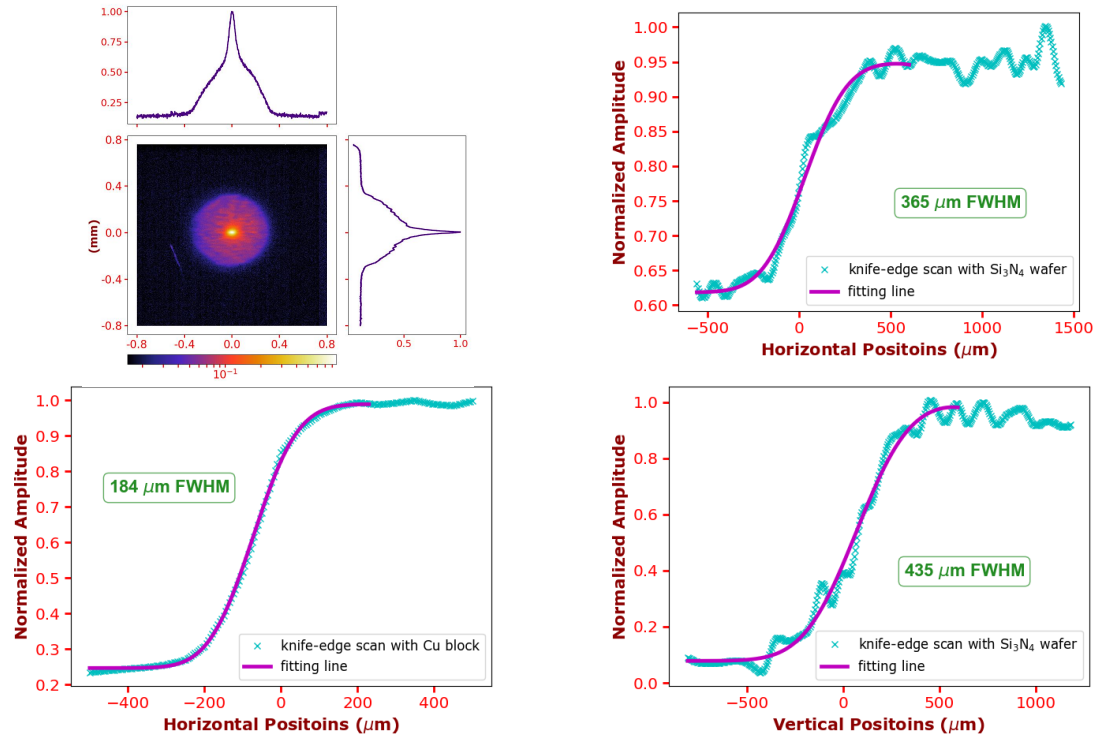


Figure 5.10. Upper left: scintillator imaging in the same condition. Lower left: Cu knife scan in horizontal. Right:  $\text{Si}_3\text{N}_4$  knife scan in vertical (upper right) and in horizontal (lower right).

## CHAPTER 6

**Coordination Compound**

A transition metal complex is a central metal atom or ion surrounded by a set of ligands. A ligand is an ion or molecule that can have an independent existence. For instance,  $\text{Ni}(\text{CO})_4$  is a transition metal complex in which the Ni atom is surrounded by four CO ligands, as shown in Fig. 6.1. A coordination compound is a neutral transition metal complex or an ionic compound in which at least one of the ions is a transition metal complex [72]. In a typical covalent bond, each atom is considered to contribute one electron. However, both of the electrons come from a single atom in the bond between a metal and ligands in a transition metal complex. This type of bond is known as a dative covalent or a donor-acceptor bond. The atom which provides the two electrons is known as the donor; the other is the acceptor. In a transition metal complex, a metal is usually an acceptor and ligands are the donors [73].

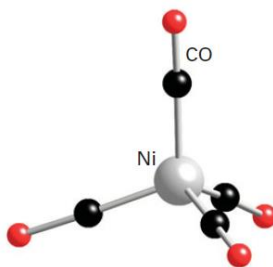


Figure 6.1.  $\text{Ni}(\text{CO})_4$  transition metal complex [72]

Coordination compounds play a critical role in structural or catalytic functions of an organism's physiology. For instance, an estimated 30% of proteins contain transition

metal complexes. In addition, catalysis is a major application of coordination compounds for the production of organic substances. For instance, a photocatalytic system consisting of a iron complex was investigated to demonstrate its function of catalyzing the conversion of methane to methanol [74].

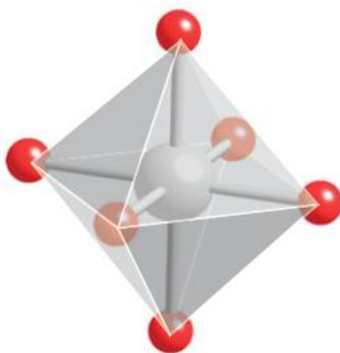


Figure 6.2. Octahedral transition metal complex [72]

Element specificity and high penetration of x-rays make it a power probe for geometry and electronic structure information of transition metal complexes either by diffraction or spectroscopy. In this project, an octahedral complex  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  was employed to demonstrate the application of the pink beam XES in the charge transfer dynamics (refer to Section 7.2 for a full story). This chapter is dedicated to introduce the electronic structure of octahedral transition metal complexes and the unique characteristics of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ .

### 6.1. Octahedral Transition Metal Complex

The most common arrangement for six-coordination transition metal complexes is highly symmetric octahedral, as shown in Fig. 6.2 if we consider the ligands as represented by structureless points.

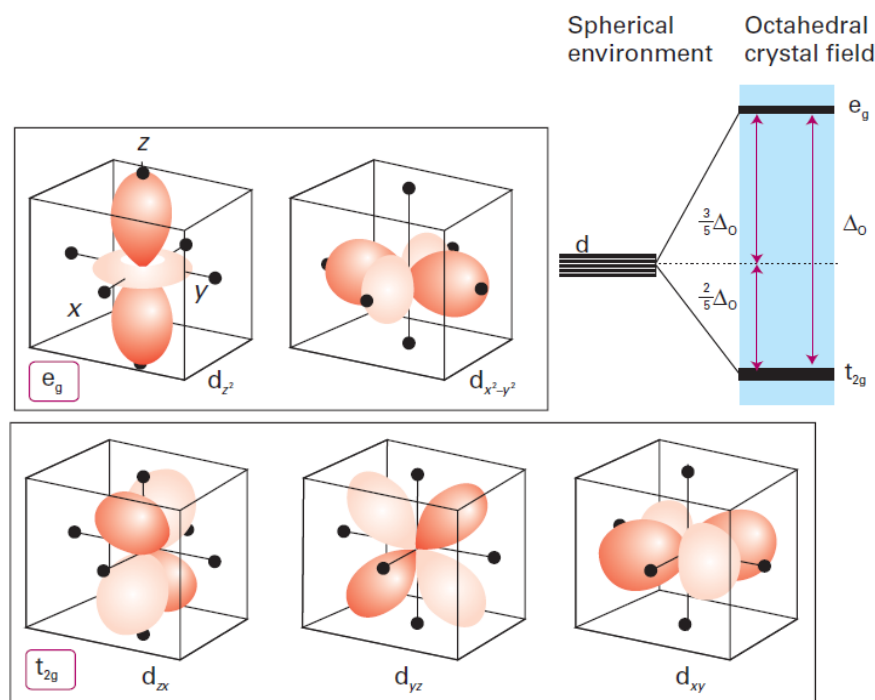


Figure 6.3. Splitting of d orbitals in octahedral transition metal complexes [75]

A ligand lone pair could be viewed as a point negative charge that repels electrons in the d orbitals of the central metal atom in an octahedral transition metal complex. Electrons in  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are concentrated close to the ligands, along the axes, whereas electrons in  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals are concentrated in regions that lie between the ligands, illustrated in Fig. 6.3. The former are repelled more strongly by the negative charge on the ligands than the latter and lie at a higher energy. As a result, the d orbitals split into two groups, called  $e_g$  and  $t_{2g}$ . This primitive theory which can explain the splitting of the d orbitals into two groups with different energies is called crystal field theory [75].

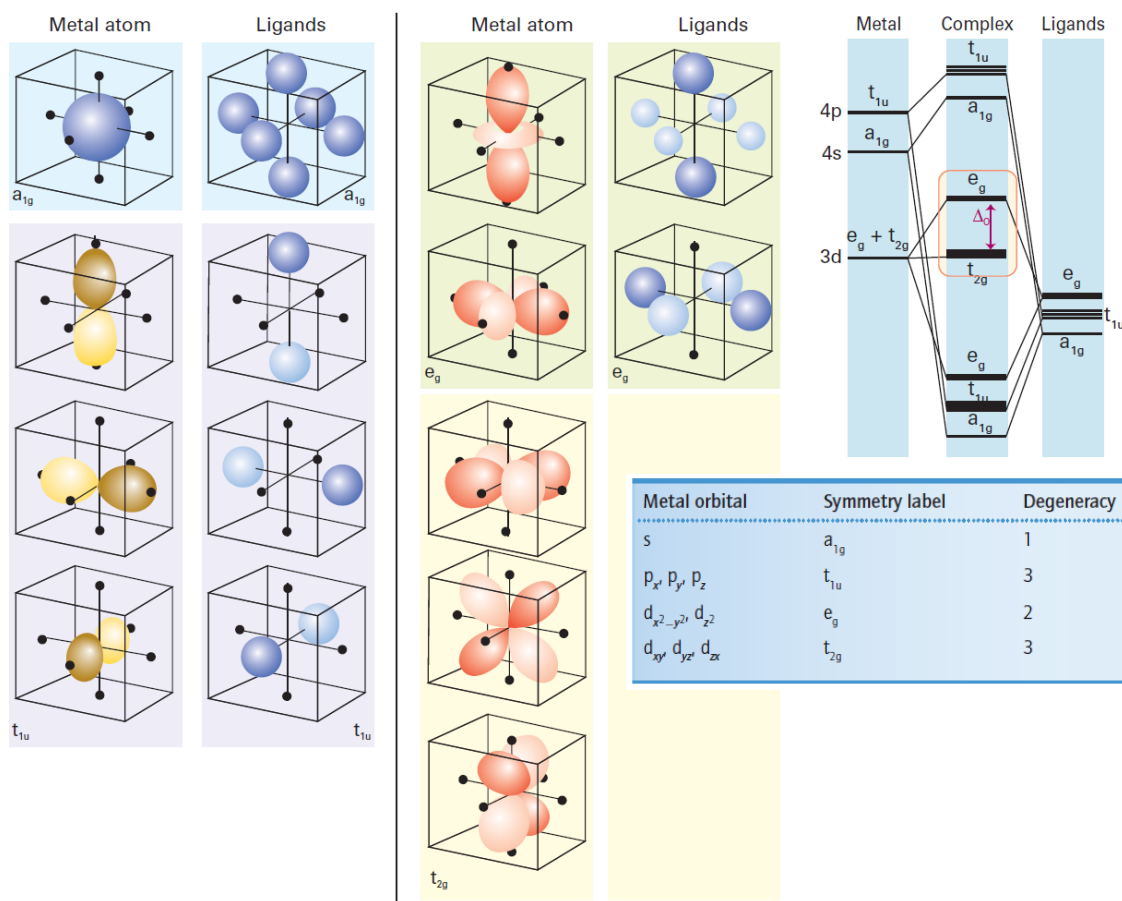


Figure 6.4. Molecular orbitals of octahedral transition metal complexes ( $\sigma$  bonding) [75]

A more sophisticated ligand field theory exploits molecular orbital theory to provide a more substantial framework to understand the origins of d orbital splitting. According to the space symmetry, the orbitals of the metal atom as well as the group orbitals of all the ligands can be categorized into different groups in a octahedral transition metal complex. In this theory, the  $e_g$  orbitals of the metal and ligands constitute  $e_g$  bonding and  $e_g^*$  antibonding molecular orbitals. The  $e_g$  bonding orbitals are occupied by electrons from donor atoms in the ligands. The electrons of d orbitals of the metal stay in the  $t_{2g}$  or  $e_g^*$  orbitals. The  $t_{2g}$  orbitals of the metal are nonbonding if only the  $\sigma$  bonding is taken into

account. As a result,  $e_g^*$  antibonding molecular orbitals are higher than the nonbonding  $t_{2g}$  orbitals in a energy diagram, as shown in Fig. 6.4. (The meaning of these labels for molecular orbitals is: **a** denotes a nondegenerate orbital; **e** denotes a doubly degenerate orbital; **t** denotes a triply degenerate orbital. The orbital is designated **g** (for gerade, even) if it is identical under inversion, and **u** (for ungerade, odd) if it changes sign.)

Besides  $\sigma$  bonding in a octahedral transition metal complex,  $t_{2g}$  orbitals of the central metal can form  $\pi$  bonding with p orbitals of ligands. There are two different scenarios depending on ligands acting as  $\pi$  donors or acceptors. If ligands' donor electrons occupy and fill the  $\pi$  bonding molecular orbitals, the electrons originally in the d orbitals of the central metal atom occupy the  $t_{2g}^*$  antibonding orbitals which are closer in energy to the  $e_g^*$  orbitals. On the contrary, if ligands have  $\pi$  orbitals available for occupation, d electrons of the central metal atom can occupy the  $t_{2g}$  bonding orbitals, which increases the energy gap to the  $e_g^*$  orbitals for the d electrons, as illustrated in Fig. 6.5. In conclusion, the  $\pi$  bonding affects the splitting strength between  $e_g$  and  $t_{2g}$  orbitals in energy:

$\pi$  donor < weak  $\pi$  donor < no  $\pi$  effect <  $\pi$  acceptor.

According to Hunds rules:

1. For a given configuration, the term with the greatest multiplicity lies lowest in energy.
2. For a term of given multiplicity, the term with the greatest value of L lies lowest in energy.

The d electrons' spins tend to be parallel to one another to achieve the lowest energy configuration. However, the energy splitting between  $e_g$  and  $t_{2g}$  orbitals might be larger than the energy difference among the configurations of different multiplicities. To take  $d^6$  complexes as an example, Fig. 6.6 depicts two different configurations based on the field

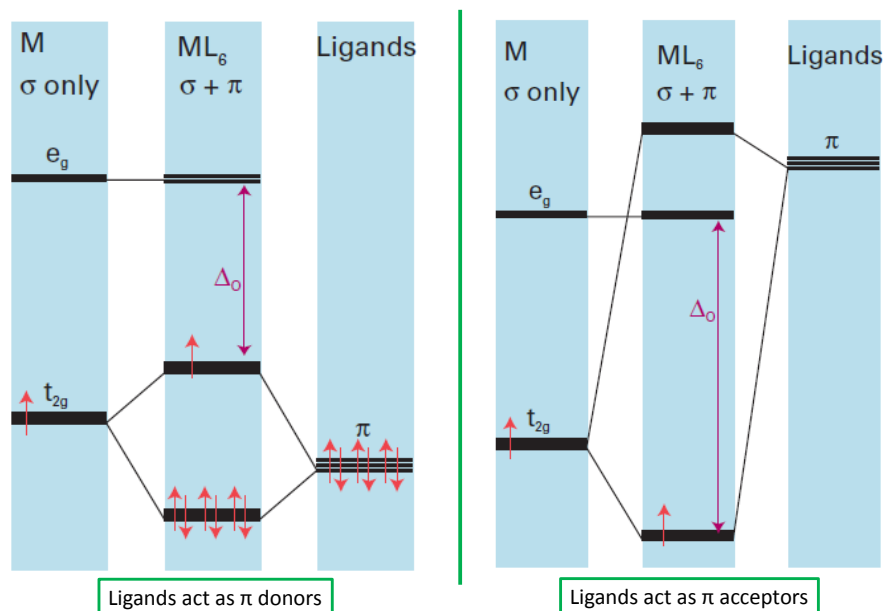


Figure 6.5. The effect of  $\pi$  bonding on the ligand field splitting. (Only the  $\pi$  orbitals of the ligand are shown) [75]

strength (the splitting strength). In the weak field the term energy of keeping greatest multiplicity is lower than that of all occupying the  $t_{2g}$  orbitals which results in the high spin state of the transition metal complex; the situation is opposite in a strong field and results in the low spin state.

Charge transfer (CT) transitions commonly happen in transition metal complexes. That is an electron migrates between orbitals that are predominantly of ligands in character and orbitals that are predominantly of the central metal in character. The transition is categorized as a ligand-to-metal charge-transfer transition (LMCT transition) if the migration of the electron is from the ligand to the metal, and as a metal-to-ligand charge-transfer transition (MLCT transition) for the opposite migration direction. Fig. 6.7 illustrates various CT transitions. LMCT is predominant if transition metal complexes



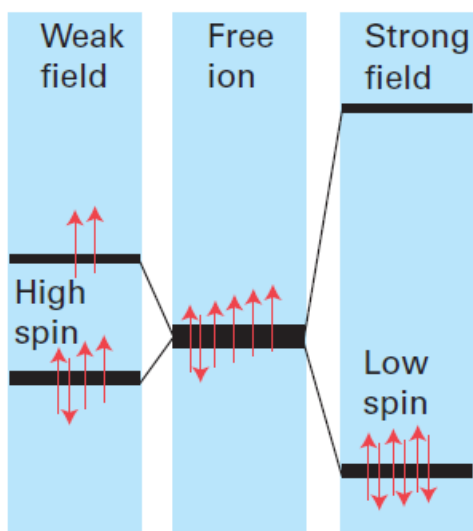


Figure 6.6. The effect of weak and strong ligand fields on the configuration of electrons for a  $d^6$  complex. The former results in a high-spin configuration and the latter in a low-spin configuration [75]

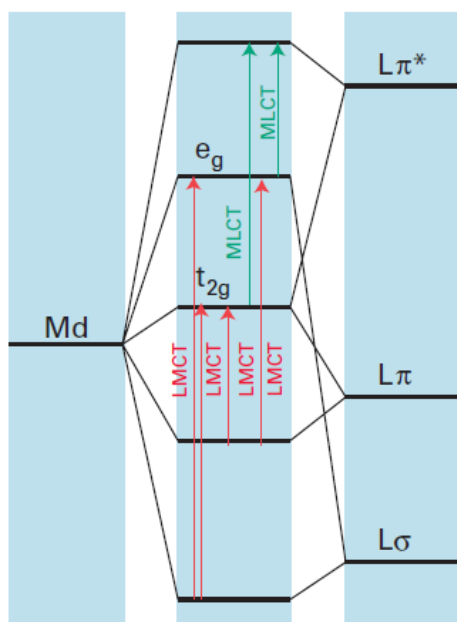


Figure 6.7. Schematic of LMCT and MLCT transitions in transition metal complexes [75]

have ligands with relatively high-energy lone pairs (such as S or Se) or if the metal has low-lying empty orbitals. MLCT is most commonly observed in transition metal complexes with ligands having low-lying  $\pi^*$  orbitals. Either type of the transition is in the visible and UV range.

## 6.2. Spin Crossover and Fe<sup>II</sup> Complex

Owing to the competition between ligand-field splitting and spin-pairing energies in transition metal complexes, some d electron configurations are at higher energy and spin-forbidden to the ground state. The lowest energy configuration among them becomes metastable and takes much longer time to non-radiatively relax to the ground state configuration. The phenomenon is designated as spin crossover (SCO). The possible applications of SCO include molecular switches, data storage devices and optical displays. It offers advantages in the miniaturization of the components in information technology [77].

A large number of SCO transition metal complexes contain Fe<sup>II</sup> in a 3d<sup>6</sup> electron configuration and an octahedral coordination. Therefore, Fe<sup>II</sup> octahedral transition metal complexes have been extensively investigated [78].  $^1A_1(t_{2g}^6)$  is the low-spin (LS) ground state configuration; the lowest excited state  $^5T_2(t_{2g}^4e_g^2)$  is a high-spin (HS) metastable state, as illustrated in Fig. 6.8. The  $t_{2g}$  orbitals are basically nonbonding and  $e_g$  orbitals are anti-bonding. The metalligand bond length increases by as much as 0.1 Å per electron that is promoted from the  $t_{2g}$  to the  $e_g$  orbital. The transition metal complex can be excited to the  $^1MLCT$  state and then relaxes to the  $^5T_2$  (HS) state within 1 ps. Then it takes  $\sim 0.65$  ns to  $\sim 150$  ns to relax non-radiatively to the LS ground from the HS metastable state [80].

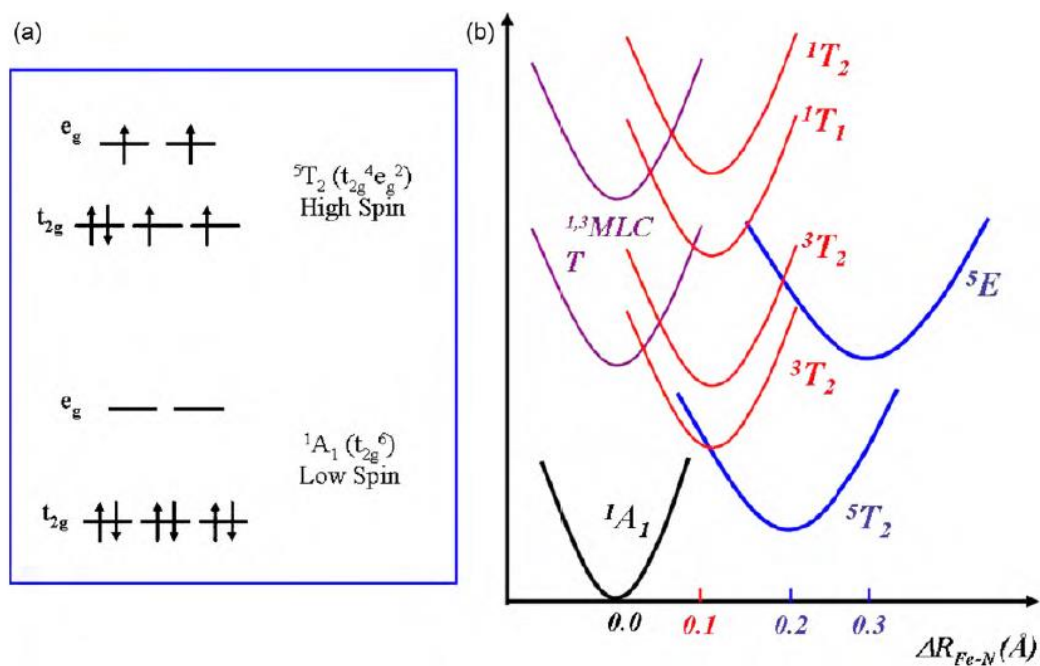


Figure 6.8. Schematic of d electron configurations and energy level of  $\text{Fe}^{\text{II}}$  octahedral complexes [80]

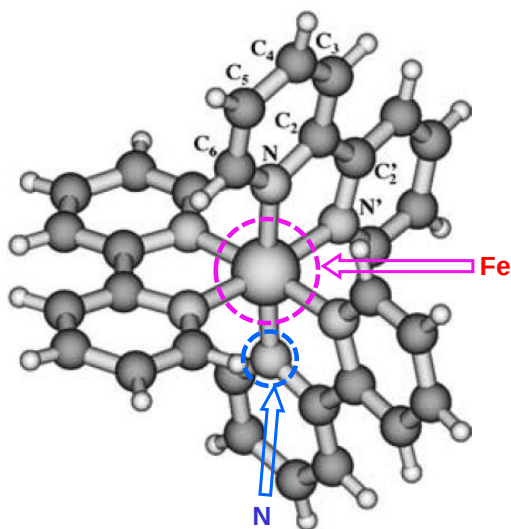


Figure 6.9. Ball-and-stick representation of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  complex [81]

Among the SCO transition metal complexes, the SCO process of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  can only be triggered by light. (For other SCO transition metal complexes, it could be a variation of temperature, pressure, an influence of a magnetic field or light irradiation.) Moreover, the HS state of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  relaxes nonradiatively to the LS ground state in less than 1 ns. (For other SCO materials, lifetimes of light-induced HS states at low temperatures can be hours.) As a result,  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  has become a model compound to investigate the light-triggered SCO transition process [79]. Figure 6.9 is the ball-and-stick representation of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ . In LS, the bond length is centered around 1.96 Å with a spread of  $\pm 0.04$  Å ; in HS, the bond length increases by 0.20 Å [80].

## CHAPTER 7

**XES Application for Charge Transfer Dynamics**

Charge transfer (CT) between metal centers and ligands in transition metal complexes is one of the most studied subjects owing to its central role in applications, such as solar energy conversion and photocatalysis [82]. Owing to the inherent element specificity and high penetration of x-ray, it has been a powerful tool to probe the electronic and geometric structures of transition metal complexes. By combining the pink beam microprobe with the existing ultrafast laser at the 7ID beamline [43], we demonstrated the laser-pump/x-ray-probe scheme on the photoexcited  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  complex. In our experiment  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  was excited to a Metal-to-Ligand Charge Transfer (MLCT) state with laser pulses, then the pink beam was utilized to probe the evolution after the excitation by capturing the XES.

In the scheme of this project, the focused pink beam is for 1s electron ionization and the spectra of the emitted photons were measured by a scanning Johann spectrometer as well as a dispersive von Hamos spectrometer [2] [16] simultaneously, as shown in Fig. 7.1.

The scanning Johann spectrometer is composed of a 10 cm diameter Ge(440) crystal analyzer and an APD detector. Both of them are placed in a 1 m diameter Rowland circle along with the sample. The fluorescence from the sample impinges on the crystal analyzer and is diffracted by the spherically bent analyzer and focused at the position sensitive detector. It's a point-to-point focus scheme and can only measure a single emission energy at a time. In contrast, the dispersive von Hamos spectrometer can collect a full range

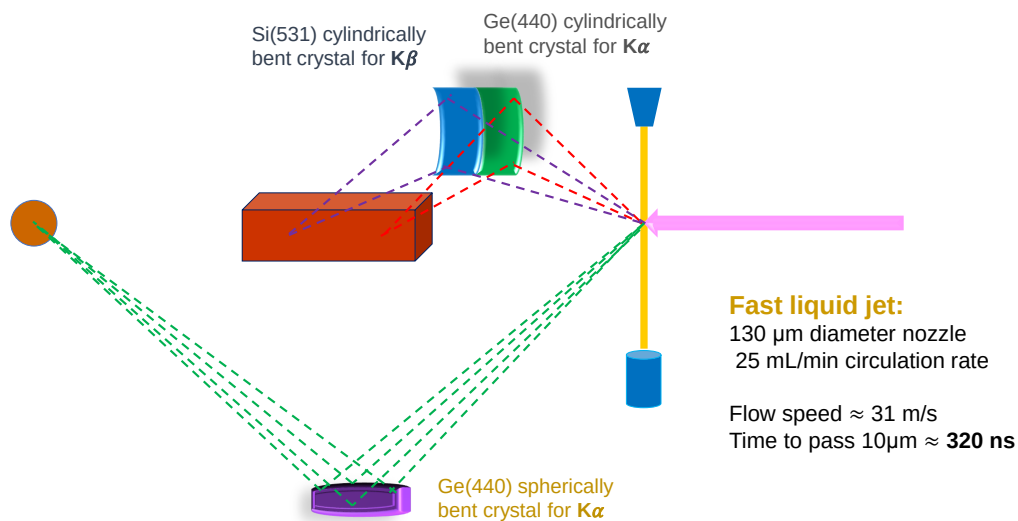
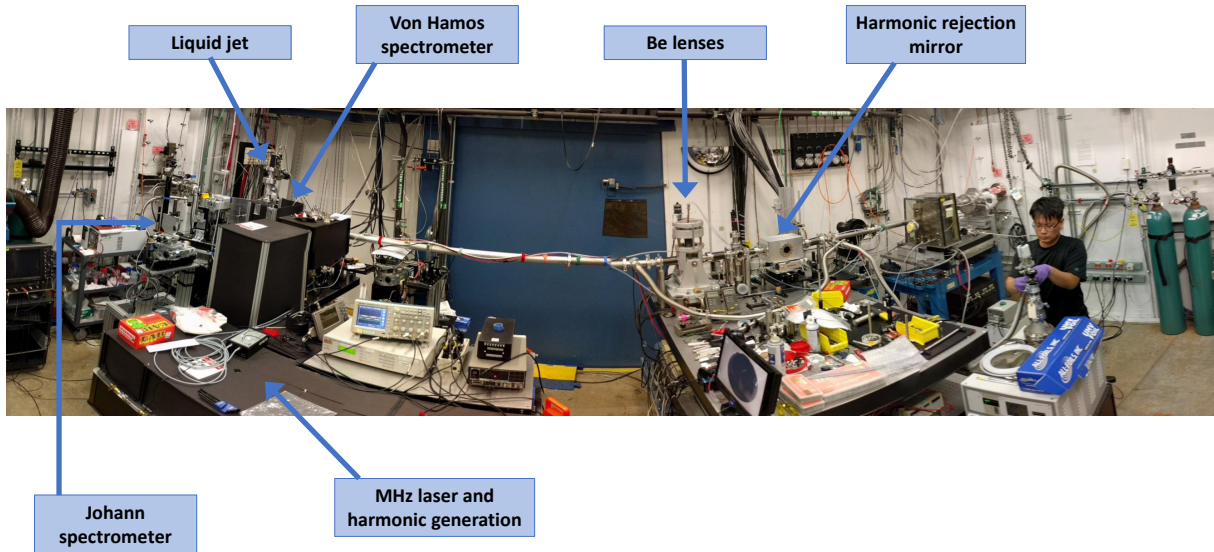


Figure 7.1. Spectrometer configuration

of  $K\alpha$  and  $K\beta$  spectra. The primary advantage of a scanning Johann spectrometer is the capability to collect a large solid angle at a single fluorescence energy resulting in a higher photon flux (higher luminosity) per energy unit, or equivalently, a better signal-to-background ratio. However, the positions and angles of the crystal analyzer and the detector of a scanning Johann spectrometer must be synchronously scanned to cover a full emission spectrum. It takes much more time than a dispersive von Hamos spectrometer and becomes impractical for a full range of time-resolved spectra of transient species. In practice, its big advantage of much higher luminosity was utilized to detect XES signals before the von Hamos spectrometer was employed to obtain a full emission spectrum. In addition, it was also used to measure the time evolution of the most intense  $K\alpha_1$  line

to gain the lifetime information of the laser-excited state. Furthermore, the  $K\alpha_1$  signal collected by the Johann spectrometer can work as a real-time reference for other emission lines measured by the von Hamos spectrometer, once the von Hamos spectrometer was engaged.



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Figure 7.2. The full experiment setup in 7ID-B. The pink beam was reflected by a harmonic rejection mirror and focused by beryllium CRL at liquid jet samples with a 2.955 m focal distance. XES signals were acquired with Johann spectrometer and von Hamos spectrometer. High repetition rate MHz laser and harmonics generation provided photoexcitation capability. The beamline was in vacuum 20 cm before the liquid jet, and a water-cooled 25  $\mu\text{m}$  thick exit beryllium window separated vacuum and air. The vacuum pressure went up from  $4.4 \times 10^{-5}$  to  $8.5 \times 10^{-5}$  Torr as the x-ray beam was turned on mainly owing to the outgas of mirror copper heat sink and CRL.

The von Hamos spectrometer in this project is comprised of a Ge(440) crystal for  $K\alpha$ , a Si(531) crystal for  $K\beta$ , and a position sensitive detector (PILATUS 100K, DECTRIS).

Both of the crystals are 25 mm wide, 100 mm high, and 250 mm radius of curvature. The emitted photons were diffracted by the cylindrically bent crystal analyzers which focus the fluorescence in one direction and spatially separates different energies in the other direction [16]. Then the fluorescence of different energies is detected by the position sensitive detector.

Once the focused pink beam was characterized with scintillator imaging (refer to Section 5.1), a few questions remained about its application to nonresonant XES. Can we collect an unperturbed XES spectrum from a liquid jet target with this very high x-ray average flux at MHz repetition rate? Is the harmonic rejection sufficient to make the high harmonics negligible for XES? Can we successfully transfer our established methods for time-resolved XES from the monochromatic case to the pink beam case? Can we efficiently collect complete time-resolved XES from low to moderate concentration solutes? In this chapter, all these questions will be answered.

### 7.1. Static XES of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$

We demonstrated our successful implementation with the static XES performance of our pink beam setup in comparison with published data on  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  (iron(II) hexacyanide) using monochromatic beam at 7.5 keV [83].

Figure 7.3 and Table 7.1 present the comparison of static XES of  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  400 mM in water with pink beam and with mono beam [83]. The pink curves in Fig. 7.3 are the static XES with the focused pink beam and the data are collected for only 1 second. The data of mono beam are calculated to the corresponding results of the same measurement condition as that of pink beam, including data acquisition time, x-ray probe beam size



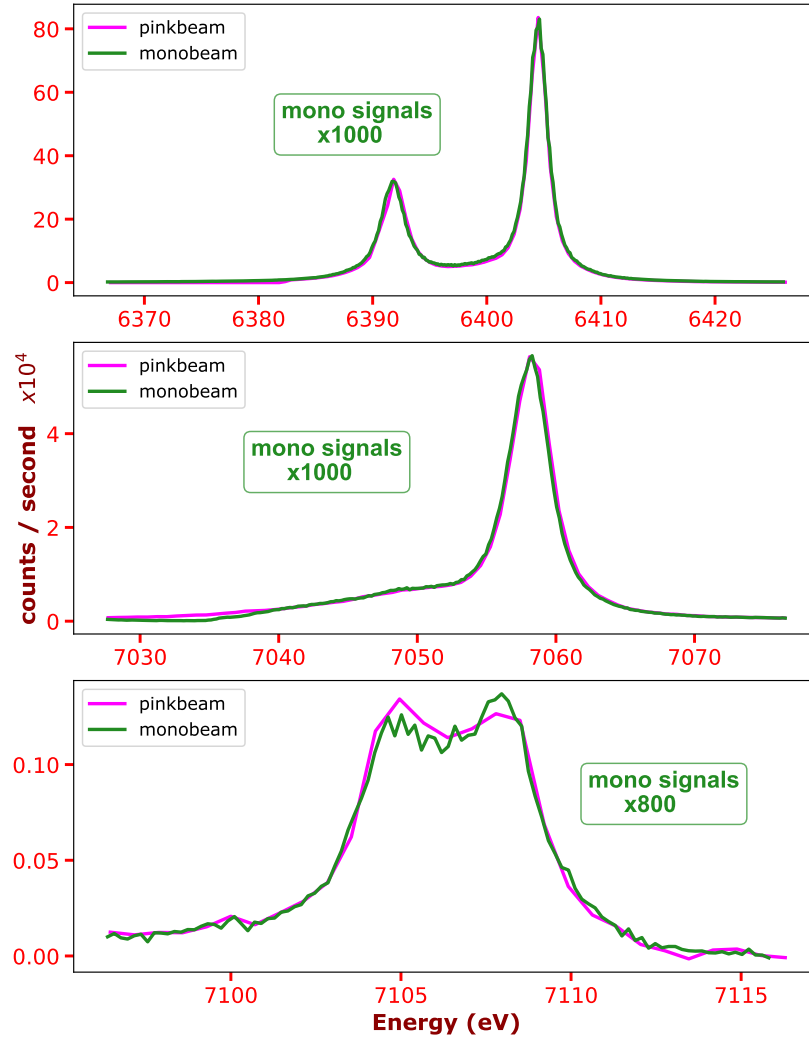


Figure 7.3. Comparison of static XES with pink beam and with mono beam. The pink curves are the static XES with the focused pink beam and the data are collected for only 1 second. The green curves are the corresponding results of the same conditions (Table 7.1) multiplied by different numbers to reach the magnitudes of XES with pink beam. From top to bottom are  $K\alpha$ ,  $K\beta$  mainline and vtc features. The signals of  $K\alpha$  and  $K\beta$  mainlines by focused pink beam are 1000 times bigger than those by mono beam and 800 times bigger for vtc signals.

and so on. The green curves are the corresponding results multiplied by different numbers to reach the magnitudes of pink beam XES. The top plot of Fig. 7.3 is  $K\alpha$ , the middle is

Table 7.1. Experimental conditions of static measurement

|                   | Monochromatic Beam                                                                                                 | Pink Beam                               |
|-------------------|--------------------------------------------------------------------------------------------------------------------|-----------------------------------------|
| sample            | $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ , 400 mM in water                                                      |                                         |
| analyzer crystals | 250 mm radius of curvature, cylindrically bent, Ge(440) (for $\text{K}\alpha$ ) and Si(531) (for $\text{K}\beta$ ) |                                         |
| jet thickness     | 200 $\mu\text{m}$ flat jet @ $45^\circ$                                                                            | 130 $\mu\text{m}$ cylindrical jet       |
| acquisition time  | 81 minutes                                                                                                         | 1 second                                |
| x-ray spot size   | 5 $\mu\text{m}$ x 5 $\mu\text{m}$                                                                                  | 40 $\mu\text{m}$ x 12 $\mu\text{m}$     |
| detector          | Mythen (55 $\mu\text{m}$ pixels)                                                                                   | Pilatus 100K (172 $\mu\text{m}$ pixels) |

$\text{K}\beta$  mainline and the bottom is vtc features. The spectrum shapes and the peak energy acquired with pink beam are nearly identical to those with mono beam which directly demonstrates that we can replicate previous results with much shorter acquisition time. Furthermore, the plots indicate that with the same condition the signal strength of  $\text{K}\alpha$  and  $\text{K}\beta$  mainlines by focused pink beam are 1000 times larger than those by mono beam and 800 times larger for vtc signals. The slightly lower signal strength for vtc may be due to a shortcoming in setup.

Furthermore, the magnification number can be adopted to estimate the flux of the pink beam available to probe the liquid jet sample. It has been previously determined that the flux of the mono beam is around  $10^{12}$  -  $10^{13}$  photons/second [43], and based on

this information we further estimate that the flux of the focused pink beam is around  $10^{15}$  -  $10^{16}$  photons/second.

On the other hand, a flux estimate on target can be made with the parameters selected from the simulated properties, taking into account the beryllium windows (totally 750  $\mu\text{m}$  thick) permanently installed on the 7ID beamline, the white beam slits opening, the harmonic rejection mirror reflectivity, the CRL absorption, as well as the short air path right before the interaction region. This air path is necessary to be able to insert laser optics when performing time-resolved pump-probe experiments. (Absorption by a water-cooled beryllium exit window (25  $\mu\text{m}$  thick) is ignored). Table 7.2 summarizes the calculations for the first three harmonics, with the first harmonic set at 8 keV. The estimate predicts that the flux of the focused pink beam is around  $10^{15}$  photons/second. In conclusion, the measured enhancement in signal matches the simulation estimate.

Table 7.2. Flux estimate

| Harmonic        | Output of<br>main slit<br>0.6x0.6mm<br>(XOP) | Be<br>windows<br>750 $\mu\text{m}$<br>(CXRO) | Si Mirror<br>10 nm<br>Rh coating<br>(CXRO) | CRL<br>7-stack<br>200 $\mu\text{m}$<br>(RXOPTICS) | Air<br>path<br>20 cm<br>(CXRO) | Available<br>to<br>liquid jet     |
|-----------------|----------------------------------------------|----------------------------------------------|--------------------------------------------|---------------------------------------------------|--------------------------------|-----------------------------------|
| 1st<br>(8 keV)  | $8.8 \times 10^{15}$<br>(11.0 W)             | 0.87                                         | 0.84                                       | 0.51                                              | 0.82                           | $2.7 \times 10^{15}$<br>(3.3 W)   |
| 2nd<br>(16 keV) | $2.2 \times 10^{15}$<br>(5.4 W)              | 0.97                                         | $2.8 \times 10^{-3}$                       | 0.83                                              | 0.98                           | $4.8 \times 10^{12}$<br>(11.7 mW) |
| 3rd<br>(24 keV) | $1.3 \times 10^{15}$<br>(5.0 W)              | 0.98                                         | $5.4 \times 10^{-4}$                       | 0.87                                              | 0.99                           | $6.0 \times 10^{11}$<br>(2.3 mW)  |

## 7.2. Time-resolved XES of Photoexcited $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$

In order to demonstrate the time-resolved XES with the established pink beam as well as its feasibility to efficiently collect complete time-resolved XES spectra from low to moderate concentration solutes, we chose to measure the transient XES spectra of photoexcited Iron(II) Tris(2, 2'-bipyridine), ( $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ ), capturing the spectroscopic properties of the high spin state following optical excitation and comparing results to our previous studies [4] [84]. This prototypical transition metal complex has been extensively studied.

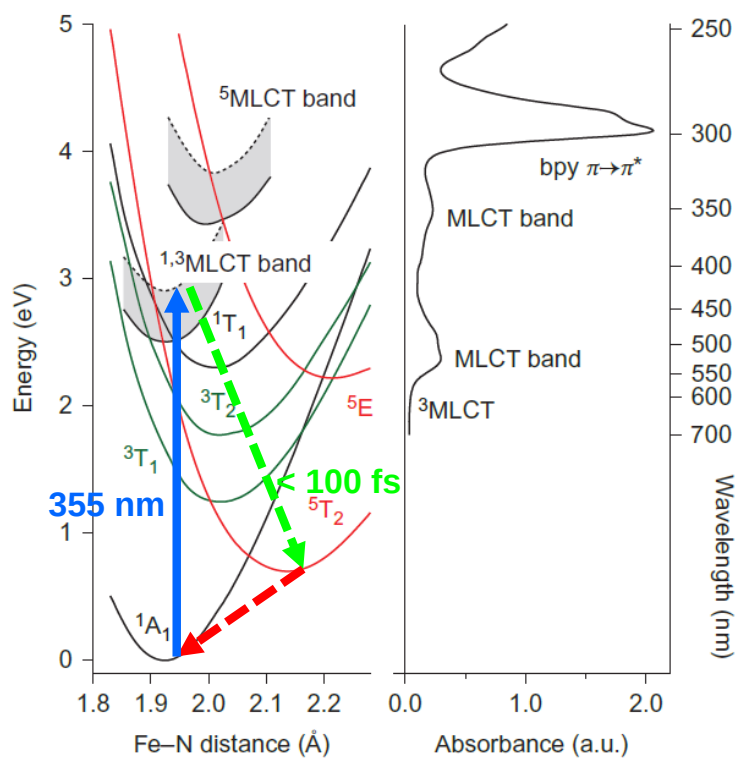


Figure 7.4. Schematic of photoinduced process of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  [79]

The schematic of the photoinduced process of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  is shown in Fig. 7.4. In this process, after pumping to a MLCT (Metal to Ligand Charge Transfer) band from its

low spin singlet state, it quickly ( $\sim 100$  fs) evolves into a high spin quintet excited state. A 355nm laser photon source which is within the energy range to excite the transition metal complex to the MLCT band, is available in the 7ID beamline. In addition, we used a solution of acetonitrile, where the high spin state had been characterized with a lifetime of 960 ps [85]. Another big advantage is that this transition metal complex has been shown to be especially robust to both optical and x-ray exposure, and yields high excitation fractions and thus large XES difference signals. All the characteristics make it an excellent test sample for our setup.

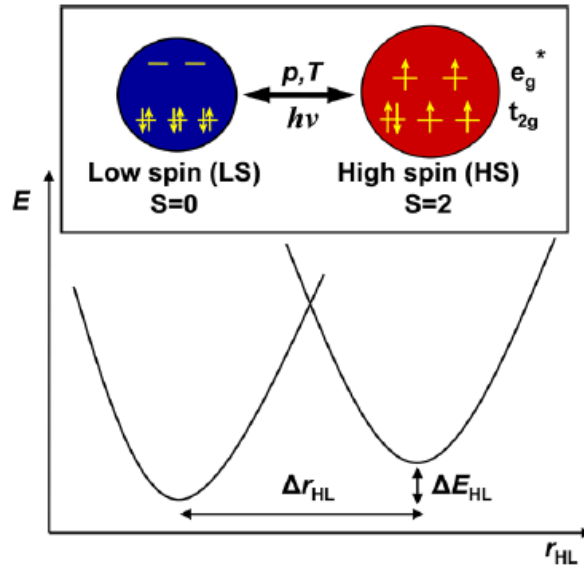


Figure 7.5. Schematic illustration of the LS  $\leftrightarrow$  HS transition in Fe<sup>II</sup> complexes with 3d<sup>6</sup> electron configuration. [86]

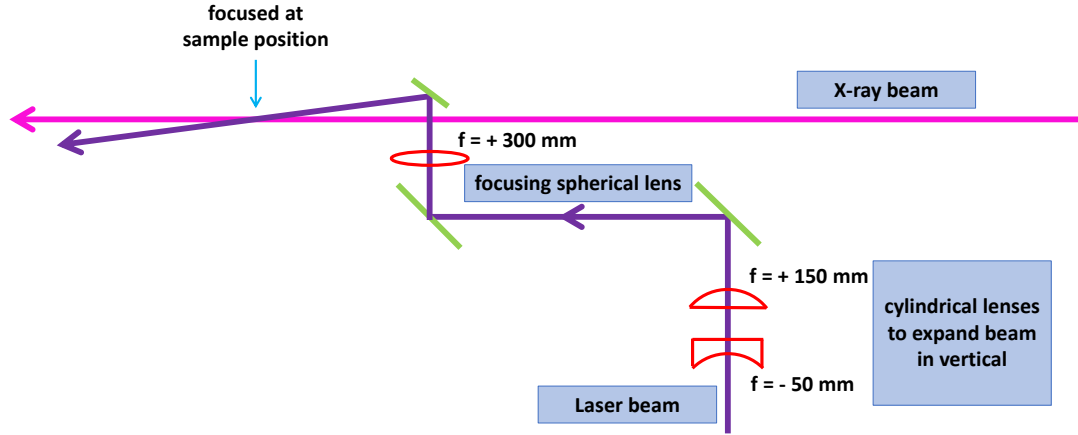
As the transition from LS to HS happens, two of the six Fe 3d electrons originally residing in the nonbonding  $t_{2g}$  orbitals now populate antibonding  $e_g^*$  orbitals, as illustrated in Figure 7.5 [4] [86]. This transition causes the elongation of the Fe-ligand bonds, diminishes orbital overlap and results in a destabilization of the MOs.

The pink beam x-ray microprobe was operating at a repetition rate of 6.5 MHz (153 ns interbunch spacing) in a standard 24-bunch operating mode (refer to Section 2.3). The 355 nm laser pumping source was generated by frequency tripling our high repetition rate 10 ps-duration laser (Duetto, Lumentum). The laser was synchronized to the storage ring rf signal, and the laser repetition rate was set at 1.3 MHz, i.e. each laser pulse can be overlapped with every 5th x-ray pulse.

In order to match the laser spot shape and size to the  $40\text{ }\mu\text{m} \times 12\text{ }\mu\text{m}$  FWHM x-ray spot measured previously, we positioned a cylindrical lenses telescope ( $f = -50\text{mm}$  and  $f = +150\text{mm}$ ) before our spherical focusing lens ( $f = +300\text{mm}$ ). The arrangement is shown in the Figure 7.6. The laser and the x-ray beam crossed with a small ( $\sim 5$  degrees) angle. By expanding the beam in the vertical direction before the lens, we were able to produce a  $50\text{ }\mu\text{m} \times 17\text{ }\mu\text{m}$  FWHM elliptical beam profile at the sample position. This is slightly larger than the x-ray beam, which should ensure that only excited regions of the target are probed, as shown in the Figure 7.7. A total laser power of about 2 W on target was used in this experiment.

In addition, this laser spot size is small enough that operating our liquid jet target at 25 m/s is sufficient to fully refresh the sample volume between laser shots. Although for  $[\text{Fe}(\text{bpy})_3]^{2+}$  this is not a concern since the decay of the excited state is much faster than the laser pulses separation, this is very important in case of long lived or permanent photoproducts.

To spatially overlap the focused laser spot with the focused pink beam spot at the sample position, a  $50\text{ }\mu\text{m}$  diameter tantalum pinhole was placed in the sample position and scanned horizontally and vertically in the plane perpendicular to the pink beam



1

Figure 7.6. Schematic of laser beam spatially overlapped with pink beam at the sample position

propagation direction and the transmitted x-ray power was measured by a PIN diode. The pinhole was scanned to find the beam edges and then centered to the pink beam. And then the last mirror of the laser beam was adjusted to center the laser beam through the pinhole as the transmitted laser power was monitored by a power meter. Both beams were heavily attenuated to avoid damaging the detectors. For the x-ray beam, the attenuator was a multilayer of aluminum and copper foils. An attenuator comprised of a waveplate and polarizer was utilized to control and reduce the laser power delivered to the sample position.

After spatially overlapping the laser and the focused pink beam at the sample position, the pinhole was replaced by a GaAs MSM (Metal-Semiconductor-Metal) photodetector

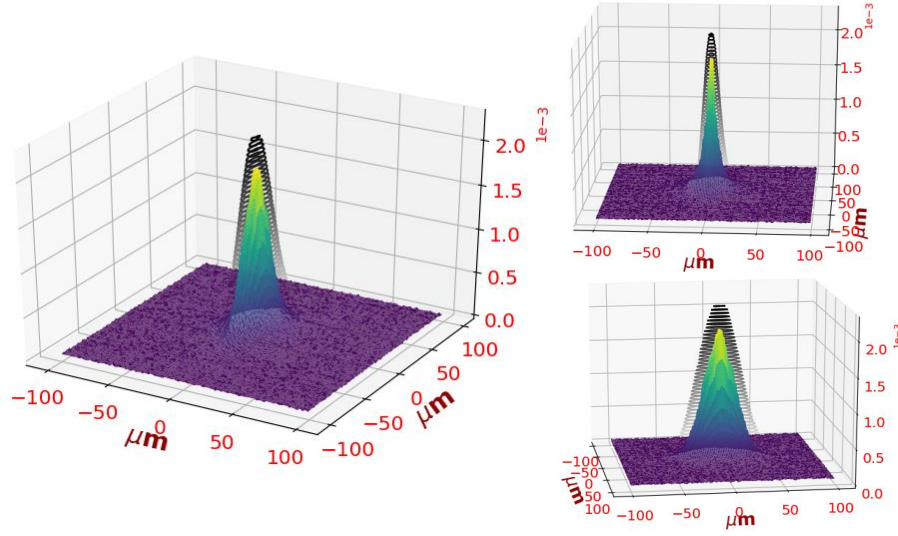


Figure 7.7. The grey contour represents the normalized laser beam profile distribution; the colormap represents the normalized pink beam profile distribution. The 3D beam profiles indicate that the focused pink beam is spatially within the range of laser beam at the sample in different angle views, either vertical (upper right plot) or horizontal (lower right plot).

(Hamamatsu, G4176-03) to temporally overlap the laser and pink beam pulses. This GaAs MSM photodetector features ultrafast 30 ps response time for both rise and fall. The attenuated pink beam and the attenuated laser beam were shone on the MSM photodetector. Pulses from each beam were monitored with a 3.5 GHz, 40 GS/s digital oscilloscope (LeCroy, WavePro 735Zi) on a single trace. The signal amplitudes of each beam were tuned to be comparable on the oscilloscope. The delay of the laser pulses was adjusted electronically to have the laser pulses and pink beam pulses temporally overlapped to an estimated precision of  $\pm 10$  ps (refer to Section 2.3). The temporal overlap can then be optimized according to the XES signals. After the overlap work was done, the attenuator of the pink beam was removed.



The sample was circulated by a HPLC pump with a flow rate of 25 mL/min through a 130  $\mu\text{m}$  diameter quartz nozzle to produce a cylindrical jet. Then the liquid jet was positioned at the intersection of the x-ray and laser beams, a 10 mM solution of  $[\text{Fe}(\text{bpy})_3]^{2+}$  in acetonitrile was circulated and the  $\text{K}\alpha$  emission signal was captured by the Johann spectrometer. The spectrometer was set at the peak of the  $\text{K}\alpha_1$  line, where signal is strongest, and also where the difference with the high spin state is maximized [84]. This signal can then be used for fine tweaks in the spatial overlap between the two beams, and to measure the lifetime of the HS (high spin) excited state.

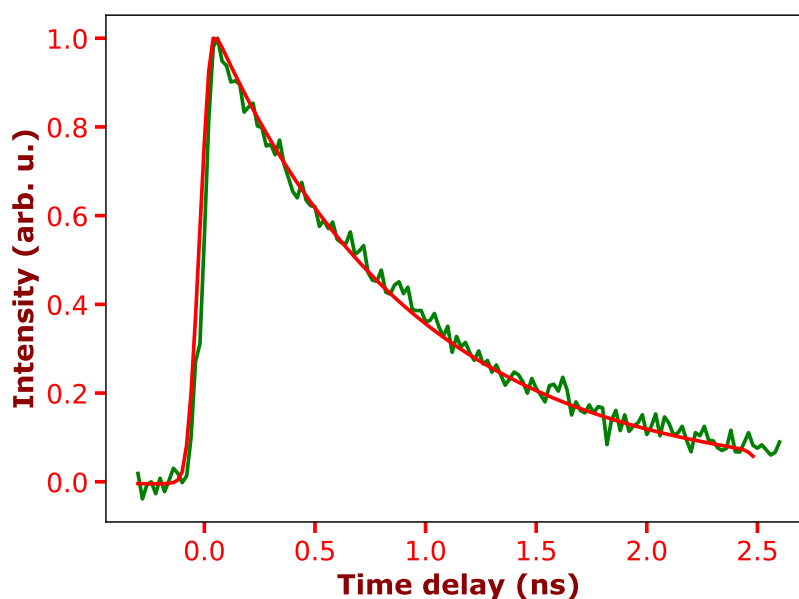


Figure 7.8. The time evolution of the  $\text{K}\alpha_1$  relative intensity of the laser-excited state of  $[\text{Fe}(\text{bpy})_3]^{2+}$  10 mM in acetonitrile with 20 ps resolution (green curves). The red curve is the fitting line with 910 ps lifetime.

Figure 7.8 presents the normalized difference between the laser-OFF (ground state) and laser-ON (ground state mixed with HS excited state) signals as a function of delay between the laser and the x-ray pulses. Within our time resolution, the formation of the

HS state is instantaneous, so we can fit this data with a simple kinetic model with single exponential decay and an instrument response function largely due to the x-ray pulse temporal profile (with a small contribution from the 10 ps laser pulse). Therefore, the IRF (instrument response function) is the convolution of a 10 ps FWHM Gaussian profile of the laser pulse and a 80 ps FWHM real profile of the x-ray pulse. The time evolution is fitted by an expression of the form

$$(7.1) \quad I(t) = \int_{-\infty}^{\infty} H(t-y)e^{-(t-y)/\tau} IRF(y)dy$$

where  $H$  is the Heaviside step function and  $\tau$  stands for the lifetime of the HS state. We obtain a lifetime of 910 ps, in very good agreement with previous measurement of 960 ps [85]. For all subsequent measurements, we set the delay to 100 ps, corresponding to the maximum difference signal.

Then the full Fe  $K\alpha$  and  $K\beta$  time-resolved XES was recorded by the von Hamos spectrometer and the gated Pilatus detector which recorded only either the laser OFF or the laser ON signal. Figure 7.9 presents the result. The top and the middle panels are  $K\alpha$  lines and  $K\beta$  mainlines respectively. In each case, we plot the ground state and laser-excited signals, their difference, as well as the emission from a reference sample known to be in high spin state in its ground state ( $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ ). The measured difference signal shape can then be directly compared to the difference between HS and LS states. The two peaks in  $K\alpha$  ( $2p \rightarrow 1s$ ) are  $K\alpha_1$  ( $2p_{3/2} \rightarrow 1s$ ) and  $K\alpha_2$  ( $2p_{1/2} \rightarrow 1s$ ). The unpaired 3d electrons cause tiny splitting within  $K\alpha_1$  and  $K\alpha_2$  emission lines owing to the weak (2p, 3d) exchange interaction. As a result, a broadening of the  $K\alpha_1$  and  $K\alpha_2$  lines is observed in HS. On the other hand, the strong (3p, 3d) exchange interaction

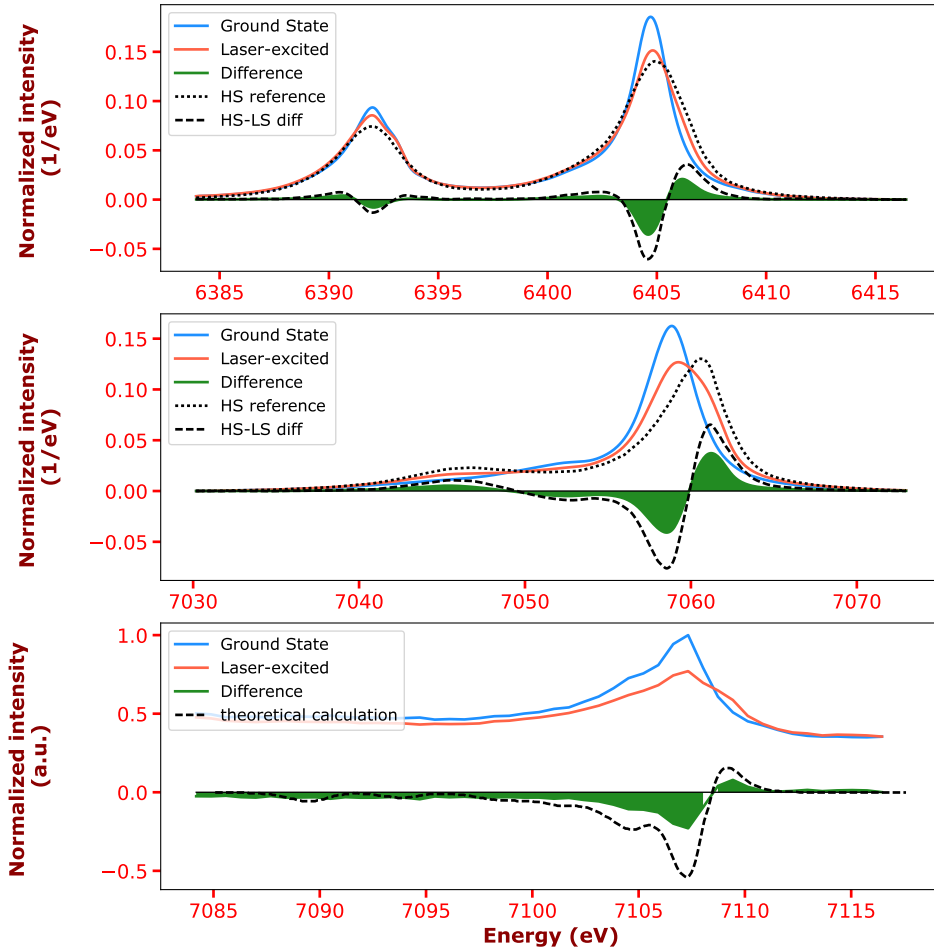


Figure 7.9.  $\text{K}\alpha$  (top) and  $\text{K}\beta$  mainline (middle) XES spectra of  $[\text{Fe}(\text{bpy})_3]^{2+}$  10mM in acetonitrile and the analysis of the high spin (HS) state fraction  $\gamma$  of the laser-excited spectra by means of integrated absolute difference (IAD) [1] [21] [84] [87]. The blue lines denote the spectra of the  $[\text{Fe}(\text{bpy})_3]^{2+}$  solution without laser excitation (ground state) and work as low spin (LS) reference as well; red lines denote the spectra measured 100 ps after laser excitation. The green filled areas show the spectral variation. The high spin (HS) reference spectra were acquired on a powder sample of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , as shown in black dotted lines [84]. The black dashed lines indicate the differences of HS and LS reference spectra.

causes a clear blue shift of the  $\text{K}\beta_{1,3}$  feature and an intensity transfer from  $\text{K}\beta_{1,3}$  to the

$K\beta'$  satellite in transition from LS to HS. Neither  $K\alpha$  nor  $K\beta$  mainline feature is directly sensitive to the valence electrons, but they reflect the spin state.

The difference signals can be used to quantitatively assess the fraction of high spin state molecules in the probed volume. To analyze the HS fraction  $\gamma$  of the laser-excited spectra, an approach called integrated absolute difference (IAD) is adopted [1] [21] [84] [87]. In this approach HS, LS and the laser-excited spectra are normalized to unit area at integration. The IAD value for the complete spin transition, referred to as  $IAD_{HL}$ , is calculated by taking the absolute values of the differences between HS and LS reference normalized spectra and integrating them. Through similar steps the IAD value of the laser-excited spectra is obtained with the LS reference and laser-excited normalized spectra. Then the scaling factor between  $IAD_{HL}$  and the IAD value of the laser-excited spectra is the HS fraction,  $IAD = \gamma IAD_{HL}$ . Consequently the HS fractions in  $K\alpha$  and  $K\beta$  mainline spectra are obtained respectively:  $\gamma_\alpha \approx 0.57$  and  $\gamma_\beta \approx 0.53$ . This excitation fraction around 55% confirms that our pink beam microprobe is able to efficiently probe a volume corresponding to the center of the laser excited region, and is consistent with previous experiments with this molecule.

The bottom panel of Fig. 7.9 presents the signal in the valence-to-core region, following about 2 hours of acquisition. Dipole-allowed transitions dominate the vtc XES, so MOs (molecular orbitals) with Fe 4p character are the primary contributors to the spectrum. In transition metal complex  $[Fe(bpy)_3]^{2+}$ , the orbitals with Fe 4p mixing have mostly ligand character. The  $K\beta''$  feature (at the lower energy part of vct XES) is attributed to the MOs with ligand 2s character and  $K\beta_{2,5}$  features (at the higher energy part) are attributed to ligand 2p character respectively [4] [22]. As the transition from LS to HS

happens, two of the six Fe 3d electrons originally residing in the nonbonding  $t_{2g}$  orbitals now populate antibonding orbitals. It results in the elongation of the Fe-ligand bonds, diminishing orbital overlap and a destabilization of the MOs, illustrated in Fig. 7.10.

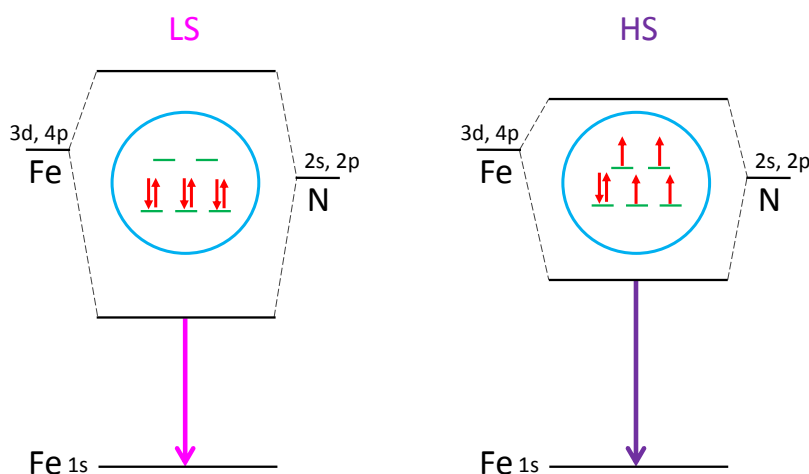


Figure 7.10. Schematic of MOs and electronic configurations of  $[\text{Fe}(\text{bpy})_3]^{2+}$  in LS and HS

The experimentally observed energy blue shift of vct XES in HS indicates that the probed MOs are destabilized. The intensity reduction is owing to the decreased amount of Fe p character contributing to the populated MOs. Moreover, a subtle shoulder appears on the high energy side of the  $\text{K}\beta_{2,5}$  feature in HS. It originates from MOs based on the mixing of Fe 3d and N 2p (of ligand) orbitals, which have reduced symmetry that makes the vtc transitions dipole allowed in HS [4]. Obtained with a single analyzer crystal, this result shows that the pink beam microprobe fully enables time-resolved valence-to-core XES at synchrotrons, especially when combined with a multi-crystal spectrometer [4]. This two-hour continuous pump-probe acquisition did not show obvious weird, unexpected

features at the end of the experiment in terms of the spectrum energy and features. It demonstrates that this robust sample can endure the high flux of pink beams.

Finally, some useful cases were demonstrated to illustrate the potential of the setup. Fig. 7.11 presents the total XES spectra obtained in a single minute of acquisition (i.e. 30 seconds OFF, 30 seconds ON) of  $[\text{Fe}(\text{bpy})_3]^{2+}$  10mM (a relatively modest concentration) in acetonitrile. Both the  $\text{K}\alpha$  and mainline  $\text{K}\beta$  signals exhibit very good signal to noise. In particular, the quality of the  $\text{K}\beta$  difference signal is sufficient to clearly identify the spin of the transient excited state. This result is very promising for a number of possible applications. While this particular sample is known to produce strong difference signals, the implementation of a multicrystal spectrometer would open the possibility to either use much lower concentration, or detect smaller difference signals with the same short acquisition time. For samples that exhibit strong x-ray or laser damage, or permanent photoproducts, single pass measurements are now possible, even without very large quantity of sample.

In the case of low concentrations, signal to background is the main consideration. Using our simple lead shielding to block scattered x-rays, we demonstrated that our setup is easily sensitive to 1 mM solute concentration. Fig. 7.12 presents the result of 10 min acquisition (5 min OFF, 5 min ON) with  $[\text{Fe}(\text{bpy})_3]^{2+}$  1 mM in acetonitrile. The low concentration sample definitely shows a little higher background in  $\text{K}\beta$  mainline and vtc features. While the vtc region becomes statistical limited, the contrast for the  $\text{K}\alpha$  and mainline  $\text{K}\beta$  signals is very good, such that no significant difference is observed from the 10 mM case.

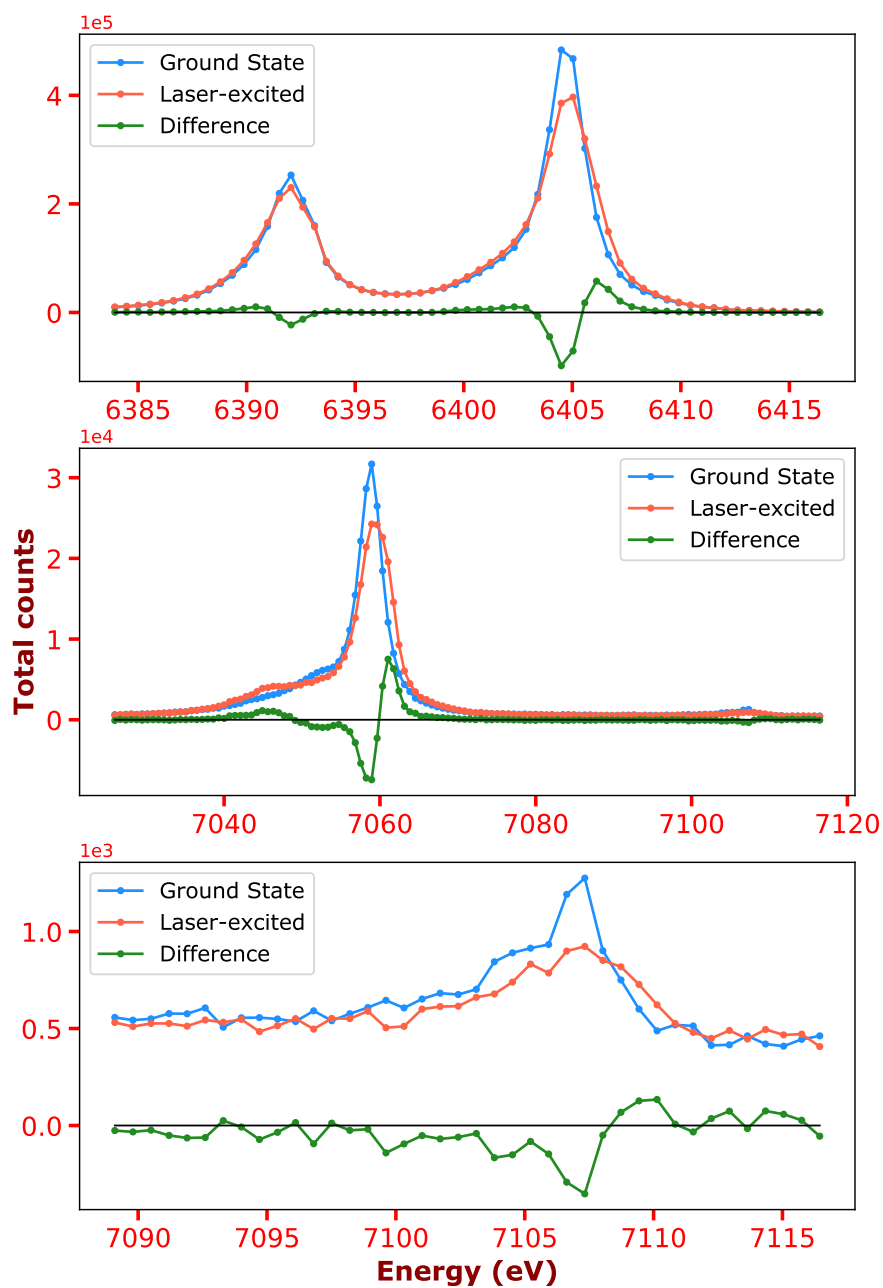


Figure 7.11. One minute data acquisition of  $[\text{Fe}(\text{bpy})_3]^{2+}$  10 mM in acetonitrile. From top to bottom are K $\alpha$ , K $\beta$  full range, and vtc features. It is demonstrated that merely a very short acquisition time is capable of having clear K $\alpha$  and K $\beta$  mainline features.

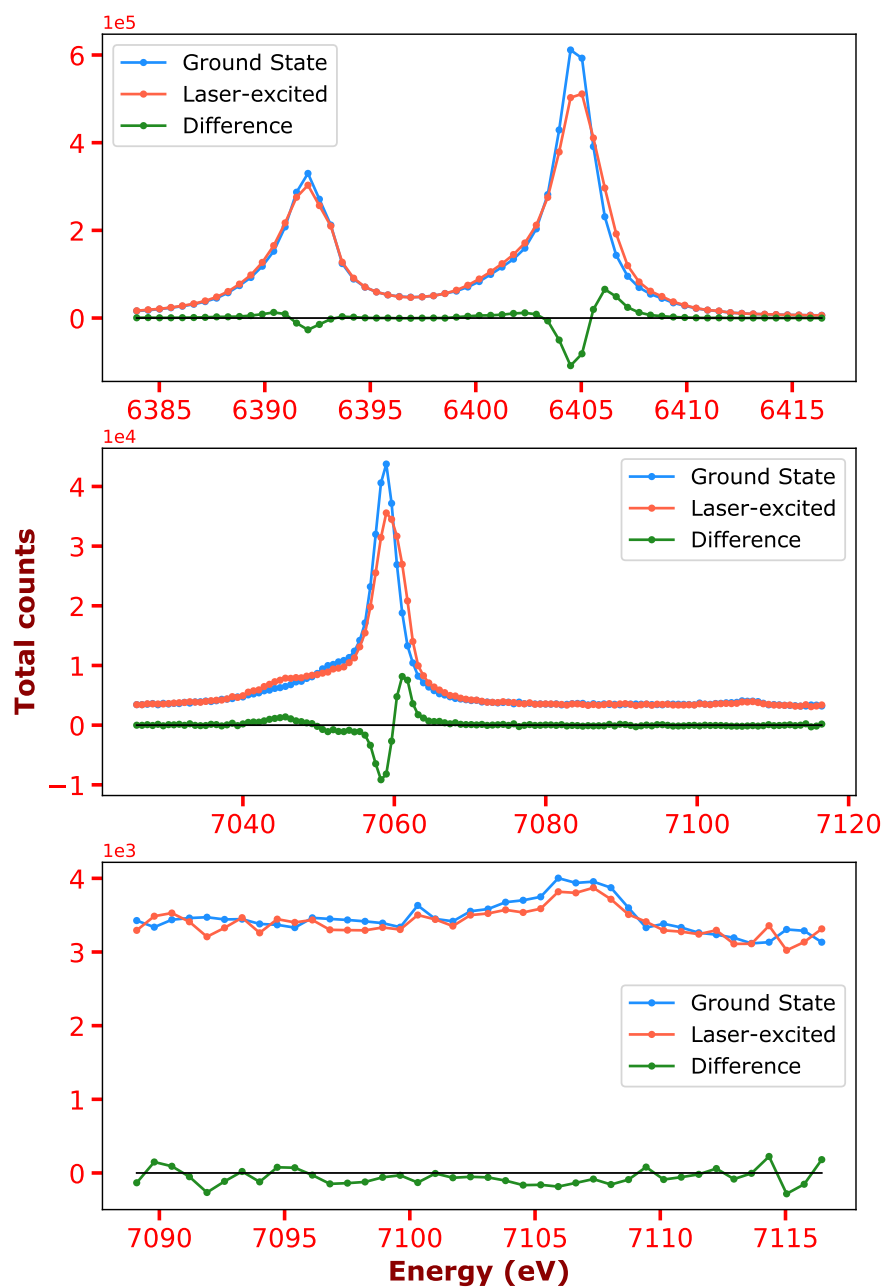


Figure 7.12. The capability of focused pink beams on gaining XES of a low concentration sample,  $[\text{Fe}(\text{bpy})_3]^{2+}$  1 mM in acetonitrile, over a short data acquisition time, 10 minutes. The top plot is  $\text{K}\alpha$ , the middle is the full range of  $\text{K}\beta$ , and the bottom plot is the vtc signal. The blue curves are for ground state, red for laser-excited state and the green shows the differences of the previous two signals (transient signals).



## CHAPTER 8

**Conclusion and Outlook**

A new capability of pink beam XES at APS has been designed and achieved. In the layout, a water-cooled flat mirror effectively suppresses high harmonics of undulator radiation to avoid thermal damages on x-ray optics and unwanted excitation on samples. A beryllium CRL focuses the reflected pink beam to a  $40\text{ }\mu\text{m} \times 12\text{ }\mu\text{m}$  FWHM elliptical spot at the sample position. The small spot size in vertical guarantees a fresh sample volume between subsequent laser shots in a high speed liquid jet setup. In combination with a ultrafast laser, the average high flux of  $10^{15}$  x-ray photons/second remarkably promotes the applicability of the time-resolved XES spectroscopy in a laser-pump/x-ray-probe scheme. A first application to nonresonant XES was demonstrated, with game-changing new capabilities being offered now, as acquisition times are reduced by about 3 orders of magnitude. With a model SCO molecule,  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ , we succeeded in demonstrating that this pink beam capability is able to efficiently probe the photoexcited state and characterize the charge transfer dynamics happening in the molecule. Besides establishing time-resolved valence-to-core XES as a viable technique on solvated systems, it is also possible to measure sensitive samples where volume recirculation is not an option, based on the successful experience on low concentration samples and short data acquisition.

This capability offers direction advantages to experiments involved in measuring weak valence-to-core (vtc) transition features of transient species. Since the vtc features have

intensity of two or three orders of magnitude lower than the  $K\alpha$  transition, it is impractical to measure the features in time-resolved spectroscopy with a mono beam to elucidate the dynamic process. The pink beam XES opens an avenue for research which needs to interrogate the dynamic changes of bond length, valence electron distribution, and geometric properties in a molecule, on which vtc-XES can provide direct information. For instance, the pink beam XES can be utilized to characterize the dynamical properties of the artificial enzyme catalyzing the conversion of methane to methanol which I investigated with time-resolved x-ray absorption spectroscopy (XAS) before [74].

In addition to XES, a potential application of the pink beam excitation capability is Auger electron spectroscopy (AES) where the focused pink beam is utilized to create a core hole of atoms in high efficiency to prepare the core-ionized initial state for AES. Another potential application is time-resolved x-ray liquid scattering. It is a technique that can accommodate large incident bandwidth, and is often coupled to XES at XFELs since it can provide structural information complementary to the electronic information.

Further enhancements are being currently implemented by adding a multi-crystal von Hamos spectrometer for more efficient signal collection coupled to a higher resolution gateable detector (Lambda 750k, X-Spectrum). While our simple setup as implemented is able to provide a microprobe in the range of 5 to 12 keV, a natural way to increase the range consists in using a multilayer monochromator with several reflective stripes. Another direct advantage of such a setup is the possibility to easily switch between monochromatic beam (crucial for x-ray absorption spectroscopy and resonant x-ray emission spectroscopy) and pink beam. Such a setup is being designed for a new beamline part of the APS-U project, the Advanced Spectroscopy Beamline, scheduled for late 2020.

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