

UPGRADE THE BEAMLINER PF-AR NW14A FOR THE HIGH-REPETITION-RATE X-RAY PUMP-PROBE EXPERIMENTS

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Abstract

The time-resolved X-ray measurements at storage ring has achieved successfully in investigating the structural dynamics of excited states, however the most of its experimental repetition rate has been limited to about ~ 1 kHz. The low repetition rate decided by the frequency of the pump laser system leads to a lack of photon in the time-resolved experiments. In this study, the high-repetition-rate time-resolved X-ray experimental system is reconstructed at PF-AR, NW14A. To use full of the x-ray flux without the x-ray isolation, the precise transient structure could be visualized. This study demonstrated the high-repetition-rate time-resolved X-ray measurements offer an opportunity to understand of the detailed photoreaction process and can be available as a fundamental observation technology for the development of new photo-functional materials.

INTRODUCTION

Time-resolved X-ray measurement is a powerful tool for the investigation of ultrafast science in various research fields ranging from local photochemical or photobiological processes, such as photocatalyzed reaction and photodissociation to photo-induced phase transitions in crystals[1]. Time-resolved X-ray experiments that have been developed with the rapid progress of synchrotron sources have made it possible to study photo-induced ultrafast transformations by synchronizing X-ray pulses with ultrashort laser pulses. This pump-probe synchronization can be combined with established X-ray techniques, such as absorption, diffraction, and scattering experiments [2]. Especially, time-resolved X-ray absorption fine structure (XAFS) is important for studying the molecular dynamics.

The Photon Factory Advanced Ring (PF-AR) is a full-time single-bunch synchrotron radiation source operated for time-resolved X-ray studies with pulsed X-rays. Electrons with a ring current of 60 mA (75.5 nC per bunch) are stored in a single bucket with a lifetime of about 20 h. The radio frequency (RF) for cavities and harmonic number of the PF-AR are 508.58 MHz and 640, respectively. Therefore, the X-ray pulses are delivered at a frequency of ~ 800 kHz with a pulse duration of about 100 ps.

Previously, the typical laser system, installed in the beam line for time-resolved experiments is a fs Ti:sapphire regenerative amplifier laser system. The Ti:sapphire laser system, which is operated at 800 nm fundamental wavelength, is capable of reaching up to 1 mJ pulse with a repetition rate of ~ 1 kHz. At that time, the experimental frequency of the laser pump and x-ray probe experiment was limited to ~ 1 kHz to excite sam-

ples with an ideal pulse energy. The low-flux condition, attributed to the about one thousandth isolated x-ray, sometimes prevents advanced researches for the dynamic structural analysis [3].

In recent years, the developments of high-repetition laser systems and x-ray focusing technologies has provided the pump-probe experiments without the x-ray isolation. Also at PF-AR, NW14A, the high-repetition-rate time-resolved X-ray experimental system was reconstructed. The improvement of measurement efficiency is described in this paper with an example from time-resolved XAFS.

X-RAY FOCUSING OPTICS

The X-ray focusing optics are a bent cylindrical focusing mirror and a poly-capillary focusing optics (XOS, USA). In regard to the bent cylindrical mirror, the mirror is coated with rhodium (100 nm thick). The mirror can be bent at a range of bending radii between -2000 m and $+2000$ m by a mechanical bender. The glancing angle is adjusted by tilting the mirror at the mirror's center. A bending mechanism directly applies the bending momentum to the mirror. By the bent cylindrical mirror, the beam is focused at the sample position with $464 \mu\text{m}$ (H) $\times 236 \mu\text{m}$ (V). In this focusing condition, to add the poly-capillary focusing optics with the 5mm working distance, the beam size at the sample position with $60 \mu\text{m}$ (H) $\times 60 \mu\text{m}$ (V) is achieved.

HIGH REPETITION LASER SYSTEM

For the pump laser with the high repetition rate, a 350 fs Yb fiber laser system (Tangerine, Amplitude Systèmes) was installed. The Yb fiber laser system is operated at 1030 nm fundamental wavelength. The fundamental wavelength can be converted to second (515 nm), third (343 nm), and fourth (257 nm) harmonics by a higher harmonics generator for the Tangerine. The fiber laser is capable of reaching up to $30 \mu\text{J}$ with a repetition rate of the 794 kHz. The fiber laser is installed at near the sample in the experimental hutch.

TIME RESOLVED XAFS WITH HIGH REPETITION RATE

The time-resolved Ru K-edge X-ray absorption fine structure (XAFS) were measured with the 400 kHz repetition rate by using a scintillation counter, a gated integrator and the fiber laser system. Through the metal filter and the solar slit, the fluorescence signal was detected by the fast scintillation counter, which has a 50 mm diameter of acceptance surface. The experimental condition, where the frequency of laser pulses is a half of the 800 kHz x-ray frequency, removes the low frequency noise components from the laser on/off difference of XAFS spectrum.

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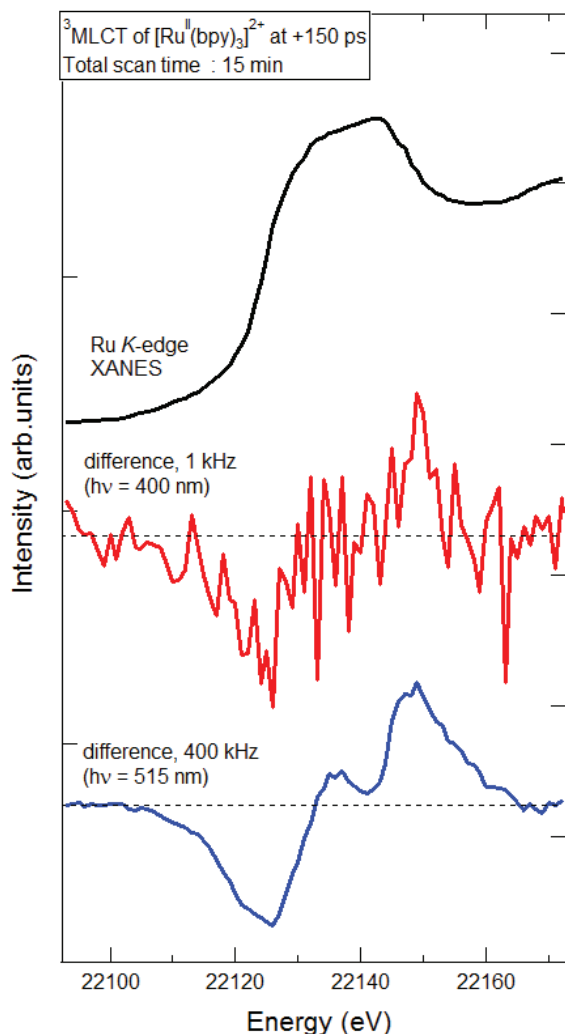


Figure 1: The Ru K-edge XANES spectrum of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and its transient differences measured with 1 kHz and 400 kHz repetition rates.

The ground state of Ru K-edge XANES spectrum and its transient differences measured with 1 kHz and 400 kHz repetition rates are shown in Fig. 1. The metal to ligand charge transfer (LMCT) band of the 10 mM aqueous solution of Ruthenium(II)-tris-2,2'-bipyridine ($[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$) was excited with the 100 mJ/cm^2 laser pulse density. By the LMCT excitation, the edge shifts were shown in both XANES transient differences due to the change of the Ru oxidation state from Ru(II) to Ru(III). The both transient differences were measured for 15 min, which is the typical measurement time for the conventional static XANES measurement. According to the increase of ~ 400 times in the repetition rate, the improvement of $\sim 20 = \sqrt{400}$ times in the S/N ratio was obtained in the transient difference.

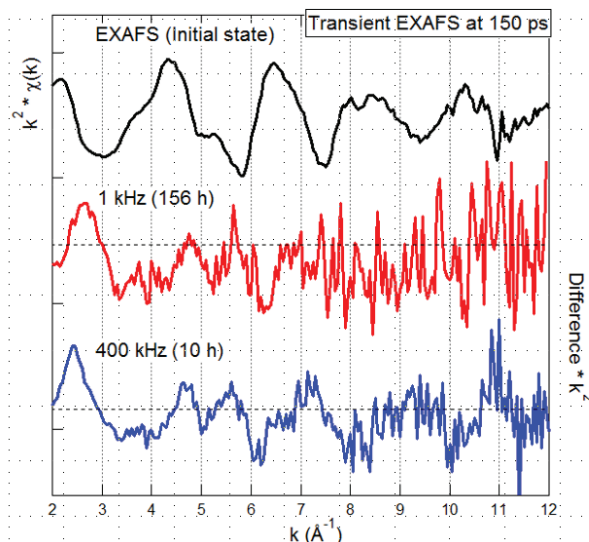


Figure 2: The Ru K-edge EXAFS oscillation of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and its transient EXAFS differences measured with 1 kHz and 400 kHz repetition rates.

Also, to analyze the transient structure in detail, it is necessary to measure the wide range of EXAFS oscillation. The Ru K-edge EXAFS oscillation of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and its transient EXAFS differences measured with 1 kHz and 400 kHz repetition rates are shown in Fig. 2. In the 1 kHz repetition rate, it is hard to measure transient EXAFS difference above $k \sim 7$ even the spectrum was accumulated in 156 hours. On the other hand, in the 400 kHz repetition rate, the transient EXAFS difference around $k \sim 12$ was observed by only the 10 hours scan. The improvement of the transient EXAFS detection capability makes it possible to visualize a precise transient structure.

CONCLUSION

In the x-ray pump-probe experiment, the great improvement of measurement efficiency was achieved by the installation of the high-repetition-rate experimental system. The improvement of experimental efficiency make it possible to visualize the detailed transient structures. In future dynamic studies, the ultra-low emittance ring allows us to obtain the inhomogeneous information in photochemical reactions.

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