Current status of 50-Picosecond Resolved X-ray Diffraction at Photon Factory Advanced Ring (PF-AR)

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Abstract. Ultra-fast time-resolved X-ray crystallography using electron-accelerator-based X-ray sources has been becoming a general and powerful tool to explore structural dynamics of crystalline state in material and biological sciences. Photon Factory Advanced Ring (PF-AR) is a full-time single-bunch synchrotron radiation source operated for such time-resolved X-ray studies using pulsed X-rays. Here we report instrumentation, feasibility, and applications of time-resolved X-ray diffraction at PF-AR. The time-resolved X-ray diffraction equipment consists of an X-ray pulse selector, an X-ray diffractometer, a femtosecond laser system and their timing modules which provide synchronized X-ray pulses with 50-picosecond duration (rms) and 150-femtosecond laser pulses for laser-pump-X-ray-probe experiment. The current status of the beam lines NW2 and NW14, and their applications are described.

1. Introduction
Time-resolved X-ray studies using synchrotron radiation sources have been successfully applied to various dynamics studies of chemical or biological systems and condensed matters [1-3]. These experiments mostly require relatively sparse bunch-filling mode of the storage ring operation such as single-bunch or hybrid modes, because these experiments require detectors with relatively slow (nanosecond to sub-microsecond) response time. In particular, for time-resolved diffraction experiments that utilize two-dimensional area detectors to record a series of time-dependent diffraction patterns, isolation of a single X-ray pulse from X-ray pulse train is a must, because the two-dimensional area detectors such as CCD or imaging plate do not have fast gating capabilities so far.
Therefore, in order to isolate a single pulse by using a fast shutter like a mechanical chopper, the sparse bunch-filling modes (single-bunch or hybrid mode) are strongly needed.

Photon Factory Advanced Ring (PF-AR) at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan is a full-time single-bunch synchrotron radiation source operated for such time-resolved X-ray studies using pulsed X-rays. By utilizing the full advantage of the sparse bunch structure of PF-AR ring, we aimed to develop sub-nanosecond-resolved X-ray structural analysis capabilities, and an in-vacuum undulator beam line NW2 has been constructed for time-resolved XAFS and X-ray diffraction studies. Primary scientific targets of time-resolved X-ray diffraction at NW2 are photo-induced phenomena which can be triggered reversibly by ultrafast laser pulses. In particular, photo-induced phase transition in molecular charge-transfer crystals is one of the major interests of our research. Time-resolved X-ray diffraction equipment with 50-ps X-ray and 150-fs laser pulses at NW2 enables us to study dynamics of electronic, atomic and molecular motions in such systems at 50-ps resolution.

2. X-ray source
PF-AR is operated in the single-bunch mode for about 5000 hours/year. Electrons with the ring current of 60 mA (75.5 nC per bunch) are stored in a single bucket with life time of ~20 hours. The X-ray pulses are delivered at a frequency of 794 kHz with the pulse duration of ~50 ps (rms). X-rays are generated by an in-vacuum undulator with period length of 40 mm, which covers an energy range of 1-40 keV with 1st, 3rd, and 5th harmonics. Graphite filters and beryllium windows absorb low-energy part of the beam, and energy cutoff of rhodium-coated focusing mirror limits the higher-energy part, which results in the energy range of 5-20 keV at the sample position. The focused beam size at the sample position is 0.2 mm (V) x 0.6 mm (H). The typical photon flux of the monochromatic beam at 18 keV is $1 \times 10^{12}$ photons/sec, which corresponds to $1 \times 10^6$ photons/pulse.

3. X-ray-laser synchronization and monitoring of the timing
The timing control of the X-ray and laser pulse is based on the radio frequency (rf) master clock (508.58 MHz) that drives an electron bunch in the storage ring. Figure 1 shows a block diagram of the X-ray-laser synchronization system. The reference rf signal is provided as sinusoidal wave ($V_{pp}=1V$), amplified and used for further synchronization.

![Figure 1. Laser and X-ray timing diagram at NW2, PF-AR.](image-url)
A high speed chopper (X-ray pulse selector, XPS) was assembled by Forschungszentrum Jülich, and is used for isolation of a single X-ray pulse from X-ray pulse train (Figure 2). The XPS is synchronized at 945 Hz to a 1/537600 subharmonic of the rf frequency (1/840 subharmonic of the revolution frequency). The physical opening window of the chopper is ~ 1 µs, and when it is phase-locked to select a single bunch in PF-AR single bunch mode, the exposure time becomes 50-ps duration (rms) of the x-ray pulse. The jitter of the opening timing of XPS is less than 2 ns. One can thus produce a 945 Hz pulse train of 50 ps pulses from X-ray pulse trains at 794 kHz emitted from PF-AR ring.

**Figure 2.** Beam line NW2 (left) and a high speed chopper (X-ray pulse selector, XPS), a diffractometer, and a cryogenic system in the experimental hutch (right).

A femtosecond regenerative amplifier system (Spectra-Physics Lasers (SP), Spitfire) seeded by a mode-locked Ti:sapphire oscillator (SP, Lok-to-Clock Tsunami) is installed at NW2 laser booth. The oscillator is phase-locked to 84.76 MHz reference signals (1/6 of the rf master clock) by controlling the cavity length of the laser externally. The mode-locked Ti:sapphire oscillator is pumped by a second harmonic of a diode laser pumped Nd:YVO4 laser (SP, Millenia), which produces pulses with 80 fs duration, 700mW average power at 800nm. The laser beam is guided to the regenerative amplifier, which is pumped by the second harmonic of a diode laser pumped Q-switched Nd:YLF laser (SP, Evolution). The external trigger of the Q-switched laser is also synchronized at 945 Hz to a 1/537600 subharmonic of the rf frequency (1/89600 subharmonic of oscillator frequency), which enables synchronization of X-ray and laser pulses. The relative delay time between X-ray and laser pulses are controlled by a digital delay pulse generator (Stanford Research Systems, DG535), and is further finely controlled by an optical delay line. Finally, light pulses with 150 fs duration and a 500 µJ per pulse at 800 nm phase-locked to the X-ray pulses are delivered at the sample position.

Timing of the synchronization is monitored with an InGaAs metal-semiconductor- metal (MSM) photodiode detector (Hamamatsu Photonics), coupled to a high-frequency preamplifier and a 500 MHz digital oscilloscope (LeCroy). The diode detector has response time (rising) less than 50 ps, and is directly placed in the X-ray beam close to the sample position. The specification and performance of the photodiode detector will be reported elsewhere.

4. Diffractometer
The diffractometer consists of a four-circle (Ω, φ, χ, 2θ) goniometer with a CCD area detector (Rigaku/MSC, MercuryCCD) as shown in Figure 3. The goniometer has a partial χ-circle, which allows open geometry for ease of mounting crystals, positioning of low-temperature devices and aligning laser beam to the sample position. The CCD detector, which is based on a Peltier-cooled, single taper CCD camera, is mounted on the 20 arm. The taper ratio is 2.85:1, and the X-ray sensitive
area is 70 mm x 70 mm with 1024 x 1024 pixels (512 x 512 pixels in 2x2 binned mode) image size and with 16-bit analog-to-digital converter. The data collection is controlled by a program CrystalClear (Rigaku/MSC). Sample crystal can be cooled down to 20 K by using cryogenic helium gas flow (Rigaku, XR-HR10K).

Figure 3. The diffractometer system at NW2 which consists of a four-circle goniometer with a CCD area detector (Rigaku/MSC, MercuryCCD)

5. Feasibility of pump-probe X-ray diffraction
In order to demonstrate feasibility of time-resolved X-ray crystallography at NW2, we have examined time-resolved structural analysis of tetrathiafulvalene-chloranil (TTF-CA) crystal by using 50-ps X-ray pulses and 150-fs laser pulses. TTF-CA shows neutral-ionic phase transition around 80K due to the competition between the energy gain of the long range Coulomb attractive interaction and the effective ionization energy of the donor-acceptor pair [4]. This transition can be triggered reversibly by photo irradiation [3-5]. We have carried out a time-resolved measurement of diffraction intensities at 60K, and changes of the integrated diffraction intensities are observed as previously reported (Figure 4) [5]. A series of time-resolved diffraction datasets was successfully collected for watching a “molecular movie”, and further analysis of the structural dynamics is in progress.

Figure 4. Temporal profile of normalized structure factor amplitude of (0 3 0) reflection at 60 K.
6. A new beam line NW14
We have started construction of a new time-resolved X-ray diffraction beam line NW14 at PF-AR owing to a funding from ERATO Non-equilibrium Dynamics Project, Japan Science and Technology Agency (JST). The conceptual design and the experimental setup of the NW14 will be also presented in this conference as a separated work by Nozawa et.al.

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