Chapter 4

Synergy with X-ray Free-Electron Laser

4.1 Introduction

At SPring-8, a synchrotron light source and an X-ray Free Electron Laser (XFEL) are neighboring each other in the same campus. This provides SPring-8 with a unique opportunity for synergetic experiments using the two different kinds of light sources. To exploit this opportunity to its full potential, it is essential to upgrade SPring-8 so that it can deliver a diffraction limited beam with ultra high brilliance matching the XFEL.

One of the promising techniques that would be enabled by the synergetic use of a synchrotron light source and XFEL is correlative imaging, where, e.g. the 1st step analysis is performed using SPring-8II beam which dramatically enhances the efficiency of the measurements using XFEL. Such technique would be powerful for atomic resolution imaging. Although the light from XFEL is considered to be useful for solving the three dimensional atomic structure of nanocrystals, the number of nanocrystals needed for a complete dataset would be larger than ten thousand if the crystal orientation is completely random [1]. The number of necessary images is expected to be greatly reduced by using nanocrystals with a pre-determined orientation using the SPring-8 II beam.

Synergetic experiments using SPring-8 II and XFEL would allow pioneering scientific experiments in the imaging of non-crystalline samples as well. Using both sources, the imaging capability in different length scale and comprehensive understanding of them could be achieved. The high-resolution imaging in general has the severe drawback of radiation damage to the sample. This is why combined measurements would be useful, where a large area of the sample such as a whole cell is imaged with SPring-8 II, followed by a successive very high-resolution imaging of a particular region such as an organelle within the cell using the XFEL. For the large area imaging, multiple coherent X-ray diffraction images with overlapping fields of view (ptychography method [2–4]) would be powerful. On the other hand, the high-resolution image of a local area could be extracted from an extended object by using the keyhole imaging method [5].

These two measurements would provide key insights, e.g., about the organization inside the cell.

The XFEL pulsed beam contains a huge number of photons, 5×10^{11} photons per pulse, in an extremely short temporal duration of less than 100 femtoseconds. By using a delayed beam from SPring-8 II, unique X-ray pump-probe experiments could be performed. For example, the XFEL beam is used as a pump beam which excites specific elements into highly ionized states or many hole states [6]. SPring-8 II beam, on the other hand, is used as the probe beam to analyze using signals of, such as X-ray diffraction and/or energy dispersive EXAFS, with varied delay time. For each measurement at different time delay, materials under investigation need to be unchanged even after repeated excitation. This condition is easily fulfilled for gaseous or liquid samples. Even for crystalline or homogeneous amorphous materials, movement of the illuminated position has proven to be effective for obtaining consistent pump-probe data [7]. With extremely high spatial coherence of XFEL and SPring-8II, pump and probe experiments on a 10 nm area of the sample would be possible. This technique would enable us to measure a sharp initial distribution of the ionization state and its temporal evolution, which are especially important for surface science applications.

4.2 Atomic resolution imaging

4.2.1 Correlative imaging in protein nanocrystallography

Protein crystallography provides the 3D structural information of proteins indispensable for rational drug design and high-level medical services. However, many important proteins for industrial application are yet to be analyzed due to the difficulty in producing large single crystals. Thus, microfocus beamlines, allowing structural determination from microcrystals with dimensions more than 1 micrometer, are rapidly developed. However, mainly due to the radiation damage during data collection, analysis of protein nanocrystals with dimensions less than 1 micrometer is difficult to date.

Protein nanocrystallography using XFEL is a promising approach to overcome this problem [1]. In this method, intense X-ray pulses with ultra short durations, less than 100 fs, enables one to collect a ‘still’ diffraction pattern from a single nanocrystal before its destruction. However, the current system in protein nanocrystallography needs tens of thousands of still images from different single nanocrystals with random orientations to reconstruct a full data set. Furthermore, the liquid jet apparatus utilized in the current system produces a droplet containing small numbers of nanocrystals in a stochastic Poisson process. This indicates a limited crystal hit rate in the data collection, typically of around 20%. The first XFEL nanocrystallography experiment on the photosystem I protein consumed 10.3 billion nanocrystals to reconstruct a

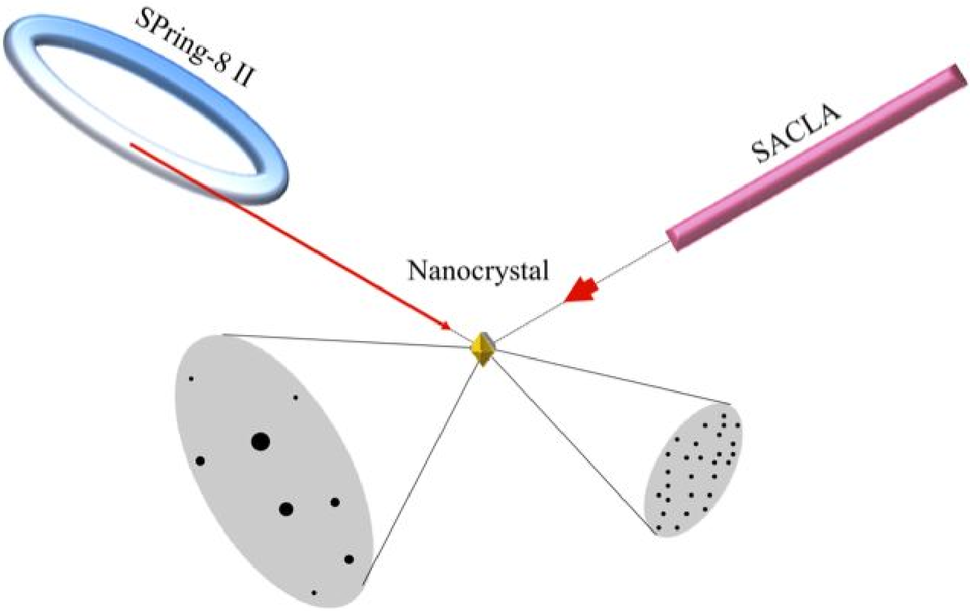

Figure 4.1: Schematic illustration of correlative diffractometry proposed for protein nanocrystallography where oscillation image using SPring-8 II and a high-resolution still image using SACLA are successively taken. In typical cases, a few hundred nanocrystals with random orientations would be enough to reconstruct a complete data set.

full data set at 8.5 Å resolution [1]. In addition, the liquid jet apparatus requires preliminary optimization of operating conditions which may consume over ten times the amount of crystals than that required for the actual experiment. Thus the current protocol would be unrealistic for most of the important proteins to be analyzed.

A complementary use of SPring-8 II and SACLA could reduce the required number of nanocrystals dramatically (see the schematic diagram in Fig. 4.1). This new system adopts a deterministic approach in which a precise determination of crystal parameters, using a nano-focused continuous X-ray beam from the storage ring, allows us to utilize most of the partially recorded reflections in the still images captured from the XFEL. Nanocrystals are mounted using a conventional cryogenic method that ensures much higher success rates in data collection. After the centering of a single nanocrystal, by X-ray scanning or a detection of fluorescence, one or a few oscillation diffraction patterns, including fully recorded reflections, are taken using the SPring-8 II X-rays with a small scanning angle that is larger than the crystal mosaicity. Radiation damage should be minimized by reducing the X-ray dose and/or using a liquid helium cryostat. Subsequently, the XFEL pulse irradiates the same nanocrystal from the opposite direction to take a high-resolution still diffraction pattern. This combination of taking two different kinds of shots from a single nanocrystal using SPring-8 II and SACLA is repeated on many independent nanocrystals with random orientations. Fully recorded reflections in the oscillation

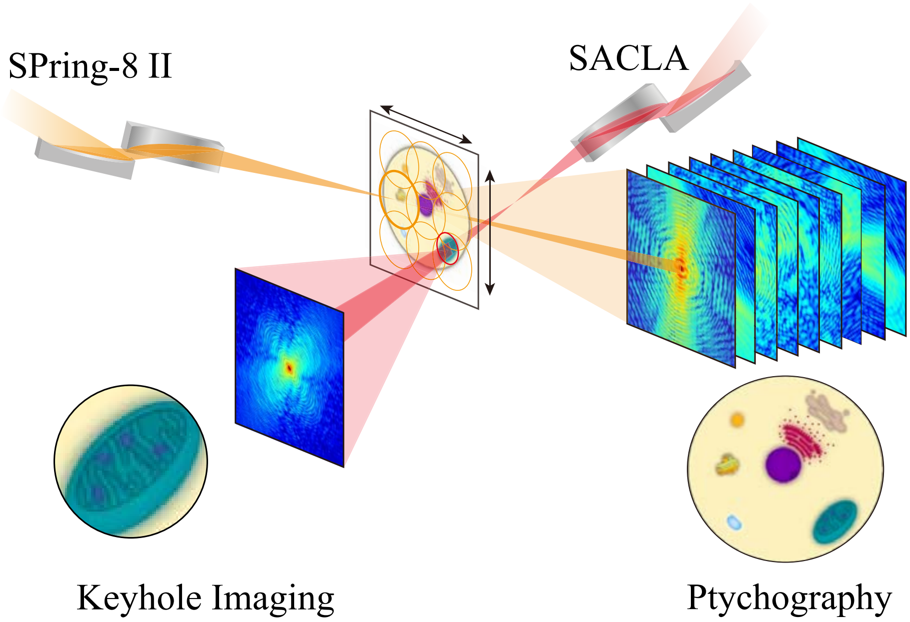

Figure 4.2: Schematic illustration of combined coherent diffractive imaging taking data for a wide area using SPring-8 II and for a specific local area using SACLA.

images are favorable in the determination of precise crystal parameters, thereby serving as a useful guide for the data reconstruction.

Alternatively, we could combine a complete low-resolution data set from SPring-8 II and many independent still data from SACLA. Even in this case, only the complementary use of SPring-8 II and SACLA allows the protein nanocrystallography at high resolution, suggesting the importance of the nano-focused continuous X-ray beam of SPring-8 II.

4.2.2 Coherent diffractive imaging of non-crystalline samples

Coherent diffractive imaging [8] (CDI) with iterative phasing methods offers X-ray imaging with extraordinarily high spatial resolution. The spatial resolution of CDI is limited, in principle, only by the X-ray wavelength and the largest recorded scattering angle. The use of highly focused incident X-ray beams is effective for collecting large angle diffraction data with a high signal-to-noise ratio [9]. A diffraction limited hard X-ray beam of SPring-8 II matched with the numerical aperture of the total reflection mirrors with ultimate surface roughness [10], makes it easy to increase the flux density by orders of magnitudes and improve the achievable resolution of CDI. On the other hand, the field of view becomes narrow as the X-ray spot size becomes small. In addition, the radiation damage of samples due to high-density radiation doses would be serious. For biological samples, the acceptable dose is limited by the radiation damage of the sample, thus limiting the spatial resolution to around 10 nm [11].

A new strategy for high-resolution and large-field-of-view CDI is provided by synergetic experiments using SPring-8 II and XFEL (see the schematic diagram in Fig. 4.2). Using SPring-8 II, ptychographic CDI [2–4] would be carried out using a focused synchrotron X-ray beam, in which a probe is scanned across the sample and the diffraction pattern would be measured at each beam position. Using XFEL, keyhole CDI [5] would be performed using a tightly focused single pulse, in which a finite expanding beam would be used to define a finite extent for the exit wave field of the object. For example, a 10-um-sized cell would be observed by ptychographic CDI with a 10-nm resolution in SPring-8 II. The shape of the cell and the spatial distribution of the organelles would be observed. Successively the region of interest, e.g. the nucleus or mitochondrion of the cell, would be measured by keyhole CDI with a resolution of less than a nanometer. Although keyhole CDI with XFEL destroys the area of the sample irradiated by X-rays, a coherent diffraction pattern could be collected faster than the relevant damage processes [12] as thermalization of the ejected electrons through collisional electron cascades is not completed within the time frame of a single XFEL pulse [13, 14]. This approach could also be used as a tool for studying the dynamics of various materials. For example, spatial distribution of catalytic nanoparticles, their individual nano-mesoscale structures, and the atomic-scale catalytic reactions they perform could be visualized. To realize this combined technique, various elementary techniques are necessary as follows: the mirror figuring and alignment technique, the positioning technique for alignment of X-rays from both X-ray sources at the same sample position, and the stabilization technique of optical systems. In addition, the illumination function must be defined beforehand or be derived in parallel to the object reconstruction. It is important to establish the technique for characterizing the X-ray probe beam [15, 16].

4.3 X-ray pump-probe experiment

X-ray free electron lasers (XFEL), such as LCLS and SACLA, would stimulate various pioneering research exploring the highly excited states in atoms, molecules, and materials. The FELs can create a specific excited state in one shot. XFEL-SPring-8 Experimental Facility, constructed in 2011, would offer an unique chance of X-ray pump-probe experiments, by overlaying the two X-ray beams from two ultimate sources on the same sample position with an appropriate time delay (see schematic diagram in Fig. 4.3).

4.3.1 Exploring elementary processes in highly-excited matters

In XFEL-irradiated systems, it is predicted that multiple inner shell electron excitation, producing multiple core-hole state and/or multiple photon excitation, occurs in addition to the simple inner shell electron ejection. The highly excited states must induce secondary process, which includes Auger process in sequence, leading to a Coulomb explosion. However, nobody has

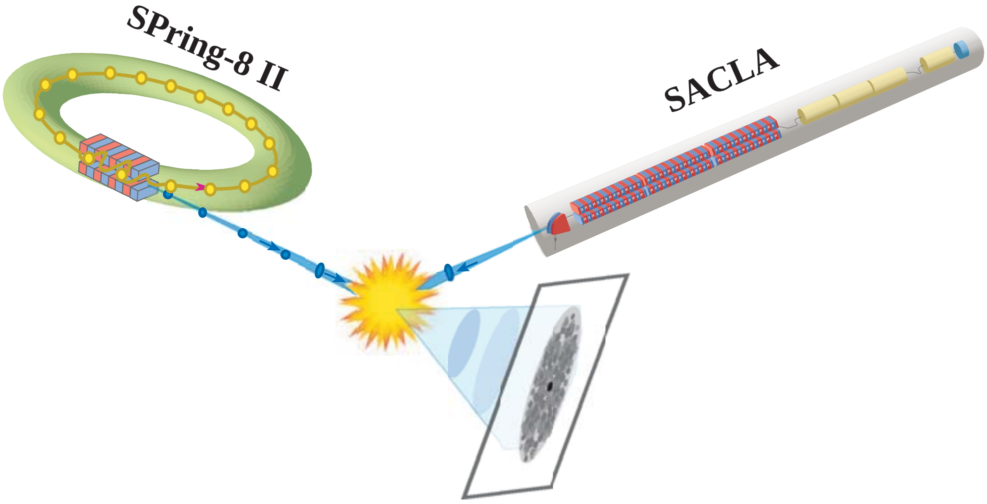

Figure 4.3: Schematic illustration of x-ray pump and x-ray probe experimental setup at SPring-8 campus.

observed the real process and experimental evidence is highly sought after. The advanced synchrotron radiation source, SPring-8 II, will become one of the most powerful tools for this observation. For this purpose, the following four features of SPring-8 II would be powerful: wide tunability of X-ray photon energy, ultra-short pulse, ultra-high brilliance, and high spatial coherence.

The energy tunability is important for probing the X-ray excited states using spectroscopic methods which require X-rays with different energy from the pumping X-rays. The two features, ultra-short pulse and ultra-high brilliance, are important for monitoring the X-ray excited states, which generally have a short life-time and relax to a ground state through higher energy intermediate states in less than picoseconds. Higher energy states in general have higher relaxation rates. Thus, SPring-8 II should provide a short pulse close to a sub-picosecond timescale. For example, the SPring-8 II SR with a sub-picosecond pulse duration would help to monitor the transient states of multiply-charged ions of neon (observations of product ions is reported by the LCLS group [6]). The high spatial coherence would help cultivating the new scientific frontier. The ultra-intense X-rays would produce new states or new phases in crystalline materials due to the proximity of the wavelength of the X-rays and the lattice constant. In the highly-excited transient state, the sample crystal may no longer keep its periodic atomic arrangements. The excited state cannot be expressed by applying perturbation theories. New states or new phases in crystalline materials are easily detectable by observing coherent diffraction patterns at a particular Bragg spot. The superior spatial coherence of SPring-8 II (Section 6.1.5) is indispensable for quantitative evaluations of the unknown states of materials.

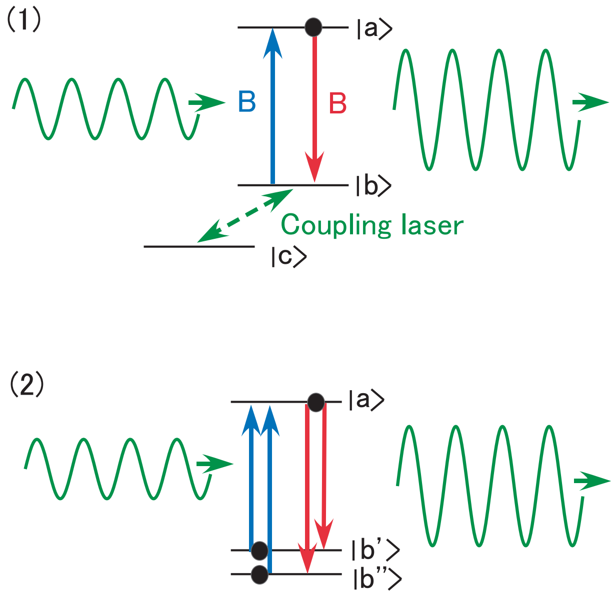

Figure 4.4: Schematic diagram of laser without inversion. (1) In normal laser condition, population inversion condition is indispensable. If an atom in which the laser field (coupling laser) is coupled to two levels rather than to one lower level, that is, the atom is prepared in a "coherent superposition" of the two lower levels of $|b'\rangle$ and $|b''\rangle$ as shown in (2), the two dipole moments for absorption are destructively interfered and canceled. On the other hand, the dipole moment for emission contributes to amplification. Therefore lasing without population inversion is achieved.

4.3.2 Coherent optical processes in the hard X-ray region

Combination of the two X-ray sources and a visible laser, makes it possible to conduct another challenging experiment, the coherent amplification of X-rays achieved in a coherent atomic system as described below. When a coherent visible (or infrared) laser is strongly coupled with the two levels of excited states in gas phase atoms, the resulting destructive interference of transition moments modifies the absorption coefficient. This phenomenon is well known as EIT (Electromagnetically Induced Transparency), which gives reduced absorption coefficient at a limited energy window [17]. At the ALS beamline, where femto-second SR pulses are generated by a laser slicing method, EIT was observed in the soft X-ray region with a high peak power femto- or pico-second pulsed laser [18]. The beams for pumping and probing should have pulse durations shorter than that of the coupling laser in this experiment. We can potentially realize EIT in the X-ray region, by modifying the population of the excited states using X-ray excitation with SACLA. One of the requirements to achieve a conventional laser is the population inversion, which requires the same value of Einstein's B coefficients between absorption and emission processes. However, if only the absorption coefficient becomes zero, the population inversion would not be required any more. Therefore, X-ray pumping to the excited states leads to the induced emission and coherent amplification of radiation. By using SACLA and SPring-8 II as the pump and probe X-ray beams, respectively, “laser without inversion” [19] may be achieved in the hard X-ray region (as schematically shown in Fig. 4.4). The coherent X-ray process may be also useful for the development of temporally- and spatially-coherent intense X-ray beams, by using the monochromatized SPring-8 II SR as a seeding light.

In summary, the SPring-8 II SR with a short pulse duration and a high spatial coherence would contribute to the probing of high energy transient systems produced by XFEL irradiation. It would open the research fields that elucidate ultrafast dynamics in highly excited states and coherent phenomenon in the X-ray region.

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