X-ray laser illuminates the local motion of water molecules

Liquids are essential to our daily life and energy-related applications, but many fundamental questions remain unanswered. A major challenge is understanding the molecular-level correlated dynamics in liquids, which helps bridge the knowledge gap between microscopic motions in liquids and macroscopic transport properties such as viscosity and electronic conductivity. Now, split-pulse X-ray photon correlation spectroscopy (XPCS) enables the measurement of molecular-level correlated motion in the pico- to nanosecond range, taking advantage of unprecedented brilliance and short pulse duration of an X-ray free electron laser (XFEL) [1]. The nearly fully coherent X-ray beam at SACLA allows the determination of the correlation in speckled scattering.

Analyses of molecular-level correlated dynamics in liquids using XPCS have been explored globally since the project of XFEL was initiated. In conventional XPCS, the temporal correlation of speckled scattering images provides the intermediate scattering function—the temporal correlation function of electron density in reciprocal space. Its temporal resolution is set by the frame rate of the detector (in synchrotron facilities) or the repetition rate of X-ray pulses (in XFEL), making it difficult to measure the dynamics in picoseconds and nanoseconds. The limitation is mitigated by using two X-ray pulses generated from a single XFEL pulse. The X-ray pulses are separated in time, and the sum of speckle scattering patterns from a sequence of two separate X-ray pulses is recorded in a single scattering image. The scattering images are then analyzed using the concept of speckle visibility spectroscopy (SVS) [2], which was originally developed using visible light. The contrast of speckled scattering images is related to the intermediate scattering function, so the dependence of contrast on the time separation between the two pulses provides information about the molecular-level dynamics. The accessible timescale in this approach is determined by the time separation between the two pulses, making it possible to study the dynamics at the femtosecond, picosecond, and sub-nanosecond scales.

The key components to realizing this approach are the split-delay optics (SDO) installed in SACLA **BL3** and the self-seeding of X-rays (Fig. 1) [1]. Reflection self-seeding produced bright X-ray pulses at a photon energy of 10 keV [3]. Each X-ray pulse was split into two sub-pulses using wavefront-division SDO [4]. The time difference Δt between the sub-pulses was controlled by the path length difference between the variable-delay branch and the fixed-delay branch. The exiting beams were overlapped and focused at the sample position with X-ray mirrors. The focused X-ray beam irradiated a continuous stream of water with a flow rate of 0.7 mL/min, and three multiport charge-coupled devices recorded the scattering from the sample. The water stream diameter was 50 μm, which is larger than the variation in beam position at the sample during the experiment (Fig. 2). The relative position between two sub-pulses, ΔX and ΔY, remained stable enough to assume that the two sub-pulses overlapped on the sample. The high stability of the SDO system is a crucial factor for successful measurement.

A major concern about this approach was a possible heating effect by the first sub-pulse. Because of the high pulse energy, the sample temperature may have risen before the second sub-pulse hit the sample. Figure 3(a) shows the scattering intensity around Q = 2 Å^{-1}, which was binned on the basis of the pulse energy of the first pulse (I_{fixed}), where Q is the magnitude of momentum transfer. The peak position shifted to a high Q with a larger Δt and a higher I_{fixed}. Using the temperature dependence of the peak position, we estimated the temperature rise ΔT (Fig. 3(b)). The result shows a heating effect for the water samples only after Δt = 0.5 ps when the X-ray pulses with $I_{\mathrm{fixed}} < 3$ μJ were selected.

The speckle visibility $\beta(Q = 2.0$ Å^{-1}, $\Delta t)$ was determined by maximum likelihood estimation on the assumption that the probability of observing photons at a single pixel is determined by a negative binomial distribution (Fig. 3(c)). With $I_{\mathrm{fixed}} < 3$ μJ, the

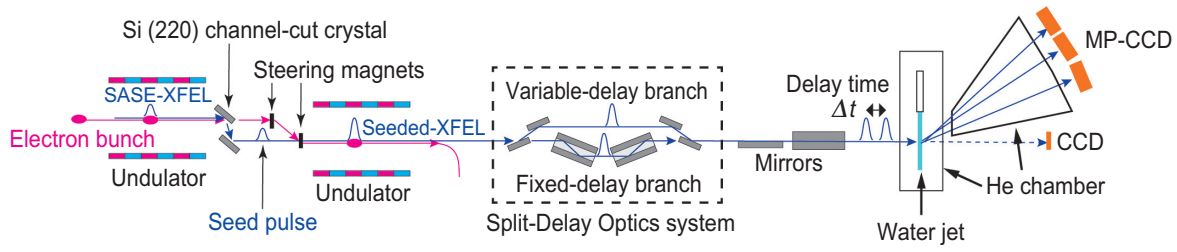

Fig. 1. Experimental setup using the SDO and reflection self-seeding at SACLA BL3. [1]

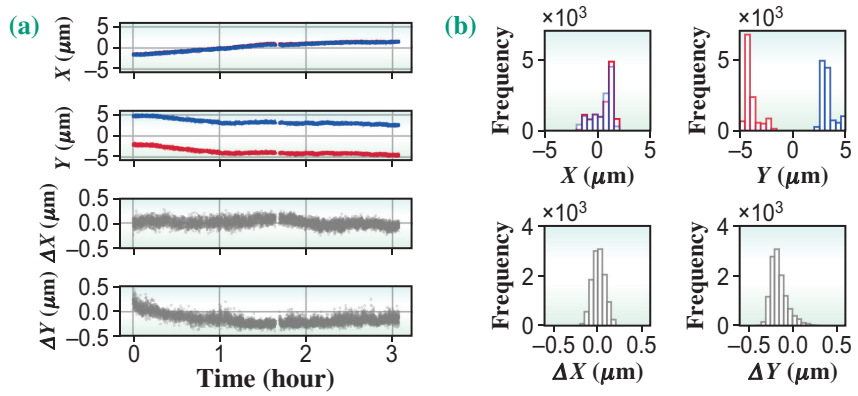

Fig. 2. **(a)** Time course of X-ray beam position of two sub-pulses at the sample position, X and Y, and their relative position, ΔX and ΔY. **(b)** Histograms of X, Y, ΔX, and ΔY. The position of two X-ray pulses was shifted in the Y direction for ease of viewing. [1]

visibility decreased as Δt increased, reflecting the dynamics of water molecules. The baseline values at a larger Δt agree with the values determined using the uncorrelated beams without spatial overlap. The decaying behavior of the visibility is comparable to those calculated from the result of inelastic X-ray scattering [5], indicating that the decrease in the visibility at short timescales with $I_{fixed} < 3$ μJ is reliable. With $I_{fixed} < 1$ μJ, meaningful estimations of β were not possible owing to the low count rate. The number of shots with 1 μJ < I_{fixed} < 3 μJ was ~65 % of the total number of shots with the seeded X-rays. Without the seeded X-rays, the average pulse energy of all X-rays (both branches) was 0.38 μJ. This result demonstrates the capability of the X-ray SVS with the control of the picosecond-scale time delay using the SDO and the necessity of self-seeded X-rays when studying the molecular-level correlated dynamics. This success at SACLA results from the use of the highly brilliant XFEL and the high stability of X-ray optics available at SACLA. Further studies at a higher Q and a larger Δt would determine the detailed molecular-level correlated dynamics at a timescale that is difficult to measure using other techniques.

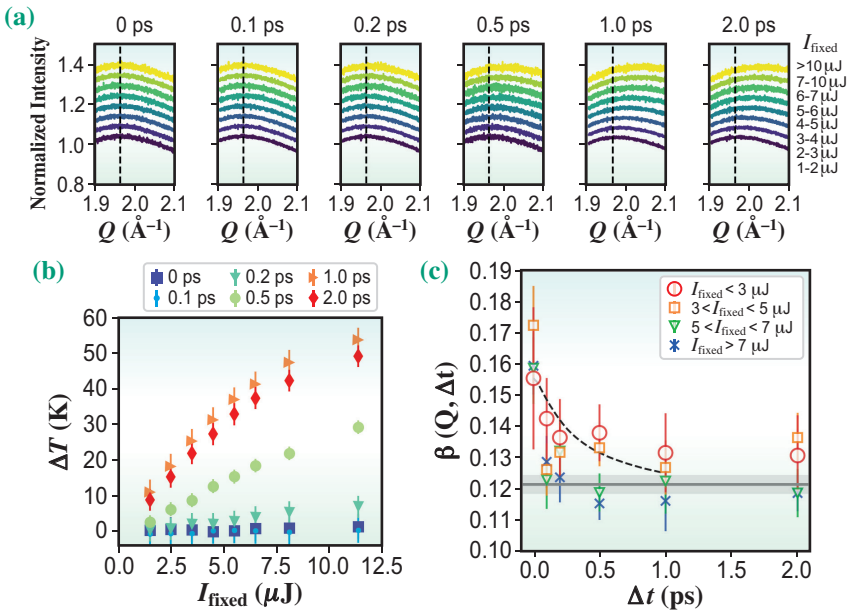

Fig. 3. **(a)** Normalized scattering intensity around Q = 2 Å^{-1}. Δt is shown at the top of the panels and the profiles are vertically shifted for clarity. **(b)** Estimated values of the temperature rise due to the energy of the sub-pulse from the fixed delay branch. The error bars represent the standard deviation of the fitting of the peak position in (a). **(c)** X-ray speckle contrast obtained by maximum likelihood estimation. The solid line represents the contrast measured when there was no overlap between the two sub-pulses, and the uncertainty was calculated using the second derivative of the log-likelihood. The dashed line represents the decaying behavior, which was estimated using the result of inelastic X-ray scattering [5]. [1]

Yuya Shinohara[a,*], Taito Osaka[b] and Ichiro Inoue[b]

[a] Oak Ridge National Laboratory
[b] RIKEN SPring-8 Center

*Email: shinoharay@ornl.gov

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