

# 100 ps time-resolved solution scattering utilizing a wide-bandwidth X-ray beam from multilayer optics

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100 ps time-resolved X-ray solution-scattering capabilities have been developed using multilayer optics at the beamline NW14A, Photon Factory Advanced Ring, KEK. X-ray pulses with an energy bandwidth of  $\Delta E/E = 1\text{--}5\%$  are generated by reflecting X-ray pulses ( $\Delta E/E = 15\%$ ) through multilayer optics, made of W/B<sub>4</sub>C or depth-graded Ru/C on silicon substrate. This tailor-made wide-bandwidth X-ray pulse provides high-quality solution-scattering data for obtaining photo-induced molecular reaction dynamics. The time-resolved solution scattering of CH<sub>2</sub>I<sub>2</sub> in methanol is demonstrated as a typical example.

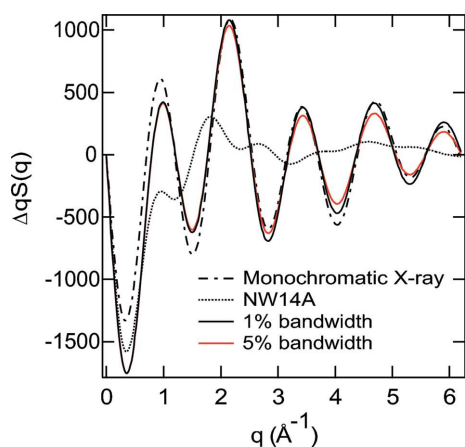
**Keywords:** time-resolved solution scattering; photodissociation reaction; liquidography; multilayers.

## 1. Introduction

Studying photo-induced reactions in the solution phase with subnanosecond time-resolution offers opportunities for understanding fundamental molecular reaction dynamics in chemistry and biology. Time-resolved X-ray diffraction using 100 ps X-ray pulses from a synchrotron source can elucidate the molecular geometry involved in photo-induced reaction pathways (Plech *et al.*, 2004; Ihee *et al.*, 2005; Georgiou *et al.*, 2006; Davidsson *et al.*, 2005; Kim *et al.*, 2006; Lee *et al.*, 2006, 2008*a,b*; Kong *et al.*, 2007, 2008). An X-ray pulse with  $\sim 3\%$  energy bandwidth has been used for solution-scattering experiments at the ID09B beamline of the European Synchrotron Radiation Facility (Plech *et al.*, 2002, 2004; Wulff *et al.*, 2004, 2006; Mirloup *et al.*, 2004; Ihee, 2009). Significant improvements in the signal-to-noise ratios of the experimental data have been reported for photochemical reactions of halogen compounds in solution. For example, the structural dynamics of C<sub>2</sub>H<sub>4</sub>I<sub>2</sub> in methanol were studied using the high-flux X-ray pulse at the ID09B beamline (Ihee *et al.*, 2005), and the reaction pathways and associated transient molecular structures in solution were resolved by the combination of theoretical calculations and global fitting analysis (Lee *et al.*, 2006; Cammarata *et al.*, 2006).

Recently, beamline NW14A at PF-AR, KEK, was constructed as a 100 ps time-resolved X-ray beamline (Nozawa *et al.*, 2007) using monochromatic or white X-rays. Its high-flux white X-rays have  $\Delta E/E \simeq 15\%$  energy bandwidth when an undulator of period length 20 mm is used. To check

the feasibility of time-resolved scattering with such a wide bandwidth and to search for the optimal bandwidth, we simulated the Debye scattering curves for the reaction C<sub>2</sub>H<sub>4</sub>I<sub>2</sub> → C<sub>2</sub>H<sub>4</sub>I + I using (i) a 15% bandwidth with the default X-ray energy distribution for the undulator spectrum on NW14A, (ii) a Gaussian spectrum with 5% energy bandwidth, (iii) a Gaussian spectrum with a 1% energy bandwidth, and (iv) a Gaussian spectrum with 0.01% energy bandwidth, as shown in Fig. 1. The photon flux of the X-ray pulse increases with the energy bandwidth, but the simulation shows that the 15% energy bandwidth with the default spectrum with a long tail is not suitable for time-resolved solution-scattering experiments owing to insufficient *q*-resolution. The long tail of the default X-ray spectrum induces a much higher extent of blurring at high scattering angles than a symmetric Gaussian spectrum with the same bandwidth. For this reason, the X-ray spectrum with a long tail at ID09B of ESRF with  $\sim 3\%$  bandwidth is comparable with a Gaussian spectrum with  $\sim 10\%$  bandwidth. In contrast, when we compare the calculated scattering curve using the Gaussian spectrum with 1% and 5% energy bandwidth X-rays with that with a 0.01% energy bandwidth, three calculated curves seem to reproduce the same quality. In addition, the total flux of the 5% energy bandwidth X-ray beam will be higher than that of the monochromatic X-rays ( $\sim 0.01\%$  energy bandwidth) from a Si single crystal by a factor of 250. The total flux of the 5% energy bandwidth X-rays is about five times more than that of the 1% energy bandwidth X-rays. Therefore, the data collecting time using the 5% energy bandwidth X-rays becomes shorter than when


**Figure 1**

Debye scattering curves calculated for the model reaction  $\text{C}_2\text{H}_4\text{I}_2 \rightarrow \text{C}_2\text{H}_4\text{I} + \text{I}$  using a 0.01% (monochromatic) Gaussian X-ray energy profile (dot-dashed line), 5% Gaussian X-ray energy profile (red line), 1% Gaussian X-ray energy profile (solid line), and 15% default X-ray energy profile with a long tail (dotted line).

using the monochromatic X-rays and the 1% energy bandwidth X-rays. These estimations clearly indicate that the preparation of X-ray pulses with  $\Delta E/E \simeq 5\%$  has a very significant merit for promoting a time-resolved X-ray solution-scattering experiment, and, thus, prompted us to reduce the bandwidth from the default 15% down to less than the  $\sim 5\%$  energy bandwidth of multilayer optics.

In our experimental set-up, the multilayer optics can produce X-rays with a 1–5% energy bandwidth, and allow us to measure the time-resolved solution-scattering with the undulator at the NW14A beamline. The purpose of this paper is to present a detailed account of achievements with the multilayer optics. We succeeded in collecting high-quality time-resolved solution-scattering data for the  $\text{CH}_2\text{I}_2$  photo-

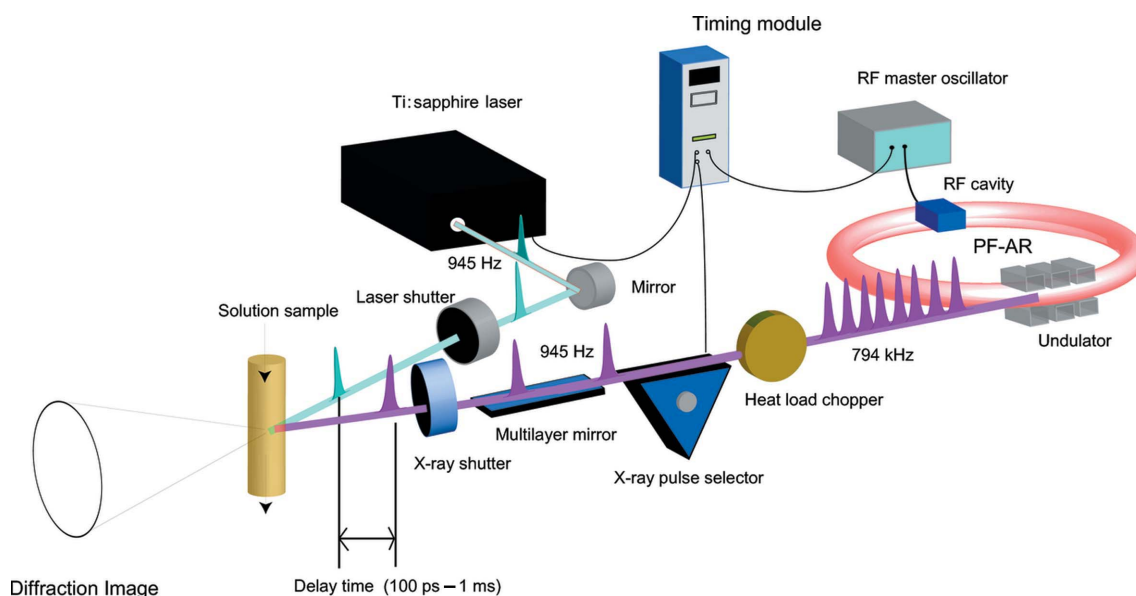
chemical reaction in methanol and briefly report the experimental aspects.

## 2. Experimental set-up

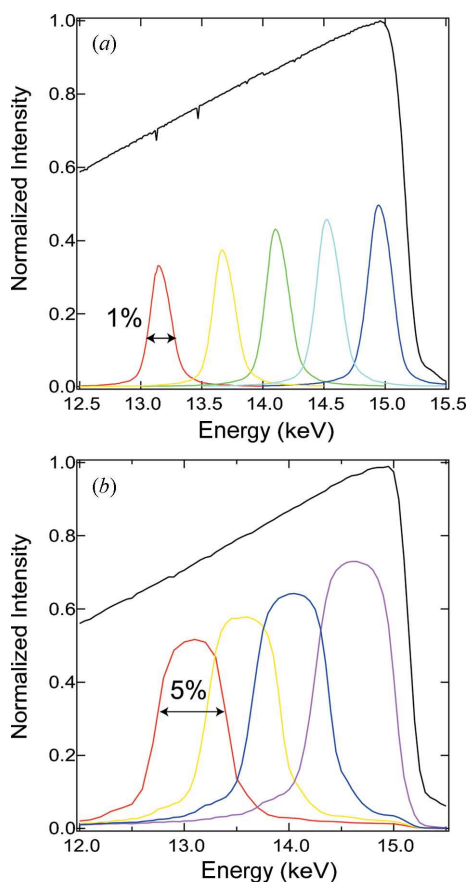
A schematic diagram of the experimental set-up is shown in Fig. 2. The experimental system consists of an amplified Ti:sapphire laser system for providing laser pulses to excite the liquid sample, an X-ray pulse selector (XPS) to select single X-ray pulses, a heat-load chopper (Gembicky *et al.*, 2007), laser and X-ray shutters, and a sapphire nozzle to provide a stable liquid jet. This beamline gives a white X-ray pulse in the energy range 13–18 keV using an undulator with a period length of 20 mm at a repetition rate of 794 kHz and with a pulse duration of about 100 ps. The scattered images were recorded on an integrating charge-coupled device detector (MarCCD165, MarUSA) of diameter 165 mm. Details of the set-up have been described elsewhere (Nozawa *et al.*, 2007).

## 3. Production of a wide-bandwidth X-ray beam using multilayer optics

We have utilized two types of multilayer optics. The first one is W/B<sub>4</sub>C ( $d = 27.7 \text{ \AA}$ , X-ray Company, Russia) on a Si single crystal with a size of  $50 \times 50 \times 5 \text{ mm}$ , which provides an X-ray spectrum with  $\sim 1\%$  energy bandwidth and in which the peak energy of the X-ray spectrum can be changed by tilting the angle of the multilayer optics, as shown in Fig. 3(a). The second multilayer, which is a depth-graded Ru/C layer ( $d = 40 \text{ \AA}$ , NTT Advanced Technology, Japan), produces a  $\sim 5\%$  energy bandwidth from the undulator spectrum, as shown in Fig. 3(b). A real image of the multilayer mirror installed in the


**Figure 2**

Schematic diagram of the time-resolved solution X-ray scattering at beamline NW14A, PF-AR. The wide-bandwidth ( $\Delta E/E = 1\text{--}5\%$ ) X-ray pulses at 945 Hz are provided from the multilayer optics downstream of the X-ray pulse selector. The laser and the X-ray pulse selector are synchronized by using the RF master oscillator.



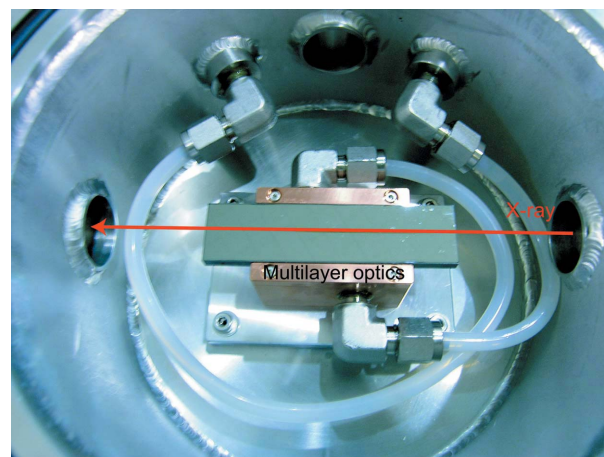
**Figure 3**

Wide-bandwidth X-ray pulses were produced by multilayer optics from the undulator spectrum. The peak energy position is controlled by changing the incident angle. The black curve is the X-ray spectrum from the undulator, with a gap of 11 mm. (a) X-ray spectra using the W/B<sub>4</sub>C multilayer optics. The X-ray bandwidth is about 1%. (b) X-ray spectra using the depth-graded Ru/C multilayer optics. The X-ray bandwidth is 5%.

vacuum chamber is shown in Fig. 4. The diameter of the vacuum chamber placed on a swivel stage is 160 mm. The multilayer optics is mounted on a water-cooled copper holder. A white X-ray pulse with a photon flux of  $1 \times 10^9$  photons per pulse is produced in the energy range at a 1 kHz repetition rate with the XPS. When multilayer optics with 1% and 5% energy bandwidths are used downstream of the XPS, the photon fluxes are  $6 \times 10^7$  and  $3 \times 10^8$  photons per pulse, respectively. We can use the discretionary wavelengths and bandwidth in the X-rays for spectra, which is an advantage for the scattering curve corresponding to the asymmetric undulator spectra.

#### 4. Time-resolved solution scattering of CH<sub>2</sub>I<sub>2</sub>

Photo-induced chemical and biological reactions have been extensively studied by time-resolved spectroscopic techniques and theoretical calculations. Time-resolved X-ray solution scattering makes it possible to probe transient molecular structures in the photo-induced reactions. We measured the time-resolved scattering signals for photodissociation of the iodine atom from CH<sub>2</sub>I<sub>2</sub> in methanol (Davidsson *et al.*, 2005).



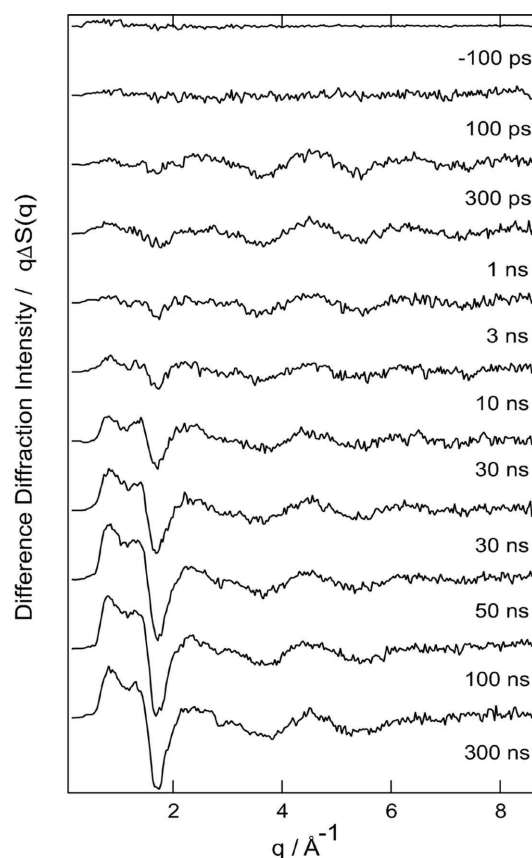
**Figure 4**

The depth-graded Ru/C multilayer in the vacuum chamber installed at the NW14A beamline at the Photon Factory Advanced Ring at KEK. The multilayer is mounted on a water-cooled holder.

We performed the measurement using X-rays with 5% energy bandwidth at 18 keV to evaluate the feasibility of this set-up. The 60 mM CH<sub>2</sub>I<sub>2</sub> (Aldrich, Japan) in methanol solution was flowed using a liquid jet of thickness 0.3 mm at a flow rate of about  $3 \text{ m s}^{-1}$ . The open jet makes it possible to remove any background signal owing to the scattering of a glass capillary. The CH<sub>2</sub>I<sub>2</sub> in methanol solution was excited by 267 nm light, the third harmonic of the Ti:sapphire femtosecond laser system. To ensure one-photon absorption, the laser pulse width was stretched to  $\sim 2$  ps by passing 150 fs laser pulses through a fused silica glass rod cut at the Brewster angle for 267 nm with 175 mm optical length. The spot size of both the X-ray and laser beams on the sample surface was 200  $\mu\text{m}$  diameter. The laser path was set almost parallel to the X-ray path ( $\sim 10^\circ$  tilt), and the intensity of the laser beam on the sample surface was adjusted to  $\sim 35 \mu\text{J}$  per pulse. The sample-to-CCD distance and the exposure time were 48.6 mm and 7 s per image, respectively. The CCD detector allowed a  $2\theta$  angle range from about  $3$  to  $62^\circ$  to be measured. Difference diffraction data were measured at time delays of  $-200$  ps, 100 ps, 300 ps, 1 ns, 3 ns, 10 ns, 30 ns, 50 ns, 100 ns, 300 ns and 1  $\mu\text{s}$ , as shown in Fig. 5. The CCD images were converted to one-dimensional curves using the *FIT2D* program (<http://www.esrf.eu/computing/scientific/FIT2D/>). To extract the diffraction intensity change alone, the data for an unperturbed sample at  $-3$  ns were subtracted from the diffraction data collected at other time delays. Photo-induced heating of the solvent is evident in the low  $q$  region ( $\leq 2 \text{ \AA}^{-1}$ ). The change in the high  $q$  region indicates the photo-induced structural changes of the CH<sub>2</sub>I<sub>2</sub> molecule. Details of the data analysis will be reported elsewhere.

#### 5. Conclusion

Wide-bandwidth X-ray pulses were generated from depth-graded Ru/C and W/B<sub>4</sub>C multilayer optics for time-resolved X-ray solution scattering. The symmetric shape and the



**Figure 5**  
Subnanosecond time-resolved diffraction signal of  $\text{CH}_2\text{I}_2$  in methanol solution as a function of time delay. The differential diffraction intensity was obtained by subtracting the diffraction signal at a reference negative time delay ( $-3$  ns) from the diffraction signal at each time delay.

bandwidth ( $\Delta E/E = 1\text{--}5\%$ ) of the energy spectra of the X-ray pulse are suitable for time-resolved solution-scattering experiments, and quantitative analysis of photo-induced molecular reaction dynamics in solution. We successfully measured the solution scattering from  $\text{CH}_2\text{I}_2$  in methanol and the time dependence of the difference scattering was presented.

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