Journal of
Synchrotron
Radiation

ISSN 0909-0495

Received 9 December 2008
Accepted 9 February 2009

Picosecond time-resolved laser pump/X-ray probe experiments using a gated single-photon-counting area detector

T. Ejdrup,[a]* H. T. Lemke,[a] K. Haldrup,[a] T. N. Nielsen,[a] D. A. Arms,[b] D. A. Walko,[b] A. Miceli,[b] E. C. Landahl,[c] E. M. Dufresne[b] and M. M. Nielsen[a]

[a]Danish National Research Foundation Centre for Molecular Movies, Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark, [b]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA, and [c]Department of Physics, DePaul University, 2219 North Kenmore Avenue, Chicago, IL 60614, USA. E-mail: ejdrup@fys.ku.dk

The recent developments in X-ray detectors have opened new possibilities in the area of time-resolved pump/probe X-ray experiments; this article presents the novel use of a PILATUS detector to achieve X-ray pulse duration limited time-resolution at the Advanced Photon Source (APS), USA. The capability of the gated PILATUS detector to selectively detect the signal from a given X-ray pulse in 24 bunch mode at the APS storage ring is demonstrated. A test experiment performed on polycrystalline organic thin films of α-perylene illustrates the possibility of reaching an X-ray pulse duration limited time-resolution of 60 ps using the gated PILATUS detector. This is the first demonstration of X-ray pulse duration limited data recorded using an area detector without the use of a mechanical chopper array at the beamline.

Keywords: time-resolved X-ray diffraction; pixel detector; α-perylene; PILATUS.

1. Introduction

In the past decade, time-resolved laser pump/X-ray probe techniques have proven to be versatile tools for investigating ultrafast dynamics in gases, solids and liquid solutions (Larsson *et al.*, 1998; Techert *et al.*, 2001; Schotte *et al.*, 2003; Plech *et al.*, 2004; Young *et al.*, 2006; Christensen *et al.*, 2009). The highest photon flux per X-ray pulse is obtained at synchrotron sources, where the time-resolution is generally limited by the X-ray pulse duration (50–100 ps). Better time resolution can be achieved using the slicing technique (100 fs) (Schoenlein *et al.*, 2000) or laser-driven sources (100 fs–5 ps) (Zhavoronkov *et al.*, 2004; Reich *et al.*, 2007) at the expense of the X-ray photon flux, limiting the use of these methods to strongly scattering sample systems. In the near future, X-ray free-electron lasers with femtosecond time resolution and a high photon flux per X-ray pulse will become operational (Saldin *et al.*, 1999, and references therein; see also http://ssrl.slac.stanford.edu/lcls/ and http://xfel.desy.de/), facilitating investigations of ultrafast processes in a wider range of sample systems. However, even with the new sources for ultrashort X-ray pulses, time-resolved experiments at synchrotron sources will still play an important role in understanding ultrafast dynamics.

In order to reach the optimal time-resolution, the signal from a single probe pulse arriving at the sample at a well defined time delay after a single pump pulse has to be detected selectively. As synchrotron sources have repetition rates in the MHz range and femtosecond lasers have repetition rates in the kHz range, reaching pulse duration limited time-resolution is not trivial. Two general schemes are used: (i) using an array of mechanical choppers reducing the repetition rate of the X-ray pulses to match the laser repetition rate (Wulff *et al.*, 2002; Nozawa *et al.*, 2007); this scheme creates pump/probe pulse pairs with a set time delay, hence it is possible to use integrating detectors; (ii) using a fast X-ray detector able to selectively detect the signal from a given X-ray pulse (DeCamp *et al.*, 2005). In both cases the time delay between the pump and probe pulses is controlled electronically with a timing jitter much smaller than the X-ray pulse duration.

Whereas the former scheme relies on highly advanced mechanical hardware installed at the beamline, the latter can be implemented using mainly electronic devices. In general, the only detectors fast enough to selectively detect the signal from a given X-ray pulse are based on photodiodes, previously limiting detector choices to point detectors or small arrays. For time-resolved experiments studying changes in the scattering signal, area detectors are favourable, as they record a full two-dimensional scattering pattern, reducing the data acquisition time considerably.

Recently, there has been a development in the area of fast detectors where arrays of silicon pixel devices have been

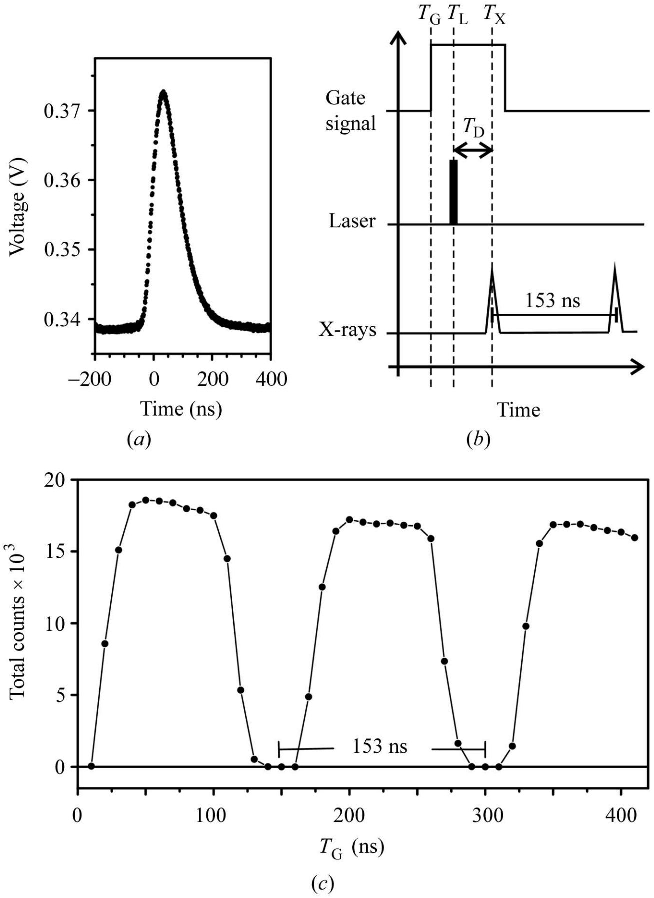
doi:10.1107/S0909049509004658

assembled to create area detectors (Brönnimann *et al.*, 2002; Ercan *et al.*, 2006), combining the advantages of the fast detectors with those of area detectors. These detectors are gateable with opening times in the nanosecond range. This opens the possibility of selectively detecting the signal from a given X-ray pulse, and thus reaching X-ray pulse duration limited time-resolution. The present paper describes the commissioning of a PILATUS100K pixel detector (Brönnimann *et al.*, 2002) for time-resolved X-ray diffraction experiments on weakly scattering organic thin films at the Advanced Photon Source (APS) storage ring.

2. Experiment and discussion

The PILATUS detector is the first commercially available gateable area pixel array detector. It is a single-photon-counting detector with a 320 µm-thick silicon sensor bump-bonded to an ASIC with a charge shaping amplifier, lower level discriminator and 20-bit counter in each pixel. It has a full frame readout time of 2.7 ms; at the fastest shaping time the dead-time of a pixel is 125 ns (http://pilatus.web.psi.ch/DATA/REPORTS/rate_scans.html). In 24 bunch mode, which is the standard mode of operation at the APS, the ring is filled with 24 equidistant electron bunches with a current of 4.25 mA and a bunch length (r.m.s.) of 40 ps (http://aps.anl.gov/Facility/Storage_Ring_Parameters/node5.html) leading to an X-ray pulse duration of about 60 ps. The PILATUS detector can be operated in an external enable mode, where the detector is only active during a gate signal. The gate signal can be shorter than the 153.4 ns separation between the individual bunches at APS in 24 bunch mode, hence it is expected that the detector will be able to selectively detect the signal from a given X-ray pulse, and thereby reach a pulse duration limited time-resolution of 60 ps.

To investigate the response of the PILATUS detector to a gate signal, the detector was gated using a 40 ns TTL pulse with a repetition rate of 1 kHz supplied by a delay generator (SRS SDG 535) locked to the ring frequency (∼272 kHz). This matches the repetition rate of the laser used for the pump/probe experiments. The fastest shaping time available on the PILATUS detector was used. The analog output of a single-pixel charge-shaping amplifier is shown in Fig. 1(*a*); the full width at half-maximum (FWHM) of the analog output is 115 ns. The arrival time of the gate pulse (T_G), see Fig. 1(*b*), was scanned over a period of 400 ns in steps of 10 ns. At each T_G a scattering image was recorded and integrated (Fig. 1*c*). This scan clearly shows a reproduction of the bunch pattern with a 153.6 ns distance between the X-ray pulses. The X-ray pulses are detected in a time window with a width about twice the duration of the gate pulse; this is attributed to the length of the comparator output in the pixel-counting circuit. No significant dependence of this effect with pixel position was found. The number of counts on the detector drops to zero between the pulses making it possible to unambiguously decide which X-ray pulse is detected by the PILATUS detector.



(*a*) (*b*)

(*c*)

Figure 1
(*a*) Analog output of the charge-shaping amplifier of a single pixel at the PILATUS fastest setting. The output was acquired using a digital sampling oscilloscope (Tektronix TDS5104) and averaged over 100 pulses. A FWHM of 115 ns is found. (*b*) Schematic of the arrival times of the various pulses in the experiment. (*c*) Total number of counts on the PILATUS detector as a function of the gate delay; the separation of 153 ns between the X-ray pulses and the ability to separate signals from neighbouring pulses is easily seen.

The timing set-up for the laser/X-ray set-up is described in detail elsewhere (Adams *et al.*, 2002). For a pump/probe experiment, the laser pump pulse arrives at the sample at time T_L with a 1 kHz repetition rate and the chosen X-ray probe pulse arrives at the sample at time T_X. T_D, the time delay between the two pulses ($T_D = T_X - T_L$), has a jitter of less than 10 ps and can be adjusted to any value between ±1 ms; this window is defined by the distance between neighbouring laser pulses. The pulse sequence is shown schematically in Fig. 1(*b*).

Before starting time-resolved experiments it is necessary to ensure that the gate pulse at T_G is timed to detect the X-ray pulse arriving at T_X, and to determine the value of T_L for which T_D is 0 (T_0). This is done through a two-step process. (i) An avalanche photodiode (APD) (http://www.aps.anl.gov/Xray_Science_Division/Beamline_Technical_Support/Detector_Pool/Detector_Information/APD/), sensitive to both laser light and X-rays inserted at the sample position, measures the arrival times of the laser and X-ray pulses (T_L and T_X). Monitoring the APD signal on a fast oscilloscope along with the gate signal, T_G and T_L are tuned to match T_X. To optimize T_G, a scan similar to the one shown in Fig. 1(*c*) can be performed. This first step allows for T_0 to be determined with a precision of 1–2 ns. (ii) A scan of a time-resolved signal from a well known sample, as described below.

A sample of weakly scattering vapour-deposited polycrystalline thin films of α-perylene was chosen to test the set-up. These thin films have been studied in detail through a series of time-resolved X-ray experiments (Lemke *et al.*, 2009), where it was determined that, within the first 100 ps after laser excitation, energy is coupled into the lattice resulting in a lattice expansion on this timescale. The fast lattice response makes these films ideal to test the time-resolution of the set-up.

A thin film sample, 5 mm × 5 mm in size, was mounted on a six-circle diffractometer. The X-ray beam was focused to 100 µm in the direction vertical to the substrate plane in order to maximize the incident flux in grazing-incidence geometry. For specular scattering, the θ and 2θ angles were kept constant, as the shift of the specular reflection was small enough that divergence of the focused X-ray beam was sufficient to keep the sample in the scattering condition. The 400 nm pump pulse was obtained by frequency doubling of the output from a Ti:sapphire laser system with a repetition rate of 1 kHz. The pulse energy at 400 nm was 300 µJ. The laser was focused to a footprint of 2 mm × 7 mm and kept at normal incidence. The PILATUS detector was controlled using software developed at the APS (Rivers, 2008).

As the second step in determining T_0, the fast response of the 001 reflection from the α-perylene film was probed. Two software regions of interest (ROIs) were defined on the PILATUS containing the top and the bottom of the 001 reflection, thus if the reflection moves vertically the ratio between the two ROIs will change accordingly. Fig. 2(*a*) shows this ratio as a function of T_L with 200 ps step size; it is easily seen at which T_L the ratio changes. This value is subsequently set to be T_0. In the present case the precision of T_0 is given by the step size chosen for the scan (200 ps); however, this can be considered an upper limit, as the sample response time is known to be <100 ps and the X-ray pulse duration is about 60 ps.

For the time-resolved experiments, pairs of images with laser delays of T_D and $T_{\rm Reference}$ were acquired and subtracted, generating difference images revealing the changes in the scattering pattern induced by laser excitation. $T_{\rm Reference}$ was chosen to be −3.68 µs (one ring period), thus both images were recorded using X-rays generated by the same electron bunch, minimizing the need for normalization. With the laser pulse arriving at the sample 3.68 µs after the X-ray pulse, the fast dynamics initiated by the previous laser pulse are over and the sample has had time to thermally equilibrate. Thus the reference may be used to normalize for long-term effects, like sample degradation and slow thermal drift. Each acquired image is an accumulation of 10000 consecutive gating events, and for each T_D multiple such T_D and $T_{\rm Reference}$ images were recorded to improve the counting statistics of the experiment; the fast readout time and low readout noise make this a viable option. In Figs. 2(*b*) and 2(*c*) two difference images of the 001 reflection are shown. Panel (*b*) shows the difference image for a negative T_D, and only statistical noise is seen. Panel (*c*) shows the difference image for a positive T_D, and the peak shift owing to the thermal expansion induced by the laser is clearly seen.

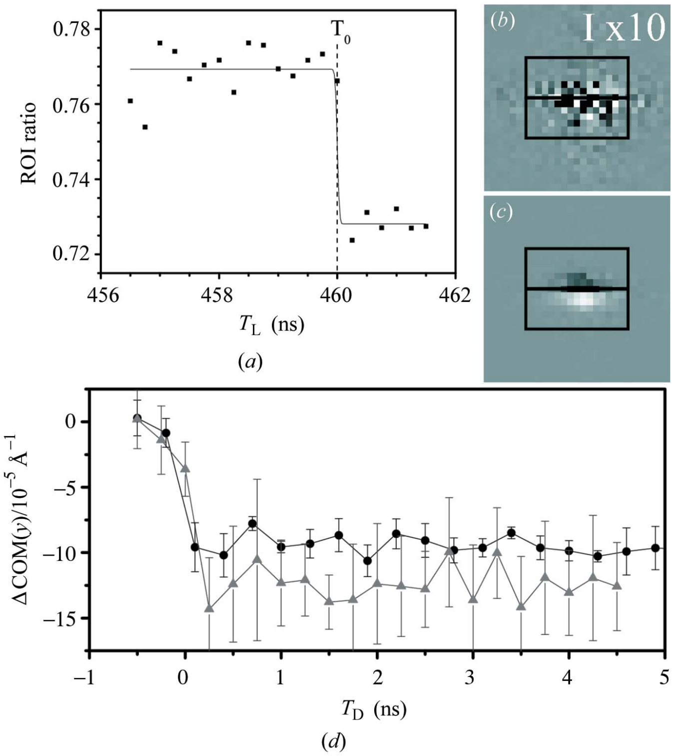


Figure 2
(*a*) Ratio between the top ROI and the bottom ROI of the 001 reflection of α-perylene as a function of the arrival time of the laser pulse T_L; the step at T_0 is fitted to an error function with a FWHM of 60 ps. (*b*) Difference image for $T_D = -200$ ps $- T_{\rm Reference} = -3.68$ µs; the laser pulse is arriving after the X-ray pulse in both images and only noise is seen. The intensity is scaled up by a factor of ten compared with the image in panel (*c*). (*c*) Difference image for $T_D = 100$ ps $- T_{\rm Reference} = -3.68$ µs; the laser pulse is arriving 100 ps before the X-ray pulse and the shift of the 001 reflection owing to thermal expansion of the lattice is seen. (*d*) The shift of the centre of mass in the vertical direction of the 001 reflection as a function of time delay for two different thin films. Circles: 700 nm-thick film; triangles: 500 nm-thick film; the error bars are the uncertainties on the fit of the centre of mass of the reflection peak. The change is proportional to the energy deposited in the film per unit volume and matches the laser intensity used in the experiment.

Time-resolved measurements of the 001 reflection were recorded for two different thin films of α-perylene with thicknesses of 500 nm and 700 nm. Fig. 2(*d*) shows a plot of the change in vertical centre of mass [COM(y)] of the 001 reflection as a function of time. The absorption length for 400 nm light is 300 nm in α-perylene films, hence the energy deposited per unit volume decreases rapidly through the film and the average energy deposited per unit volume in the film will decrease with increasing film thickness. The ratio of the average initial temperature rise between the thin and the thick film is expected to be 1.2 with the laser settings used in the experiment. The ratio of the peak shift is observed to be 1.3 ±

0.4, hence there is a good match between the expected and measured values.

3. Conclusion and outlook

The results described above show that it is possible to selectively detect the signal from a given X-ray pulse using a gated PILATUS detector and hence perform X-ray pulse duration limited time-resolved X-ray diffraction experiments at a synchrotron source using this type of detector. This has been illustrated by an experiment investigating the peak shift of the 001 reflection of α-perylene caused by laser excitation. The experimental findings match the expected thermal expansion in the thin films. These are the first X-ray pulse duration limited time-resolved X-ray experiments performed at a synchrotron source using an area detector without the use of mechanical chopper systems. The advantage of the area detector is clear, as the data acquisition time is reduced by about a factor of 60 compared with using an APD[1], even without taking into account the possibility of recording multiple reflections on a single image. The commercial availability of the PILATUS detector opens for the possibility of performing time-resolved experiments at many more beamlines than at present, as it eliminates the need for advanced mechanical chopper systems to be installed, while still making it possible to obtain two-dimensional images of scattering patterns. Similar to mechanical chopper systems, the PILATUS requires a certain bunch structure in the synchrotron ring to reach the best possible time resolution. Our data reveal that a bunch separation of at least 130 ns is needed to selectively detect only a given X-ray pulse. Signal-to-noise ratios could be further improved by virtually eliminating drift between subsequent $T_{\rm D}$ and $T_{\rm Reference}$ images with future detectors employing multiple gateable accumulation registers for each pixel, allowing for the recording of both images within one accumulation cycle. The lack of any reduction in the X-ray repetition rate in the experiments leads to increased X-ray beam damage of the sample compared with chopper-based set-ups, however. The beam damage can be significantly reduced by implementing a simple detector-synchronized heatload chopper at the beamline with opening times in the microsecond range.

This work was made possible through support from the Danish National Research Foundation, Centre for Molecular Movies. Use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We thank C. Brönnimann for valuable discussions regarding the PILATUS detector.

References

Adams, B. W., DeCamp, M. F., Dufresne, E. & Reis, D. A. (2002). *Rev. Sci. Instrum.* **73**, 4150–4156.

Brönnimann, Ch., Baur, R., Eikenberry, E. F., Fischer, P., Florin, S., Horisberger, R., Lindner, M., Schmitt, B. & Schulze, C. (2002). *Nucl. Instrum. Methods A*, **477**, 531–535.

Christensen, M., Haldrup, K., Bechgaard, K., Feidenhans'l, R., Kong, Q., Cammarata, M., Lo Russo, M., Wulff, M., Harrit, N. & Nielsen, M. M. (2009). *J. Am. Chem. Soc.* **131**, 502–508.

DeCamp, M. F., Reis, D. A., Fritz, D. M., Bucksbaum, P. H., Dufresne, E. M. & Clarke, R. (2005). *J. Synchrotron Rad.* **12**, 177–192.

Ercan, A., Tate, M. W. & Gruner, S. M. (2006). *J. Synchrotron Rad.* **13**, 110–119.

Larsson, J., Heimann, P. A., Lindenberg, A. M., Schuck, P. J., Buckbaum, P. H., Lee, R. W., Padmore, H. A., Wark, J. S. & Falcone, R. W. (1998). *App. Phys. A*, **66**, 587–591.

Lemke, H. T. *et al.* (2009). In preparation.

Nozawa, S. *et al.* (2007). *J. Synchrotron Rad.* **14**, 313–319.

Plech, A., Wulff, M., Bratos, S., Mirloup, F., Vuilleumier, R., Schotte, F. & Anfinrud, P. A. (2004). *Phys. Rev. Lett.* **92**, 125505.

Reich, C., Laperle, C. M., Li, X., Ahr, B., Benesch, F. & Rose-Petruck, C. G. (2007). *Opt. Lett.* **32**, 427–429.

Rivers, M. (2008). *Pilatus EPICS Software*, http://cars9.uchicago.edu/software/epics/pilatusDoc.html.

Saldin, E. L., Schneidmüller, E. A. & Yurkov, M. V. (1999). *The Physics of Free Electron Lasers.* Berlin: Springer.

Schoenlein, R. W., Chattopadhyay, S., Chong, H. H. W., Glover, T. E., Heimann, P. A., Shank, C. V., Zholents, A. A. & Zolotorev, M. S. (2000). *Science*, **287**, 2237–2240.

Schotte, F., Lim, M., Jackson, T. A., Smirnov, A. V., Soman, J., Olson, J. S., Phillips, G. N. Jr, Wulff, M. & Anfinrud, P. A. (2003). *Science*, **300**, 1944–1947.

Techert, S., Schotte, F. & Wulff, M. (2001). *Phys. Rev. A*, **86**, 2030–2033.

Wulff, M., Plech, A., Eybert, L., Randler, R., Schotte, F. & Anfinrud, P. (2002). *Faraday Discuss.* **122**, 13–26.

Young, L., Arms, D. A., Dufresne, E. M., Dunford, R. W., Ederer, D. L., Höhr, C., Kanter, E. P., Krässig, B., Landahl, E. C., Peterson, E. R., Rudati, J., Santra, R. & Southworth, S. H. (2006). *Phys. Rev. Lett.* **97**, 083601.

Zhavoronkov, N., Gritsai, Y., Korn, G. & Elsaesser, T. (2004). *Appl. Phys. B*, **79**, 663–667.

---

[1] To characterize a reflection in two dimensions using a point detector, scans across the peak in both horizontal and vertical directions are needed. To be able to detect the small peak shifts in time-resolved experiments, these scans would typically contain 21–41 points and each point would require about the same data acquisition time as one image recorded by the PILATUS detector.