A 100 picosecond time-resolved X-ray scattering facility at BioCARS

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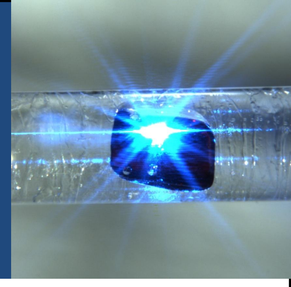


Beamline Description

The 14-ID beamline has recently undergone a major upgrade of its X-ray optics and experimental infrastructure. With the addition of a new KB mirror system, the X-ray flux density at the sample has increased by a factor of 100 compared to the old setup. A minimum focal spot size of 90(H) x 20(V) μm^2 achieved by the new mirrors also reduced the minimum opening time of the chopper system, thus allowing the beamline to operate with 100-ps time resolution for nearly 80% of the APS run cycle, taking advantage of both 24 bunch and hybrid modes. For most experiments, the critical parameter is the number of photons per 100-ps pulse impinging on the sample. The 14-ID beamline delivers as many as ~4 10^{10} ph/pulse in a bandwidth of $\Delta E/E$~4% at a maximum repetition rate of 1 kHz. By comparison, the LCLS operating in 10 fs mode has a maximum flux of 10^{11} ph/pulse in a bandwidth of 0.5% at a repetition rate of 120Hz. The nearly identical time average flux and photons-per-pulse at 14-ID and LCLS makes BioCARS a suitable for LCLS type experiments that use samples where interesting, slow dynamics occurs on time scales >100 ps. Additionally, a broadly tunable picosecond laser system was installed at BioCARS which makes the temporal width of the storage-ring electron bunch the factor that limits the overall time resolution. Each laser pump pulse is synchronized to the time of arrival of the X-ray bunch to within a 4-ps RMS jitter and can be delayed relative to the X-ray pulse over a time range from picoseconds to seconds.

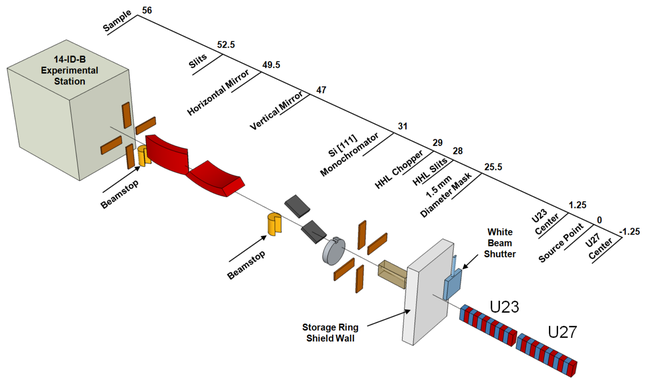


Figure 1: Layout of the upgraded 14-ID beamline. The scale indicates the distance in meters from the source point, *i.e.* between the two insertion devices. From right to left the components are: 1.5mm diameter power limiting mask (25.5 m), high-heat-load slits (28 m), high-heat-load chopper (29 m) , Si (111) monochromator (31 m), equipment safety beamstop, vertically focusing mirror (47 m), horizontally focusing mirror (49.5 m), equipment safety beamstop, pink-beam slits (52.5 m), and sample position in the 14-ID-B experimental station (56 m).

Pump Probe Technique

Figure 2 shows a schematic of a typical time-resolved, pump-probe experiment at sector 14-ID (crystallography is described however WAXS and general diffraction setups are also possible). Moving from right to left, a high-heat-load chopper reduces power on downstream components to less than 1% of the original power in the X-ray beam. This chopper typically produces a 22 µs burst of X-rays at a repetition rate of 82.3 Hz. Single pulse isolation is achieved using the fast Jülich chopper which has a minimum opening time of ~200 ns and can isolate a single pulse from the initial synchrotron pulse train at 1 kHz. Since this chopper is continuously rotating, a second shutter with a millisecond open time acts like the shutter on a photographic camera, exposing the CCD detector on demand to the X-rays scattered by the sample. The laser beam is oriented orthogonal to the X-ray beam and intersects the crystal at the center of the goniometer rotation. Two APS storage-ring modes are used for ~100 ps time-resolved experiments at BioCARS. The standard APS operating mode has 24 bunches circulating with 4.25 mA/bunch and 153.4 ns separation between bunches. The bunch length in this mode is 79 ps (FWHM). Hybrid mode has a 16 mA bunch separated from adjacent septuplets by 1.59 µs with a bunch length of 118 ps (FWHM). There are three 12-week runs per year at the APS, with hybrid mode accounting for ~17% of the total run cycle and 24-bunch mode accounting for ~60%. In both modes, periodic top-up of the individual bunches maintains the total ring current at 102 mA.

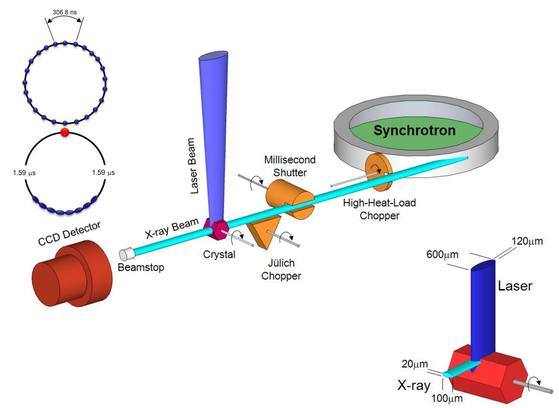


Figure 2: The laser beam is oriented orthogonal to the X-ray beam and intersects the crystal at the center of the goniometer rotation. For each crystal orientation, X-ray pulses probe a ~60-80 µm-deep layer of the crystal on the laser-illuminated side in order to match the typical laser penetration depth. A MAR165 CCD detector records the diffracted X-rays. Typical laser and X-ray beam dimensions are shown in the inset. The vertical size of the X-ray beam can be increased from the 20 mm minimum (shown) to whatever size is necessary to match the laser penetration depth.

Theoretical and Measured Beamline Parameters at 12 KeV

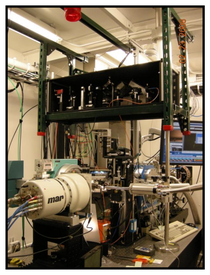
Parameter	Theoretical	Measured
White beam power U27 (K=0.92, measured at exit window)	150 W	142 W
White beam power U23 (K=1.16, measured at exit window)	329 W	329 W
Total power focused pink beam (U23+U27 measured at sample)	125 W	103 W
Number of photons in a single bunch in 24 bunch mode.	$1.0 \times 10^{10}\gamma$	$9.4 \times 10^{9}\gamma$
Number of photons in a single bunch in hybrid mode.	$3.9 \times 10^{10}\gamma$	$3.2 \times 10^{10}\gamma$
Horizontal focus size	~82.2 µm	~95 µm
Vertical focus size	~38.3 µm	~20 µm

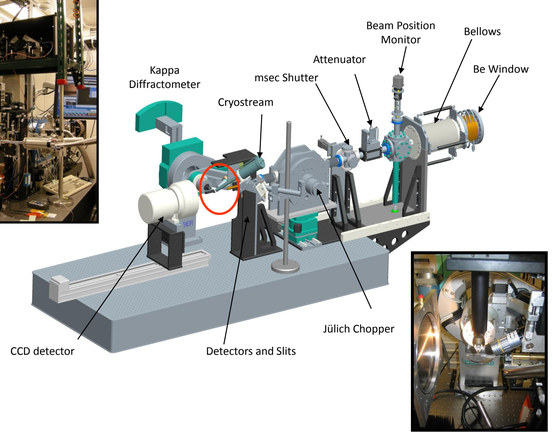
Flux comparison to the Linac Coherent Light Source (LCLS)

Source	Energy	Max Rep Rate	Photons/pulse	Integrated flux
BioCARS APS	7-17 keV	1000 Hz	3.2×10^{10}	3.2×10^{13}
LCLS	8.2 keV	120 Hz	~1×10^{12}	1.2×10^{14}
LCLS (Third harmonic)	24.6 keV	120 Hz	~1×10^{10}	1.2×10^{12}

- Time integrated Flux 25% of LCLS
- LCLS time-resolution < 80 fsec
- BioCARS ~100psec

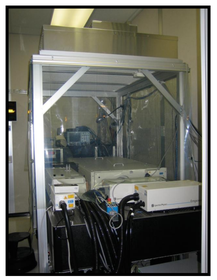
14-ID-B Station



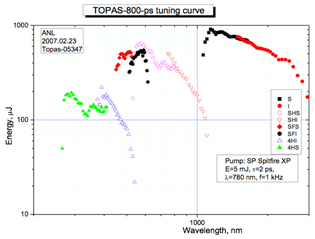


Tunable Laser Systems

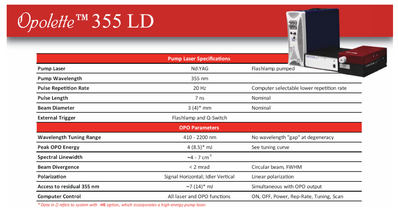
Picosecond Laser System

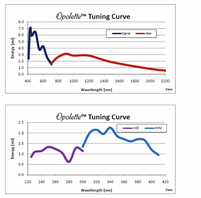


Laser	Wavelength	Pulse width	Maximum repetition rate	Energy/power
Millennia	532 nm	CW	CW	5 W
Tsunami	780 nm	100 fs	70 MHz	850 mW
Empower	527 nm	300 ns	1 kHz	15 mJ
Spitfire Pro	780 nm	1.2 ps	1 kHz	5 mJ
TOPAS	450–2000 nm	1.2 ps	1 kHz	>150 µJ (at sample)



Nanosecond Laser System





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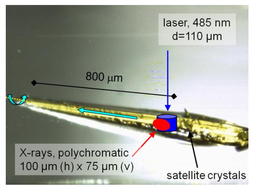
Photoactive Yellow Protein

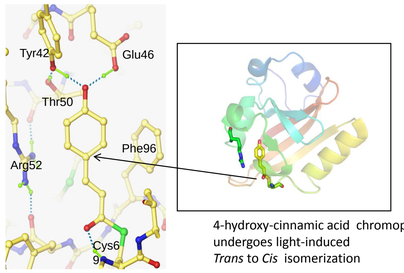
- Blue light photoreceptor from the purple eubacterium *Ectothiorhodospira halophila*
- Involved in negative phototactic response of *E. halophila* to blue light
- PYP exhibits a photocycle: several intermediates spanning time-scales from <ps to seconds



5-Dimensional Crystallography

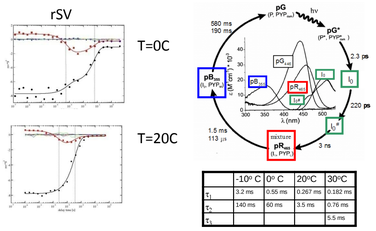
Marius Schmidt
University of Wisconsin-Milwaukee

Space, Time and Temperature
Unique Mechanism and Energetics

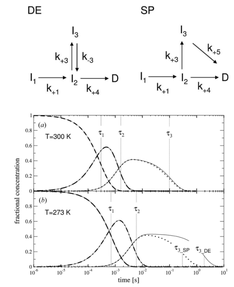


4-hydroxy-cinnamic acid chromophore undergoes light-induced *Trans* to *Cis* isomerization

Photoactive Yellow Protein photocycle as a function of time and temperature



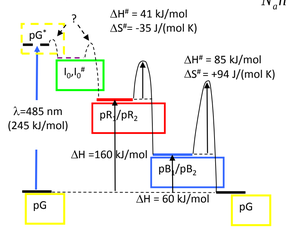
	-10° C	0° C	20°C	30°C
τ_1	3.2 ms	0.55 ms	0.267 ms	0.182 ms
τ_2	140 ms	60 ms	3.5 ms	0.76 ms
τ_3				5.5 ms



Example – temperature studies can help to distinguish between two mechanisms

Arrhenius equation & transition state theory

$$k_i(T) = 1/\tau_i(T) = Ae^{-\frac{Ea}{RT}} = \frac{RT}{N_a h} e^{\frac{\Delta S_i^{\#}}{R}} e^{-\frac{\Delta H_i^{\#}}{RT}}$$



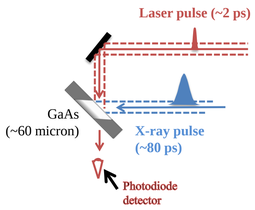
ΔH from Takeshita et al., Biochem. 2002

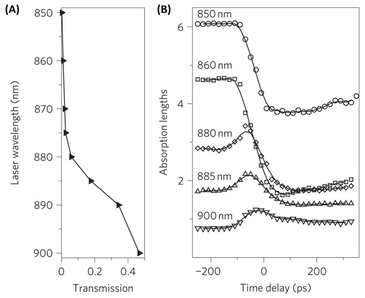
M. Schmidt, T. Graber, R. Henning and V. Srajer, Five Dimensional Crystallography, *Acta Cryst.* A**66**, 198-206, 2010.

Picosecond X-ray Pump Laser Probe: Induced Transparency in GaAs

Steve Durbin, Purdue University

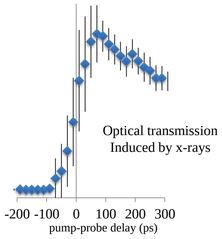
In these experiments an ~60-µm-thick GaAs specimen absorbs an intense, 80 ps full-width at half-maximum (FWHM) synchrotron X-ray pump pulse. The transmission of a monochromatic 1.6 ps (FWHM) laser probe pulse near the bandgap energy was then measured as a function of the pump–probe delay time.





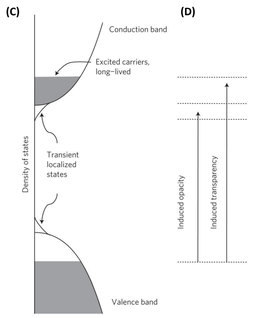
$$T \propto e^{-\mu x}$$

(A) Laser beam transmitted fraction *T* (without X-rays) versus wavelength from below-gap (900 nm) to above-gap (850 nm) values. **(B)** Exponential factor $\mu(\lambda)L$ for the GaAs specimen versus time delay for wavelengths of 850–900 nm. Note that the absorption factor profile approximates the Gaussian profile of the X-ray pulses for sub-gap wavelengths, consistent with the short-lived states induced by the X-rays (see text).



The specimen switched from optically opaque to transparent within the duration of the X-ray pulse. An 860 nm photon has just enough energy (1.44 eV) to excite a valence electron across the direct bandgap into the conduction band (~1.43 eV). The induced transparency decays with a time constant of 1.1 ns. Transparency was observed from ~880 to 840 nm, a bandwidth of ~70 meV. The 40-fold increase in transmitted signal suggests that this could be a useful X-ray/optical cross-correlator for high-intensity synchrotron and XFEL beams.

(C) Ideal semiconductor density of states, with a filled valence band separated from an empty conduction band by energy gap E_g. Photons with energy less than E_g are transmitted, and are absorbed by promoting an electron from the valence to the conduction band if the energy exceeds E_g.
(D) Intense X-ray excitation fills the states at the bottom of the conduction band, blocking absorption of photons with energies just above the bandgap energy. Induced absorption for photons with energy just below the bandgap could arise from transient localized states at the band edges, as seen with doped semiconductors.



Durbin, S. M., Clevenger, T., Graber, T., and Henning, R., X-ray pump optical probe cross-correlation study of GaAs, *Nature Photonics*, **6**,111–114, 2012.

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