Reaction Initiation in Crystals with Ultrashort Laser Pulses: What Can Go Wrong, and What Can Be Done About It

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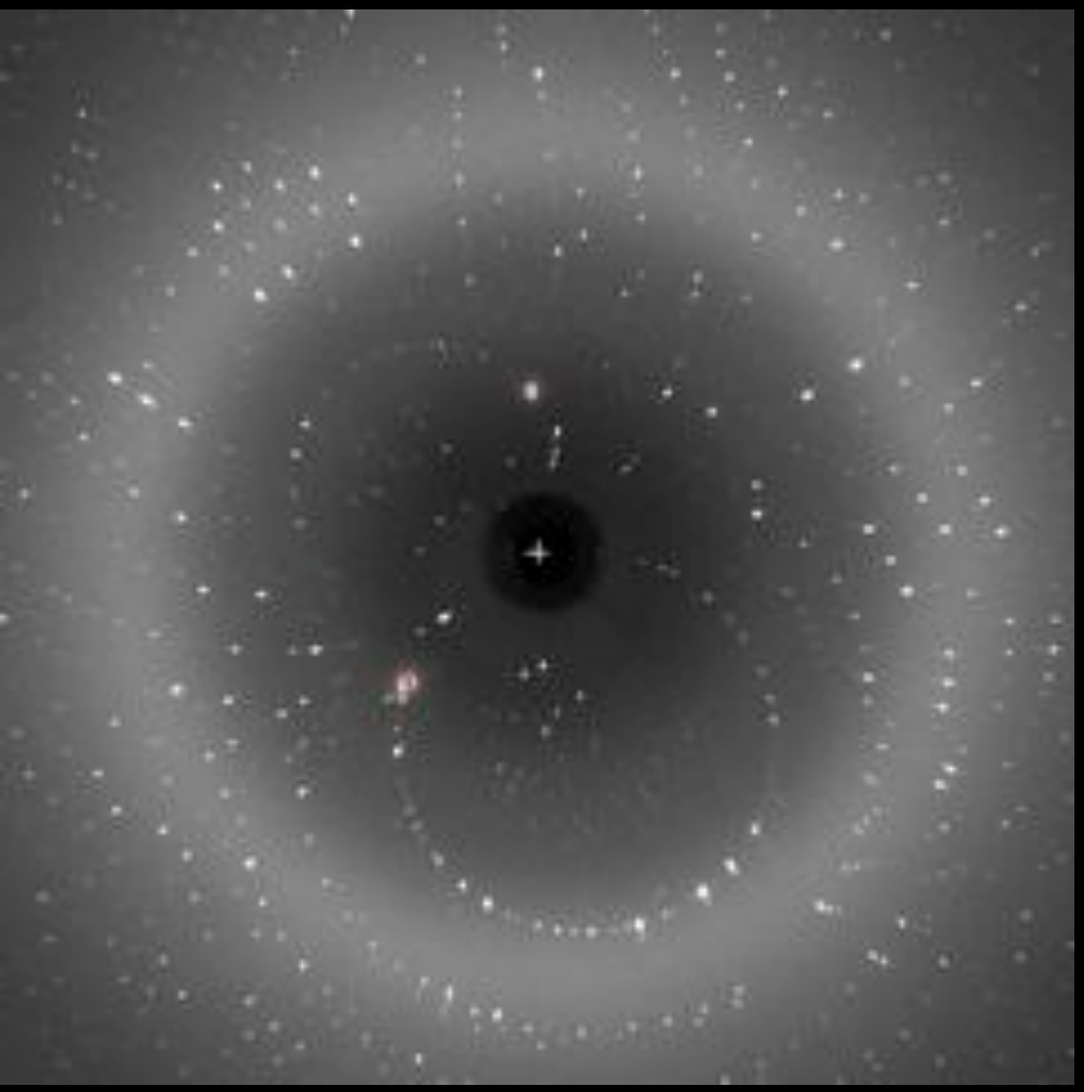
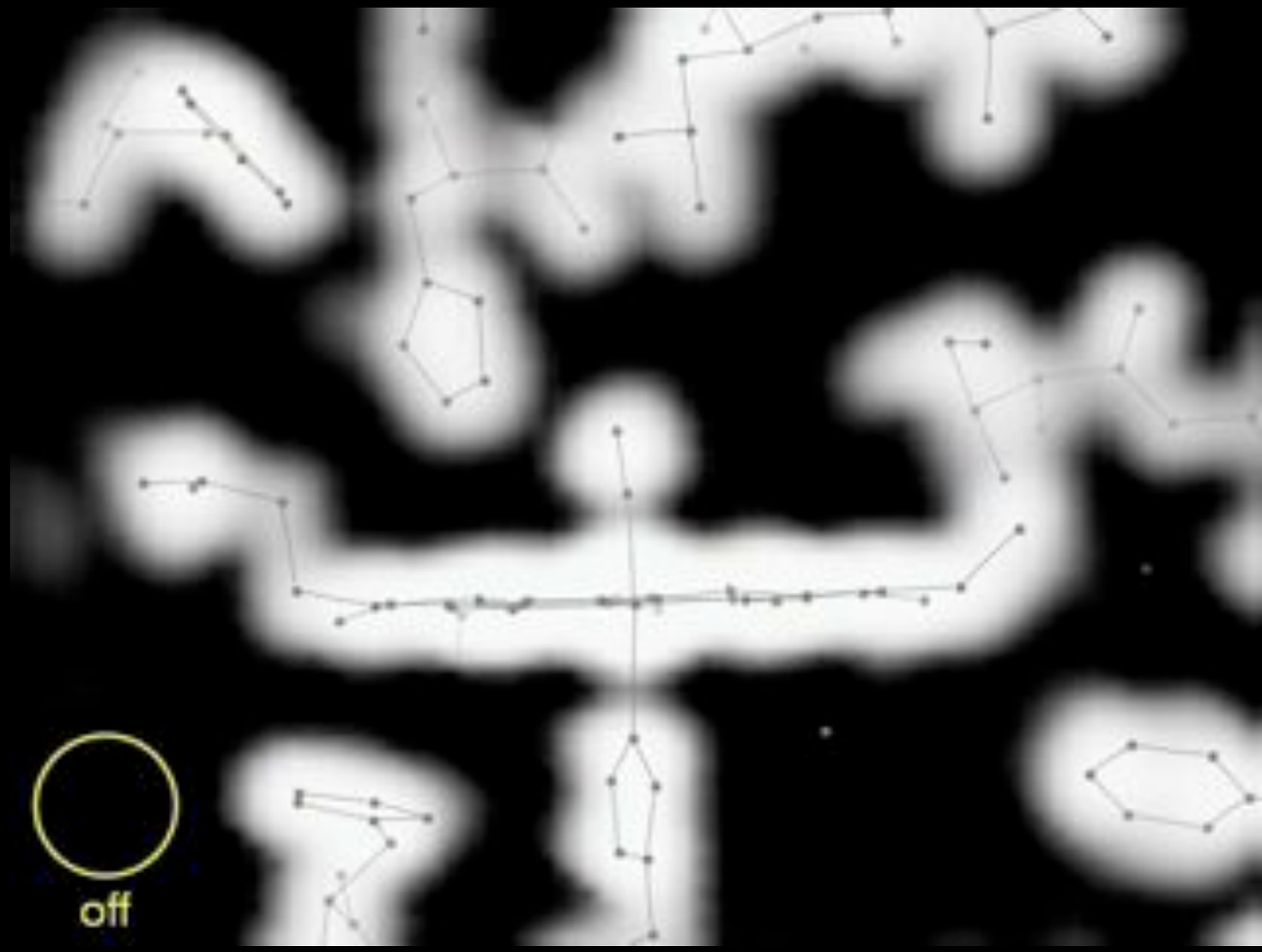
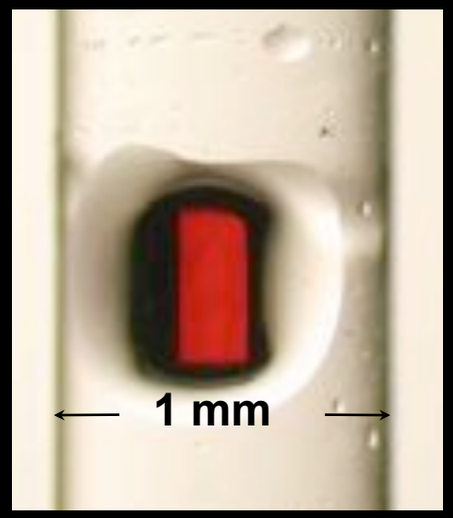
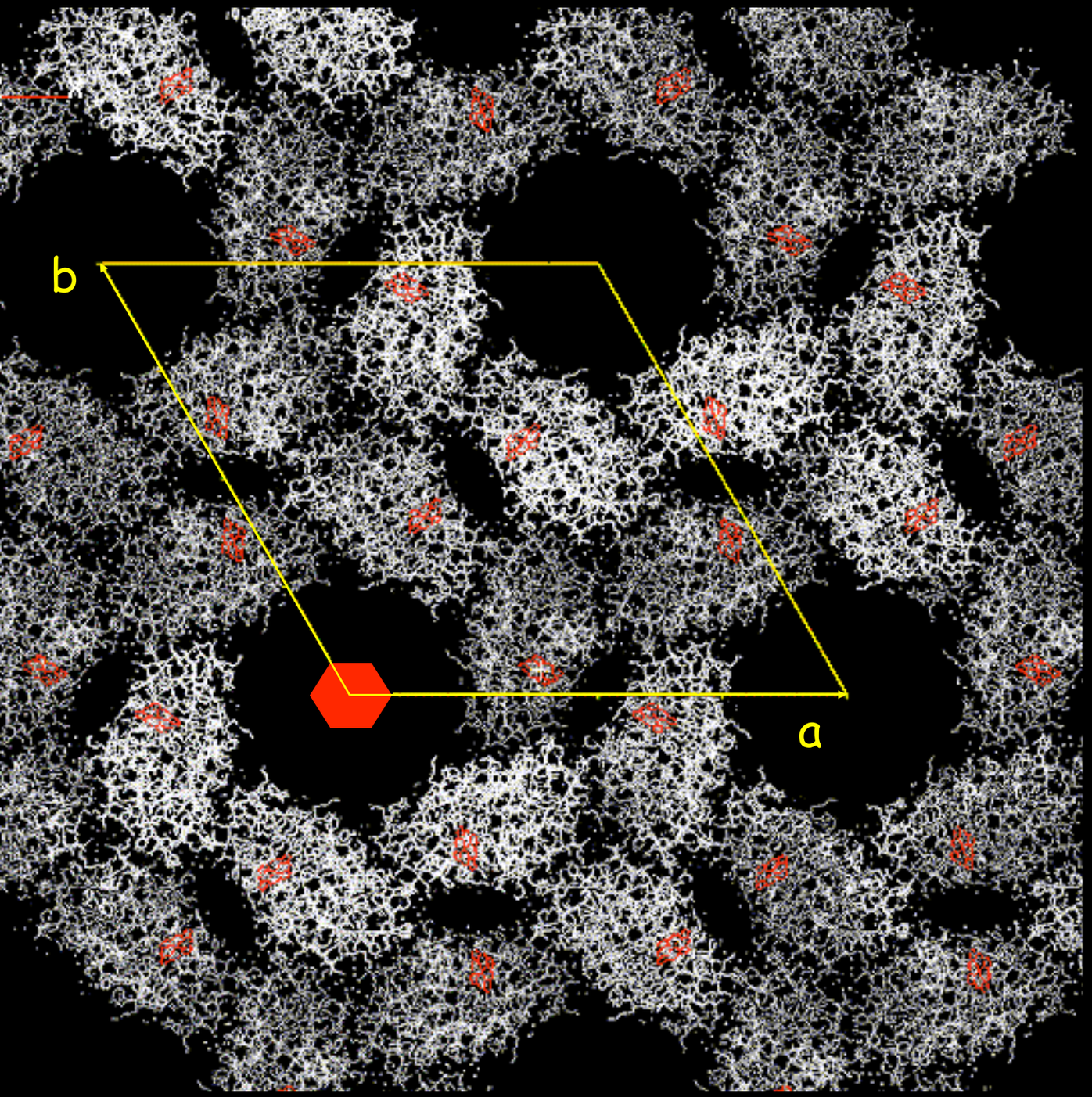
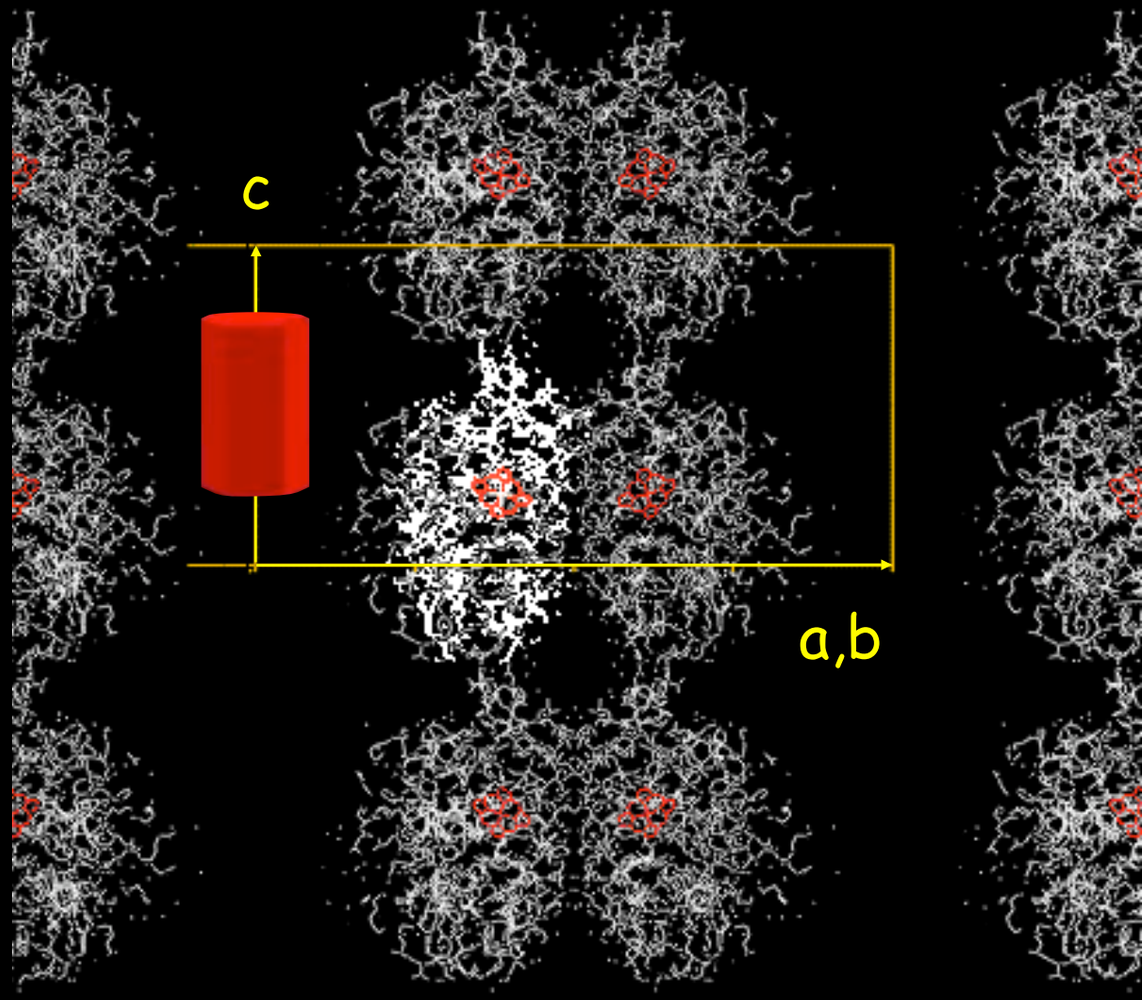




Packing of P6 Myoglobin Crystal (D122N)



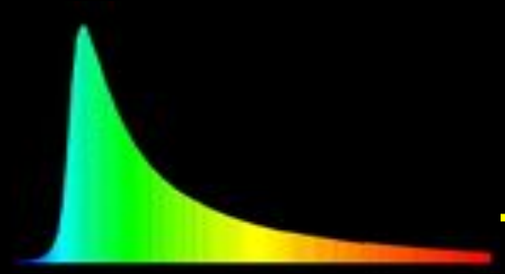




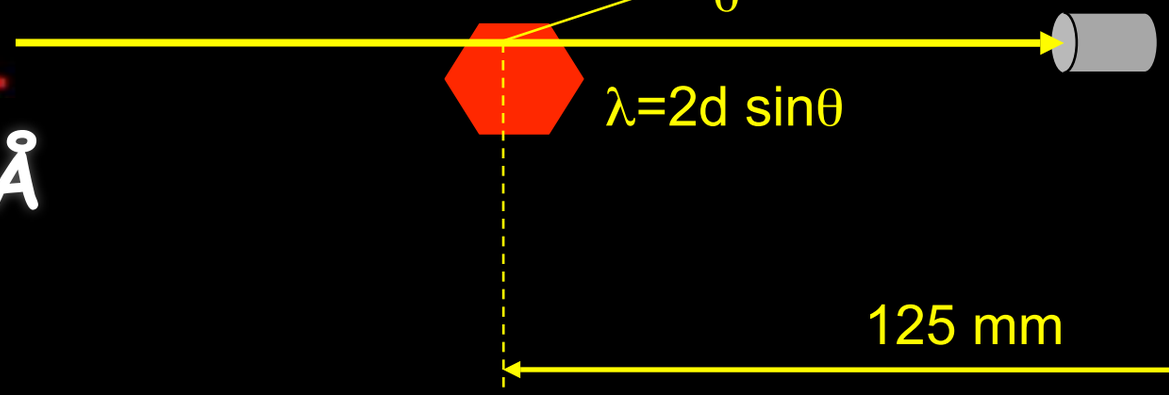
a = b = 91.20 Å, c = 45.87 Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$; heme plane to a,b plane $\angle$ = 55°

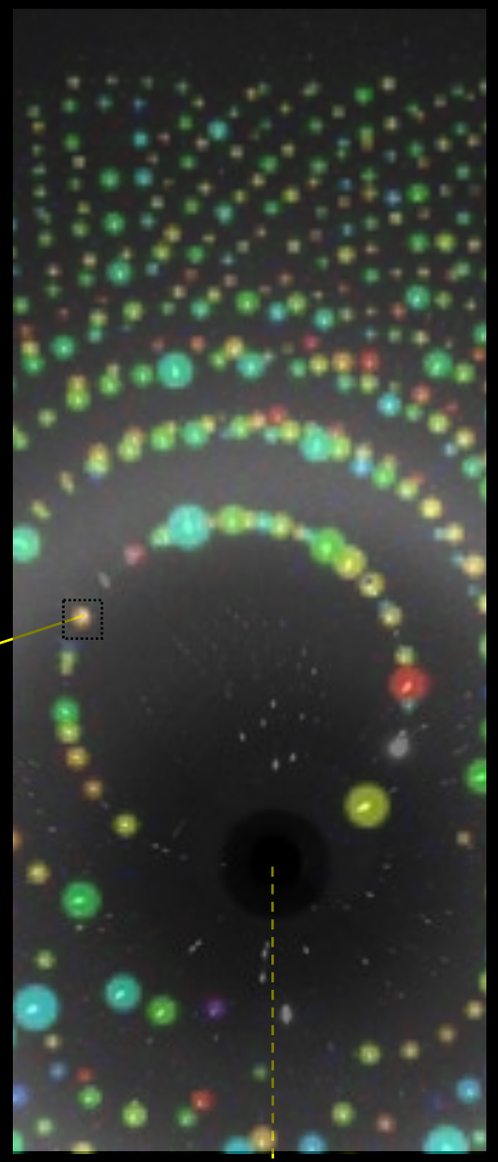
Laue Crystallography

- ~150 ps X-ray pulse
- "Pink" beam peaked at ~ 12 keV (1Å)
- ~10^{10} X-ray photons in a single bunch
- ~ 8 shots per image



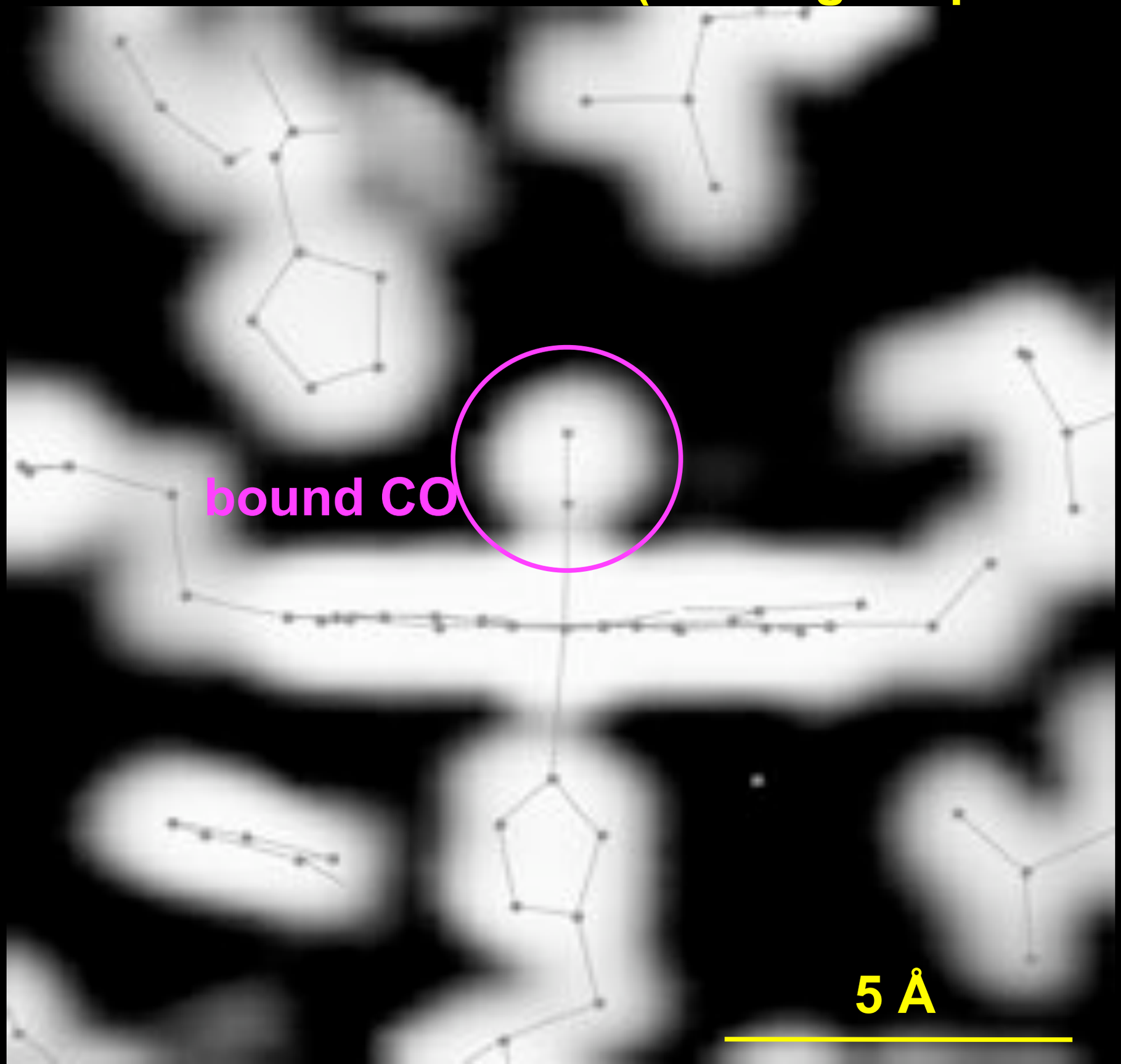
λ = 1.0...1.2 Å





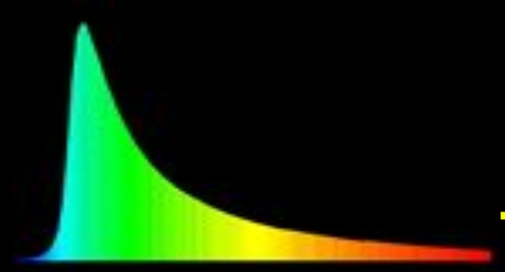
10^2
10^3
10^4
10^5
10^6

Electron Density Distribution Calculated from Measured Structure Factors (31 images spaced 2 deg.)

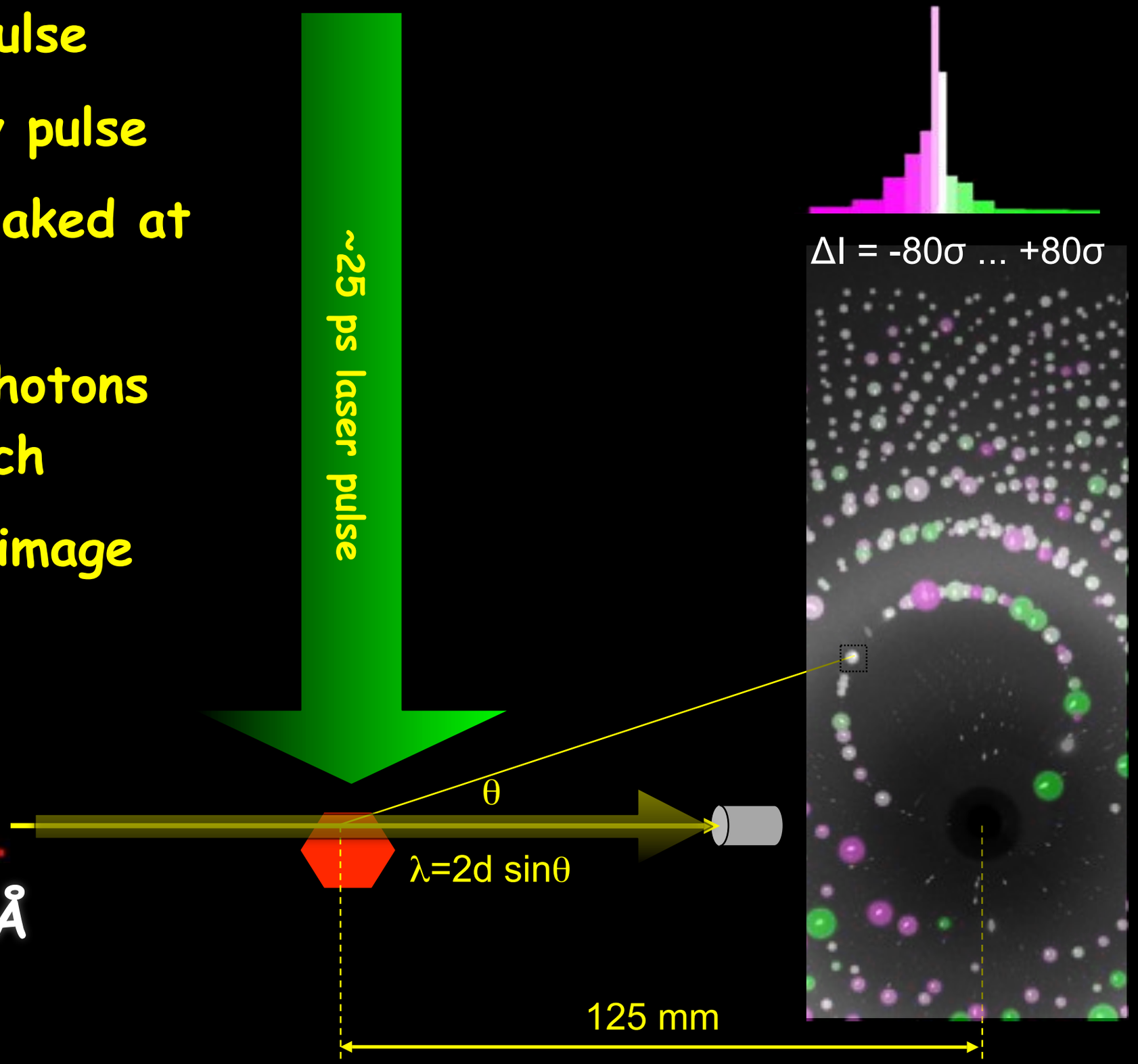


150-ps Time-Resolved Laue Crystallography

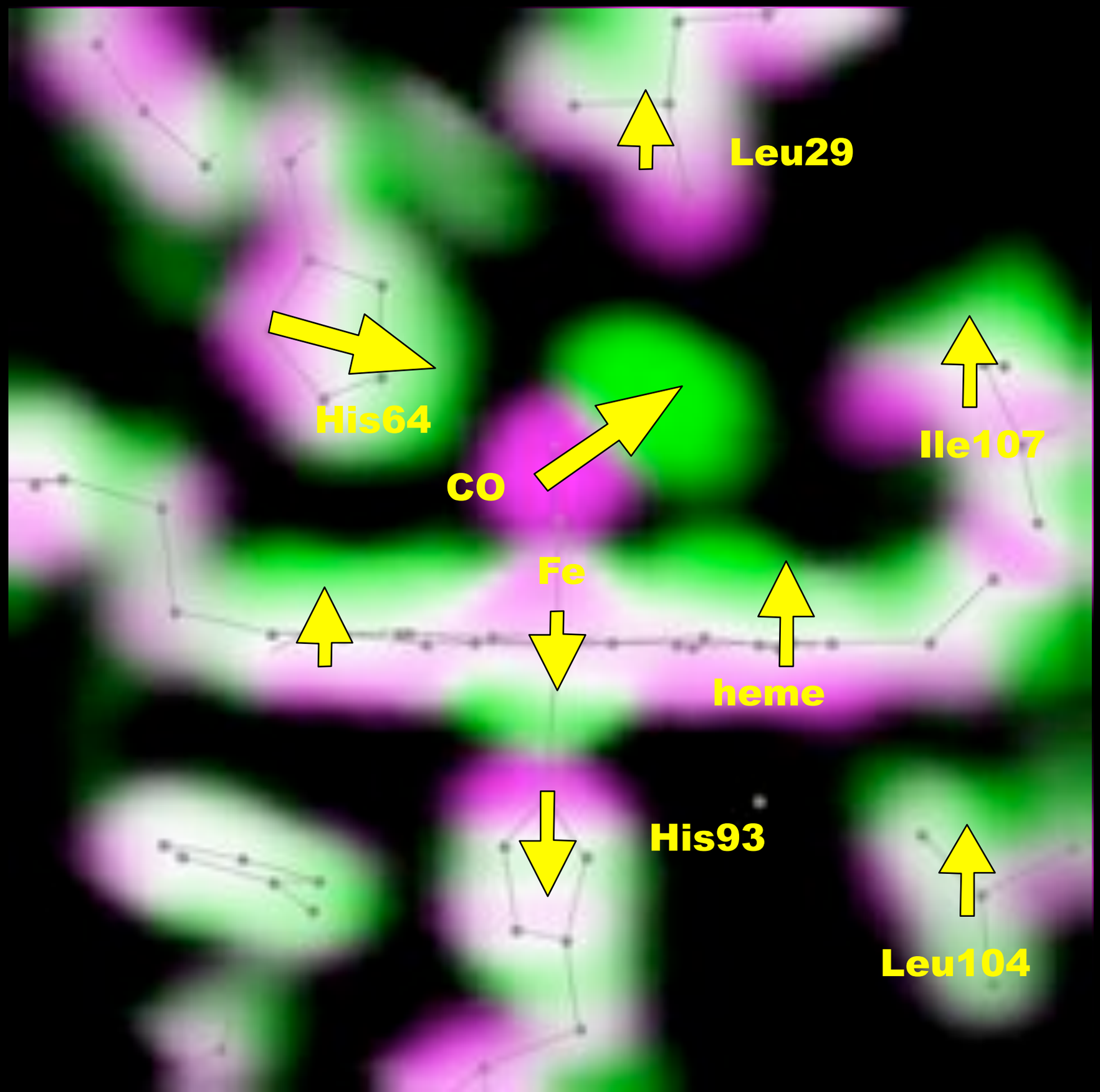
- ~25 ps laser pulse
- ~150 ps X-ray pulse
- "Pink" beam peaked at ~ 12 keV (1Å)
- ~10^{10} X-ray photons in a single bunch
- ~ 8 shots per image



λ = 1.0...1.2 Å



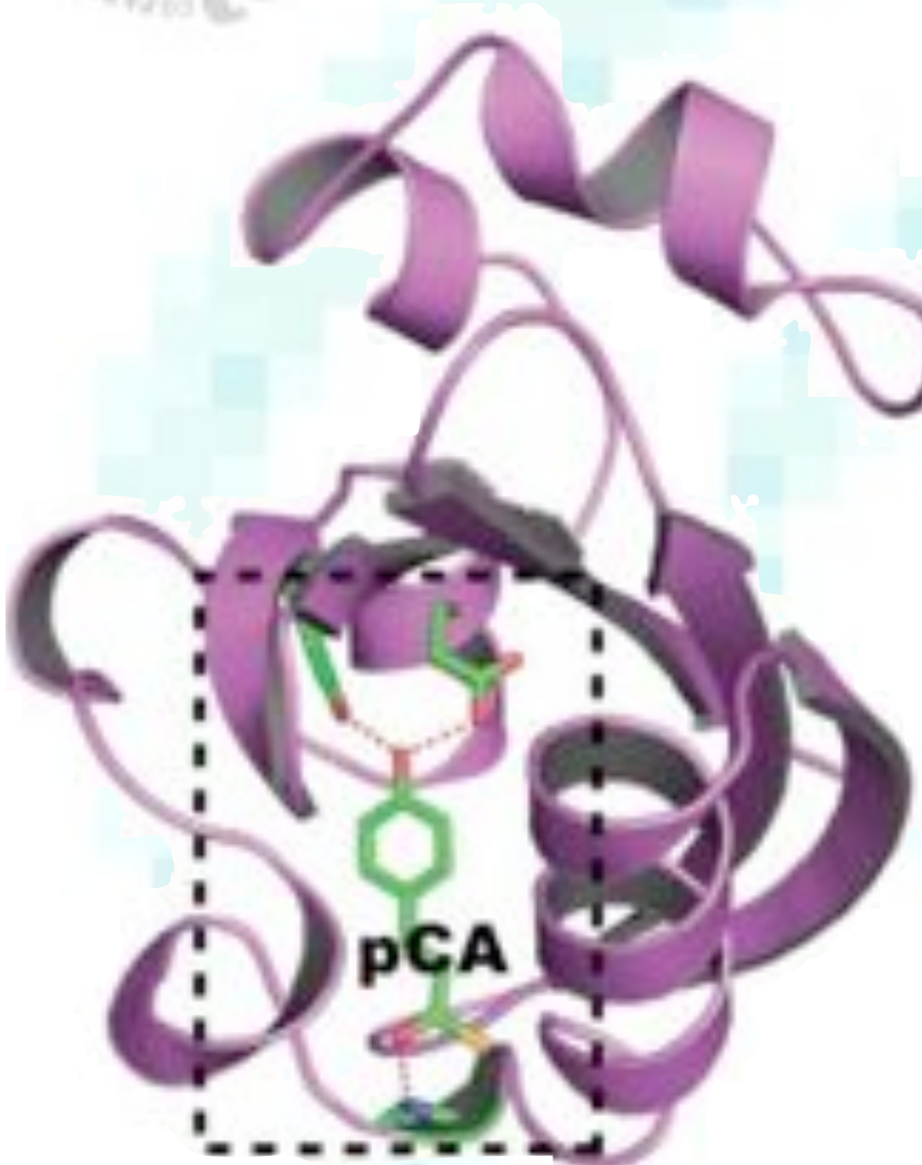
Color-coded maps superimposed: MbCO at 100 ps

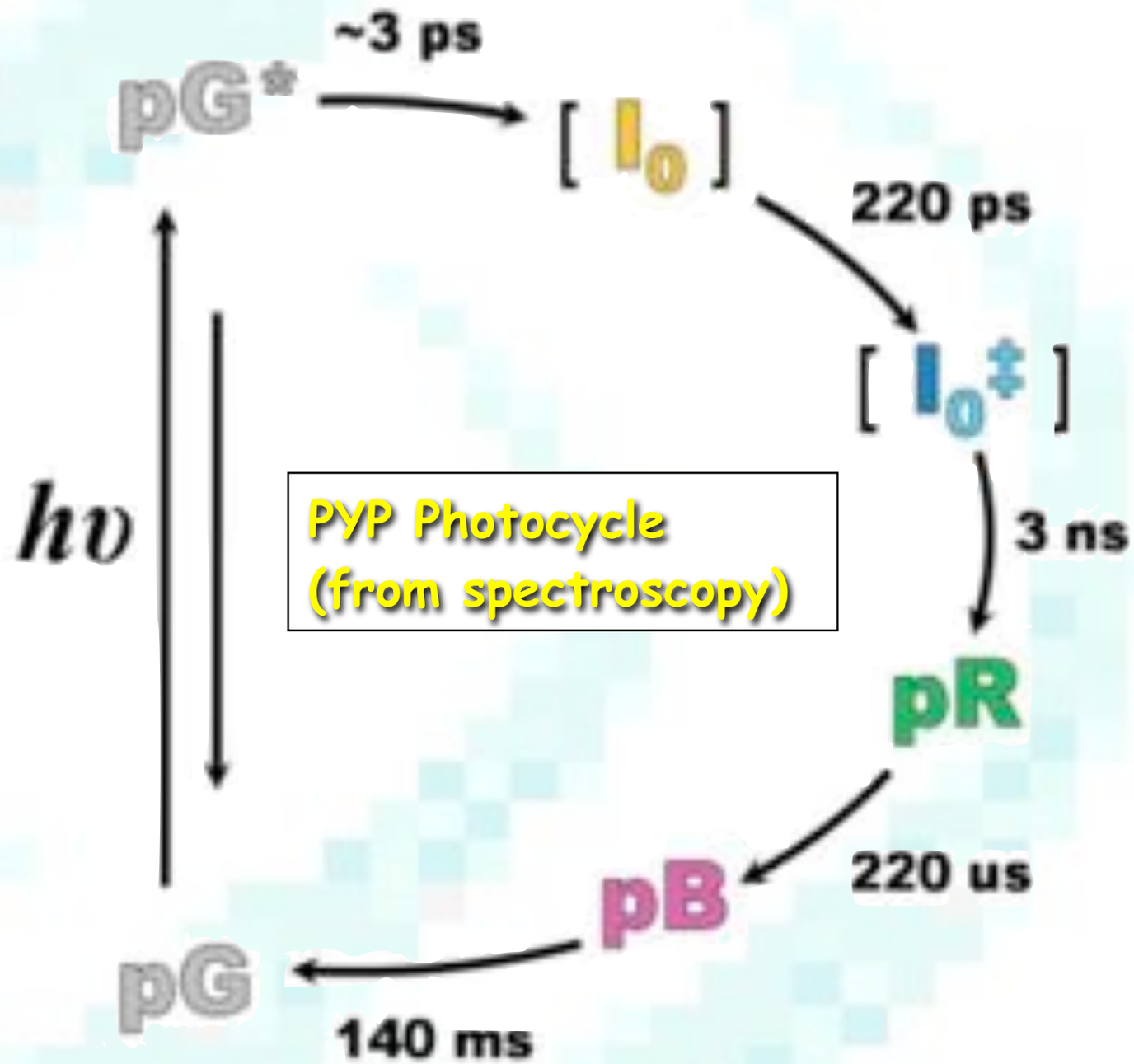


Laser Photoactivation: What are the issues?

- **Shallow laser penetration depth**
  - Orthogonal Pump-Probe geometry
- **Crystal dichroism**
  - circular polarization
- **Optimal pulse energy**
  - 1-2 mJ/mm^2
- **Excited state lifetime**
  - Stretch the laser pulses with an Echelon
- **Excited state absorption**
  - Stretch the laser pulses with an Echelon
- **Optimal focus size**
- **Pulse repetition frequency**

Photoactive Yellow Protein (PYP)

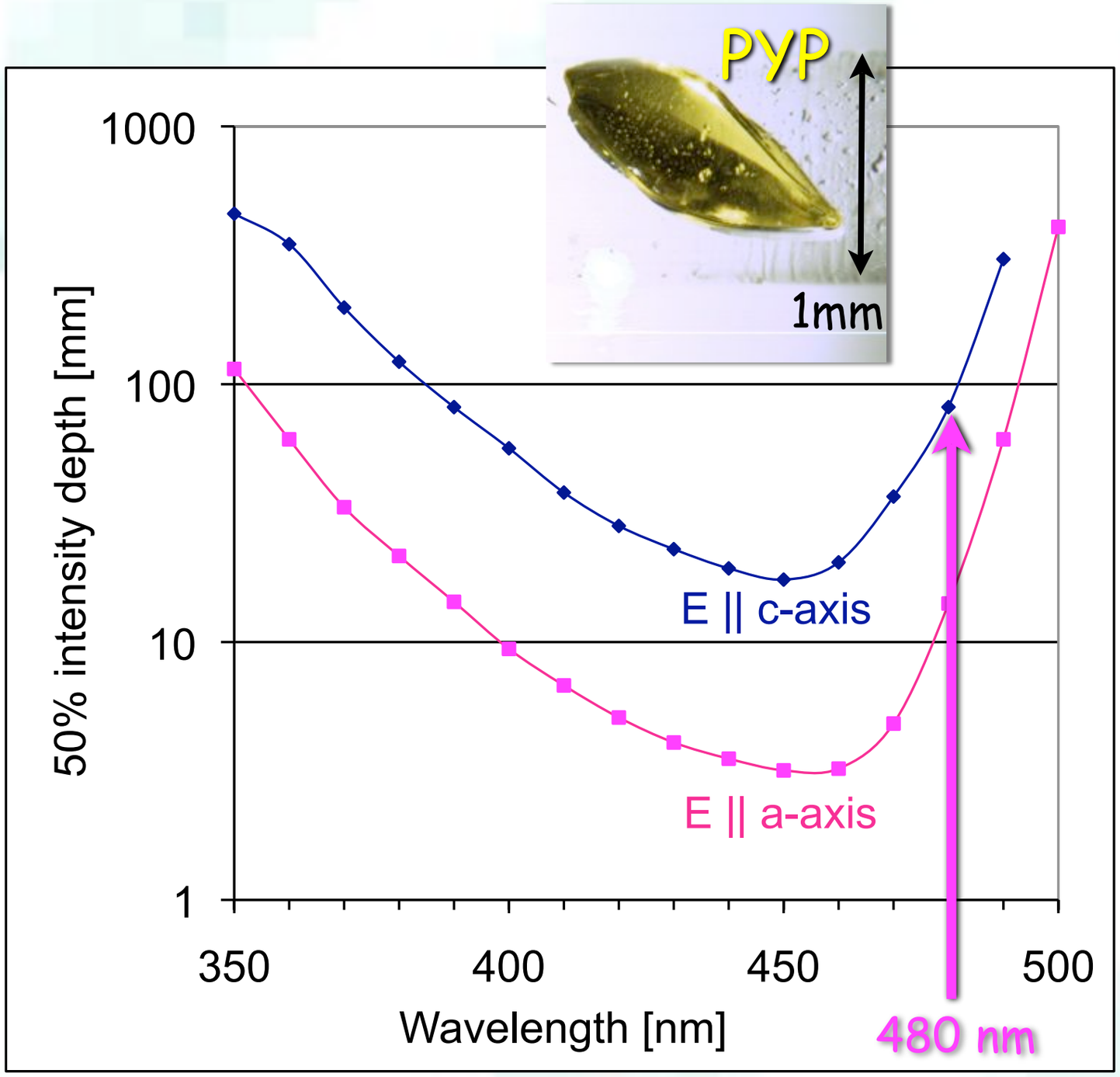




PYP Photocycle
(from spectroscopy)

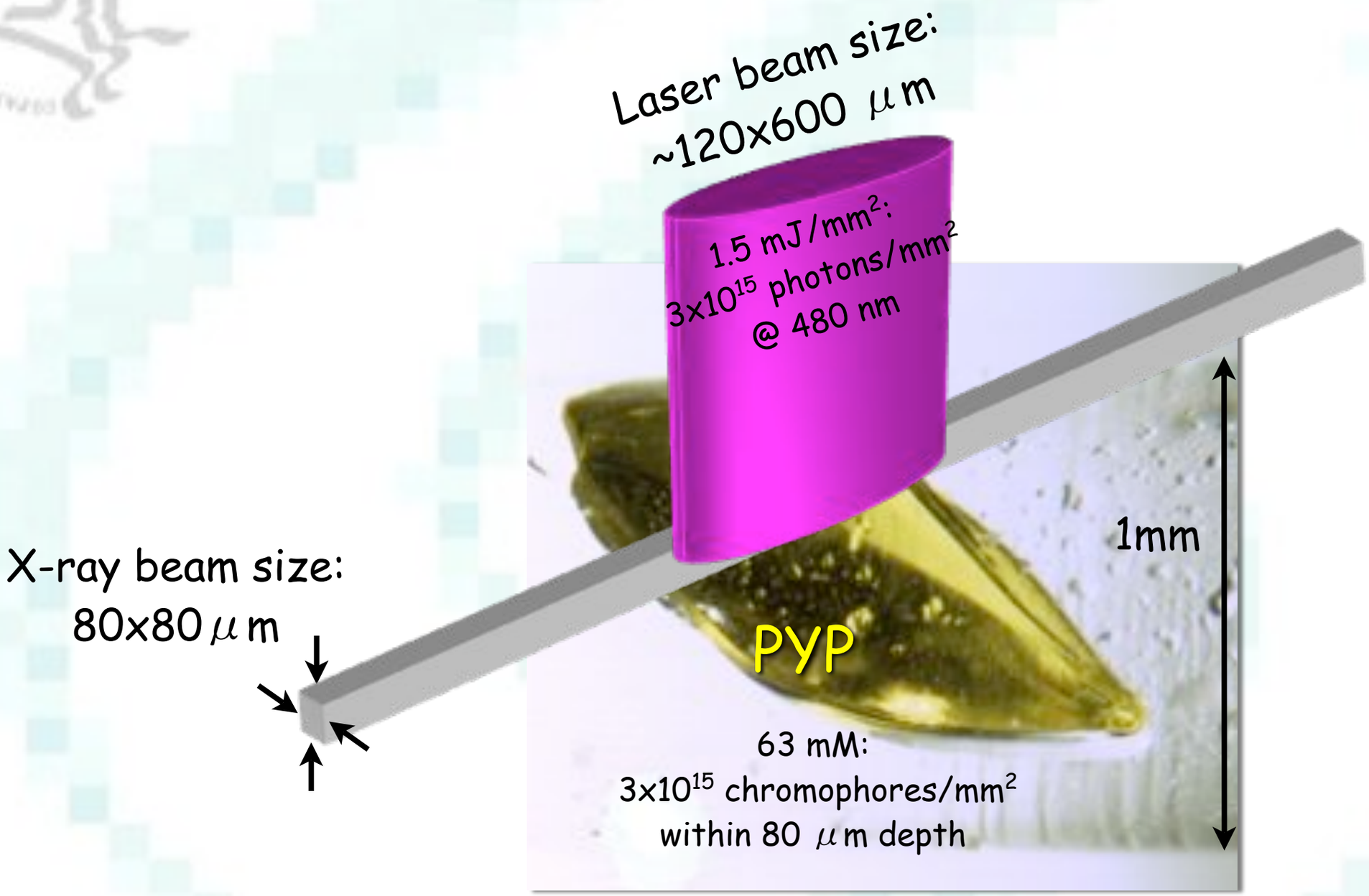
pCA (p-coumaric acid chromophore)

Laser Penetration Depth in PYP



- **PYP concentration in the crystal is high: 63 mM**
- **Protein crystal is dichroic (penetration depth depends on polarization)**
  - Excite with circularly polarized laser light

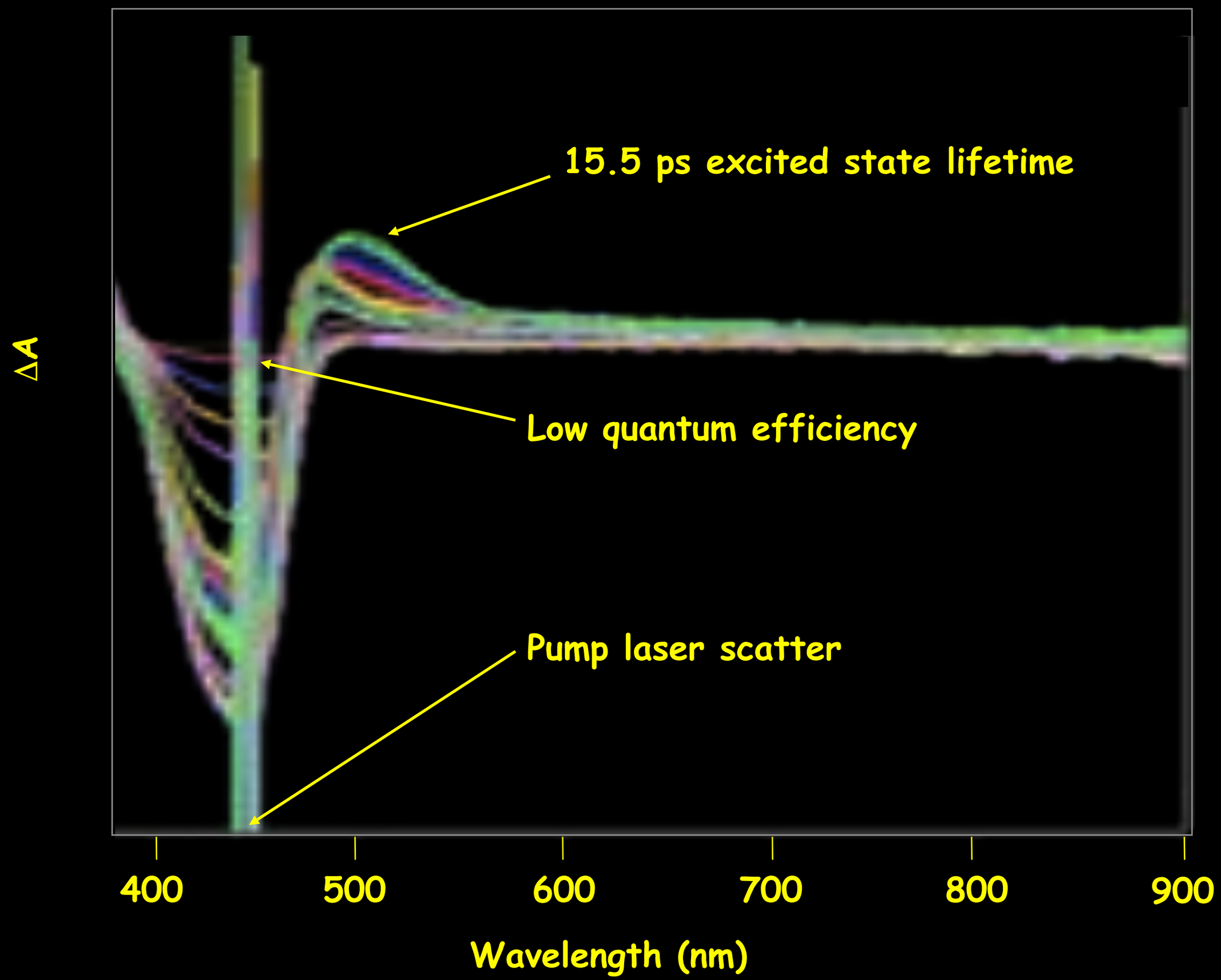
Orthogonal Pump-Probe geometry



Choose excitation wavelength for which laser penetration depth matches vertical size of x-ray beam

Orthogonal geometry minimizes total energy deposited into crystal

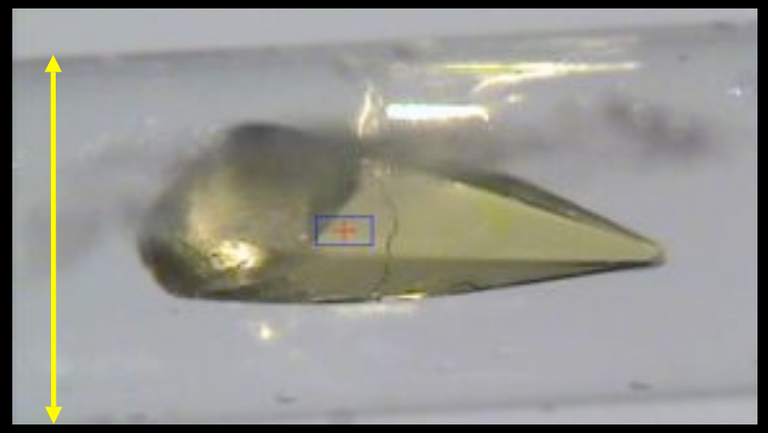
Femtosecond time-resolved absorbance of Photoactive Yellow Protein (PYP) in a crystal



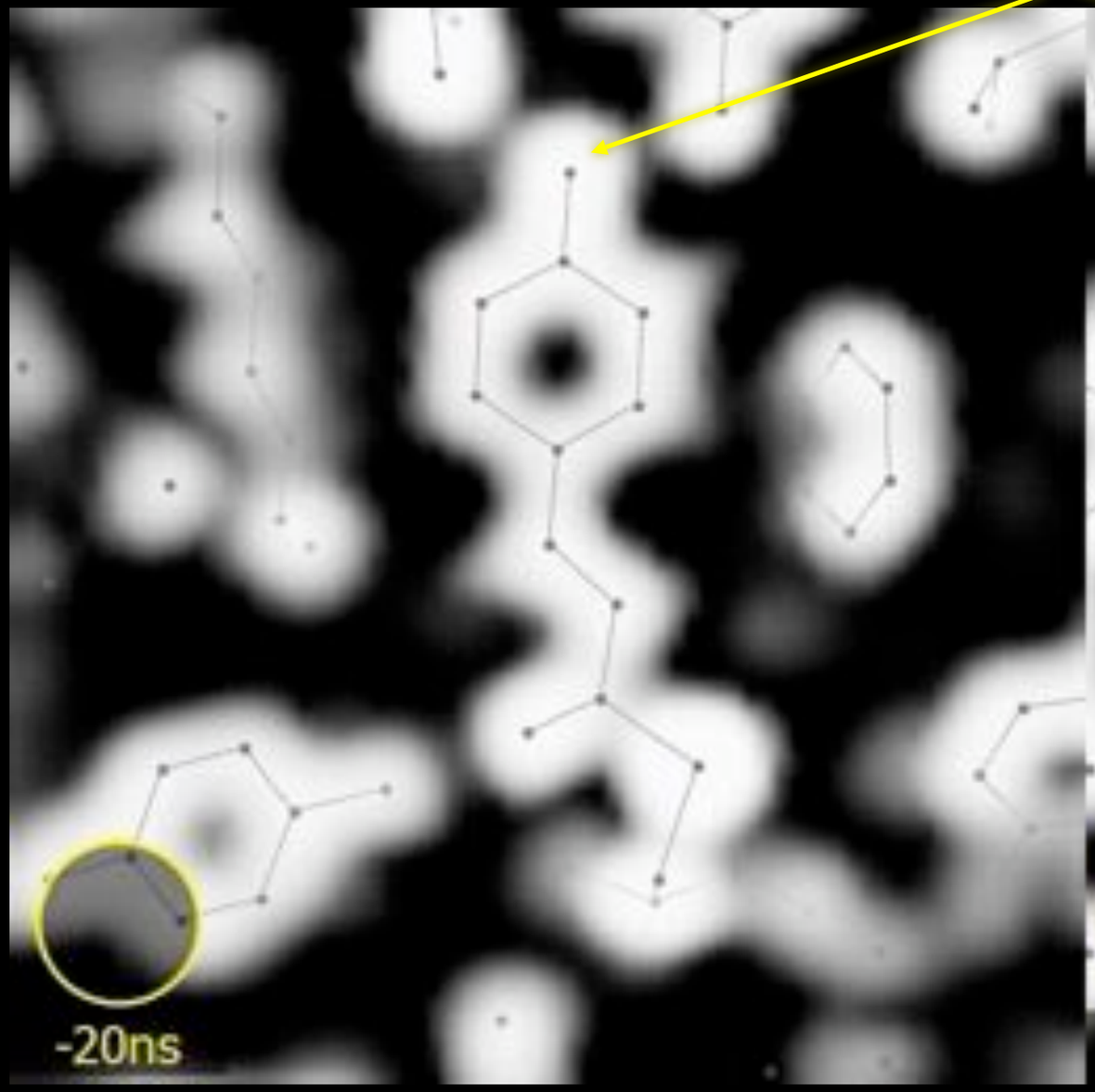
Photoactive Yellow Protein (PYP + PYP)*

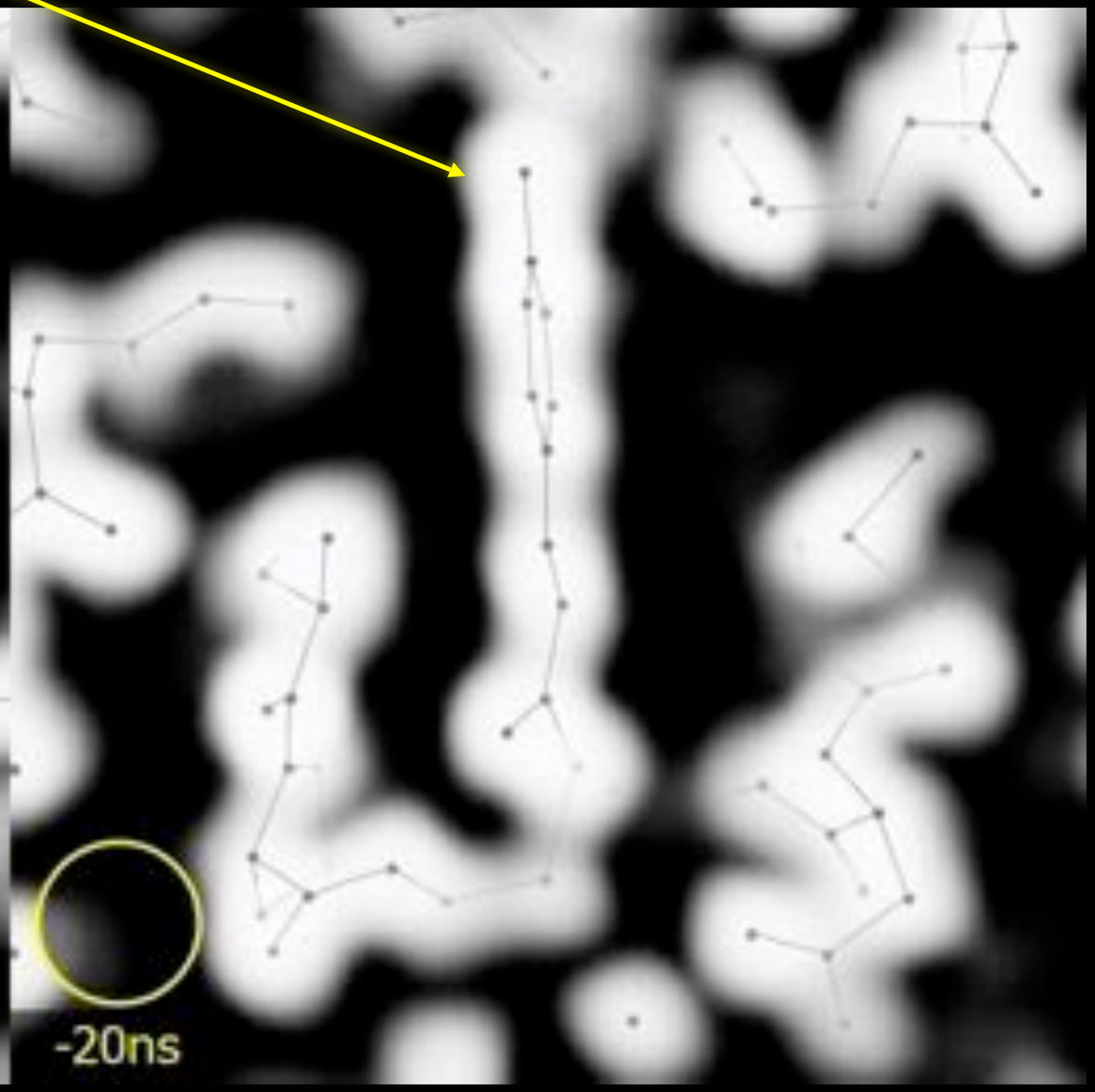
Prof. Hyotcherl Ihee
KAIST

1 mm



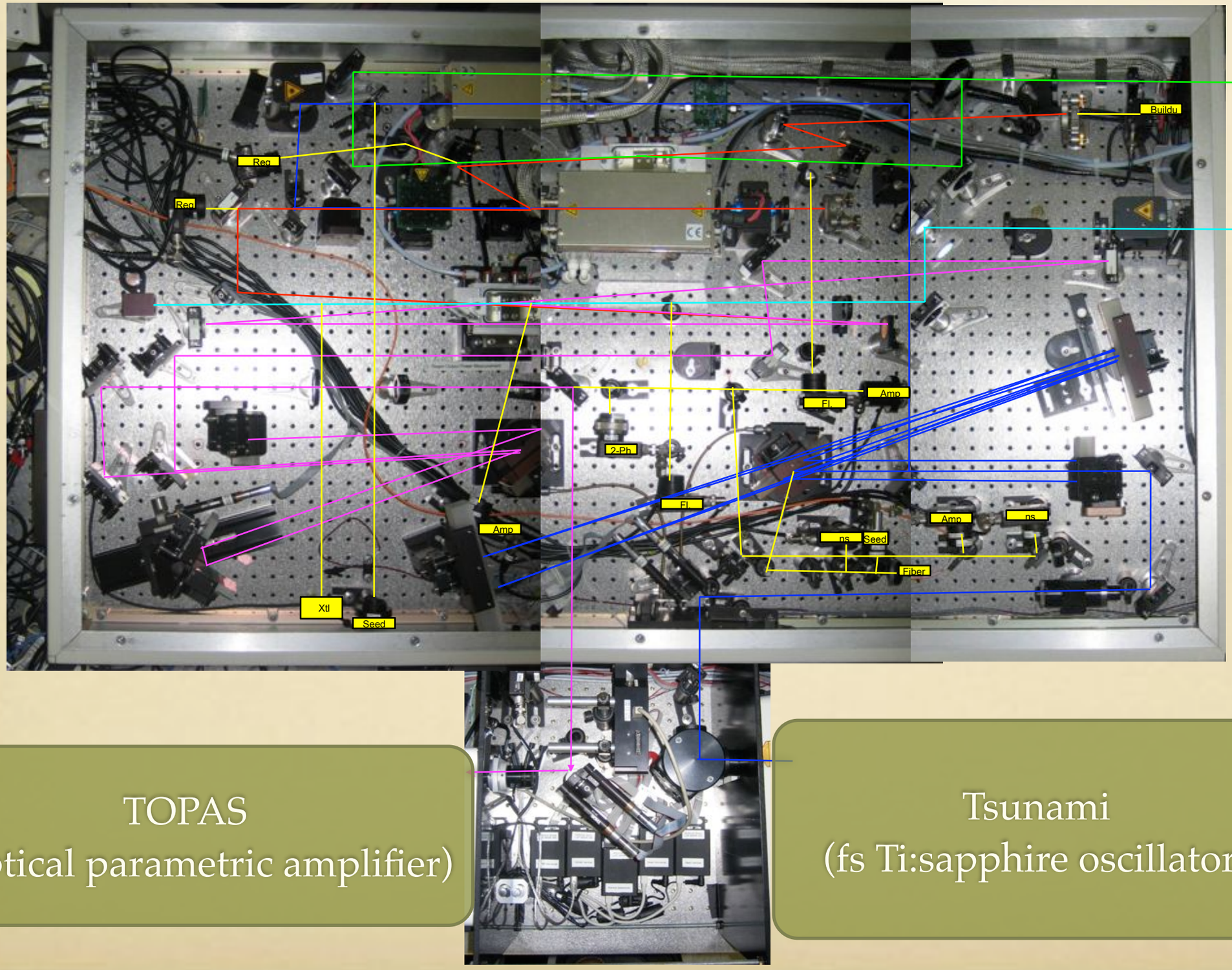
p-coumaric acid chromophore (pCA)





High-Power Picosecond Laser System

Extensively customized (integrated motorized controls; cameras; photodiodes; spectrometers; bandwidth control)



Empower Pump laser

Empower Pump laser

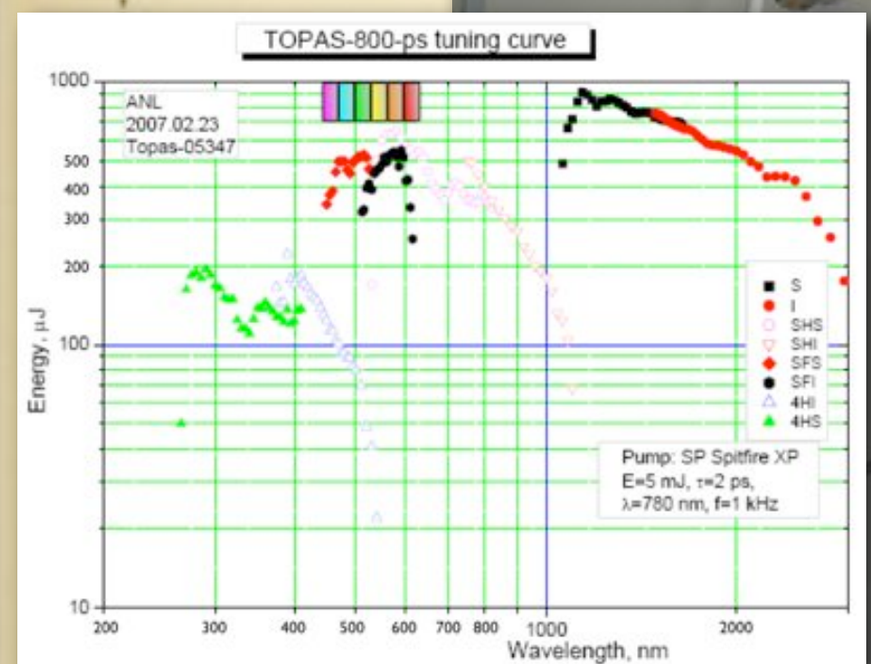
TOPAS (optical parametric amplifier)

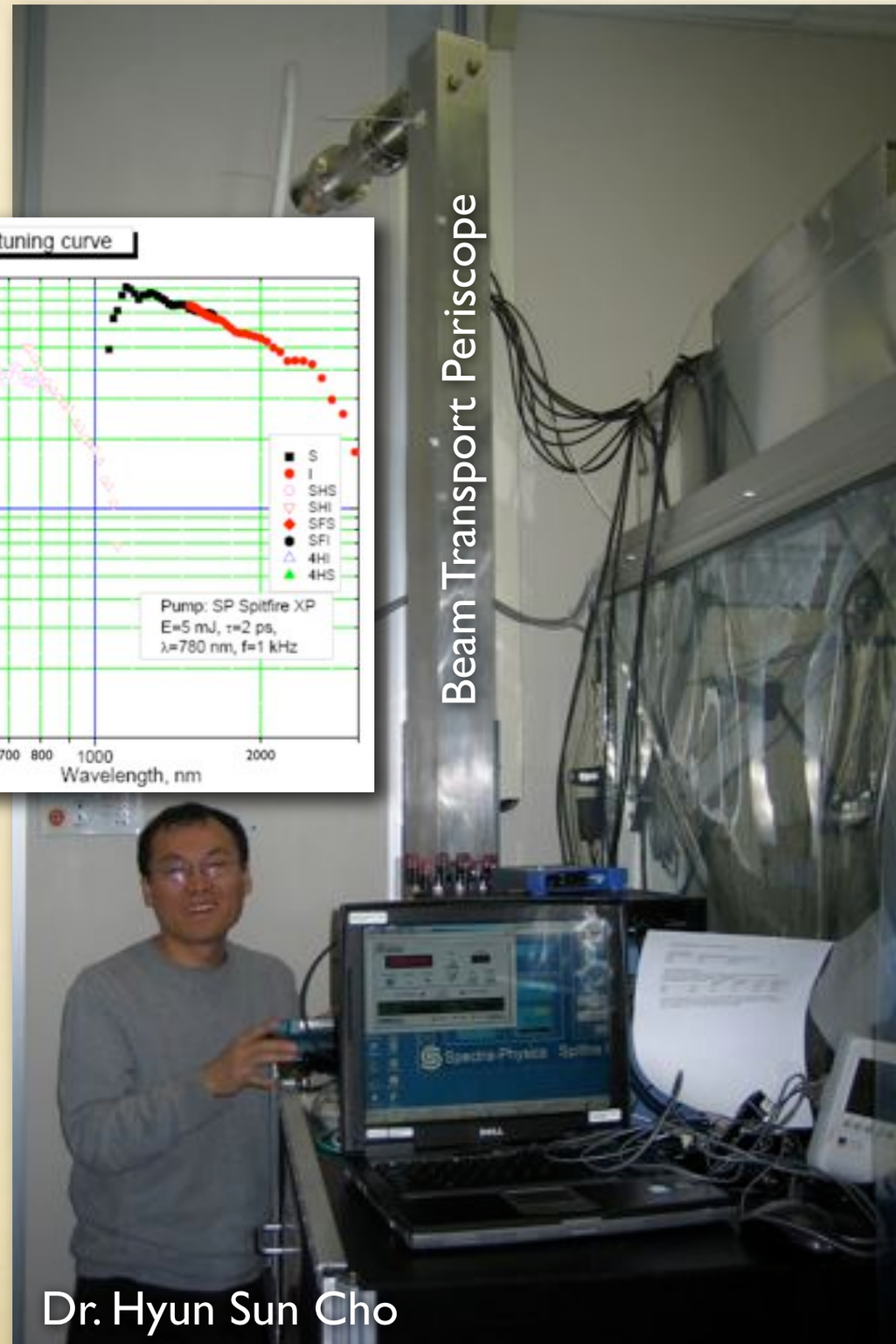
Tsunami (fs Ti:sapphire oscillator)

Millenia Pump laser

Laser Hutch

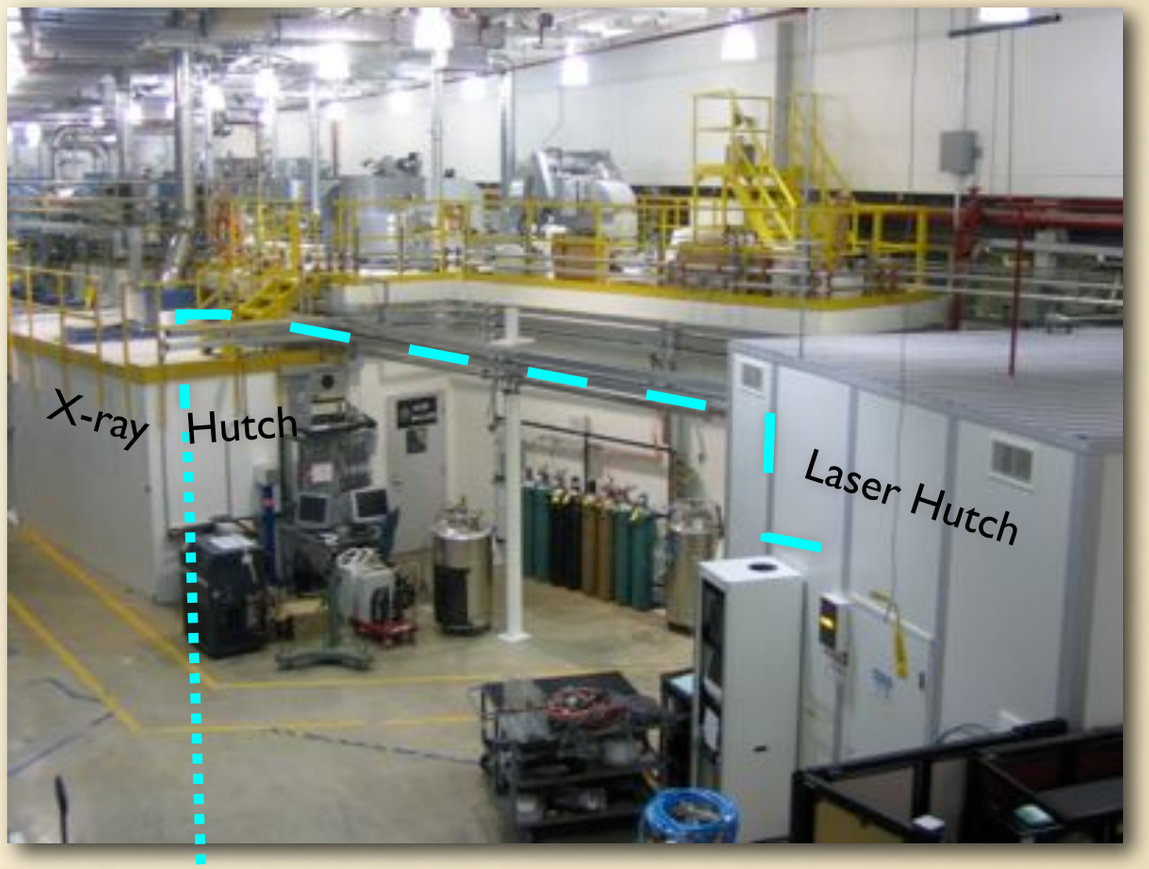
Computer-controlled generation of broadly-tunable pulses

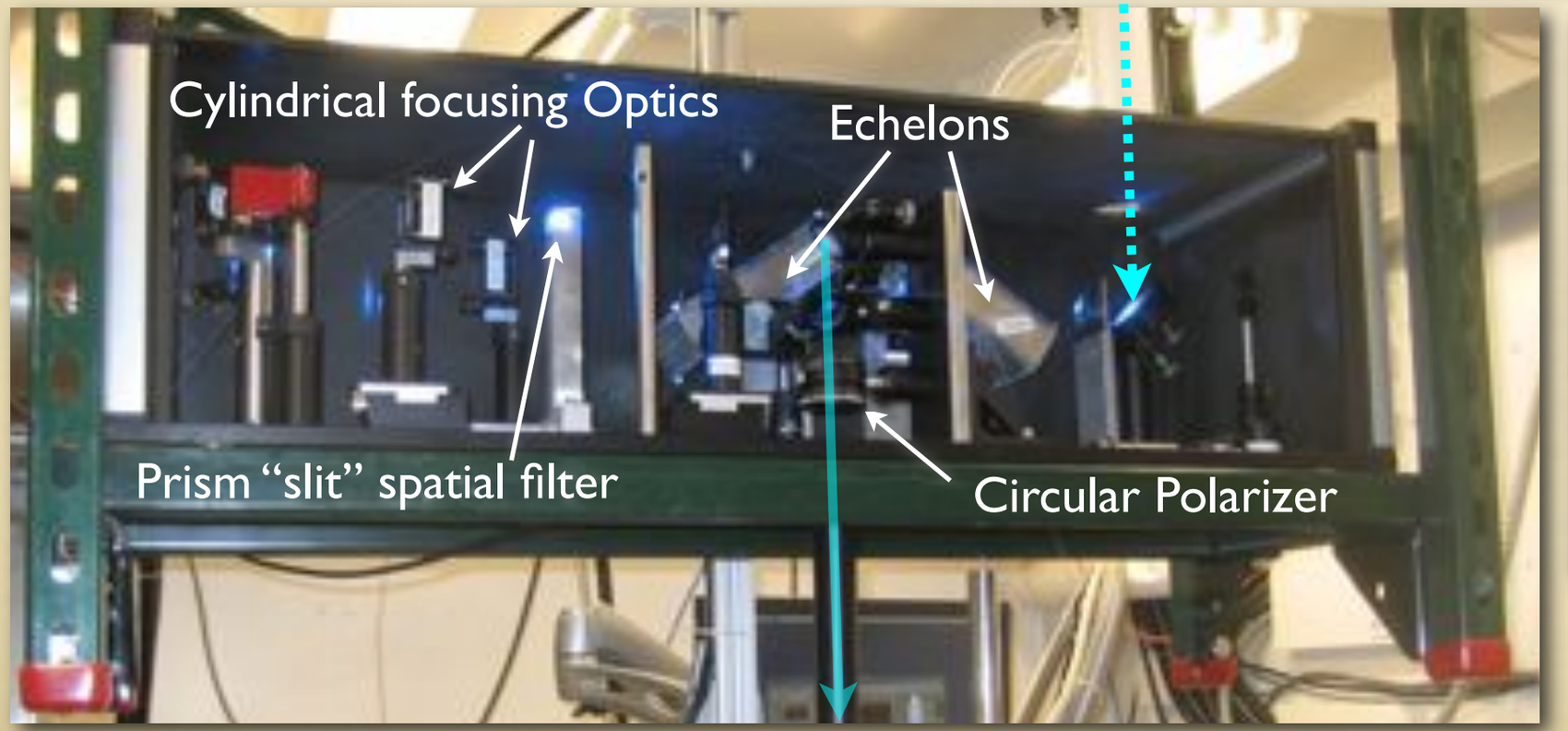




Laser Transport and Beam Conditioning

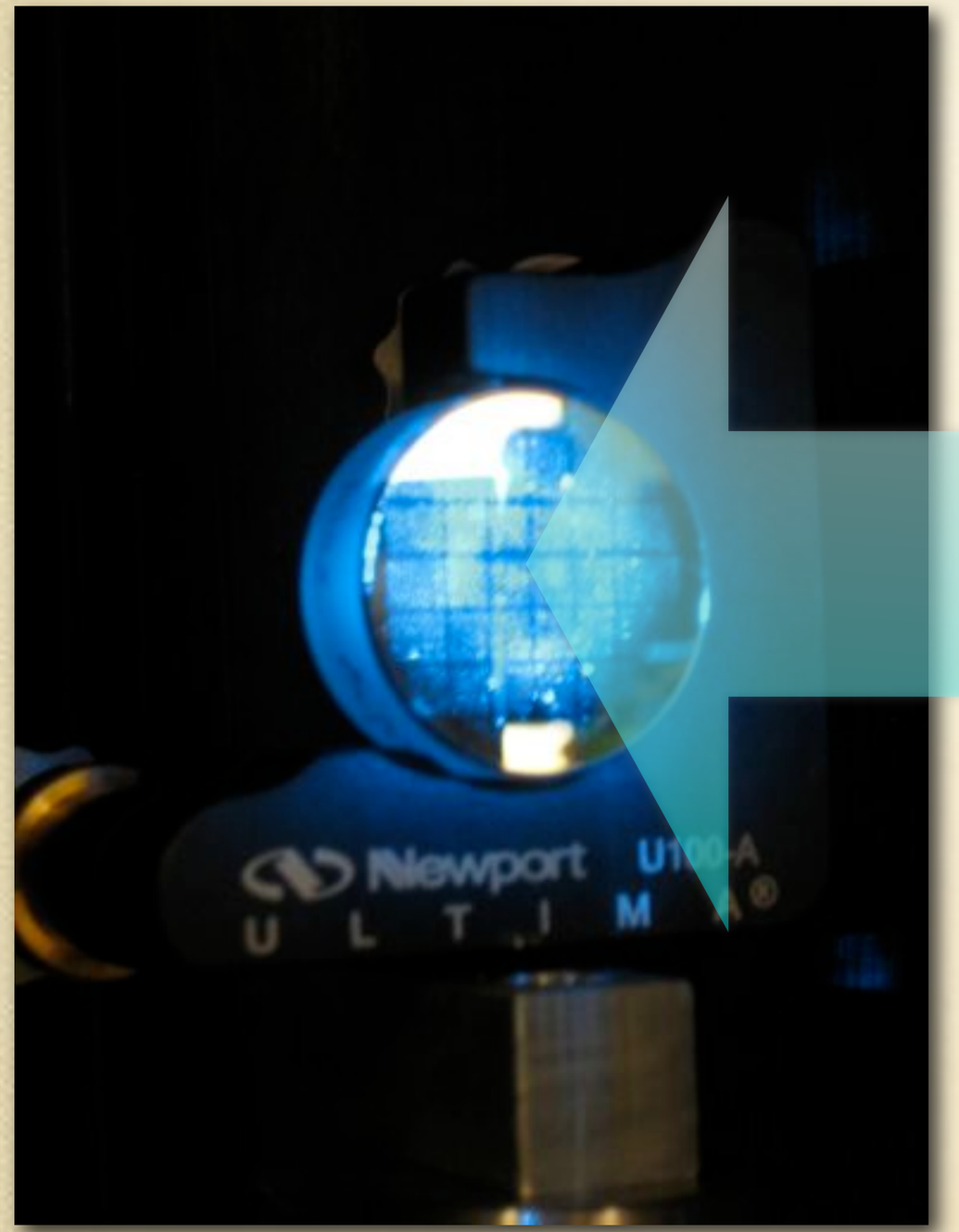
- matched echelon pair stretches pulses to ~50 ps
- cylindrical focusing to generate 5:1 elliptical spot
- High-energy 4-prism "slit" spatial filter to clean up spatial profile
- Tilt-tunable waveplate set to generate circular polarization

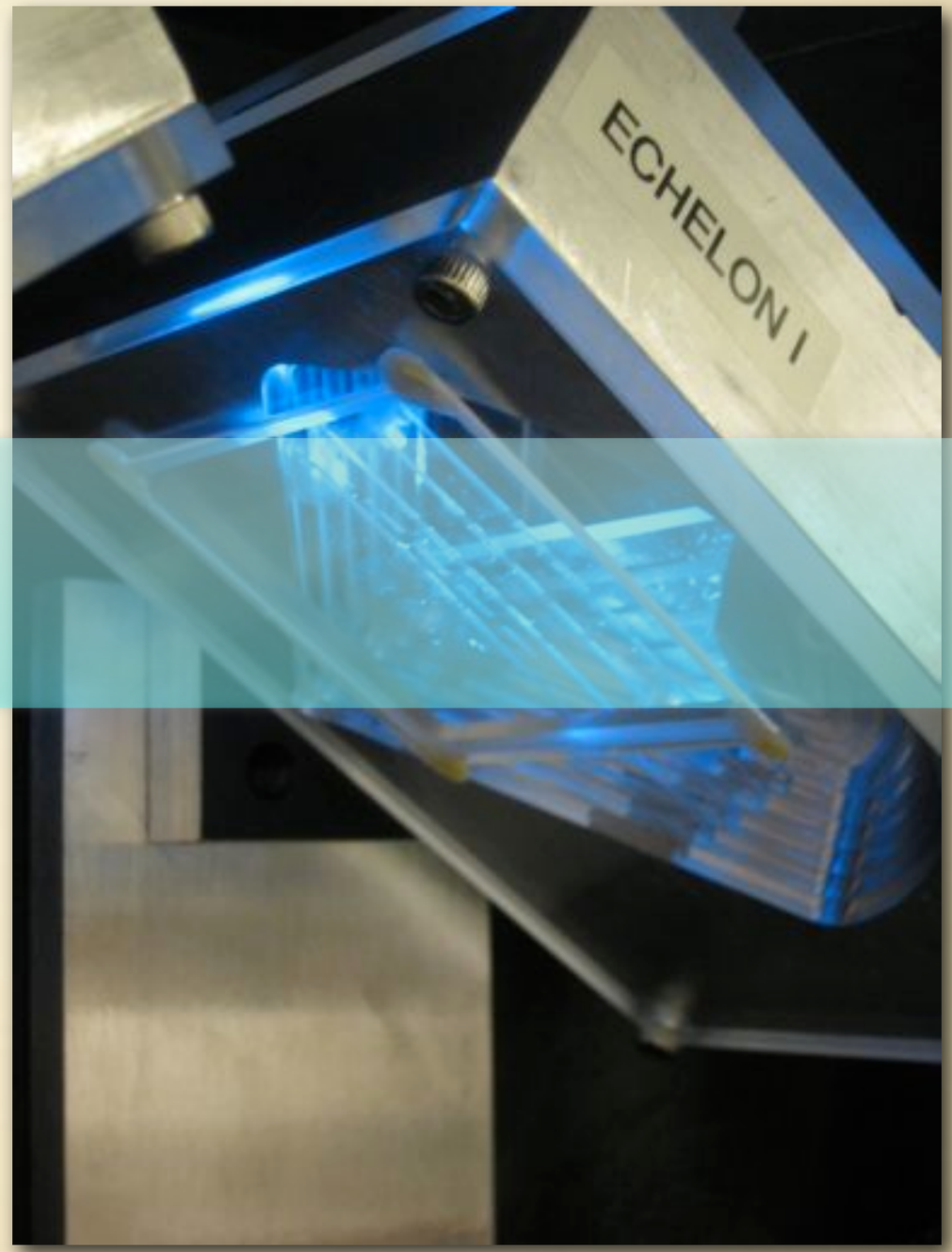




Dr. "Nara" Dashdorj

Echelon Pulse Stretcher

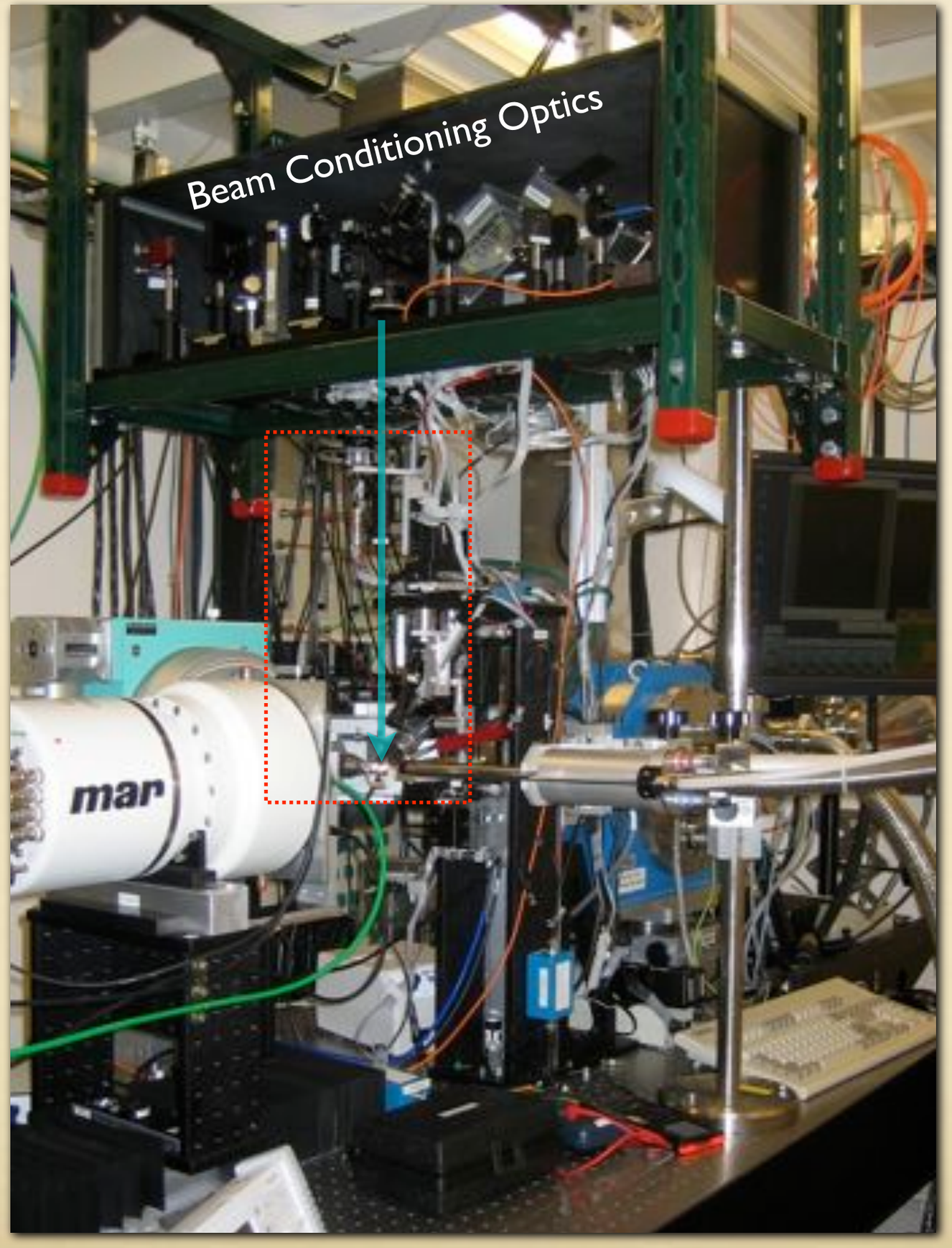




Matched echelon pair (one shown) splits 1.2 ps pulse into 36 pulses via Brewster-oriented, precision-parallel, triangular-cut, fused-silica windows.

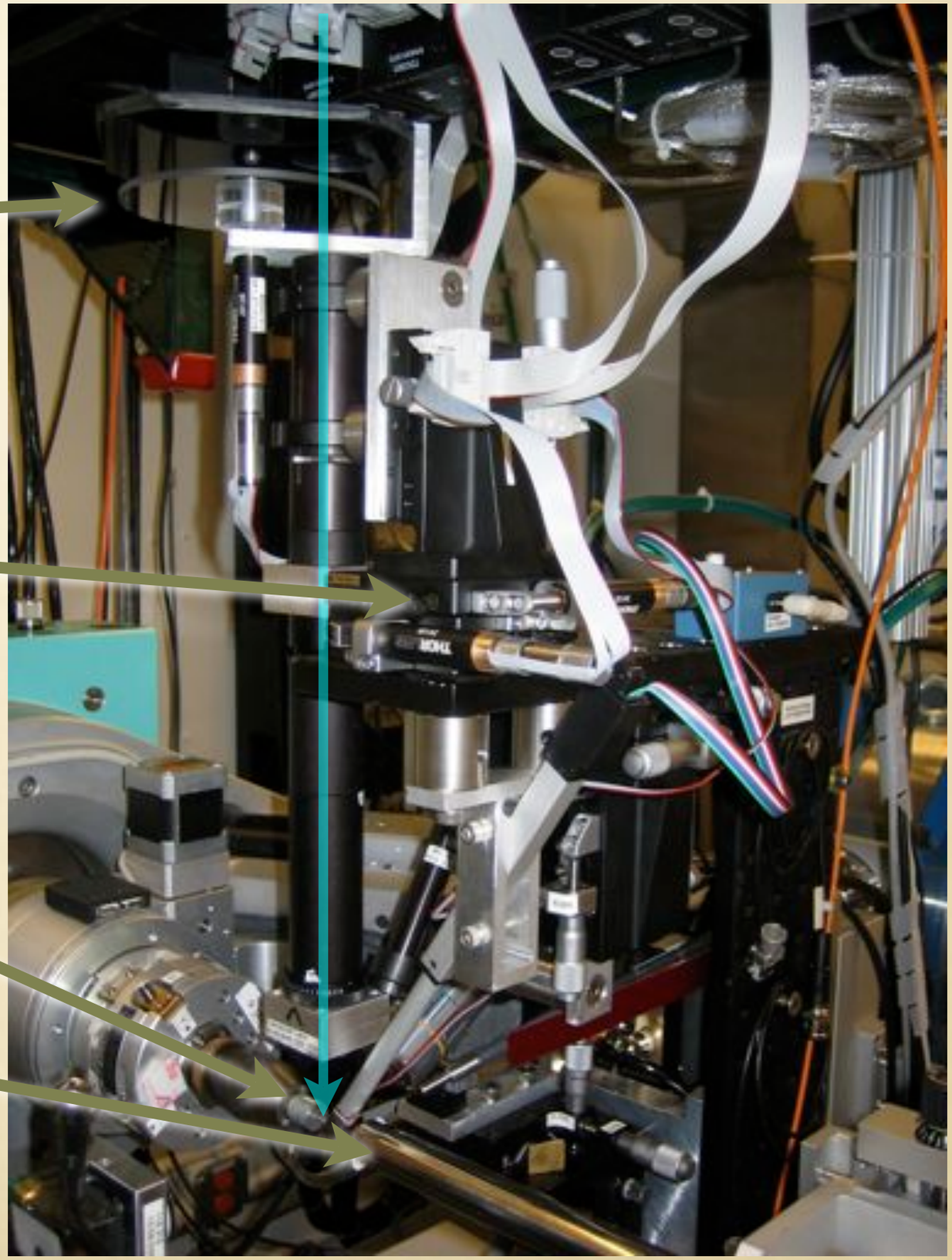
Light passing through each square “pixel” experiences a different time delay, the span of which is ~50 ps.

Experimental Hutch



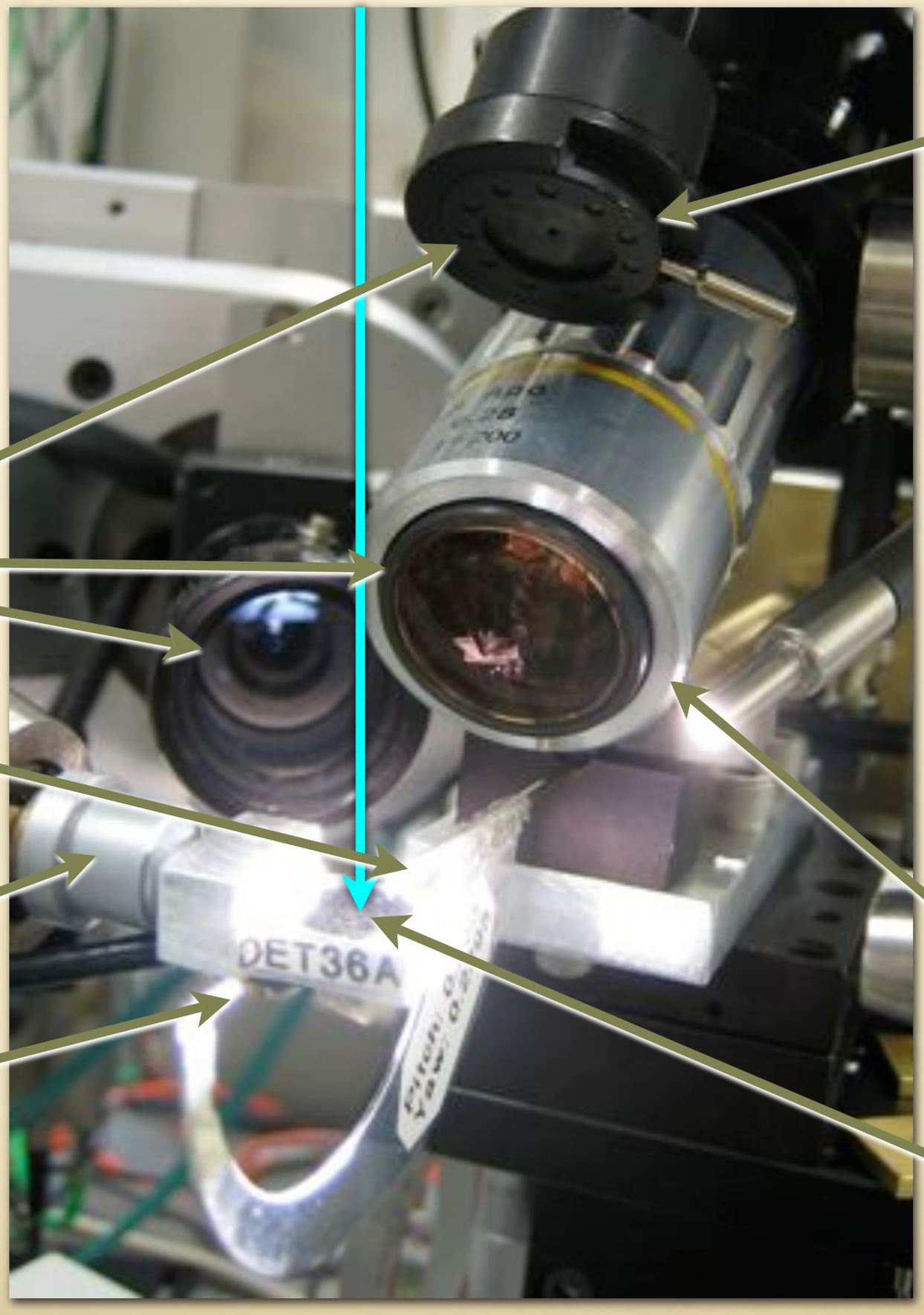
Laser Beam Delivery to Goniometer

- Motorized laser beam attenuator
- Motorized xy+z stage to focus and position laser beam
- Sample attached to Kappa goniometer
- Cryostream nozzle



Sample Environment

- 3 cameras
- 350-um tip collimator pipe
- magnetic goniometer base
- 1-mm tungsten beamstop



6-μm resolution color camera

5-μm carbon fiber

1-μm resolution color camera

25-μm tungsten alignment pinhole

Laser Beam Profile

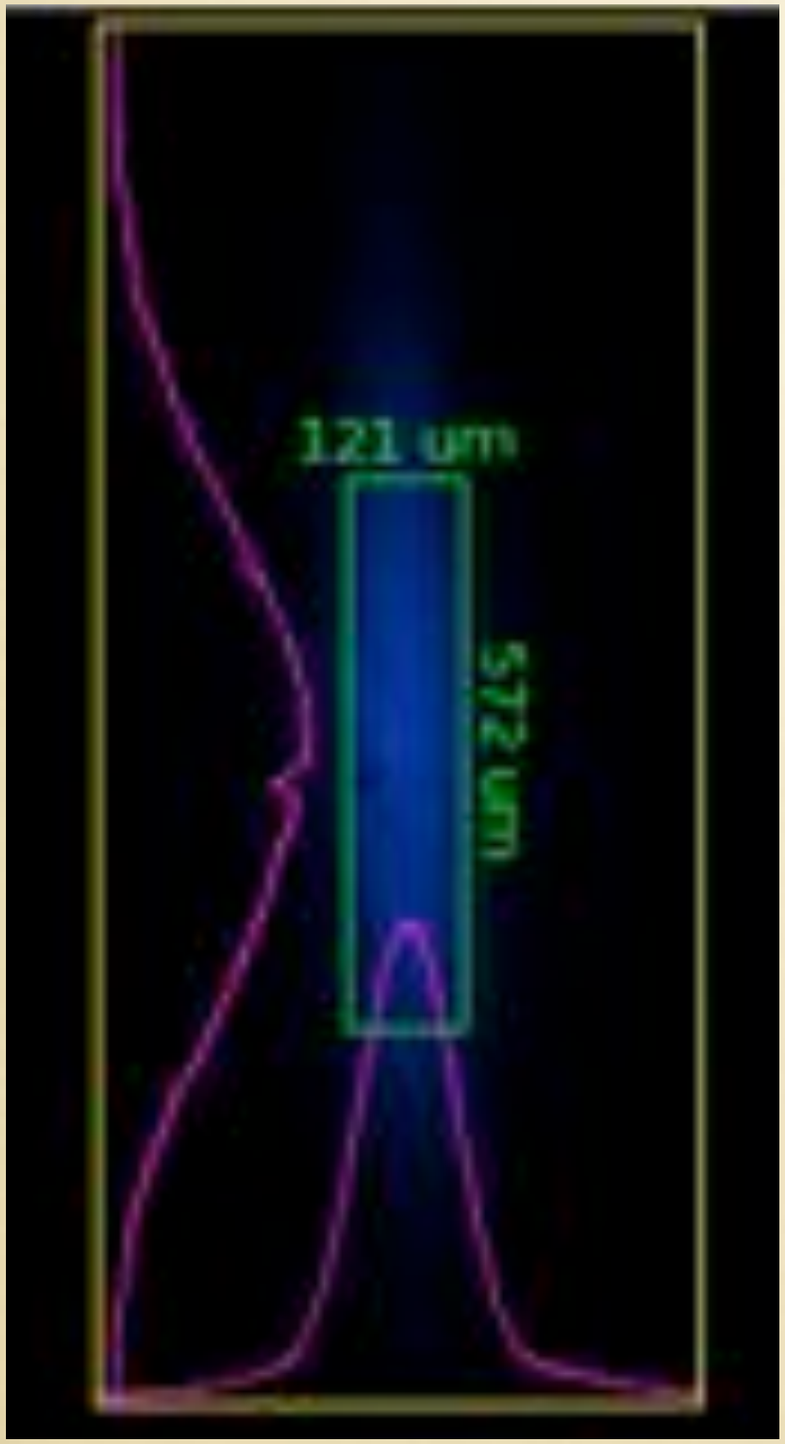
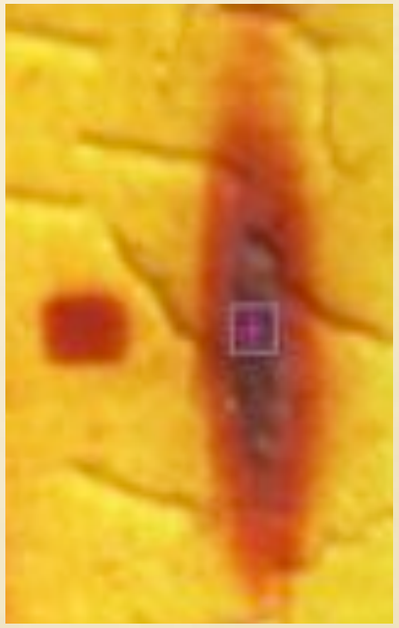


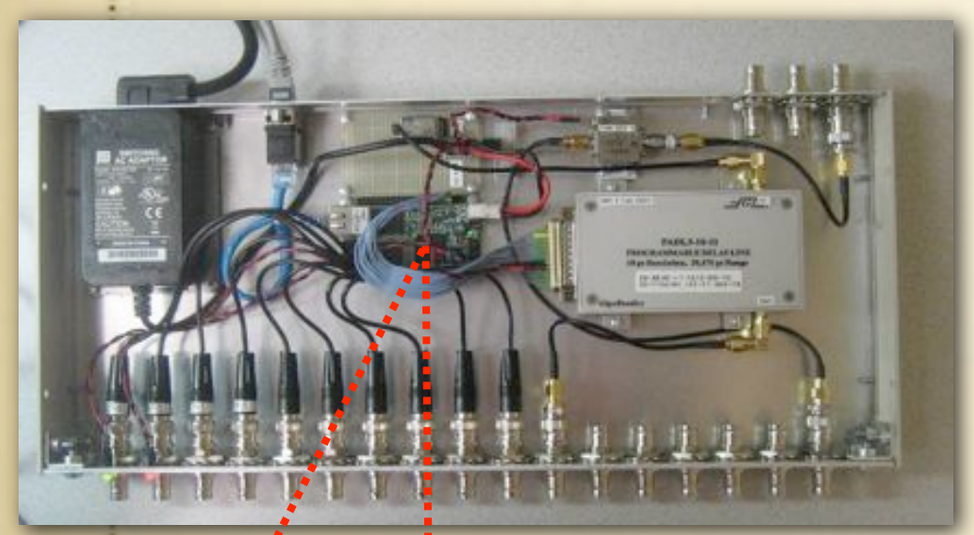
Image from medium-resolution CCD camera
Software developed by Friedrich Schotte

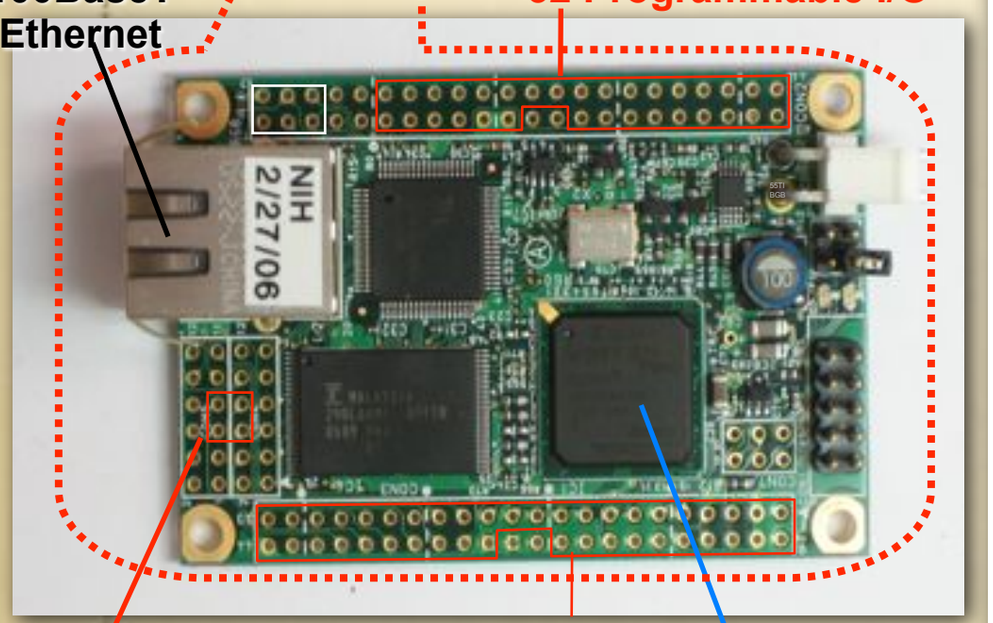


Assess alignment
with “burn” paper

Electronic Synchronization of Beam Line

Field-Programmable-Gate-Array (FPGA) generates all timing signals necessary to operate the beam line





100BaseT Ethernet

32 Programmable I/O

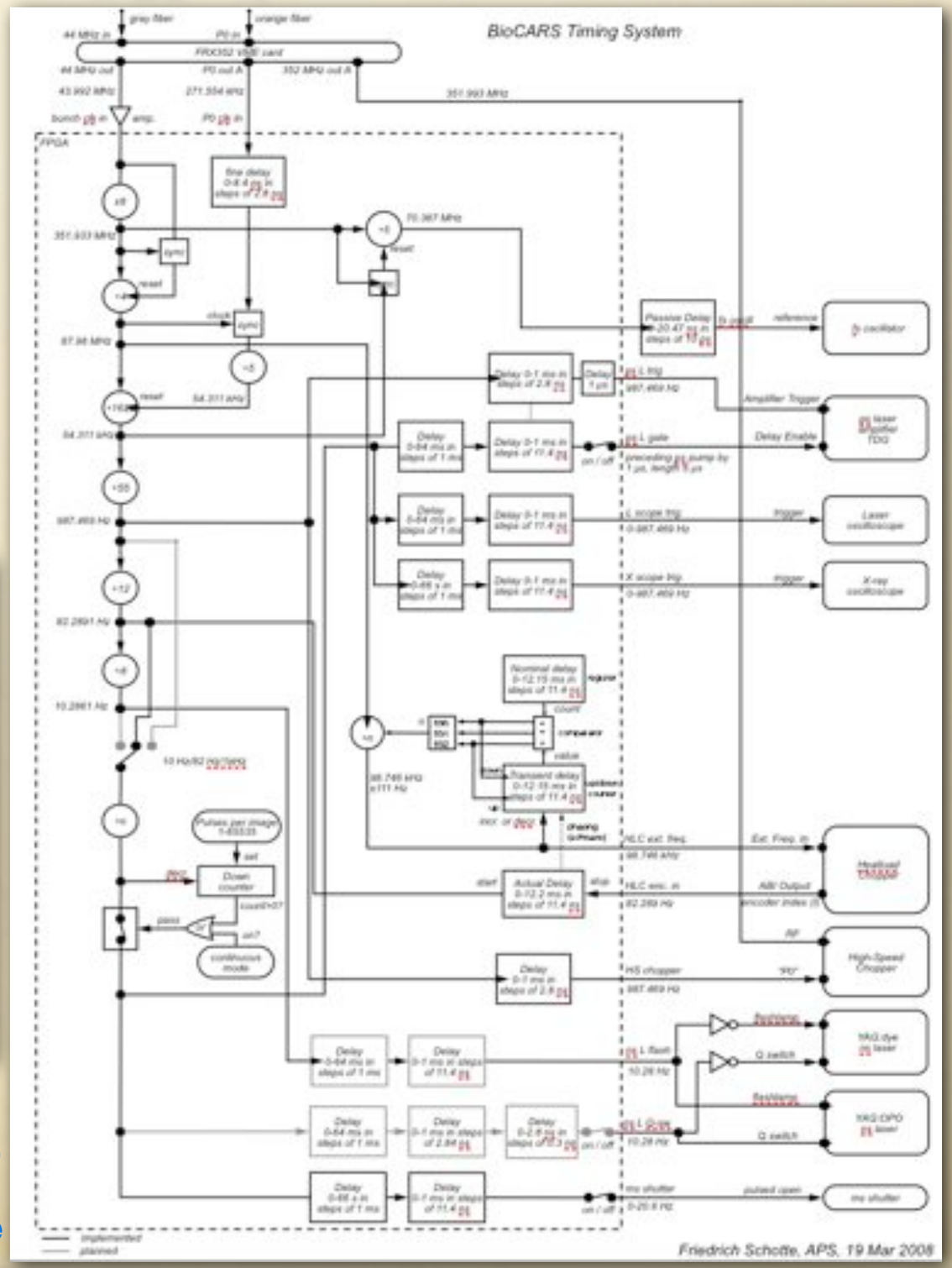
34 Programmable I/O

4 Programmable I/O

Virtex-II Pro FPGA (256 pin)
180,000 gates, 360 MHz
270-MHz PowerPC-405 core

44 MHz

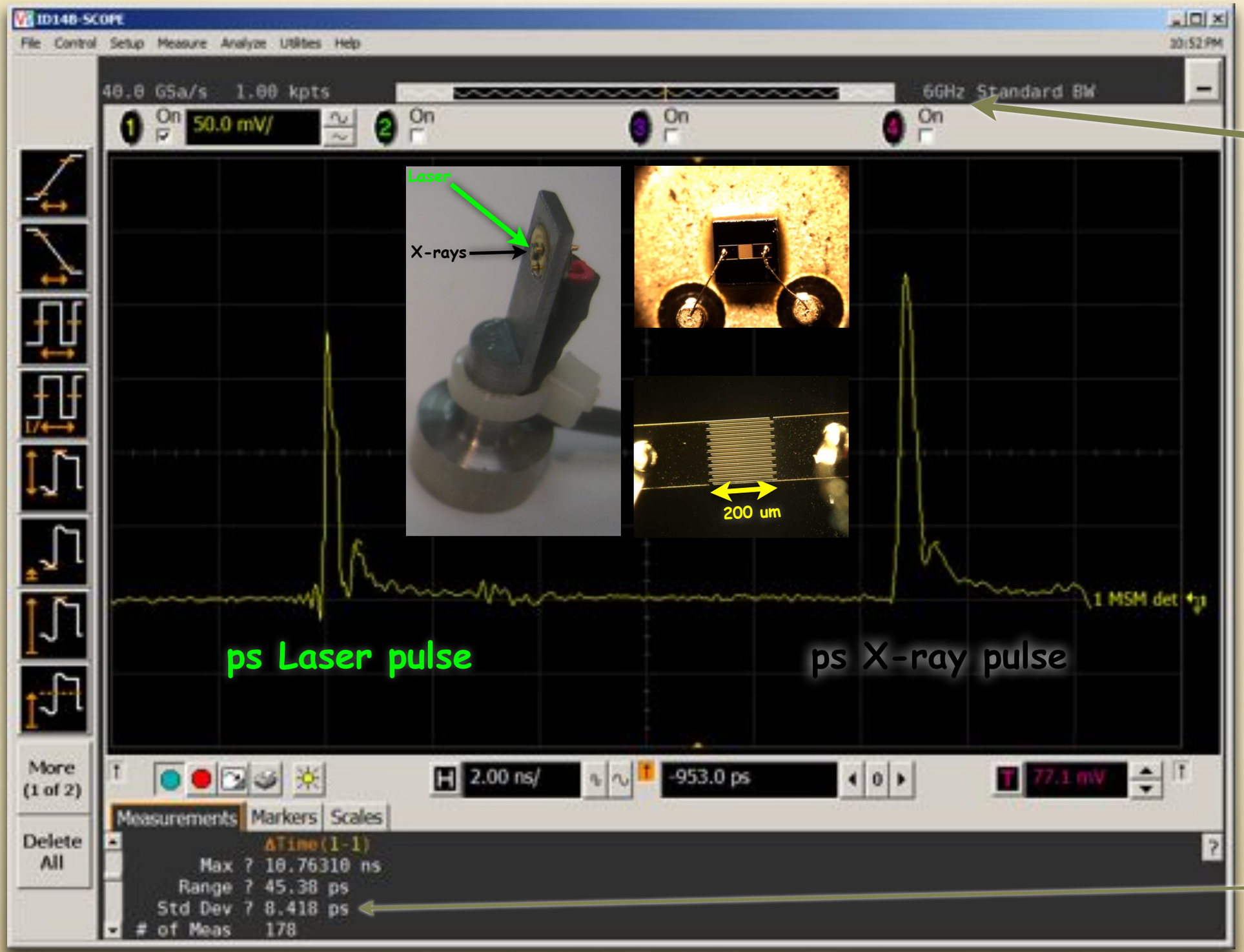
P0



Dr. Friedrich Schotte

X-ray/Laser Pulse Synchronization

Metal-Semiconductor-Metal (MSM) photo-detector is responsive to both laser and x-ray photons

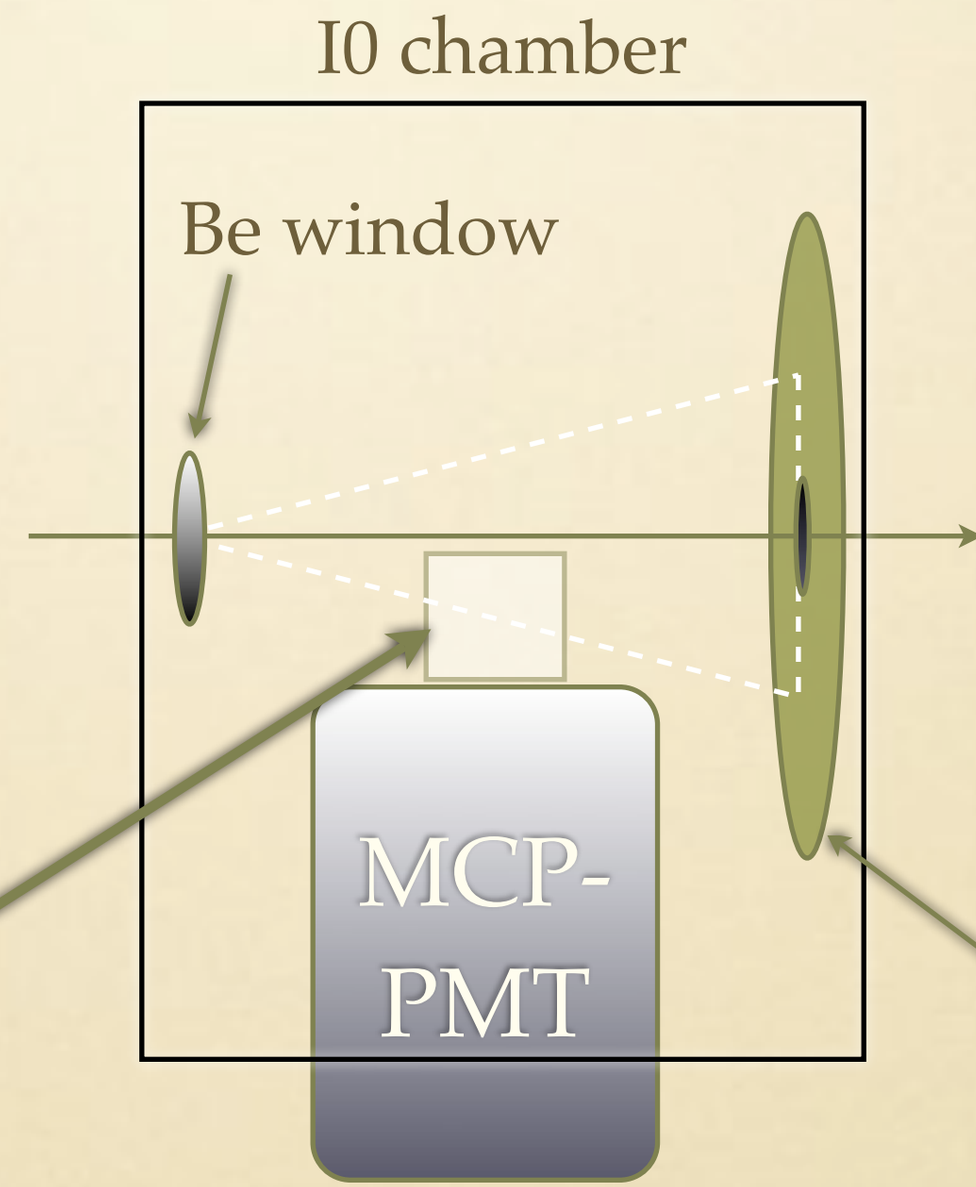


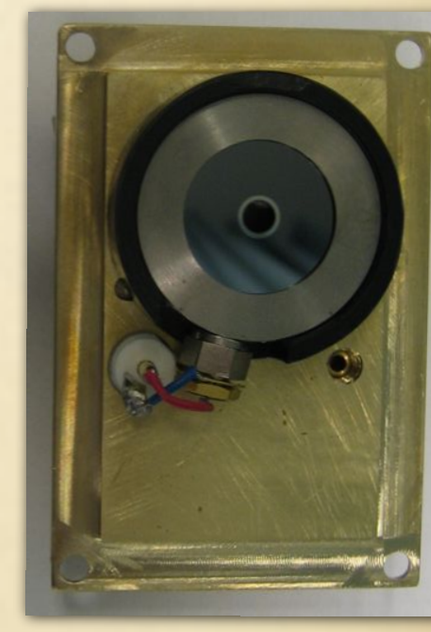
Fast!

Precise!

Non-Invasive X-ray Monitors:

Pulse intensity and **High-Speed Chopper timing** with I0 PIN diode;
X-ray Timing with Micro-Channel Plate Photomultiplier (MCP-MPT)

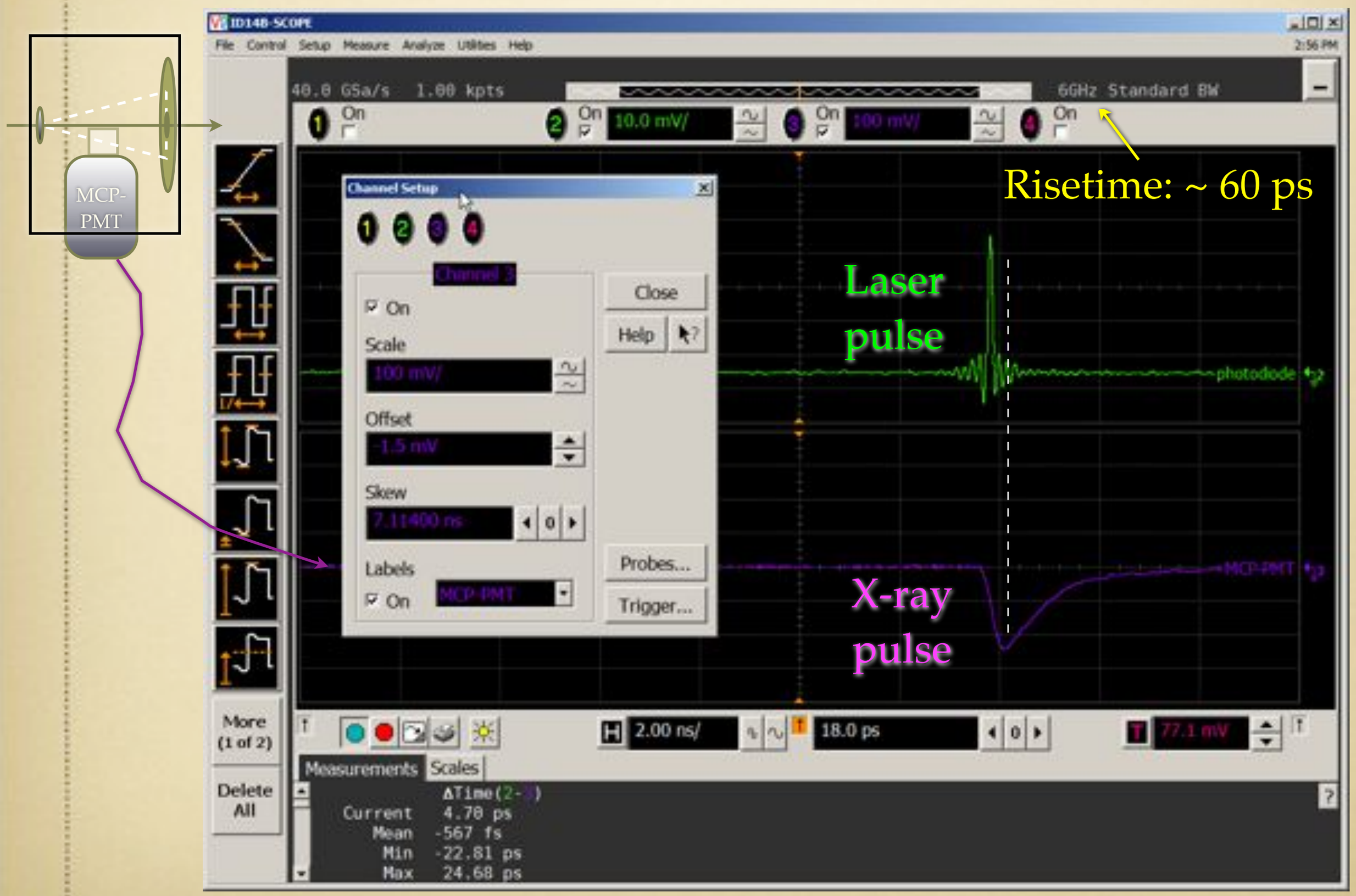




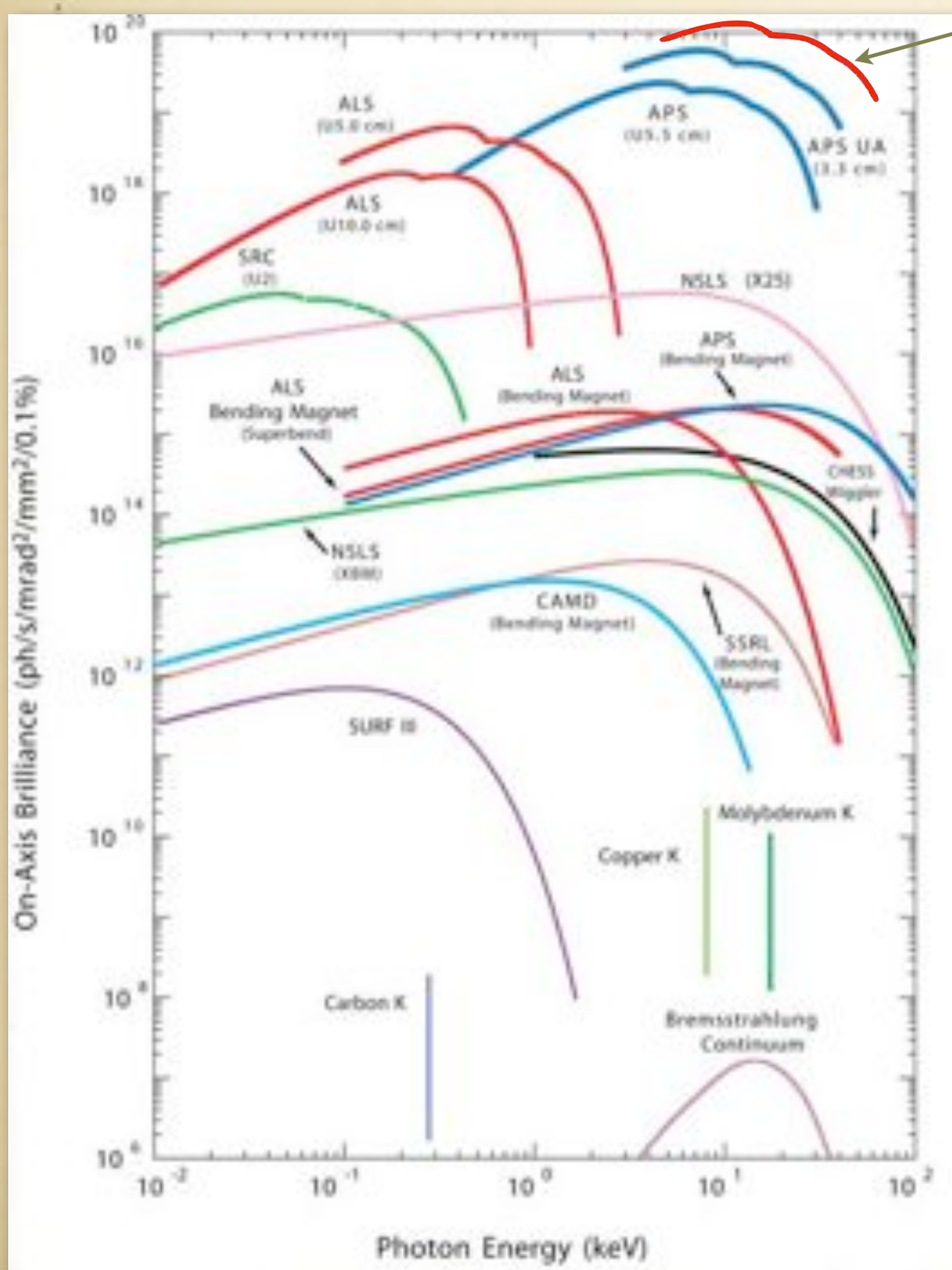
I0 PIN diode

Bicron BC422Q Scintillator
105 ps risetime
0.7 ns falltime (with 1% Benzophenone "quencher")

Non-invasive X-ray/laser timing monitor



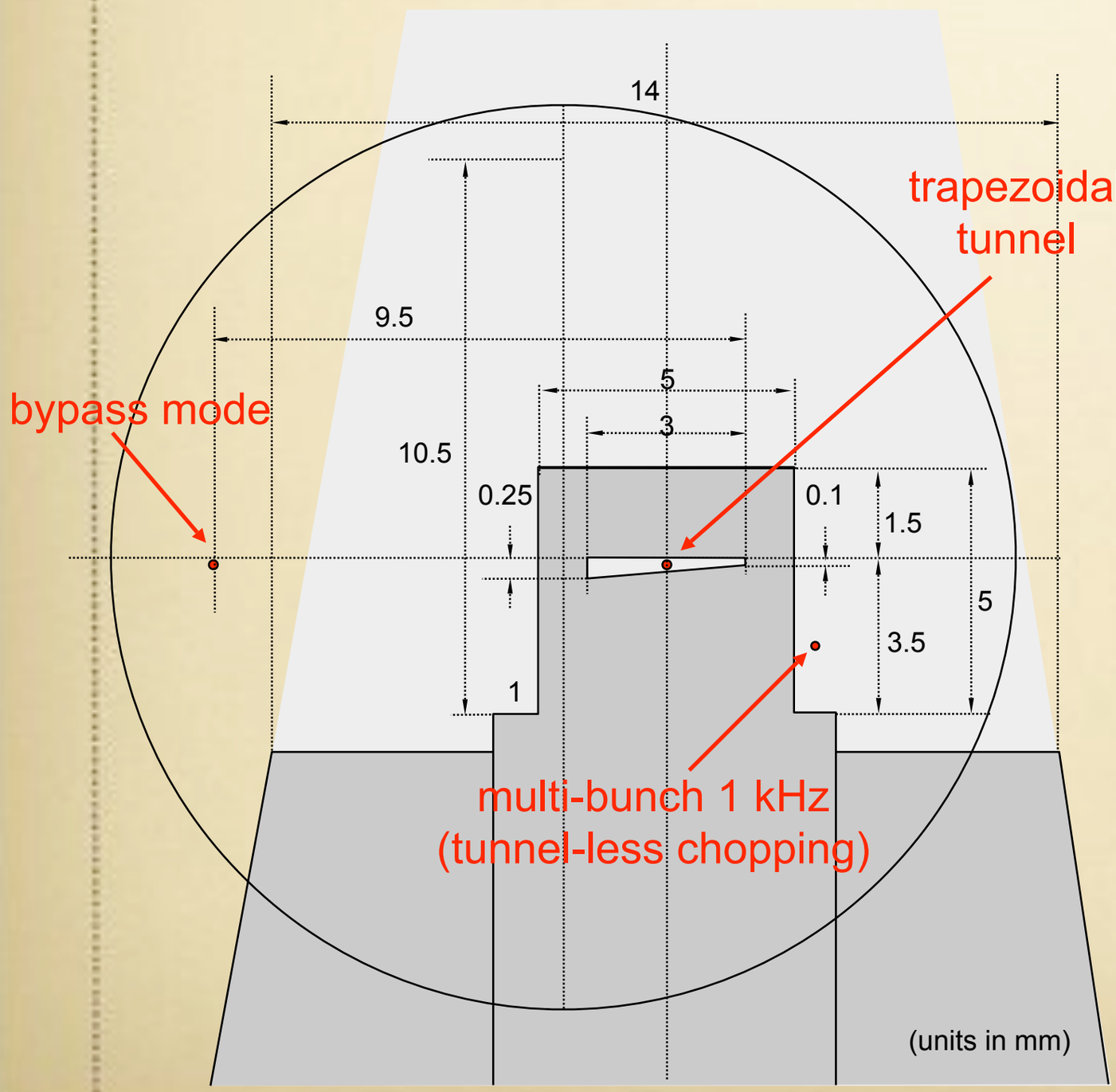
One U33 replaced by U23 and U27

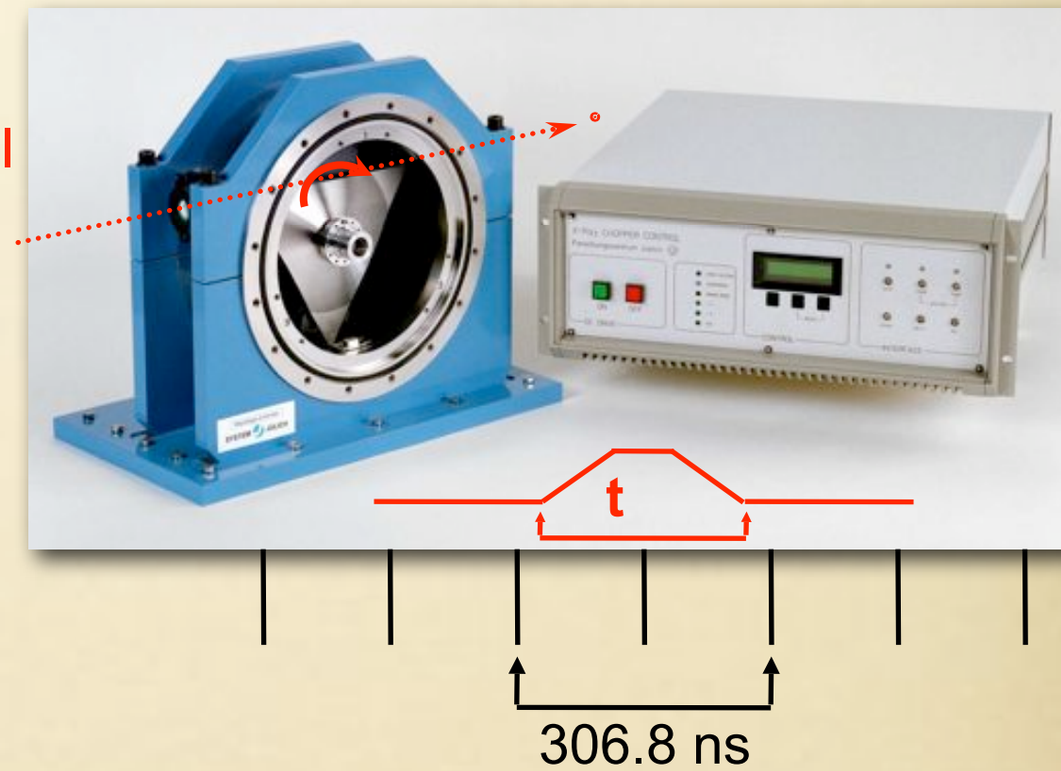


(Credit: Argonne National Laboratory)

High-Speed X-ray Chopper

- With upgraded rotor and controller electronics, can isolate 1 bunch from 24-bunch mode (pulse separation: 153.4 ns)
- Time-resolved capabilities span over 150 days per year





Trapezoidal Tunnel Opening time:

$t = h/[2\pi rf\cos(30)]$

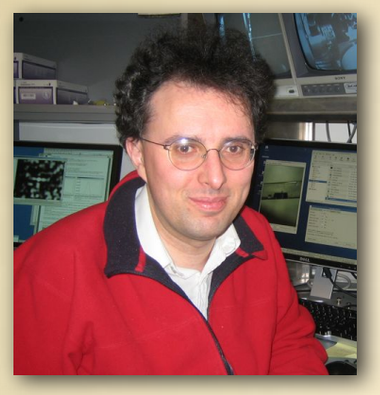
$h < 0.13$ mm

$r = 96.8$ mm

$f = 986$ Hz (supersonic!)

$t < 250$ ns

Acknowledgements



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Dr. Hyun Sun Cho

Dr. "Nara" Dashdorj

Dr. Eric Henry

Bernie Howder

BioCARS (Sector 14 at APS)

- Keith Moffat, U Chicago (PI)
- Yu-Shen Chen (beam line scientist)
- Tim Graber (beam line scientist; directed the X-ray optics upgrade)
- Rob Henning (beam line scientist)
- Zhong Ren (software development)
- Vukica Šrajer (beam line scientist)

APS, Argonne National Laboratory

- Efim Gluskin (head of APS undulator group; oversaw installation of U23 and U27 undulators on Sector 14 BioCARS ID beamline)

Juelich, Germany

- Bernd Lindenau (high-speed chopper rotor upgrade)
- Juergen Raebiger (high-speed chopper electronics upgrade)