Ultrafast x-ray absorption spectroscopy of laser-excited materials

Philip Heimann, Ernie Glover, Howard Padmore (Advanced Light Source)
Steven Johnson, Aaron Lindenberg, Donnacha Lowney, Andrew MacPhee,
Roger Falcone (UC Berkeley) and Robert Schoenlein (MSD LBNL)

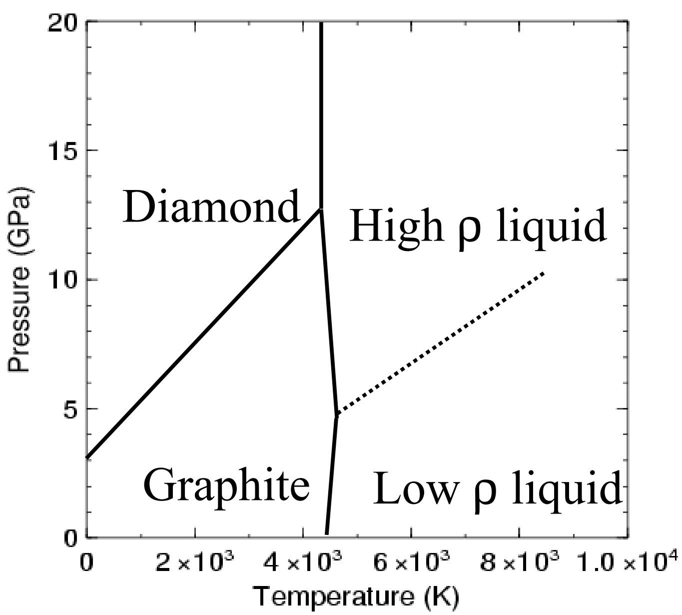
- Introduction: time-resolved x-ray absorption spectroscopy, liquid carbon
- Bunch slicing
- ALS beamline 6.0

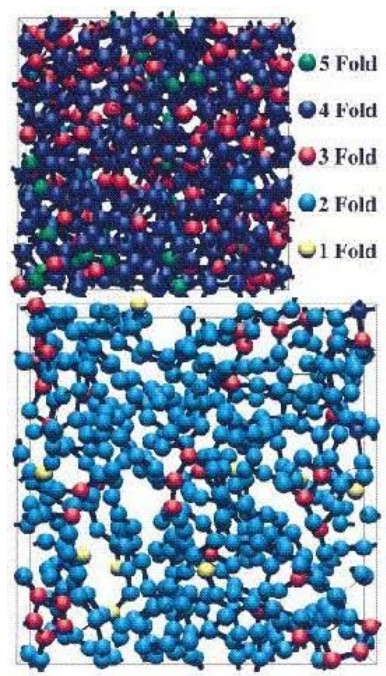
Introduction: time resolved x-ray absorption spectroscopy

- Time-resolved Near-Edge (XANES) and Extended X-ray Absorption Fine Structure (EXAFS): use these probes of electronic states and structure with time resolution approaching molecular vibration ~ 100 fs
- Applications at bend magnet BL 5.3.1: with ALS pulse duration 70 ps, streak camera ~ 2 ps, slicing 100 fs
  - Phase transitions: VO_2 insulator to metal (A. Cavalleri et al.)
  - Photochemistry in solution: $[Ru^{II}(bpy)_3]^{2+}$ -> $[Ru^{III}(bpy)_3]^{3+}$
    (W. Gawelda poster 10.6 Wed)
  - Atomic physics: K^+ (A. Belkacem et al.)
  - High temperature materials: liquid silicon, liquid carbon (S. Johnson thesis)
- Observe laser-induced transient states that cannot be made statically

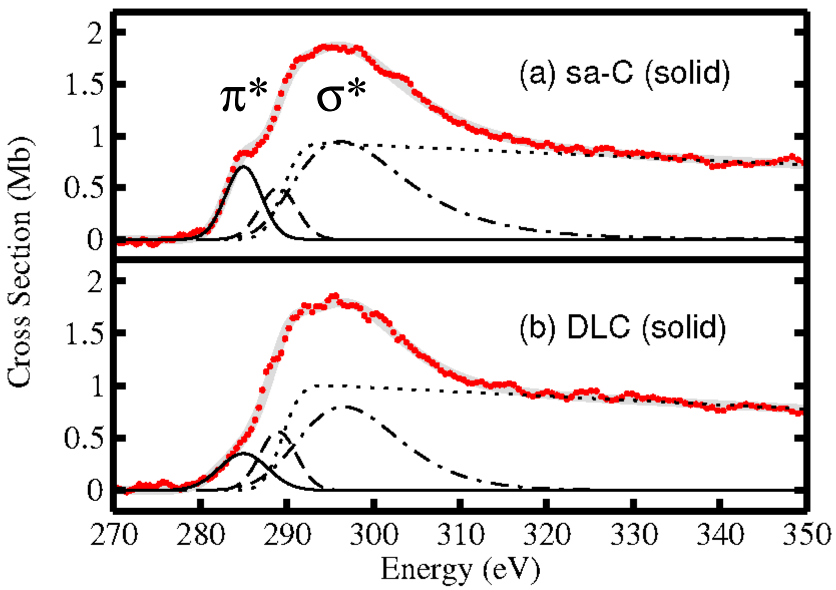
X-ray absorption of liquid carbon

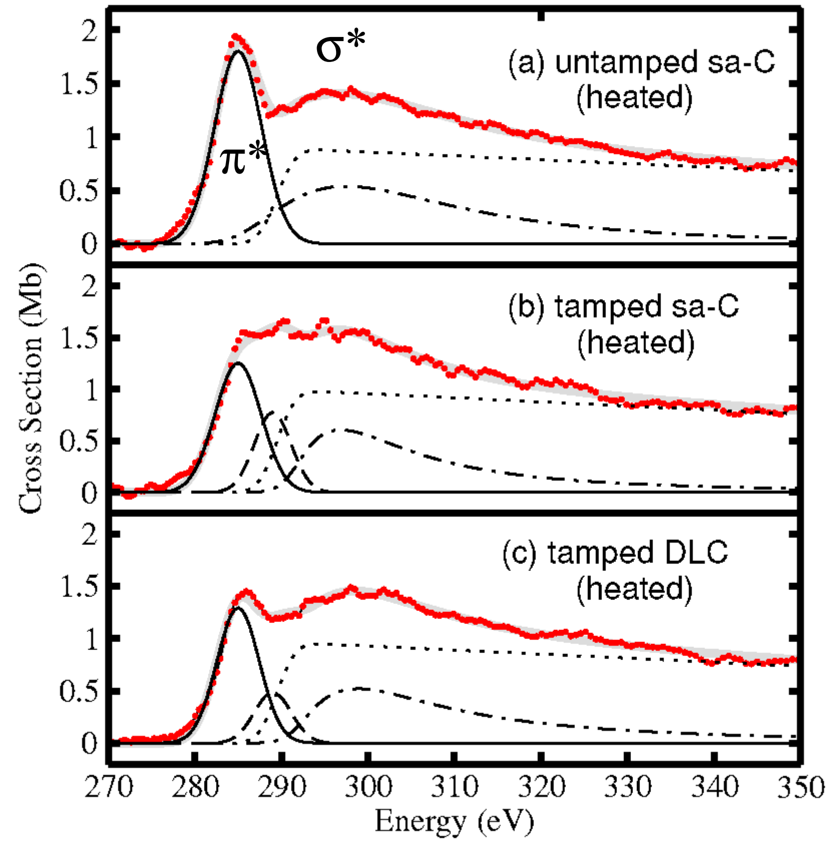
- In planets Uranus and Neptune, middle layer of CH_4, H_2O and NH_3 at high T, P. CH_4 expected to be dissociated. Liquid carbon not stable ambient pressure
- Molecular dynamics calculations
  - Low density ρ liquid predominantly sp coordination, high ρ liquid mainly sp^3, Glosli and Ree, PRL *82*, 4659 (1999)
  - Continuous change from sp sp^2 mixture to sp^2 sp^3 mixture as density is increased, Wu et al., PRL *89*, 135701 (2002)





Carbon K-edge spectra





- Initial sample: soft amorphous carbon ρ, 2.2 g/cm^3, DLC ρ, 2.6 g/cm^3,
- Heated spectrum shows increase in π* resonance, decrease in σ* resonance
- Tamp carbon with LiF, to keep density constant - spectra at 100 and 300 ps are the same

| LiF | C | LiF |

K-edge spectrum of tamped carbon

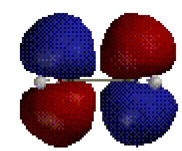
Material	π* area	π* states/site	π* states/site calculation[1]
soft a-C	0.047	0.70	
DLC	0.030	0.45	
untamped liquid	0.135	2.01	
2.2 g/cc liquid	0.090	1.35	1.29
2.6 g/cc liquid	0.087	1.29	1.16

[1]Morris et al. Phys. Rev. B 52, 4138 (1995)

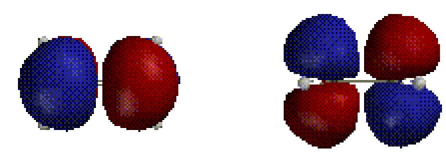
Unoccupied π orbitals

Ethane sp^3
None

Ethylene sp^2



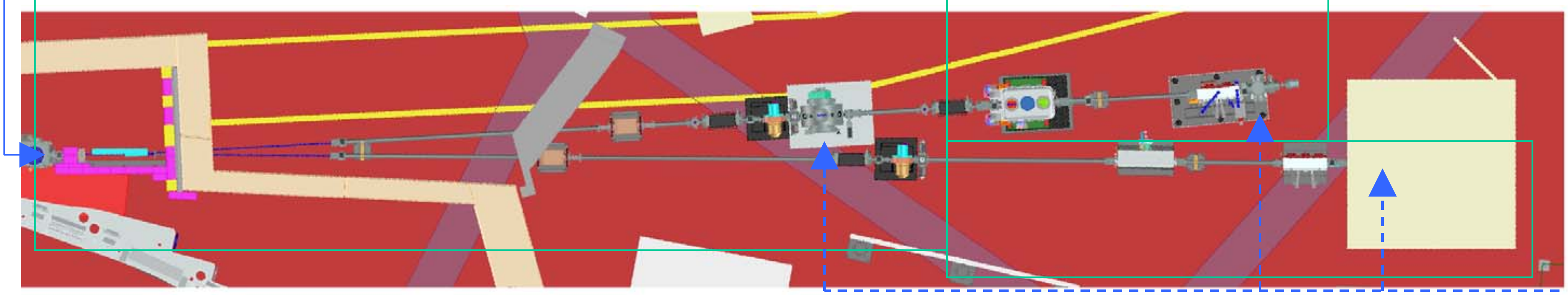
Acetylene sp



- At low density (untamped), liquid C is sp bonded
- At higher density, liquid C has mixture of different bonding, agrees with calculations
- Goals: Improved energy resolution, EXAFS sensitivity

ALS beamline 6.0

- Slicing of the electron bunch
- In-vacuum undulator
- Separation of fs x-ray pulse
- Grating spectrograph

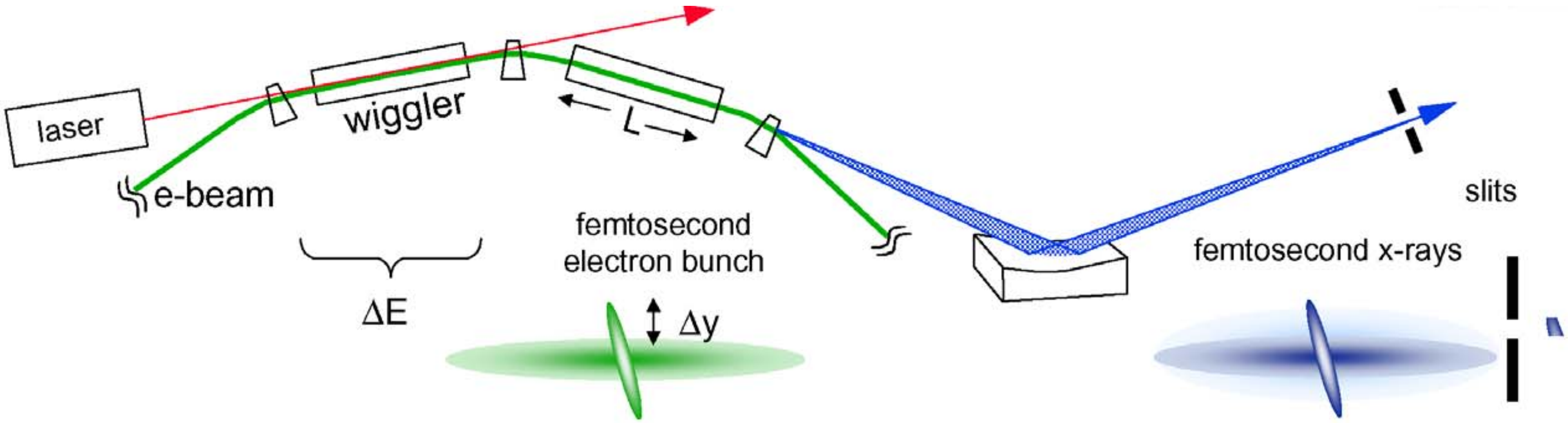


- Crystal mono
- Laser system
~ 70 fs, 40 kHz,
1 mJ, 2 arms

Goals of beamline design

- Photon energy range < 250 eV - 10 keV:
  - Use both undulator and wiggler radiation
  - Use both grating and crystal optics
- Clean separation of fs x-ray pulse
- High efficiency: relatively large angular aperture, limited number of reflections
- Dispersive soft x-ray absorption spectroscopy: grating spectrograph
- Energy resolution: 0.5 eV at Ni L edge (850 eV), for hard x-rays approach perfect crystal limited resolution
- Detectors: high quantum efficiency, gateable
- Laser system: high repetition rate, 40 kHz, to increase useable x-ray flux

Slicing and separation of fs x-rays



- Laser modulation of e-beam energy (ΔE)
- Storage ring dispersion (ΔE -> Δy)
- Beamline imaging
- Zholents and Zolotorev, Physical Review Letters **76**, 916 (1996), Schoenlein et al., Science **287**, 223 (2000).

Slicing flux

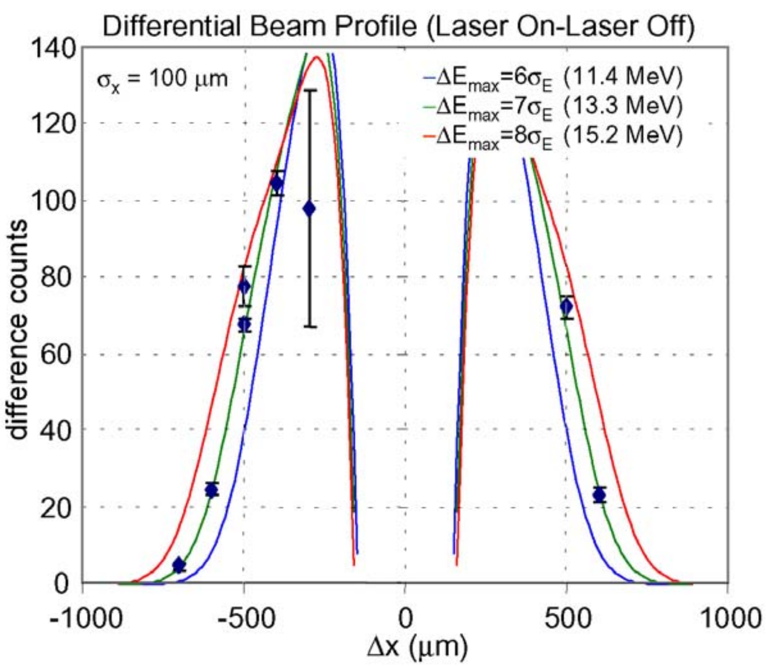
- phase factor $\eta_1 = 0.1$ (fraction of electrons in optimum phase)
- pulse duration $\eta_2 = \tau_{laser} / \tau_{synchrotron} = 10^{-3}$ ($\tau_{x\text{-ray}} \approx 170$ fs)
  (70 fs) (70 ps)
- repetition rate $\eta_3 = f_{laser} / f_{synchrotron} = 2\text{x}10^{-6}$
  (1 kHz) (500 MHz)

  $f_{laser} / f_{synchrotron}$
  (40 kHz) (500 MHz)

  $$f_{limit} \approx 3 \times \frac{\text{number of bunches}}{\tau_{damping}} = 150 \text{ kHz}$$

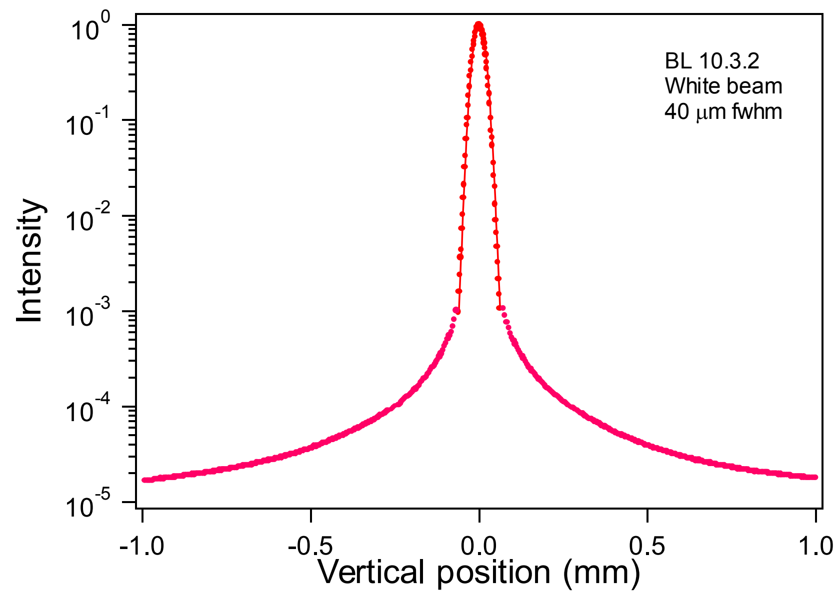
Femtosecond x-ray profile

- Measured x-ray profile with slicing



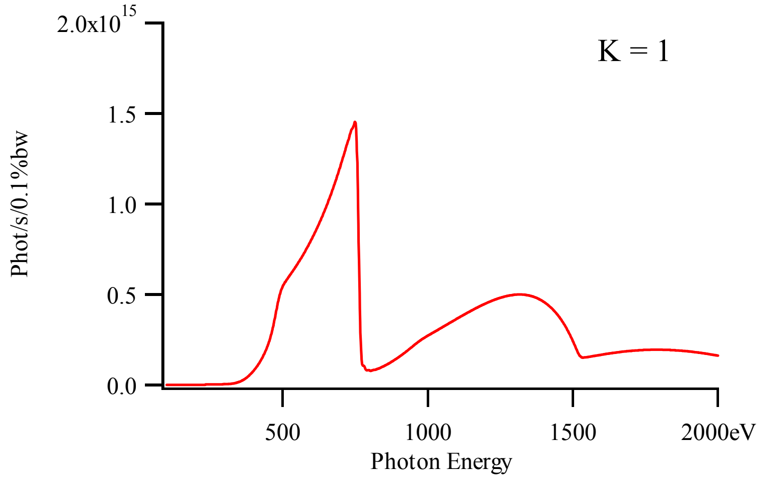
- Laser 0.8 mJ, 75 fs

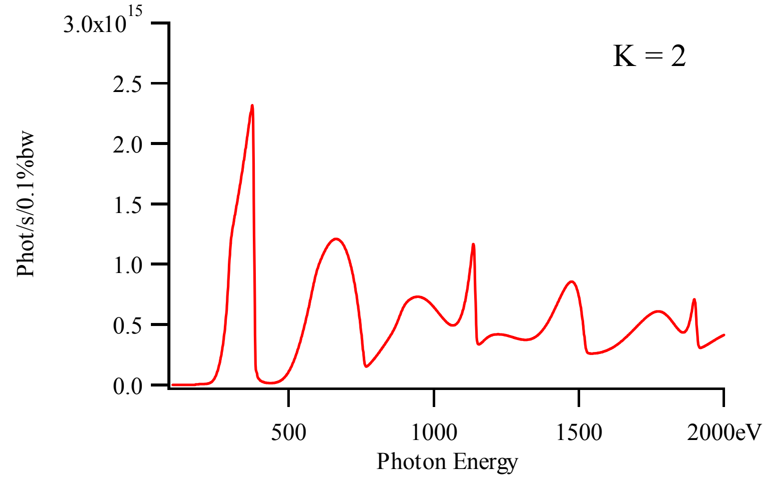
- Background from optical scattering

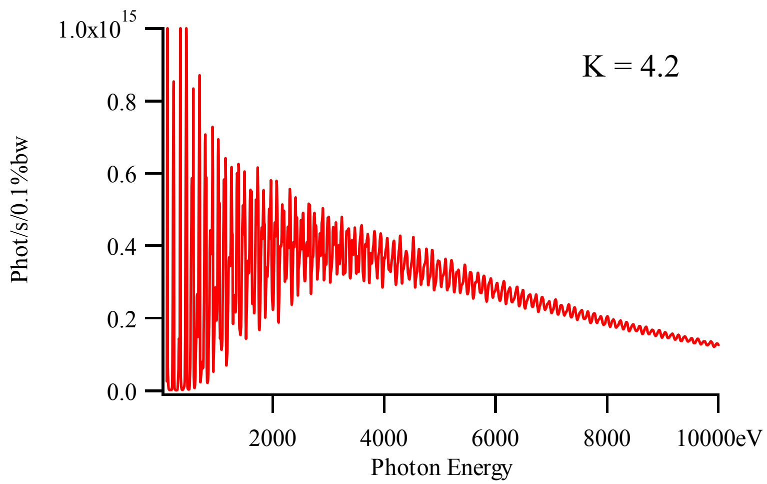


- Challenge: isolate fs x-ray intensity of 10^{-4} at displacement of 0.3 mm
- fs signal / 70 ps background, estimate ~ 1:1
- S. Khan (BESSY): scheme to use angular separation of sliced x-ray pulse, with no optic before aperture

In-vacuum undulator / wiggler source spectrum





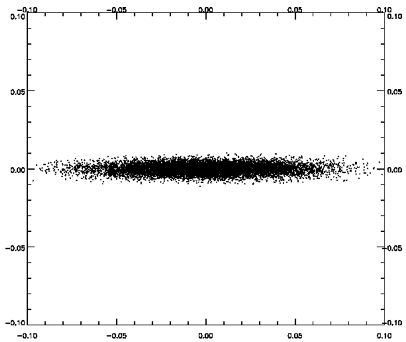


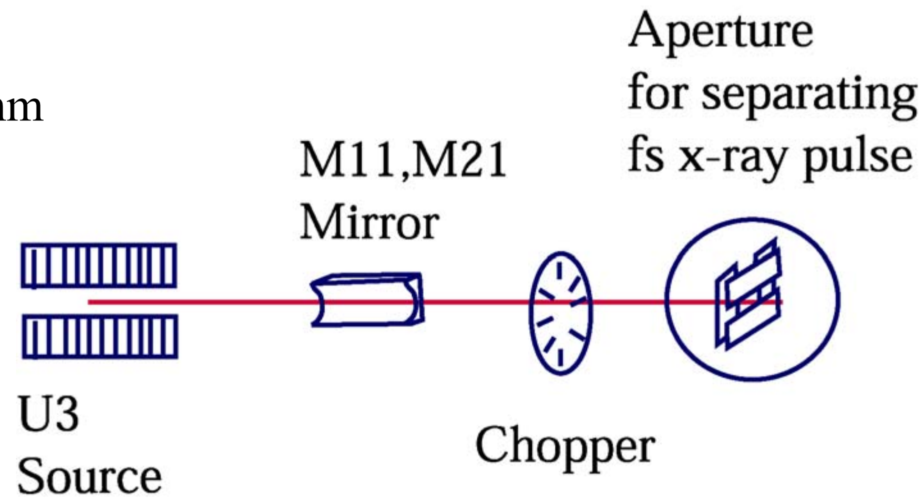
Harmonic	E	ΔE (fwhm)
1	280 eV	66 eV
2	850 eV	312 eV

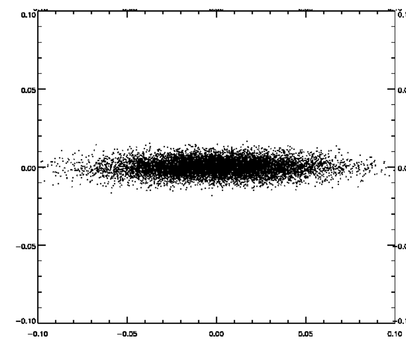
- Undulator spectrum calculated with SRW: λu = 3 cm, B(peak) = 1.5 T
  - Into 0.5 (h) x 0.5 (v) $mrad^2$ aperture, use harmonics 1, 2, 3, 4, up to 2 keV
- Wiggler radiation into 0.5 (h) x 0.3(v) $mrad^2$ aperture, up to 10 keV

Separation of fs x-ray pulse

- Source:
710 (h) x 72 µm (v) fwhm

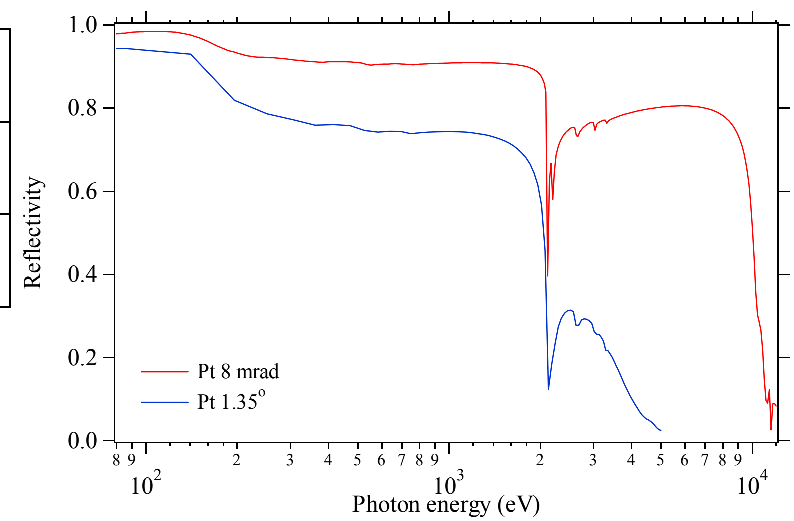






- Intermediate focus:
720 (h) x 100 µm (v) fwhm
70 µm (v) for central cone

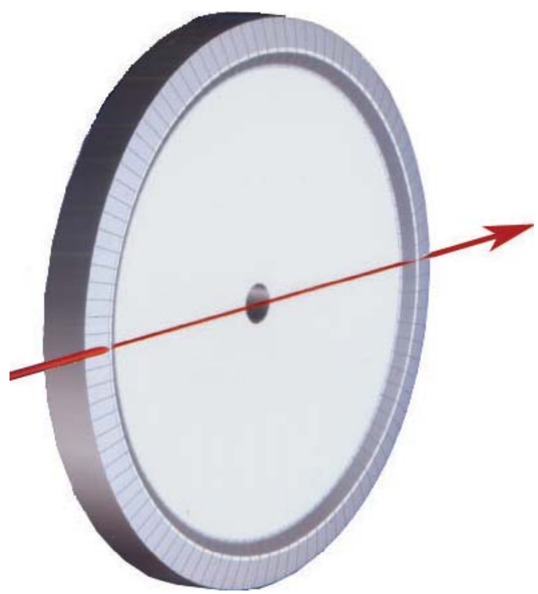
	Type	Coating and blank material	Dimensions (mm)	Radius (m)	Incidence angle (°)
M11	Toroidal mirror	Pt-coated silicon	320 x 90 x 25	449 (R) 0.2472 (ρ)	88.6552
M21	Toroidal mirror	Pt-coated silicon	800 x 40 x 75	1458 (R) 0.0933 (ρ)	89.54



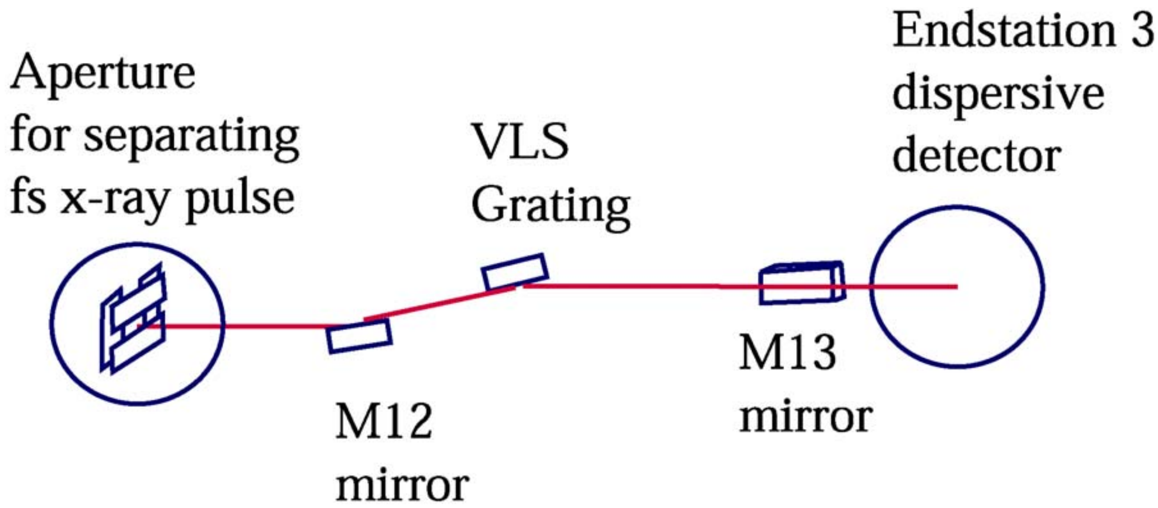
- Single reflection in sagittal focusing reduces x-ray scattering background

X-ray chopper

- Absorbed power: 430 W on hard x-ray branch, reduces power on samples in pink beam and on downstream optics
- Frequency: 40 kHz matched to laser repetition rate
- Acceptance: 2 %
- Design based on Rigaku rotating anode



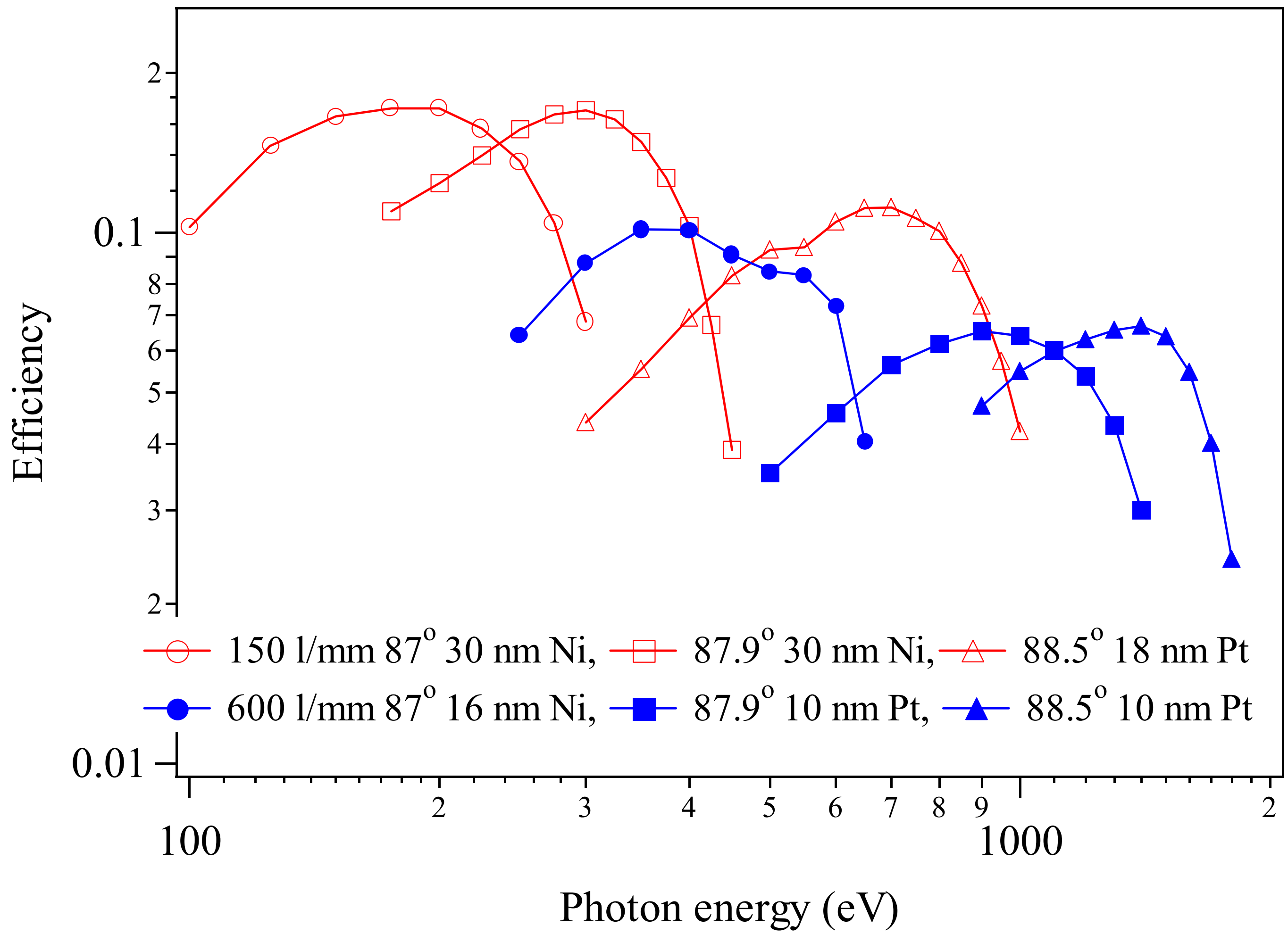
Grating spectrograph



	Type	Coating and blank material	Dimension (mm)	Radius (m)	Incidence angle(°)	Grating peri order
M12	Spherical mirror	Ni, Pt-coated silicon	60x70x25 77x70x25 100x70x25	63 90 126	87 87.9 88.5	-
G1,G2	VLS, Plane grating	Ni, Pt-coated silicon	167x36x30	∞	84 – 90	1/150, +1 1/600, +1
M13	Plane elliptic mirror	Pt-coated fused silica	240 x 40 x 25	29.5	88.5	-

- VLS grating produces flat field spectrum at detector

Efficiency of grating spectrograph

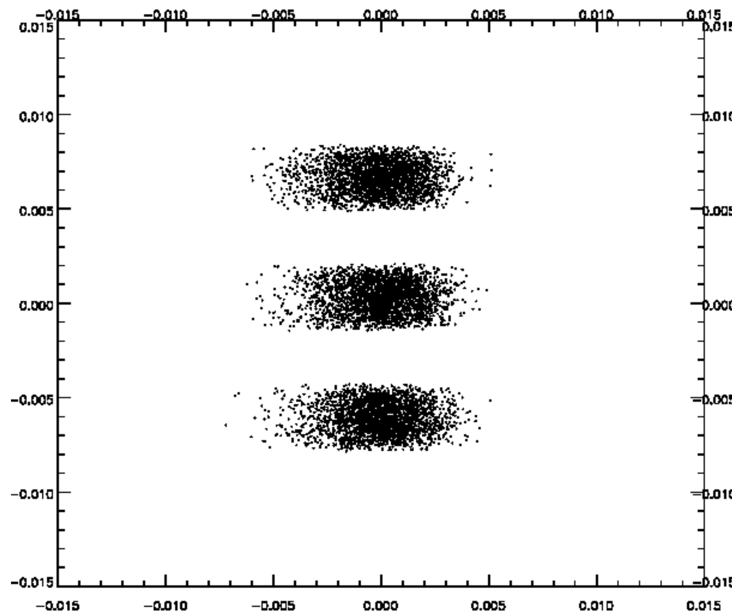


- Includes grating efficiencies from Neviere code and M11, M12 and M13 reflectivities

Energy resolution at 850 eV, range of spectrum across detector

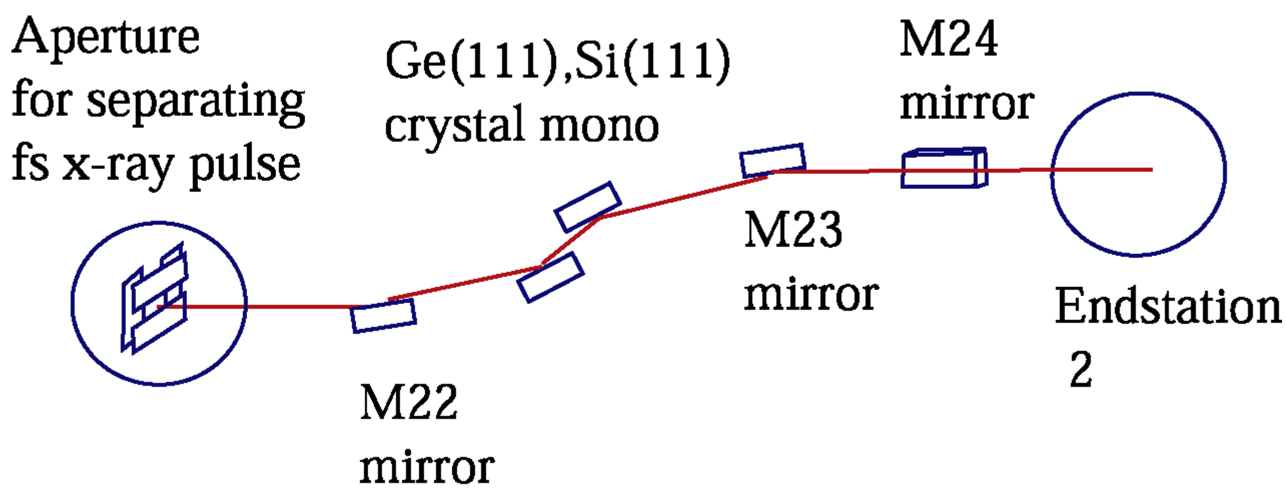
- Goals:
  - Energy resolution match core hole linewidths, 0.5 eV at Ni L edge
  - Energy range for XAS across detector, 60 eV at C K edge
- Parameters:
  - Size of spectrograph: r = r' = 3 m
  - Entrance slit matched to beam fwhm (for undulator central cone)
  - Detector: 25 μm spatial resolution, 10 mm slit length (based on streak camera)
  - M12 magnification 1

Photon energy	Grating(l/mm), m, θ	Energy resolution	Energy range
280 eV	150, +1, 87.9 °	0.27 eV	64 eV
850 eV	600, +1, 87.9 °	0.56 eV	160 eV



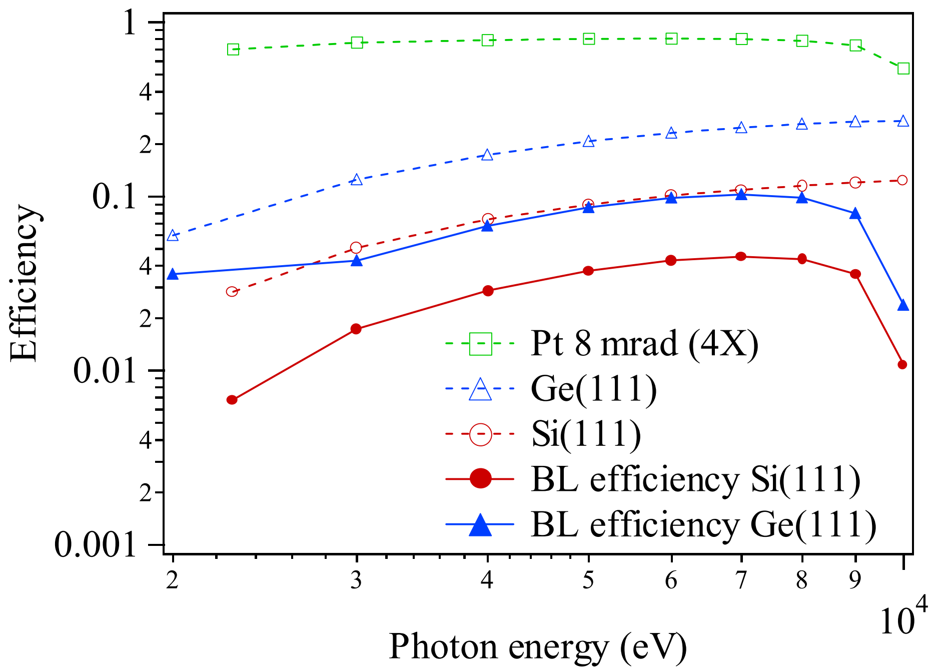
- Photon energies 849, 850, and 851 eV, 600 l/mm grating and 60 μm entrance slit.

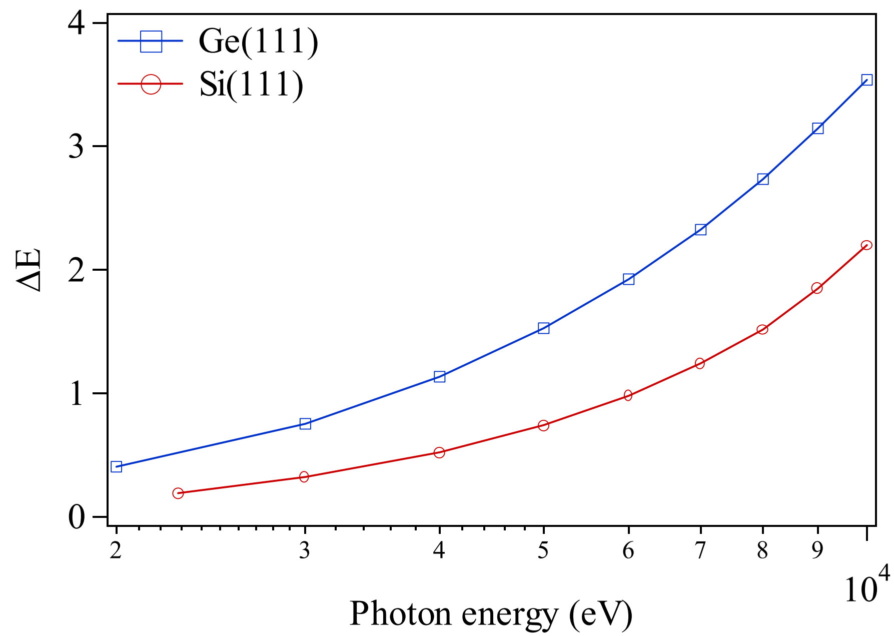
Crystal monochromator



	Type	Coating and blank materia	Dimensions (mm)	Radius (m)	Incidenc angle(°)
M22	Cylindrical mirror	Pt-coated silicon	150 x 12 x 6	750	89.54
X1, X2	Crystal	Si (111), Ge(111)	20 x 10 x 10	∞	6 - 60 (θ_{B}
M23	Cylindrical mirror	Pt-coated silicon	150 x 12 x 6	750	89.54
M24	Plane elliptica mirror	Pt-coated fused silica	600 x 40 x 50	160	89.54

Efficiency and energy resolution of crystal monochromator branchline



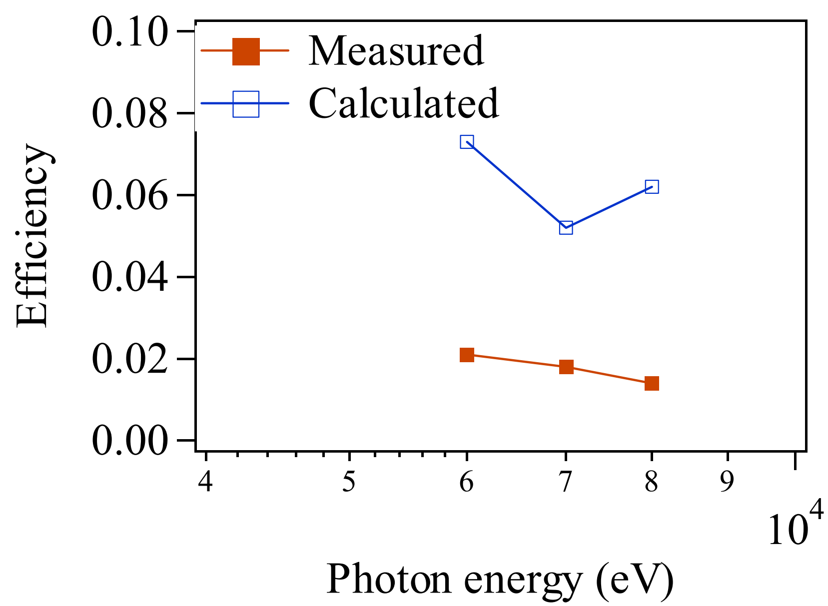


- Crystal efficiency calculated from $\varepsilon = (1/\tan\theta) \int R^2(\theta)\, d\theta$
- Normalized to 0.1 % bandwidth
- Ge(111) crystals for sliced beam, Si(111) for full beam +/- 11 µrad thermal distortion

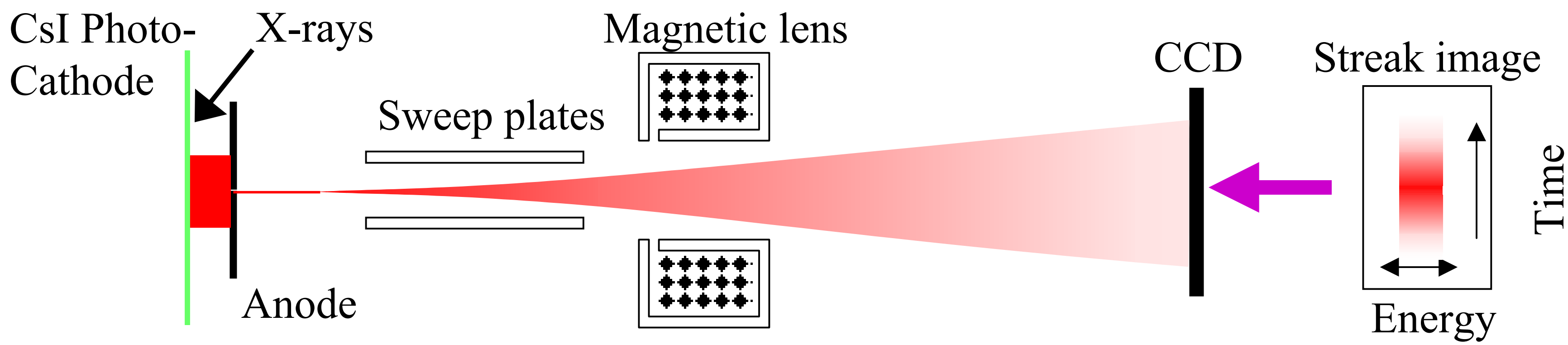
- Contributions
  - Crystal rocking widths: Si(111) 54 µrad, Ge(111) 125 µrad at 5 keV
  - Collimation of M22 mirror: s/r = 106 µm/3 m = 35 µrad,

Hard x-ray dispersive XAS

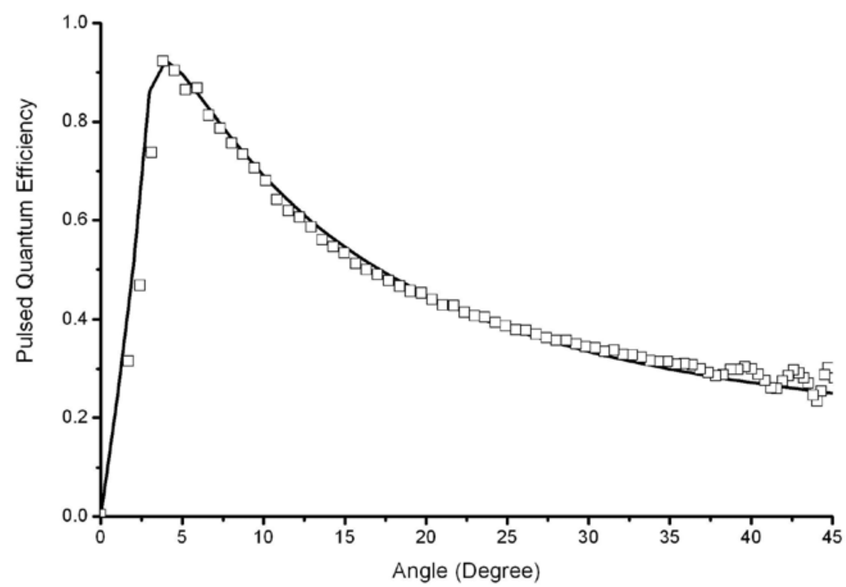
- Goal: with hard x-rays take advantage of wide bandwidth of wiggler, take whole EXAFS spectrum in parallel
- Crystal polychromator not a solution, each part of crystal diffracts narrow bandwidth
- Multilayer grating have demonstrated high efficiency 34% at 8 keV, limited bandwidth, Martynov et al. SPIE (1997)
- Total external reflection gratings
  - Tests on an available laminar grating: 380 l/mm, 12 nm groove depth, nickel coating, measured at θg = 0.4 degrees
  - Efficiency may be limited by surface roughness



Detectors: Streak Camera



- X-ray streak cameras achieved resolution of Δt ~700 fs in averaging mode
- Combined with slicing the streak camera could suppress the background because most ps x-rays will be swept to a different position on the time axis
- High quantum efficiency by using grazing incidence to match x-ray penetration depth and electron escape depth
- Quantum efficiency of CsI vs θ at 500 eV, D. Lowney et al. SPIE 5194b (2003)



Summary

- Time-resolved x-ray absorption spectroscopy, example of liquid carbon
- Source: in-vacuum undulator / wiggler
- Beamline optimized for TR XAS
  - Separation of slicing fs x-ray pulses: sagittal focusing toroidal mirrors
  - Grating spectrograph: measure entire x-ray absorption spectrum simultaneously
  - Crystal monochromator: using Ge(111) and Si(111) crystals
- Detectors: grazing-incidence streak camera and avalanche photodiodes
- Schedule:
  - Insertion device, Soft x-ray branchline, Laser system: Jan. 2005
  - Hard x-ray branchline: Sept. 2005
- Poster: R. Schoenlein (today 6.94)