Experimental aspects: synchrotron radiation, beamlines, detectors, measurement modes geometry, sample preparation methods

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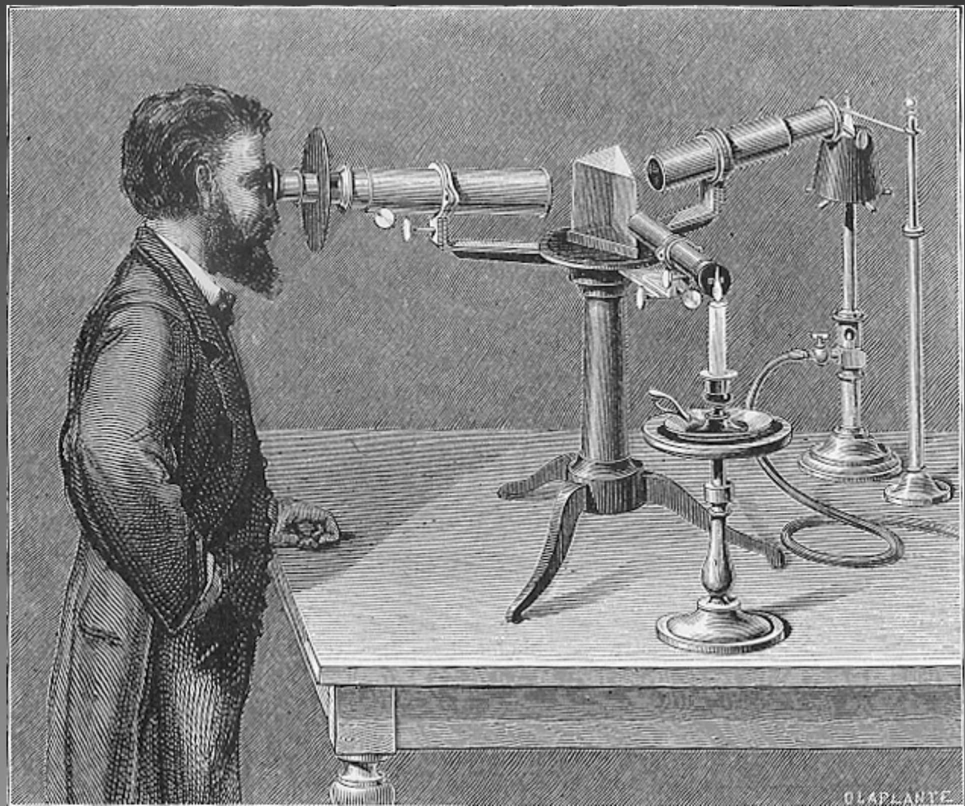
IUCr 2011 XAFS Tutorial for crystallographers and beginners
Madrid, August 22, 2011

Introduction

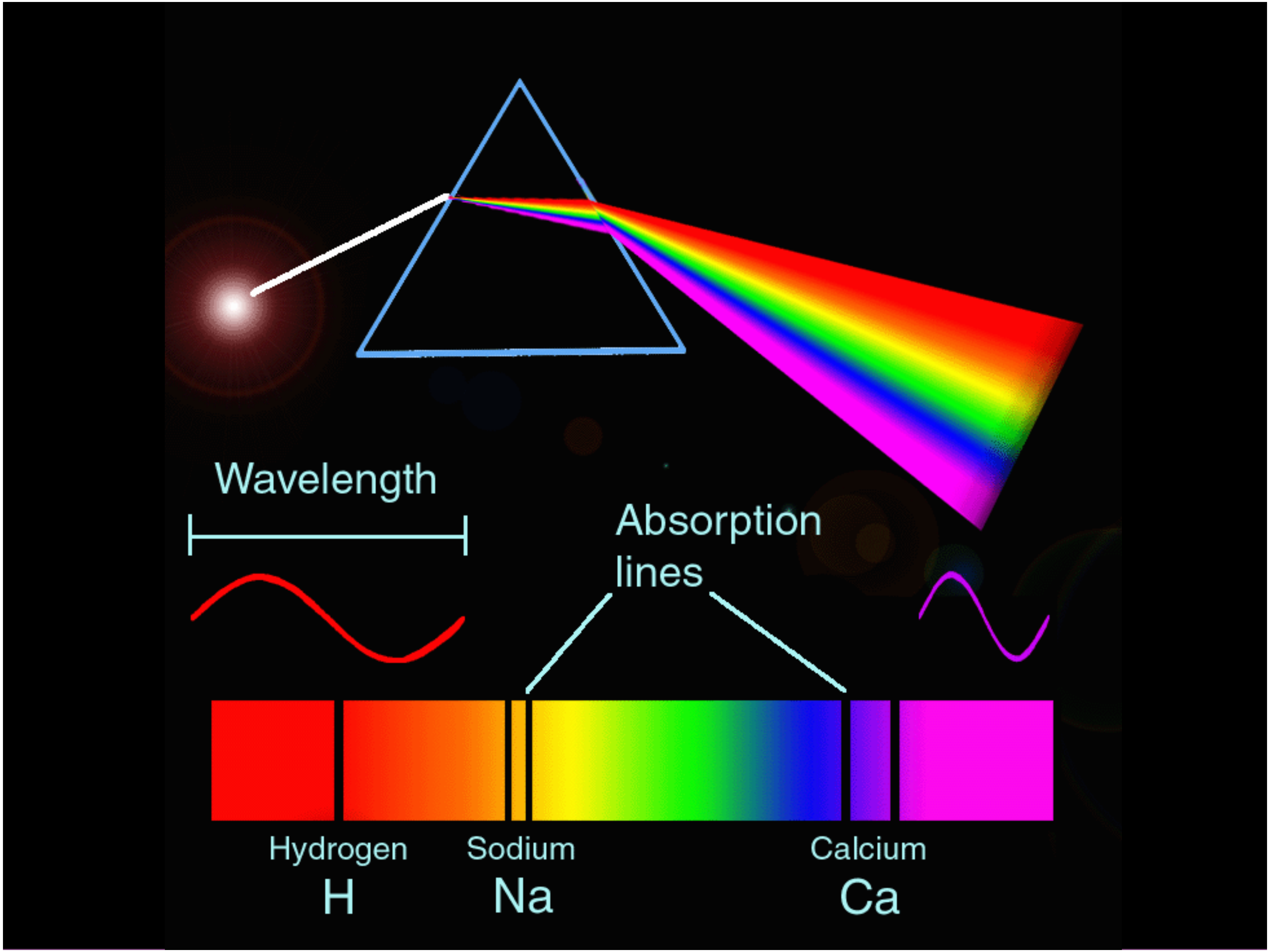
X-ray absorption spectroscopy
-brief description

What is spectroscopy?

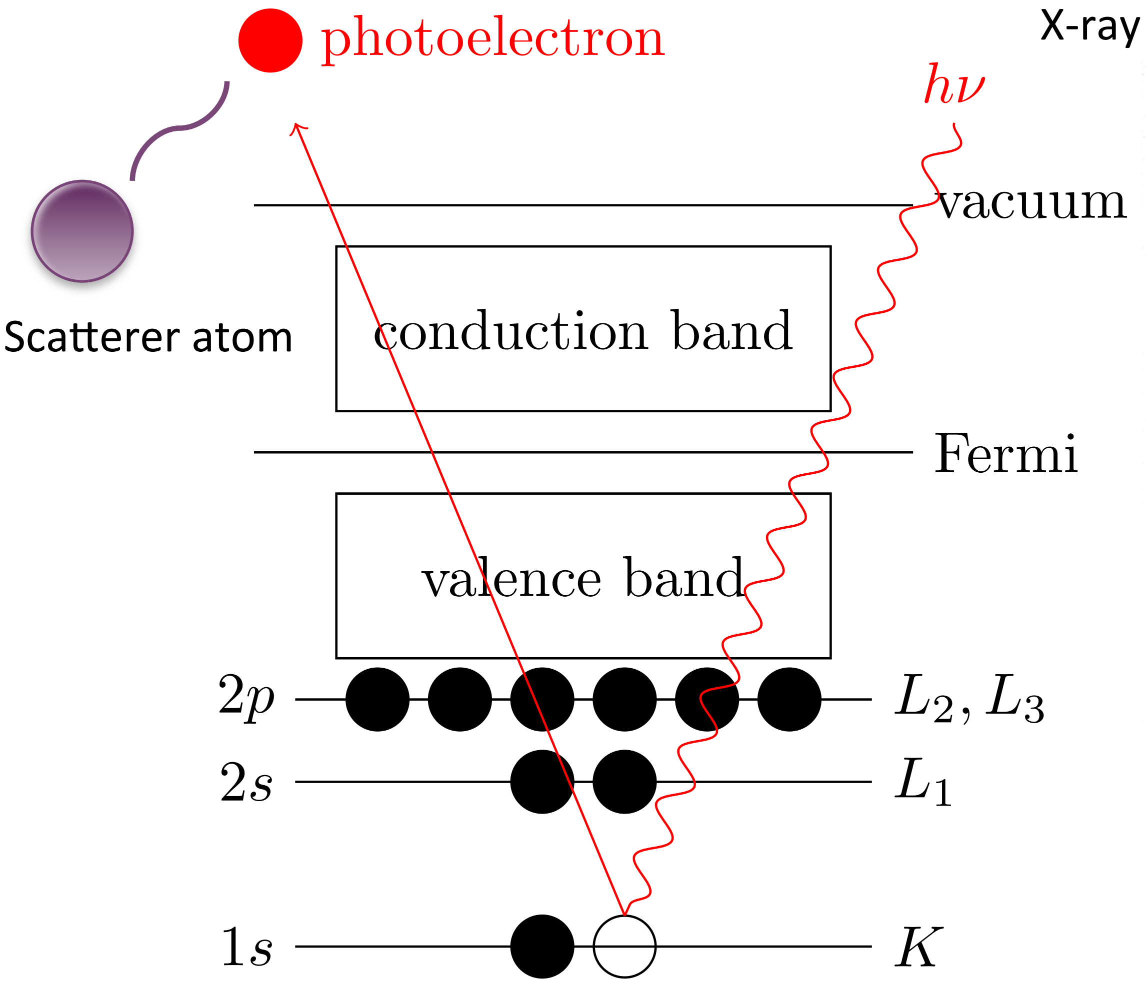
The study of molecular structure and dynamics through the absorption, emission, and scattering of light



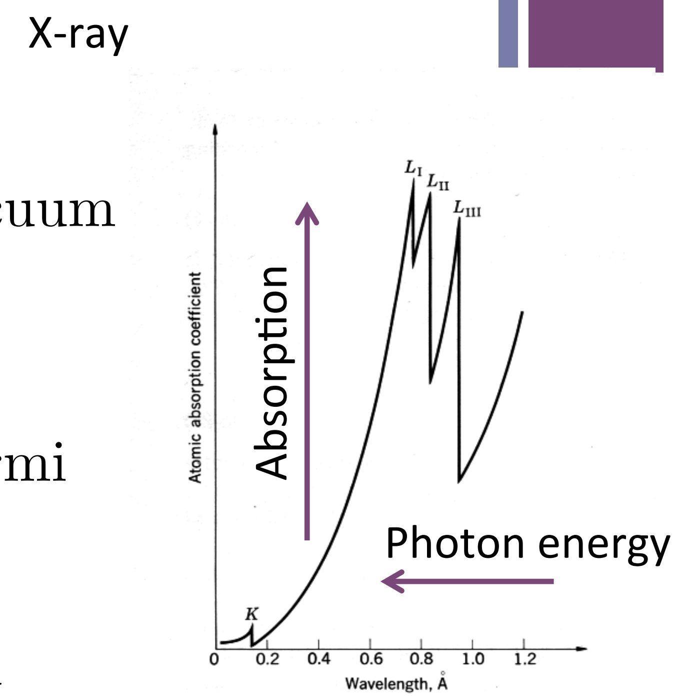
Astronomers used the "spectroscope", to observe atomic spectra.
Norman Lockyer found helium in the solar spectrum in 1868.


Wavelength
Absorption lines
Hydrogen
H
Sodium
Na
Calcium
Ca

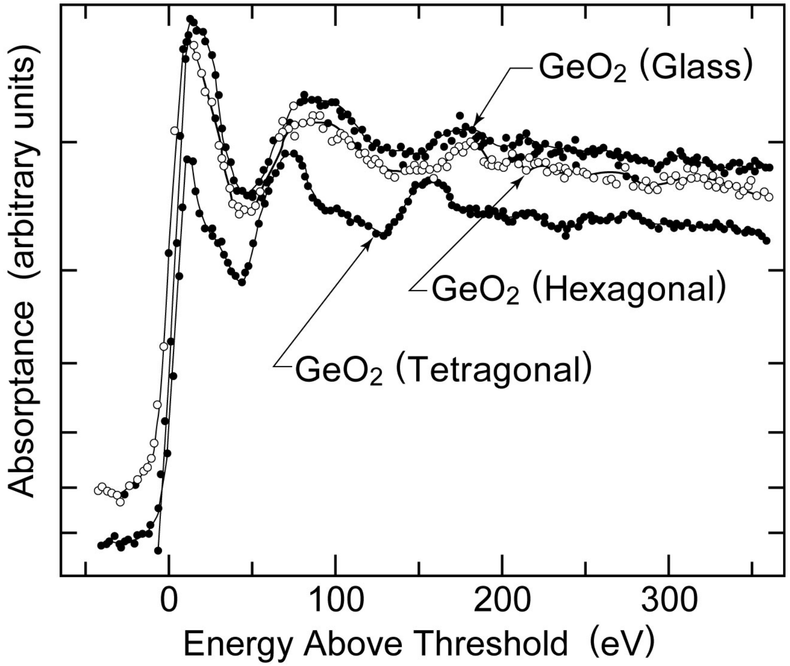
+ X-ray aborption spectroscopy -schematic presentation



Mathias Laurin

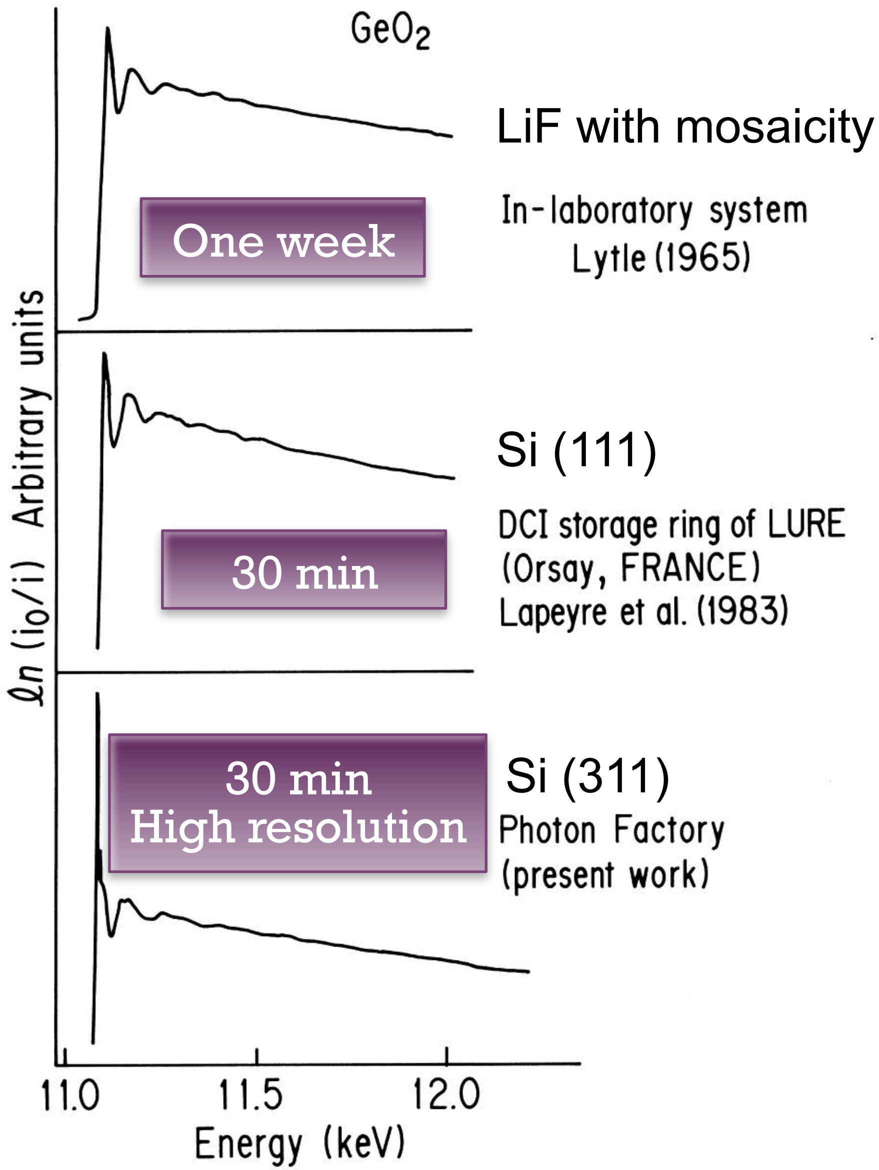


Power of Synchrotron radiation



Nelson et al., Phys. Rev. 127, 2025 (1962).
1 week for one spectrum, tube x-ray source + diffractometer

Synchrotron radiation changed quality & Quality of XAS



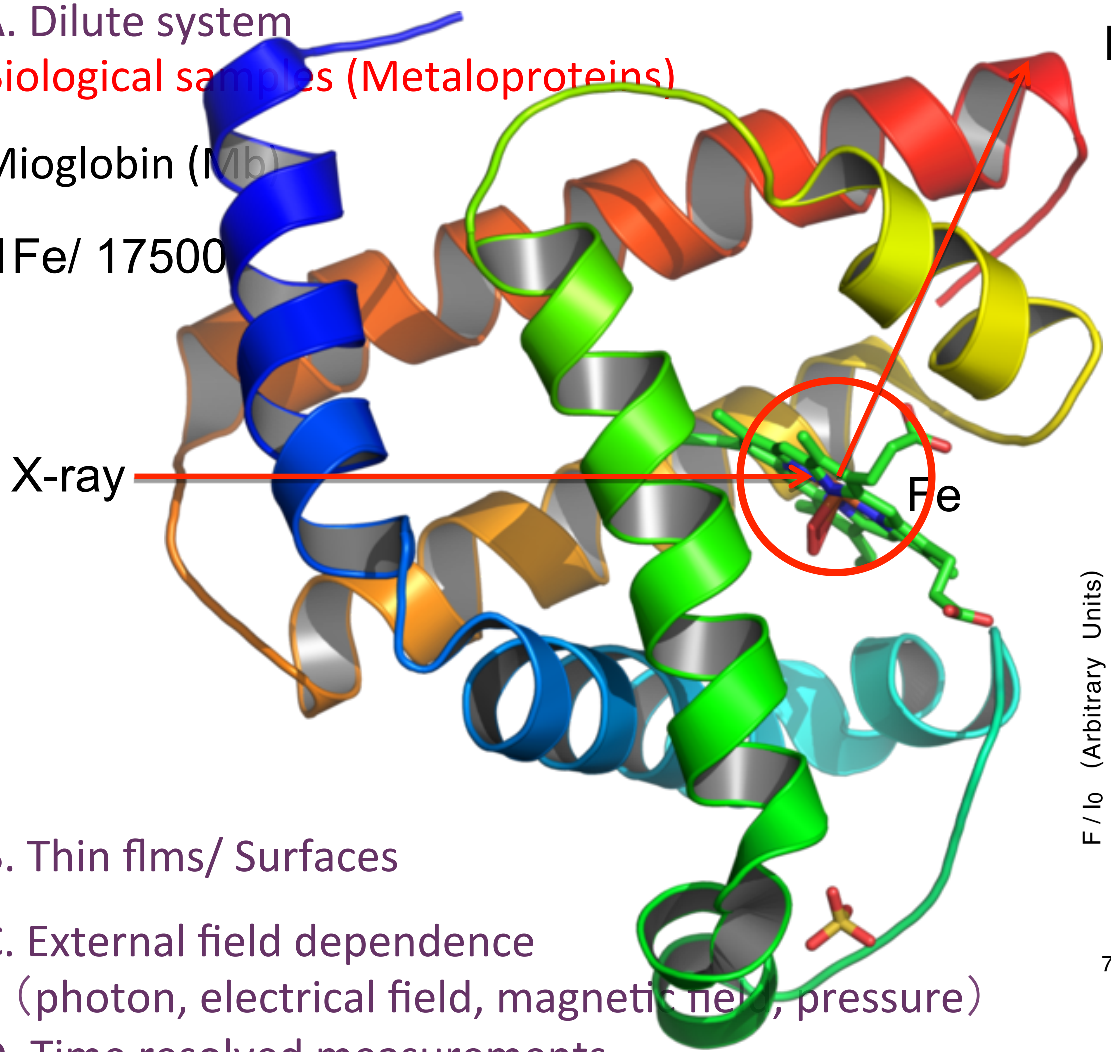
Fluorescence-XAS probing a dilute system

A. Dilute system

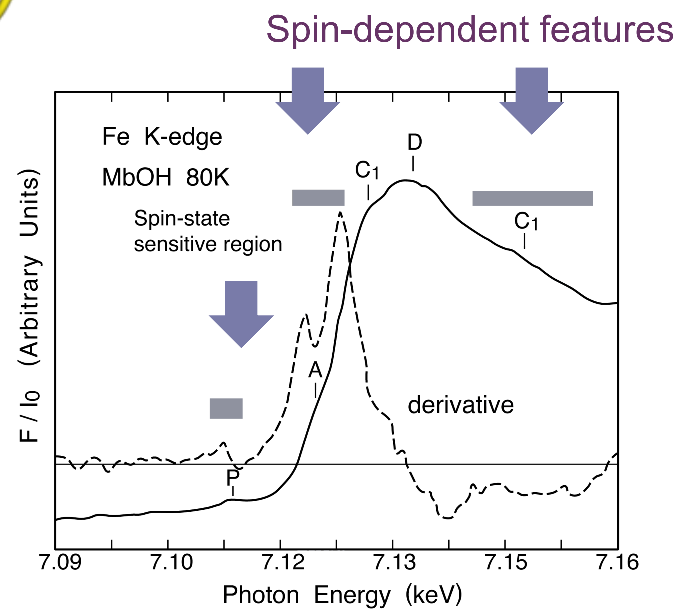
Biological samples (Metaloproteins)

Mioglobin (Mb)

1Fe/ 17500



- **SPIN-STATES**
- **LOCAL STRUCTURE**
- **FUNCTION**



Spin-dependent XANES of MbOH

Oyanagi et al., J. Phys. Soc. Jpn. 56, 1987, 3381.

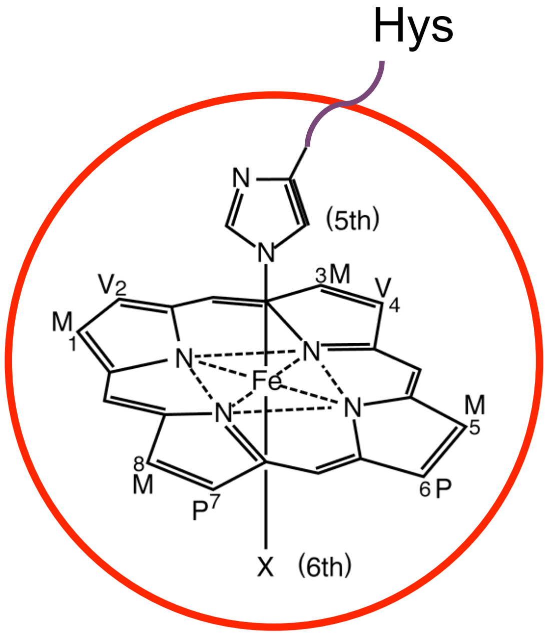
B. Thin flms/ Surfaces

C. External field dependence
（photon, electrical field, magnetic field, pressure）

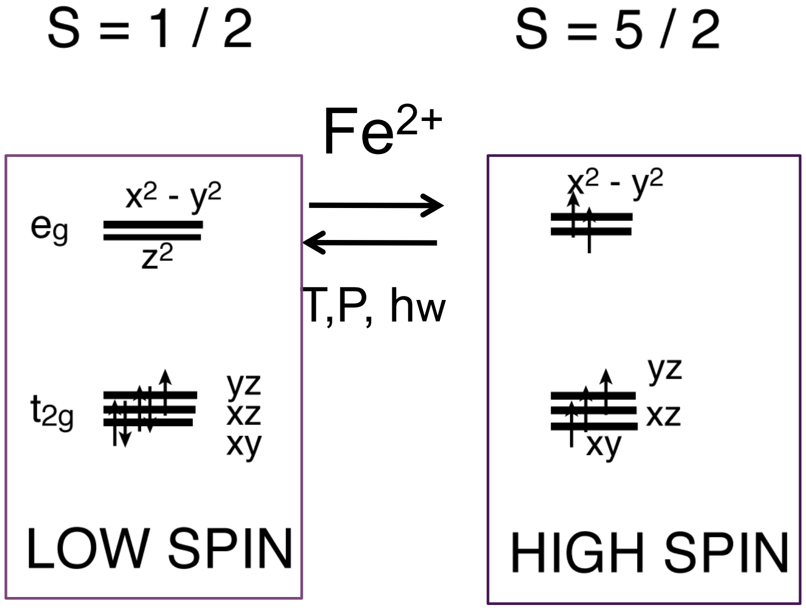
D. Time resolved measurements

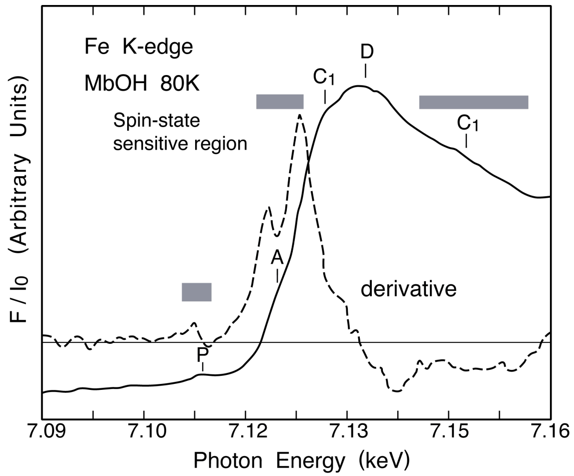
E. Small volume, nanocrystals, solutions

+ Local structure and spin states in MbOH

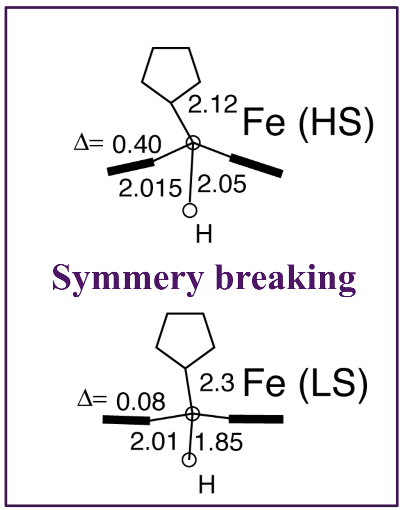


Fe's 5th bound to Hs、6th is active site (oxygen bind





Oyanagi et al., J. Phys. Soc. Jpn. 56, 1987, 3381.



In HS, Fe is popped out by 0.4A

In LS, Fe in the heme plane

Spin-dependent full mulitiple scattering
S. Della Longaet al. J. Biol. Chem. 272, 21025 (1996).

Symmetry breaking to lower ligand field

Synchrotron radiation

Donuts proliferating the world
What are they?

Synchrotron radiation

3[rd] generation (3G) synchrotron radiation facilities

Started from a "mega" facility
Now proliferating as a "compact" machine

ALBA

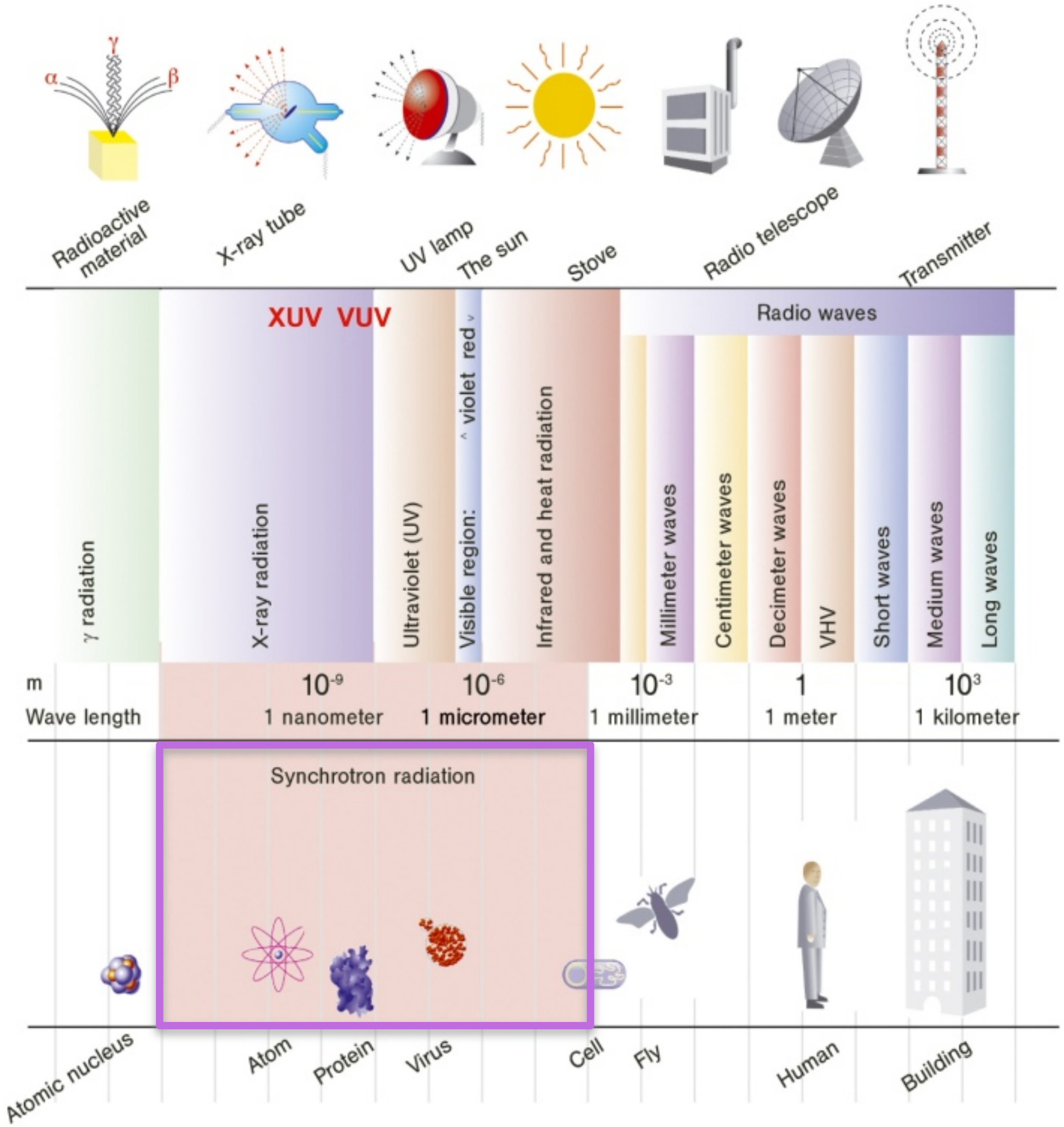
ESRF

Apple mother ship

Wavelength and object size

Wavelength

Object



DESY Hamburg

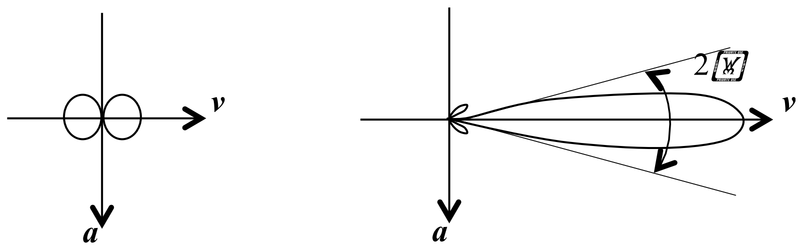
+ Synchrotron radiation –relativistic radiation

Normal radiation (b 0) and relativistic radiation (b 1)

$$\beta \approx 0 \quad dP/d\Omega \approx 1-\sin^2\theta$$

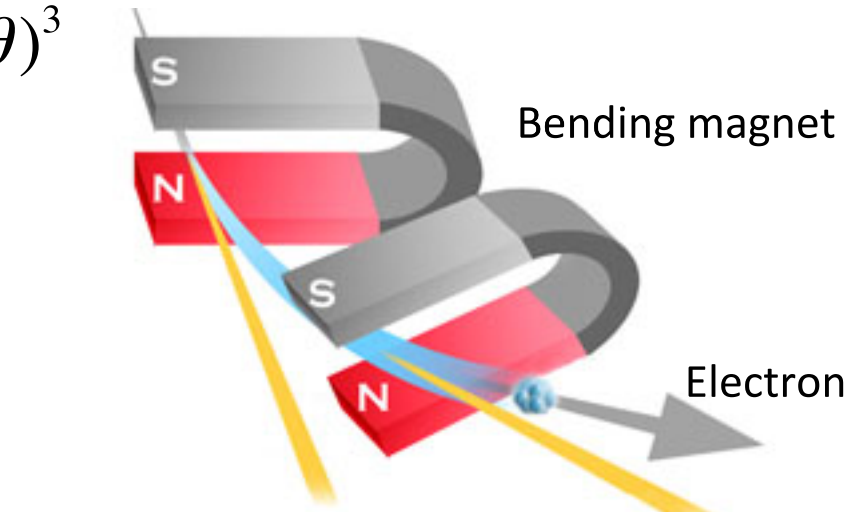
$$\beta \approx 1 \quad dP/d\Omega \approx 1/(1-\cos\theta)^3$$

$$\Psi \approx 1/\gamma = \sqrt{1-\beta^2}$$



(a) ≈ 0 (b) ≈1

Bending magnet radiation

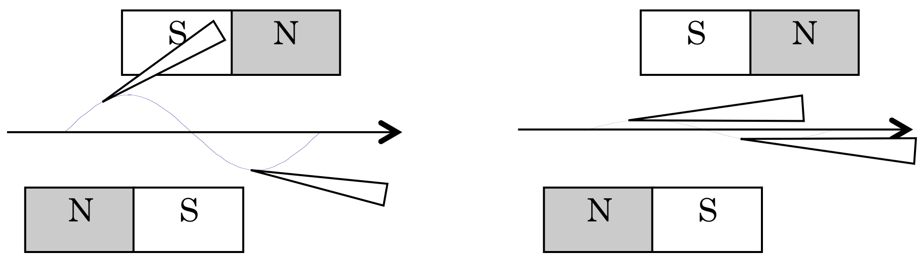


As electron velocity approaches c (that of light), radiation becomes highly directional, providing a bright white x-ray beam (synchrotron radiation)

Undulator and wiggler

$$K = \frac{eB_{\max}\lambda_o}{2\pi m_o c} = 0.934 B_{\max}[\mathrm{T}]\lambda_o[\mathrm{cm}]$$

B_{max} Maximum flux density, l_0 Period length

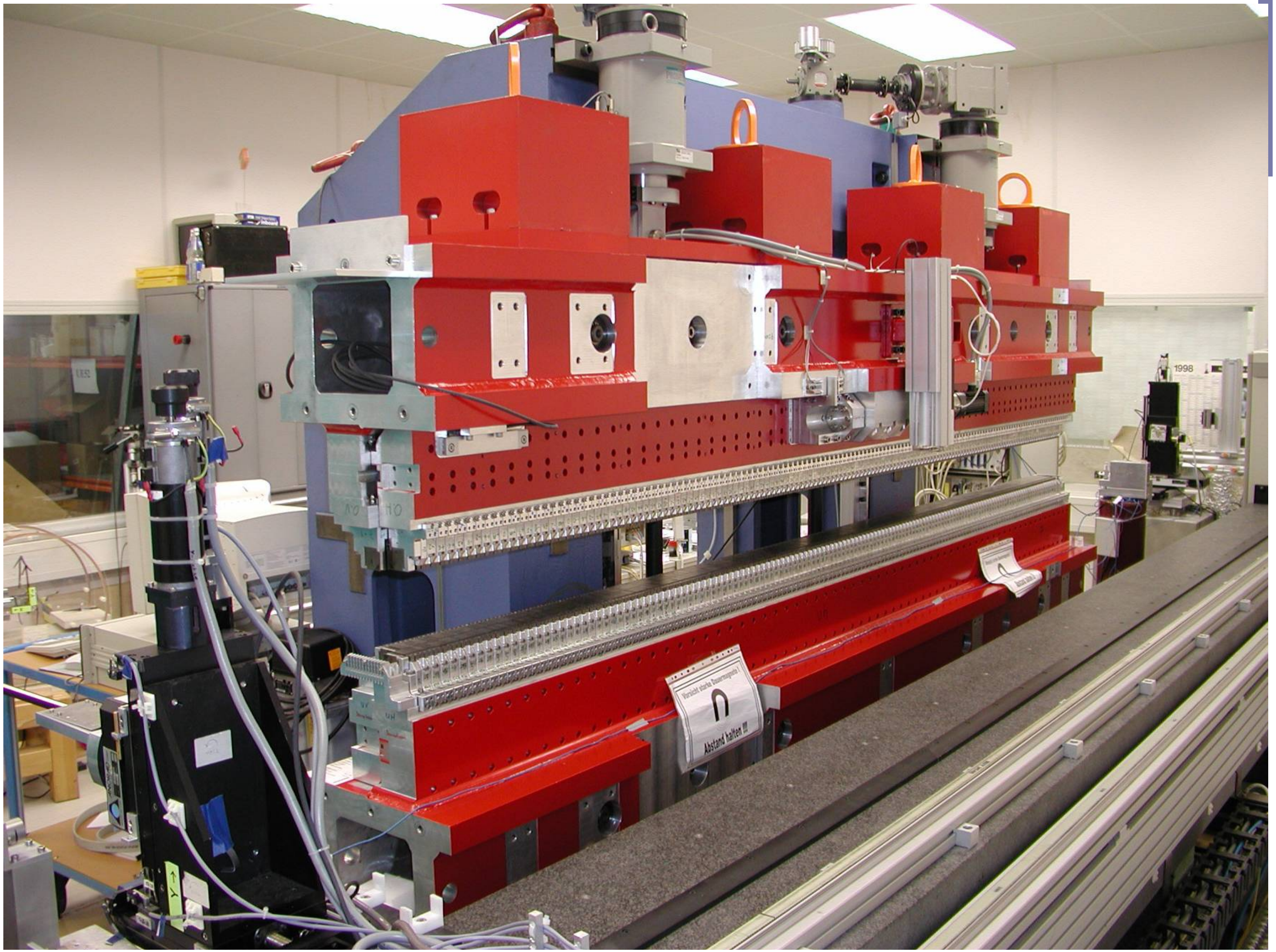


Wiggler (K >>1)   Undulator (K <<1)

High magnetic field (K >>1) — N-pole wiggler radiation enhances brilliance by N
Produces white x-ray but high heat load

Low magnetic field (K <<1) — Quasi-monochromatic high brilliance beam
Less heat load (high power density)

Undulator



@BESSY

Brilliance

Brilliance

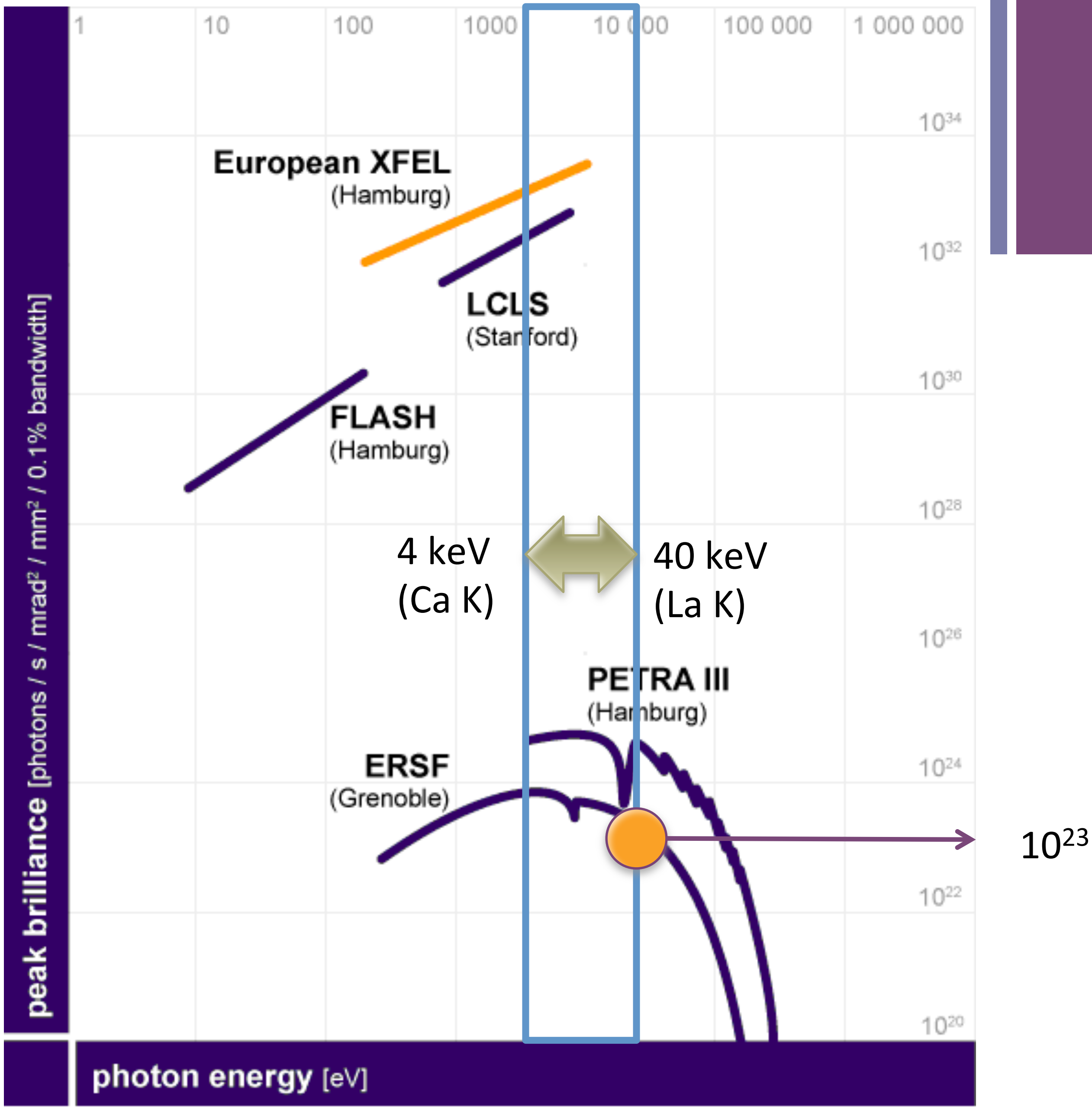
10^{23}

Phtons/s
/mrad²
/mm²
/0.1% bandwidth

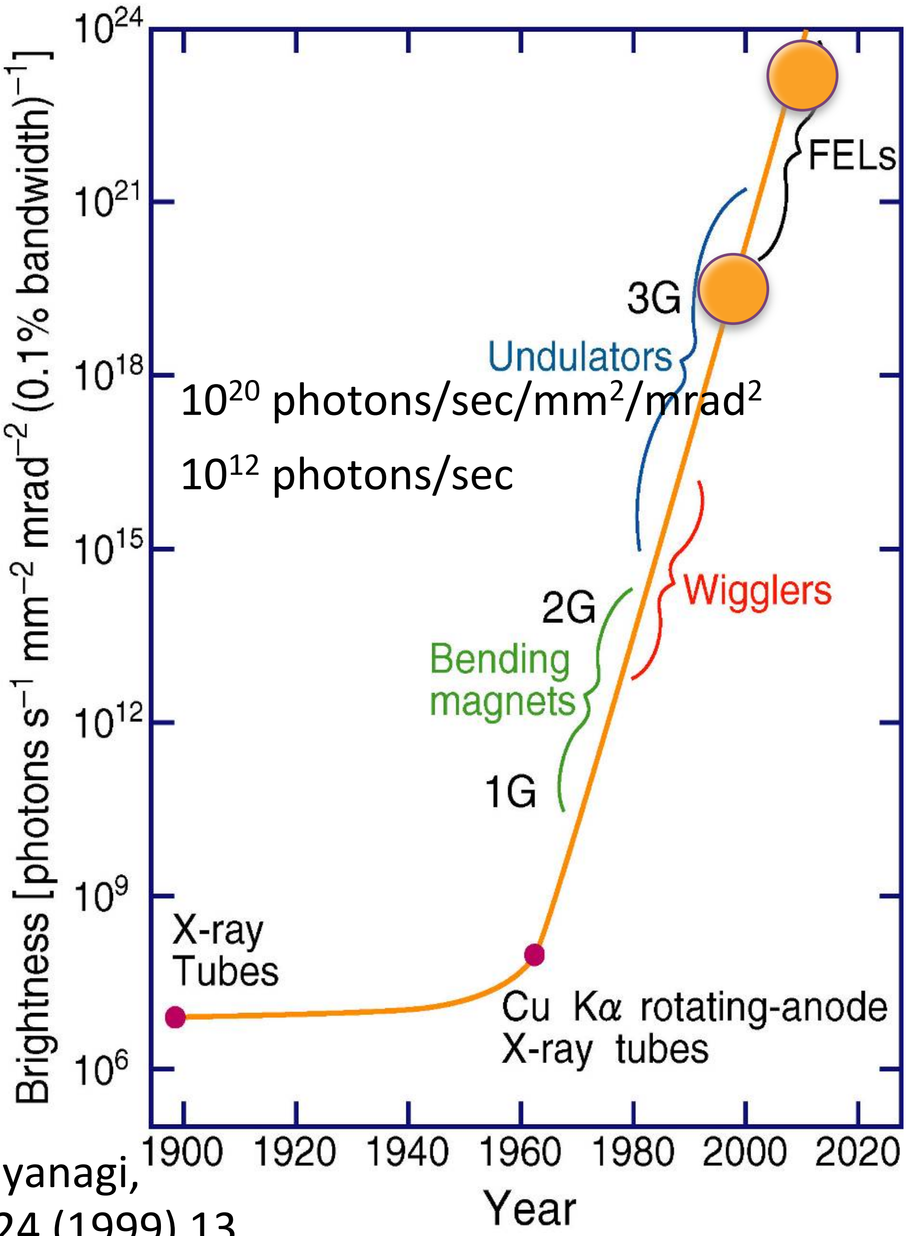
Flux

10^{12}

Phtons/s



Moore's law in Synchrotron Radiation



Montano and Oyanagi, MRS BULLETIN 24 (1999) 13.

We are here!

Note that exponential growth is due to successive inventions of different devices

10^7 times brighter beam in 30 years

NO EXPONENTIAL IS FOREVER...

Gordon E. Moore

Omittedtopics

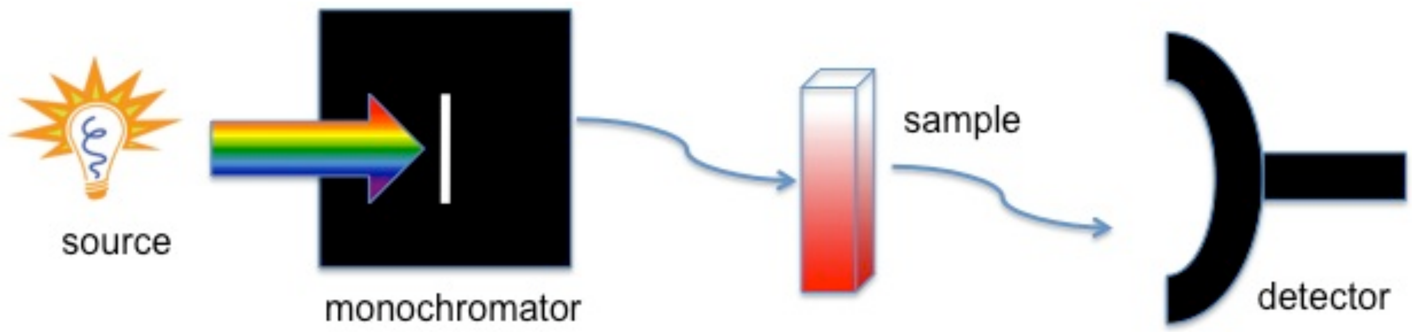
VUV beamline
Soft x-ray beamline

Beamline

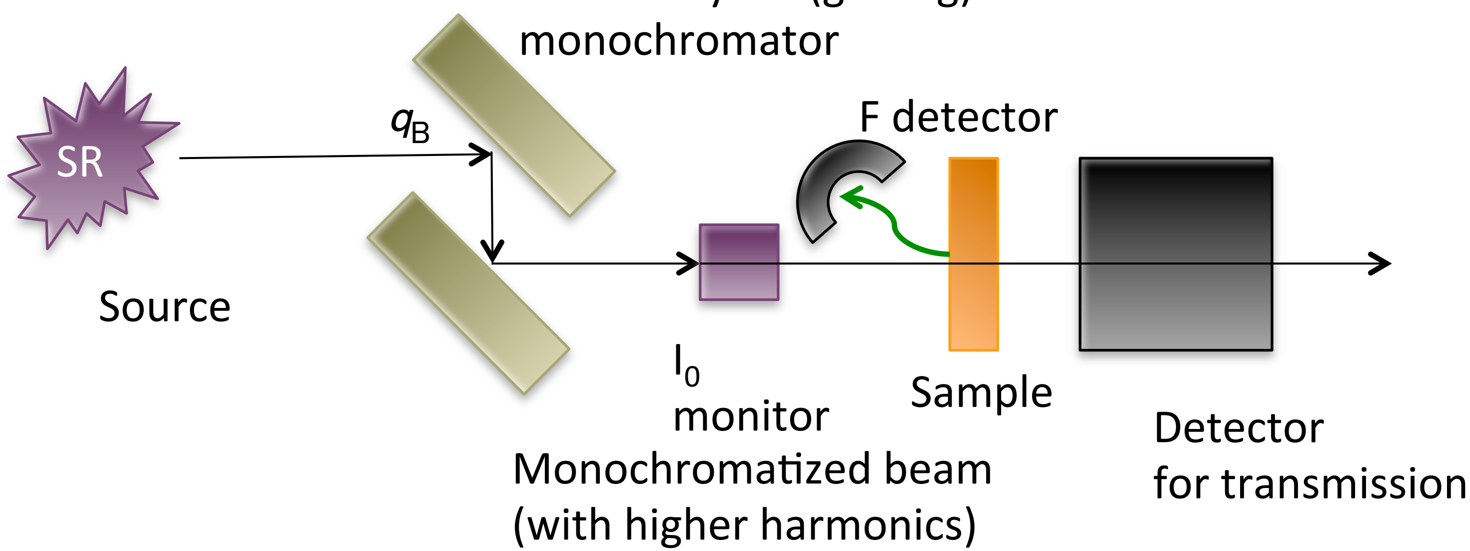
Monochromators and mirrors

XAS measurement –fundamental setup

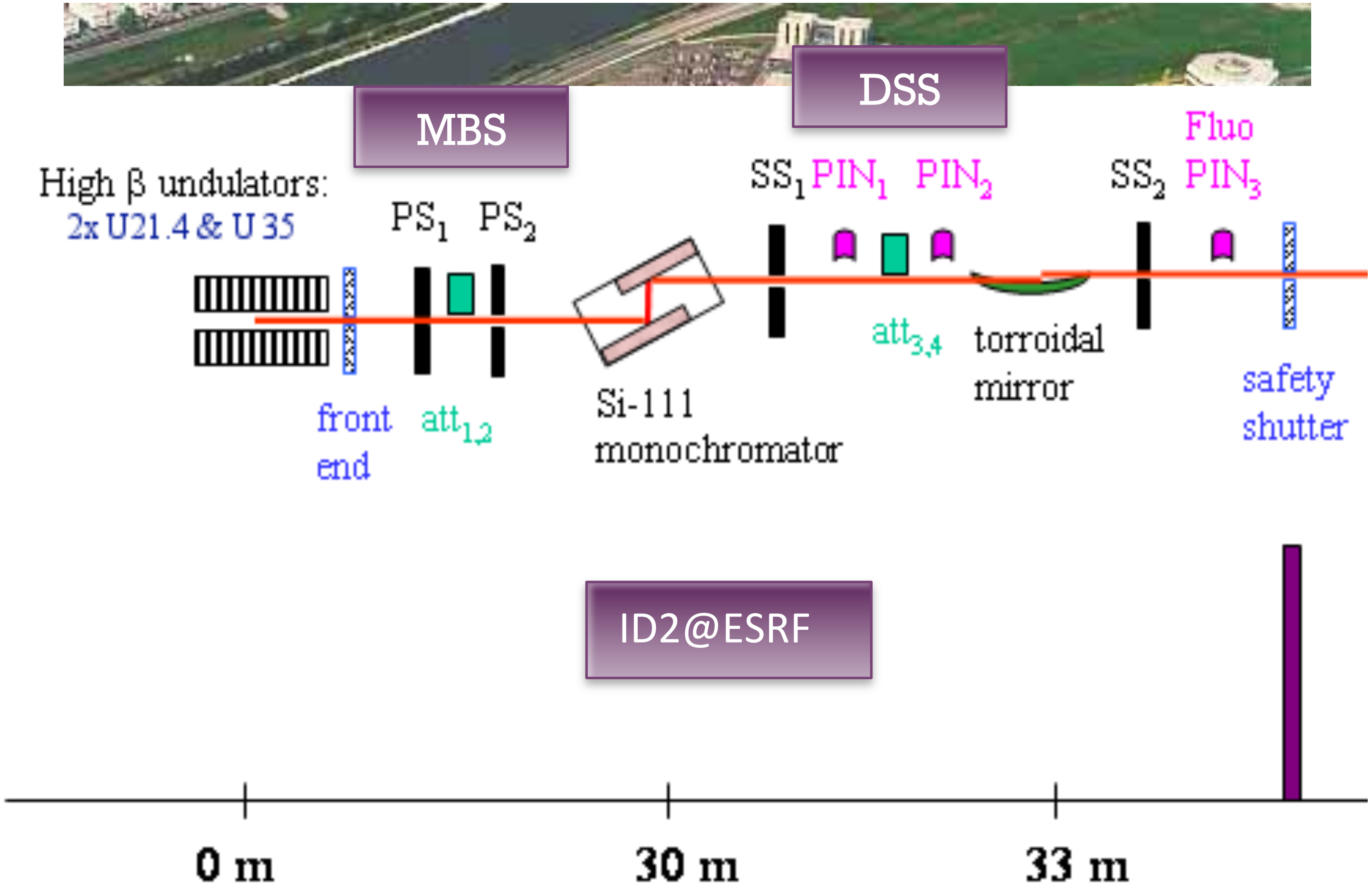
SINGLE BEAM



SR beamline



+ Storage ring and beam transport (beamline)



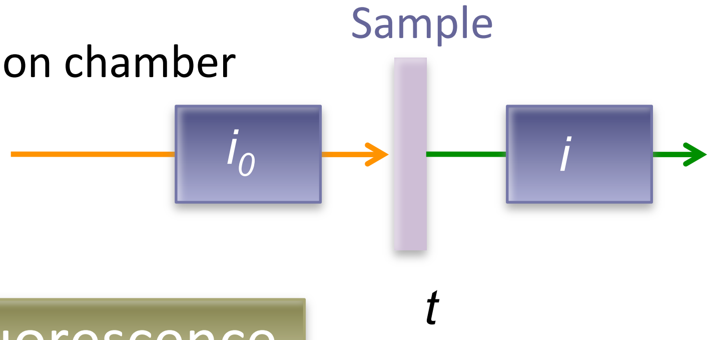
+ X-ray Absorption Spectroscopy -how to measure

XANES, EXAFS, …

Most fundamental technique is a transmission mode

Transmission

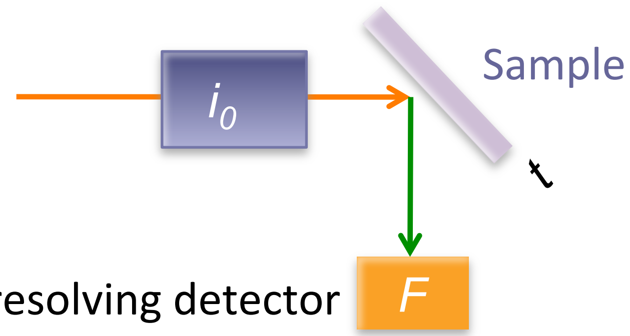
Ionization chamber



$$mt\ (E) = ln\ (i_0 / i)$$

You measure attenuated beam intensity, that" exponentially" decreases

Fluorescence



Energy resolving detector

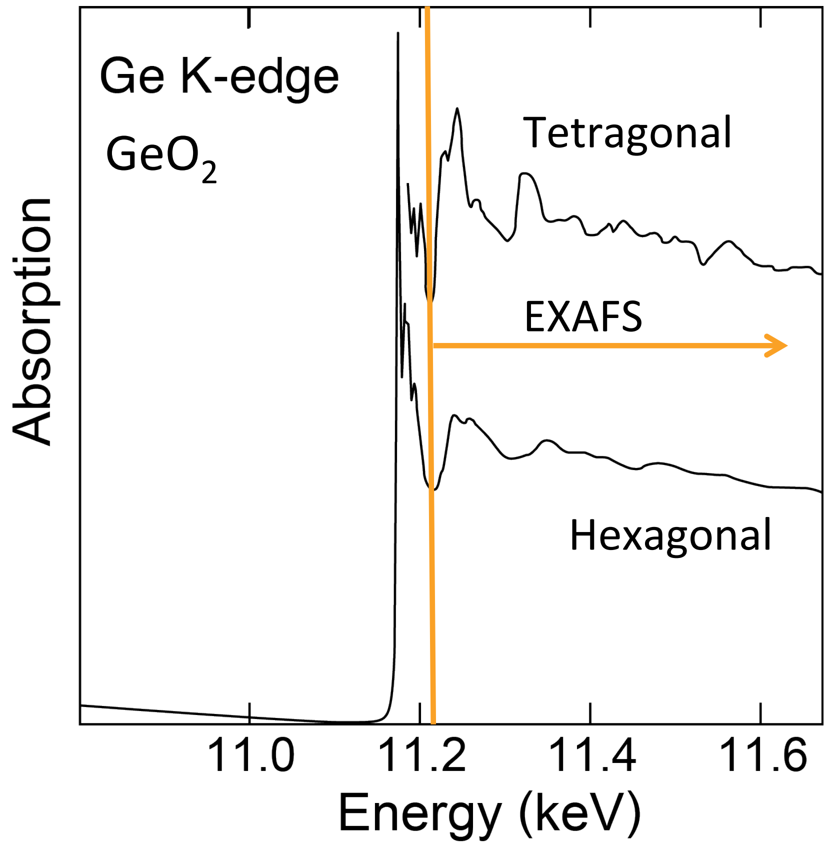
$$mt\ (E) = F / i_0$$

You measure emitted beam intensity
Which "linearly" proportional to conc.

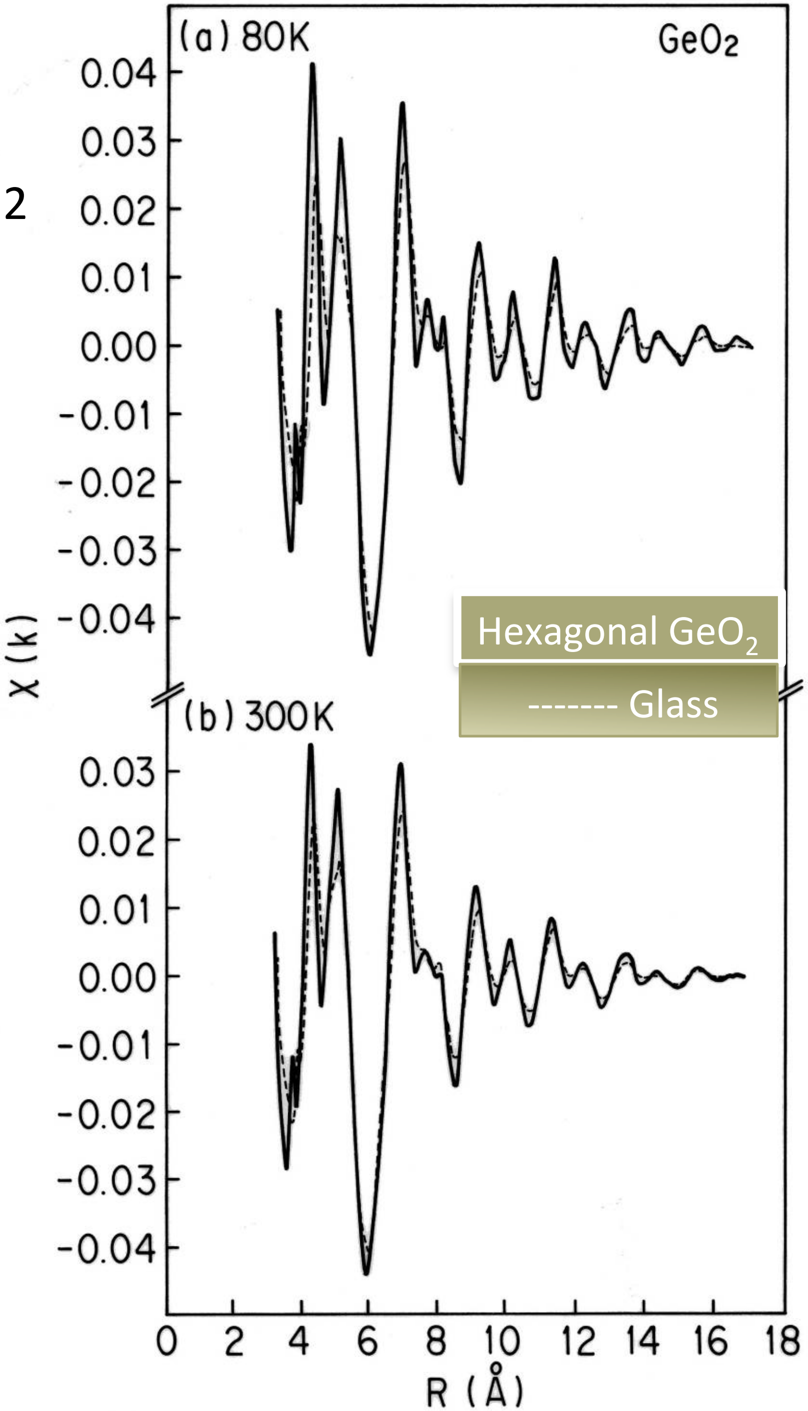
Dilute system
Impurities, surfaces, thin films

Example
- Crystalline and glassy GeO_2

Okuno et al.

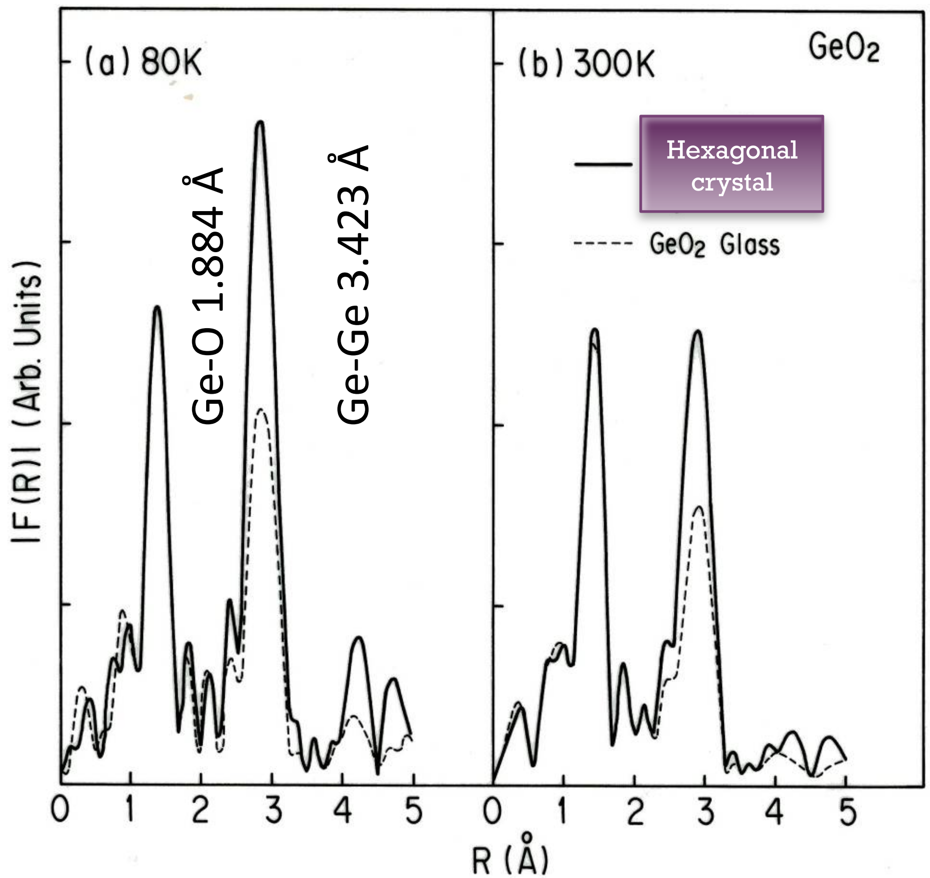


Si (311) monochromator, 10B@PF

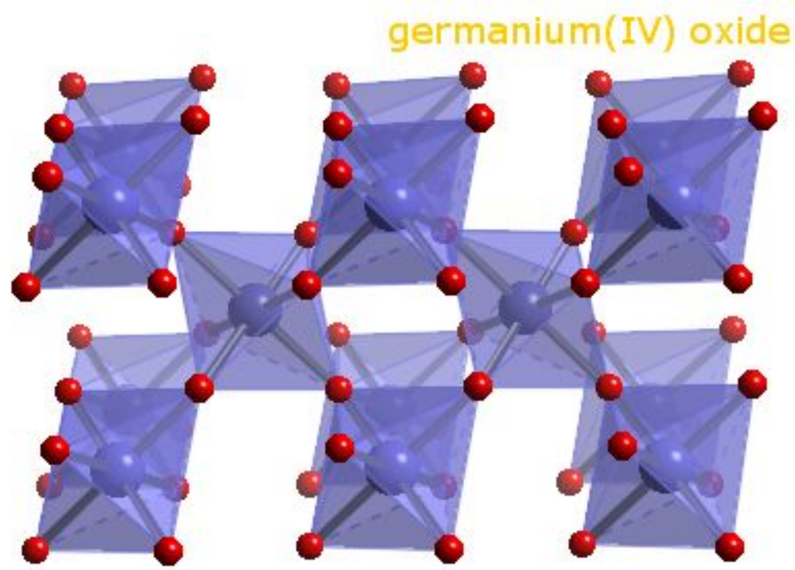


Fourier Transform -example

FT magnitude function for crystalline and glass GeO_2 Okuno et al.



Crystal structure (hexagonal)

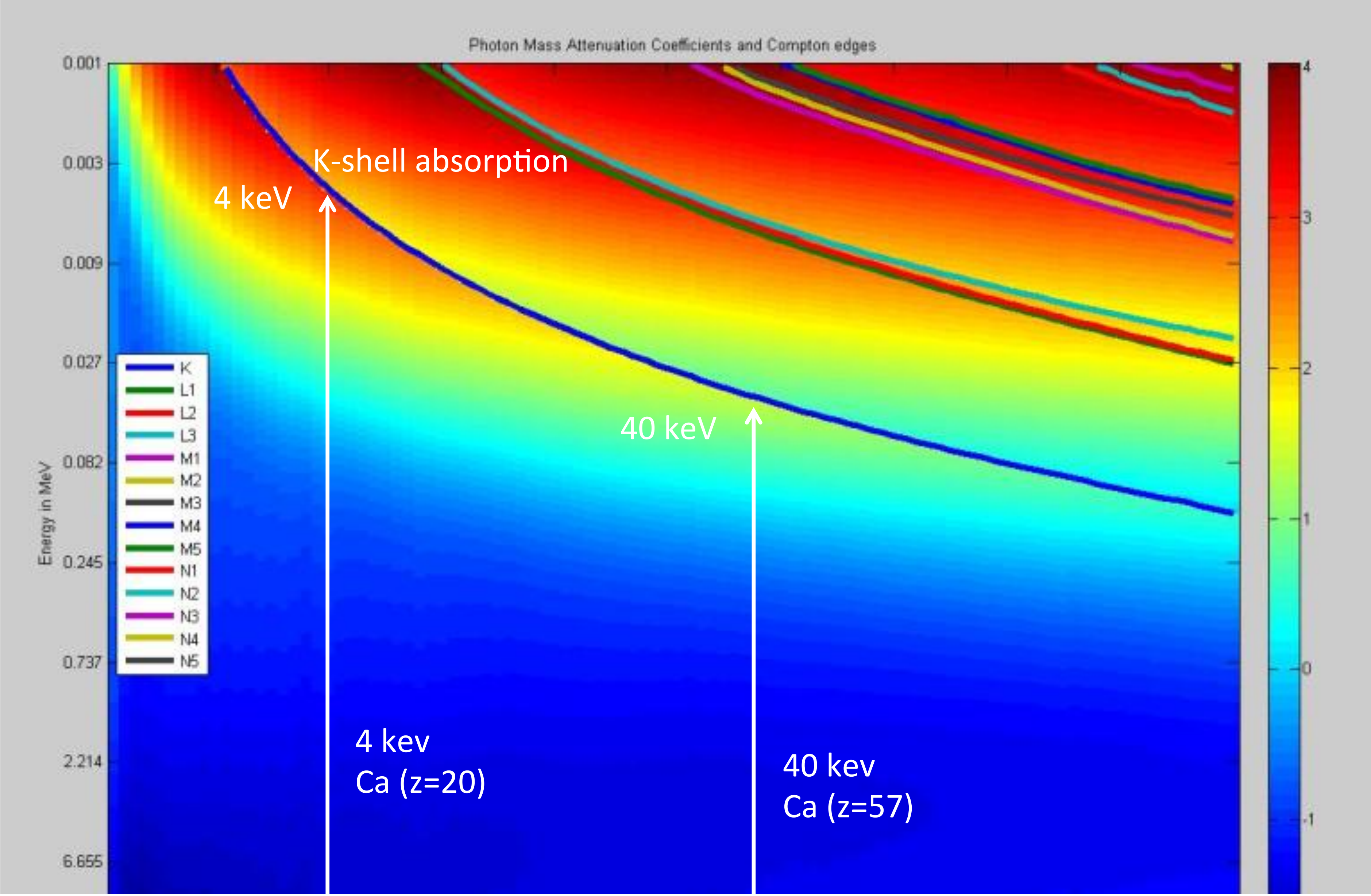


Acta Cryst. 17, 842 (1964)
Acta Cryst. B27, 2133 (1971)

Glass structure

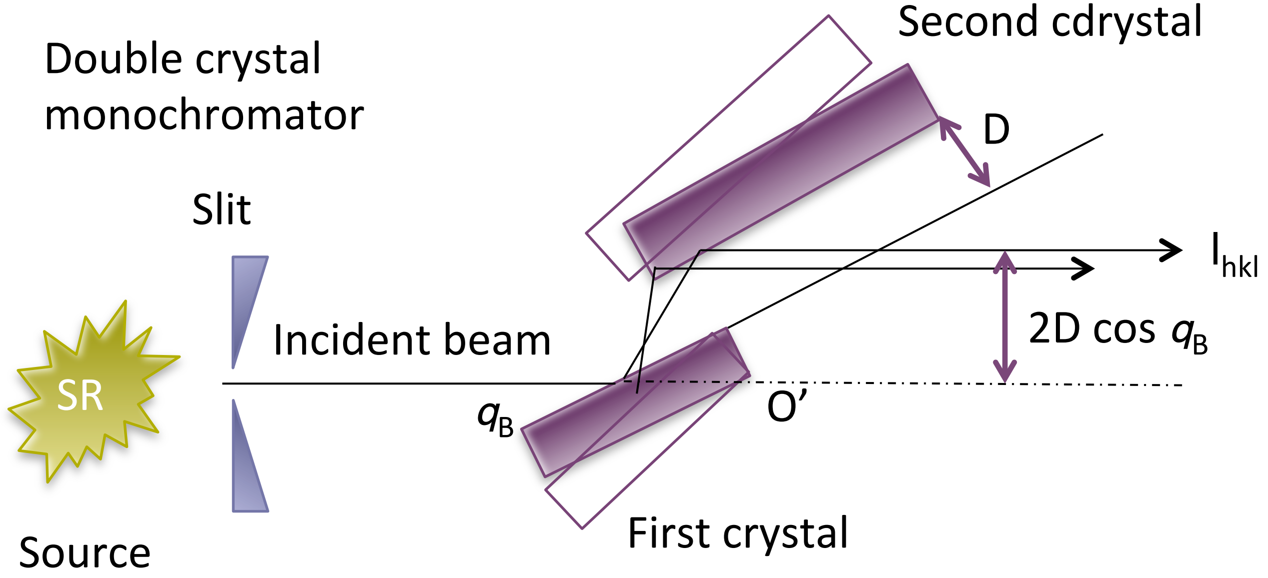
Short range order is close to the hexagonal crystal
Disorder in arrangement of GeO_4 units (connectivity)

X-ray absorption –atom and shell specific phenomena



+ Monochromator

Double crystal monochromator



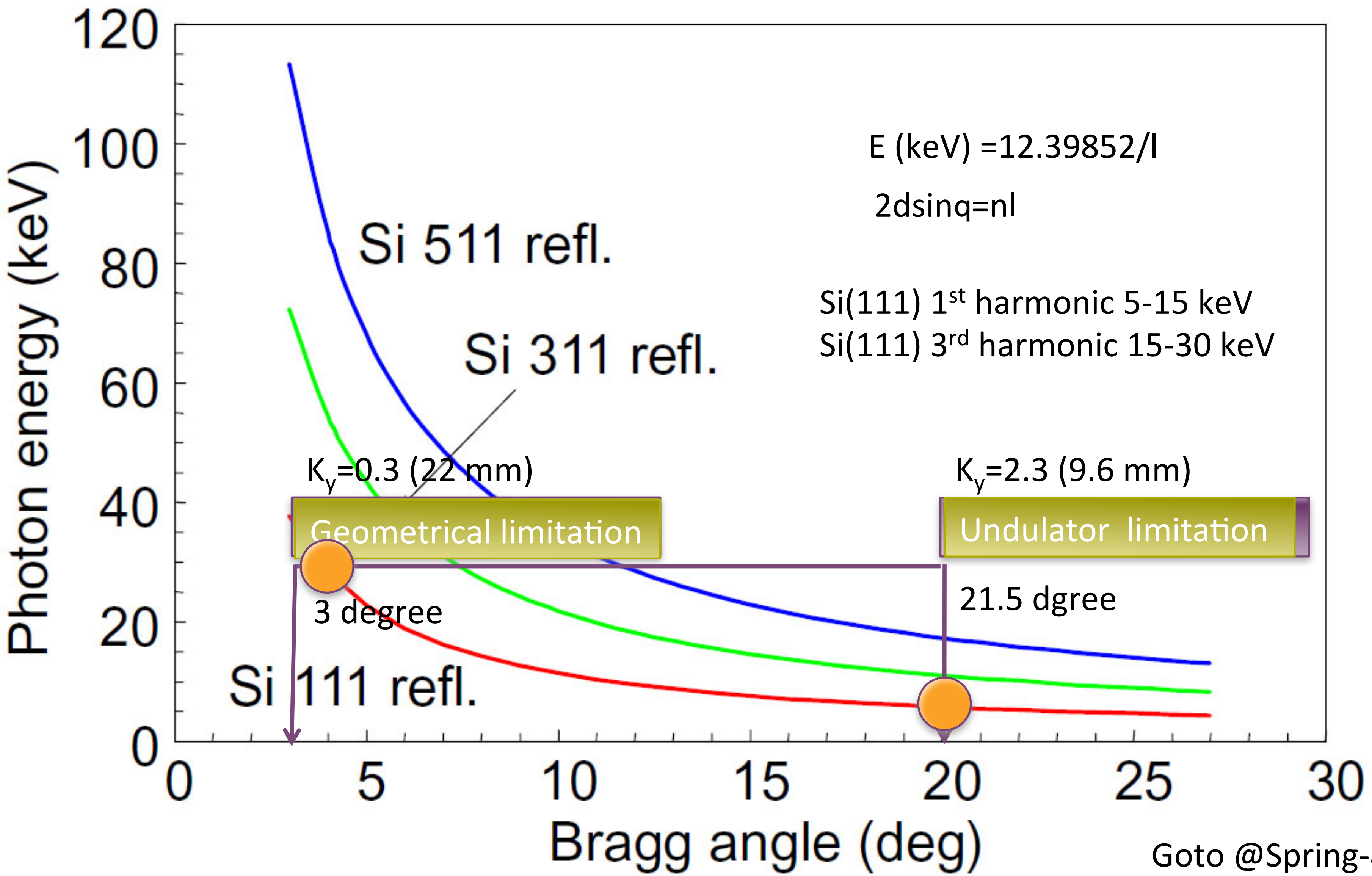
Energy scale

$$2d\sin\theta = n\lambda,\ d = 3.13551 \text{ for Si(111)}$$

$$E\ (\text{keV}) = 12.39852 / \lambda = 1.9771 / \sin\theta$$

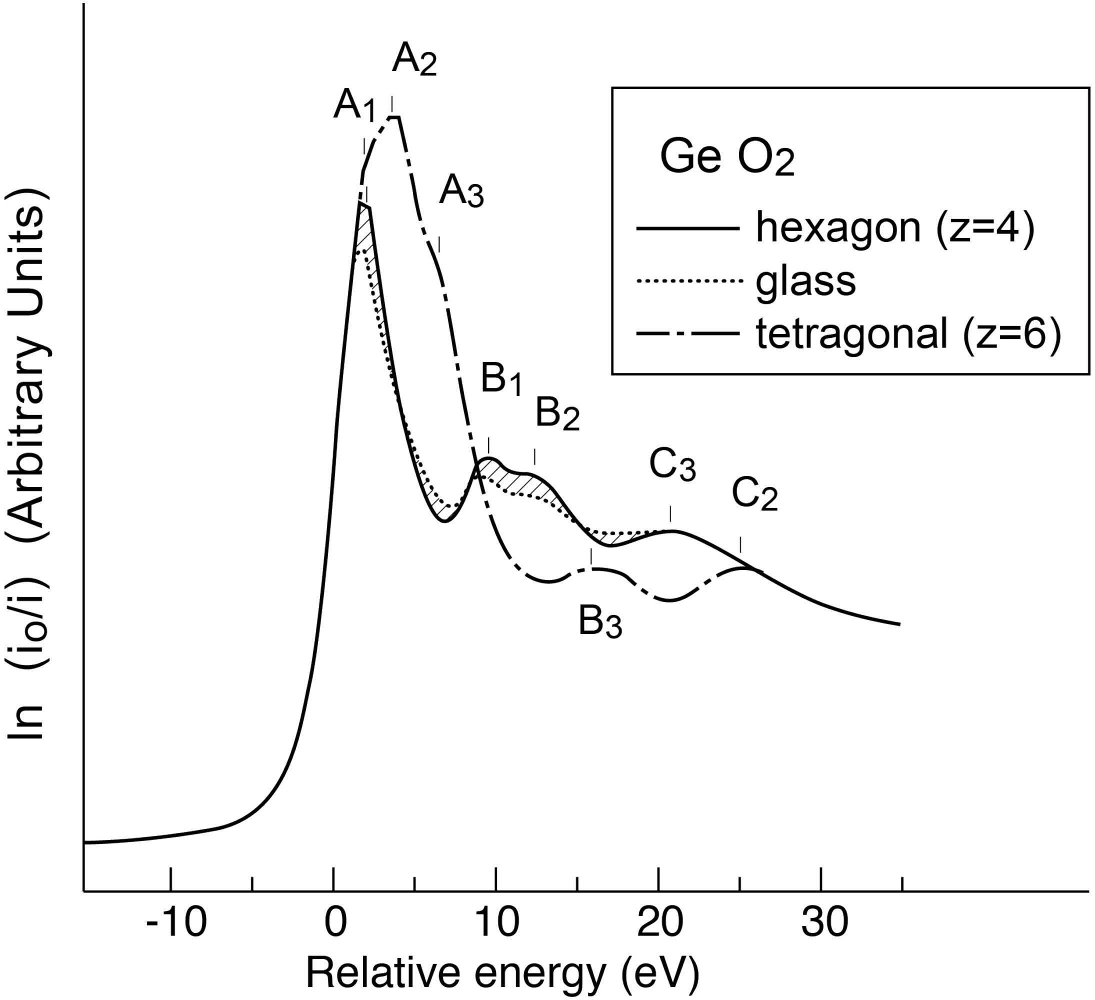
Spacing (*d*-value)	Crystal plane
1.3578 Å	Si (400)
3.1356 Å	Si(111)
1.6376 Å	Si(311)
1.0452 Å	Si(511)

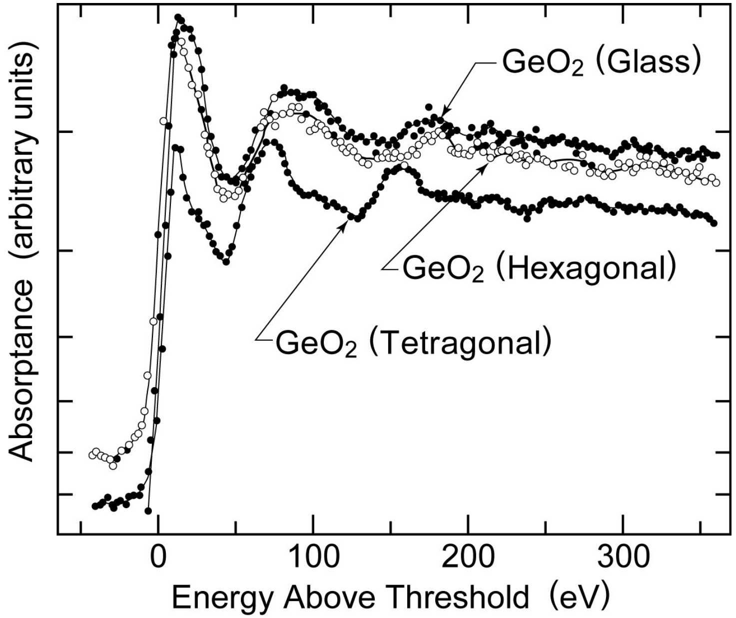
+ Monochromator –energy range



Goto @Spring-8

Example of XANES – why resolution?



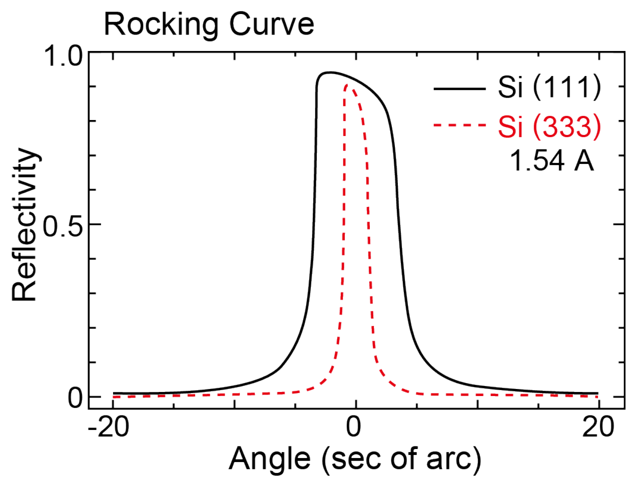


Si (311) monochromator   Okuno et al.

Nelson et al., Phys. Rev. 127, 2025 (1962).
1 week for one spectrum, tube x-ray source + diffractometer

Short range in glass sample is close to that of hexagonal crystal

+ Energy resolution



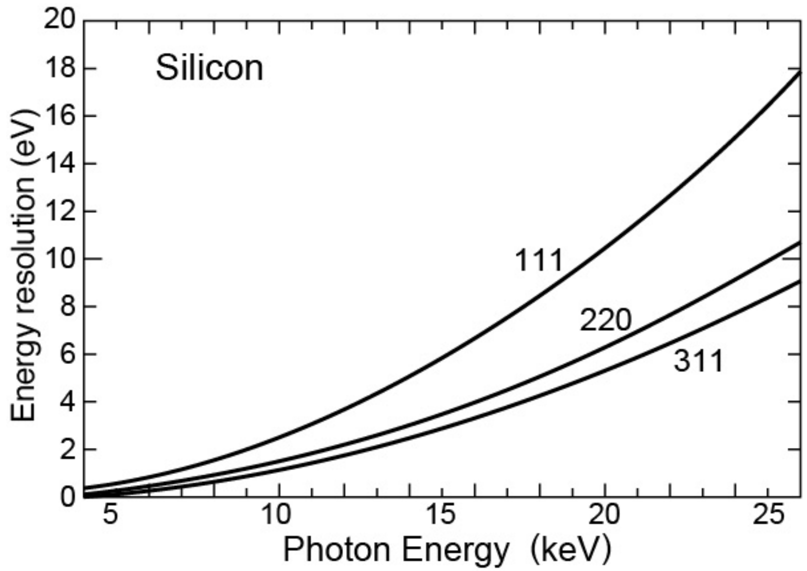
Energy resolution $\Delta E/E = \sqrt{(d\theta_g)^2 + (d\theta_w)^2}\ \cot\theta_B$

Geometrical resolution: $d\theta_g$

Darwin width: $d\theta_B$

$$d\theta_W = \frac{2e^3\lambda^2 |F|}{\pi m c^2 V \sin 2\theta_B} = 8\text{ sec. } (4\text{x}10^{-5}\text{ rad}) \text{ (Si(111), 9keV)}$$

Energy resolution is given as a convolution of geometrical resolution and Darwin width

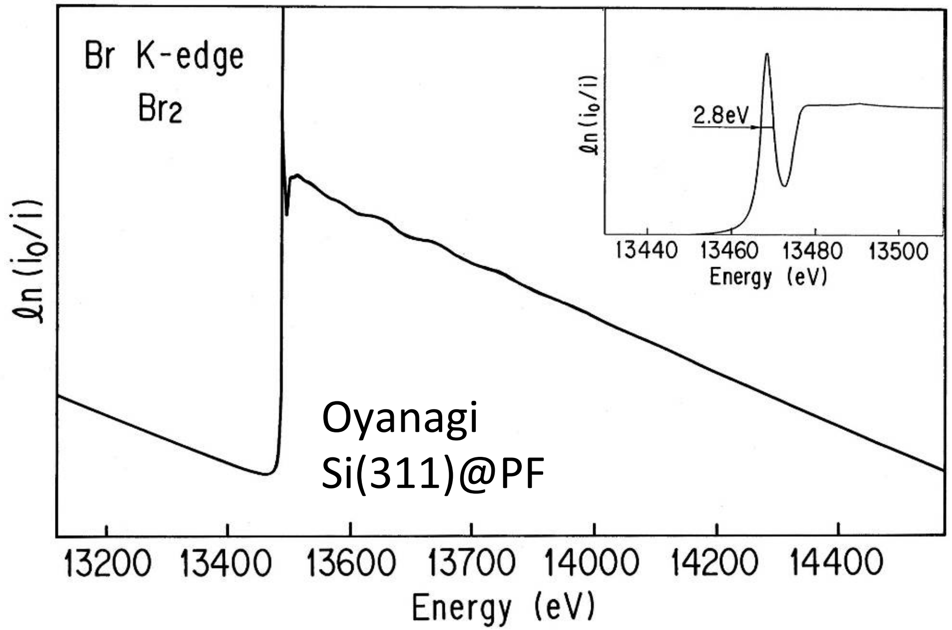


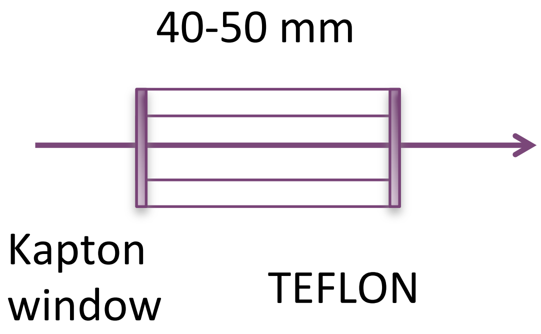
Guidelines

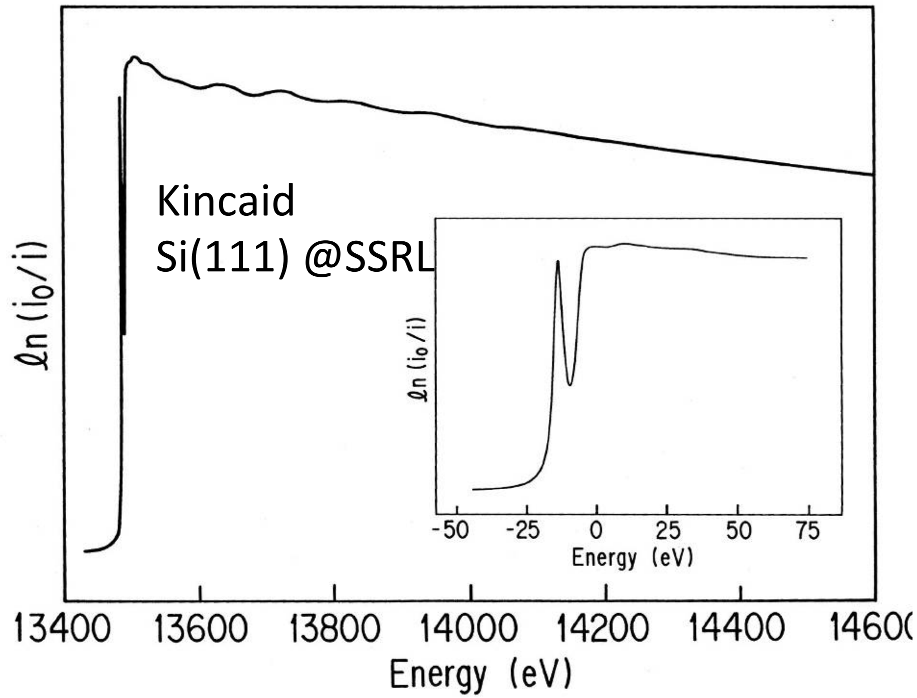
a. Bragg-angle-dependent energy resolution degrades with the increase of energy

b. Darwin width is smaller for high index planes, i.e. better resolution

Evidence for high energy resolution -bromine gas K-edge







How to evaluate the energy resolution

Br gas By K-edge (13.5 keV)

★Darwin width and angle-dependent term

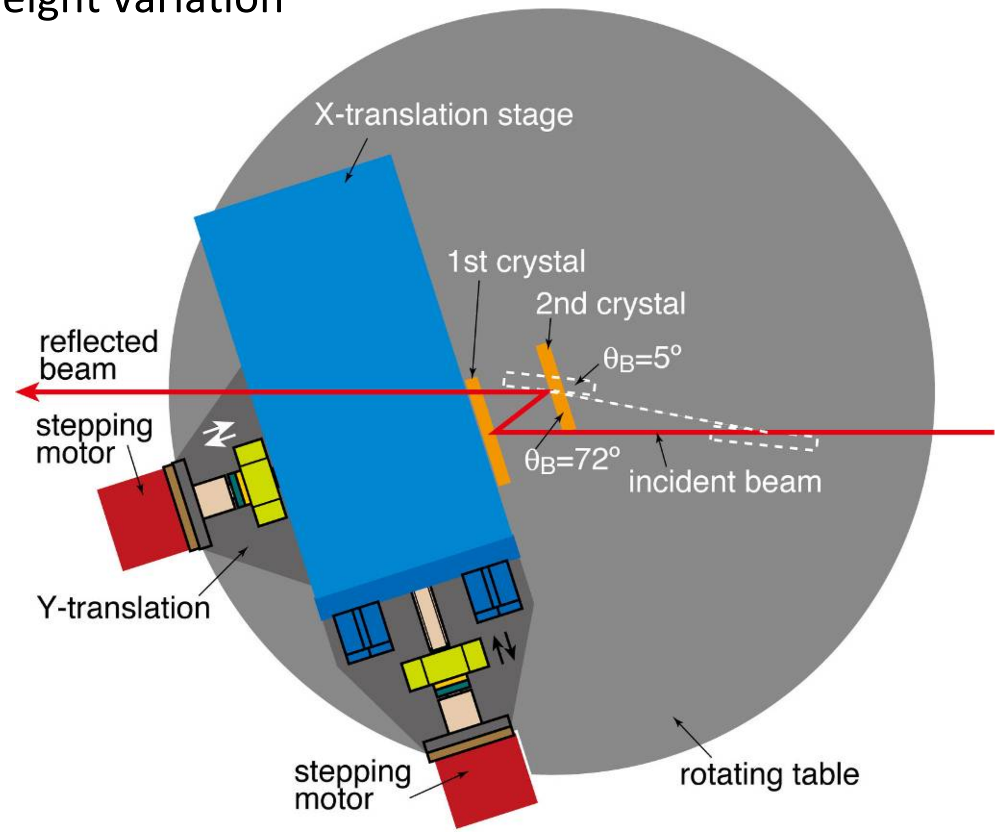
★Abberation caused by a focusing mirror placed in front of monochromator degrades energy resolution T. Matsushita@SSRL

+ Monochromator -mechanism

Rotating a double crystal results in beam height change

How to correct the beam height variation

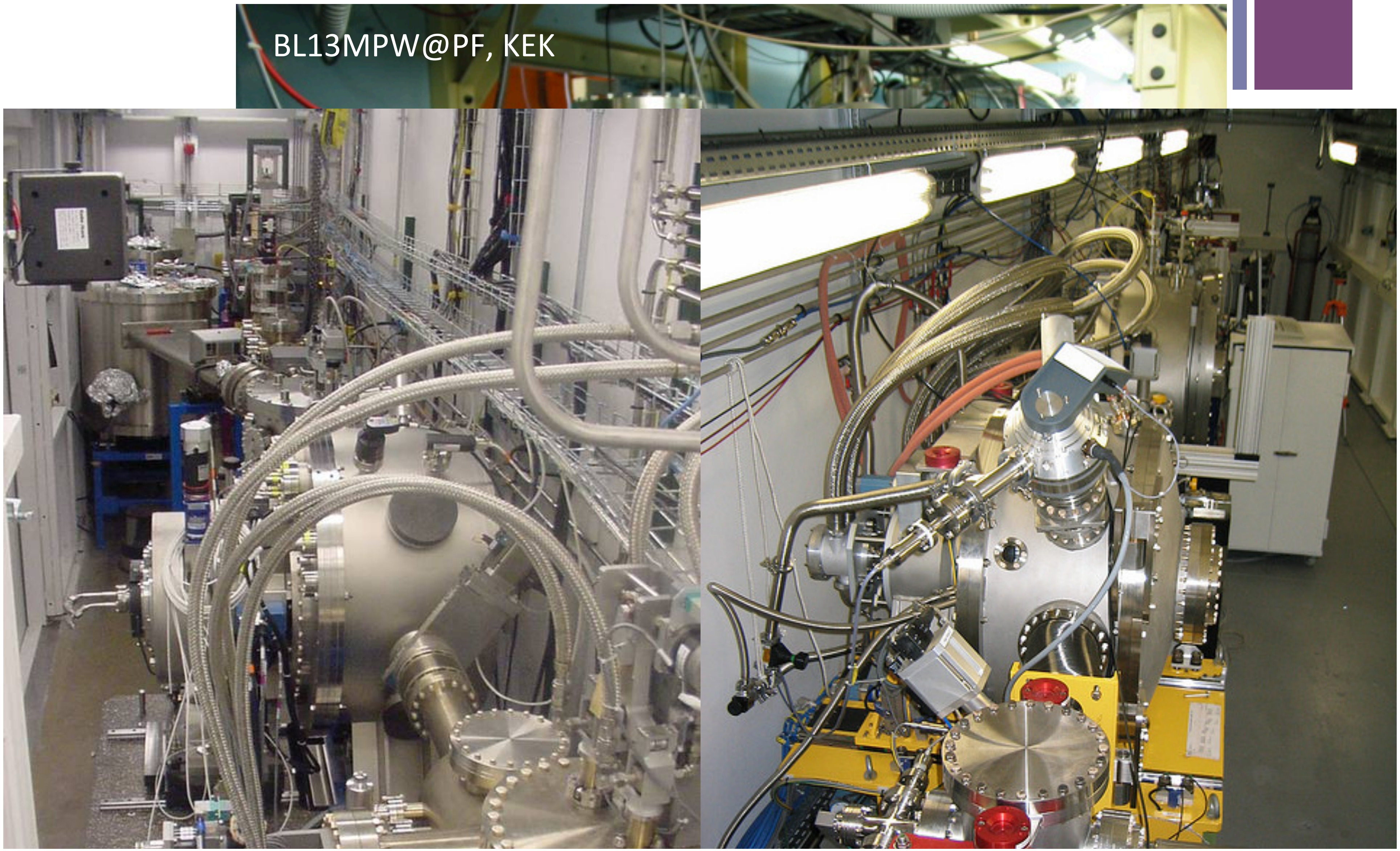
Fixed beam height or
Correction by stage



Constant beam-height
double crystal monochromator

Nucl. Instrum. Methods A246, 377 (1986)

Monochromator -outlook

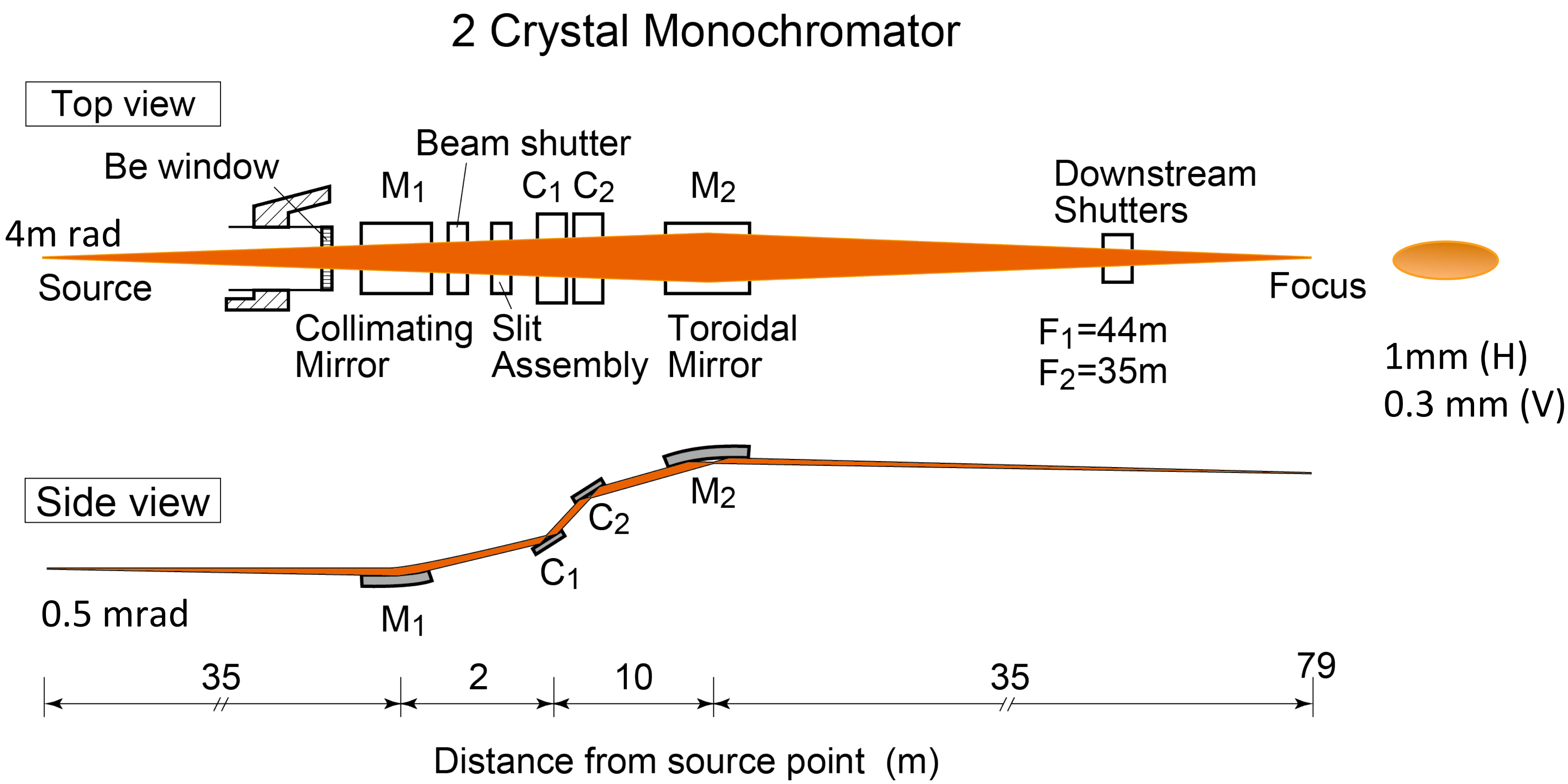


Beamline optics -strategy

Wiggler@2G

Emittance ≈ 30 nmrad

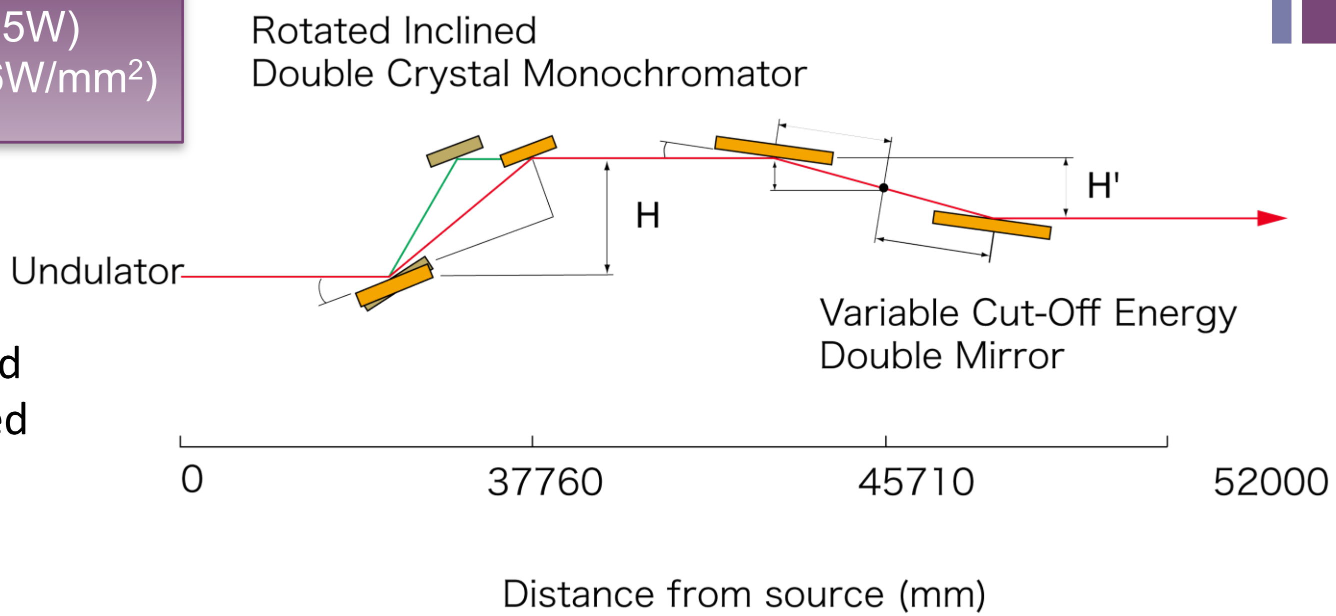
Strategy: 1:1 mirror focusing or 3:1 sagittal focusing



+ Optics of BL10XU (U032V) beamline@Spring-8

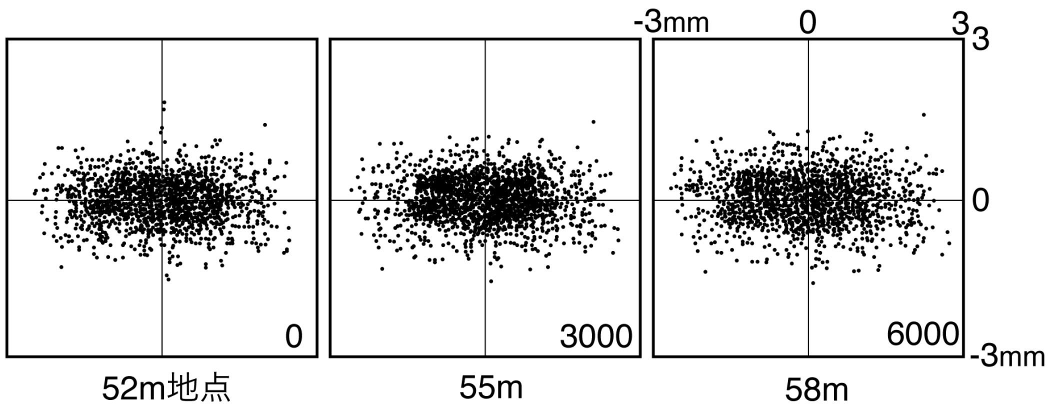
5-30 keV energy range
1st & 3rd radiation (tunable)
T.P. 12kW (465W)
P.D. (76W/mm²)

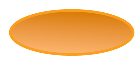
Optics of SPring-8 BL10XU



Emittance: 3 nmrad
Strategy: unfocused

Ray tracing results





1mm (H)
0.3 mm (V)