De-excitation spectroscopy II: Photon-in Photon-out spectroscopy

Excitation Source: Tunable SR (UV –X rays)

Photon-out phenomena:

- ***Scattering*** (elastic, inelastic, resonant)
- ***Fluorescence*** (core-hole decay)

  X-ray fluorescence (hard x-rays)

  X-ray emission (soft x-rays)

  Luminescence (UV-visible)

  Auger (pseudo-photon)

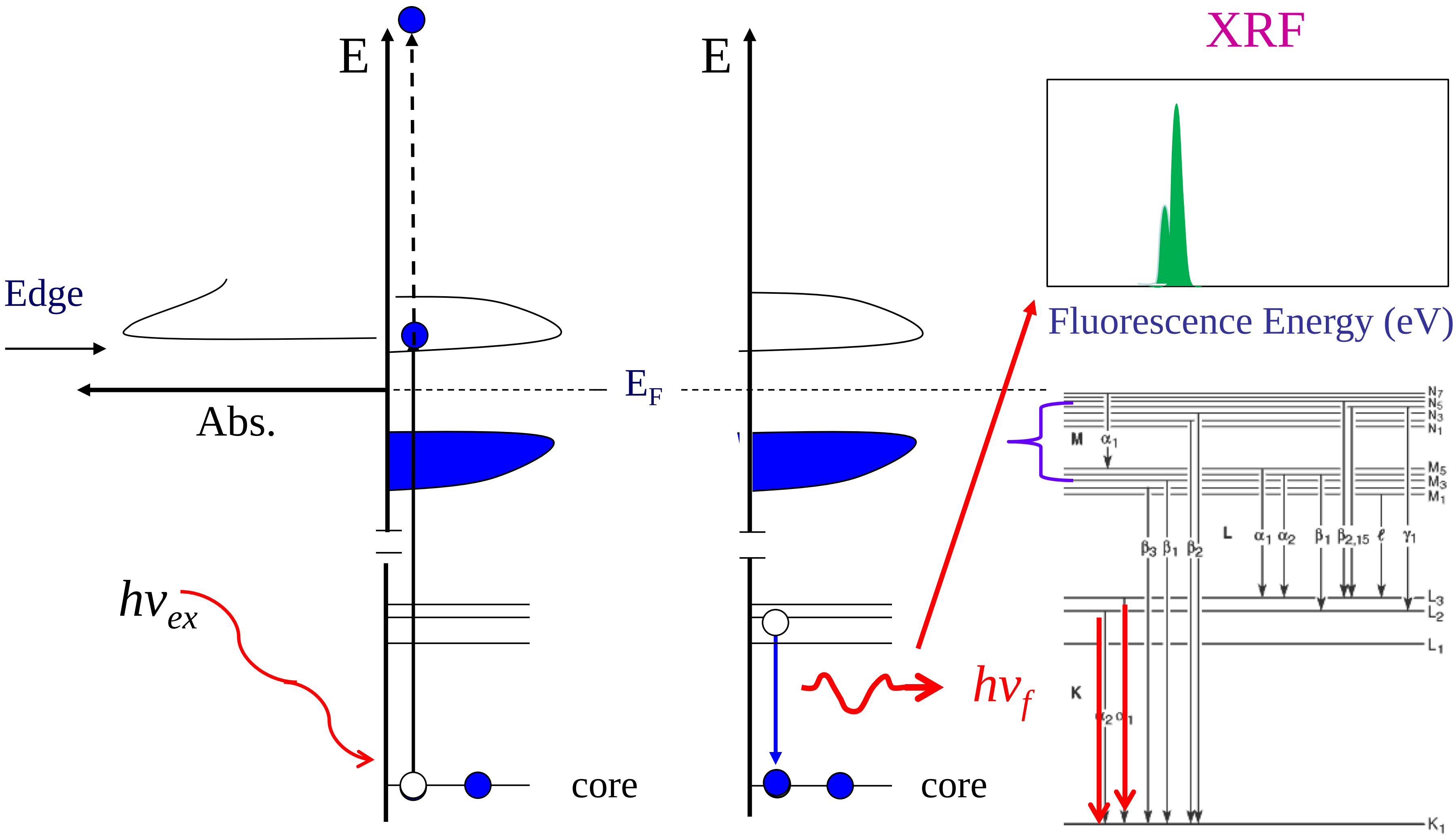
Photon-in Photon-out Spectroscopy

X-ray fluorescence (XRF)

X-ray emission (XES)

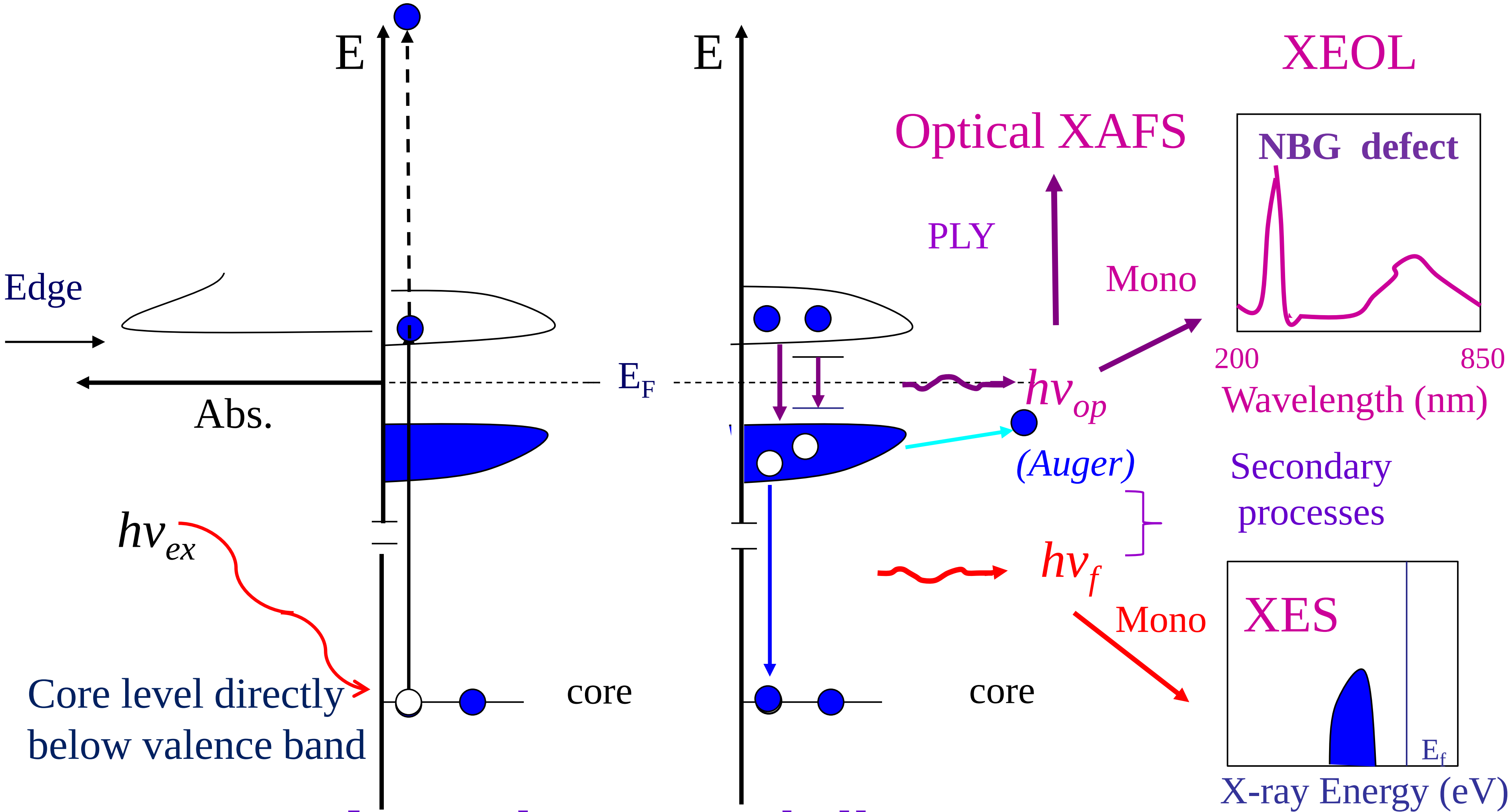
X-ray excited optical luminescence (XEOL)

X-ray fluorescence (XRF)



X-ray fluorescence: shallower **core** electron (e.g. L shell) to deeper **core** hole (K) transition

X-ray emission (XES) and X-ray excited optical luminescence (XEOL)



XES: **valence** electron to shallow **core**

XEOL: **CB** to **VB** & **defects**

X-ray Fluorescence measurements

Nondispersive (no energy resolution)

- Scintillation counter
- Ion chamber (Lytle detector) (with filters)

Moderate energy resolution

Solid state detectors (Ge, Si), order of 10 to10^2 eV

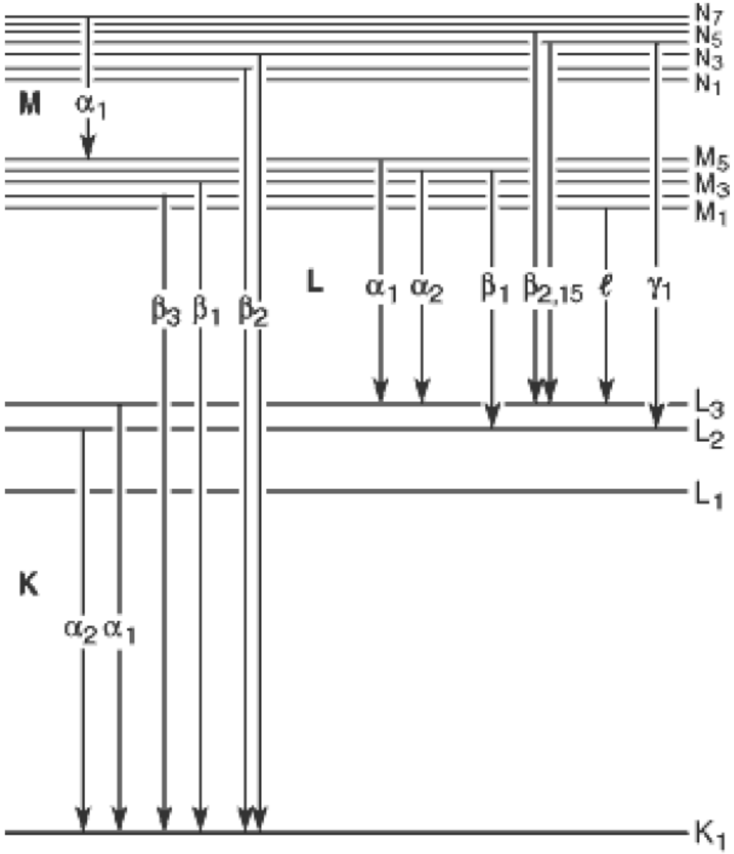
High energy resolution

WDX detector (crystal monochromator) $E/\Delta E \sim 800$

Very high energy resolution

MiniXS (Jerry Seidler, U. of Washington)
$E/\Delta E \sim 4000$

X-ray Fluorescence properties of elements



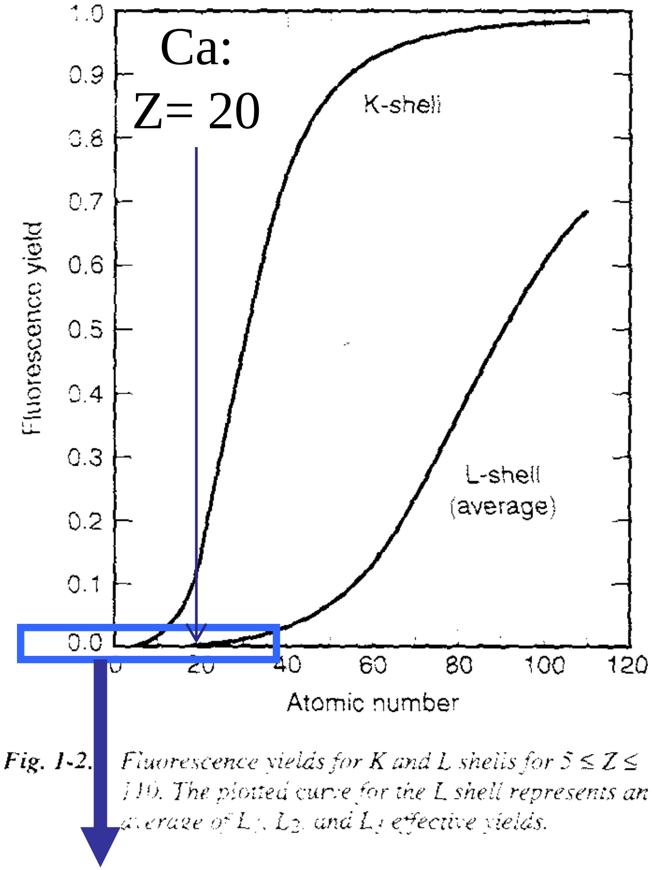


Fig. 1-2. Fluorescence yields for K and L shells for 5 ≤ Z ≤ 110. The plotted curve for the L shell represents an average of L1, L2, and L3 effective yields.

Normal Fluorescence: Core-Core
XES: L or M = valence band
Resonant: Core-CB excitation

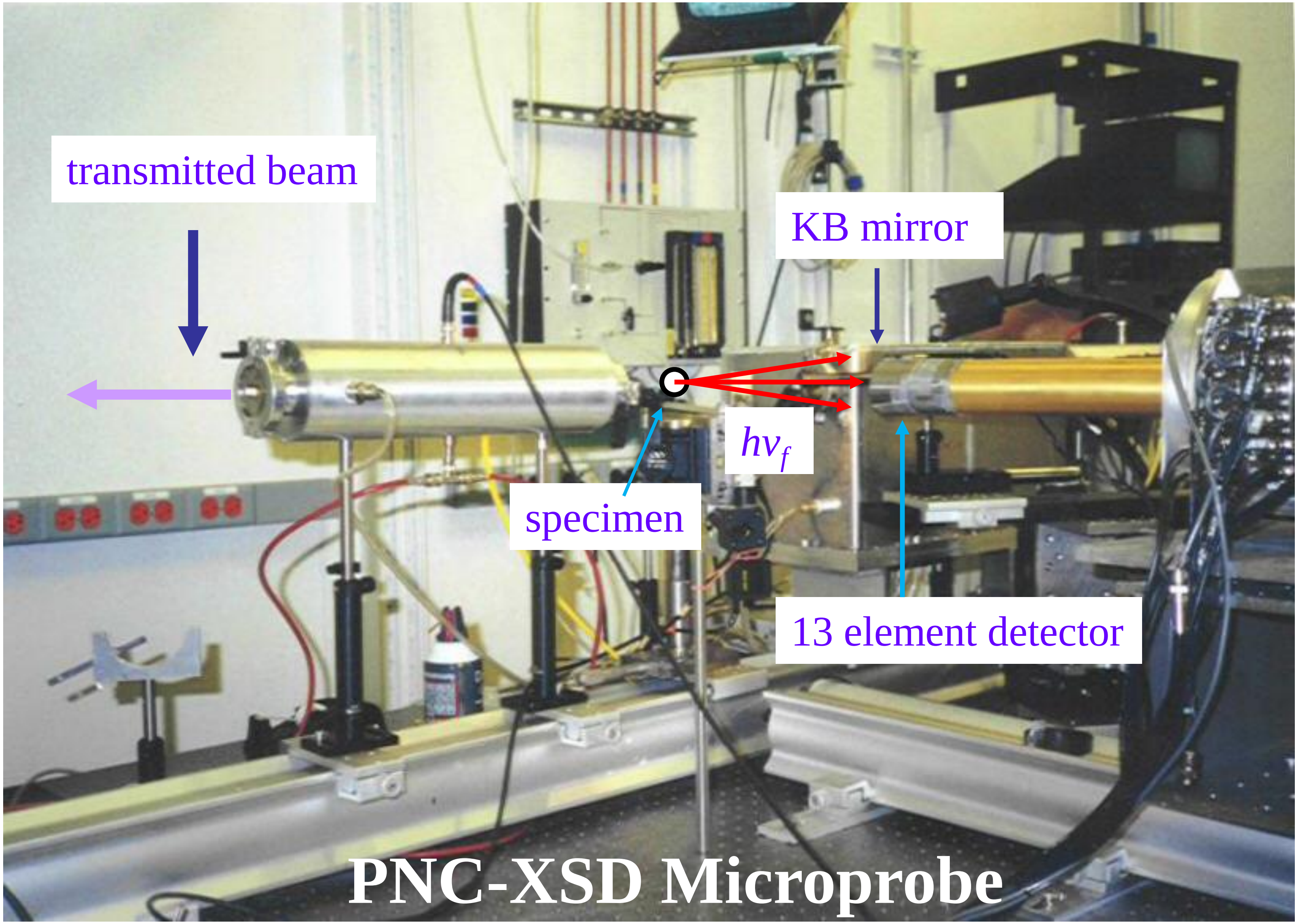
Auger yield = 1 – FLY
FLY for low z elements
(C, N, O etc.) is << 1 %

X-ray Fluorescence:

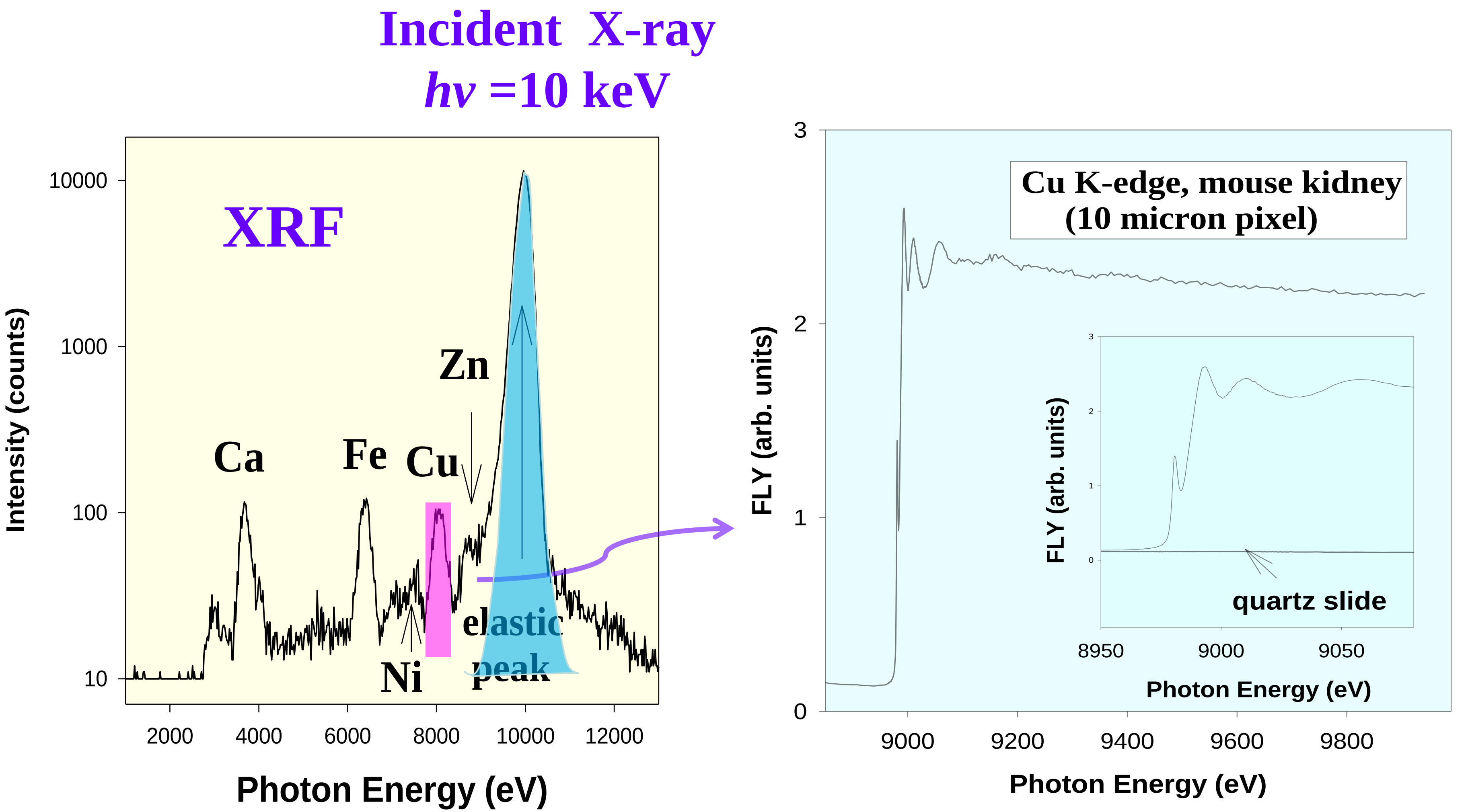
X-ray photons in, x-ray photons out.
Results from the decay of a deep core hole (e.g. K, or L)
Monitor the absorption spectrum using fluorescence yield (**FLY**) → **element specificity**

Detection Schemes

- High sensitivity, non-dispersive
  Channel plate, Ion chamber
  (solar slits, filters, e.g. Lytle)
- High sensitivity, moderate energy resolution
  Solid state detector (e.g. Canberra 13 element at PNC-CAT, Si drift detector at CLS)
  Gas proportional counters (e.g. Fisher/Ohta)
- High sensitivity, more moderate resolution
  Multi-layer Array Analyzer Detector (MAAD)
  Log spiral detector (asymmetric Laue bent)

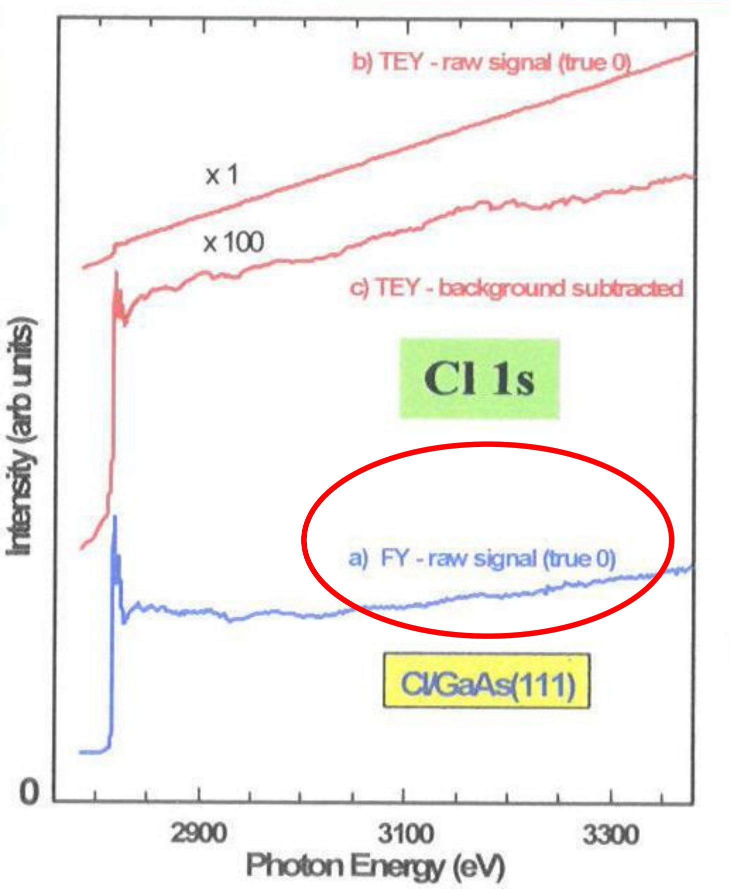

transmitted beam
KB mirror
$h\nu_f$
specimen
13 element detector
PNC-XSD Microprobe

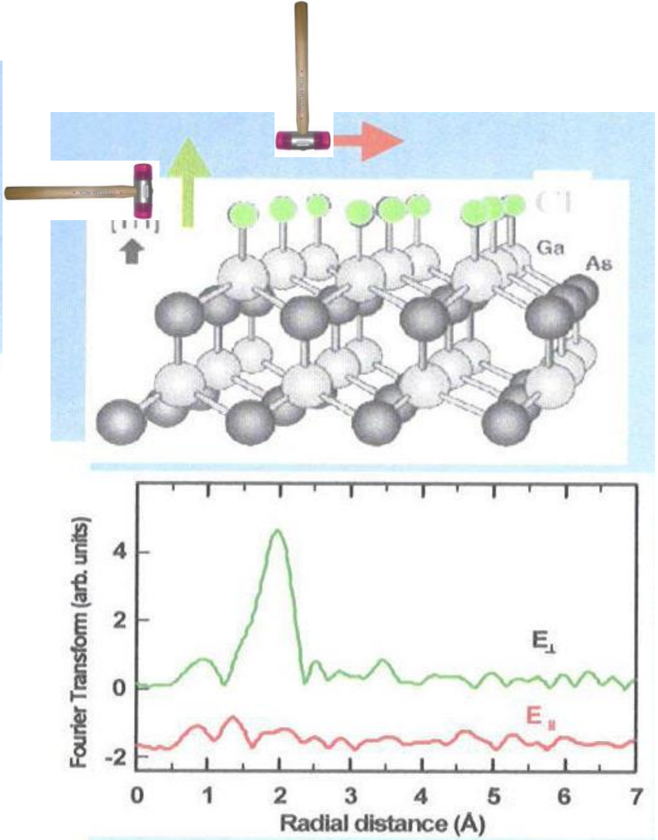
Metals in mouse kidney tissue (hard X-ray)

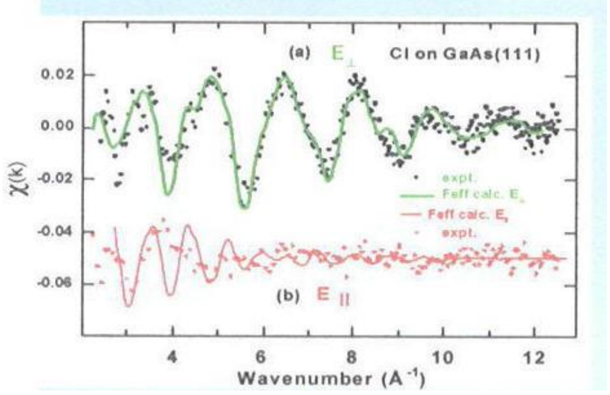


Cl / GaAs(111)

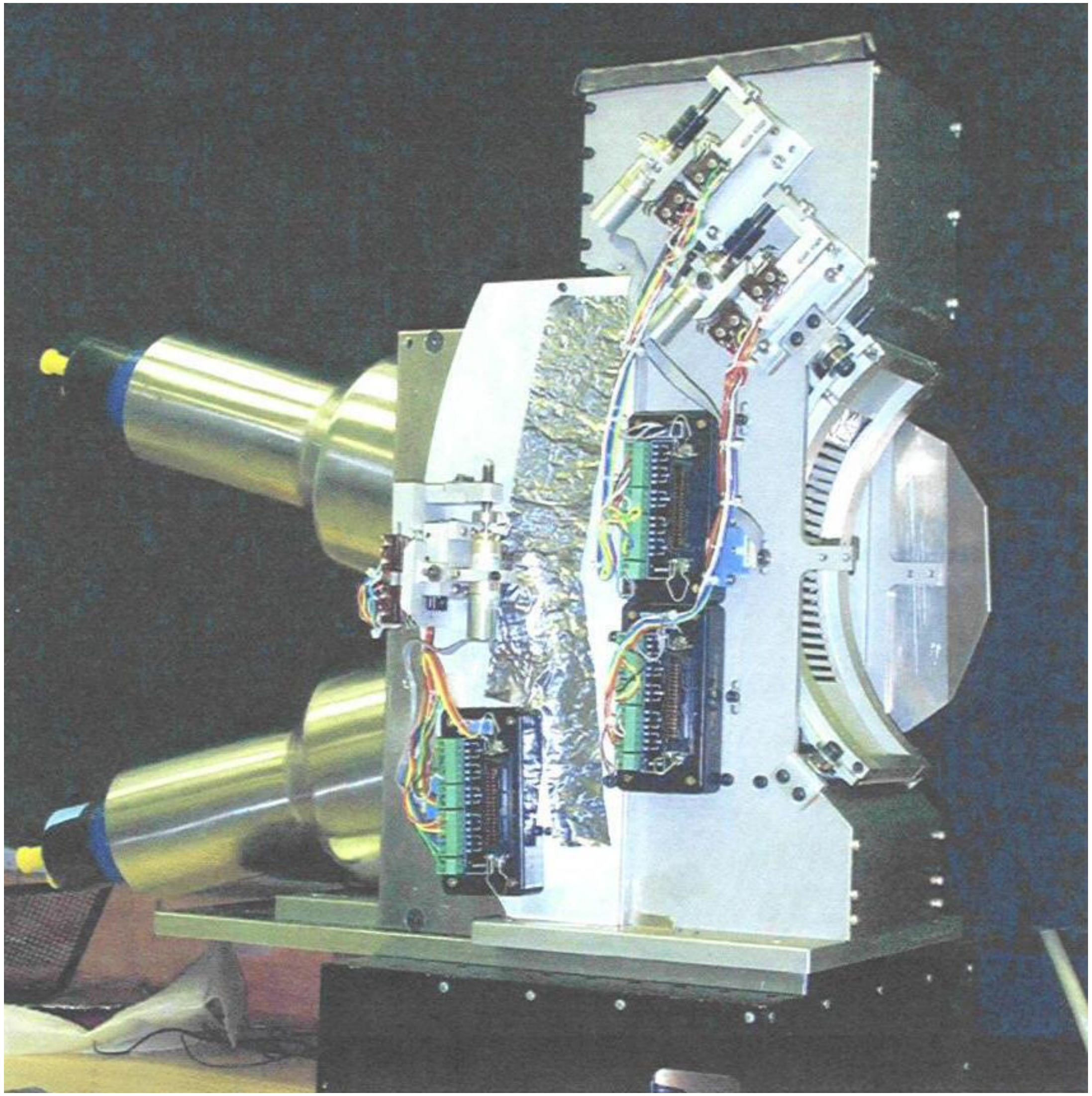
Polarization dependent X-ray absorption (EXAFS)

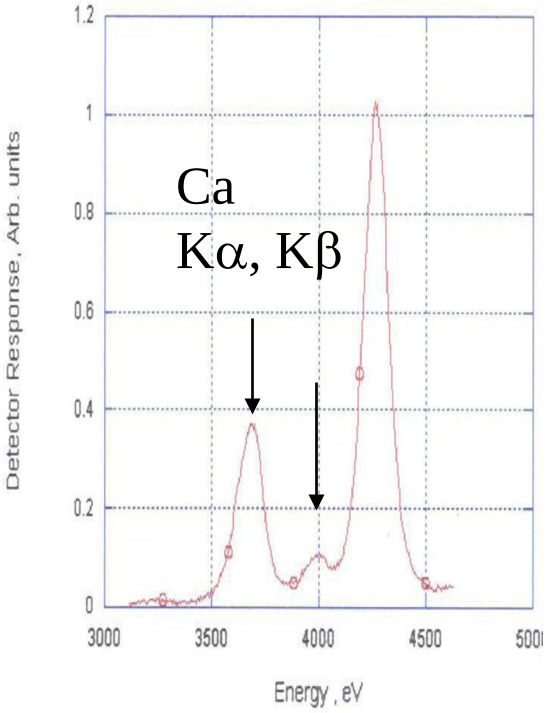






Lu, soft x-ray [Phys. Rev. B, 58 (1998)]





Energy scan: elastic,
Ca Kα and Kβ
ΔE = 150 eV at Ca Kα

20 element Multi-Array Analyzer Detector (MAAD)
[Ke Zhang et al. HD Technologies Inc.]

Variable width

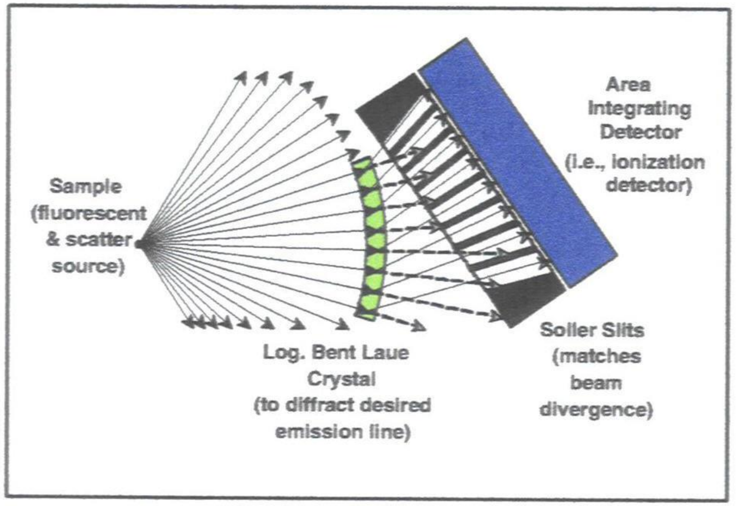


FIG. 1. A sketch of the "logarithmic bent Laue analyzer" concept.

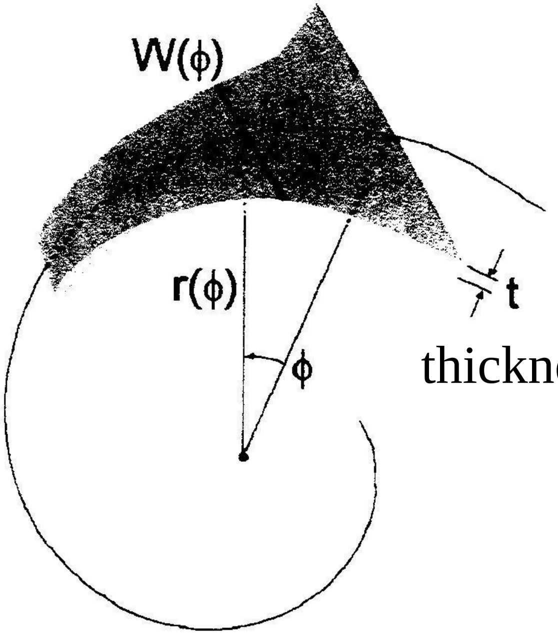


FIG. 2. Crystal bent to log spiral shape.

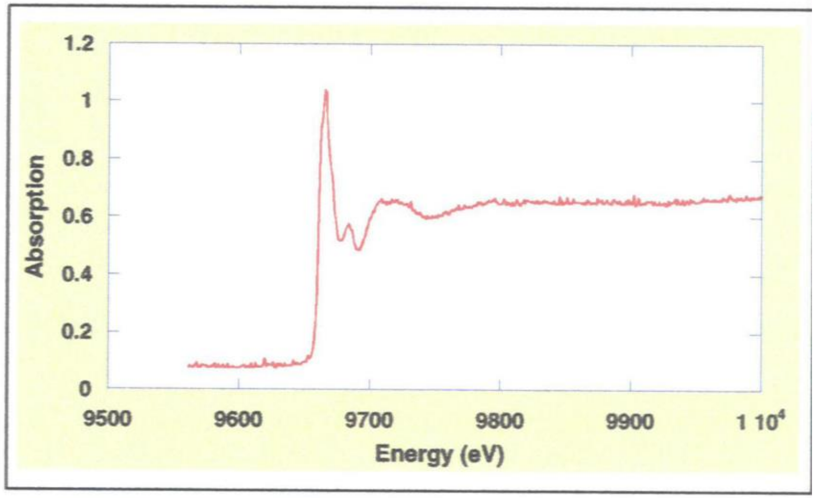


FIG. 2. An XAFS spectrum of around 65 ppm Zn - adsorbed to montmorillonite clay - measured with Logarithmic Bent Laue Analyzer.

Schematic of an asymmetric cut Si (100) wafer where in polar Coordinate: $r(\phi) = ae^{b\phi}$, $b = \tan\theta$ [Khelashvili et al. Rev. Sci. Instru. 73, 1534 (2002)]

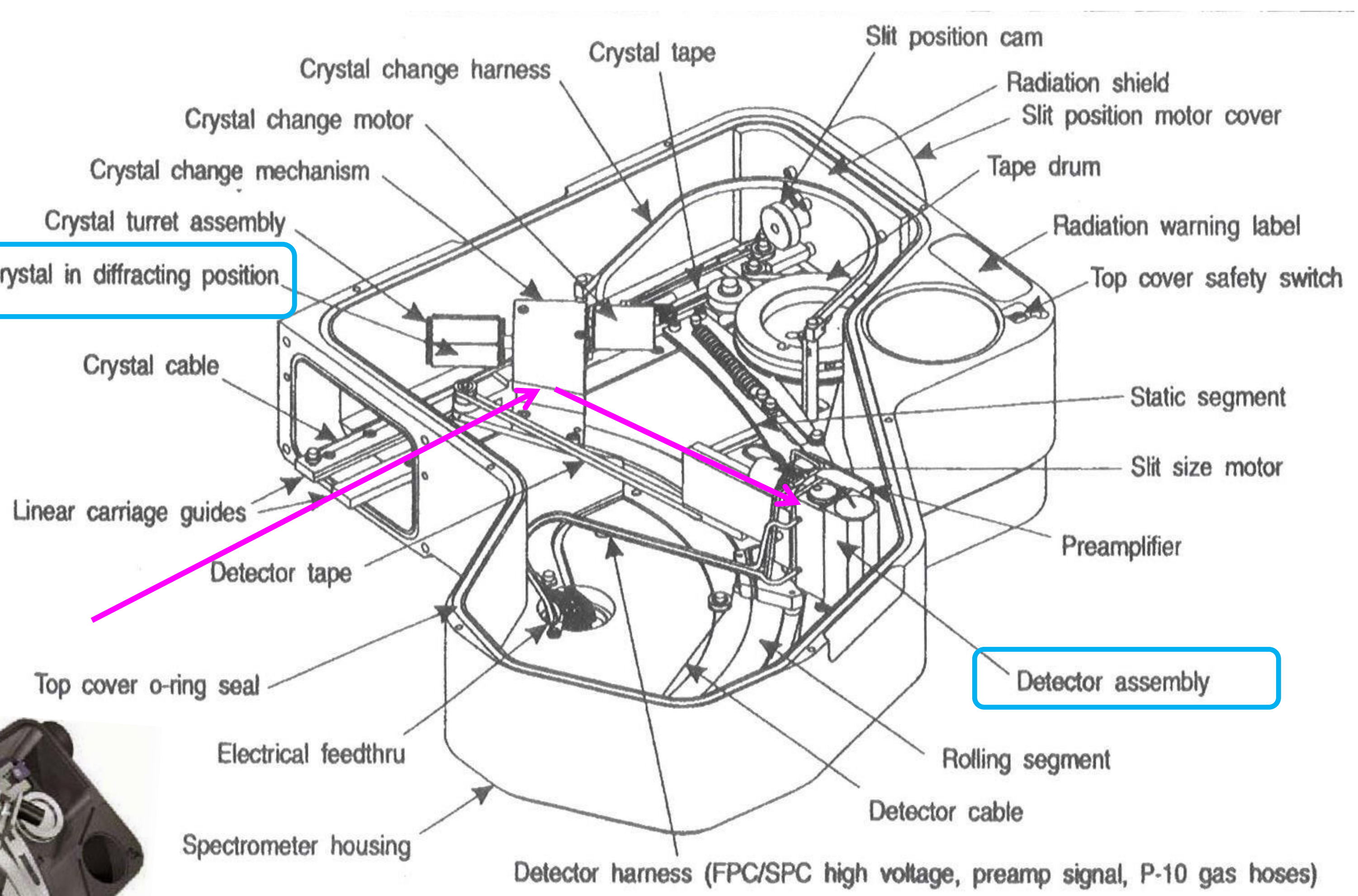
Detection Schemes (continues..)

• Low sensitivity, good resolution WDX (Rowland circle crystal optics)

LiF crystals (electron microprobes): 2-5 keV [e.g. PNC-CAT]

Ge (3,3,3), Si (4,4,0): Fluorescence > 5 keV

• Low sensitivity, good resolution (< 2 keV) Grating monochromator [e.g. BL 8.0.1, ALS]



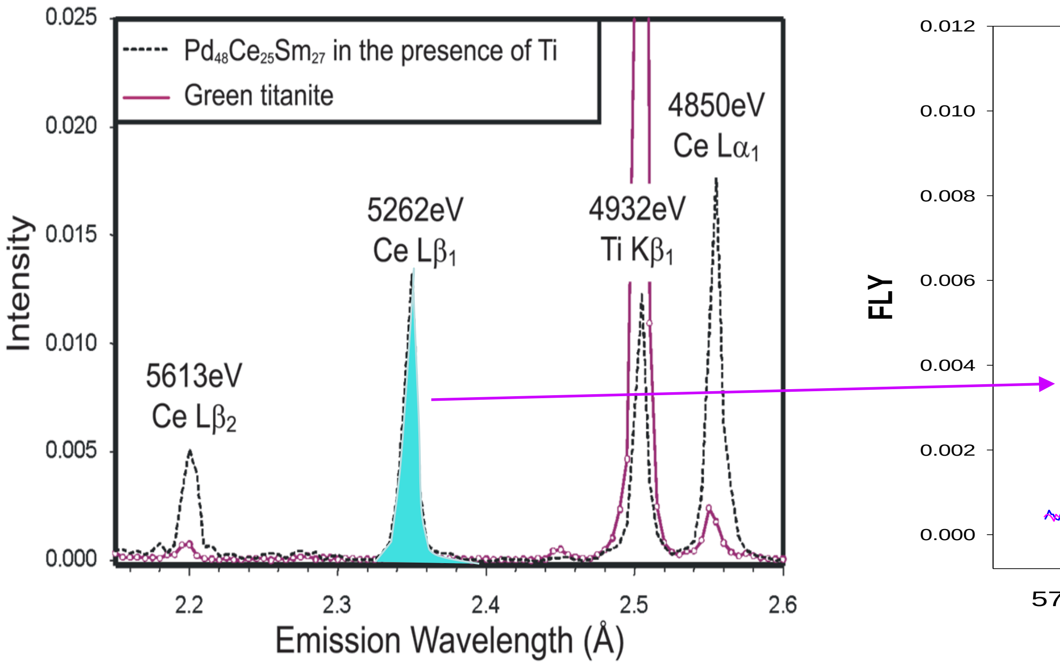
WDX from an electron microprobe

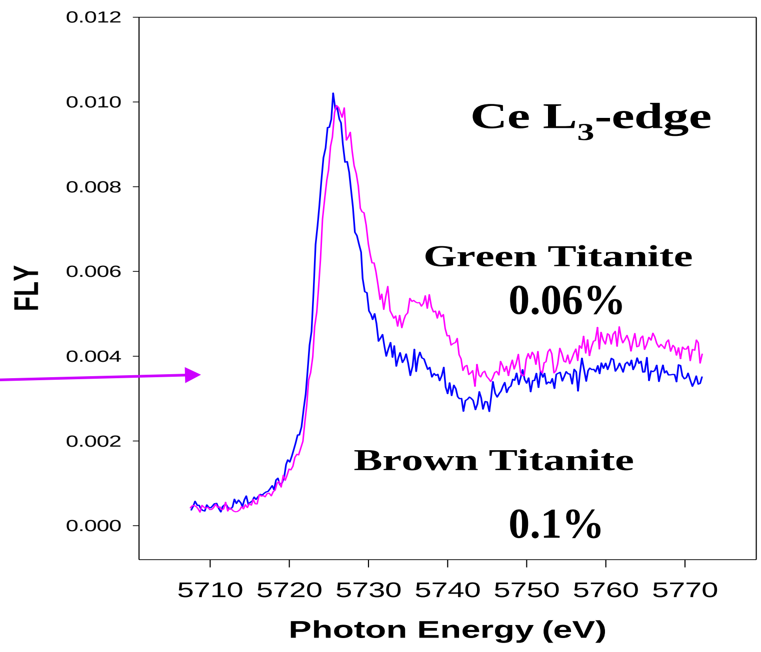
Ce L_3 edge of Ce in Titanite: WDX detection

Ti K β_1 4932 eV Ce Lα_2 4823.0 eV

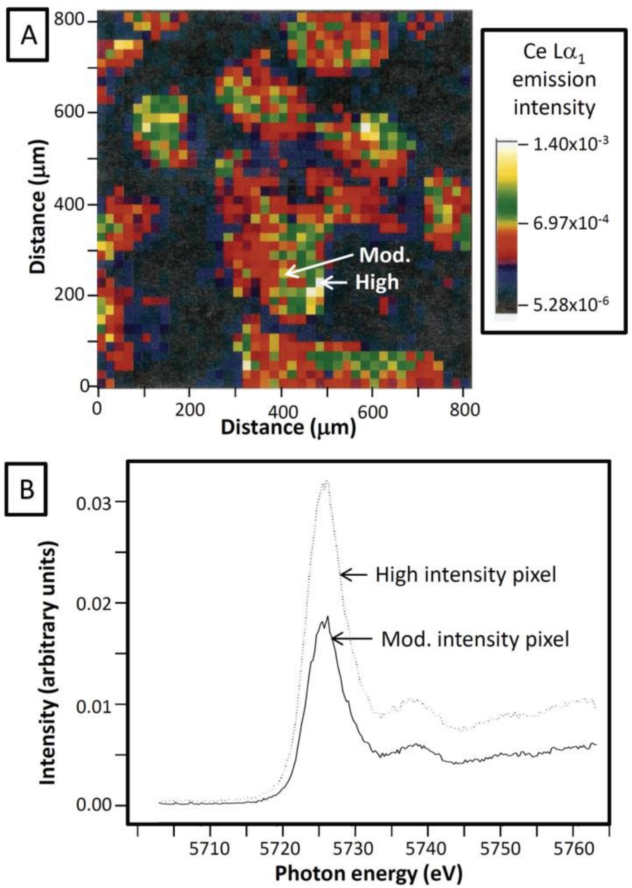
Ce Lα_1 4840.8 eV **Ce Lβ_1 5262.2 eV**

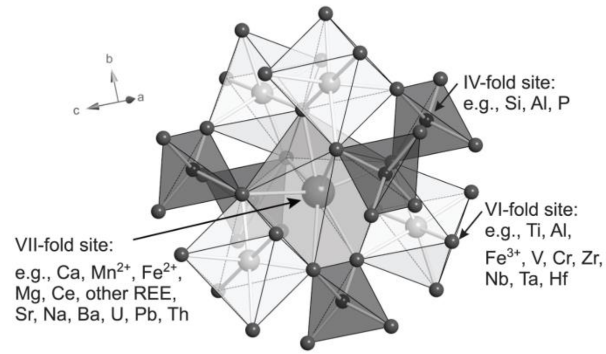
Neither SS nor WDX detector will resolve Ce Lα from Ti K β
But WDX can resolve Ce Lβ nicely



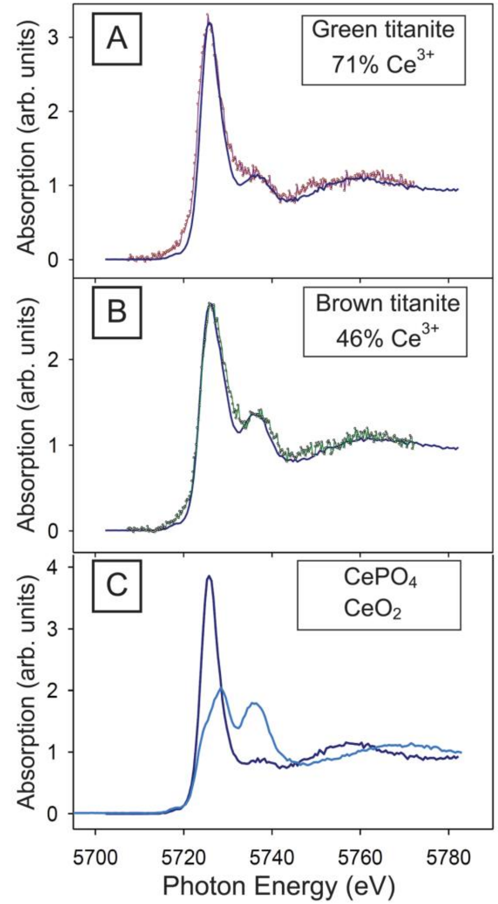


Ce in Titanite: Microprobe using WDX

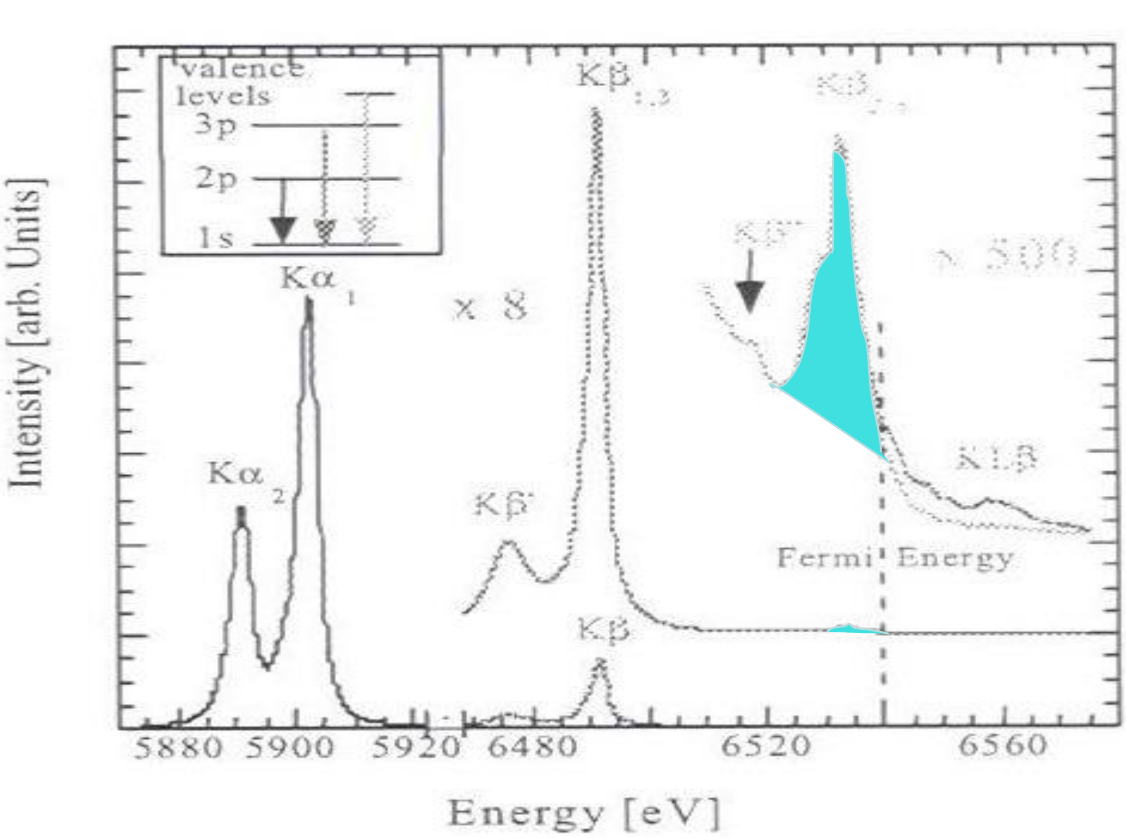


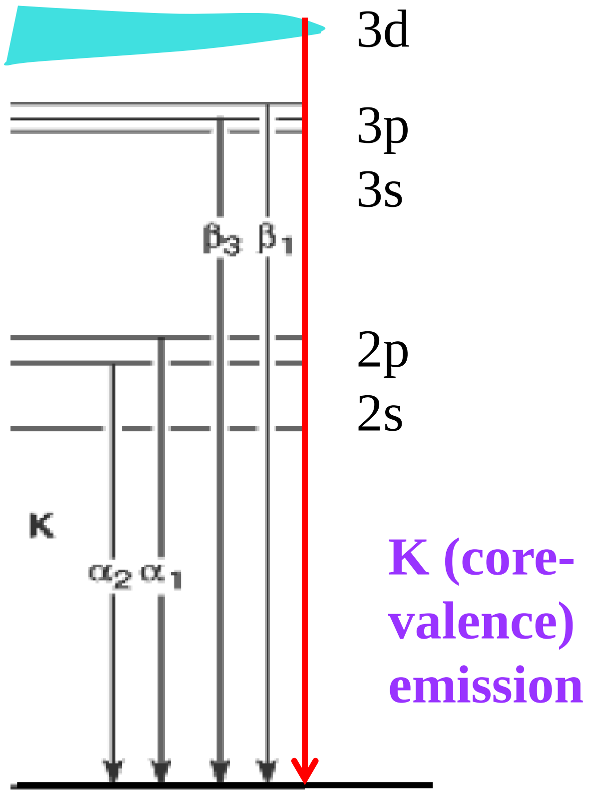


Titanite ($CaTiSiO_5$, sphene) is a common mineral in mafic-felsic igneous and meta-morphic rocks, and it is widely used for geochronologic and petrogenetic studies



American Mineralogist, Volume 98, 110–119, (2013)

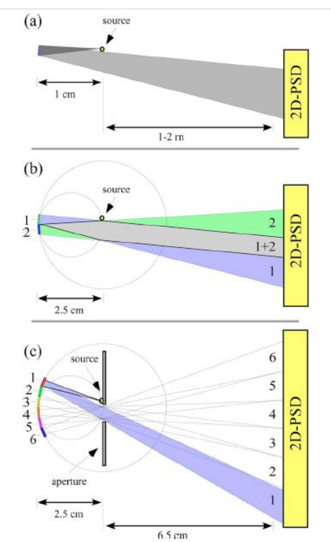


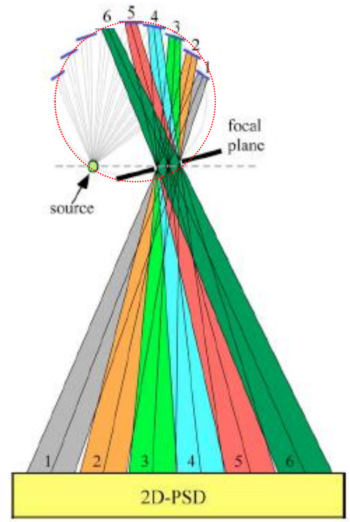


K Fluorescence of MnO using Ge(333) and Si(440) crystals (Rowland circle optics, S. Cramer X-25 NSLS, 2002)

High resolution fluorescence using Minixs

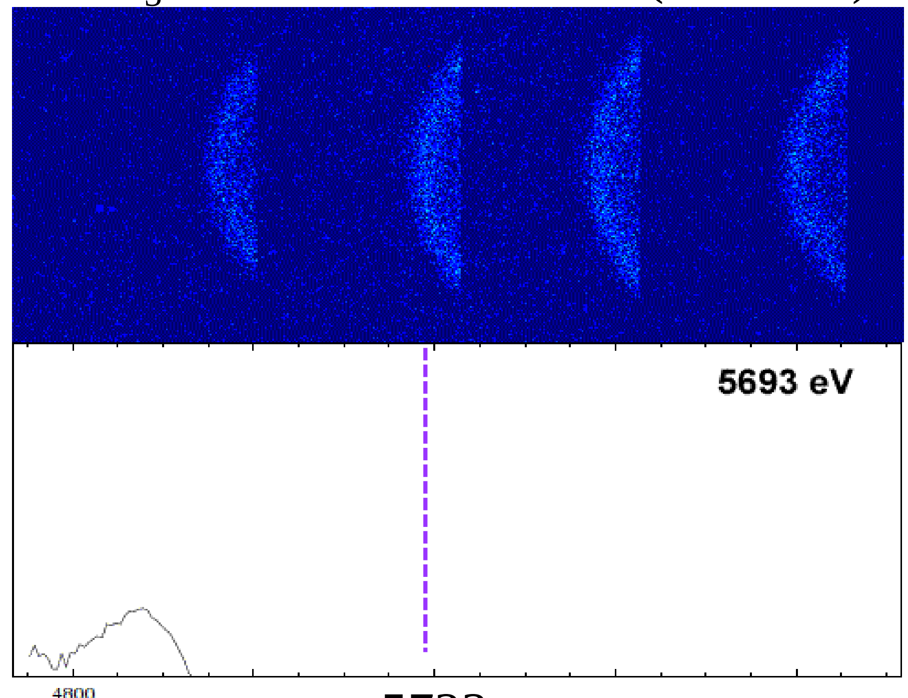
Rowland Circle



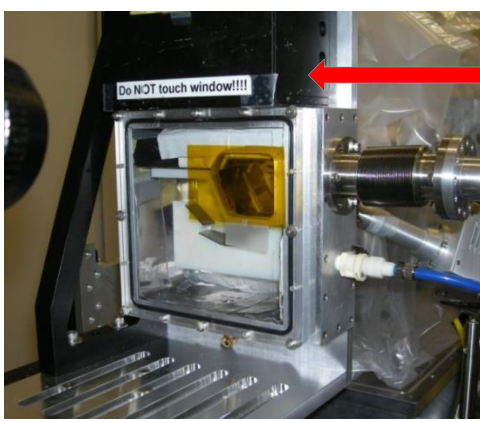


Dickinson et al. ***Rev. Sci. Instrum.*** **79**, 123112 (2008)

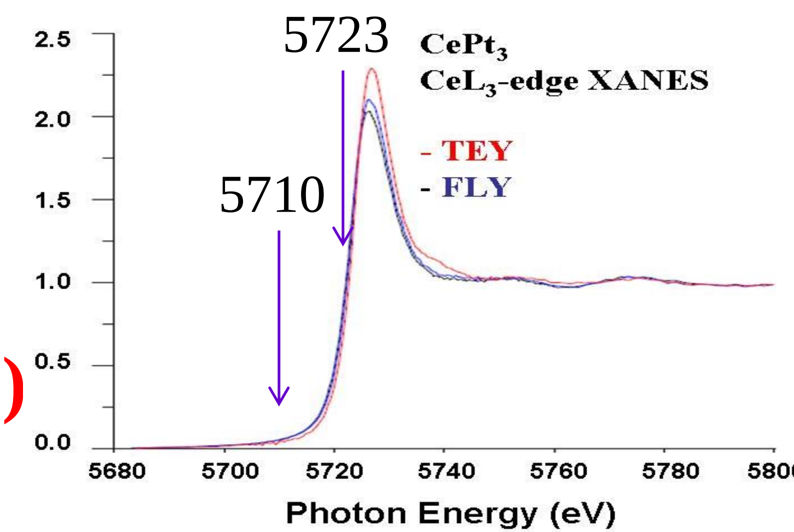
CePd$_3$ RXES data collection (~3 hours)



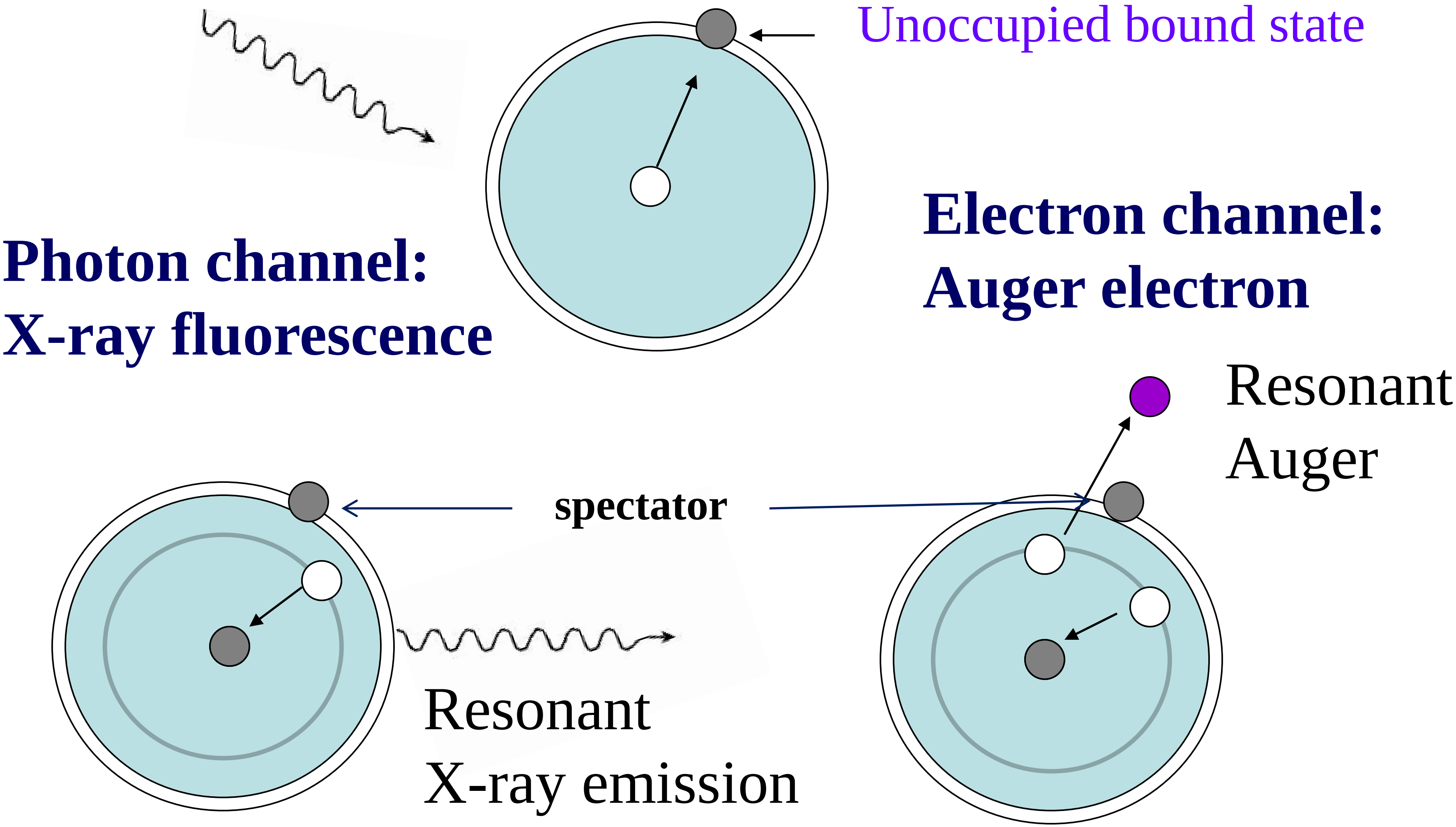
Pilatus 100K PAD



Ce L$_\alpha$ Ge(440)

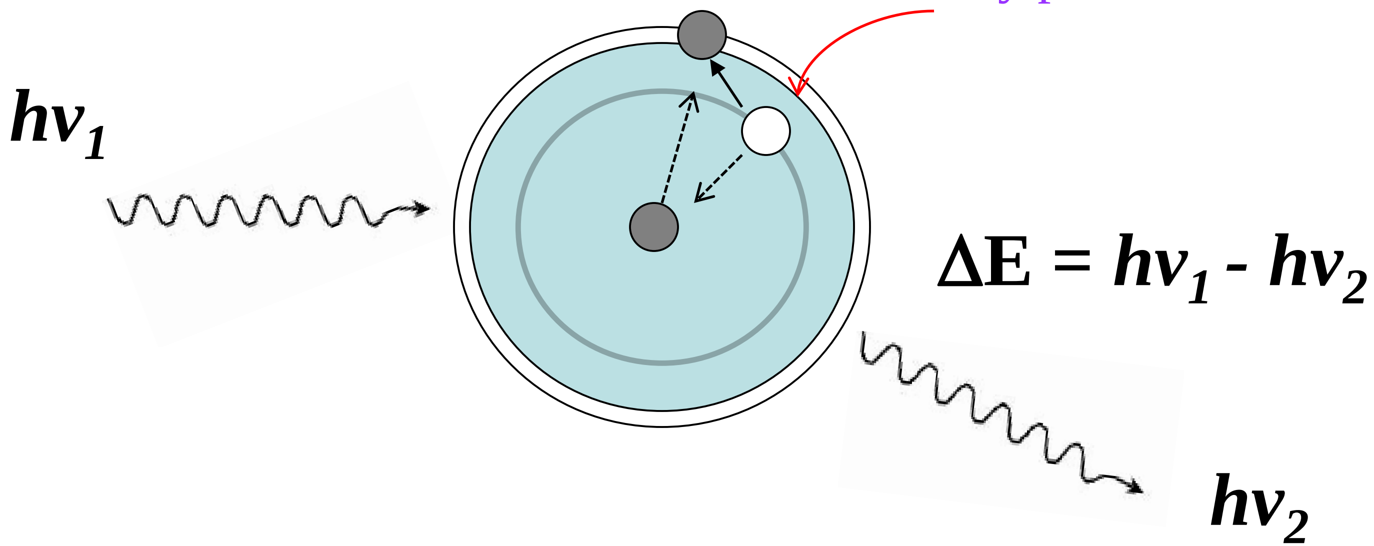


Absorption & de-excitation @ resonance:



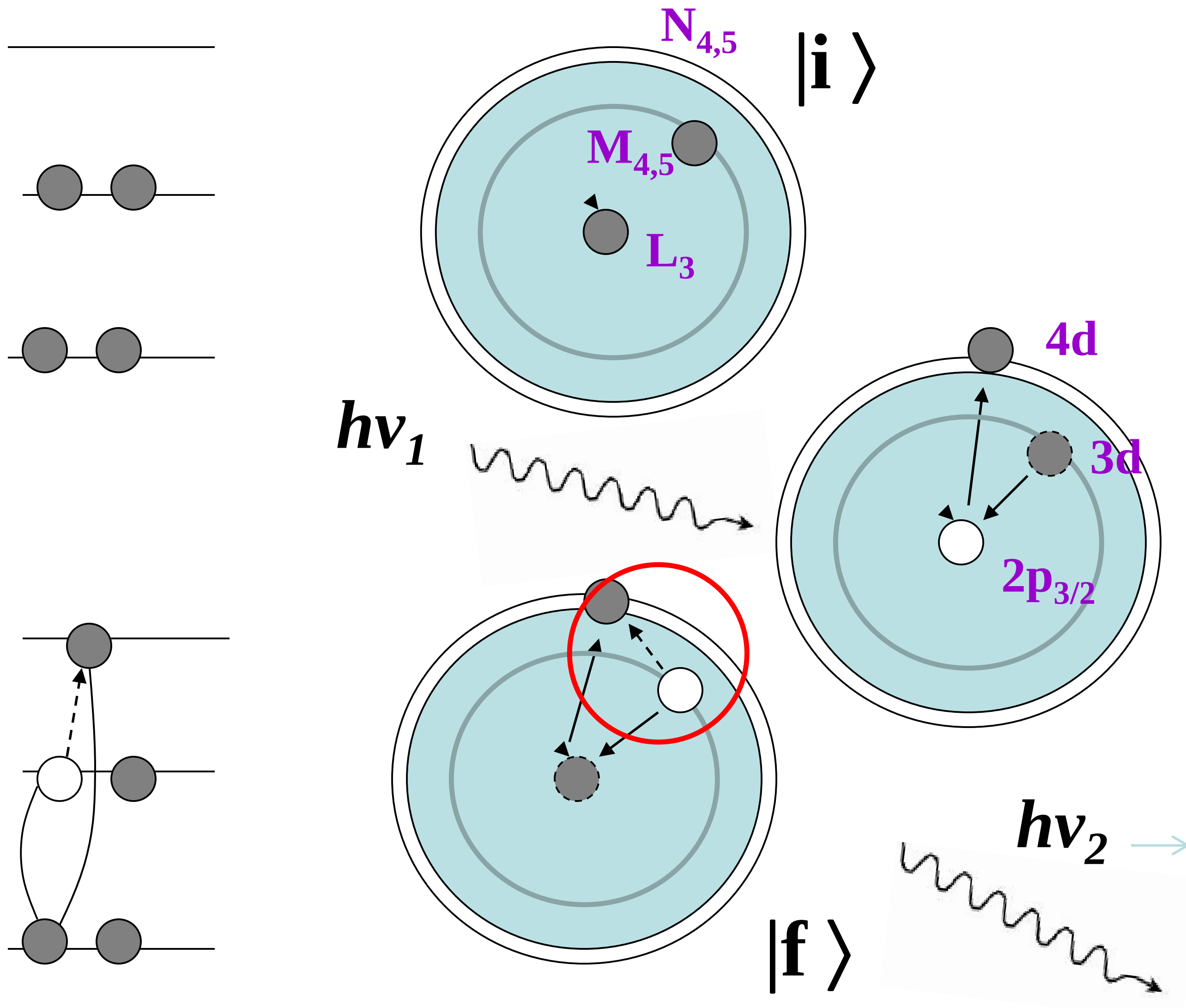
Inelastic X-ray scattering (core level excitation)

Same shallow hole left behind when the e drops down to fill a deeper core hole emitting a fluorescence X-ray photon



Cross-section is very small except at resonance
When $h\nu_1 = h\nu$ (threshold resonance)

RIXS @ Ce L_3-edge

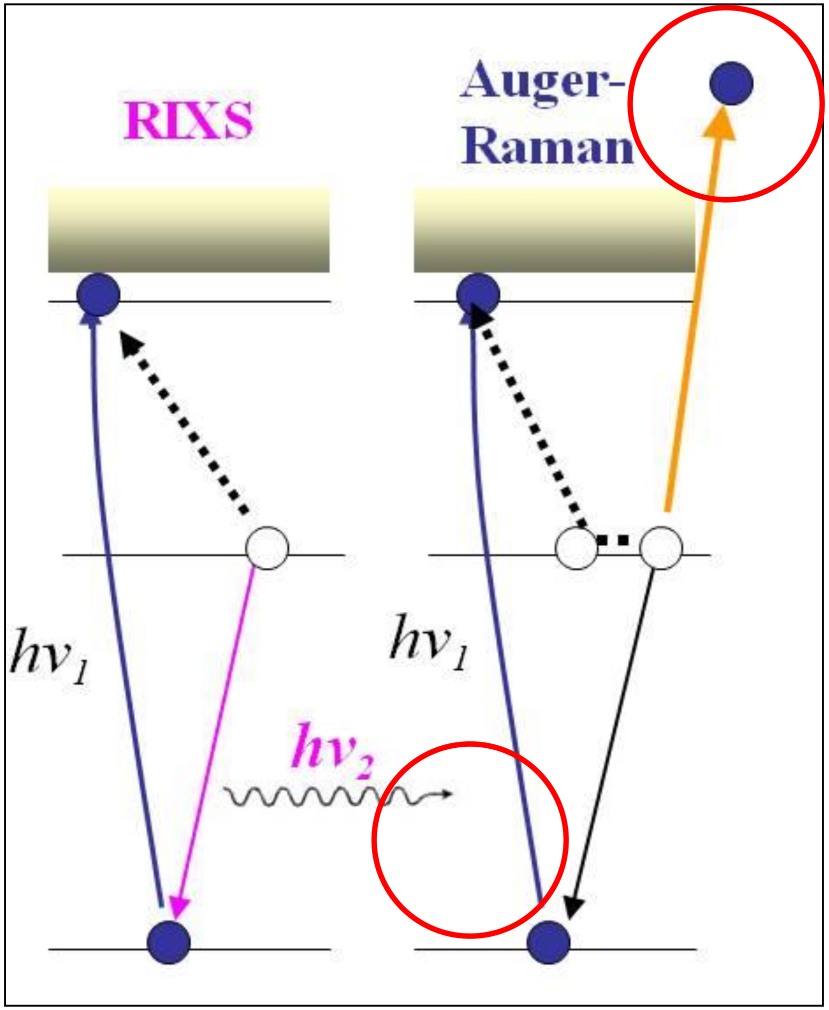


dispersion when $h\nu_1$ < threshold, constant when $h\nu_1$ > threshold

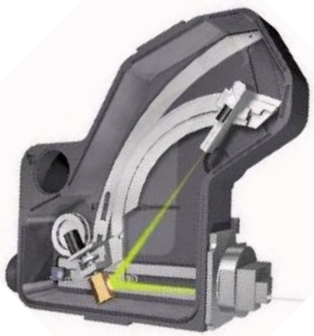
RIXS measurements (electron and photon)

- Experiment requires **high flux**, **high photon energy resolution** (incident and emission) and **high electron energy resolution**

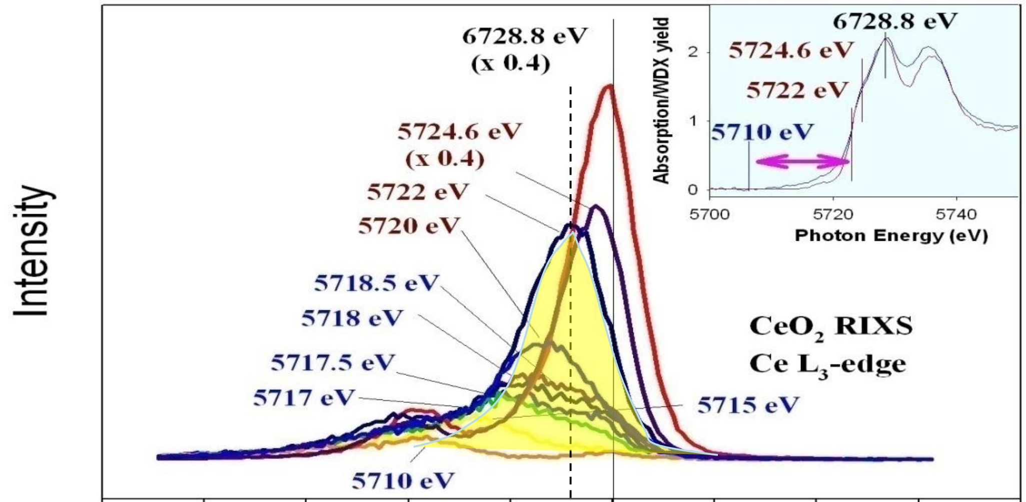
- Information: **dispersion (constant energy transfer)**; **core-hole lifetime suppression**

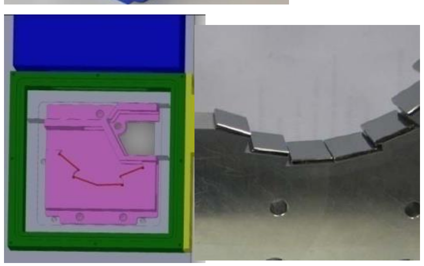


Resonant Inelastic X-ray Scattering (RIXS)

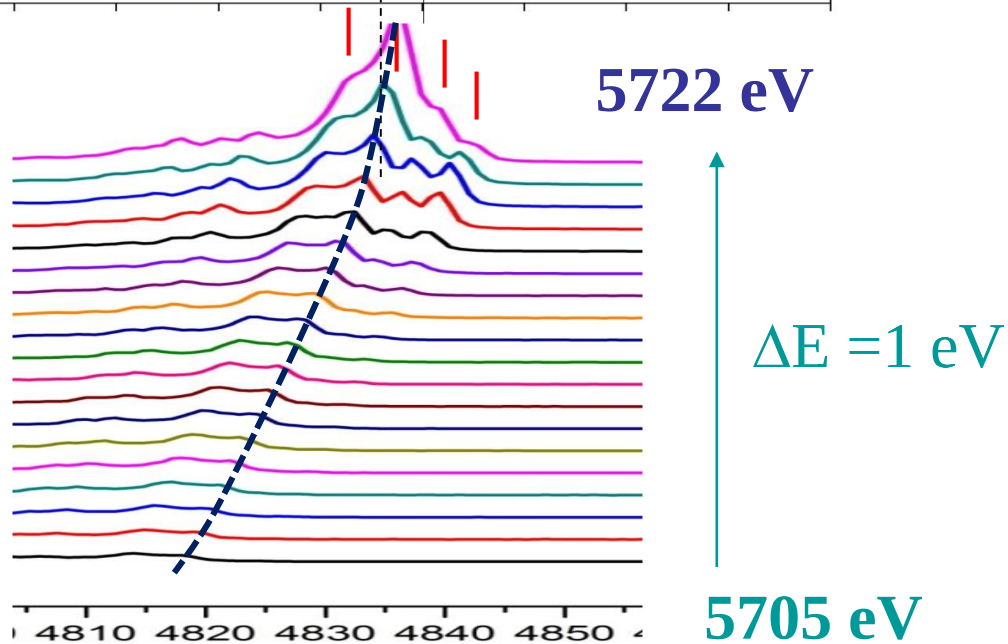


WDX
ΔE ~ 6 eV





MiniXS
ΔE <1 eV

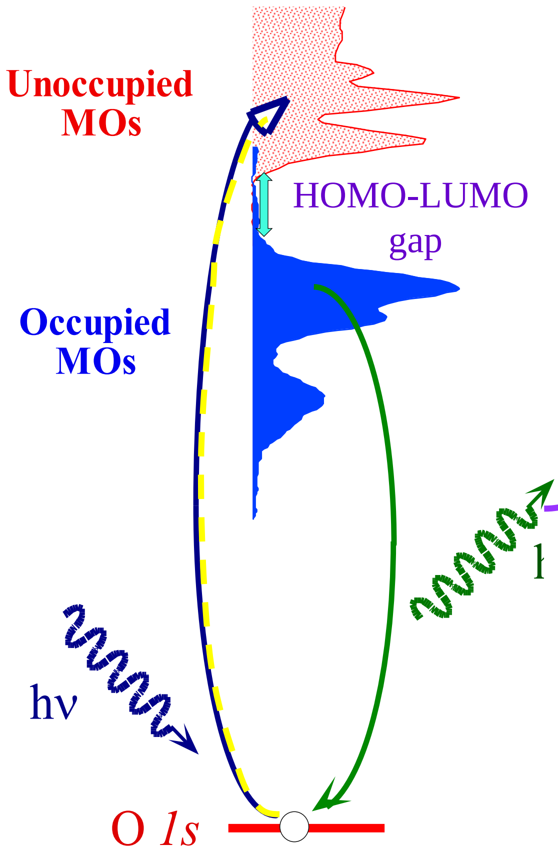


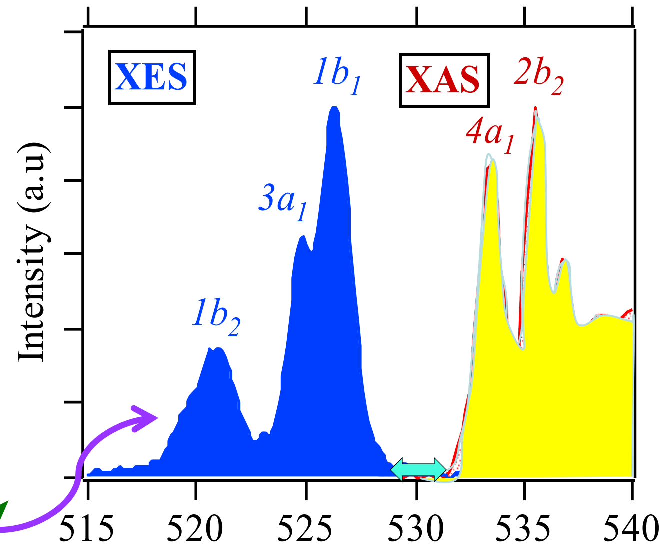
XES : X-ray Emission Spectroscopy

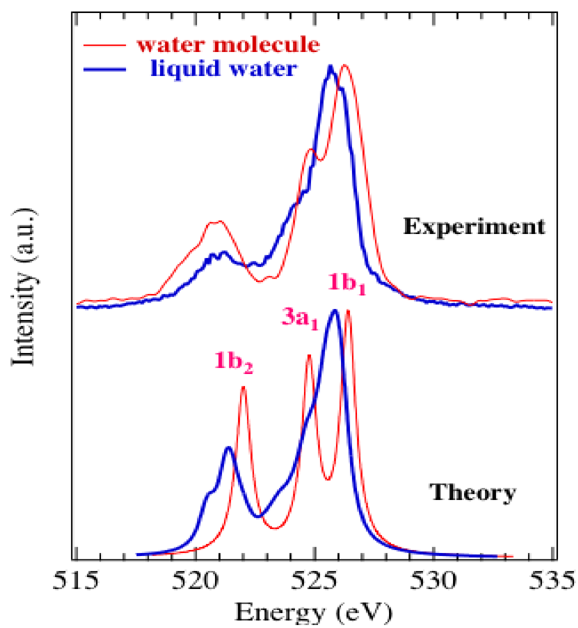
X -ray photons in, x-ray photons out

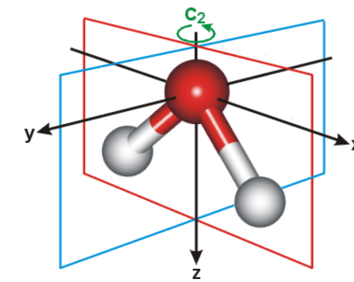
For shallow core excitations, XES measures the projected densities of states of the element in the valence band ⟶ **element and chemical specificity**

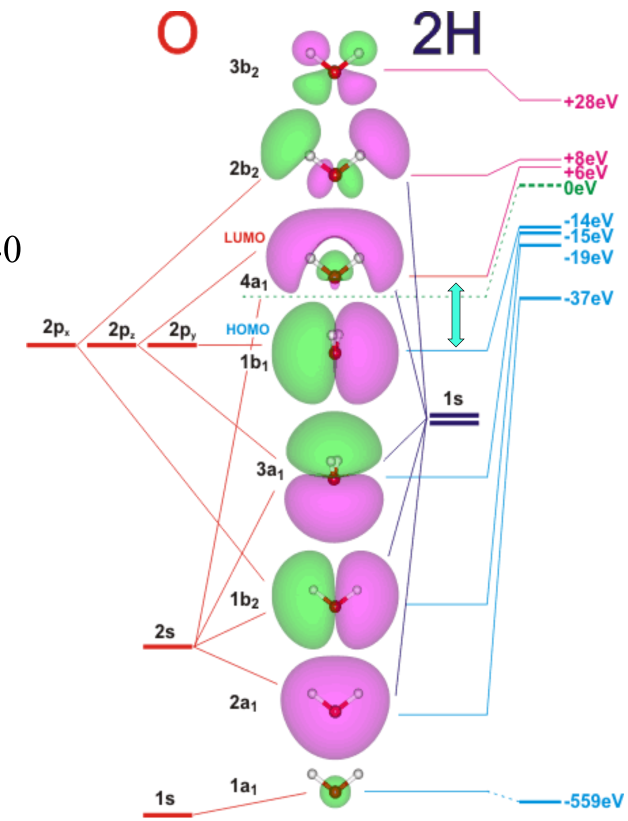
O K-edge XAS and XES of H_2O





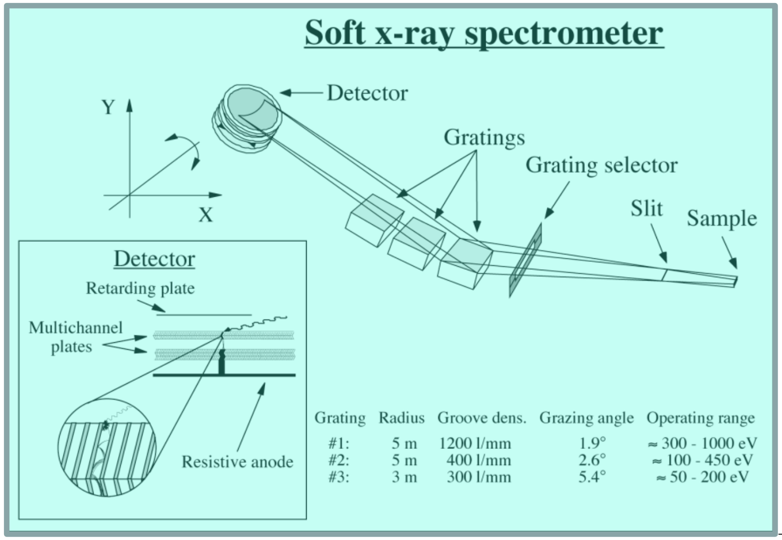






Guo et al., PRL 89, 137402 (2002)

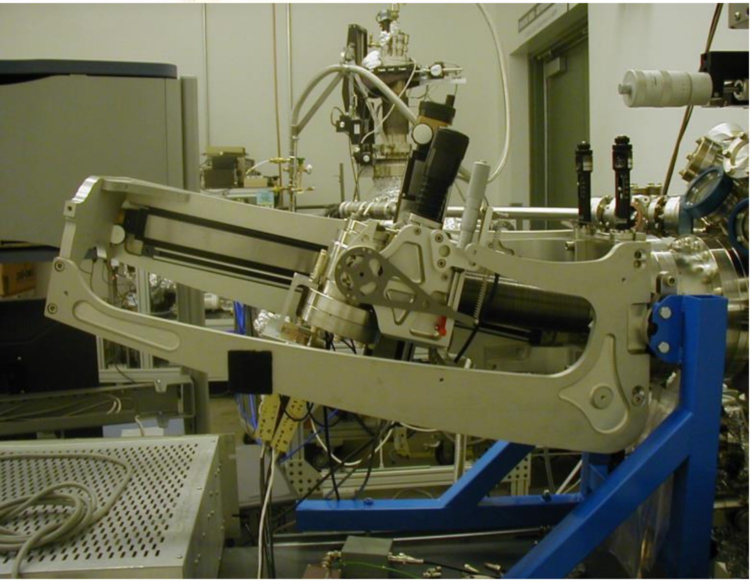
Resolution of Grating Spectrometer



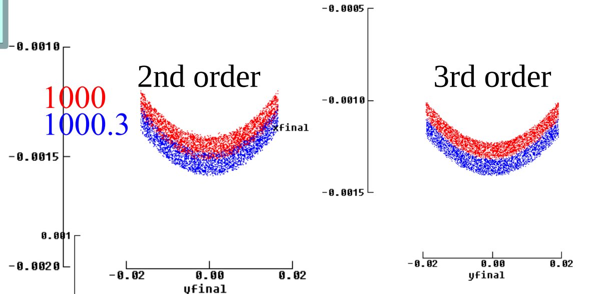
1200 lines/mm, 5 m, resolution:
670 meV (at 1000 eV)
370 meV (O K-edge at 525 eV)

400 lines/mm, 5 m, resolution:
300 meV (C K-edge at 275 eV)
100 meV (S L-edge at 150 eV)

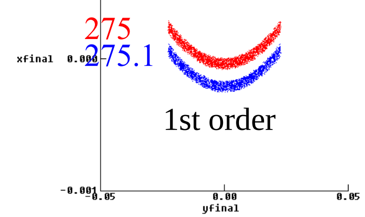
300 lines/mm, 3 m, resolution:
80 meV (Cu M-edge at 72 eV)



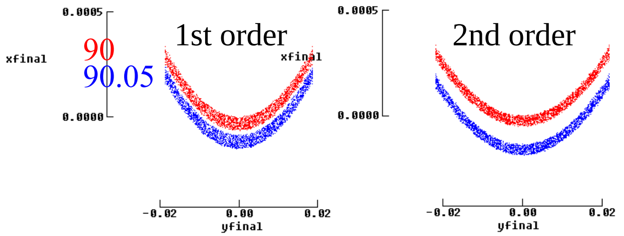
1800 lines/mm, 5 m, resolution:
300 meV (at 1000 eV)
150 meV (O K-edge at 525 eV)



1200 lines/mm, 5 m, resolution:
100 meV (C K-edge at 275 eV)



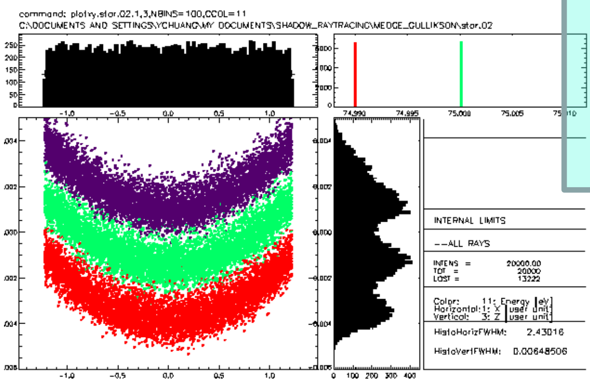
600 lines/mm, 3 m, resolution:
50 meV at 90 eV



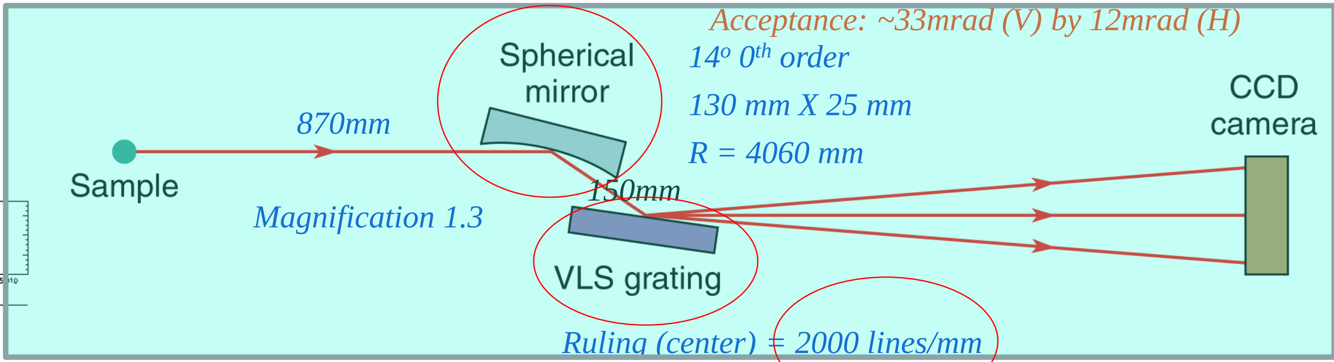
Slit size 10um, Detector resolution 50um

Very High Resolution Spectrometer

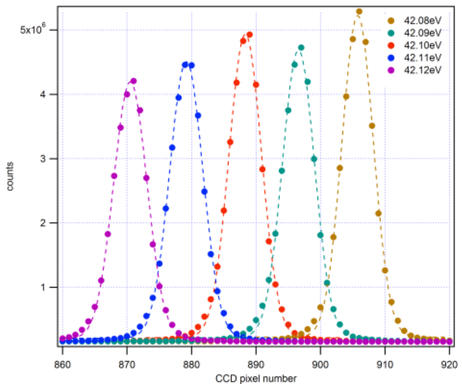
MERLIN at ALS:

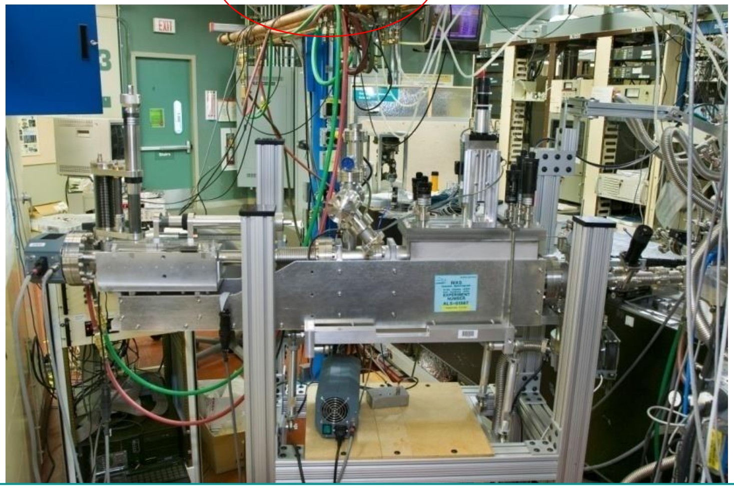


Cu 3p;
75eV+/- 10meV
RP~7,500



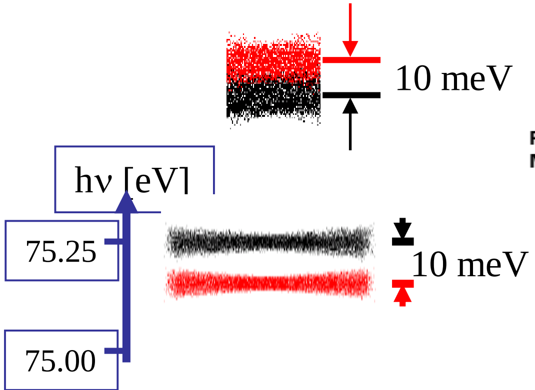
6μm by 15μm source

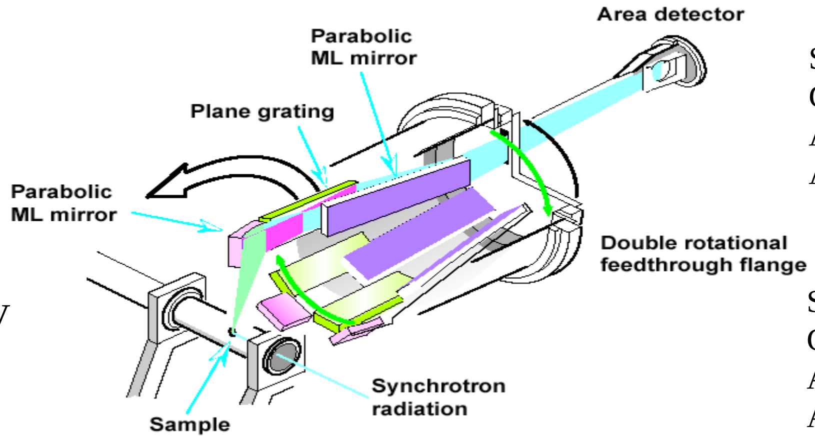




Courtesy of J.H. Guo

Uppsala University:





Source size: 6 μm x 60 μm
Grating: 1200 l/mm
Angle of incidence: 78 deg., outside order
Acceptance angle: 100 mrad x 50 mrad

Source size: 6 μm x 60 μm
Grating: 1800 l/mm
Angle of incidence: 85 deg., inside order
Acceptance angle: 20 mrad x 50 mrad

Intensity of X-ray emission Spectra

❖ Fluorescence Yield

- ➢ Photon hungry experiment
- ➢ Resonance enhancement

❖ Excitation

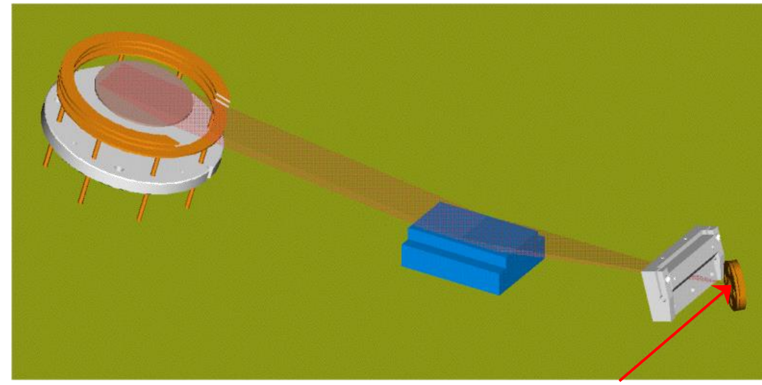
- ➢ Synchrotron radiation
- ➢ Undulator (Linear, EPU)
- ➢ Monochromator

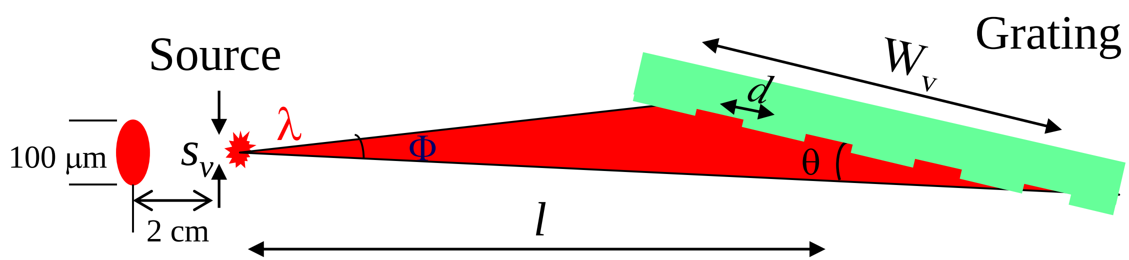
❖ Detection

- ✓ *Diffraction efficiency of grating*
  - *Blaze*
  - *Grove density*
  - *Surface quality*
- ✓ *Quantum efficiency of detector*
  - *MCP (Photon cathode coating)*
  - *CCD*
- ✓ *Beam spot size*
- ✓ *Solid angles to collected (slit size)*

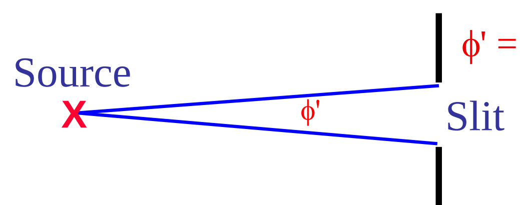
Beam size (1994):

- ➢ 1 mm at BW3 (HASYLAB) & X1B (NSLS)
- ➢ 100 µm at BL7.0.1 (ALS)



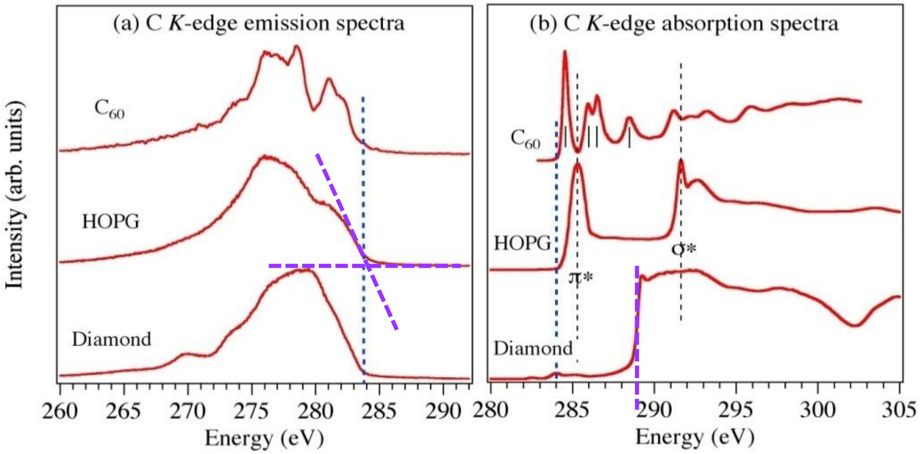


ϕ = 2.5 cm / 5 m = 5 mrad

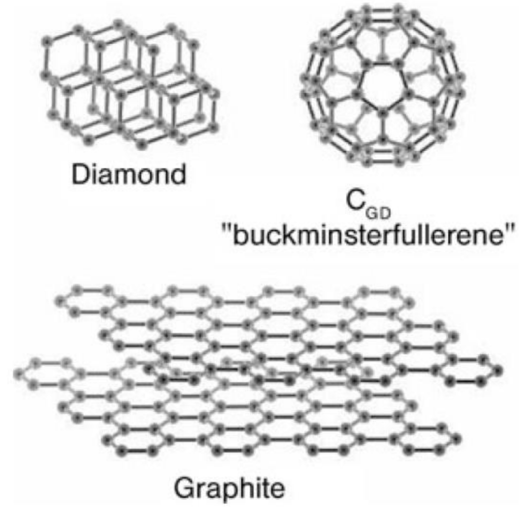


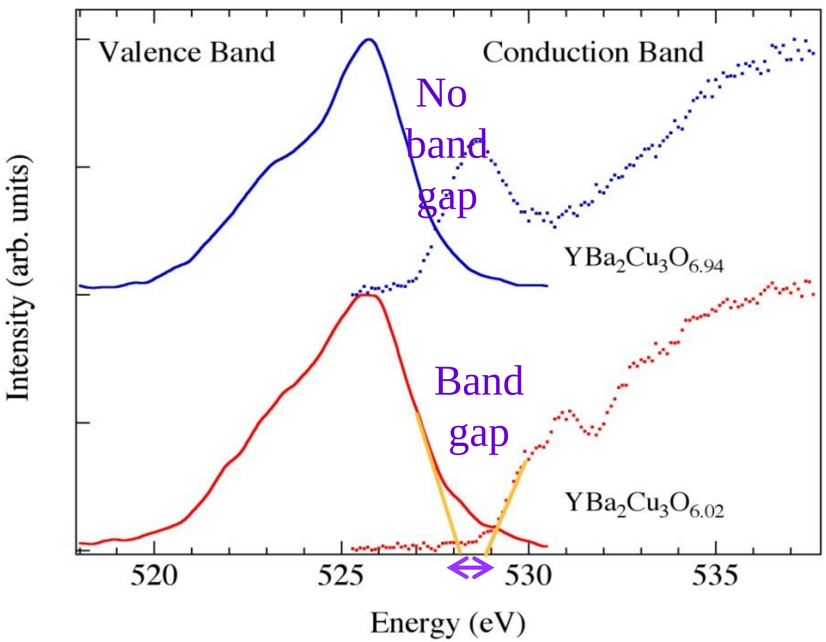
The beam size can be seen at 20 mm distance:
5 mrad x 20 mm = 100 µm

XES + XAS : Bandgap determination

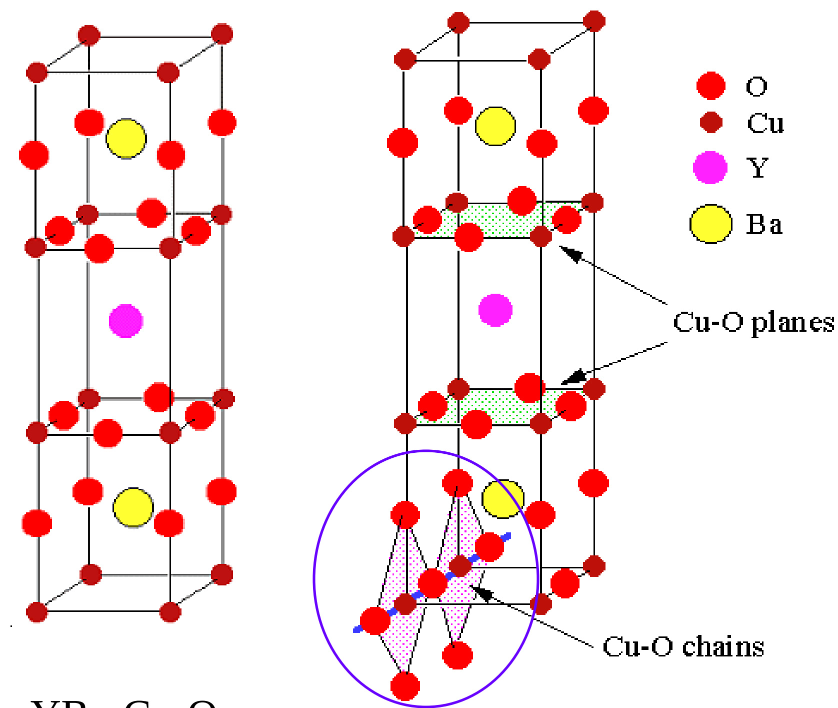


Guo, Int. J. Nanotech. 1-2, 193 (2004)



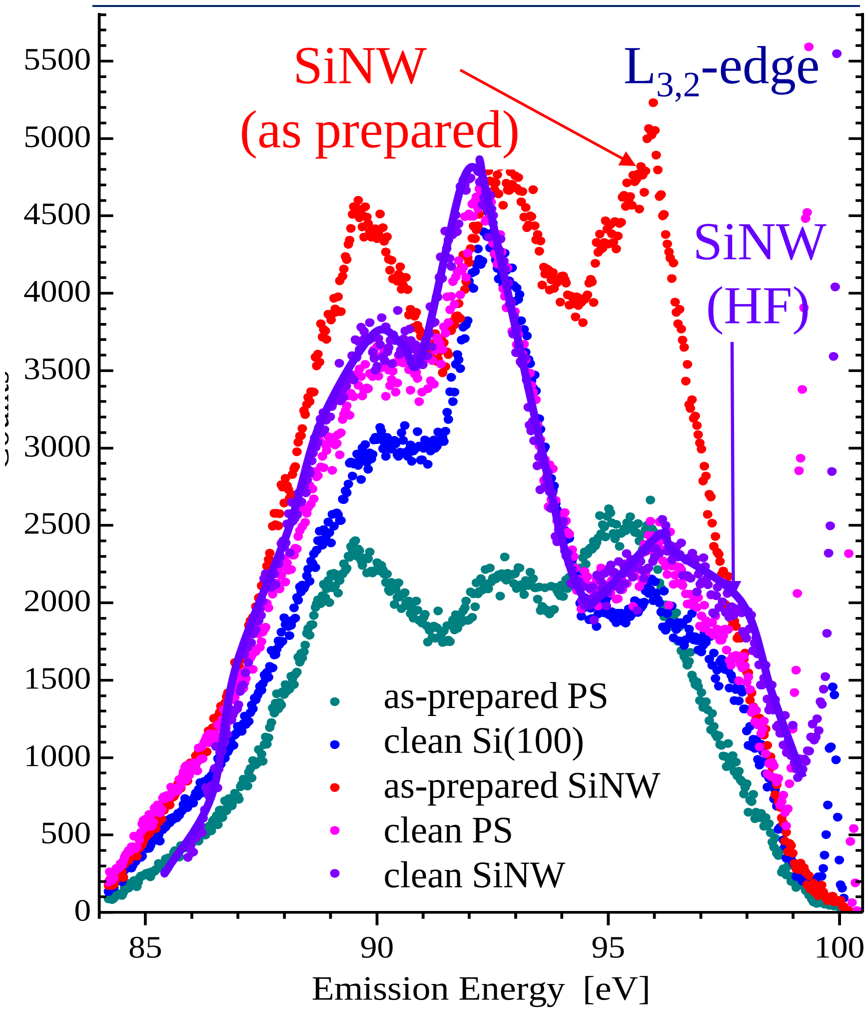


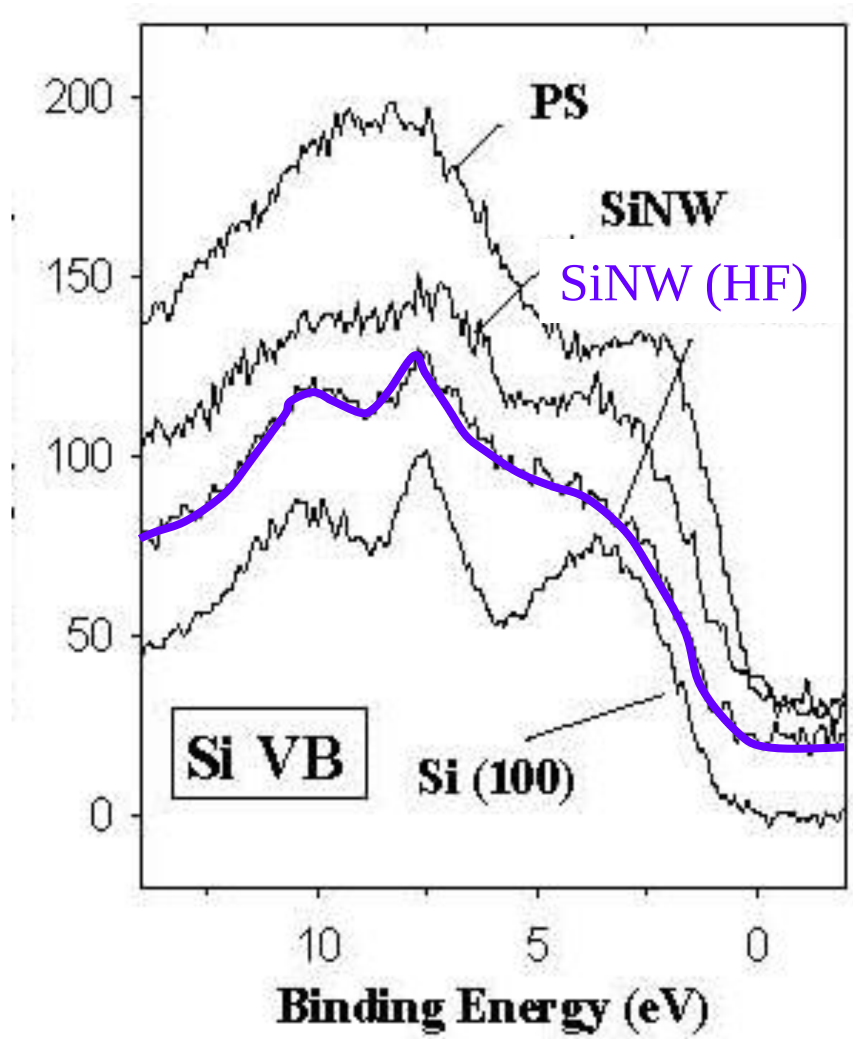
Guo et al., Phys. Rev. B 61, 9140 (2000)



$YBa_2Cu_3O_6$ $YBa_2Cu_3O_{7-\delta}$

Si L XES: Si → Valence Band   XPS: Valence Band

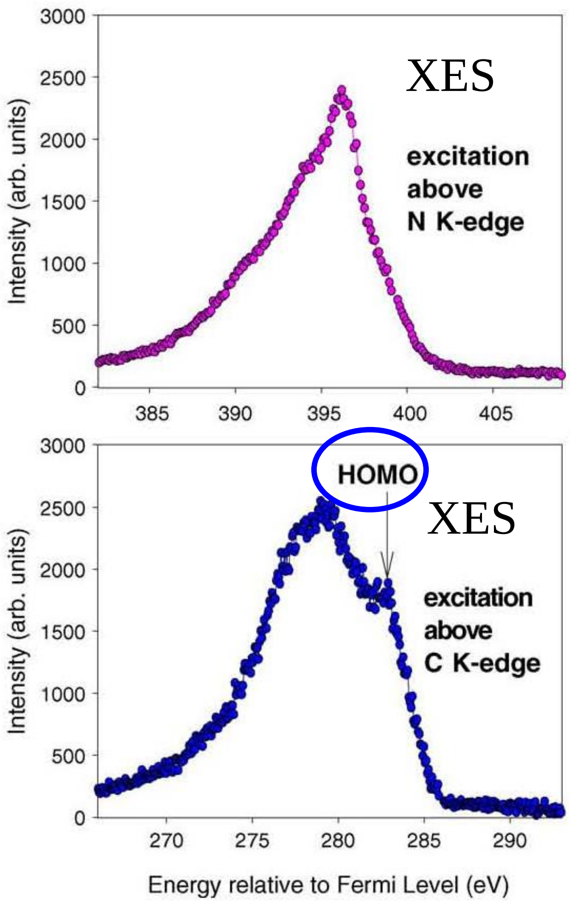


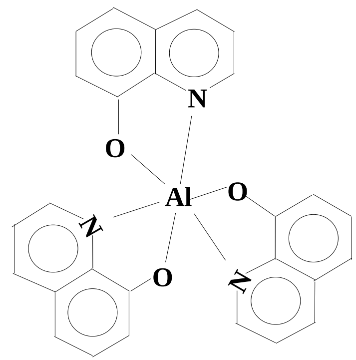


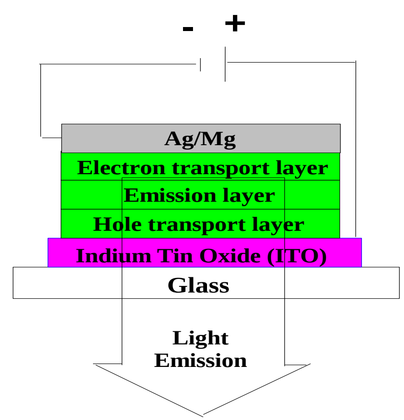
XES of Alq_3

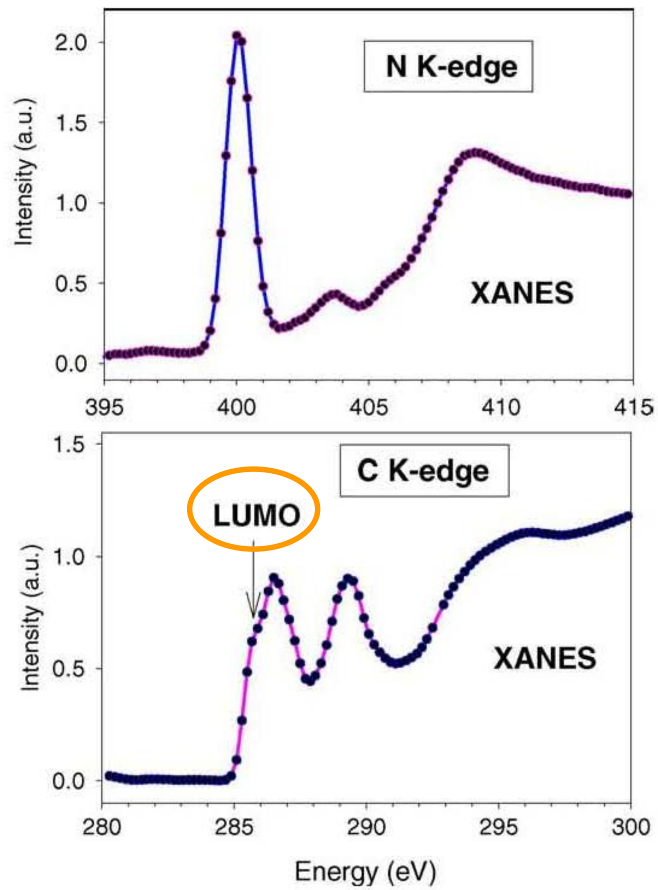
XES:PDOS (occupied)

XANES:PDOS (unoccupied)





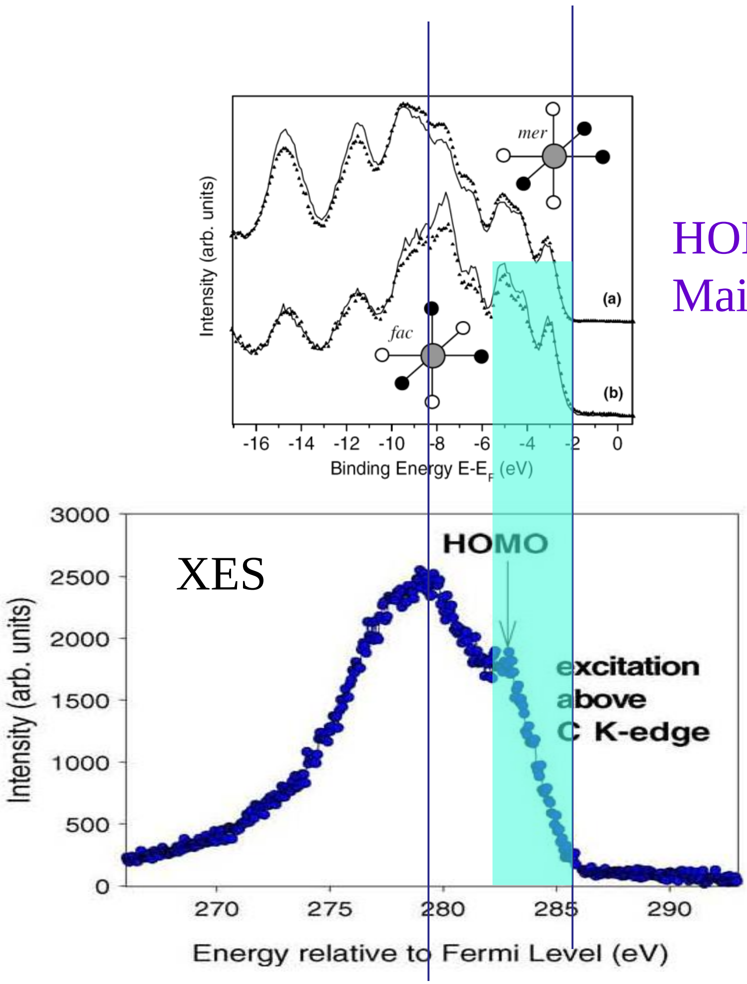




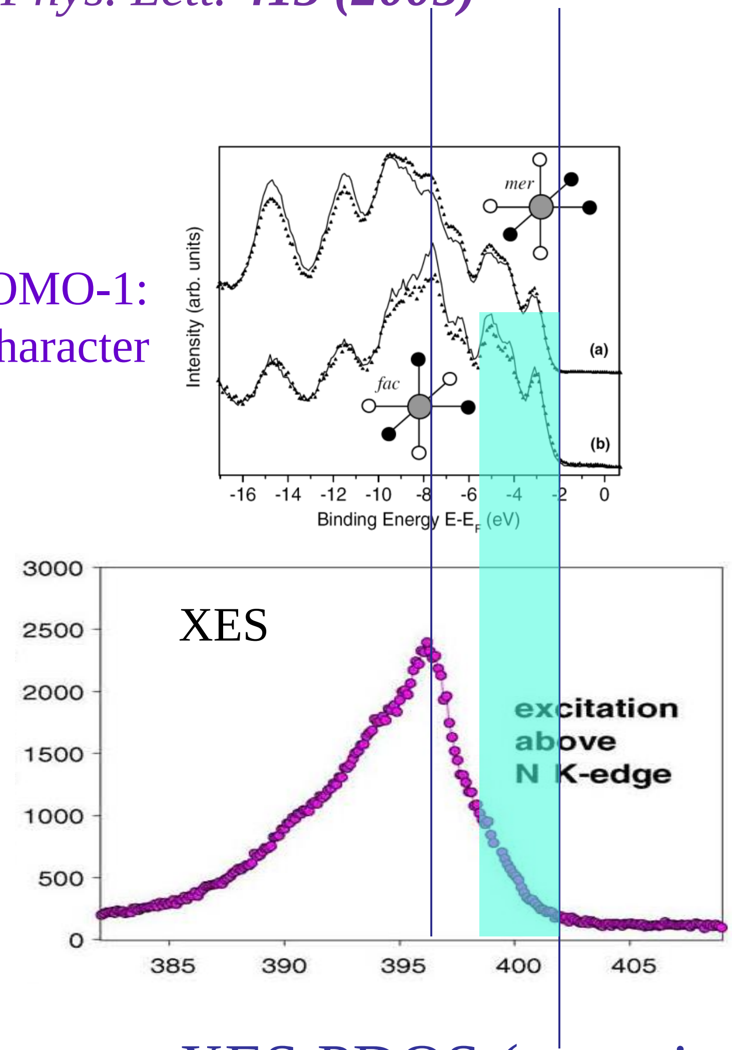
P.-S.G. Kim et. al. J. Elect. Spectros. , 901, 141(2005)

XES of Alq_3

XPS: Caruso et al. *Chem. Phys. Lett.* ***413 (2005)***



HOMO, HOMO-1:
Mainly C character



P.-S.G. Kim et. al. J. Elect. Spectros. , 901, 141(2005)

XES:PDOS (occupied)

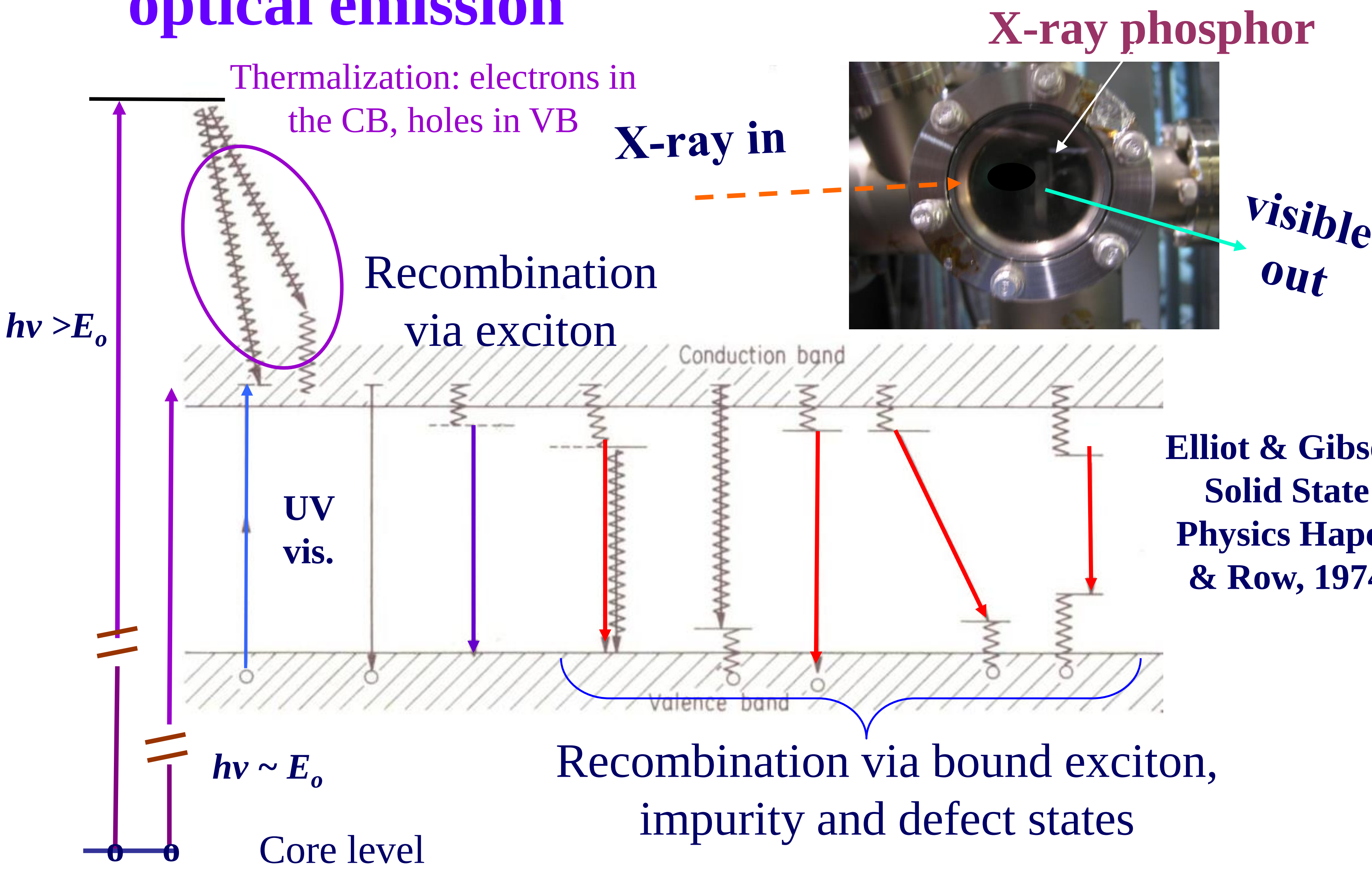
XEOL: X-ray Excited Optical Luminescence

X-ray photons in, optical photons (UV, visible, near IR) out.

Luminescence can be element and excitation channel specific.

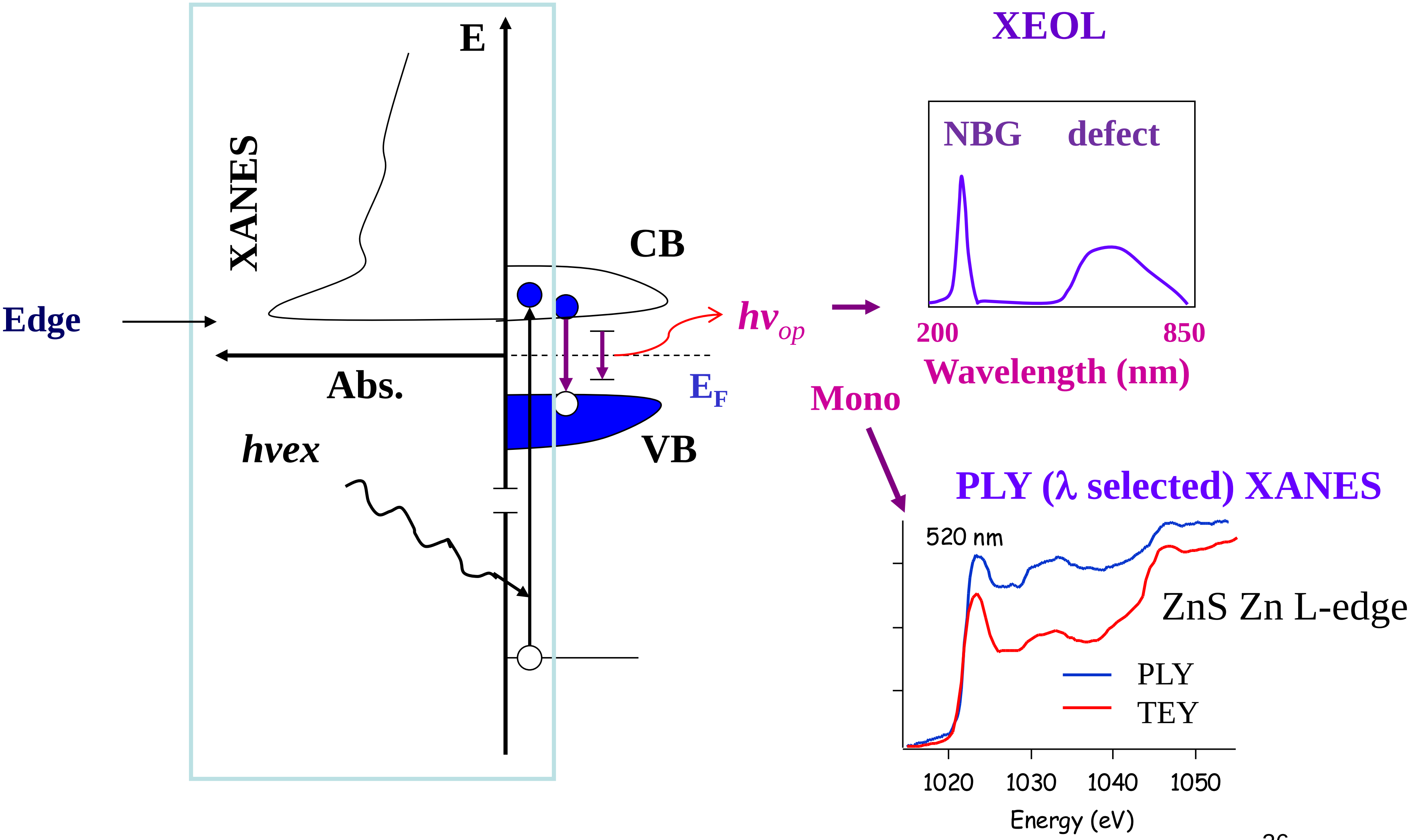
Monitor the absorption spectrum using the photo-luminescence yield (PLY) → **element and chemical specificity**

XEOL - Conversion of X-ray energy into optical emission



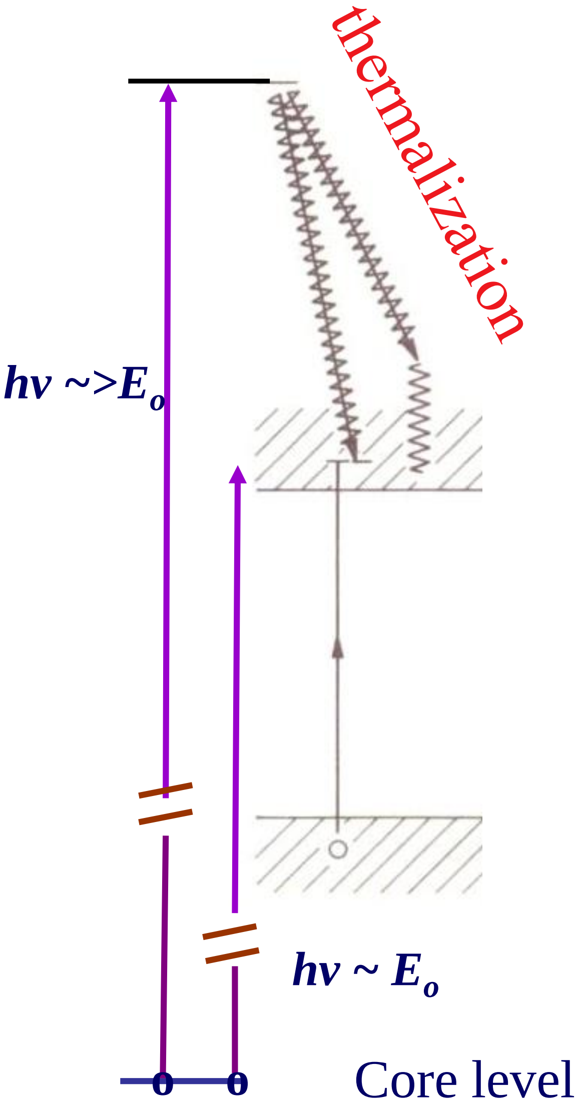
Elliot & Gibson
Solid State
Physics Haper
& Row, 1974

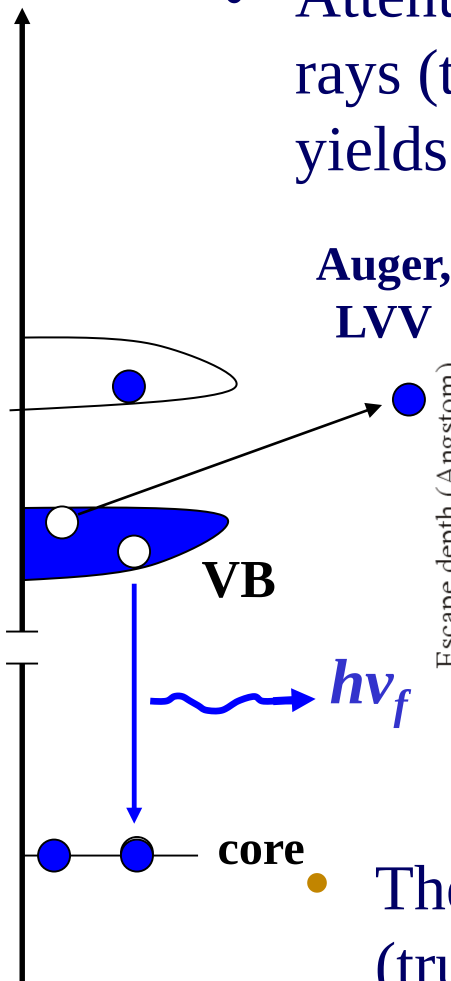
XAS and XEOL (Optical XAFS)

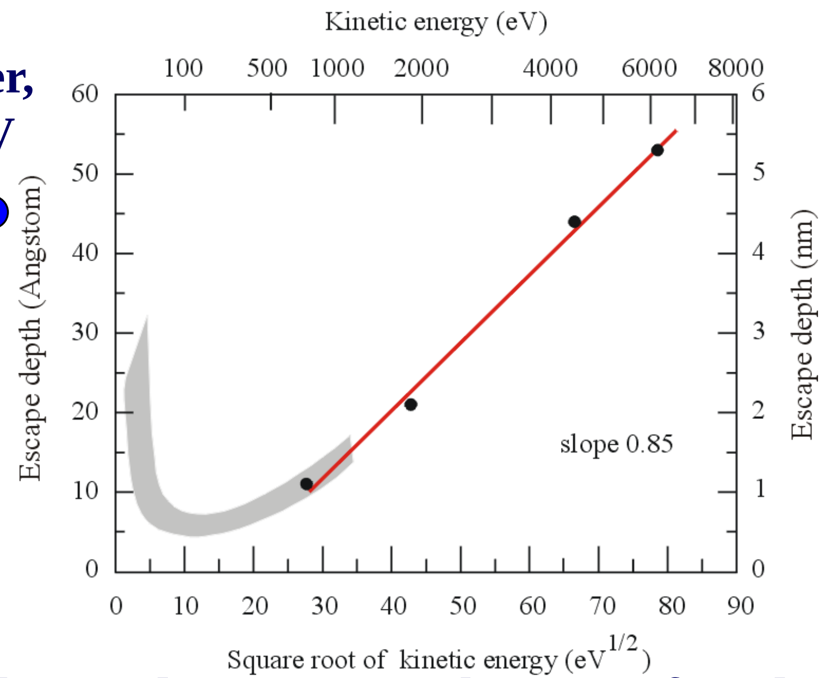


De-excitation, Energy transfer in nanostructures

- Decay channels
- Attenuation of e and fluorescence x-rays (thermalization) in the solid yields secondary electrons (holes)







- Thermalization track is confined (truncated) in nanostructures

Photon-in: Synchrotron Light

→ • Tunability → Element, edge, excitation channel specificity

• High brightness

• Polarization

→ • Time structure

XEOL Techniques

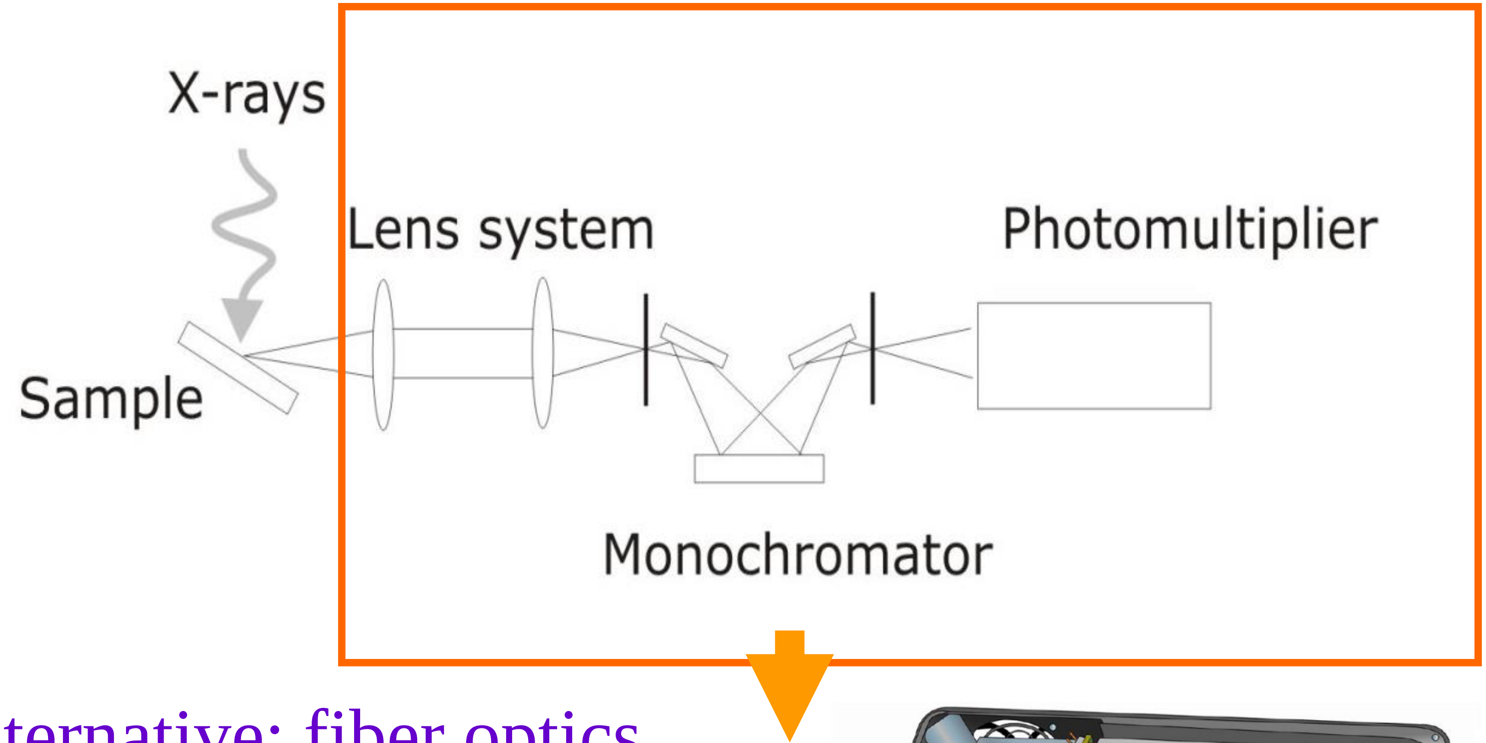
Energy Domain

XEOL: Luminescence induced by selected excitation photon energy (usually across an absorption edge)
Optical XAFS: Monitored with the optical signal

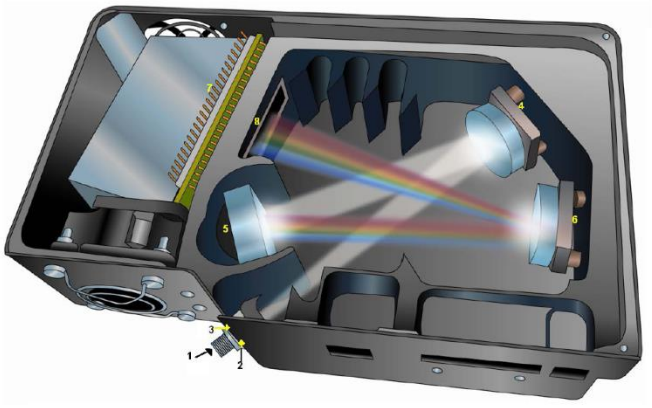
Time Domain

Lifetime: Synchrotron pulse
Time-resolved (gated) XEOL: Luminescence within a selected time window between pulses
Time-gated Optical XAFS: Time window

XEOL: Experimental Layout



Alternative: fiber optics, spectrograph with CCD detectors (e.g. Ocean Optics QE65000)

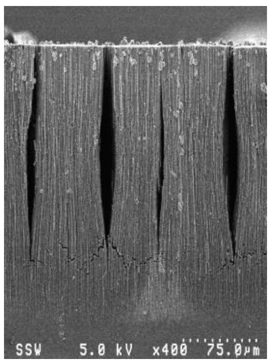


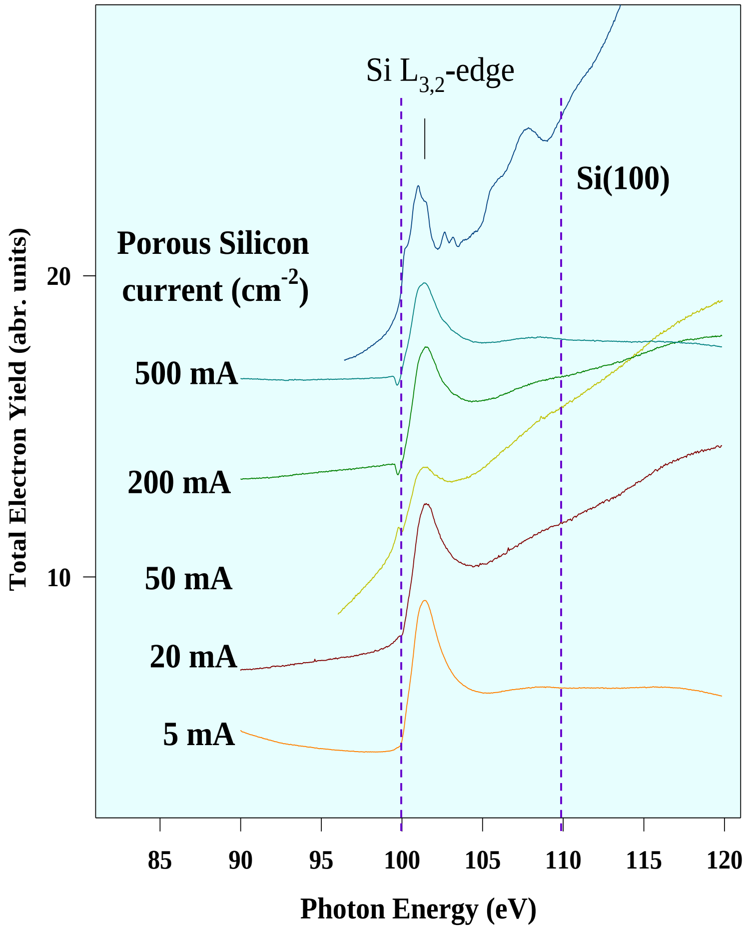
QE65000 Spectrometer with Components

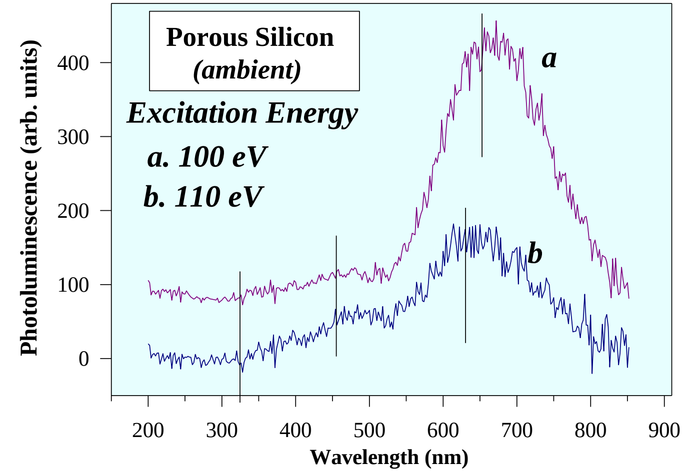
XEOL - Energy Domain

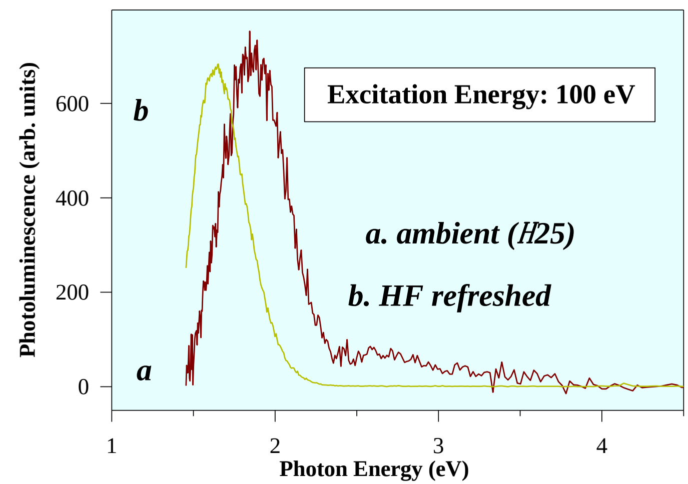
- Case studies
  - Si nanostructure
  - ZnS nanoribbons (crystal structure engineering)
  - Soft matter
  - Alq_3 (OLED materials)
  - 2D – XEOL TiO_2 nanowire

Si L-edge XEOL (porous silicon)

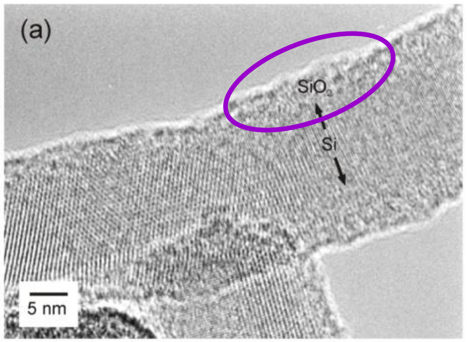








Si K-edge XEOL of silicon nanowires



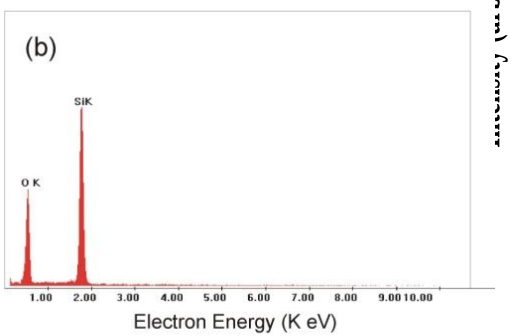
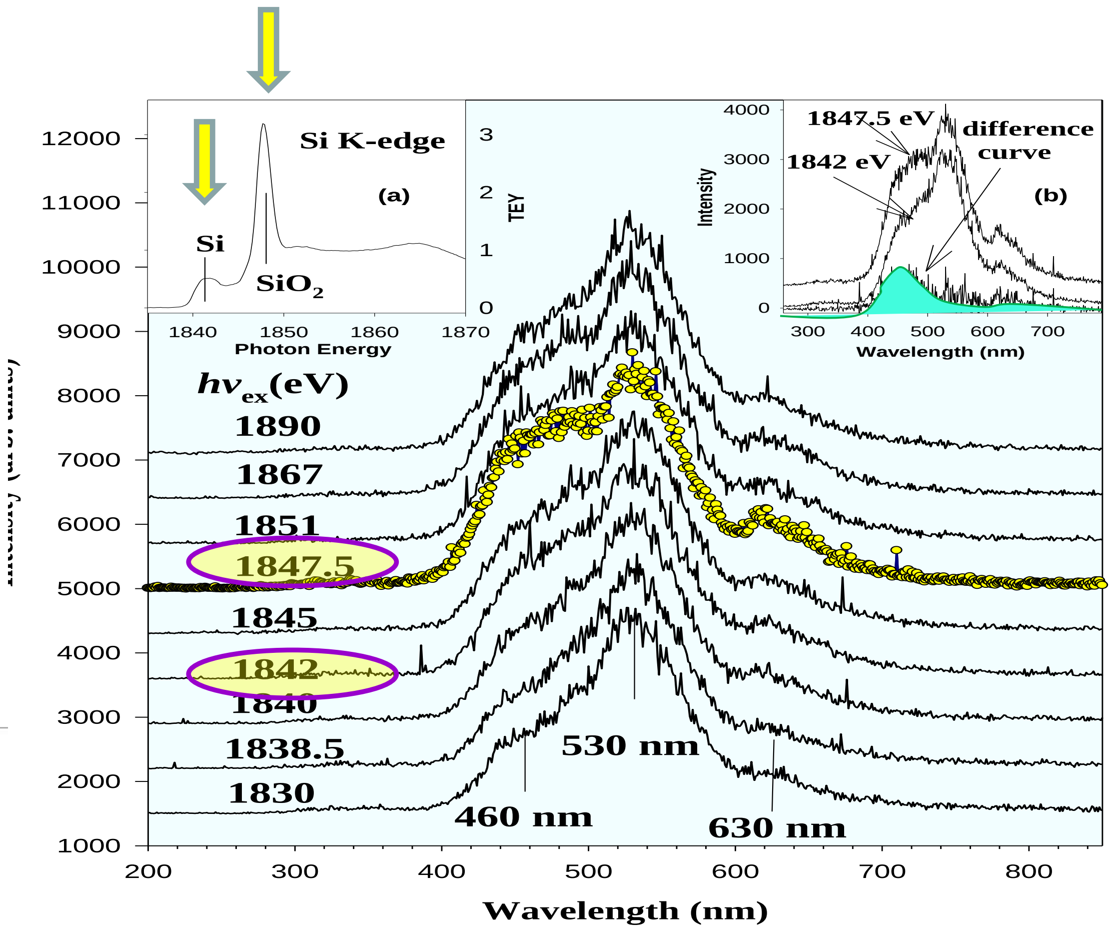
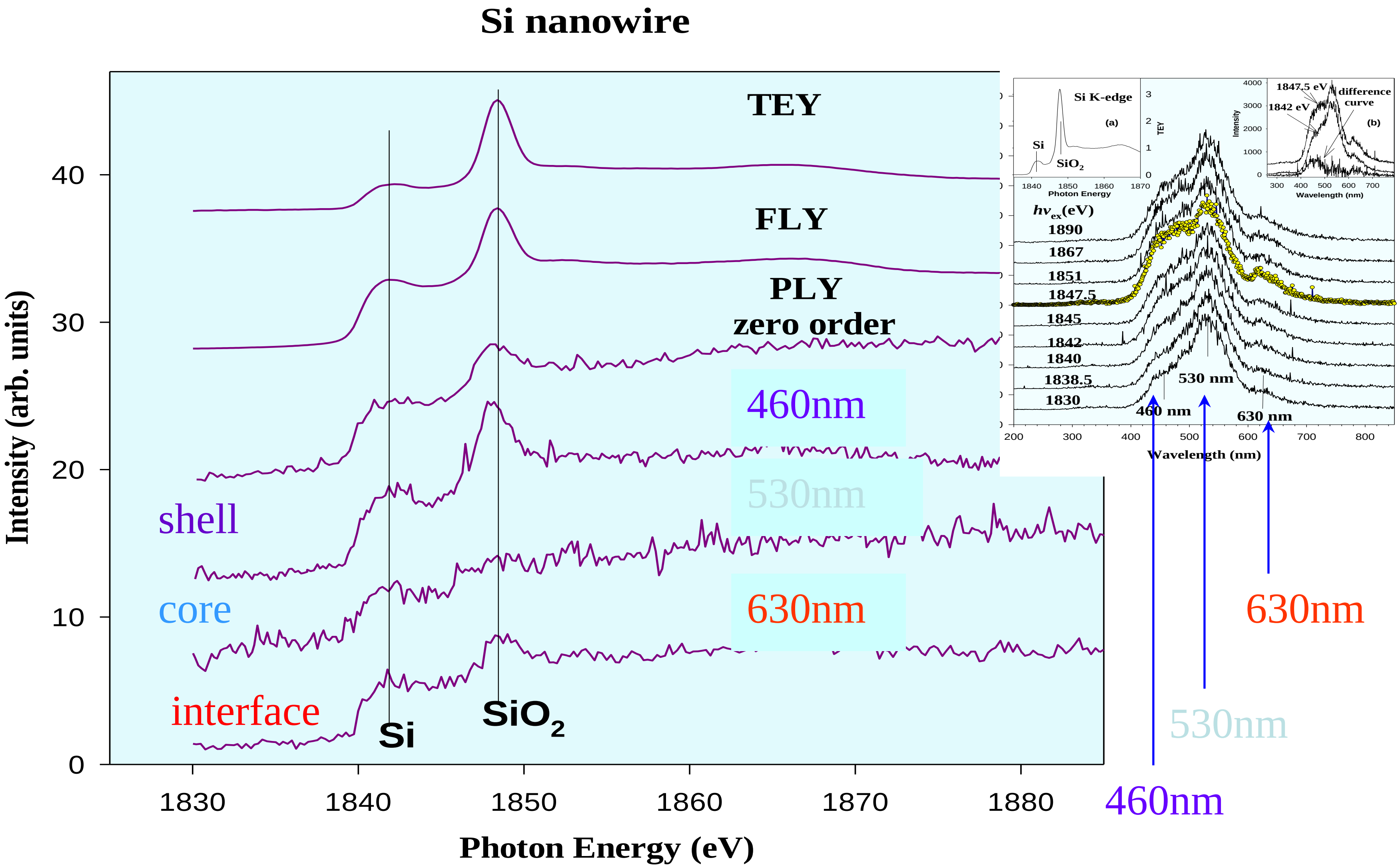


Fig. 1(a) The TEM image and (b) EDS result of as-prepared SiNWs



Phys. Rev. B 70, 045313 (2004)

Si K-edge: PLY


Si nanowire
TEY
FLY
PLY
zero order
460nm
530nm
630nm
shell
core
interface
Si
SiO2
Intensity (arb. units)
Photon Energy (eV)
0
10
20
30
40
1830
1840
1850
1860
1870
1880
Si K-edge
(a)
Si
SiO2
Photon Energy
TEY
hvex(eV)
1890
1867
1851
1847.5
1845
1842
1840
1838.5
1830
460 nm
530 nm
630 nm
Wavelength (nm)
1847.5 eV
1842 eV
difference curve
(b)
Intensity
200
300
400
500
600
700
800
630nm
530nm
460nm

XEOL and chemistry of SiNW

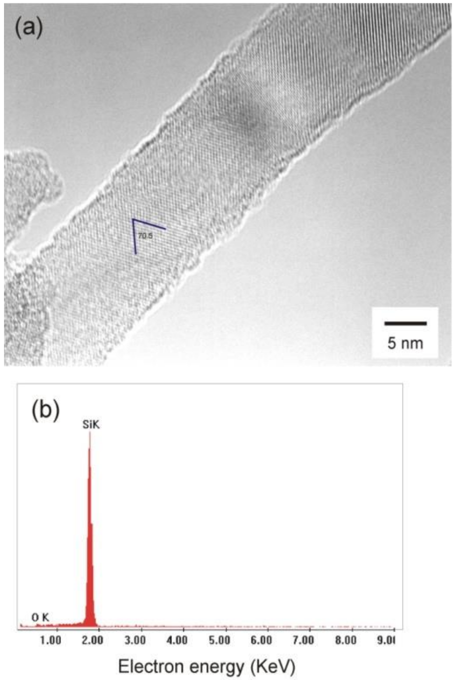
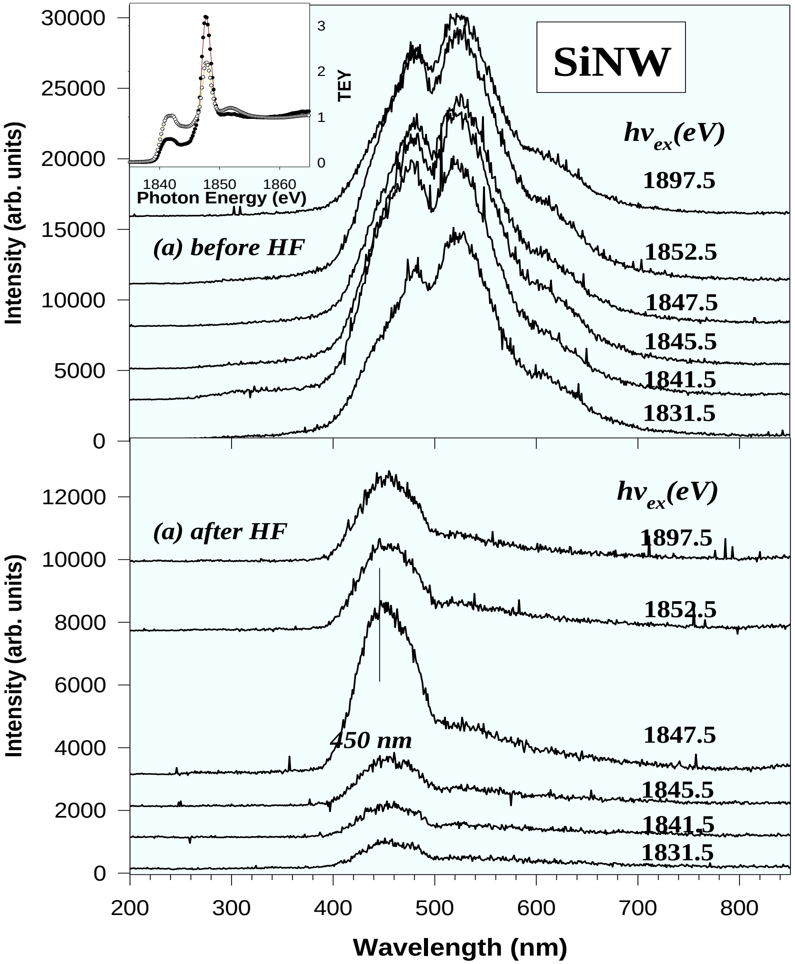
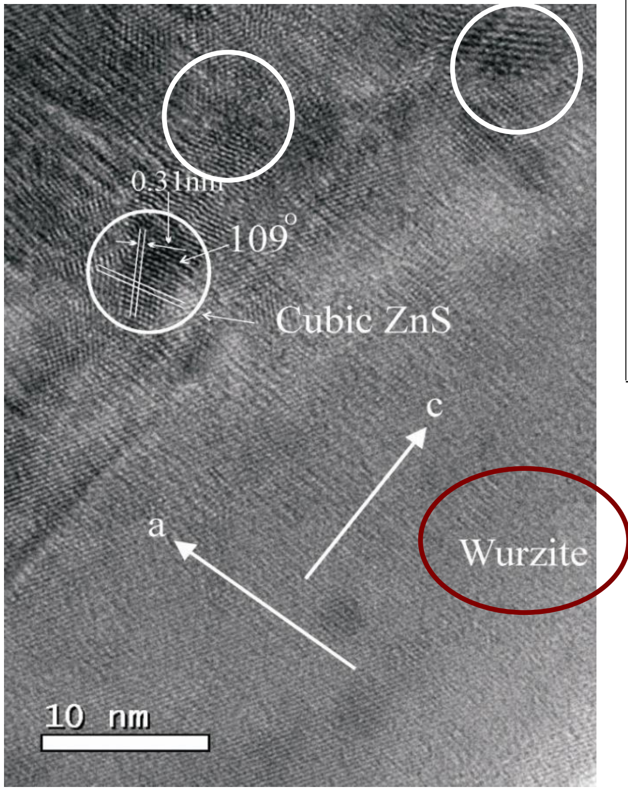


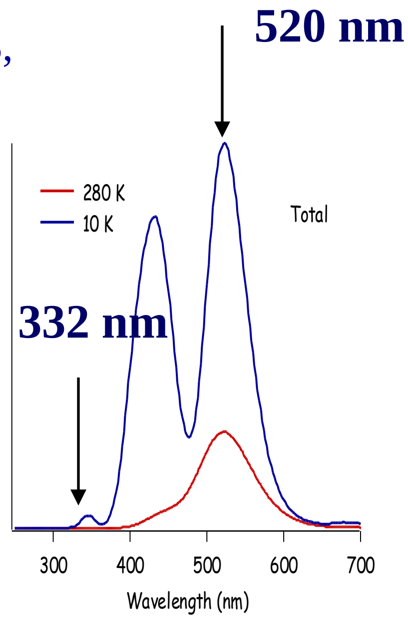
Fig. 2 The TEM image (a) and EDS result (b) of HF etched SiNWs

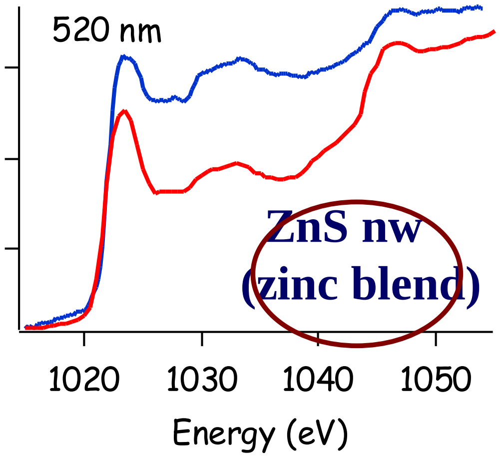


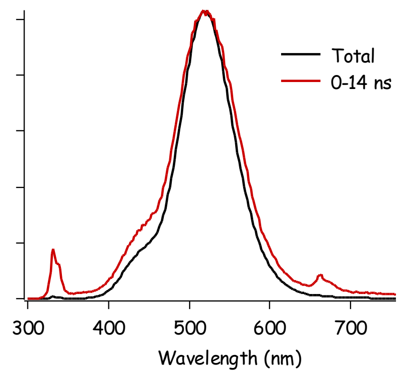
ZnS hetero-crystalline nano-ribbon

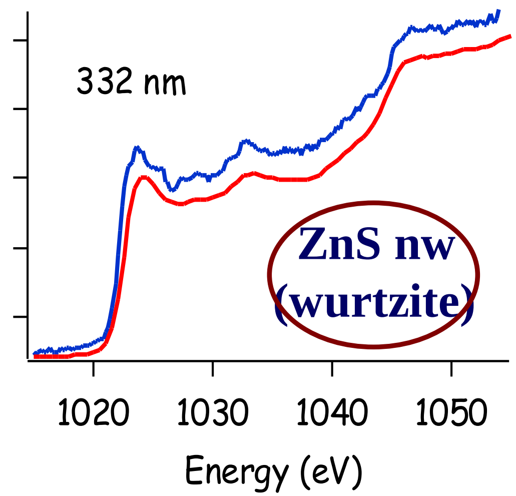
X.-T. Zhou et al., **J. Appl. Phys.** 98, 024312(2005)







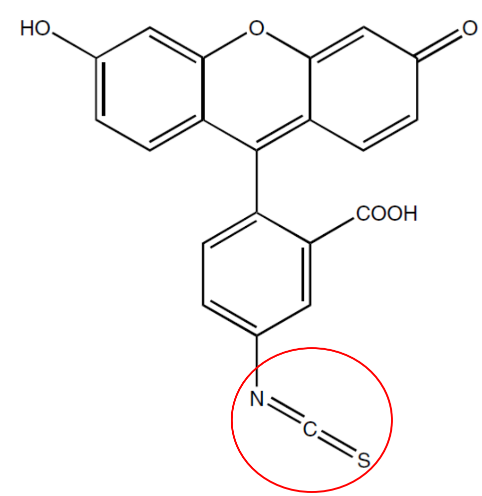




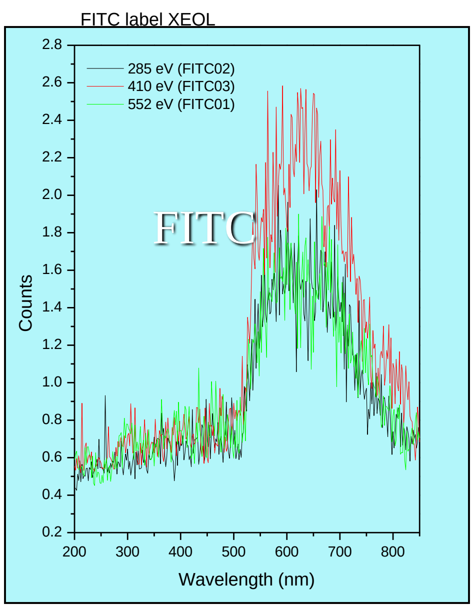
R.A. Rosenberg et al., **Appl. Phys. Lett.** 87, 253105(2005)

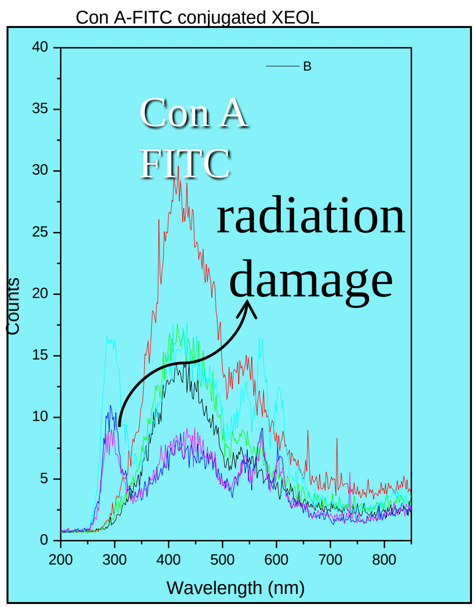
XEOL from soft matters

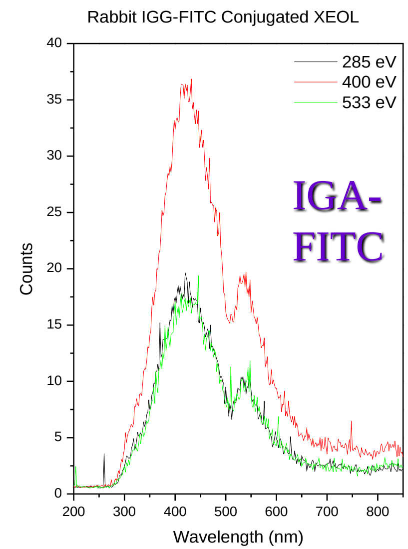
Fluorescein isothiocyanate **(FITC)** label



FITC conjugated concanavalin A (Con A) lectin **(Con A-FITC)** and goat anti-rabbit immunoglobulin G (IgG) **(IgG-FITC)**



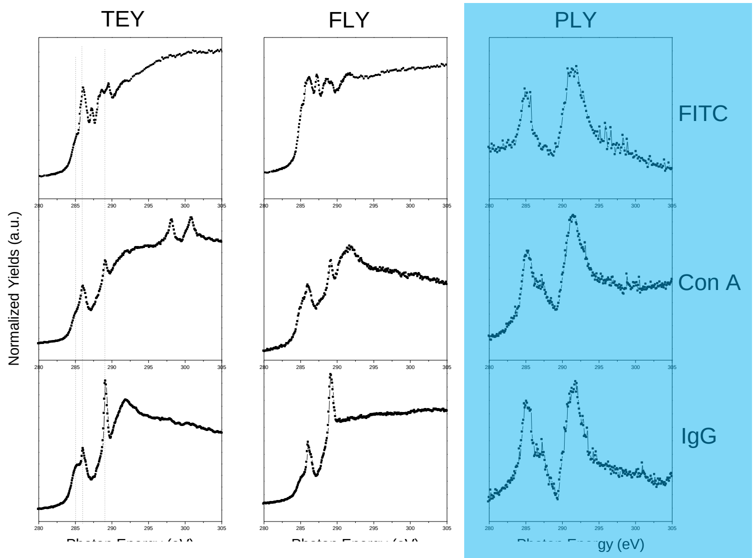


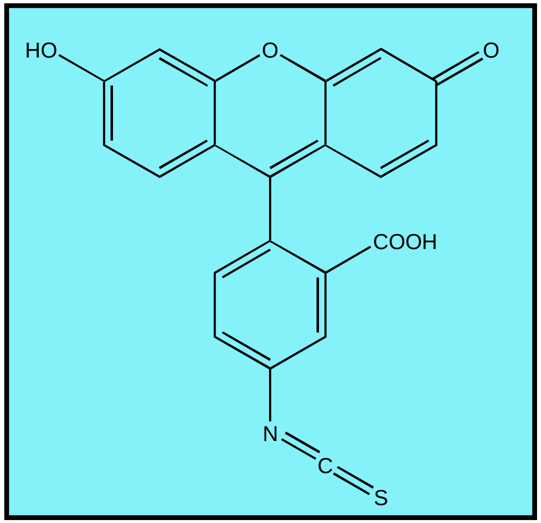


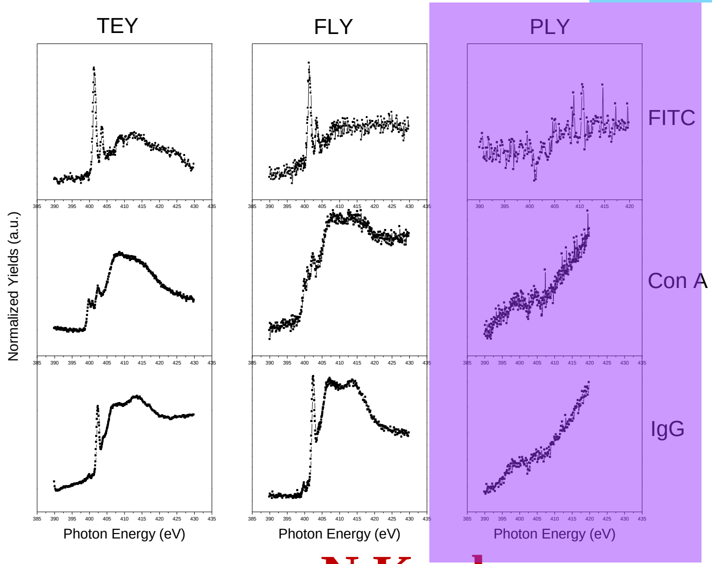
P.-S. G. Kim et al. Chem. Phys. Lett. 39, 44(2004)

PLY from labeled proteins

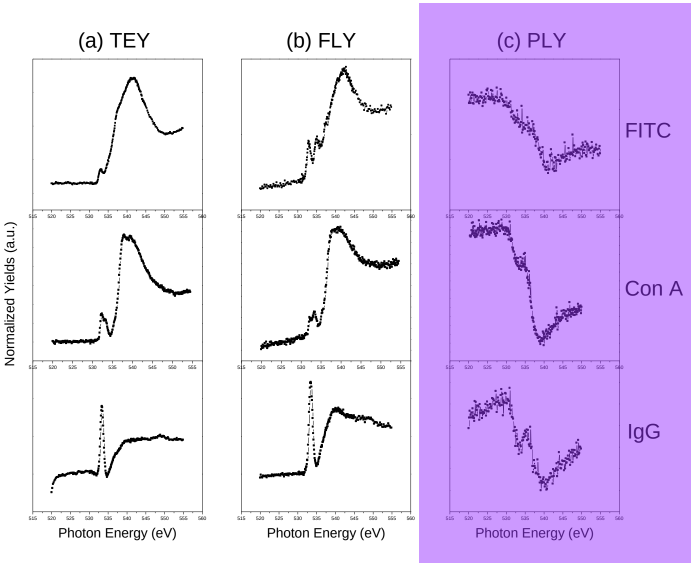
C K-edge





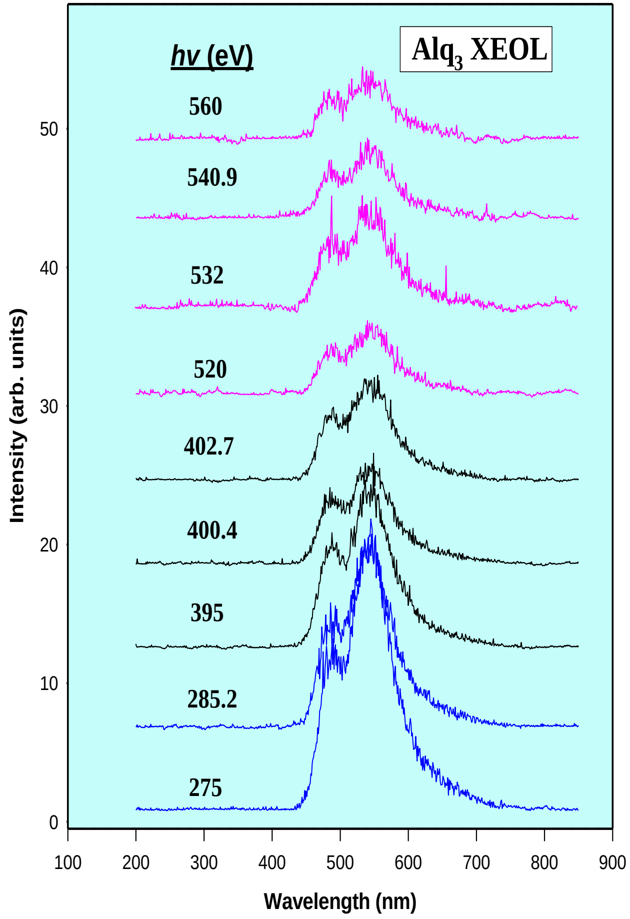


N K-edge

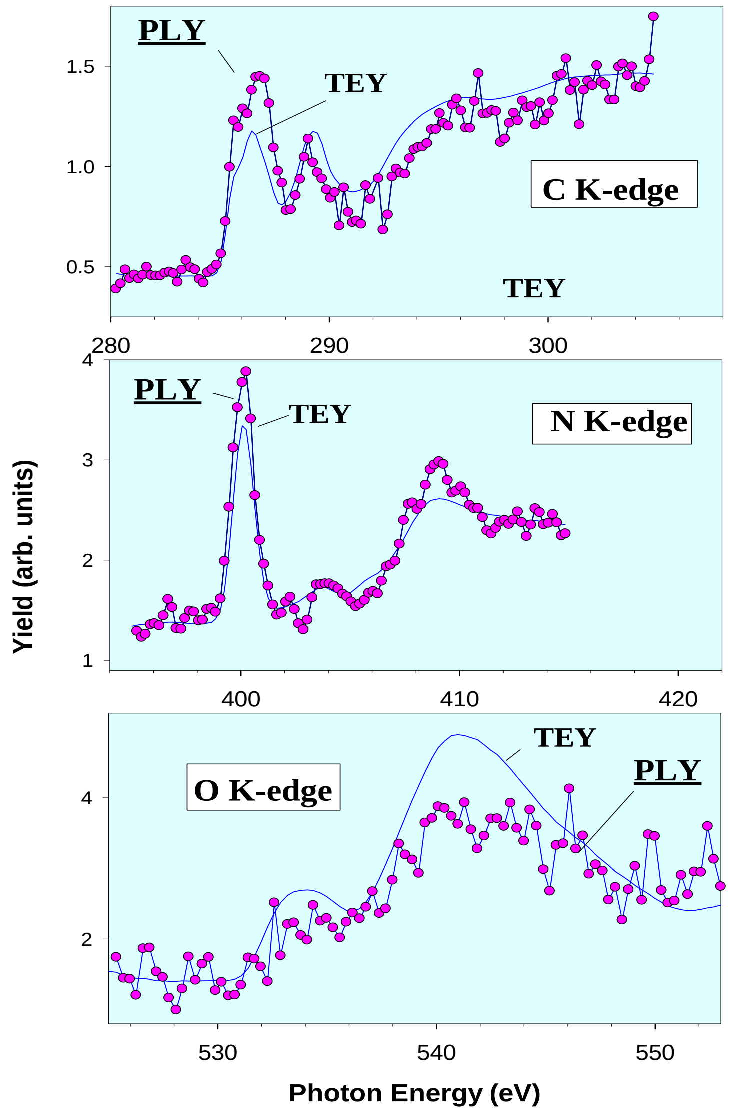


O K-edge

Alq$_3$ XEOL

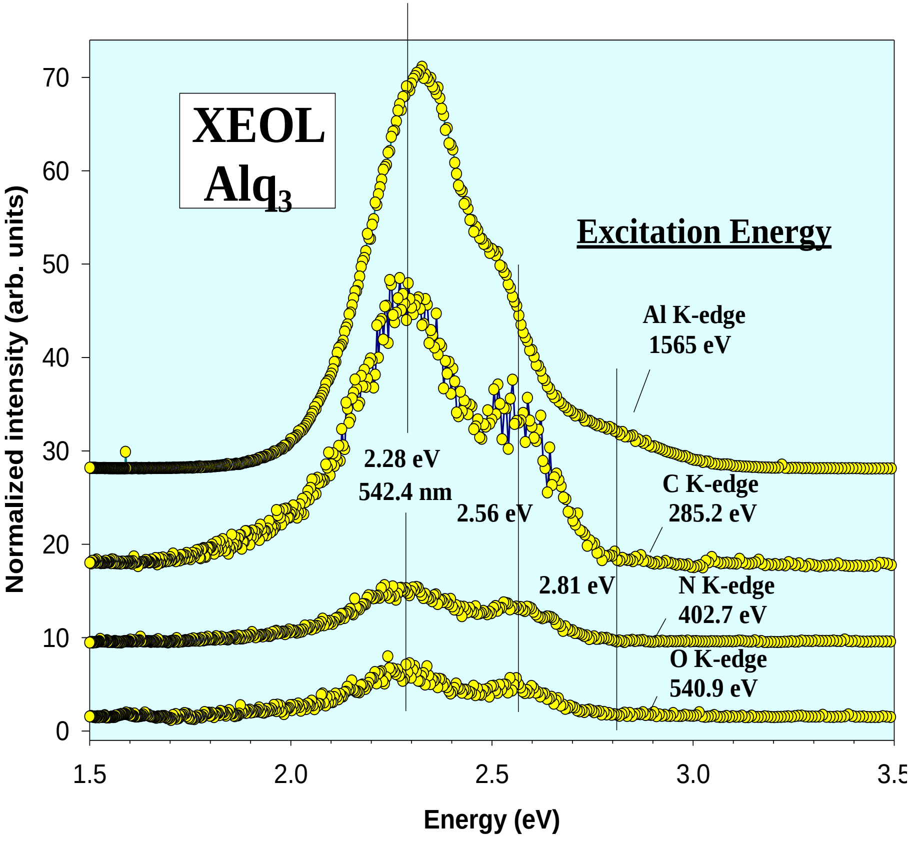


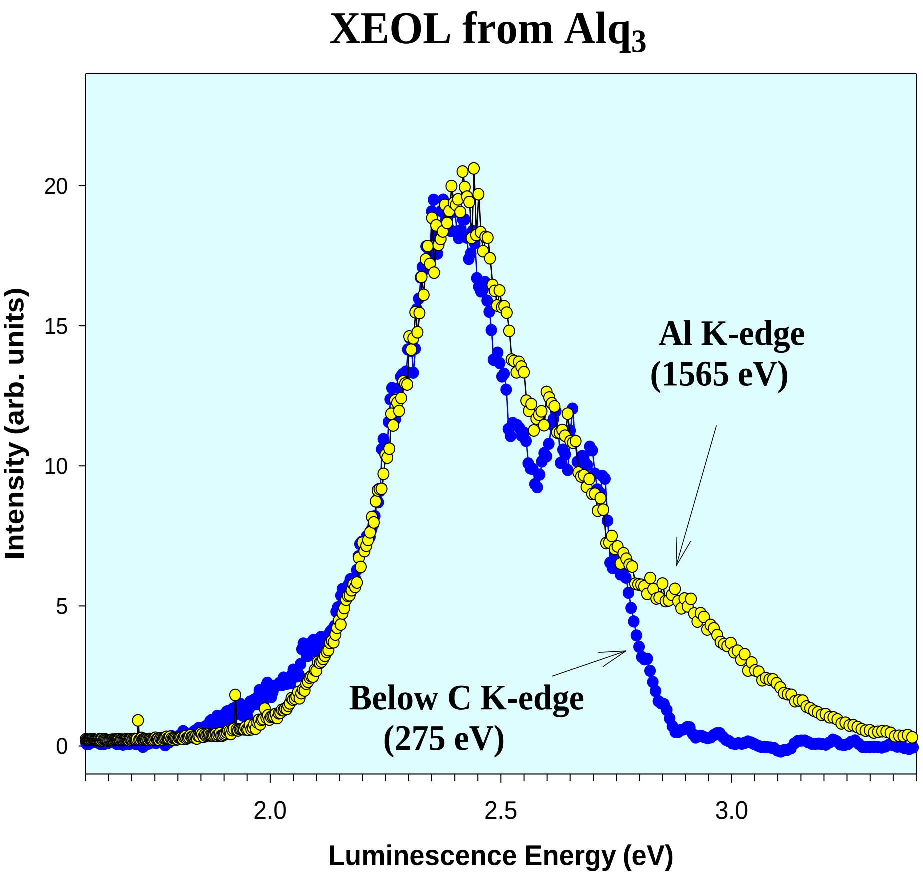
XAFS (near-edge)



Naftel et al. Appl. Phys. Lett. 78, 1847(2001).

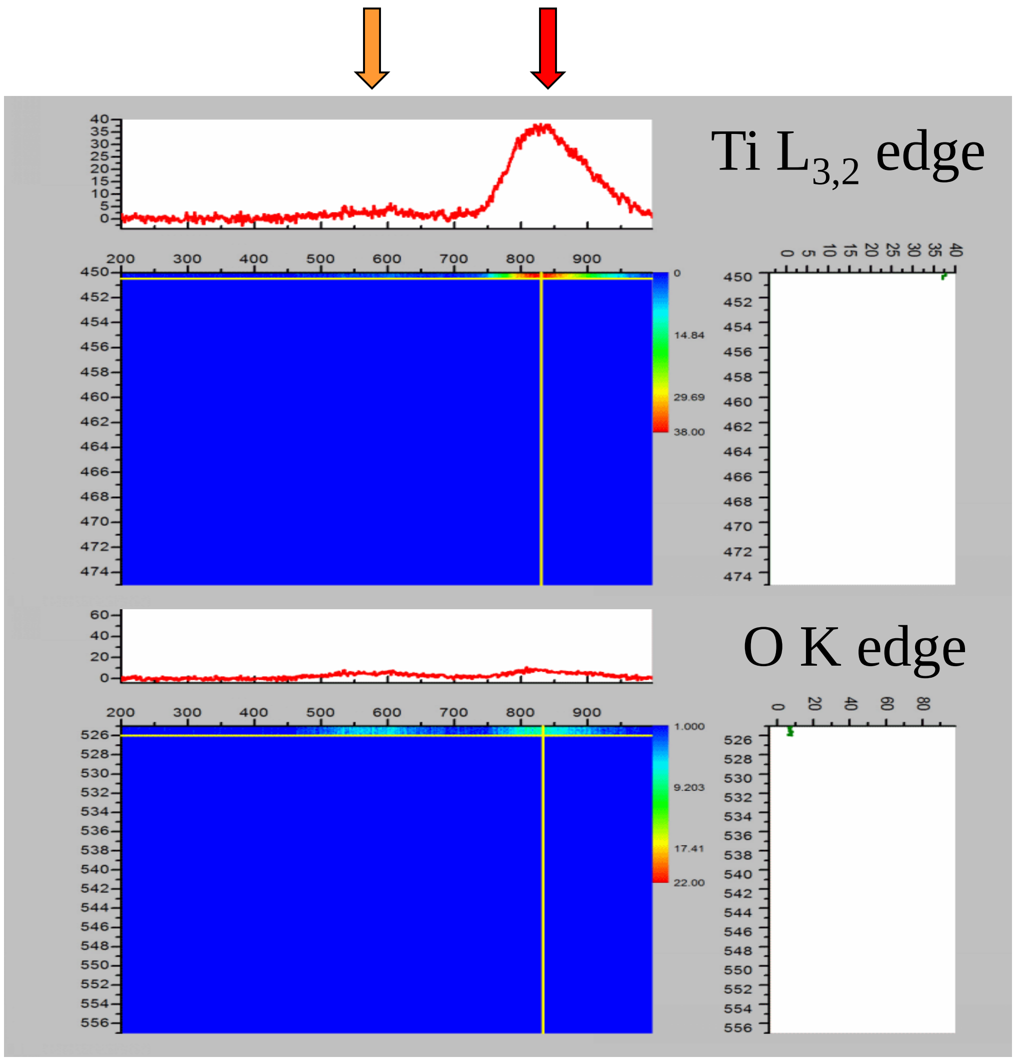
Excitation Channel Dependent XEOL



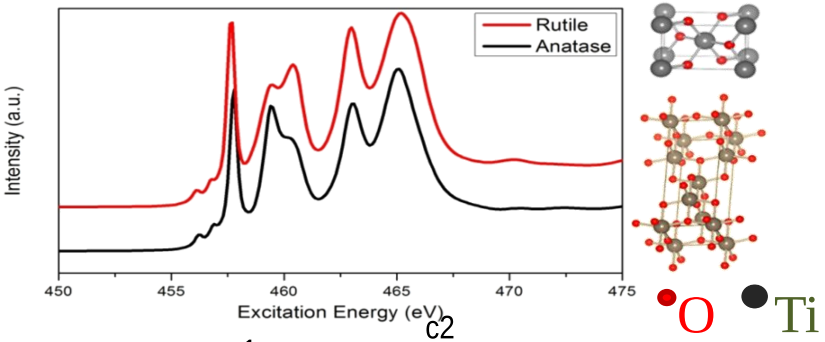


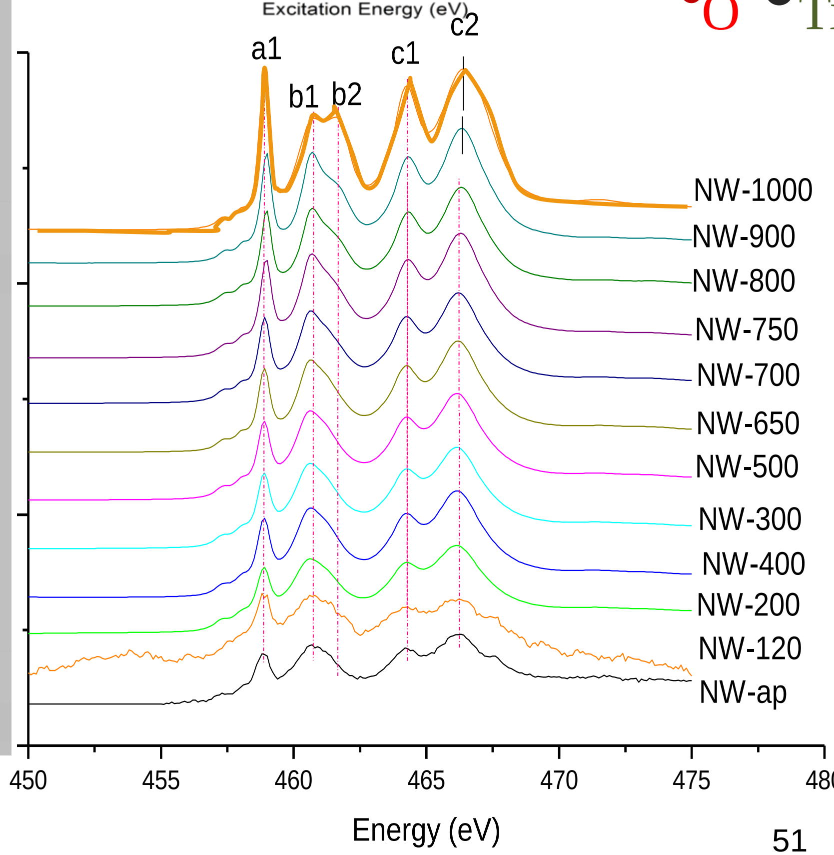
2-D XAS-XEOL TiO_2 Nanowire (1000 °C)

anatase rutile



Ti $L_{3,2}$-edge

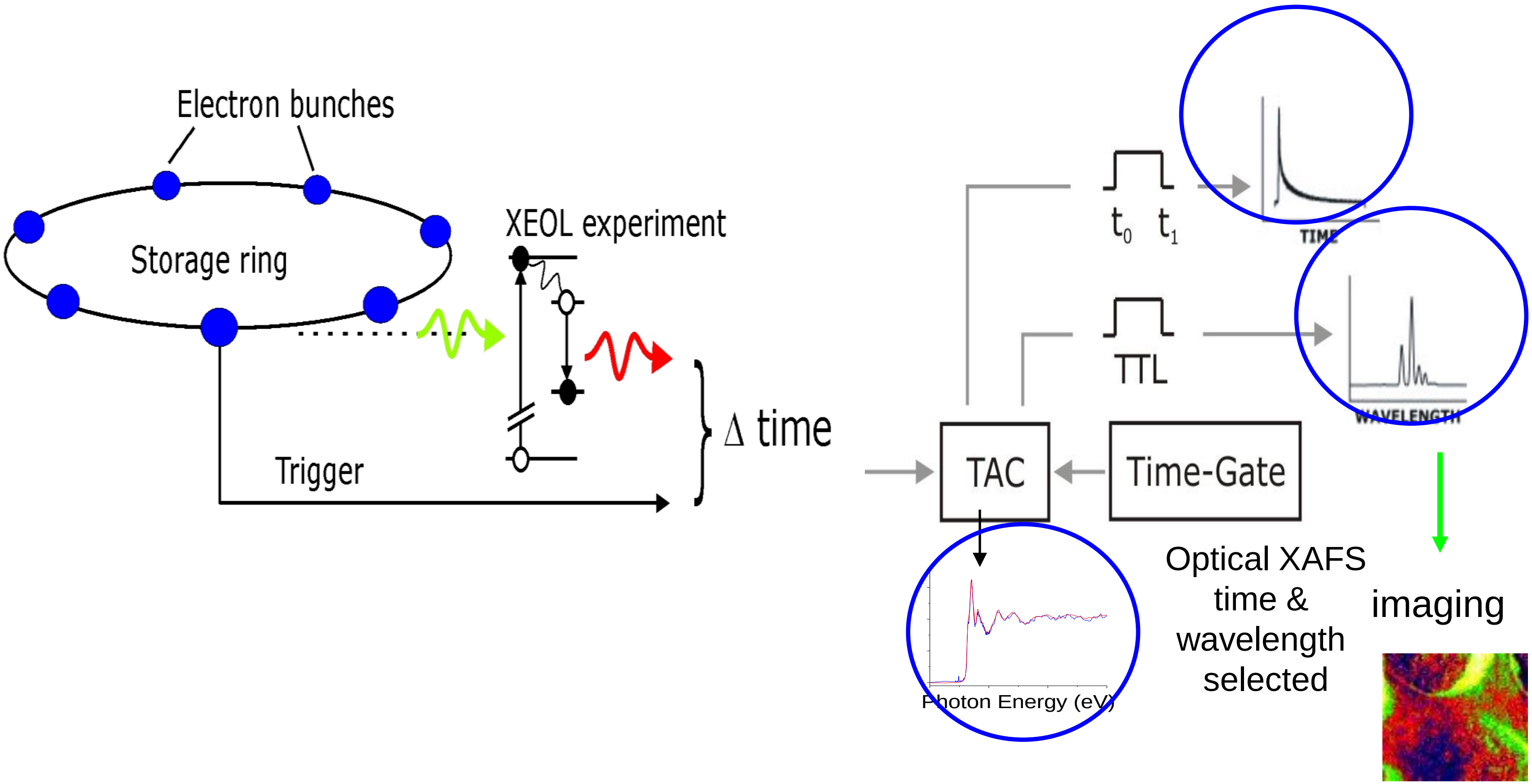




A. Zhao et al. unpublished

XEOL - Time Domain

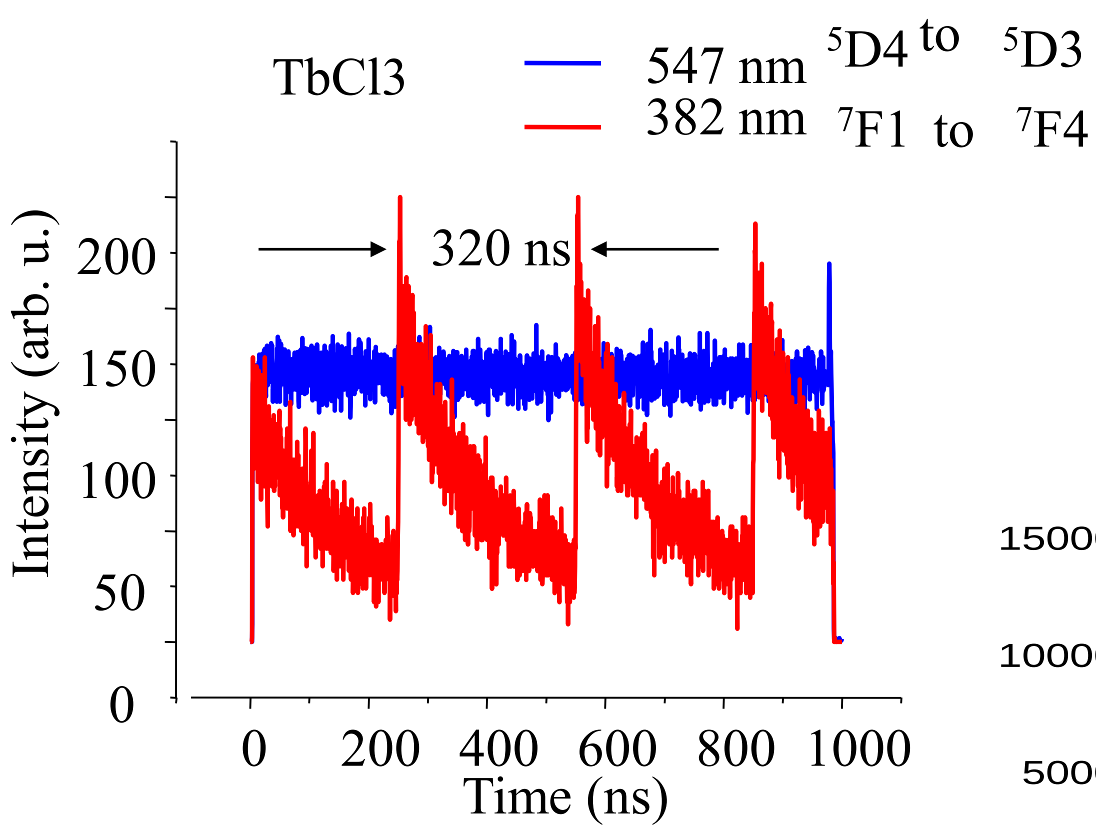
TRXEOL-Time-resolved XEOL



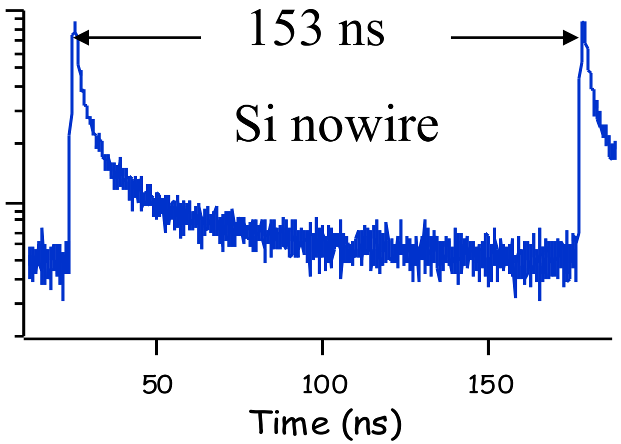
T.K. Sham and R.A. Gordon **SRI** 2009

TRXEOL from SRC, APS and CLS

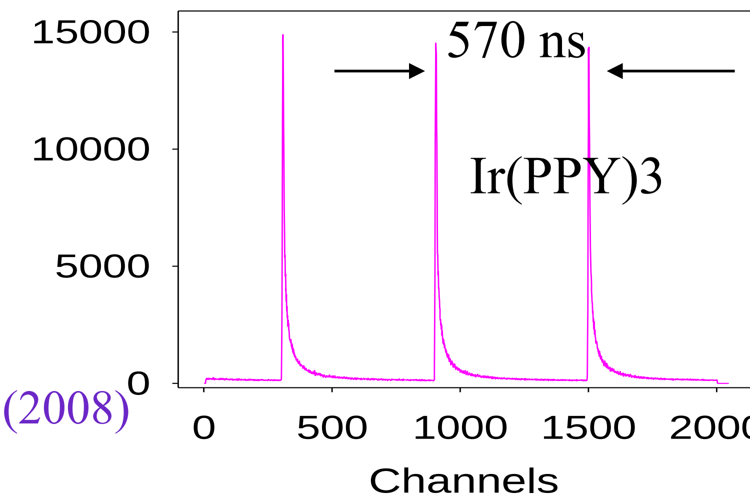
SRC single bunch



APS top up: 24 bunches



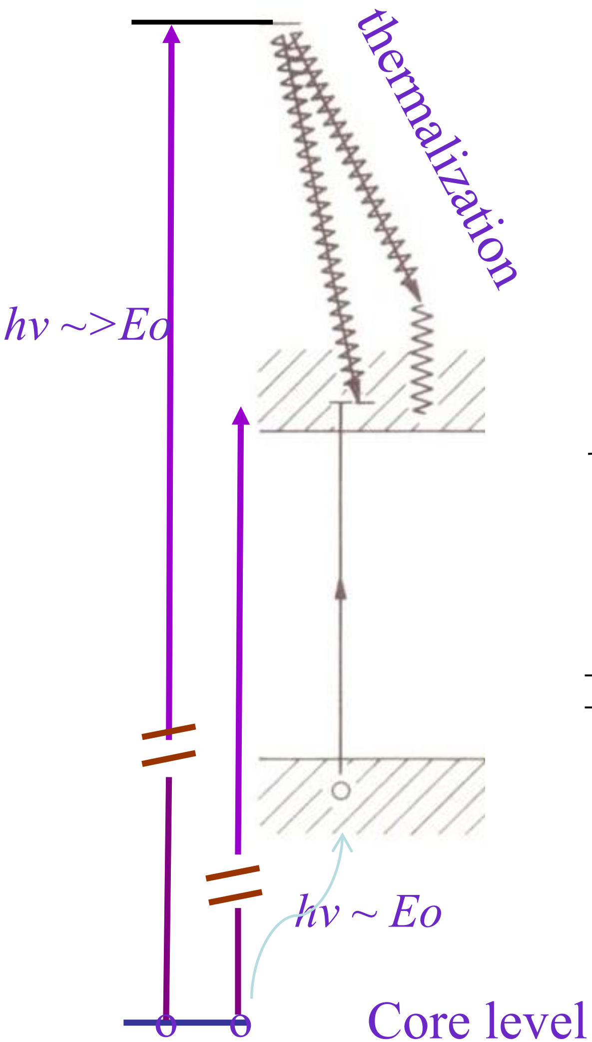
CLS single bunch

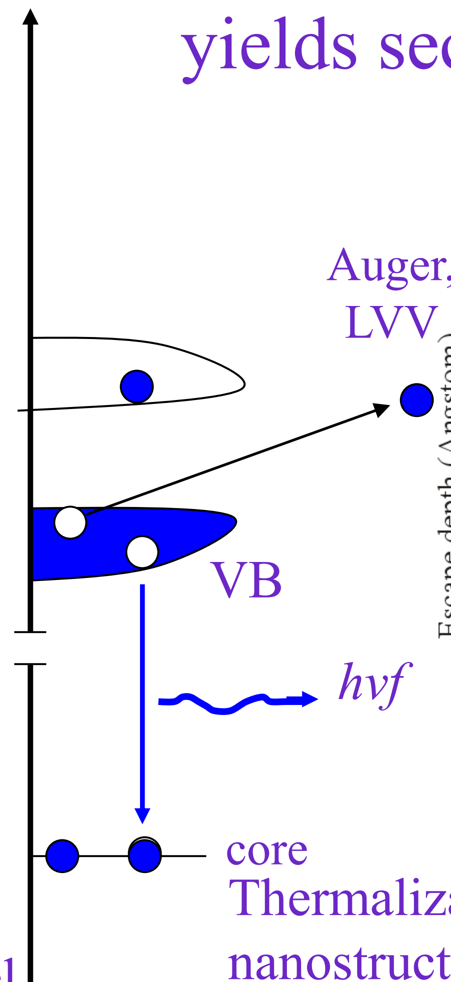


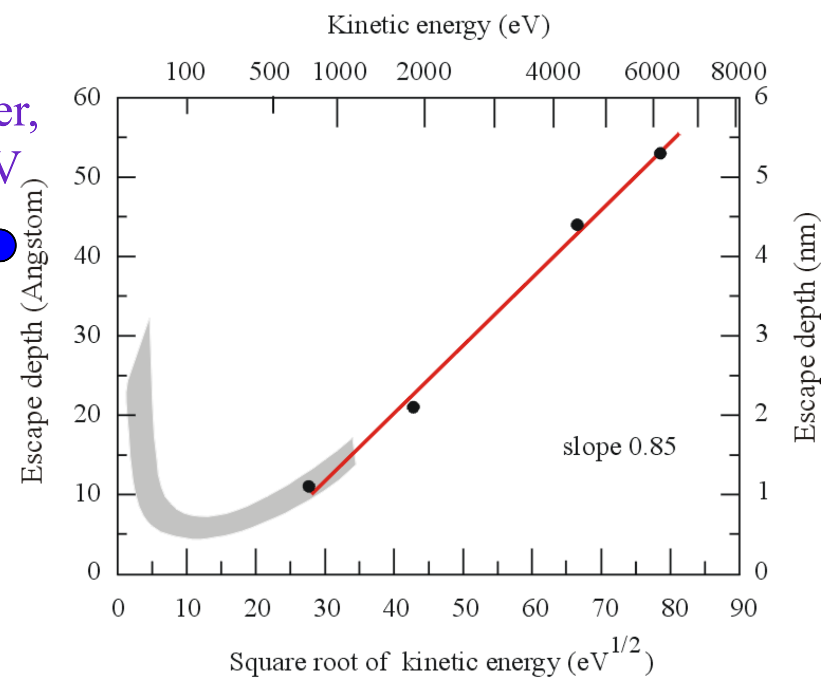
F. Heigl, et.al. SRI2006, AIP CP879, 1202 (2007)
R.A. Rosenberg et. al., J. Phys. Chem., 112, 13943 (2008)
F. Heigl, et al. JACS, 128, 3906 (2006)

De-excitation and energy transfer in nanostructures

- Attenuation of e (thermalization) yields secondary electrons (holes)





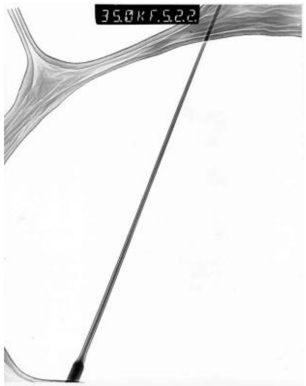


Thermalization track is confined (truncated) in nanostructures ! The smaller the size, the shorter the track, the faster the decay

TRXEOL – Case studies

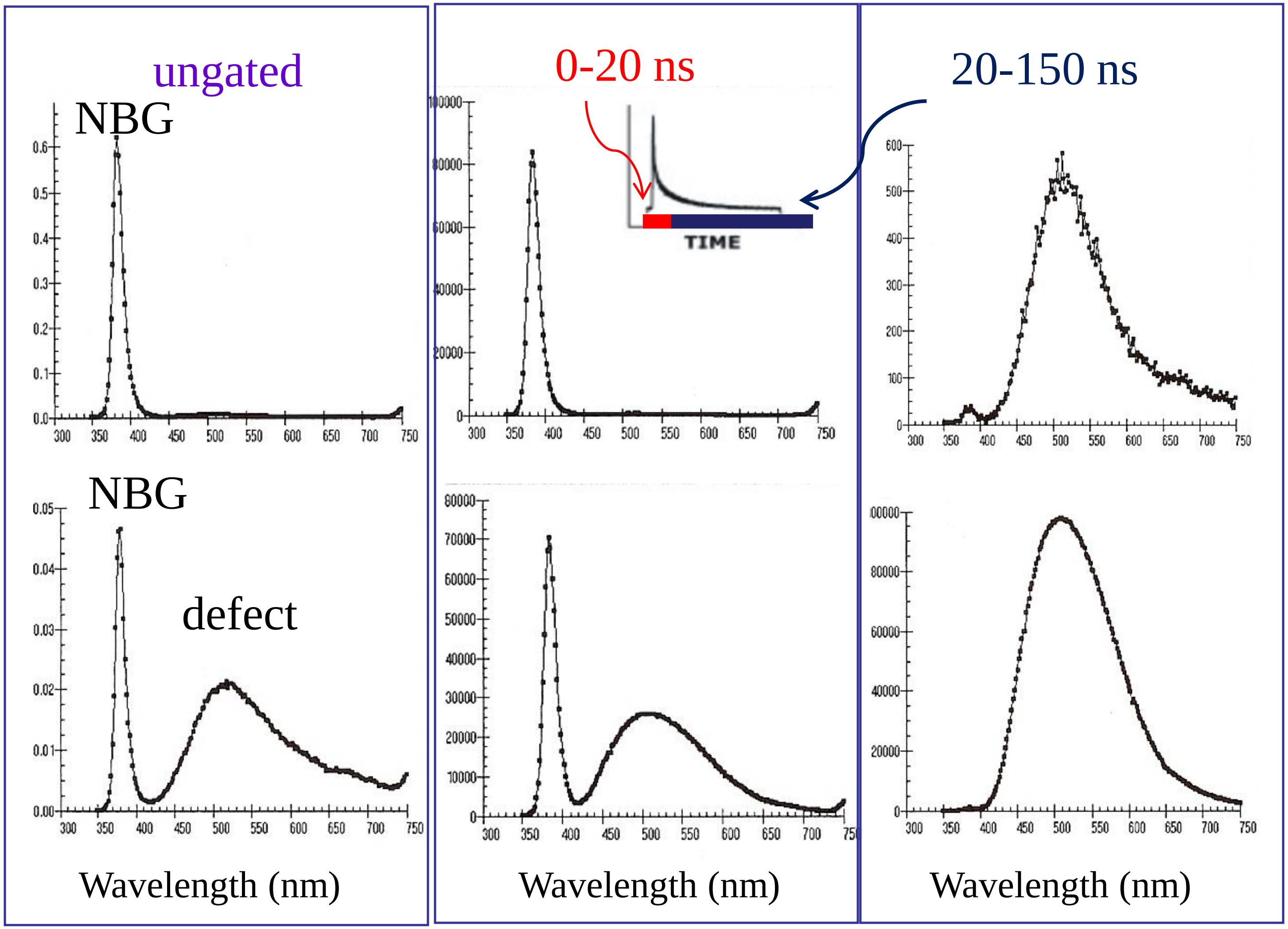
- ZnO: nanoneedle vs nanowire **(crystallinity)**
- ZnO: nano vs micro **(size)**
- $Ru(phen)_3^{2+}$: **(metal vs ligand)**

TRXEOL from ZnO nanostructure



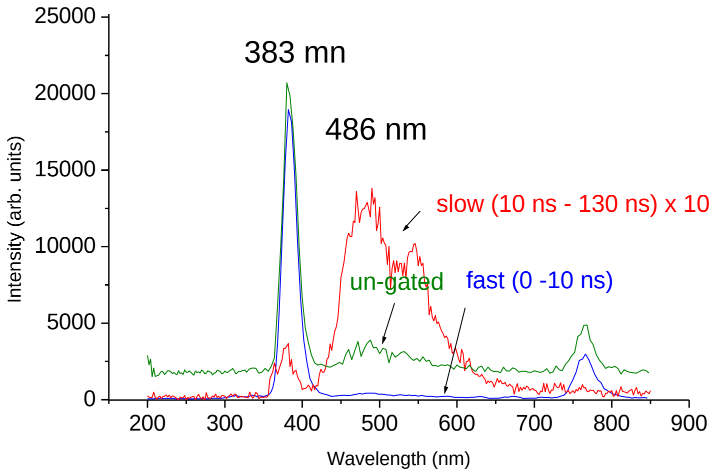
nanoneedle

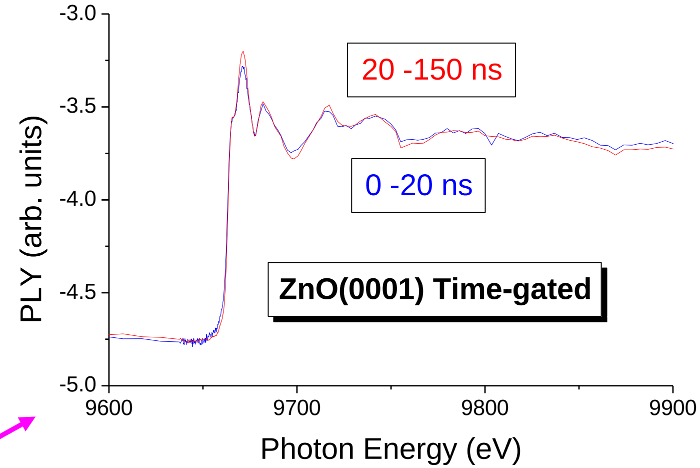
nanowire

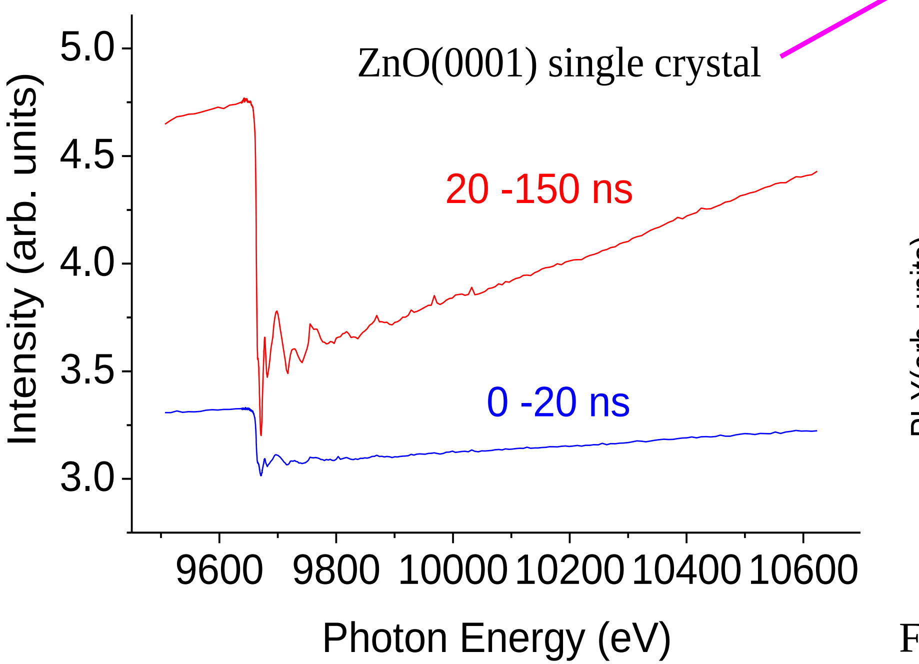


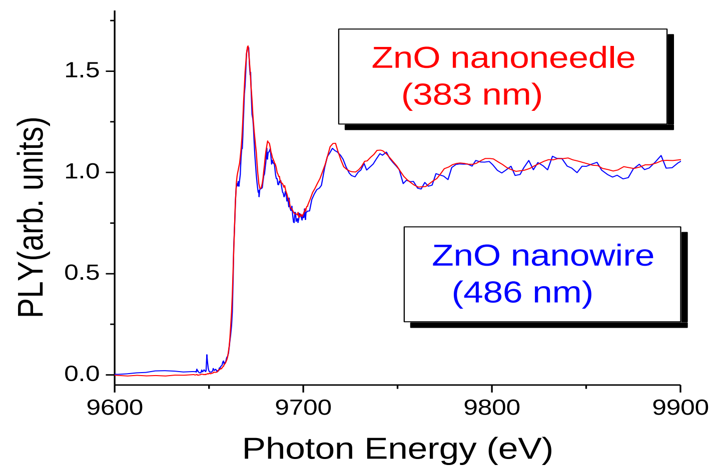
R.A. Rosenberg et. al. Appl. Phys. Lett. 89, 093118(3) (2006)

Time gated-optical XAFS



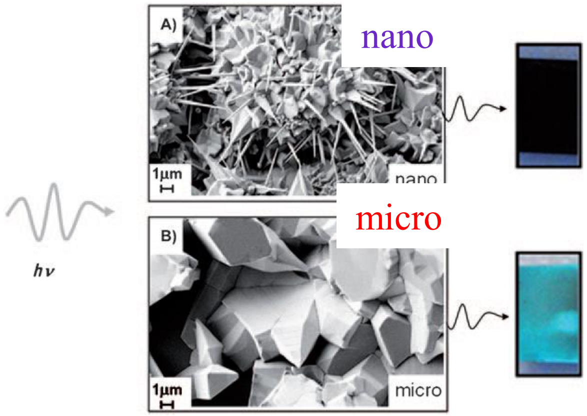




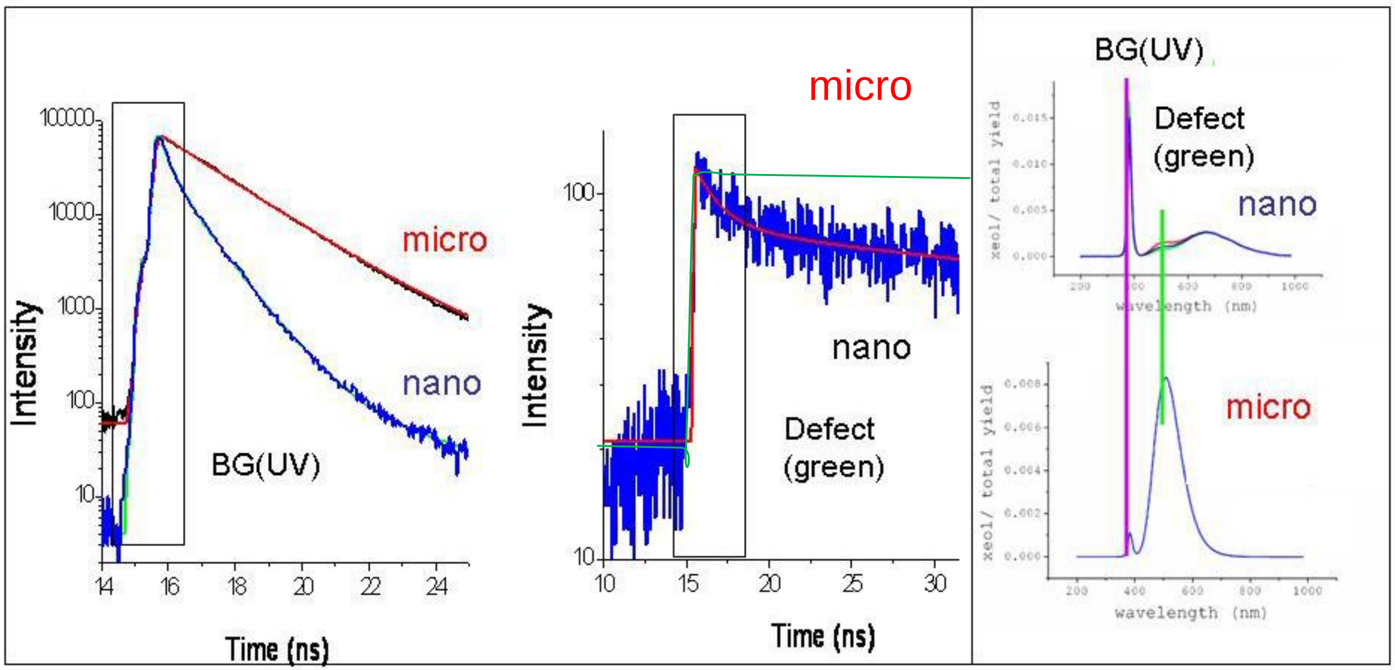


F. Heigl et al. XAFS 13 *AIP Proc.*, (2007)

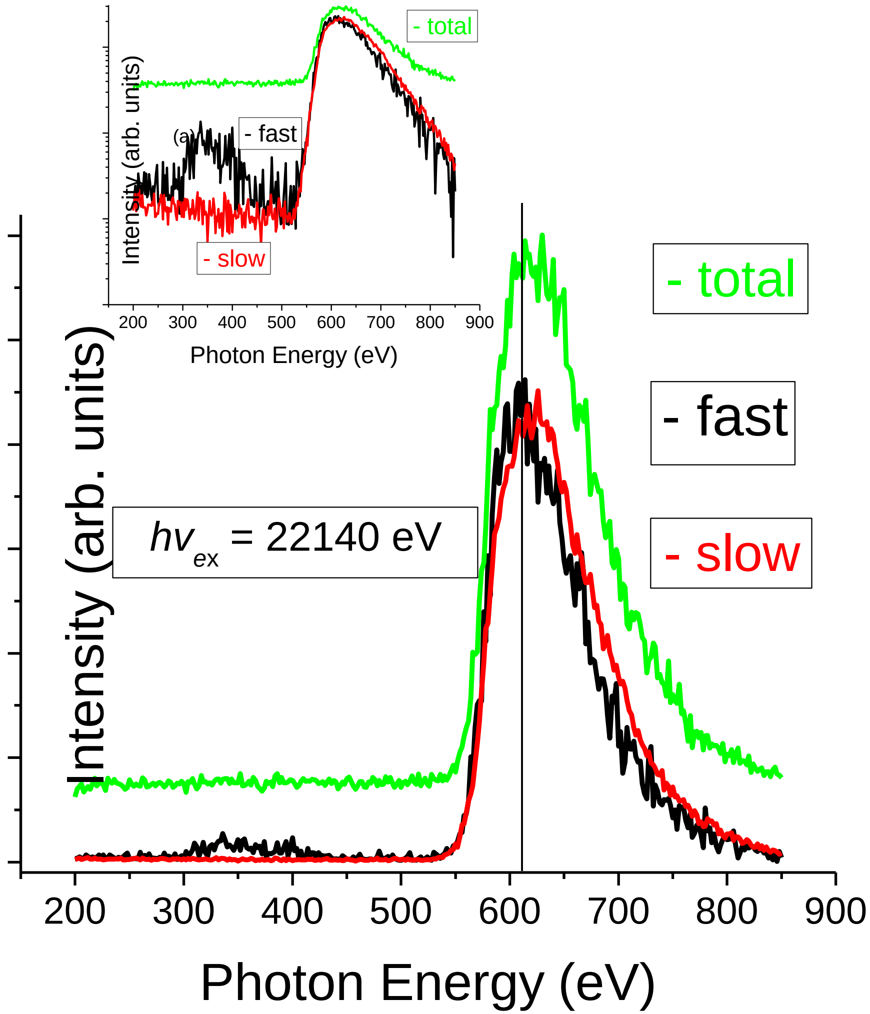
Morphology and size dependent dynamics

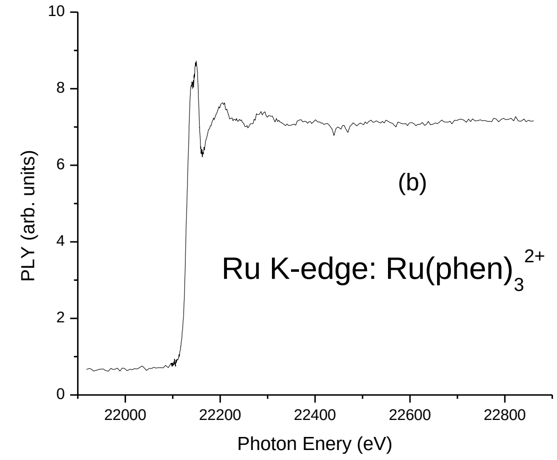


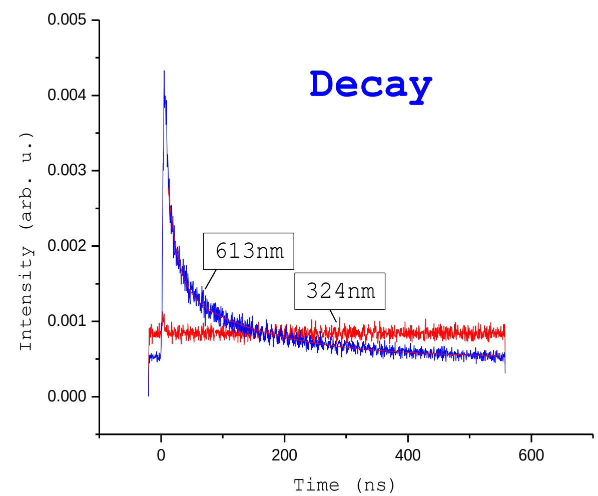
L. Armelao et. al. **ChemPhysChem** 2010, 11, 3625



TRXEOL from $Ru(phen)_3^{2+}$

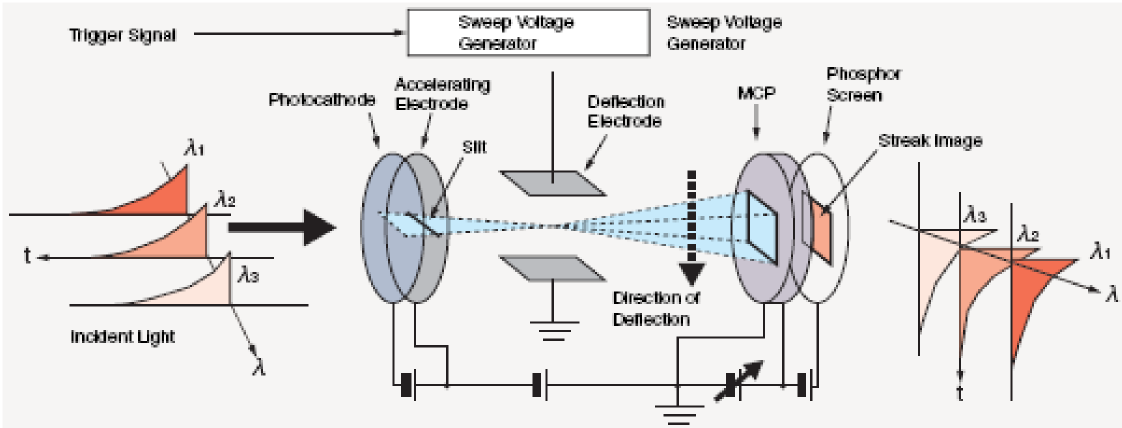


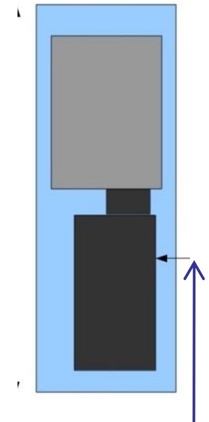




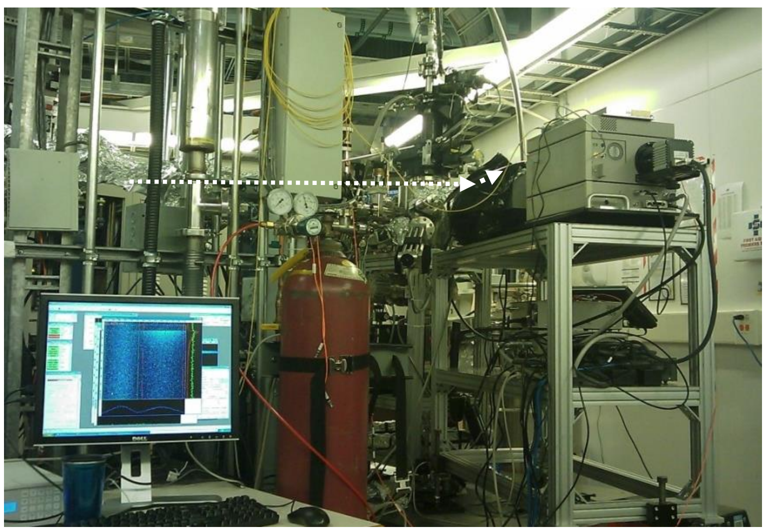
S. Lam, et al. AIP Proc., **XAFS13**, CP882, 687 (2007)

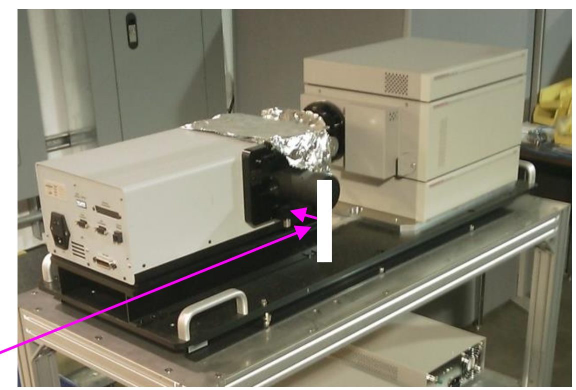
Prospect: TRXEOL with an optical streak camera





Optical photon





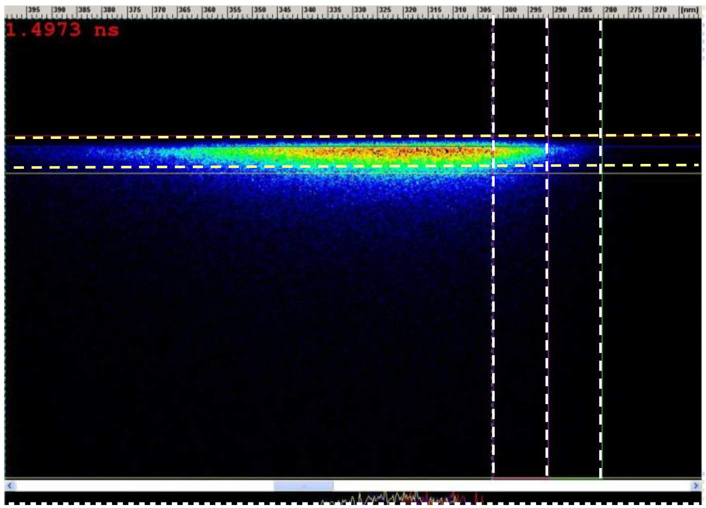
Hamamatsu C4780

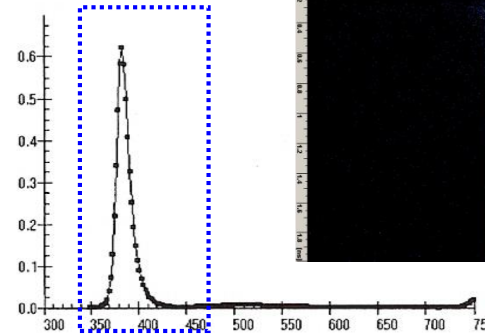
T. Regier et al. ***CLS Activity Report,*** 2009

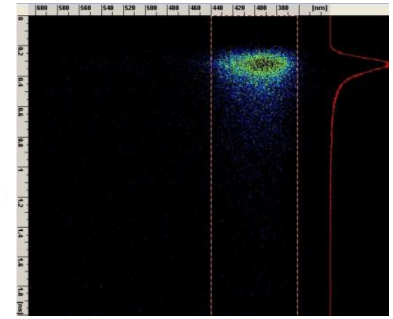
ZnO nanoneedle excitonic emission

λ_{max}~ 380 nm ($h\nu_{ex}$ = 530 eV)

Time

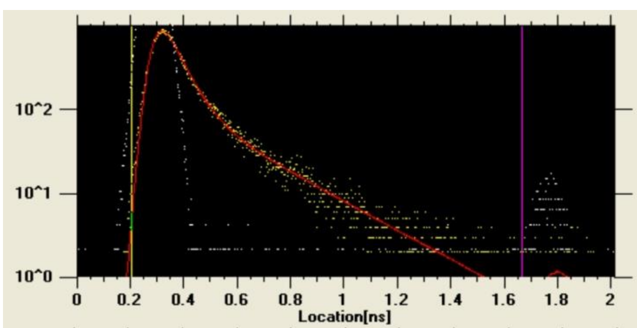


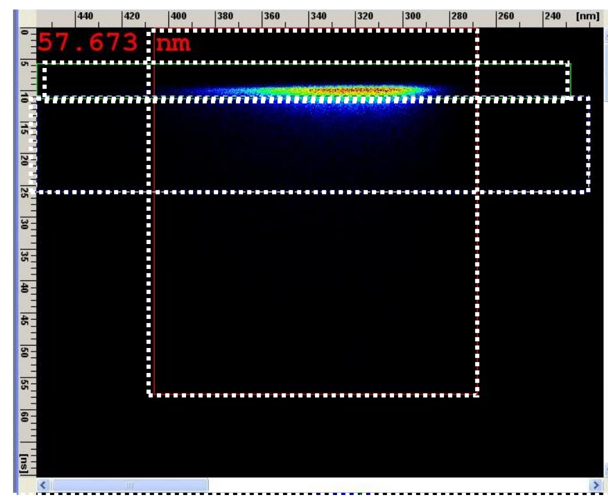


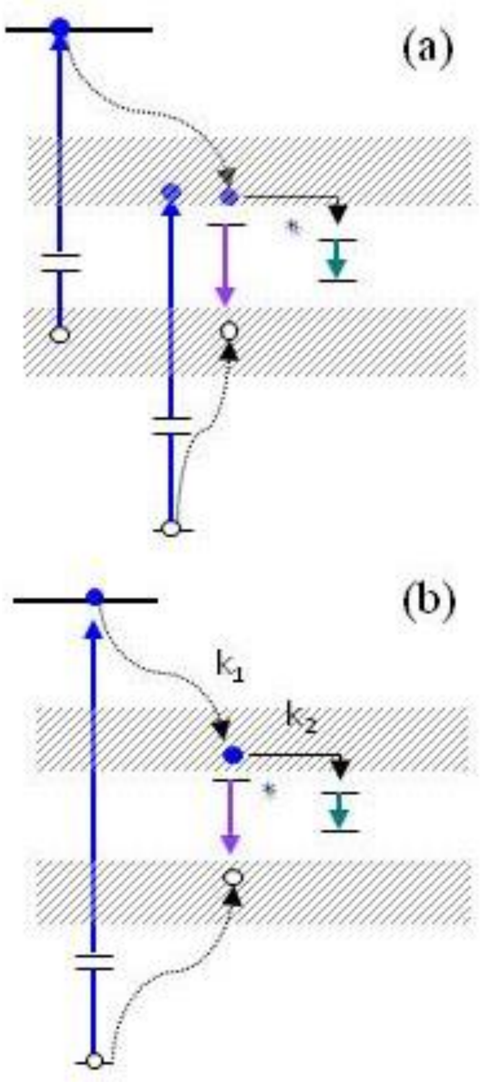


Energy

Energy







What determines the decay lifetime of XEOL ?

In general,

- The larger the energy separation the faster the decay
- The faster the thermalization, k_1, the faster the decay (nanostructures)
- The faster the energy transfer process, k_2, the faster the decay
- NBG emission is always faster than defect emission