

Core Level Spectroscopies

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Lecture I: Basics

1. Types of core level spectroscopies
2. Spectral ranges, cross sections, widths, probing depths
3. Chemical resolution vs. sensitivity to dilute species
4. Working with synchrotron radiation
5. Data analysis via reference spectra and theory
6. Spectroscopic microscopy, holography, ptychography

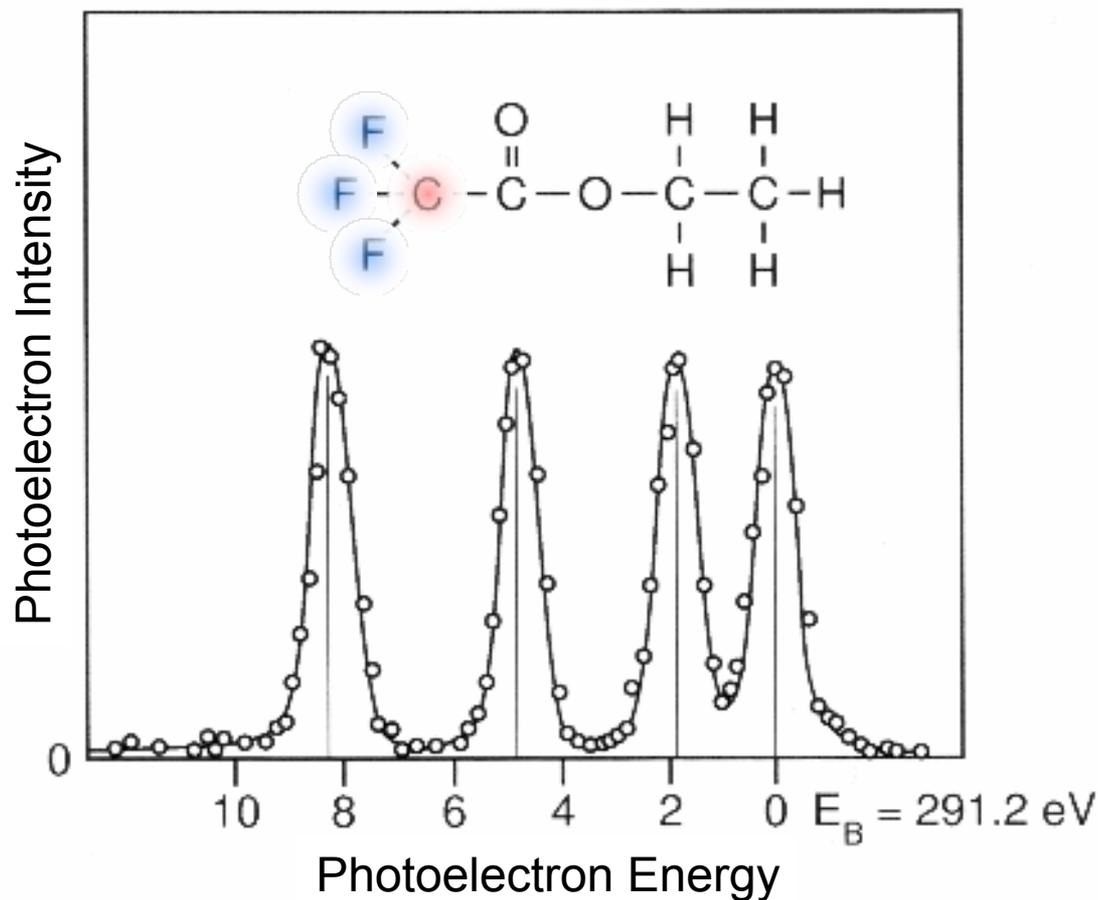
What Can Core Levels Do for you?

Spectroscopies based on core levels are **element- and bond-specific**. They are particularly useful for revealing the **chemical environment of a specific atom** (Nobel Prize in Physics 1981 to Kai Siegbahn).

Their interpretation is fairly straightforward, making it possible to **sort out complex surfaces and interfaces**.

X-ray photoelectron and absorption spectroscopy are widespread diagnostic techniques in academic and industrial research.

Example of the Chemical Sensitivity from Siegbahn's Group



This molecule contains **4 carbon atoms in different chemical environments**. They are easily separated by their C1s core level binding energies. The shifts are associated with the charge transfer between each C atom and its ligands.

Outgoing Particle

Photon

Electron

Atom/Ion

Photon

Absorption (XAS)

XAS

XAS

Emission (XES)

Photoelectron
Spectroscopy (XPS)

Photon-Stimulated
Desorption (PSD)

RIXS (X-rays out)

Auger Spectroscopy

XEOL (Visible out)

Electron

Cathodoluminescence

Electron Energy Loss
Spectroscopy (EELS)
Appearance Potential
Spectroscopy (APS)

Electron-Stimulated
Desorption (ESD)

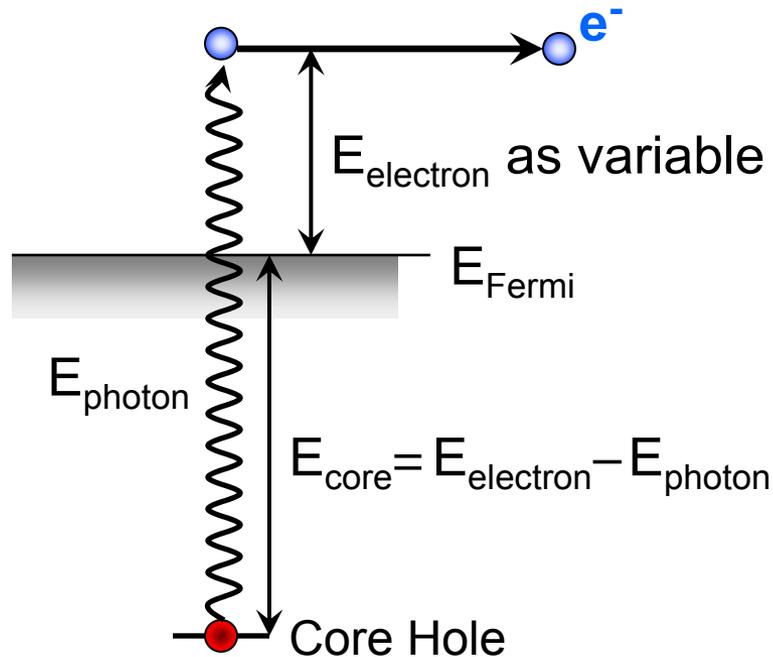
Atom/Ion

Incoming Particle

		Photon	Electron	Atom/Ion
Incoming Particle	Photon	Absorption (XAS) Emission (XES) RIXS (X-rays out) XEOL (Visible out)	XAS Photoelectron Spectroscopy (XPS) Auger Spectroscopy	XAS Photon-Stimulated Desorption (PSD)
	Electron	Cathodoluminescence	Electron Energy Loss Spectroscopy (EELS) Appearance Potential Spectroscopy (APS)	Electron-Stimulated Desorption (ESD)
	Atom/Ion			

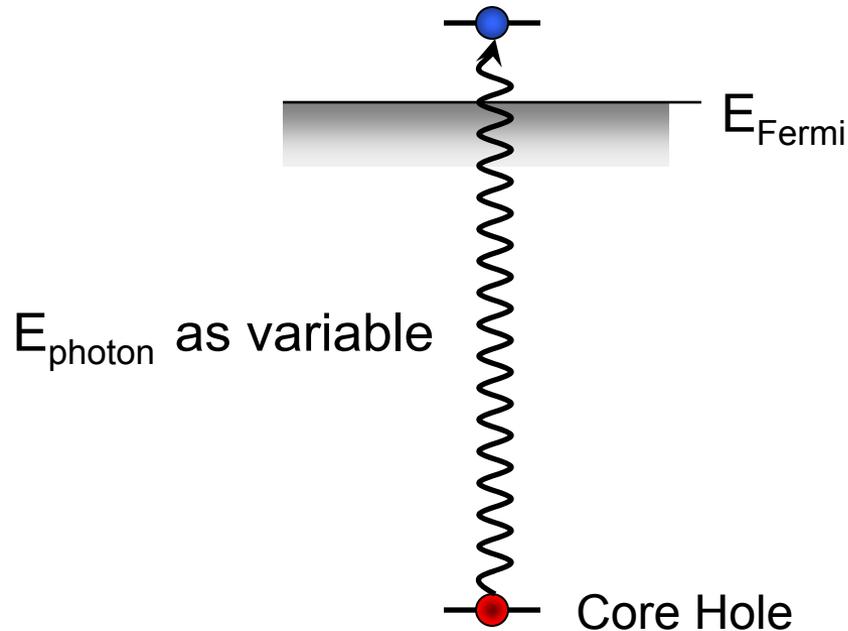
Photoelectron Spectroscopy

(XPS, ESCA)



- Determines the binding energy of a core level by ionizing it
- Provides the energy of the core level
- Involves just a single quasiparticle, the core **hole** (1 quasiparticle)

X-ray Absorption Spectroscopy (XAS, NEXAFS, XANES)

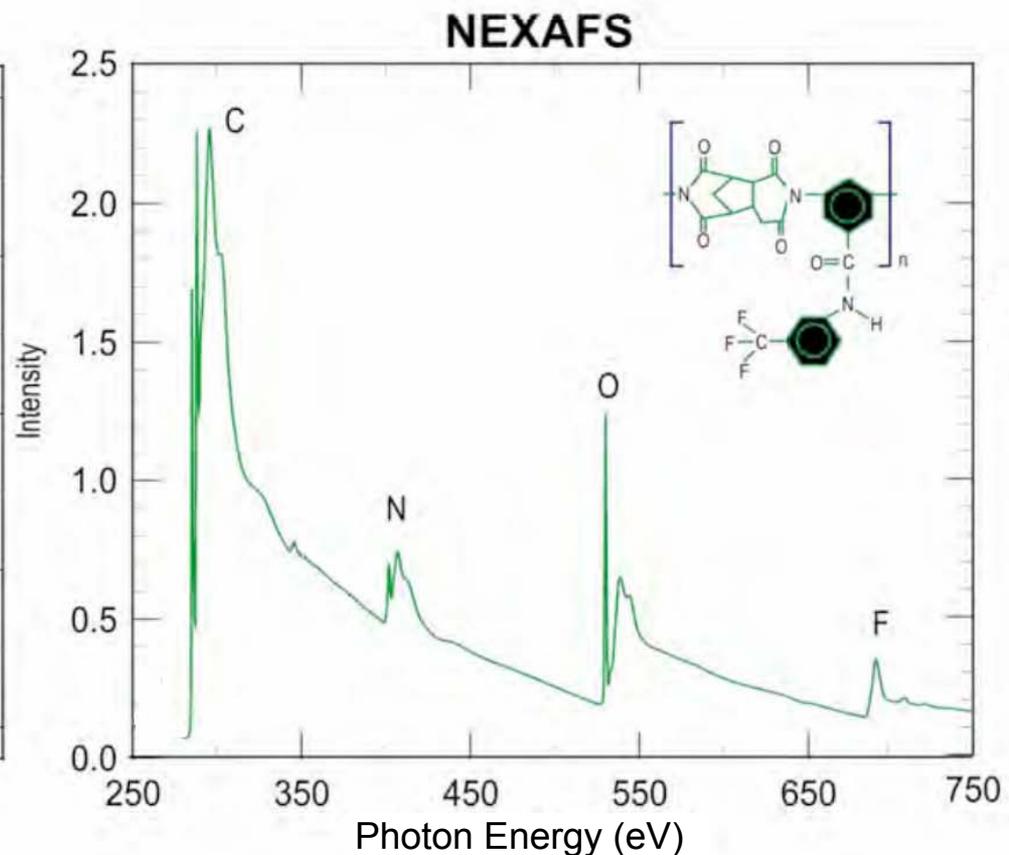
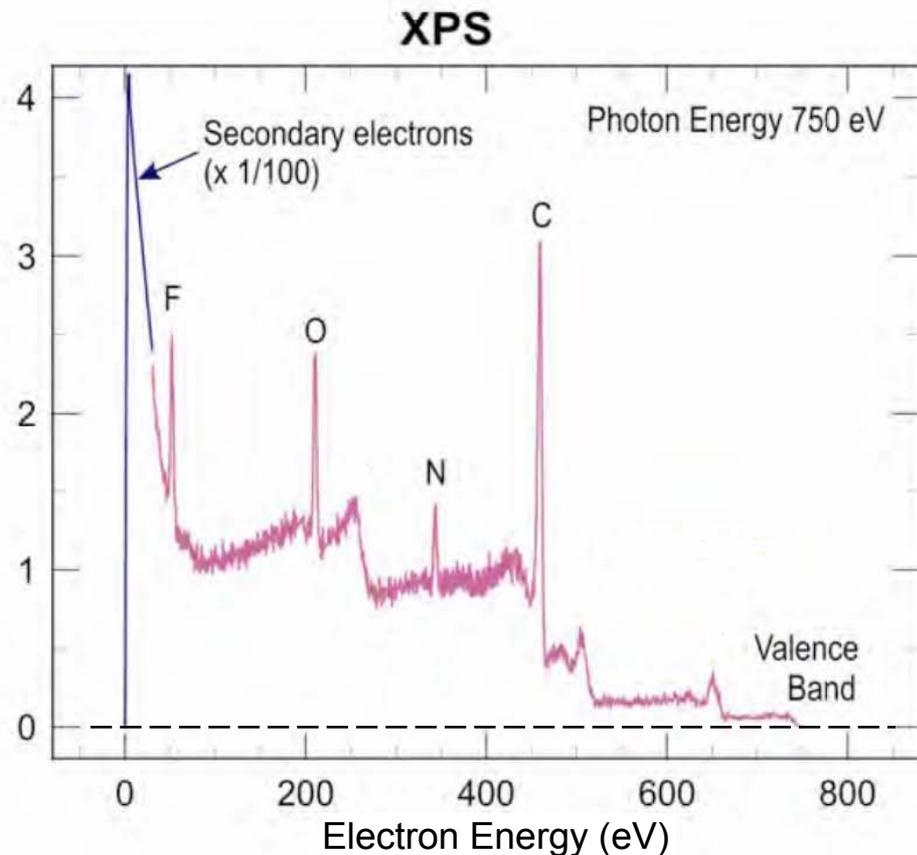


- Probes empty valence states by populating them from a core level
- Element sensitive, measures states located at a specific atom
- Need to consider **electron-hole** interaction (2 quasiparticles)

XPS versus XAS: Overview Spectra

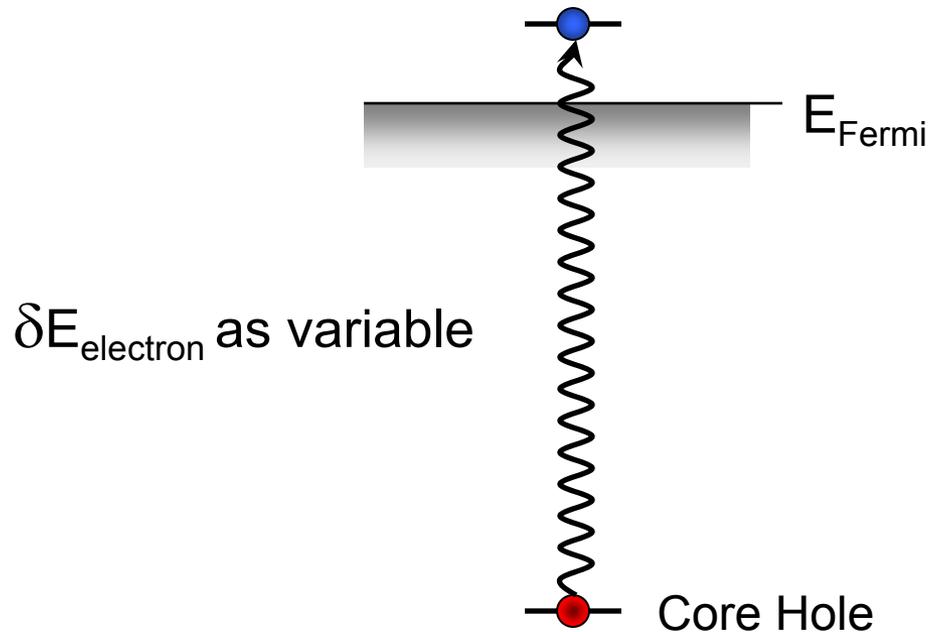
XPS analyzes a core level, while XAS analyzes empty valence states.

Focus on individual peaks in XPS and individual edges in XAS.



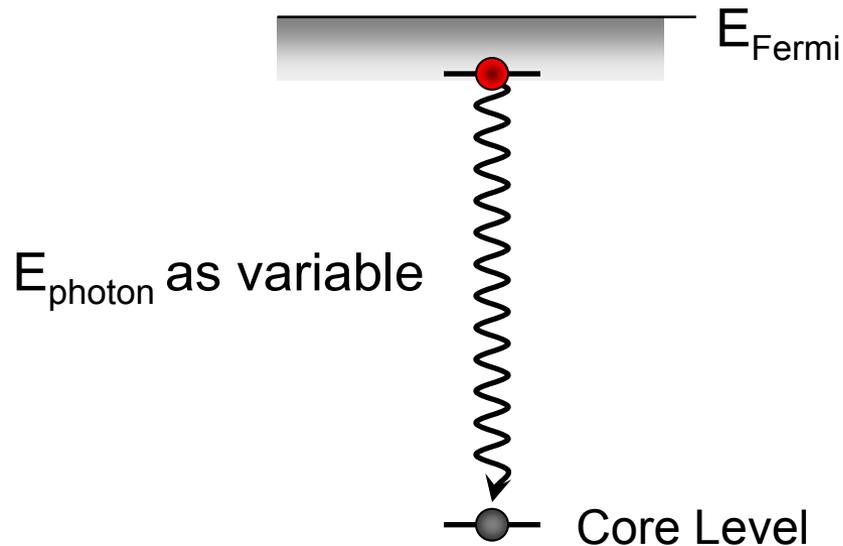
(Anders Nilsson)

Electron Energy Loss Spectroscopy (EELS)



- Same process as X-ray absorption spectroscopy, with a virtual photon emitted by a passing electron (not shown)
- Same dipole transitions in forward scattering, but extra multipole transitions with finite momentum transfer

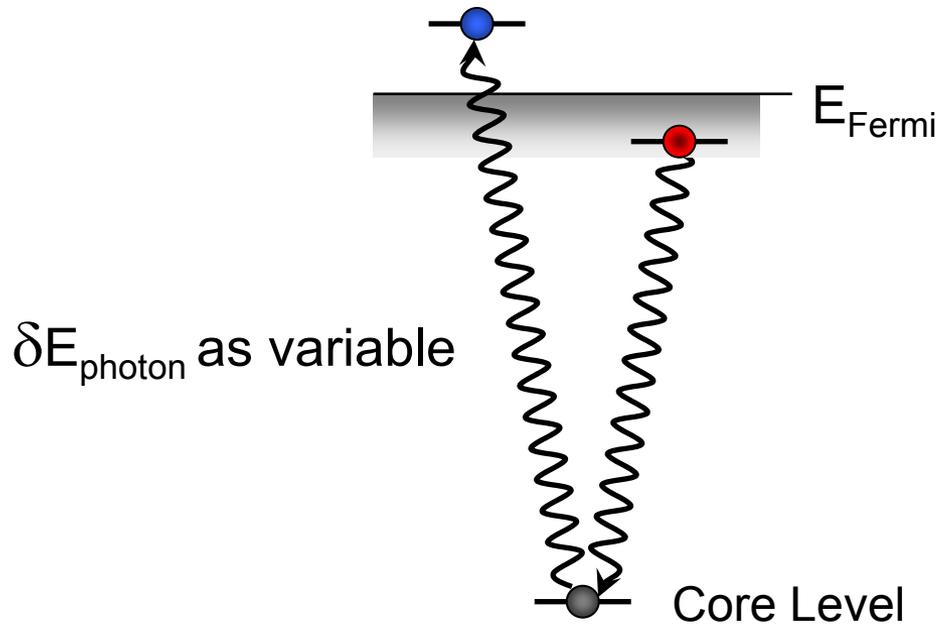
X-ray Emission Spectroscopy



- Starts with a core hole (produced by absorption or EELS)
- A valence electron falls into the core hole emitting X-rays
- The end result is a valence **hole**. Thereby one probes an “occupied” valence state near a specific atom

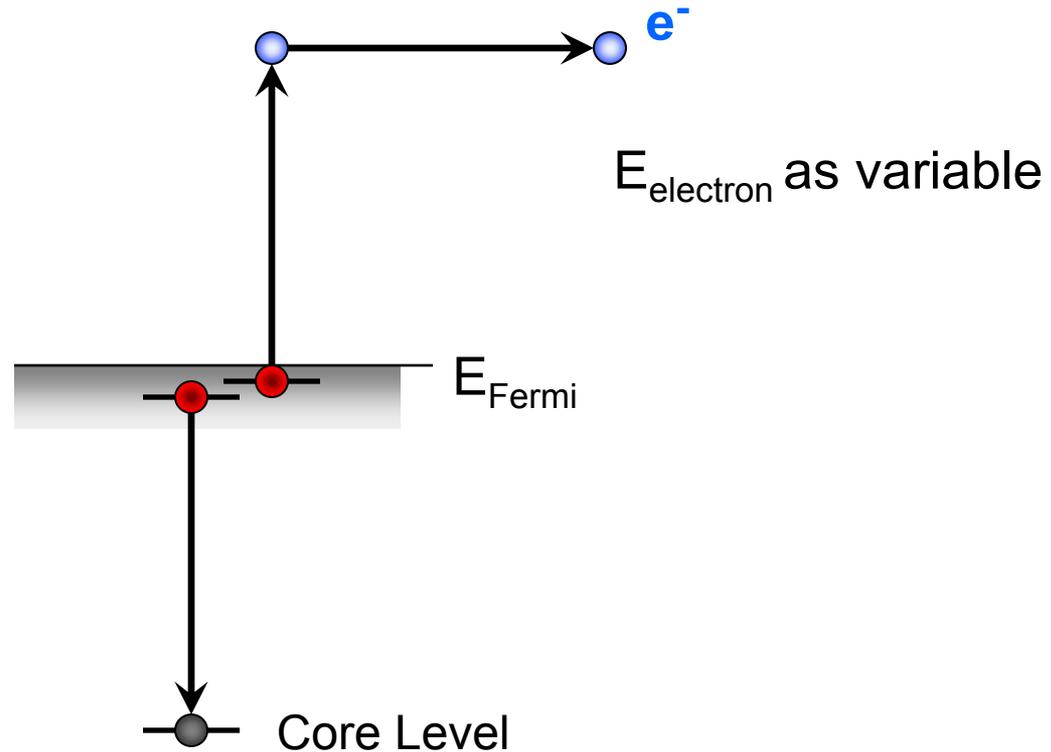
Resonant Inelastic X-ray Scattering

(RIXS, X-ray Raman)



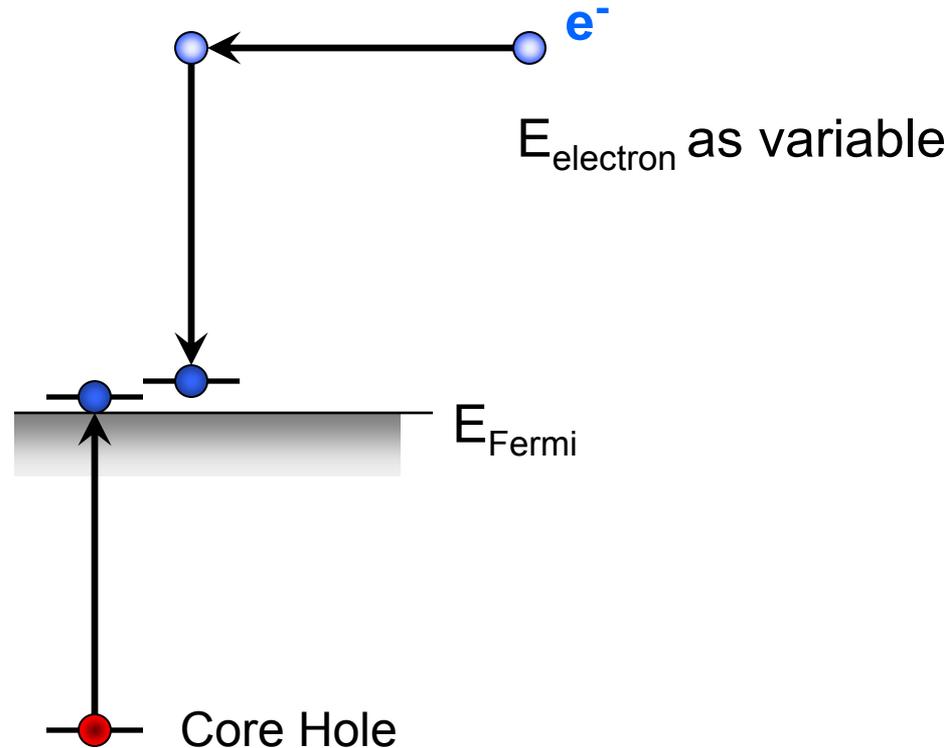
- Combines core level absorption and emission coherently
- The end result is the creation of a valence **electron-hole** pair
- Becomes element-specific by involving a core level resonance

Auger Electron Spectroscopy (AES)

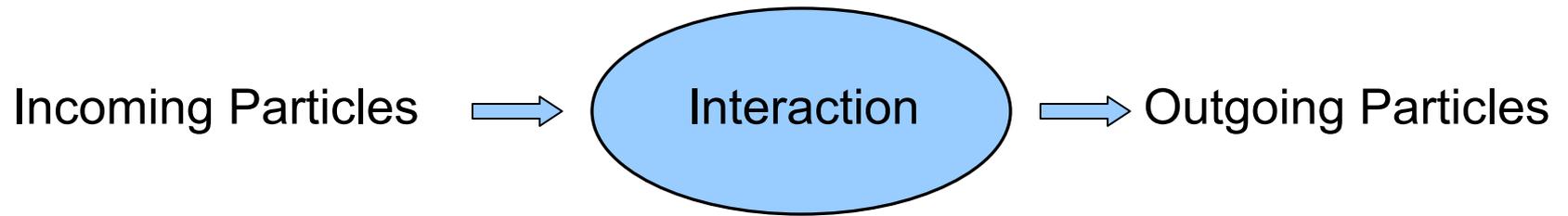


- Starts with a core hole (produced by XAS or EELS)
- Ends with **2 valence holes** plus an Auger **electron**
- Convolutates the density-of-states of two “occupied states”

Appearance Potential Spectroscopy (APS)



- Starts with a high-energy electron
- Ends with 2 valence electrons plus a core hole (detected by its decay)
- Convolutates the density-of-states of two “empty states”



Initial State

Hamiltonian

Final State

$$H_{\text{int}}$$

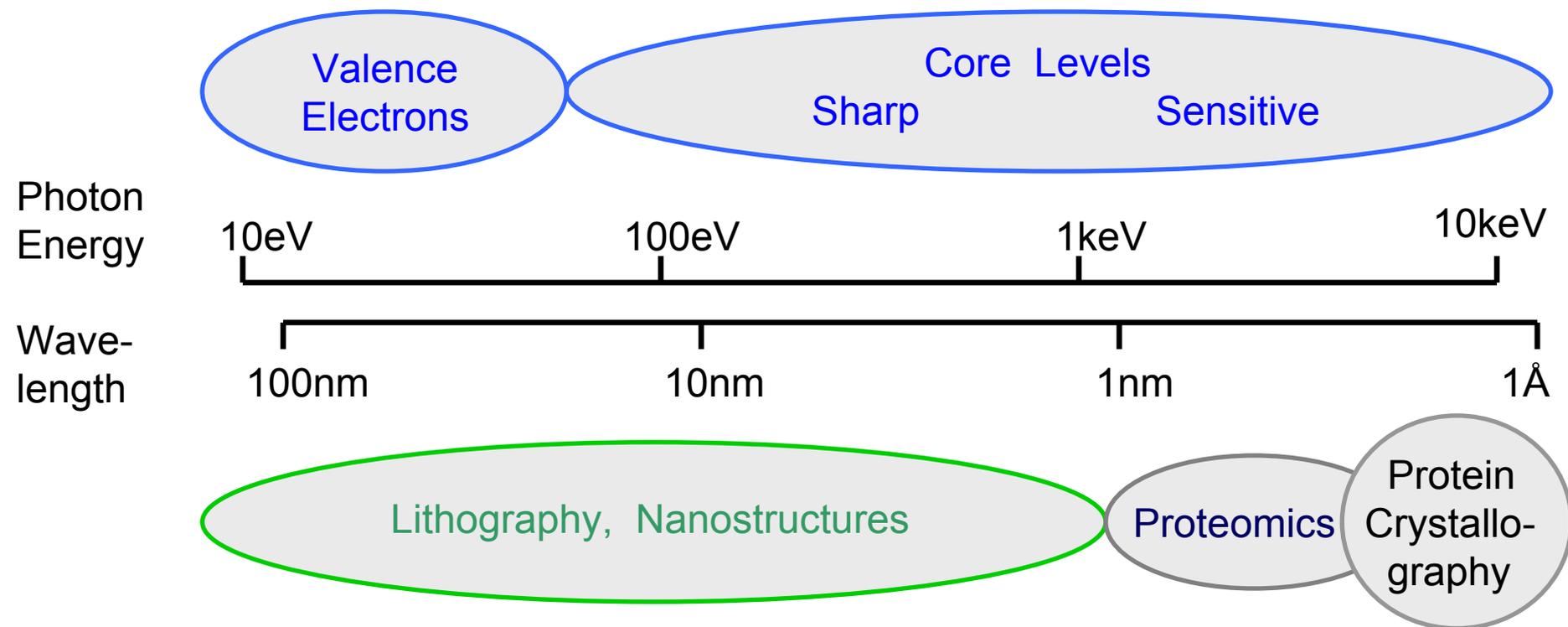
Matrix element:

$$M_{\text{fi}} = \langle \Psi_{\text{final}} | H_{\text{int}} | \Psi_{\text{initial}} \rangle$$

Fermi's Golden Rule:

Cross section = $|M_{\text{fi}}|^2$
averaged over initial states
and summed over final states

Spectral Ranges



Chemical Selectivity in Core Level Spectroscopy

List of core level binding energies: http://xdb.lbl.gov/Section1/Table_1-1.pdf

Binding energies and widths of the sharpest core levels are listed below (in eV).

These are: $nl = 1s, 2p, 3d, 4f$ (with increasing atomic number Z).

The periodic table below shows core level binding energies in eV for various elements. Annotations highlight specific groups: Magnetism (Fe), Catalysts (Pd), Semiconductors (Si), and Bio (N).

H 1s 14																He 1s 25			
Li 1s 55	Be 1s 112													B 1s 189	C 1s 284	N 1s 410	O 1s 543	F 1s 698	Ne 1s 870 2p 22
Na 2p 31	Mg 2p 49													Al 2p 73	Si 2p 100	P 2p 135	S 2p 163	Cl 2p 200	Ar 2p 248 3p 16
K 2p 295 3p 18	Ca 2p 346 3p 25	Sc 2p 399	Ti 2p 454	V 2p 512	Cr 2p 574	Mn 2p 639	Fe 2p 707	Co 2p 778	Ni 2p 853	Cu 2p 933	Zn 3d 10	Ga 3d 19	Ge 3d 29	As 3d 42	Se 3d 55	Br 3d 69	Kr 3d 94 4p 14		
Rb 3d 112 4p 15	Sr 3d 134 4p 20	Y 3d 156	Zr 3d 179	Nb 3d 202	Mo 3d 228	Tc 3d 253	Ru 3d 280	Rh 3d 307	Pd 3d 335	Ag 3d 368	Cd 4d 11	In 4d 16	Sn 4d 24	Sb 4d 32	Te 4d 40	I 4d 50	Xe 4d 68 5p 12		
Cs 4d 78 5p 12	Ba 4d 90 5p 15	La 4d 103	Hf 4f 14	Ta 4f 22	W 4f 31	Re 4f 41	Os 4f 51	Ir 4f 61	Pt 4f 71	Au 4f 84	Hg 5d 8	Tl 5d 13	Pb 5d 18	Bi 5d 24	Po 5d 31	At 5d 40	Rn 5d 48 6p 11		
Fr 5d 58 6p 15	Ra 5d 68 6p 19	Ac 5d 80																	
Ce 4d 109 4f 1	Pr 4f 3	Nd 4f 5	Pm 4f 5	Sm 4f 5	Eu 4f 2	Gd 4f 8	Tb 4f 2	Dy 4f 4	Ho 4f 5	Er 4f 5	Tm 4f 5	Yb 4f 1	Lu 4f 7						
Th 5d 85	Pa 5d 94	U 5f 1	Np 5f	Pu 5f 2	Am 5f	Cm 5f	Bk 5f	Cf 5f	Es 5f	Fm 5f	Md 5f	No 5f	Lw 5f						

Intrinsic Lifetime Broadening of Core Levels (Lorentzian, $\Gamma = 2\pi/\tau$)

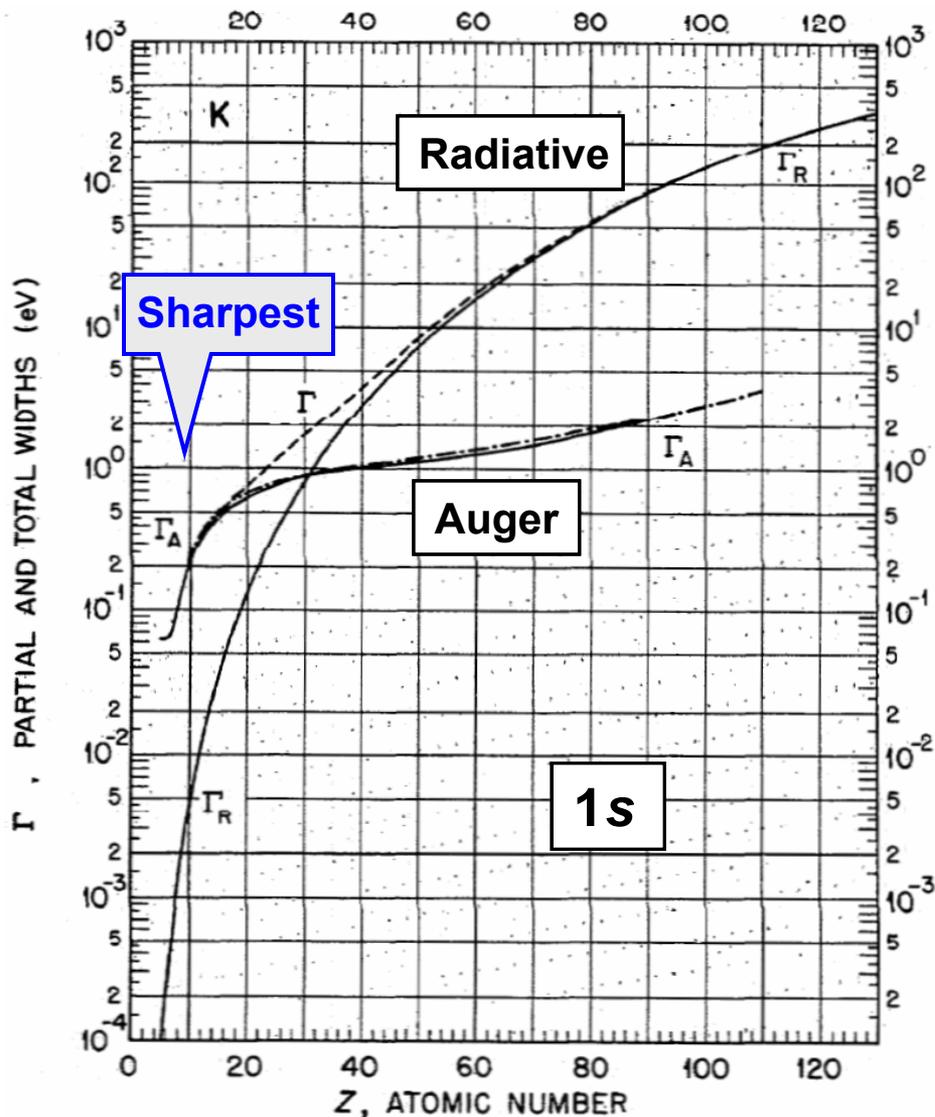


FIGURE 1. Theoretical partial and total atomic level widths for K shell. Γ_A = Auger width, Γ_R = radiative width, Γ = total width.

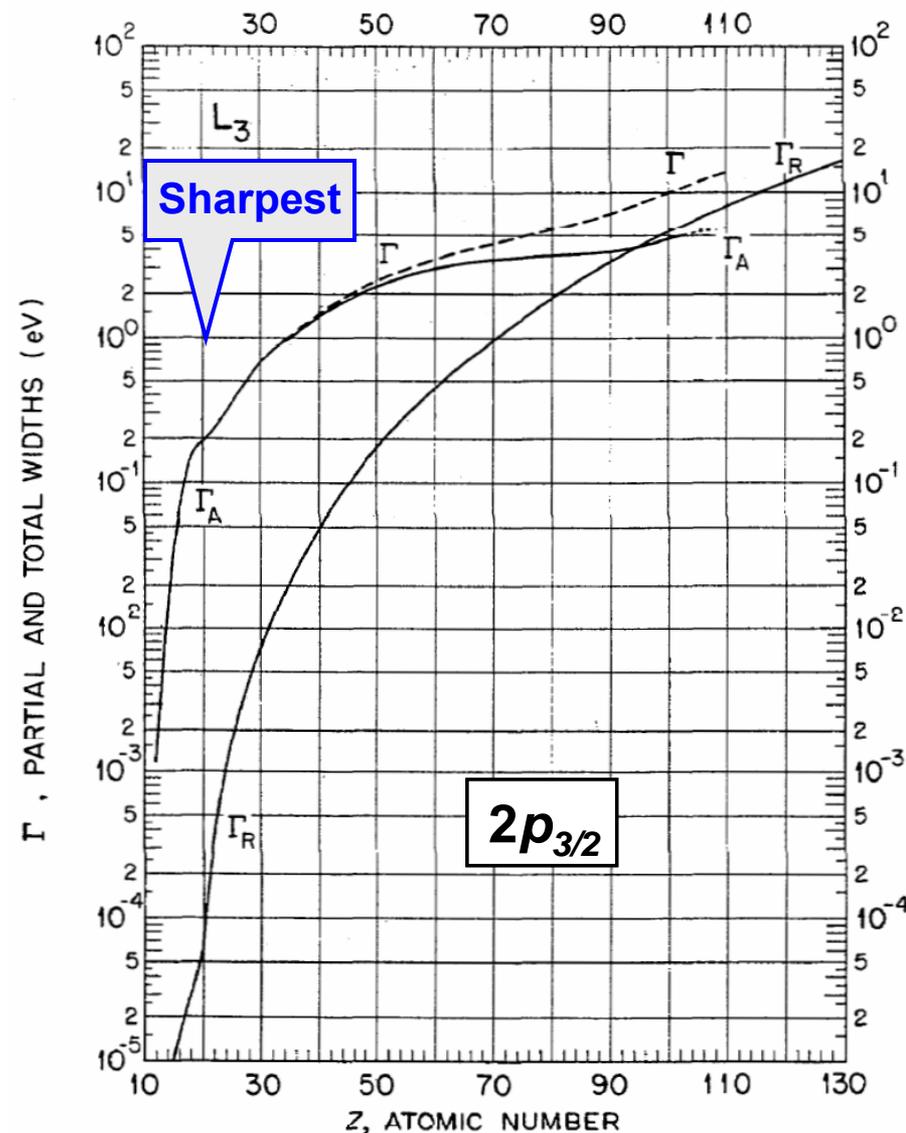


FIGURE 4. Theoretical partial and total atomic level widths for L_3 subshell. Γ_A = Auger width, Γ_R = radiative width, Γ = total width.

Branching Ratio between Fluorescence and Auger Decay of Core Holes

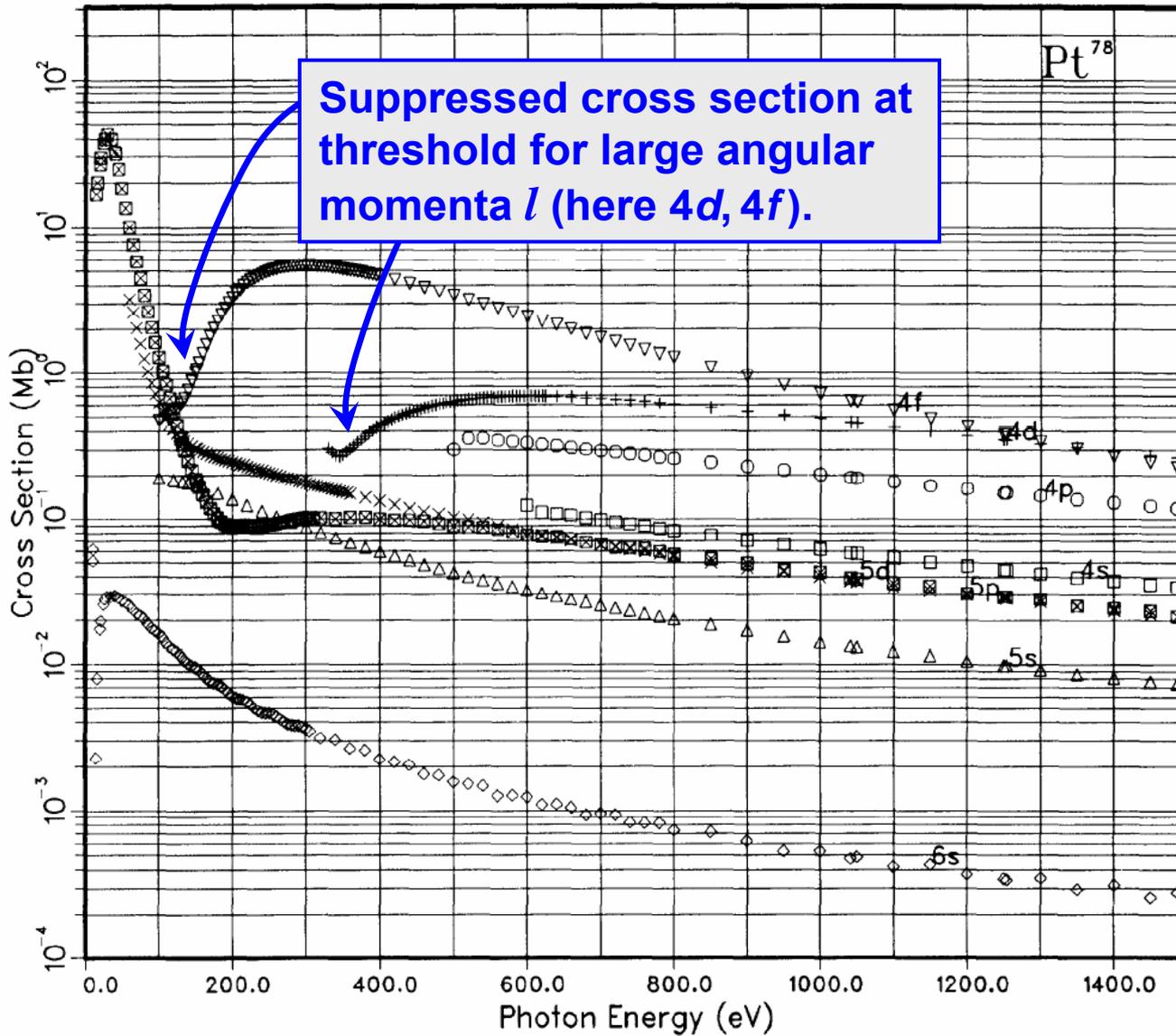
Table 1. Fluorescence, Auger and Coster-Kronig yields for light atoms in condensed matter.^a ($9.0 \text{ E-5} \equiv 9.0 \times 10^{-5}$).

K Shell			L ₂ Subshell			
Z	ω_K	a_K	Z	ω_2	a_2	$f_{2,3}$
3	9.0 E-5	1.000	22	1.1 E-3 ^b	0.75 ^b	0.25 ^b
4	3.3 E-4	1.000	23	1.8 E-3 ^b	0.71 ^b	0.29 ^b
5	7.0 E-4	1.000	24	2.3 E-3 ^b	0.65 ^b	0.35 ^b
6	1.4 E-3	0.999	25	3.1 E-3 ^b	0.61 ^b	0.39 ^b
7	3.1 E-3	0.997	26	3.6 E-3	0.58	0.42
8	5.8 E-3	0.994	27	4.4 E-3	0.57	0.43
9	9.2 E-3	0.991	28	5.1 E-3	0.54	0.45
10	0.016	0.984	29	5.7 E-3	0.52	0.47
11	0.021	0.979	30	9.5 E-3	0.75	0.24
12	0.028	0.972				
13	0.036	0.964		X-rays	Auger	
14	0.048	0.952				
15	0.061	0.939				
	X-rays	Auger				

Light elements:

- Auger decay dominates.
- Little photon emission ($\approx 10^{-3}$).

Cross Sections for Producing Core Holes with Photons



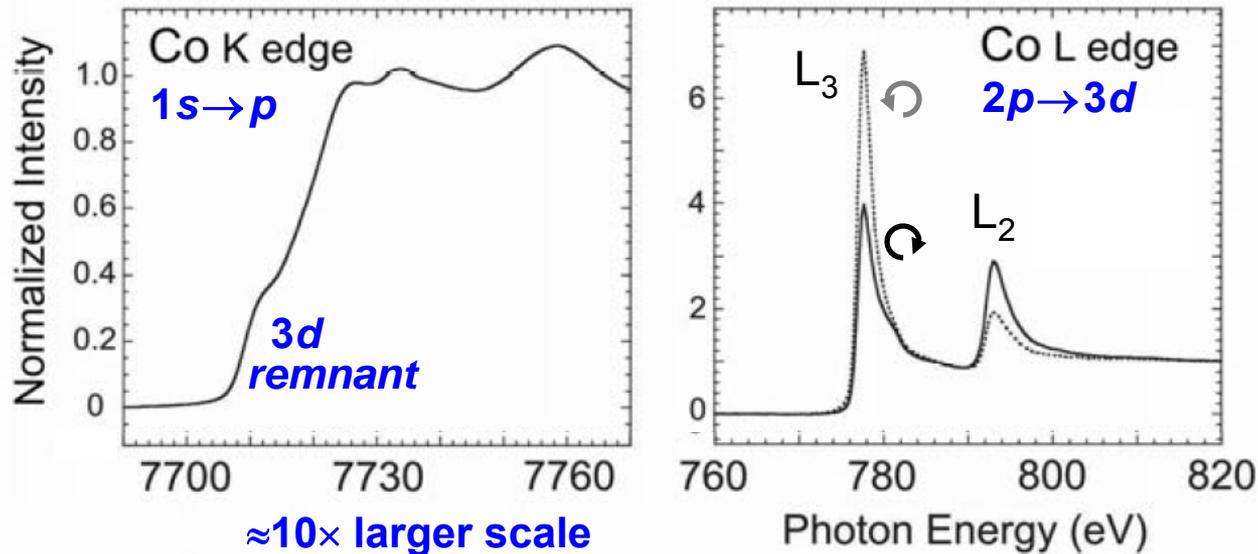
Choosing a Suitable Core Level

For XPS and XAS:

There is a trade-off between chemical selectivity and sensitivity

For selectivity: Shallow core level, Low Z, electron detection

For sensitivity: Deep core level, High Z, photon detection



(J. Stöhr)

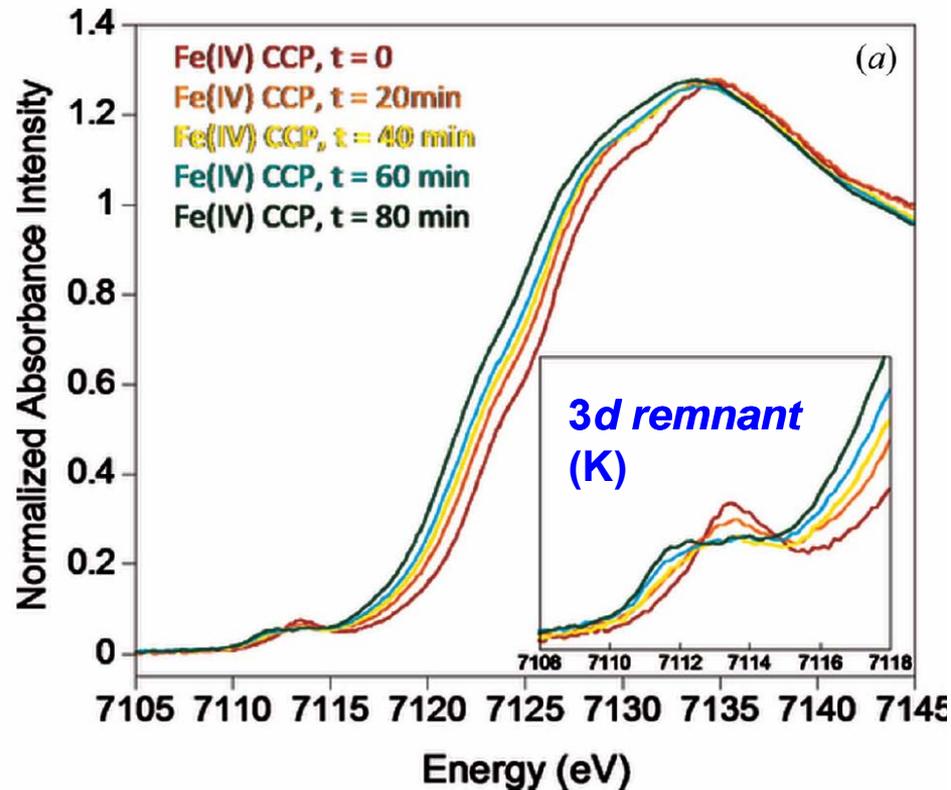
For XAS:

The absorption cross section near threshold is suppressed by the centrifugal barrier with increasing angular momentum (see previous slide). Use *s*- or *p*-levels (K- or L_{2,3}-edges).

Sensitivity vs. Chemical Selectivity for Metalloproteins

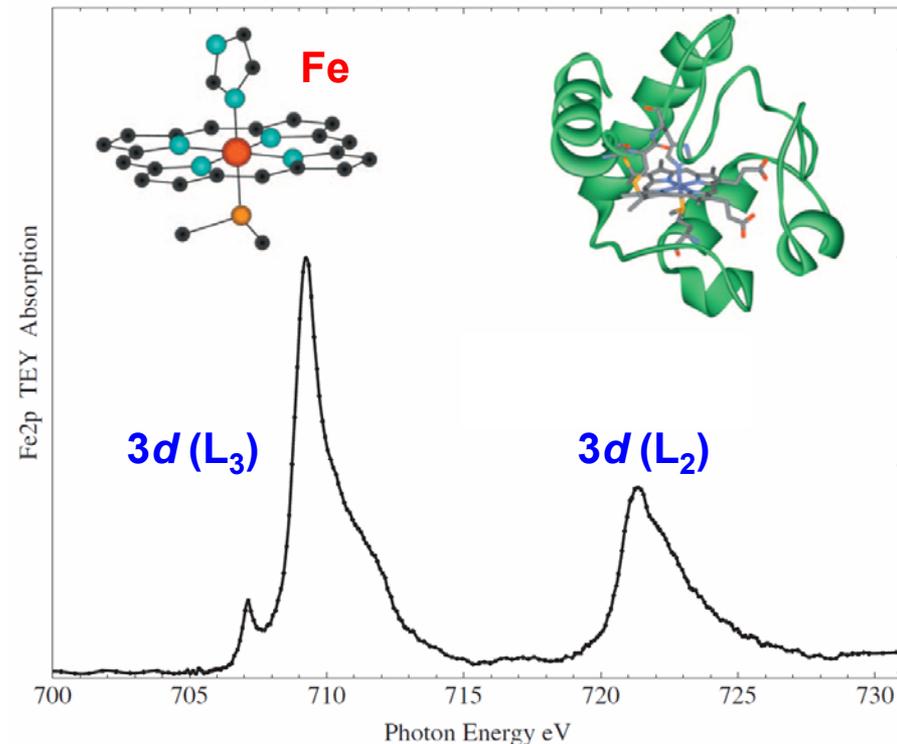
Need high sensitivity (highly dilute, prone to radiation damage)

Cytochrome c peroxidase
(293 amino acids)
Fe K edge with photon detection



J. Synchrotron Rad. **19**, 875 (2012)

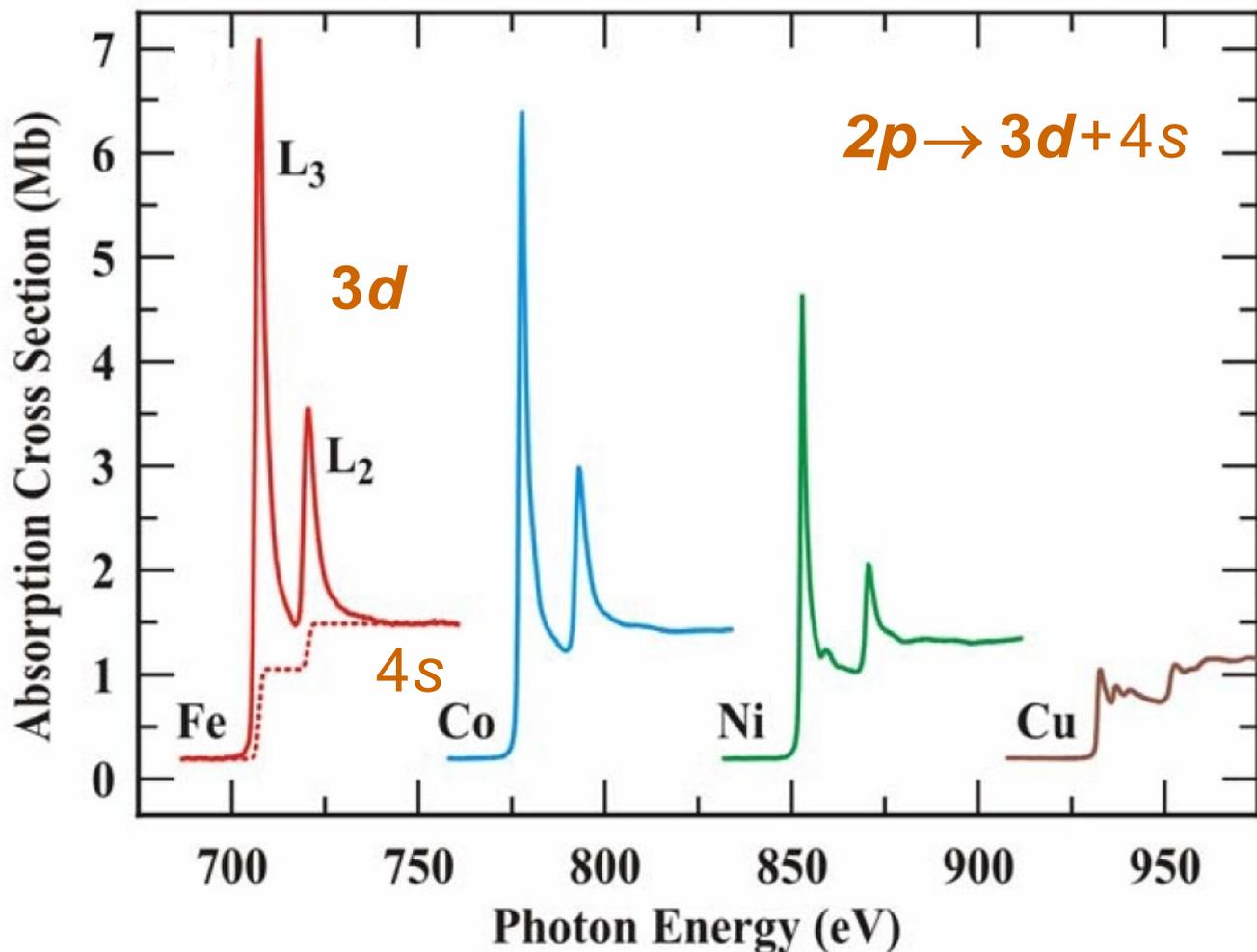
Cytochrome c
(104 amino acids)
Fe L edge with electron detection



J. Chem. Phys. **131**, 194701 (2009)

Dipole Selection Rules

$l \rightarrow l \pm 1$, with $l \rightarrow l + 1$ dominant: $s \rightarrow p$, $p \rightarrow d + s$, $d \rightarrow f + p$



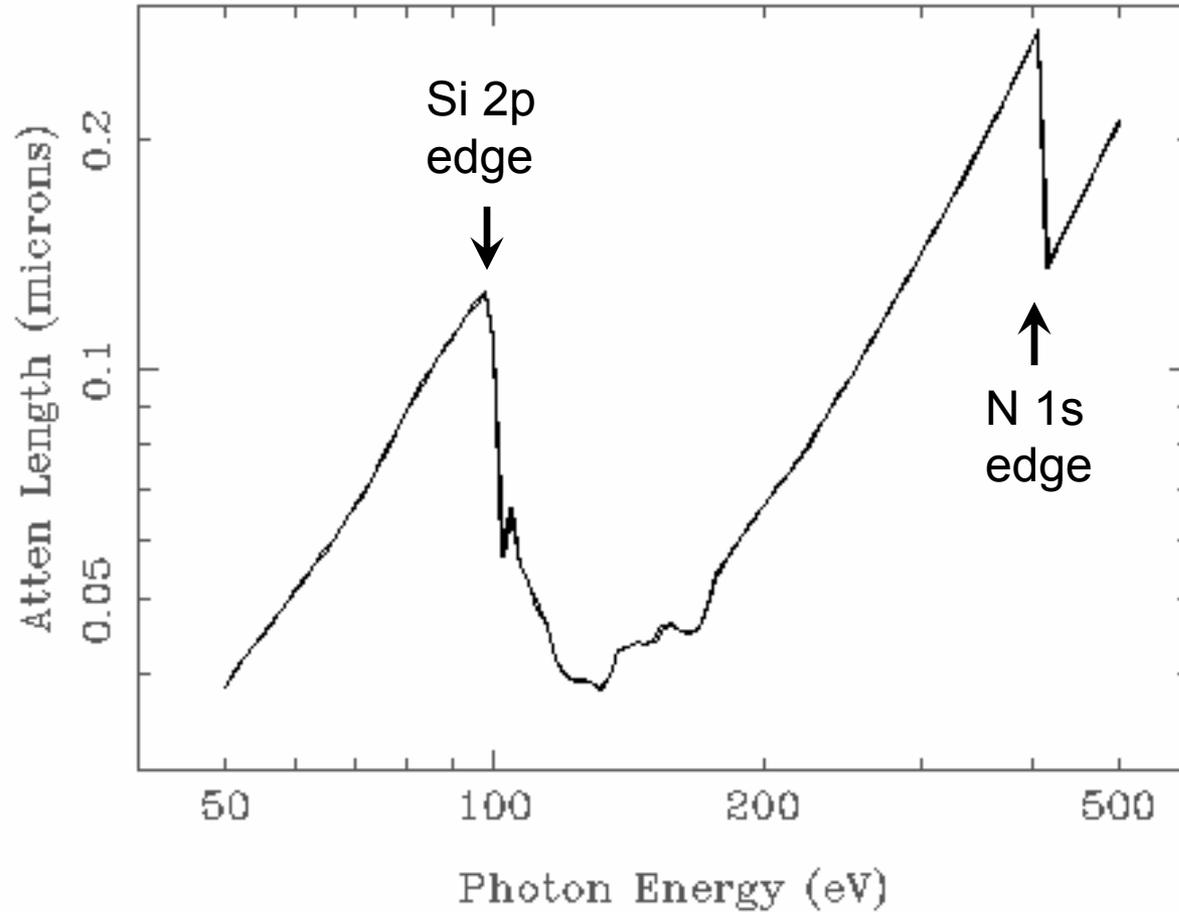
3d states are more localized than 4s states and therefore overlap better with the 2p core level in $\langle \psi_{\text{final}} | H_{\text{int}} | \psi_{\text{initial}} \rangle$

The density of empty 3d states decreases while the 3d shell becomes filled, leading to a decrease of the 2p → 3d intensity.

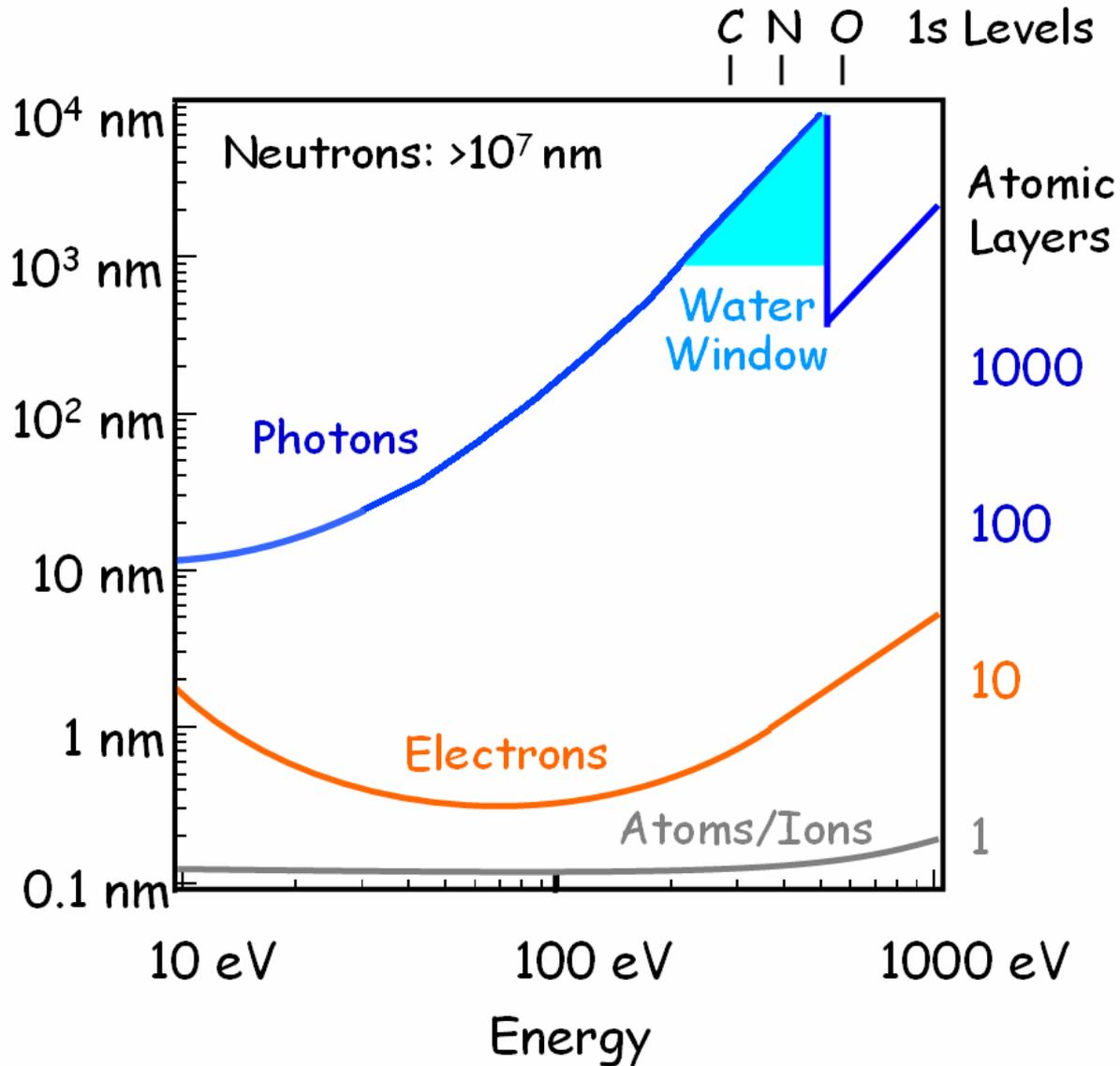
(J. Stöhr)

Probing Depth of Photons

Si₃N₄ Density=3.44, Angle=90.deg

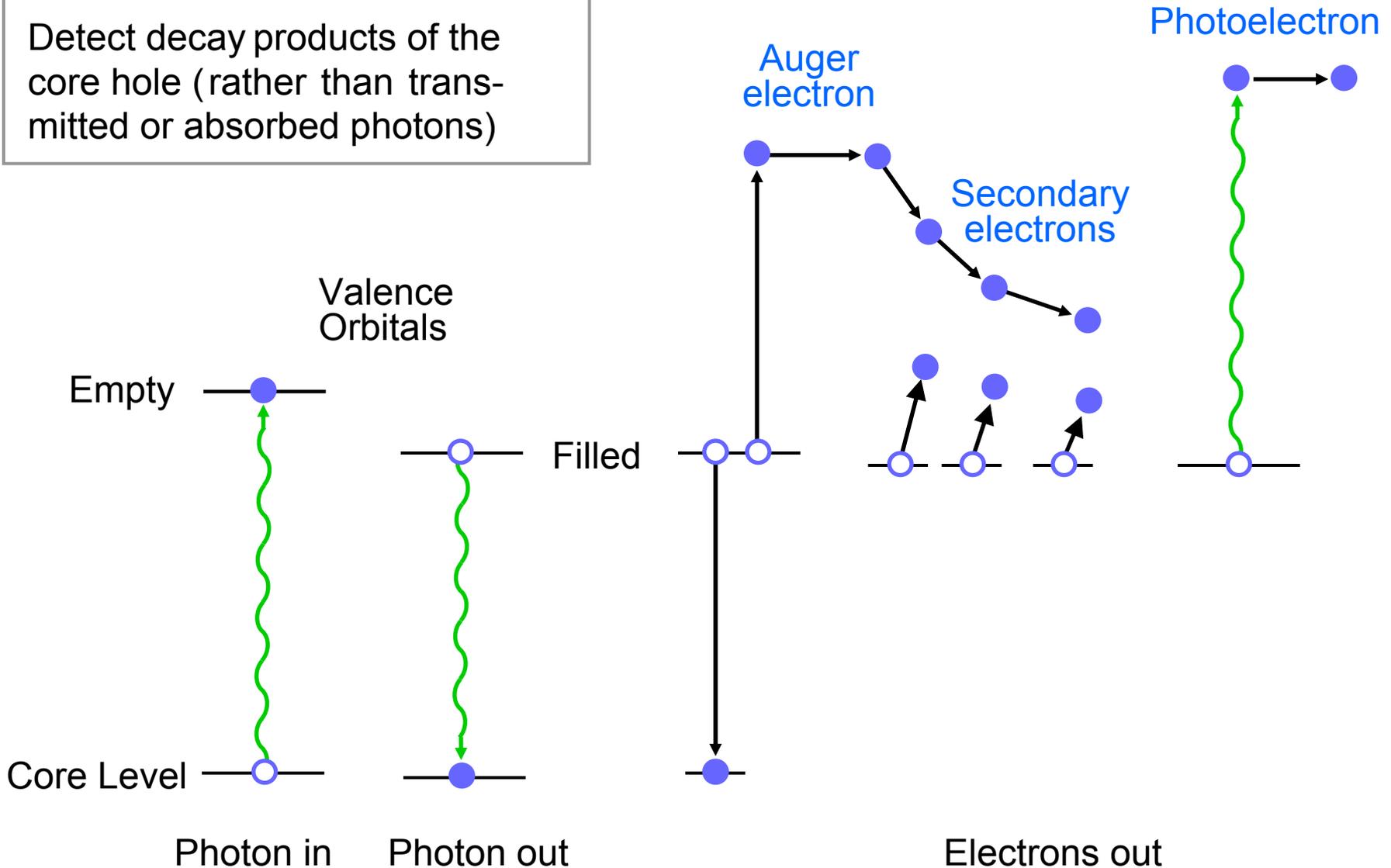


Probing Depths of Various Particles

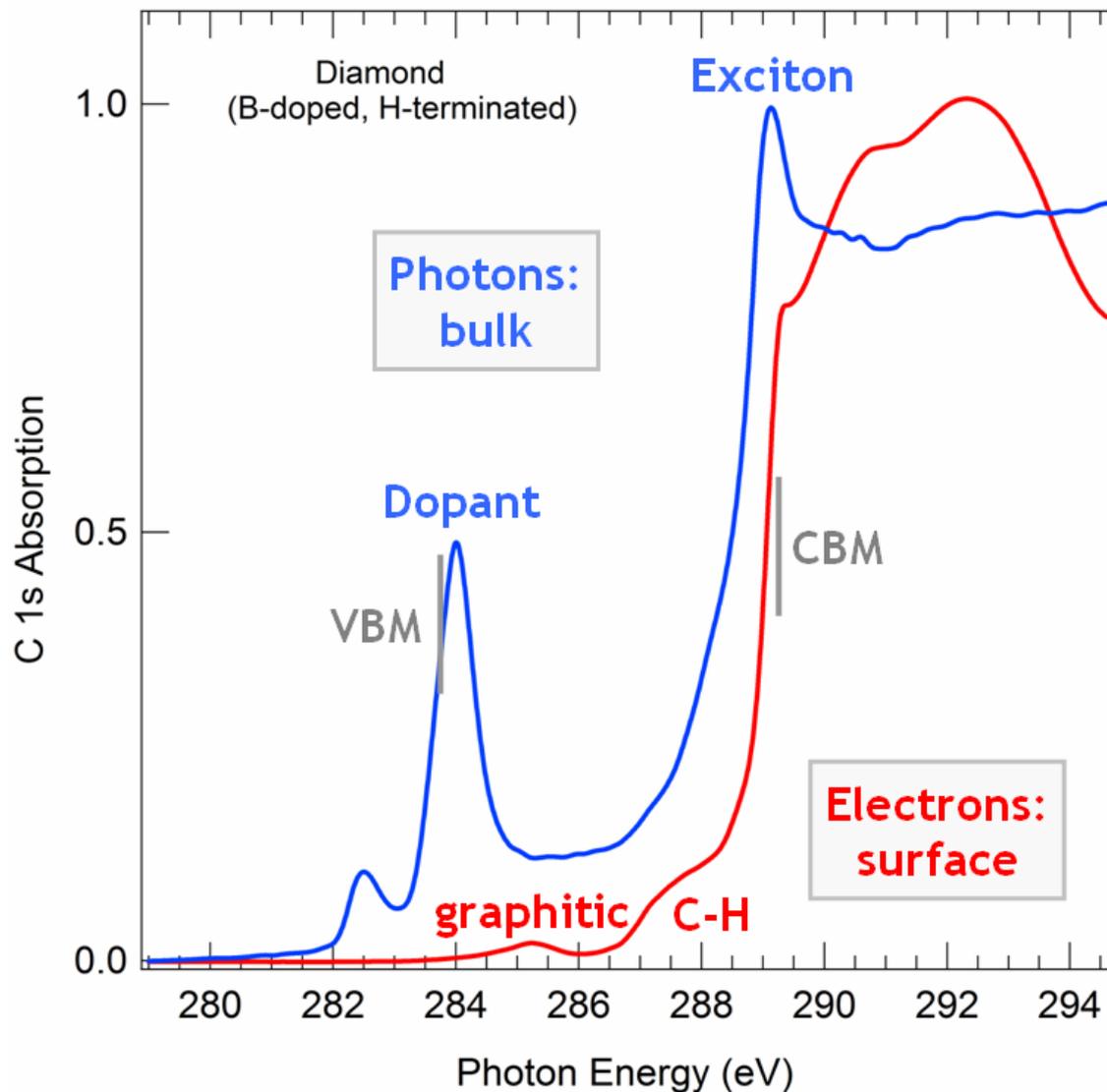


Decay Processes after X-Ray Absorption

Detect decay products of the core hole (rather than transmitted or absorbed photons)



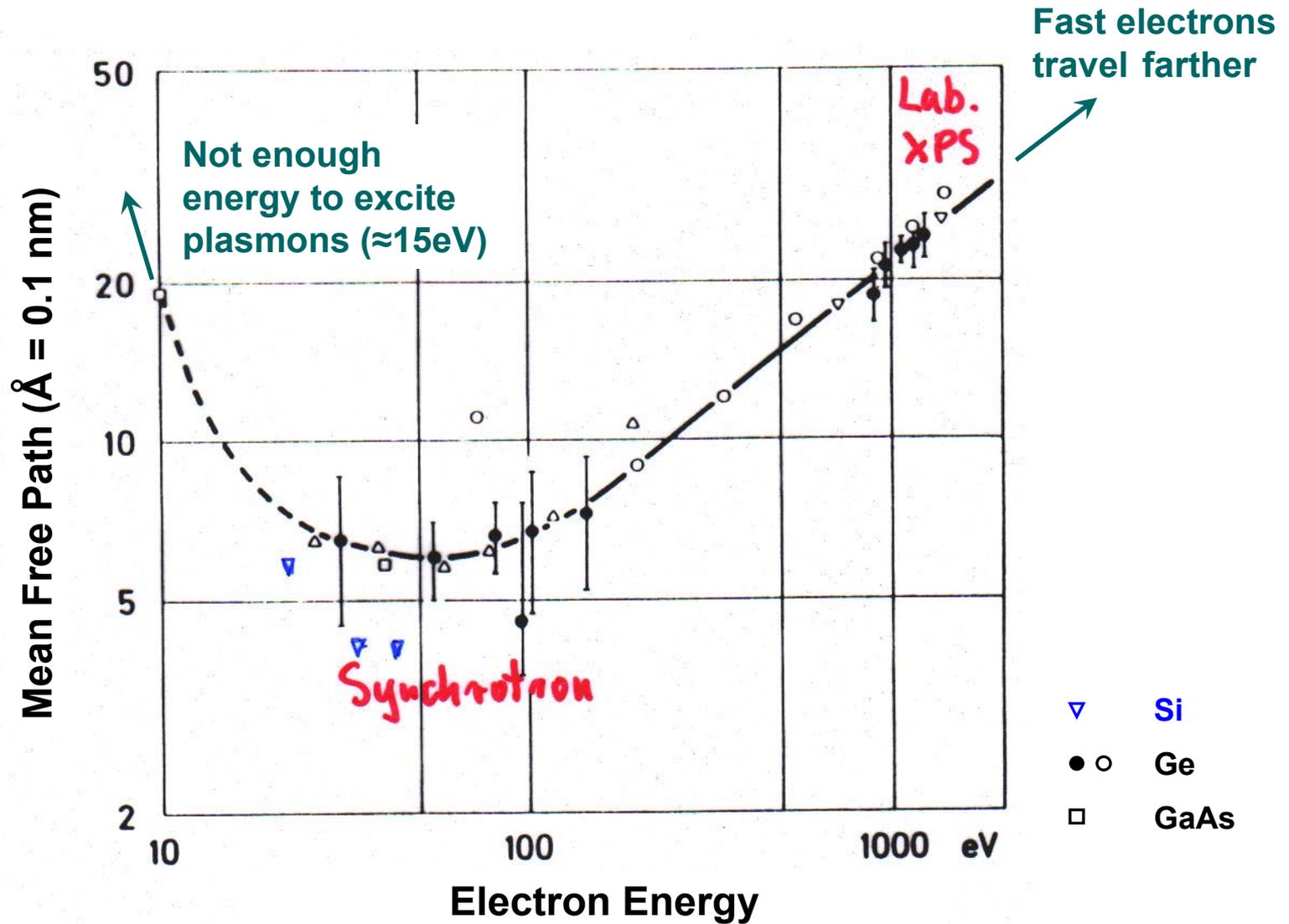
Vary the Probing Depth in XAS by Detecting Electrons + Photons



Polycrystalline diamond films as inert electrodes in photovoltaics and catalysis

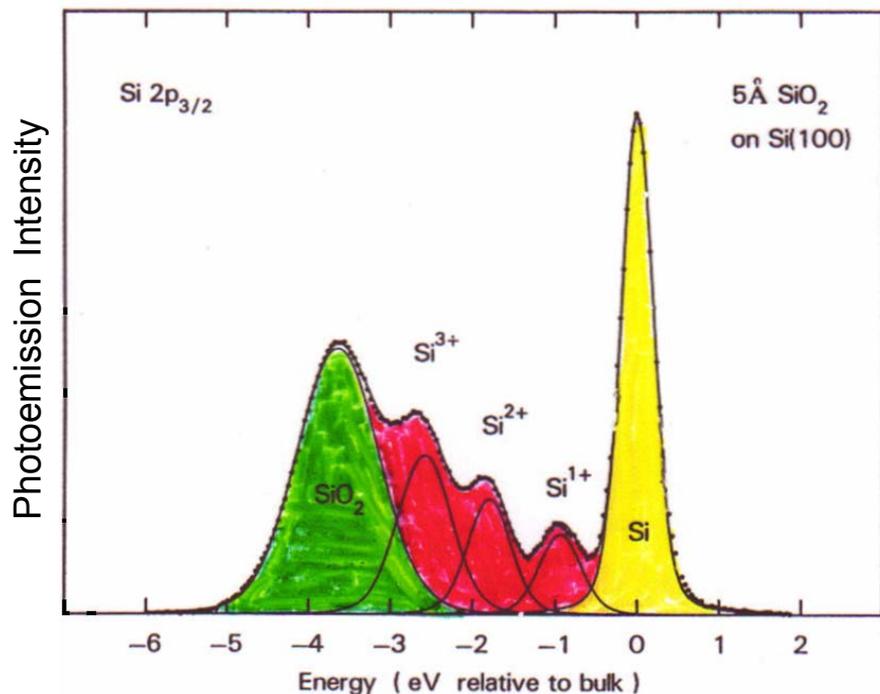
Spectra taken simultaneously with two detectors.

Probing Depth of Electrons



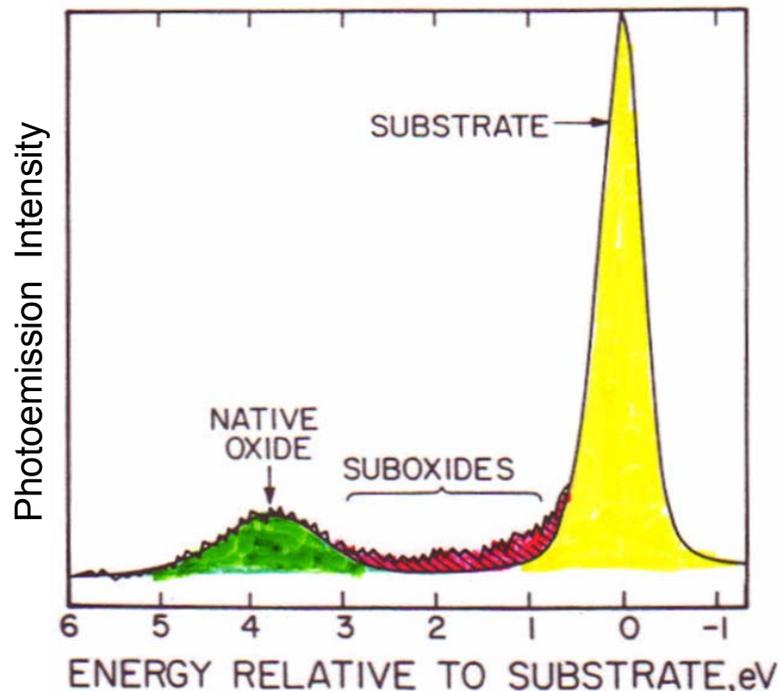
Vary the Probing Depth in XPS by Changing the Photon Energy

Synchrotron radiation ($h\nu = 130$ eV)



Phys. Rev. B **38**, 6084 (1988)

X-ray tube ($h\nu = 1487$ eV)



(F. Grunthaner)

The Si/SiO₂ interface: the key to Si technology (see Lecture II).

The intermediate oxidation states exist only at the interface.

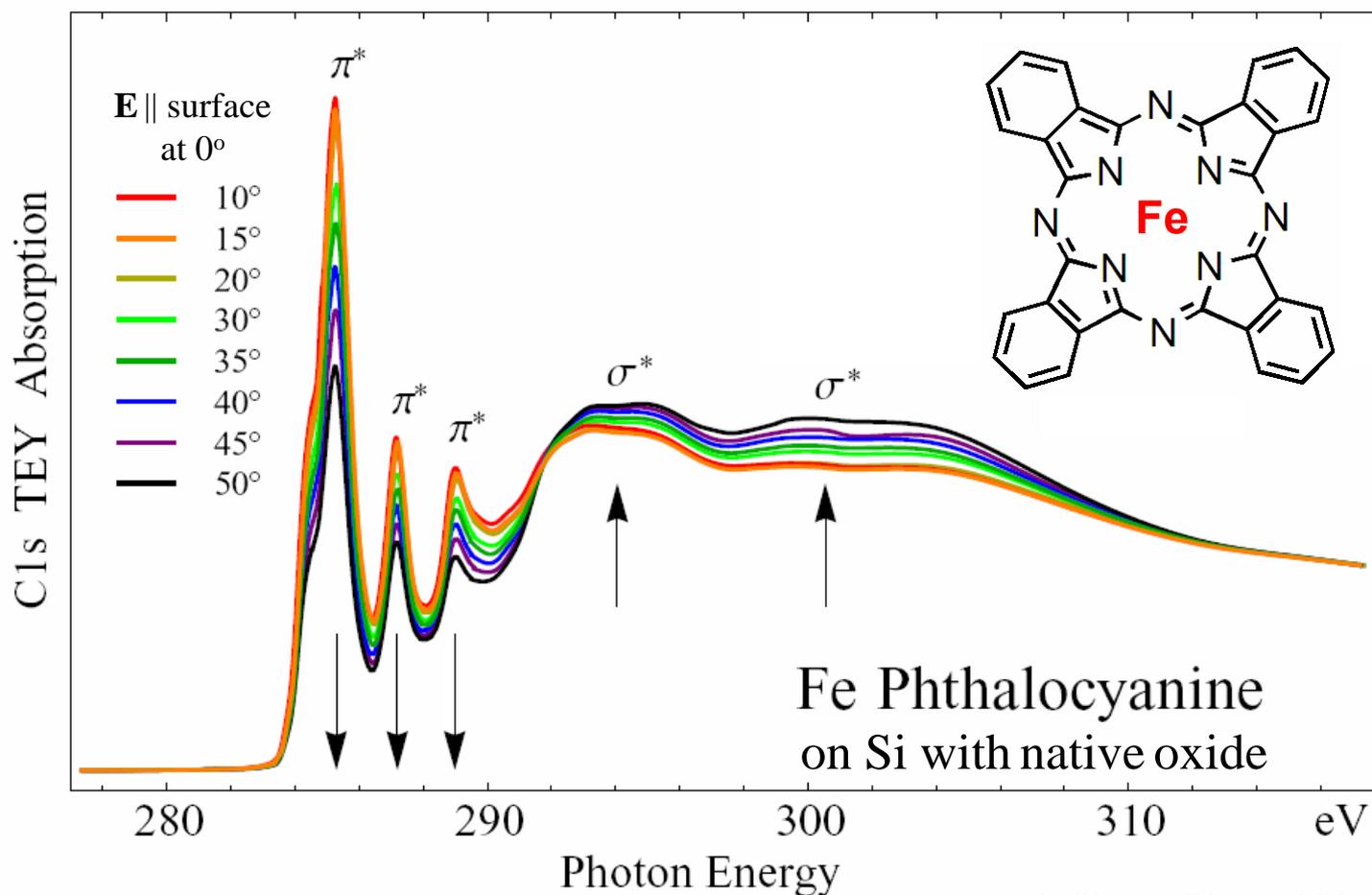
They disproportionate into Si and SiO₂ in the bulk.

Orbital Orientation from the Polarization Dependence

For $1s \rightarrow 2p$ transitions in XAS:

$\cos^2\theta$ dipole pattern, with a maximum when the polarization vector E is parallel to the $2p$ orbital. Opposite behavior of π^* and σ^* orbitals.

Rotate the sample instead of the synchrotron or use special undulator.



Want a Tunable, Polarized Source of X-rays

Advanced Light Source (ALS) at Berkeley



Synchrotron light sources have captured the interest of architects

Shanghai Light Source



Swiss Light Source



Generating Synchrotron Radiation

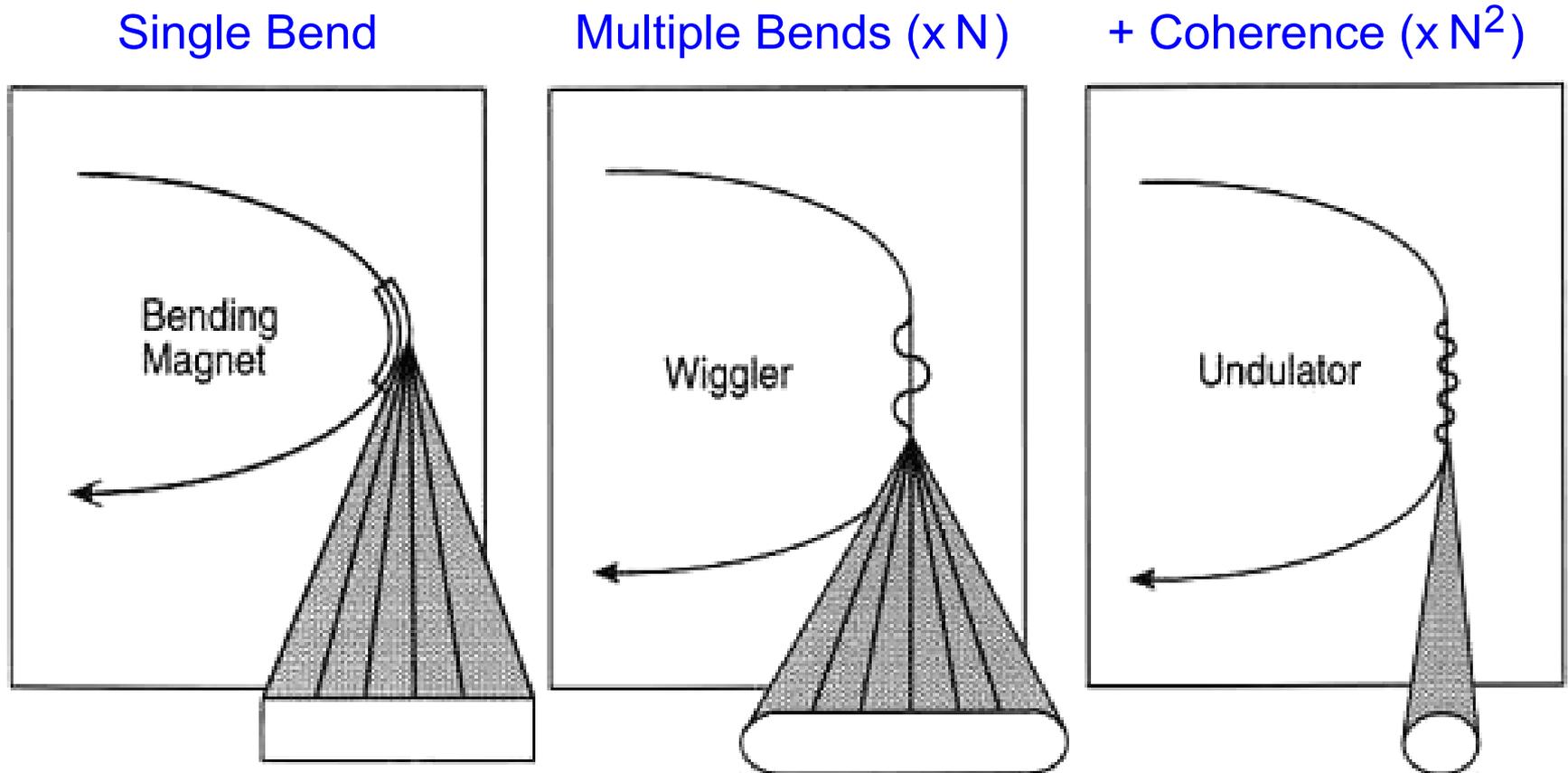
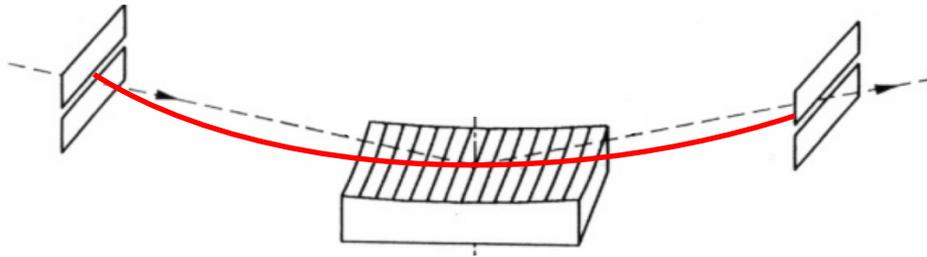


Fig. 1 Schematic of the three approaches used for synchrotron light generation. Bending magnet light is available at all sources. Wigglers or undulators, which are periodic magnet structures installed in straight sections, provide much enhanced flux and brightness. (Figure courtesy of ALS, LBNL)

Producing Monochromatic Synchrotron Radiation

Diffraction Grating (< 2 keV)

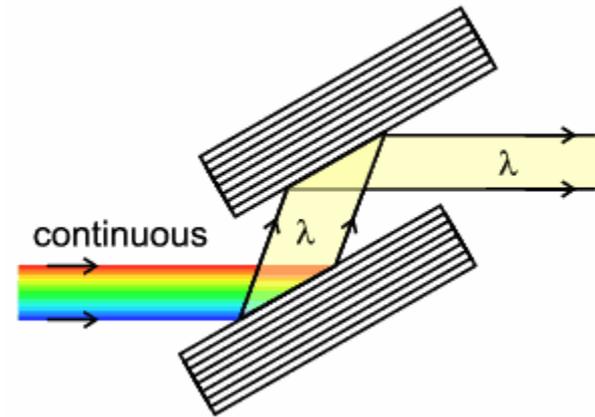


Slits and grating all have to lie on the **Rowland circle** for best focusing. Its radius is half the radius of the spherical grating.

At higher photon energies the angle of incidence gets closer to grazing (down to 1 degree).

Spherical Grating Monochromator

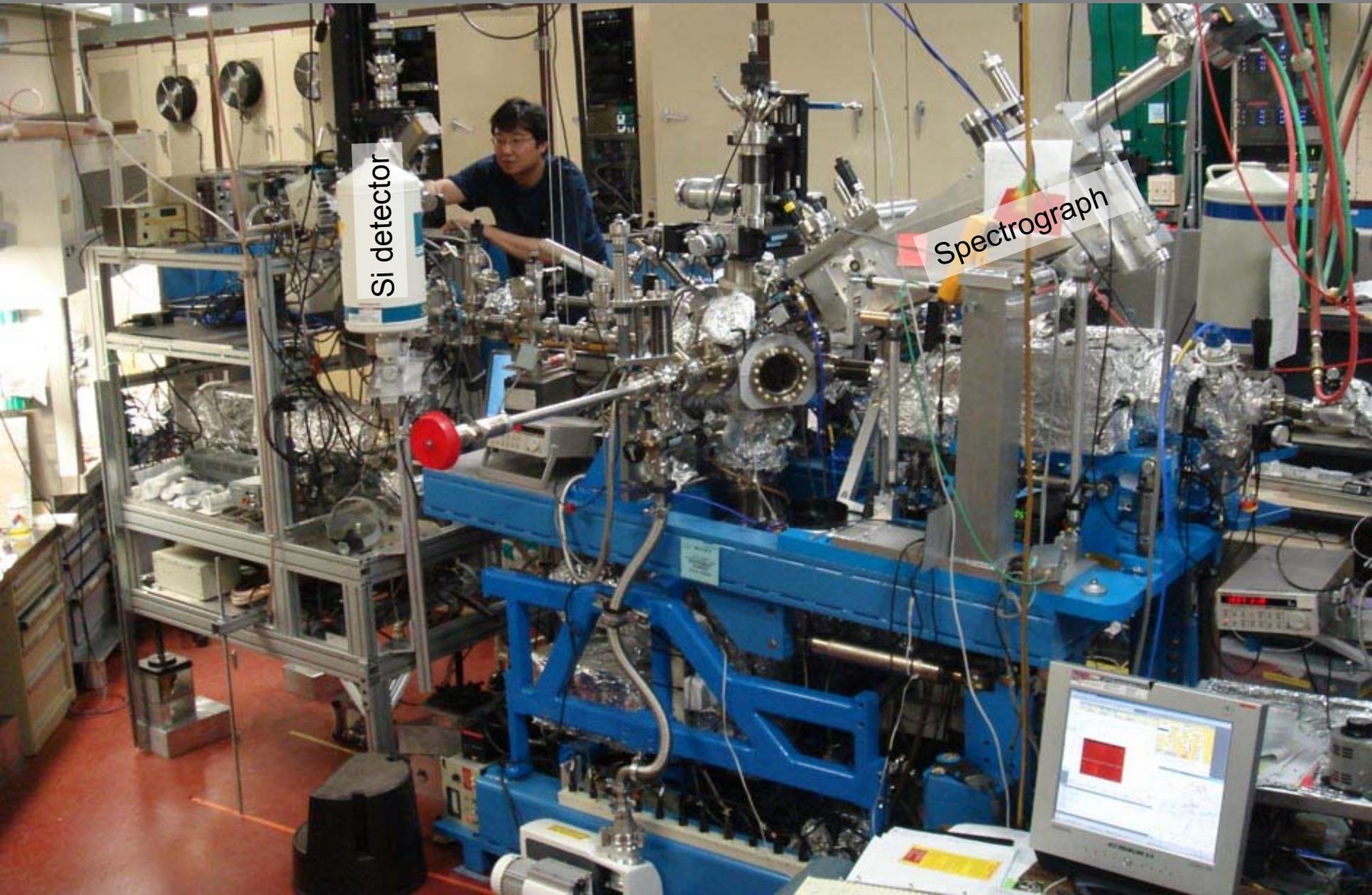
Bragg Reflection (> 2 keV)



Bragg's condition for diffraction of X-rays at the lattice planes of a crystal selects a specific wavelength for each incidence angle.

Double Crystal Monochromator

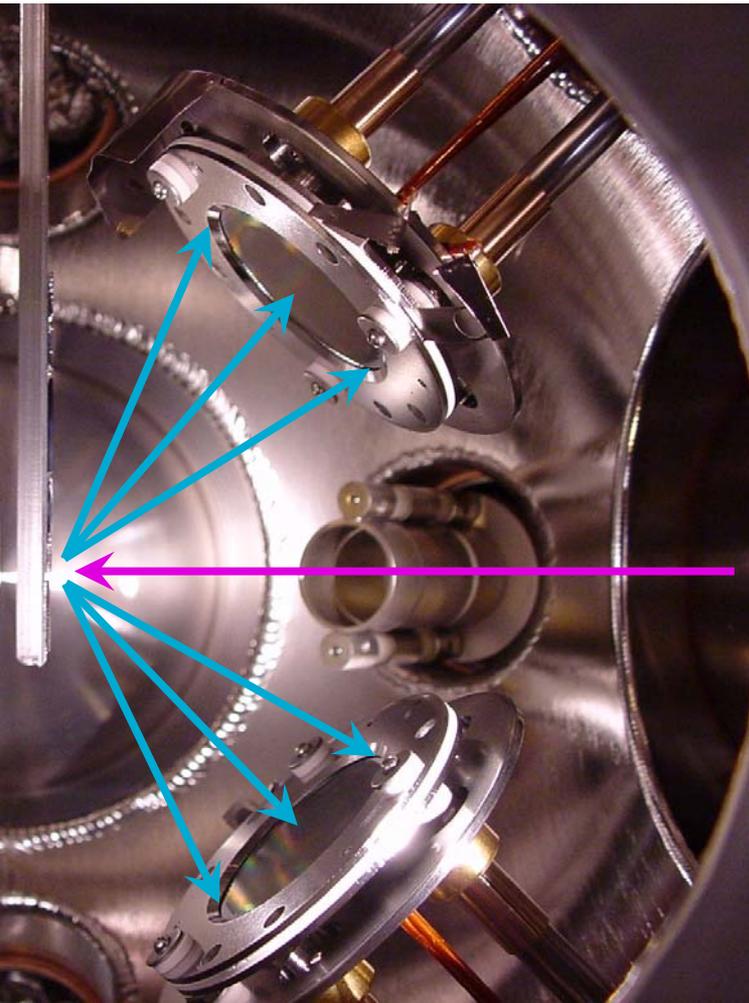
XAS+XES Endstation at an Undulator Beamline



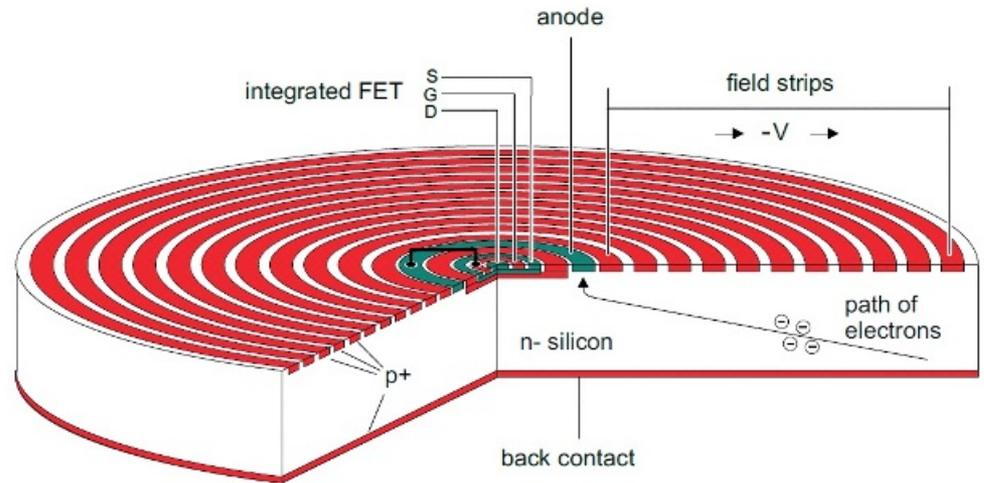
Photon Detectors

Trade-off between high efficiency in 1) and high energy resolution in 3):

1) Channelplates (+ filter)
Large solid angle



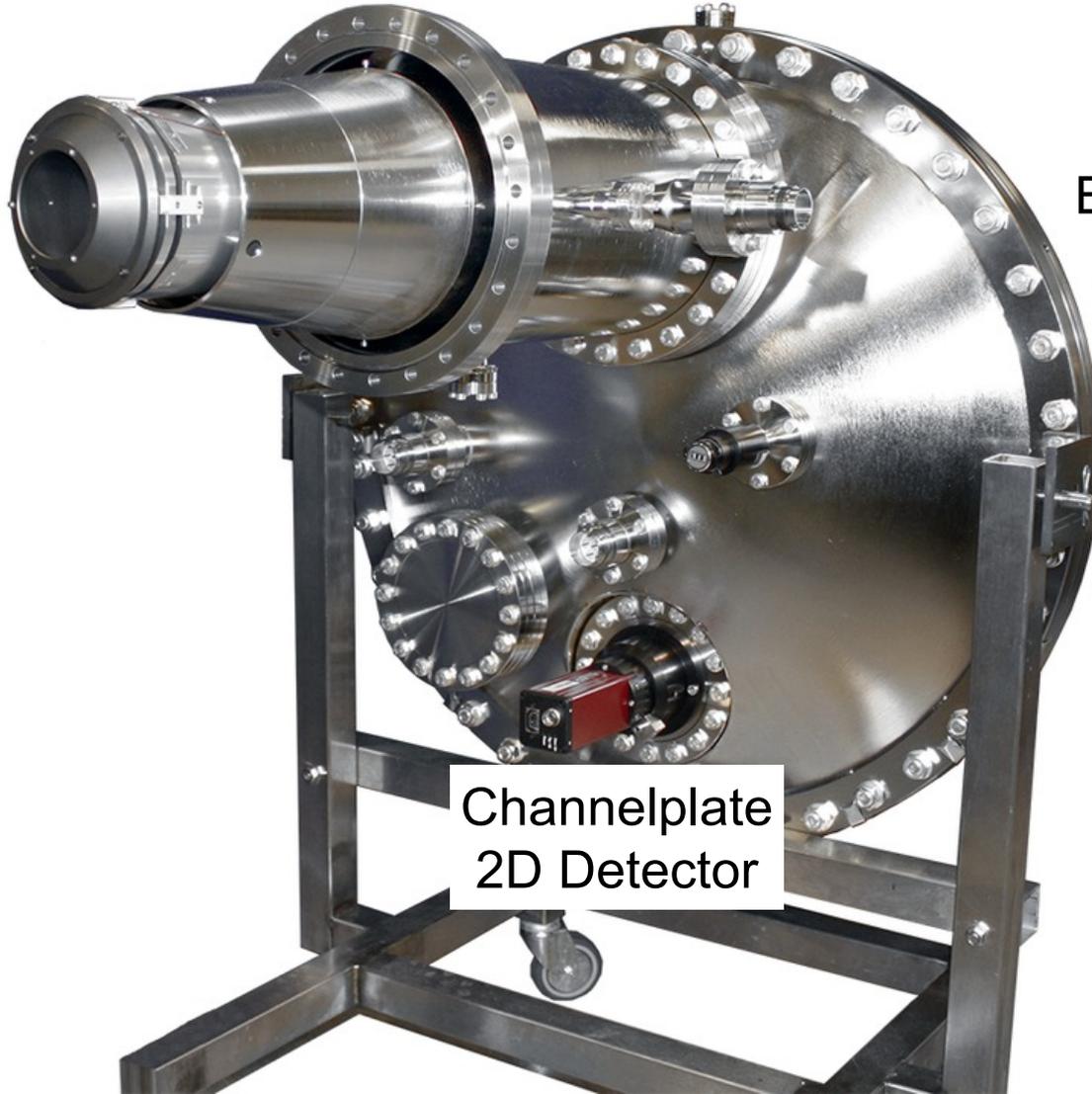
2) Silicon drift detector (SDD)
Separates core levels



3) Spectrograph (monochromator with multidetection replacing the exit slit)
High energy resolution

Electron Spectrometer with Multidetector

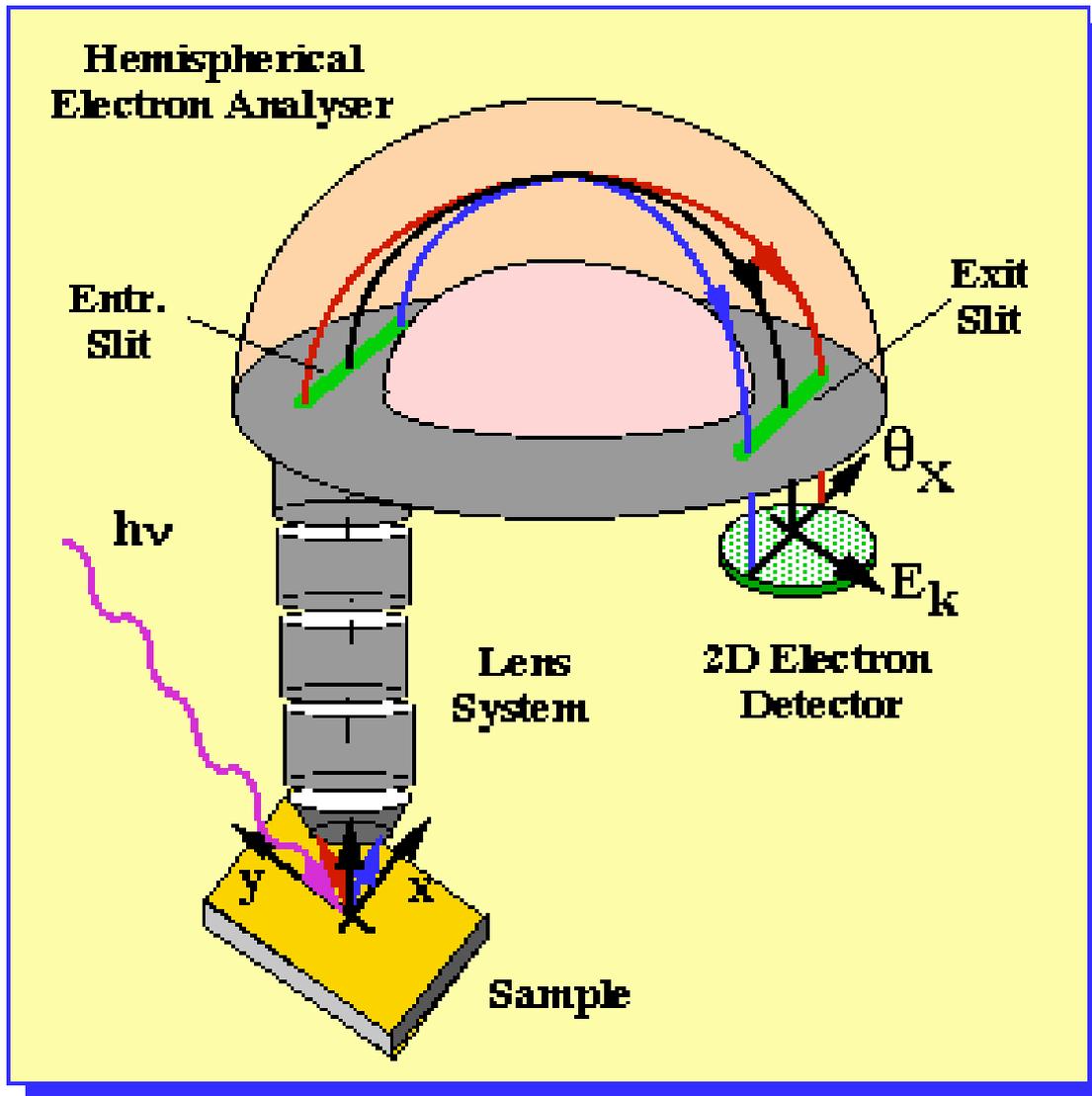
Electron
Lens



Hemispherical
Energy Analyzer

Channelplate
2D Detector

Electron Spectrometer with Multidetetection



Kepler orbits between the charged spheres.

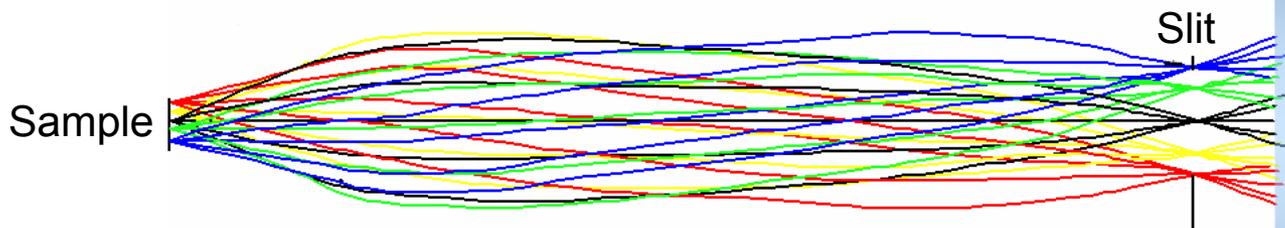
Larger orbits for faster electrons.

Angles and/or positions mapped along the slits.

50×50 = 2500 Spectra in one scan!

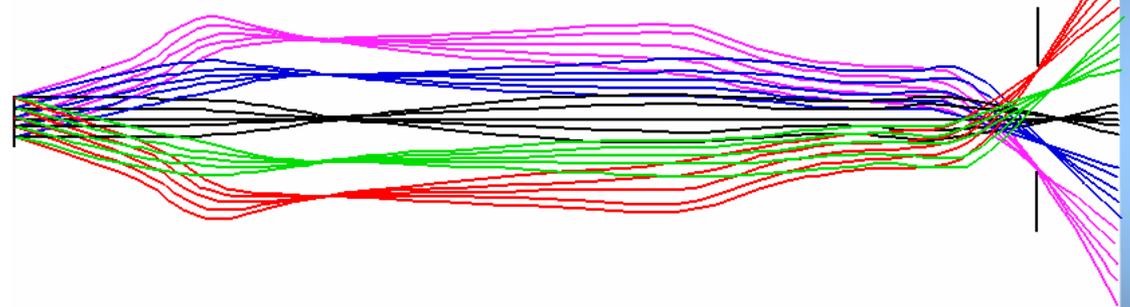
Imaging Mode

Lens focused on sample



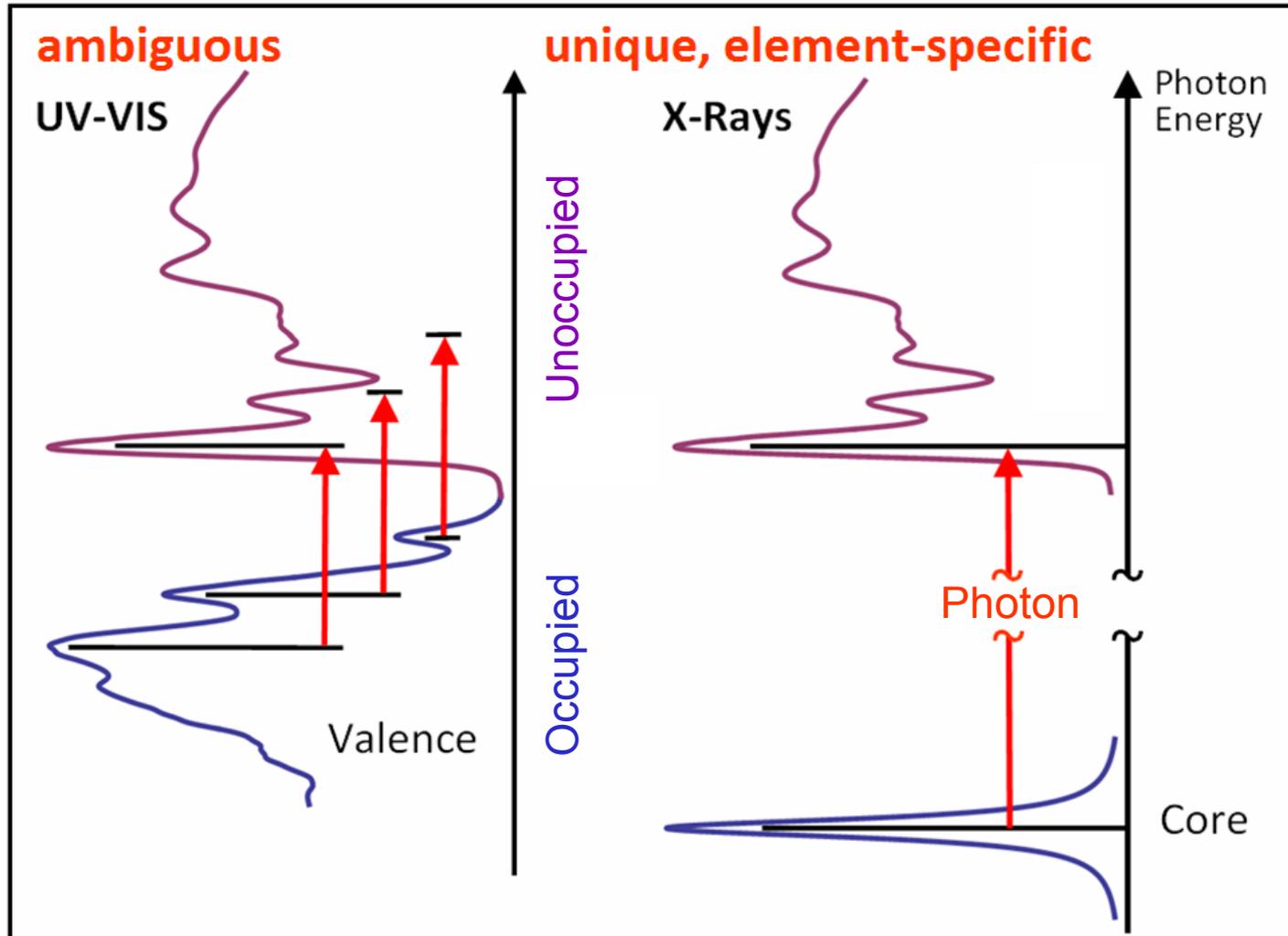
Angle-resolved Mode

Lens focused to infinity



Circular orbits out of plane

X-ray vs. Optical Absorption Spectroscopy



Data Analysis in XPS and XAS

First step: Use **reference spectra** from model compounds to identify the bonding environment (oxidation state in XPS, orbital assignment in XAS). Compare the photon energy calibrations in XAS (varies significantly).

XPS binding energies:

Physical Electronics (Φ) handbooks of XPS and Auger electron energies:
<https://www.phis.com/support/reference-material/handbook.html>

NIST: <https://srdata.nist.gov/xps/Default.aspx>

XAS/EELS transitions:

J. Stöhr, NEXAFS Spectroscopy, Springer Series in Surface Sciences **25**

Molecules: <http://unicorn.mcmaster.ca/corex/cedb-title.html>

Polymers: J. Phys. Chem. B **106**, 8531 (2002); Polymer **49**, 643 (2008).

Nitrogen K-edge: J. Synchrotron Rad. **14**, 500 (2007).

Transition metal oxides, coordination complexes:

J. Phys. Condens. Matter **21**, 104207 (2009); (K-edge)

J. Electron. Spectrosc. Relat. Phenom. **61**, 529 (1994); (L-edge)

Data Analysis Assisted by Theory

Semiempirical modeling:

A multiple scattering code for modeling of absorption edges has evolved over a number of years (currently FEFF9):

<http://leonardo.phys.washington.edu/feffproject-feff.html>

The complex (but highly-informative) multiplet structure of the $2p \rightarrow 3d$ edges in transition metals and rare earths can be modeled by CTM4XAS:

<http://www.anorg.chem.uu.nl/people/staff/FrankdeGroot/>

First principles calculations:

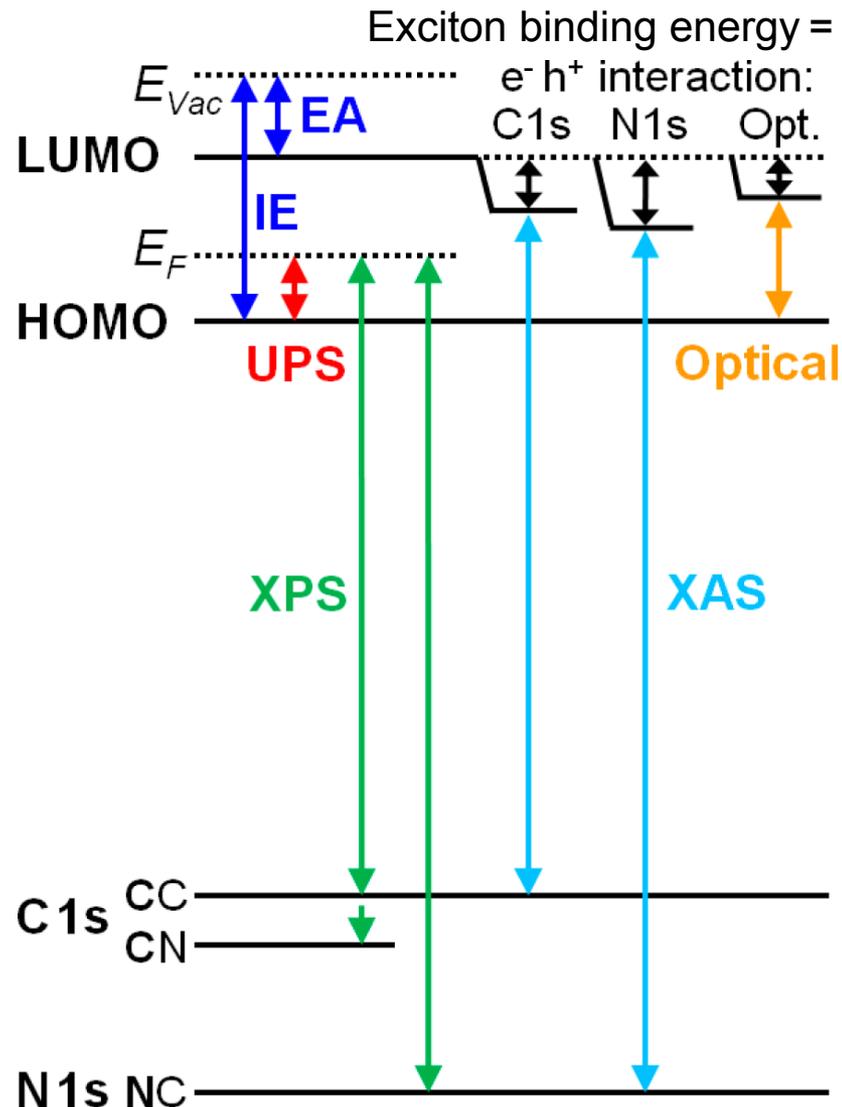
The difficulty increases strongly with the number of quasiparticles involved: XPS and XES involve only a single quasiparticle (if shake-up and plasmon satellites are ignored). They can be handled with standard density functional theory (DFT). XAS/EELS involve an electron-hole pair (exciton) which requires time-dependent DFT (TDDFT) or the Bethe-Salpeter equation. It is possible to get by with simpler calculations with input from other experiments (see the next slide).

Combination of Core and Valence Spectroscopy with Theory

For both optical and core level absorption spectroscopy one needs to take the electron-hole interaction into account (black double-arrows). To avoid complex two-body calculations one can combine a simple Δ SCF calculation of the ionization energy (IE) and the electron affinity (EA) with XPS, UPS, and XAS data. Following the double-arrows for XAS, XPS, UPS, IE, EA clockwise, the remaining gap for completing a loop is the exciton binding energy.

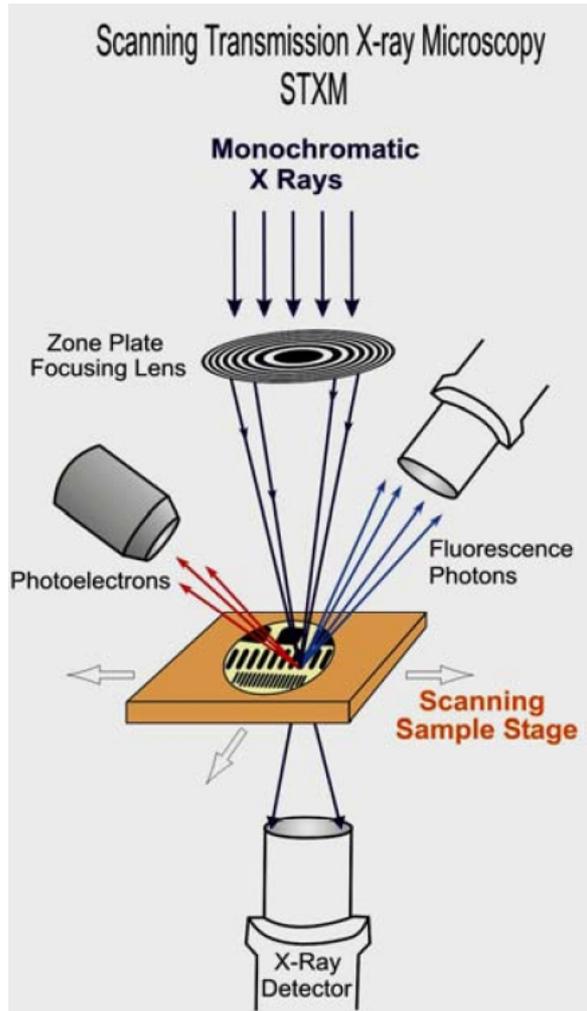
The energy reference for XPS, UPS is the Fermi level E_F . For XAS (optical absorption) it is the core level (HOMO), and for theory the vacuum level E_{Vac} .

J. Phys. Chem. C **120**, 1366 (2016)

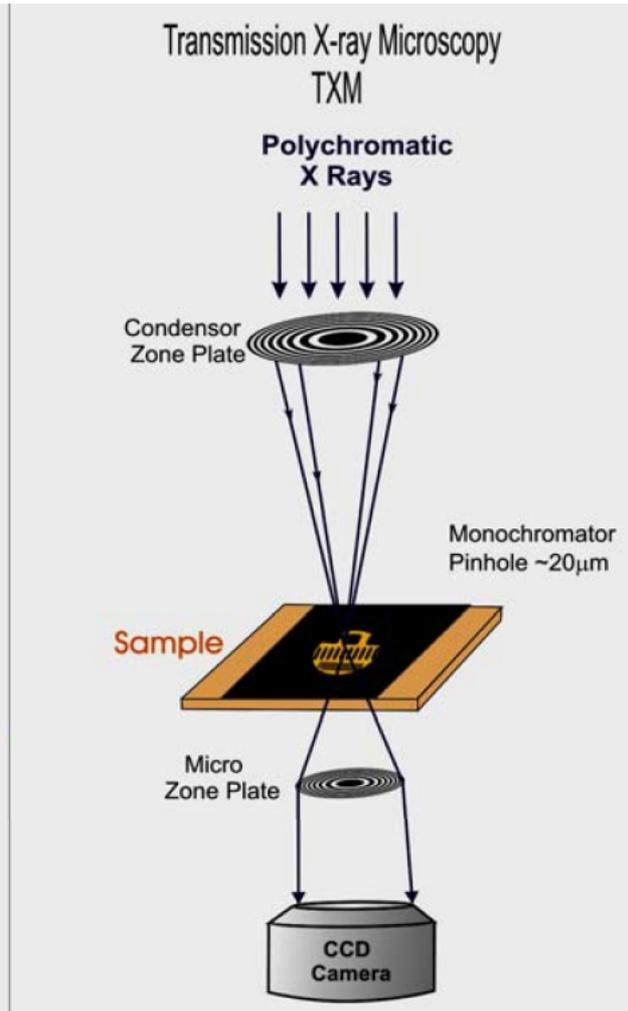


Microscopy with Chemical Resolution Using Core Levels

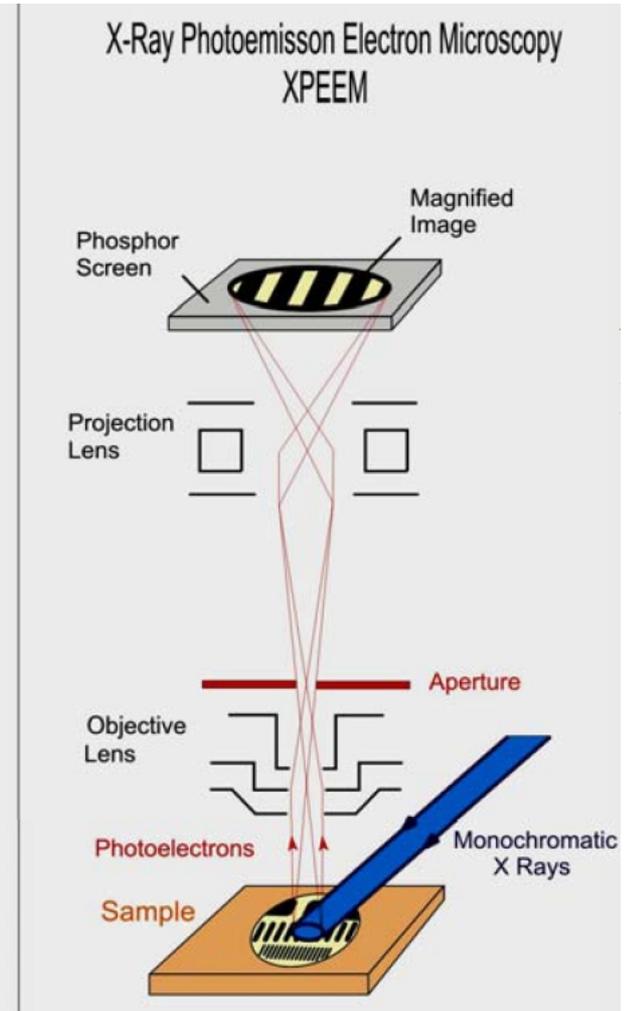
Scanning focused X-rays



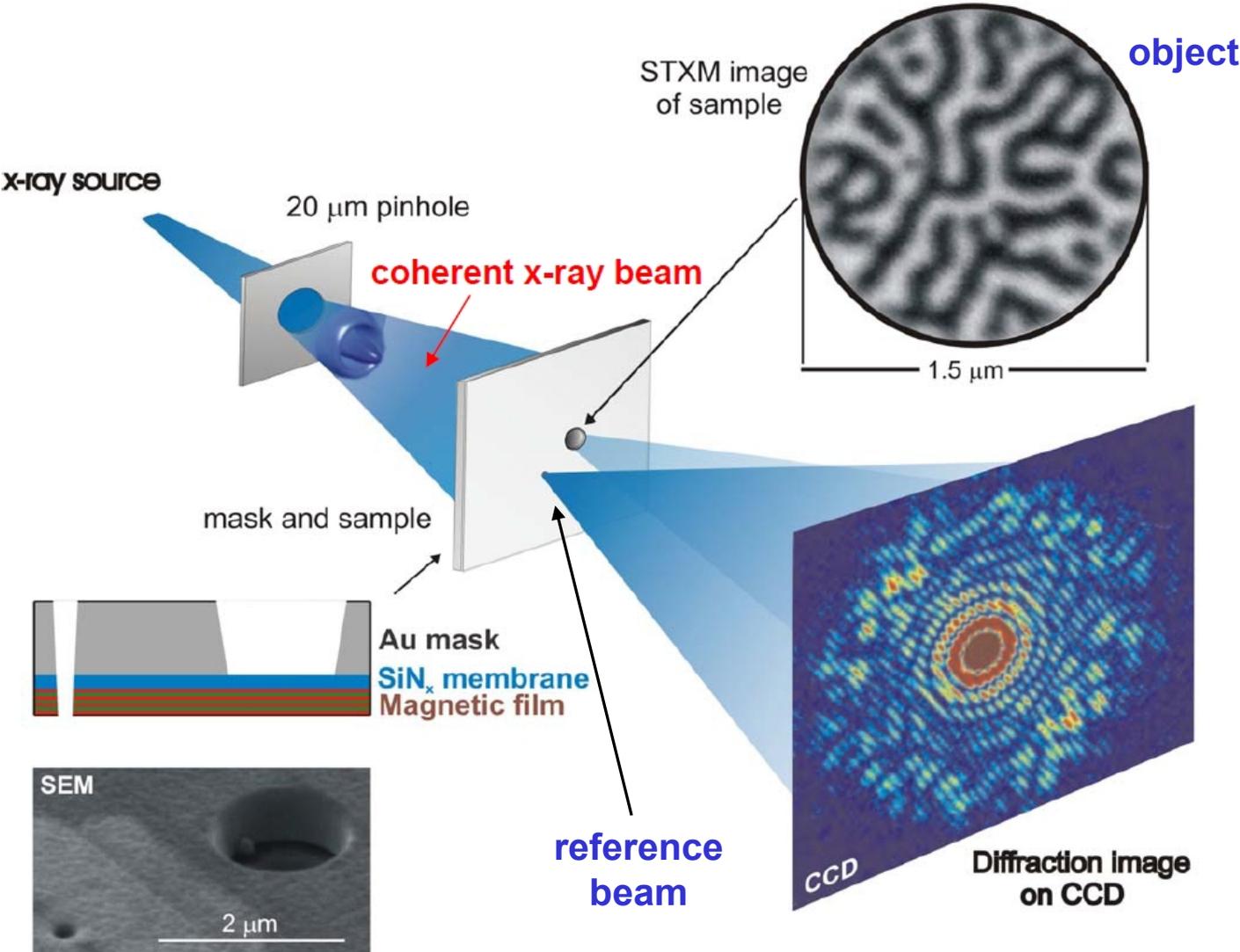
Imaging with X-rays



Imaging emitted electrons



Holography and Ptychography



Ptychography = Holography without a Reference Beam

In favorable circumstances it is possible to reconstruct a diffraction pattern without a reference beam. The diffraction pattern is the Fourier transform of the X-rays emitted by the object. Therefore, an inverse Fourier transform should reconstruct the object. The problem is that one measures only the amplitude of the diffraction pattern, not its phase. But for an object located inside a well-defined aperture, one can obtain the phase by iteration:

- 1) Inverse Fourier transform of the diffraction amplitude with arbitrary phase from k-space to r-space.
- 2) Truncation of the amplitude outside the aperture + Fourier transform from r to k.
- 3) Replacement of the amplitude in k-space by the measured diffraction pattern + inverse Fourier transform back to r.
- 4) Return to 2).

Photoelectron Diffraction and Holography

One can also use diffraction from photoelectron rather than photons. Since the electron wavelength is shorter than the photon wavelength, one can reach atomic resolution even with soft X-rays. The spherical wave of photoelectrons emitted directly from a particular atom serves as reference, the waves scattered by neighbor atoms create the object. The analysis is more involved for electrons than for photons, because multiple scattering needs to be included.

This concept will be illustrated in Lecture II, using the Si/SiO₂ interface as example.

