Basic X-ray experimental techniques - spectroscopy

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Suggested readings (books)

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[1] David Attwood, Anne Sakdinawat, (2017). *X-Rays and Extreme Ultraviolet Radiation: Principles and Applications*. Cambridge University Press.

[2] Philip Willmott, (2011). *An introduction to synchrotron radiation: techniques and applications*. John Wiley & Sons, Ltd.

[3] Frank de Groot, Akio Kotani, (2008). *Core Level Spectroscopy of Solids*. CRC Press.

[4] Grant Bunker, (2010). *Introduction to XAFS: A Practical Guide to X-Ray Absorption Fine Structure Spectroscopy*, Cambridge University Press.

[5] Jeroen A. van Bokhoven, Carlo Lamberti, editors, (2015). *X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications*. John Wiley & Sons, Inc.

Terminology

XPS: **X**-ray **P**hotolectron **S**pectroscopy is a technique to probe electronic structure of the occupied orbitals/bands, which provide surface sensitive (few nm) information on chemical composition of materials and their valence state structure

ARPES: **A**ngle **R**esolved **P**hoto**E**lectron **S**pectroscopy is a technique to probe dispersion relation of valence electrons

XAS: **X**-ray **A**bsorption **S**pectroscopy is a technique to probe electronic structure of unoccupied orbital/bands, which provide bulk sensitive (few microns) element selective information on local atomic structure

XES: **X**-ray **E**mission **S**pectroscopy is a technique to probe electronic structure of the occupied orbitals/bands, which provide bulk sensitive (few microns) element selective information on charge, spin and valence band density of states

RIXS: **R**esonant **I**nelastic **X**-ray **S**cattering is a photon-in photon-out spectroscopy technique to probe electronic excitations resolved in energy and momentum

Outline

1. Introduction to core level X-ray spectroscopy
2. X-ray absorption spectroscopy and dichroism
3. X-ray photoelectron spectroscopy and its angular dependence
4. X-ray fluorescence and emission spectroscopy
5. Resonant inelastic X-ray scattering and related methods
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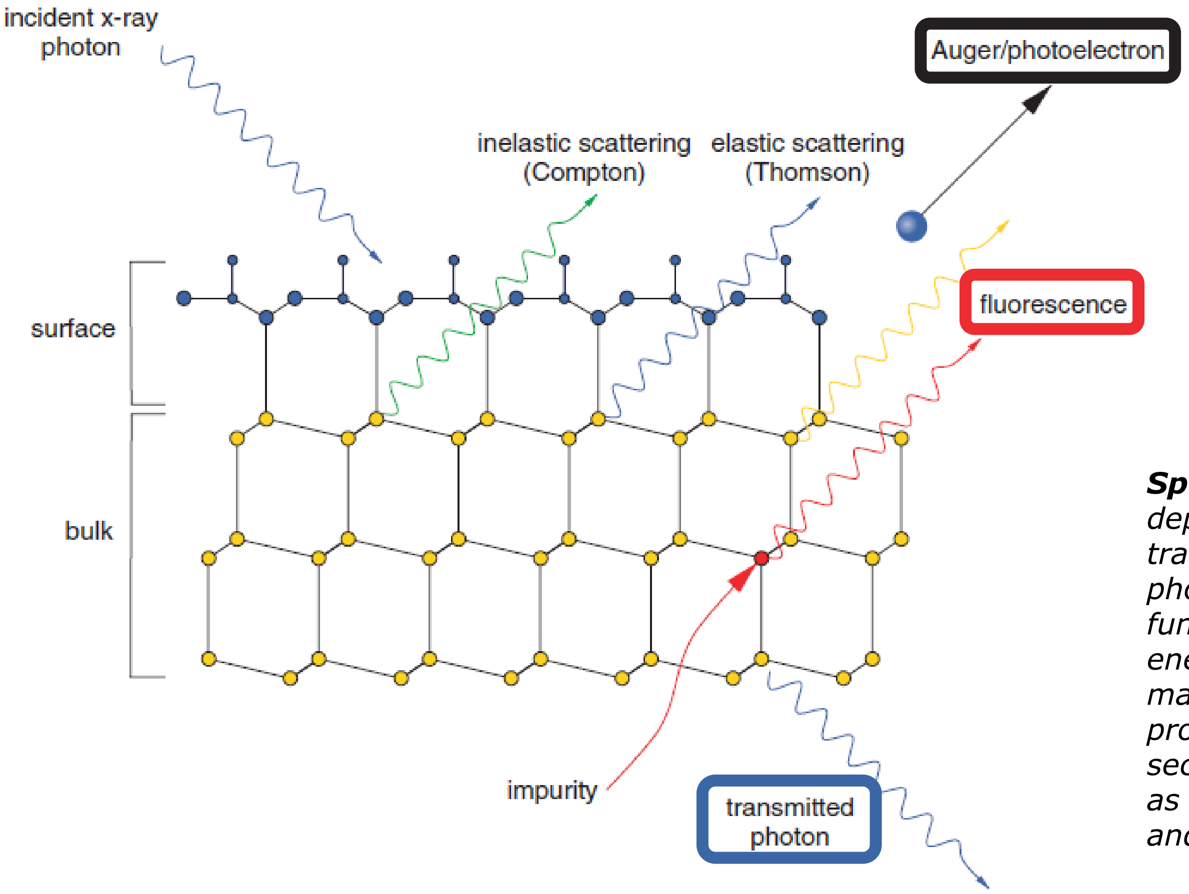
X-ray interaction with matter

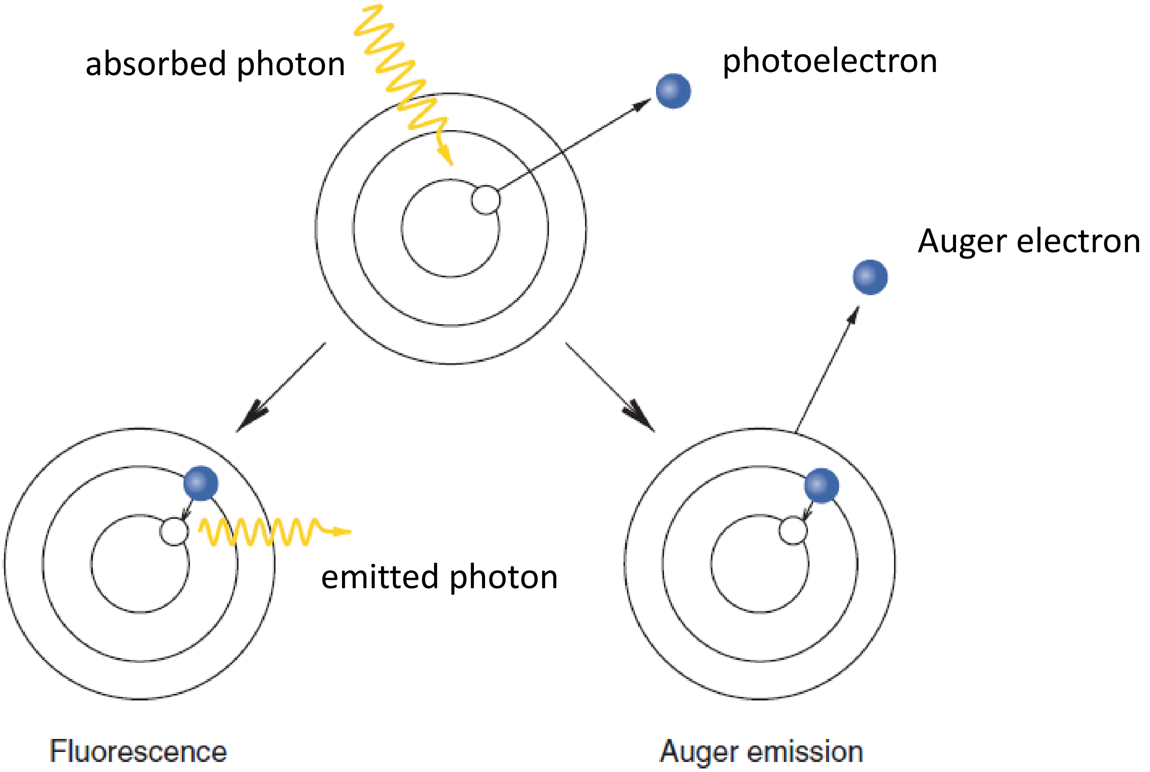


Spectroscopy *probes the dependence of transmission/absorption of photons by matter as a function of incident photon energy. Absorption process may be probed also by probing the intensity of secondary particles, such as fluorescence photons and Auger/photoelectrons.*

X-ray fluorescense and Auger emission

Photoabsorption and photoelectron emission are primary processes

Fluorescence and Auger emission are secondary processes observed as an effect of electronic relaxation of the electronic structure excited by absorption of photon energy



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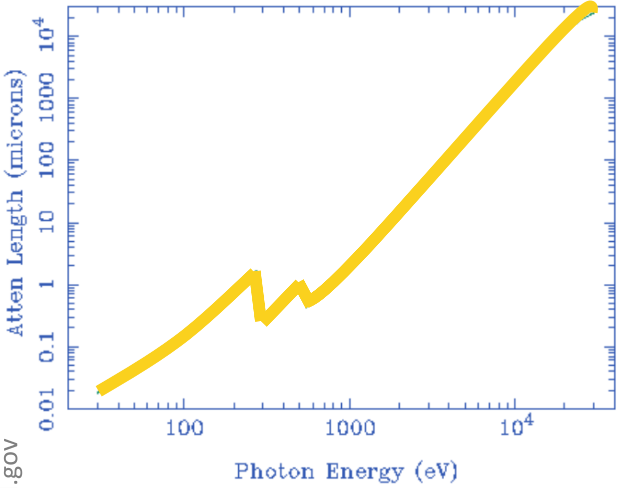
Information depth

Attenuation length of X-rays



source: henke.lbl.gov

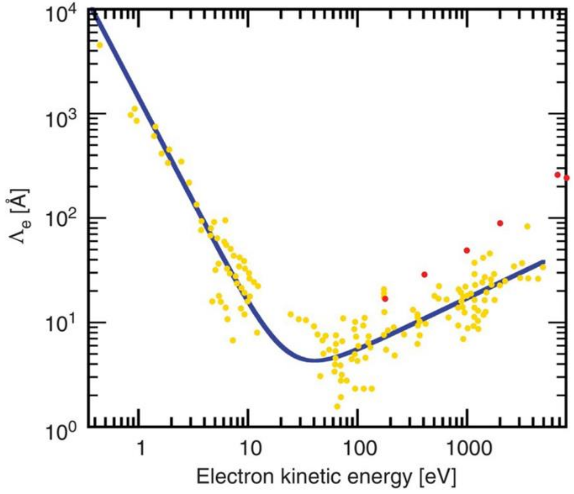
few microns

XES, RIXS, etc.

Fluorescence XAS

Probing depth of X-ray spectroscopy depends on the particles probed. In case of the detection of photons it is of the order of microns to millimeters, while in the case of electrons it is in the order nanometers

Electron mean free path



source: [2]

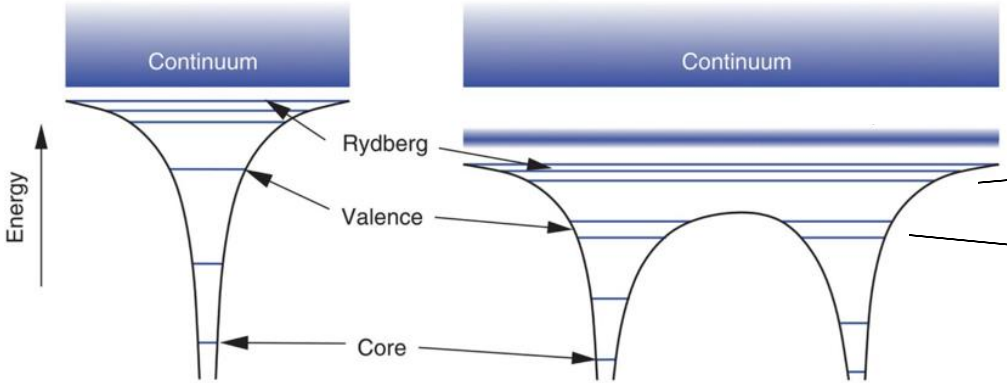
few nm

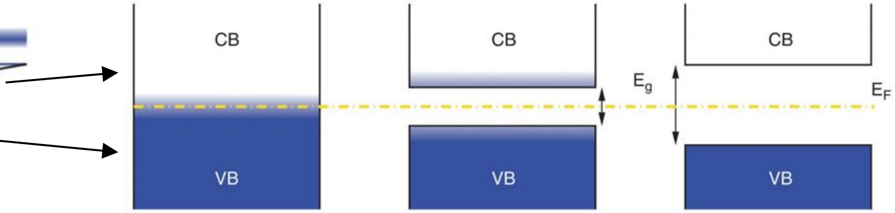
XPS (ARPES)

Electron Yield XAS

Electronic structure of matter

Isolated atom | *Molecule* | *Solid materials*





metal | *semiconductor* | *insulator*

source: [2]

Element	K 1s
1 H	13.6
2 He	24.6*
3 Li	54.7*
4 Be	111.5*
5 B	188*
6 C	284.2*
7 N	409.9*
8 O	543.1*
9 F	696.7*
10 Ne	870.2*
11 Na	1070.8†
12 Mg	1303.0†

Energy of X-ray photons (from ~100eV to >10keV) is high enough to excite electrons from the strongly bound orbitals, namely the core orbitals

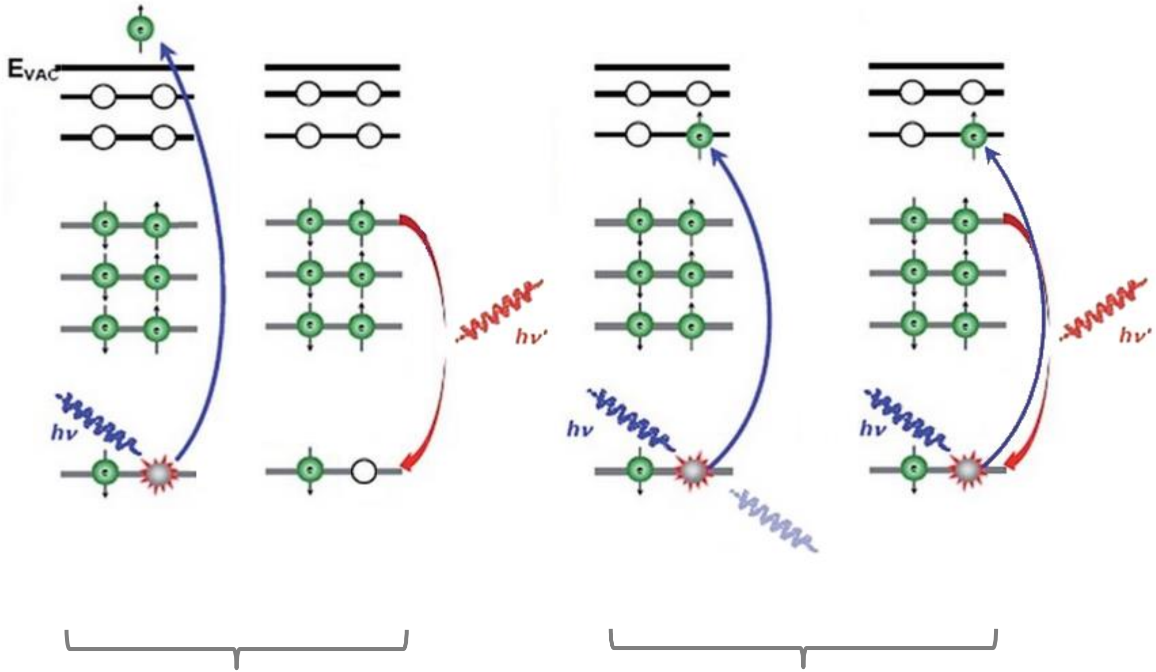
CB $\rightarrow$ conduction band
VB $\rightarrow$ valence band
E_F $\rightarrow$ Fermi energy
E_g $\rightarrow$ energy gap

Corel level X-ray spectroscopy

Empty

Valence

Core



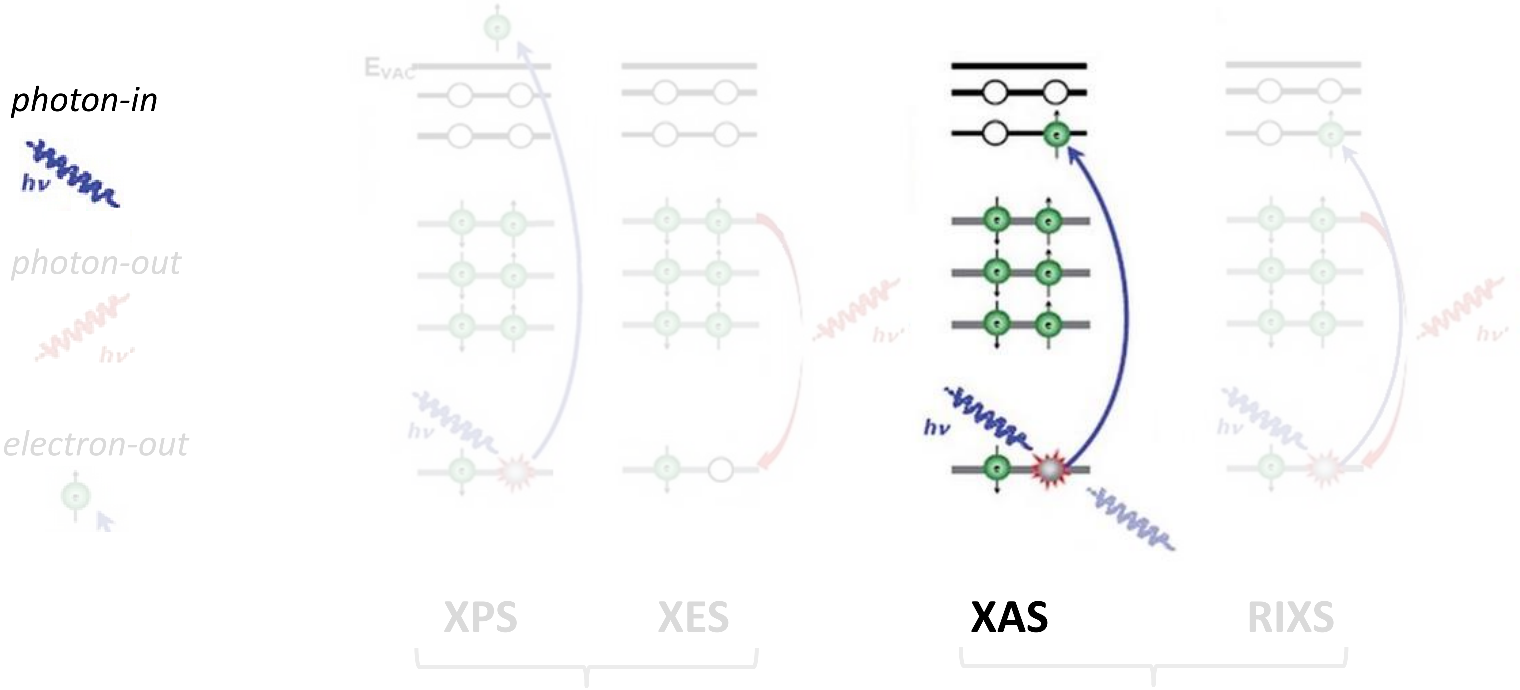
Fixed photon energy *Variable photon energy*

X-ray absorption spectroscopy

photon-in

photon-out

electron-out



Fixed photon-in energy

Tunable photon-in energy

X-ray absorption spectroscopy

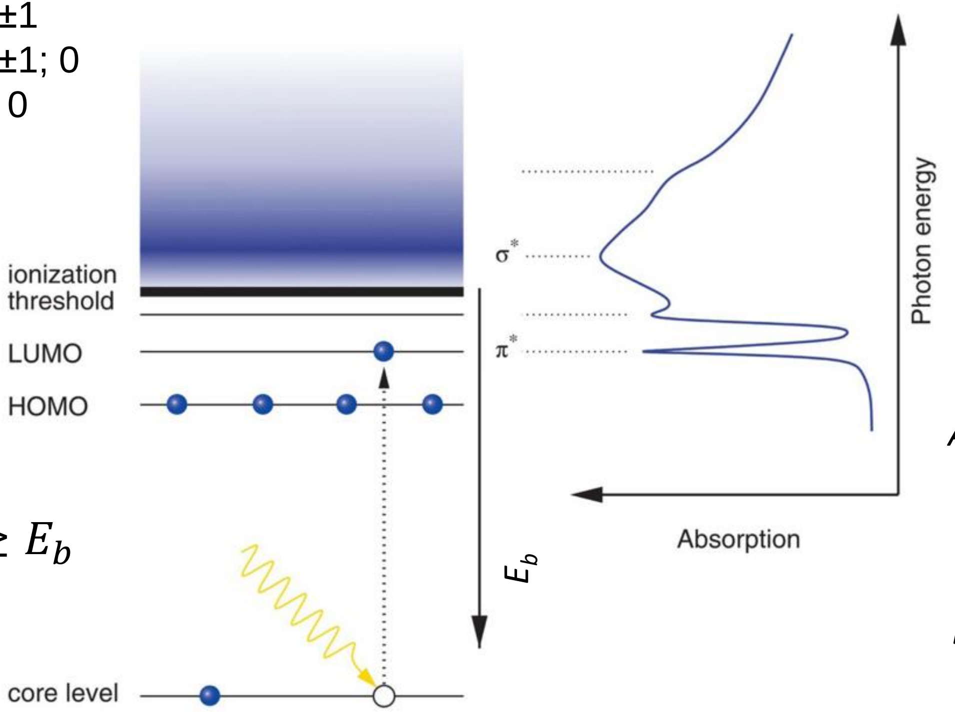
Dipol transitions

$\Delta l = \pm 1$

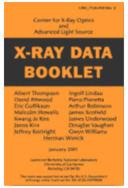
$\Delta j = \pm 1; 0$

$\Delta s = 0$

$$h\upsilon \geq E_b$$



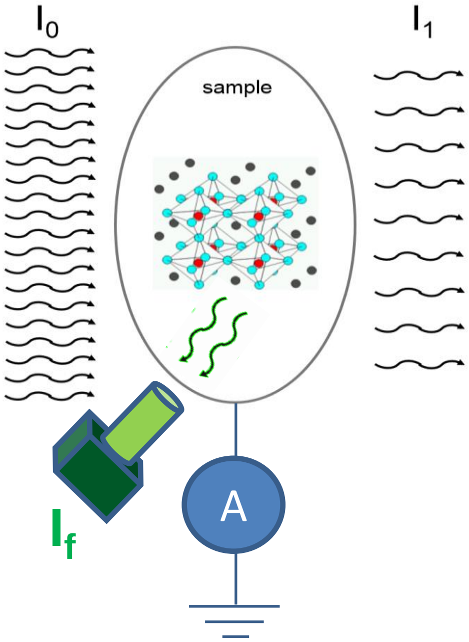
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$
1 H	13.6			
2 He	24.6*			
3 Li	54.7*			
4 Be	111.5*			
5 B	188*			
6 C	284.2*			
7 N	409.9*	37.3*		
8 O	543.1*	41.6*		
9 F	696.7*			
10 Ne	870.2*	48.5*	21.7*	21.6*
11 Na	1070.8†	63.5†	30.65	30.81
12 Mg	1303.0†	88.7	49.78	49.50
13 Al	1559.6	117.8	72.95	72.55
14 Si	1839	149.7*b	99.82	99.42
15 P	2145.5	189*	136*	135*
16 S	2472	230.9	163.6*	162.5*
17 Cl	2822.4	270*	202*	200*
18 Ar	3205.9*	326.3*	250.6†	248.4*
19 K	3608.4*	378.6*	297.3*	294.6*
20 Ca	4038.5*	438.4†	349.7†	346.2†
21 Sc	4492	498.0*	403.6*	398.7*
22 Ti	4966	560.9†	460.2†	453.8†



Absorption crosssection is proportional to density of unoccupied electronic states at the energy defined by the energy and momentum conservation principles

Binding energy probed in XAS is characteristic for element/orbital. As such the method can be used as element and symmetry selective probe of ***unoccupied electronic states***

X-ray absorption experiment



Absorption measured by

transmission

$$I_1 = I_0 e^{-\mu x}$$

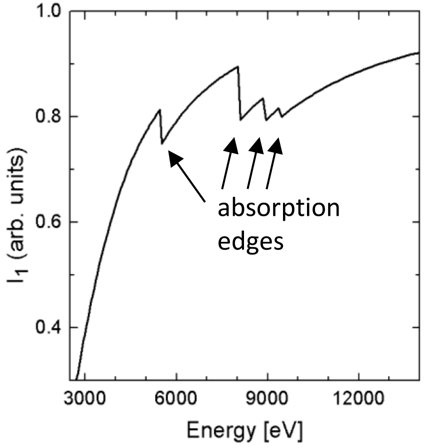
electron yield / *fluorescence*

$$TEY \sim I_0 \mu$$

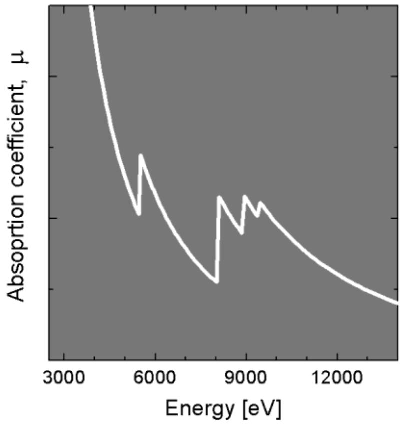
$$I_f \sim I_0 \mu$$

XAS can be probed using energy dependence of:

- *transmission*
- *fluorescence*
- *electron yield*

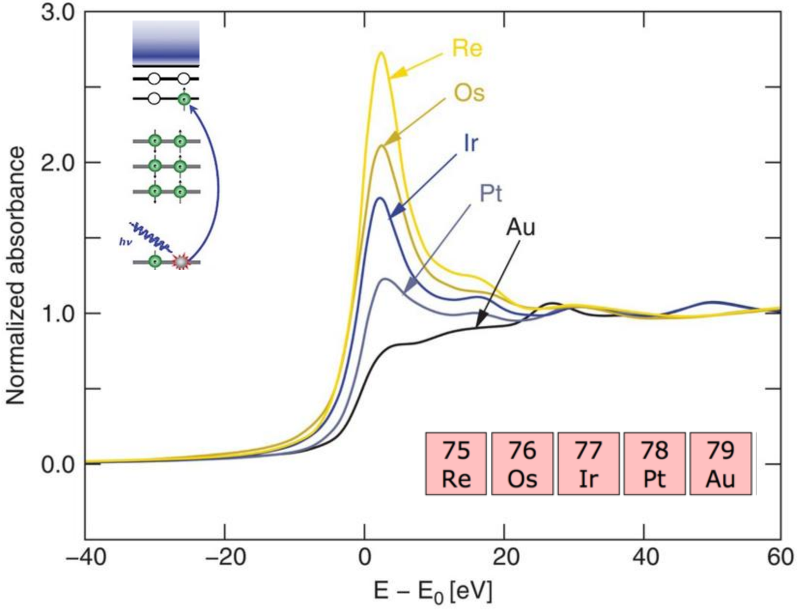


→ *absorption spectrum*

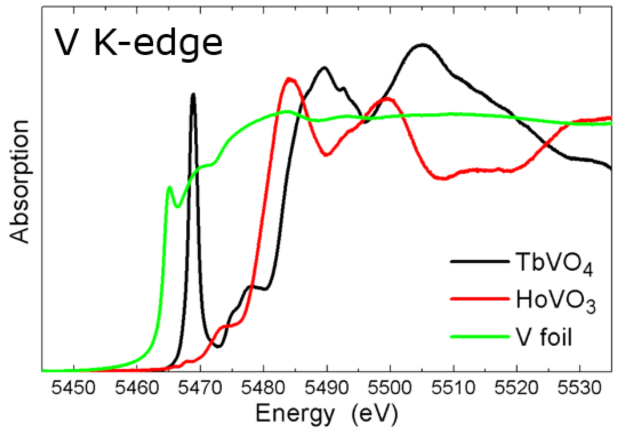


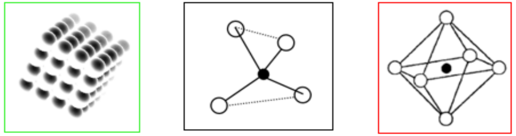
X-ray absorption near edge structure

L_3 absorption edge of the 5d-metals with different occupation of valence band



K absorption edge of V compounds of different local structure and V oxidation state





*Sensitive to **electronic occupation***

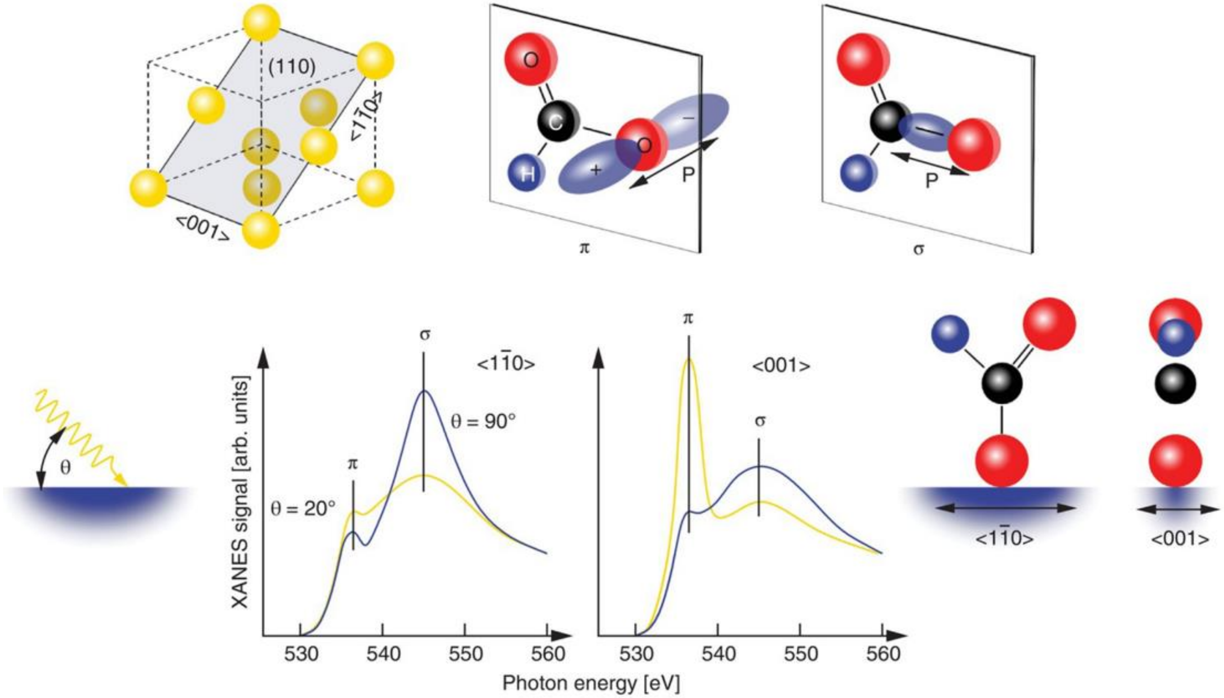
*Sensitive to **local symmetry & hybridization***

Angular and polarization dependence

X-ray linear dichroism (XLD)

***Dichroism**: the difference in spectral shape observed at distinct orientation of photon polarization with respect to crystal/molecule orientation*

Selective probe of ***structural anisotropy***



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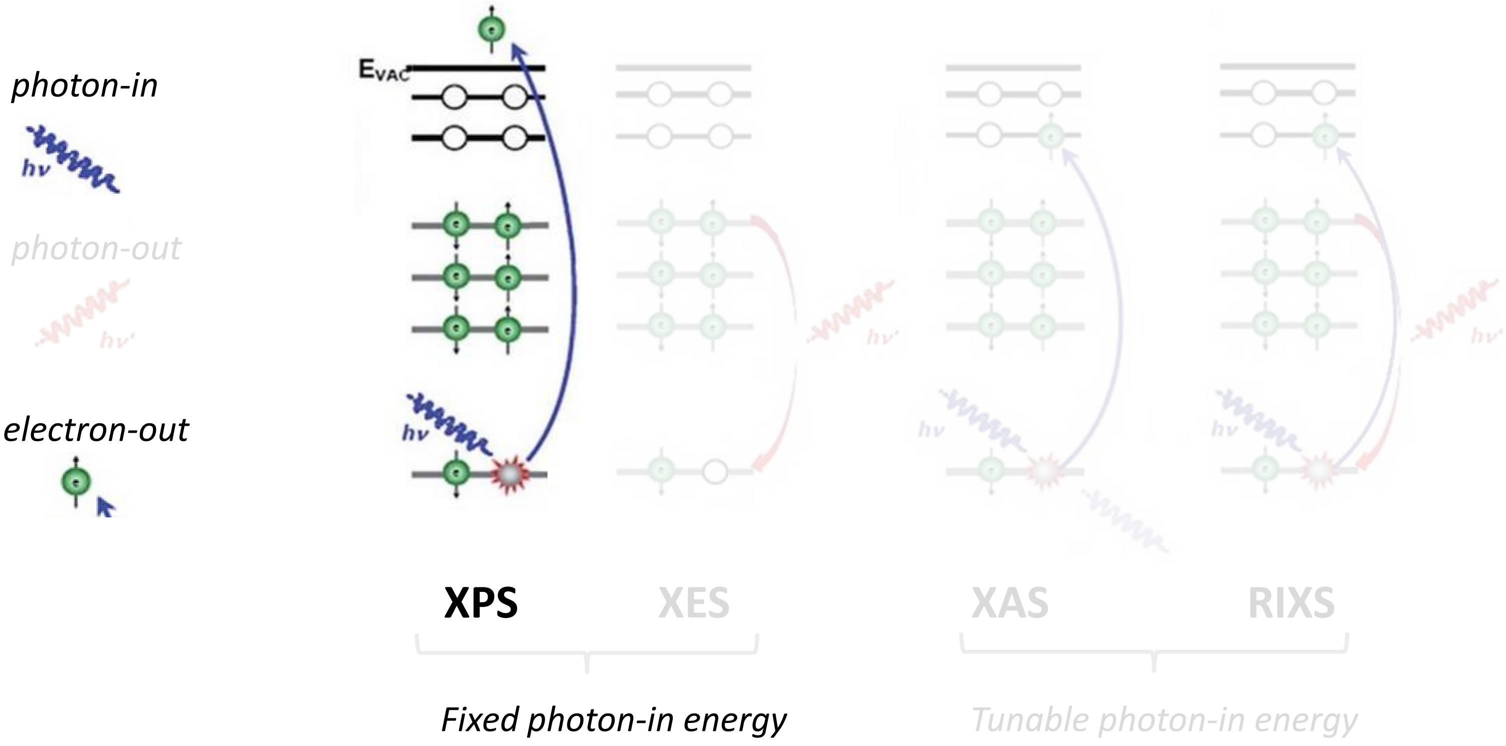
X-ray photoelectron spectroscopy



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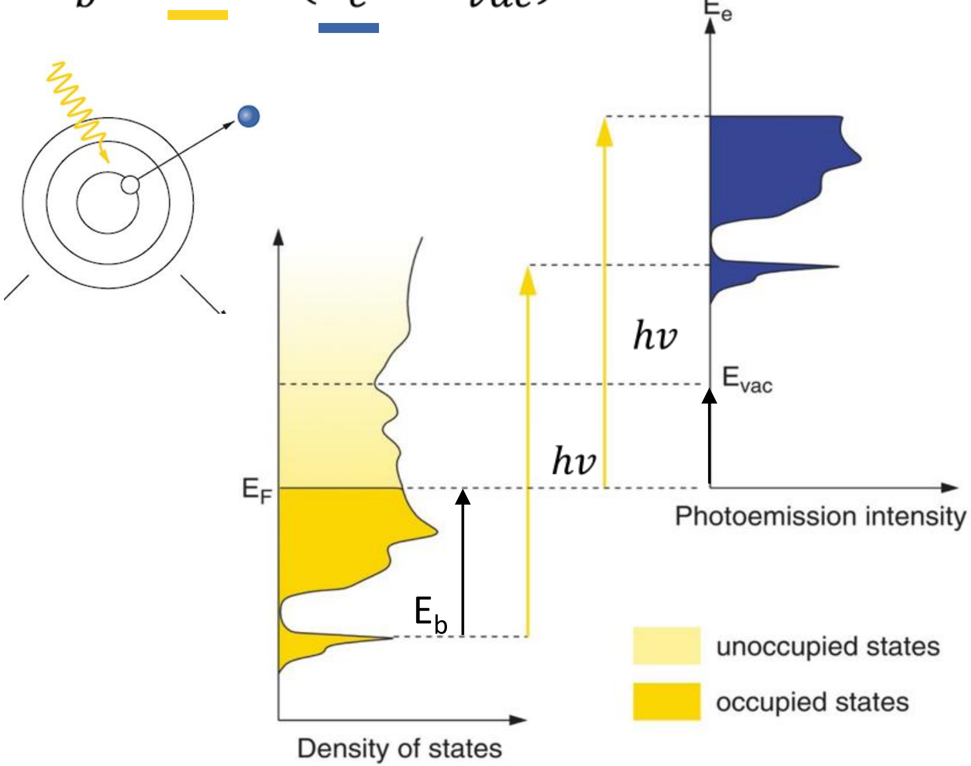
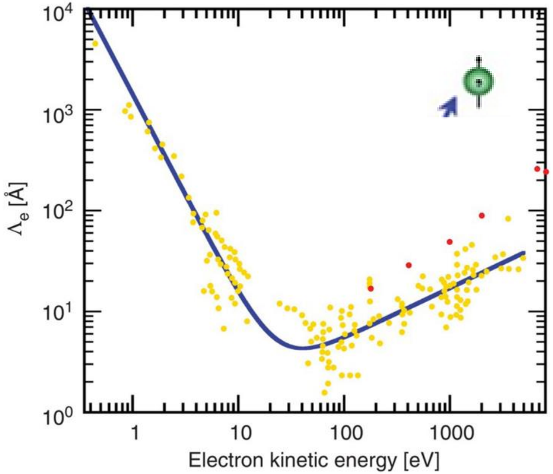
XPS principle

$$E_b = \underline{hv} - (\underline{E_e} - E_{vac})$$

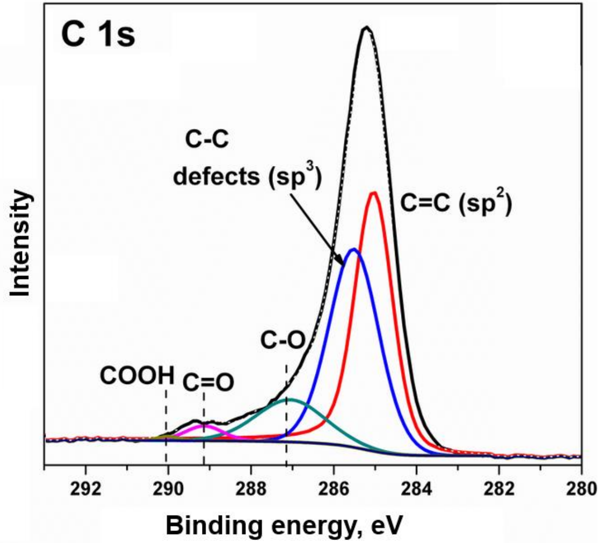




X-ray photoelectron spectroscopy probes the details of (occupied) electronic band structure with ***surface sensitivity*** *and* ***element selectivity***

Probing depth depends on kinetic energy of photoelectron, E_e, that is dependen on incident photon energy, hv

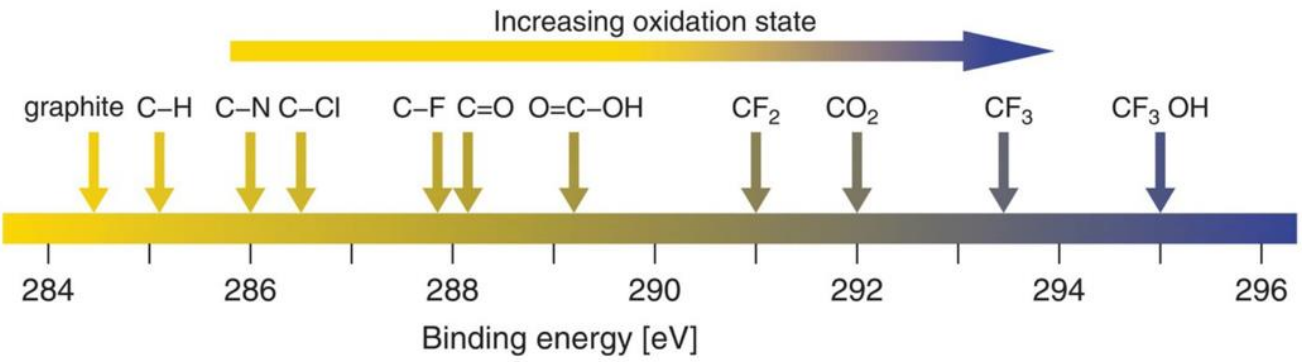
XPS applications



Determination of surface chemical composition, including speciation of organic structures

Chemical shift

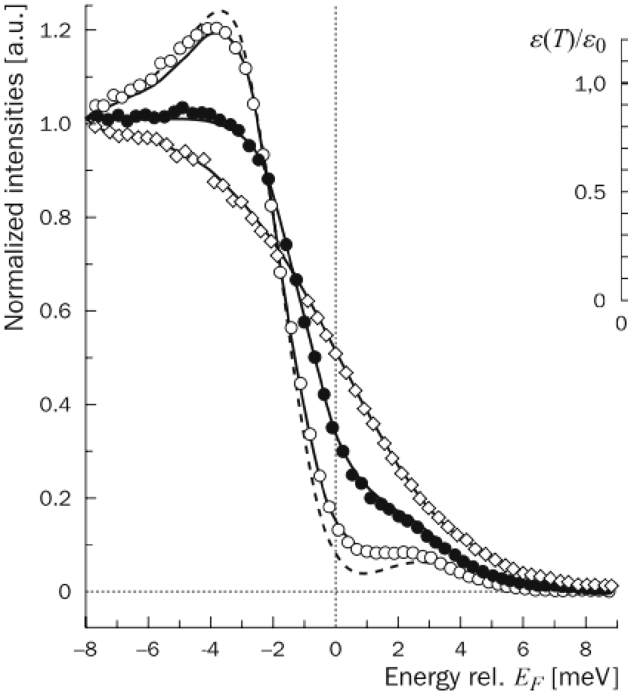
Position of the resonance (binding energy) depends on bond type

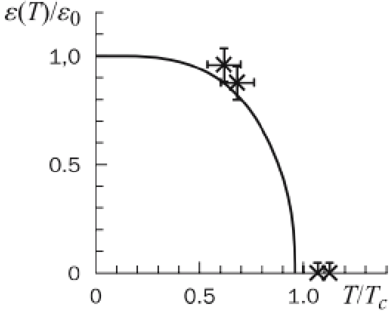


source: [2]

F. Reinert et al., Phys. Rev. Lett. 85, 3930 (2000)

XPS applications



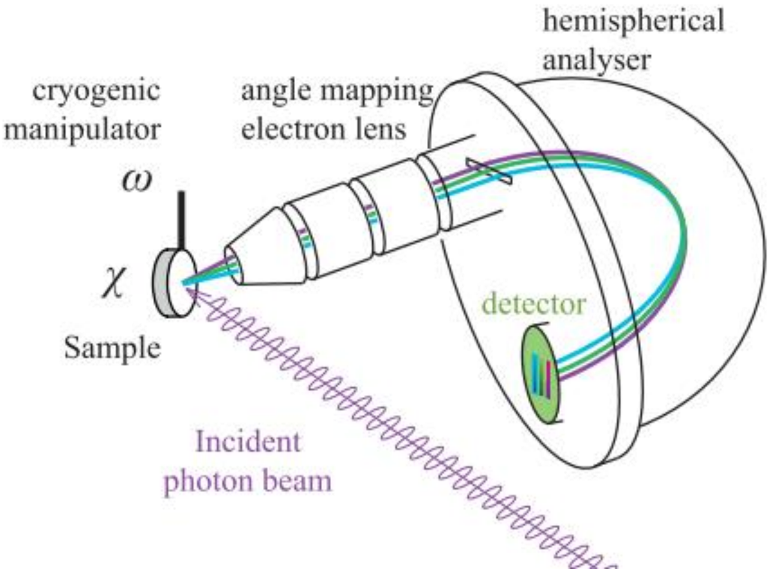


Determination of band gap in semiconductors and superconductors

XPS spectra at temperature above and below the superconducting transition in V_3Si show the shift of valence band maximum with respect to Fermi level

Modern XPS setup

Hemispherical analyzer combined with 2D pixel detector allow for simultaneous probing of energy and angle of emission (angular momentum) of photoelectrons



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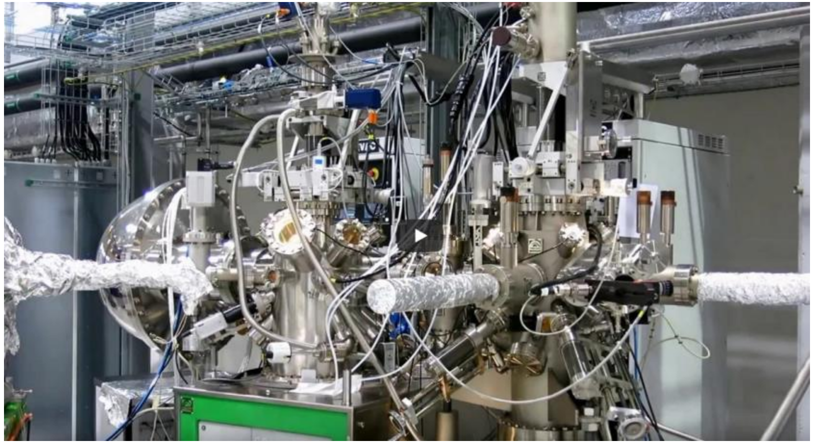
URANOS at SOLARIS



https://www.youtube.com/watch?v=jkbwOVWtHl8

Angle resolved photoemission (ARPES)

source: [2]

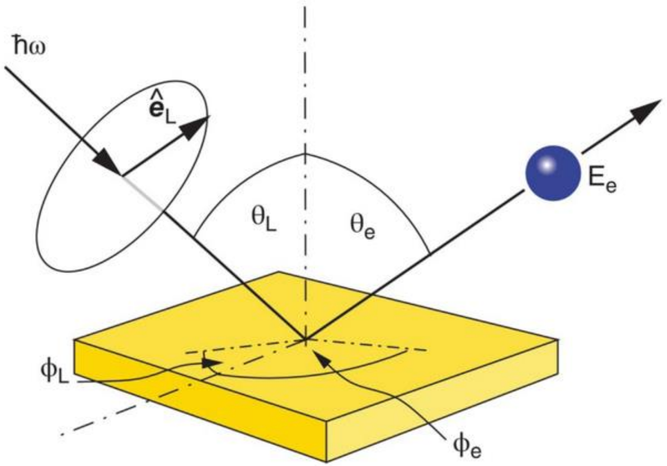
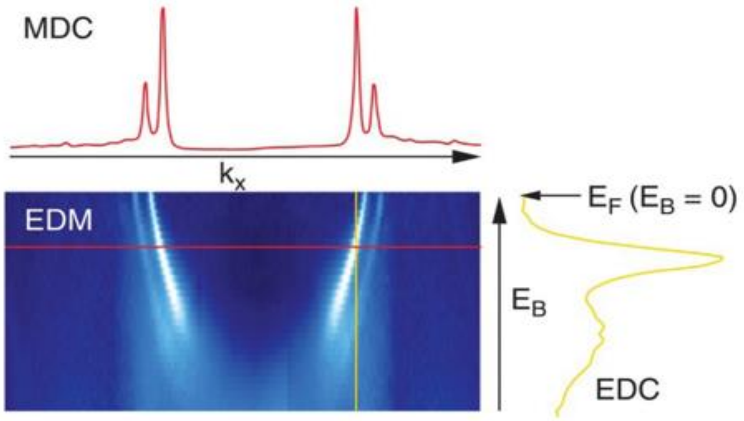


Figure 7.52 Schematic diagram of an angular-resolved photoelectron experiment, including the possible experimental variables. Those relating to the incident beam are suffixed with *L*, while those relating to the electron are suffixed with *e*. The unit vector $\hat{e}_L$ is a polarization vector. The angles are normally referenced to a high-symmetry axis of the crystal.

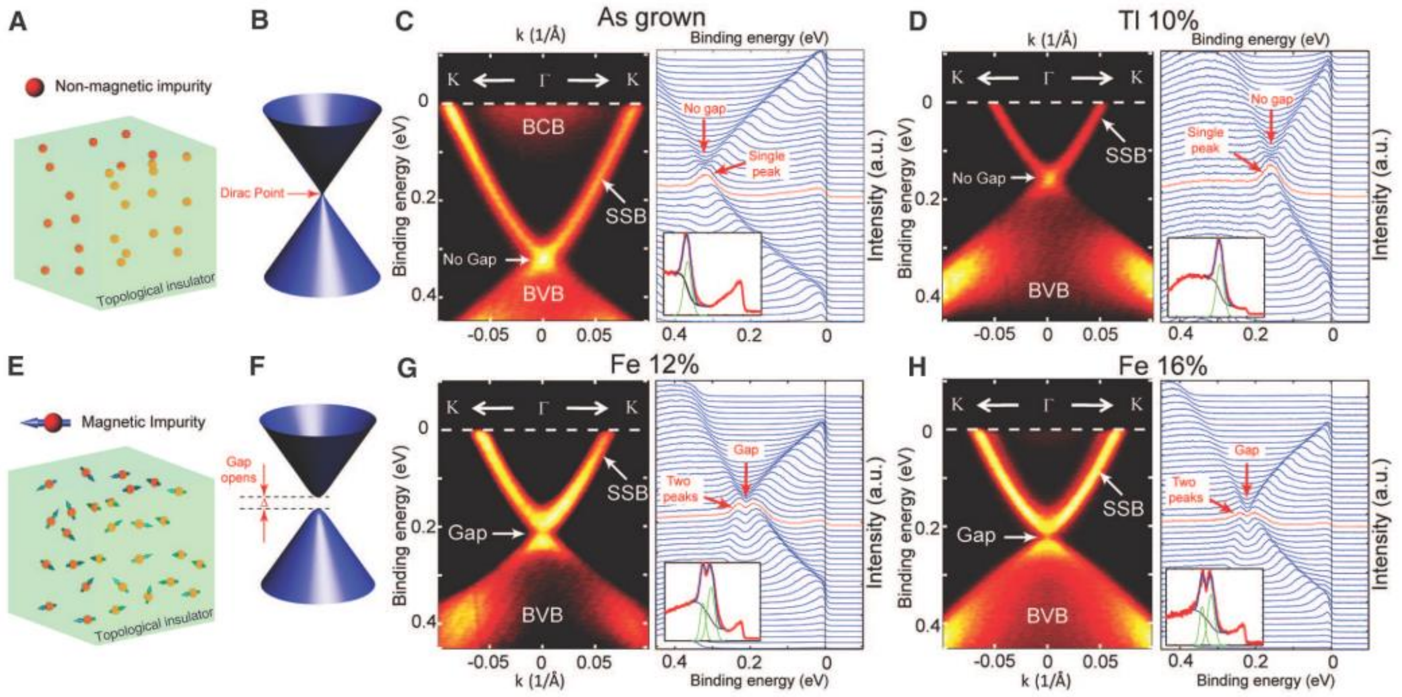


Energy density map (EDM)

Energy distribution curves (EDC)
Momentum distribution curves (MDC)

Dispersion of electronic band structure, i.e. the dependence of electron binding energy on momentum, E(k) can be probed in three directions of the reciprocal space

ARPES example – topological insulators



Y.L. Chen et al., Science 329, 659 (2010)

Nonmagnetic impurities shift Dirac point towards Fermi surface

Magnetic impurities open energy gap, i.e. destroy topologically protected surface states

Outline

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X-ray emission spectroscopy

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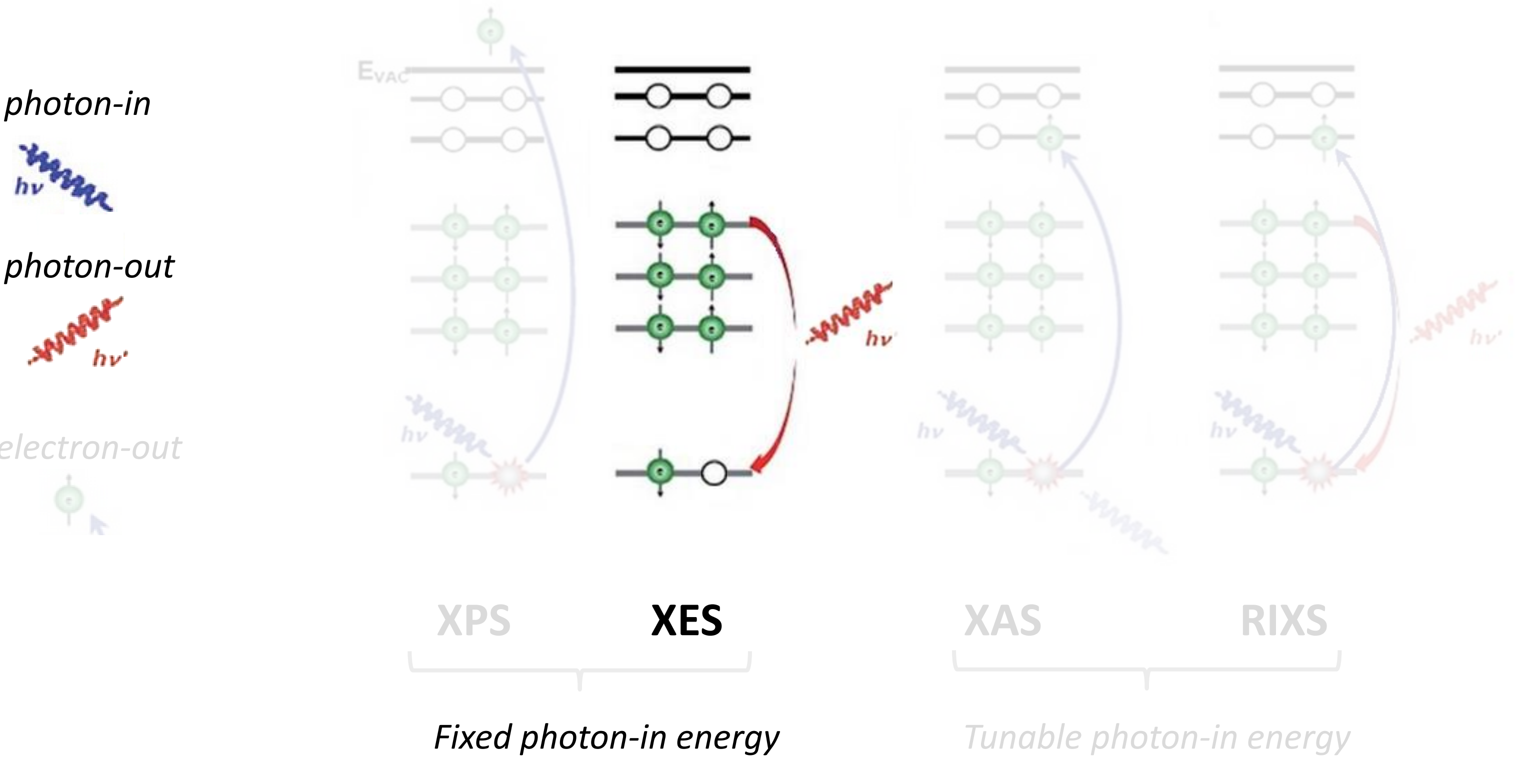
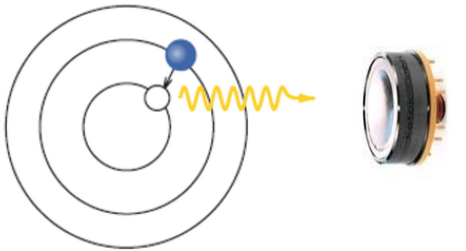
photon-in

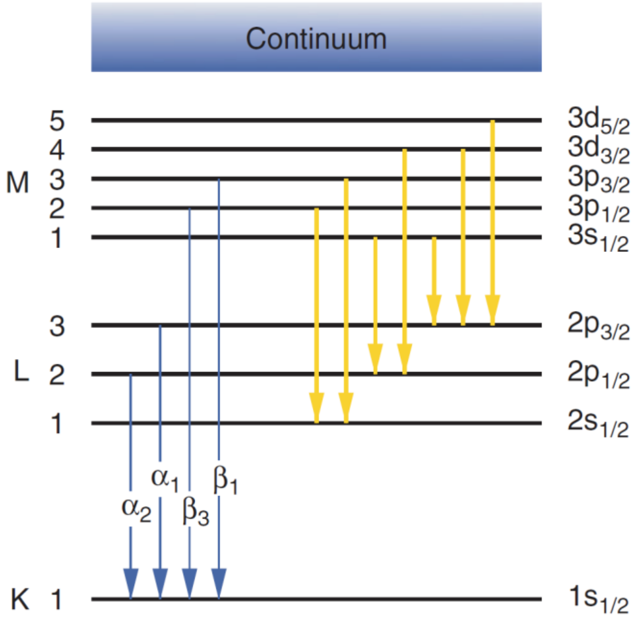
photon-out

electron-out



X-ray fluorescence (XRF)





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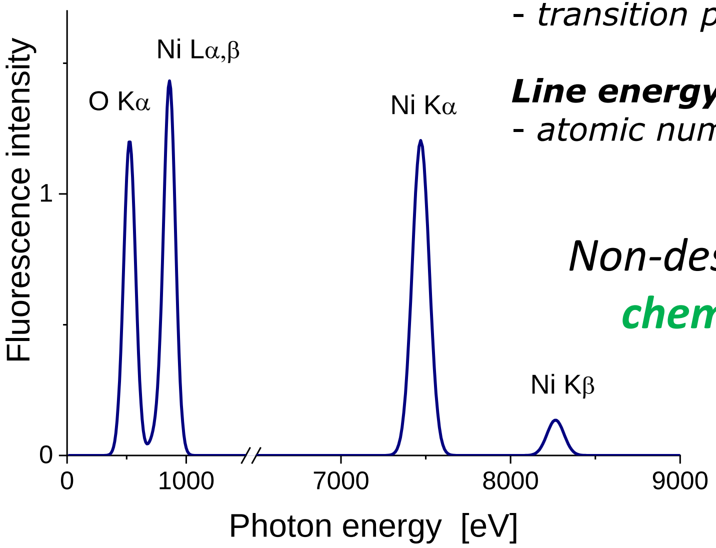


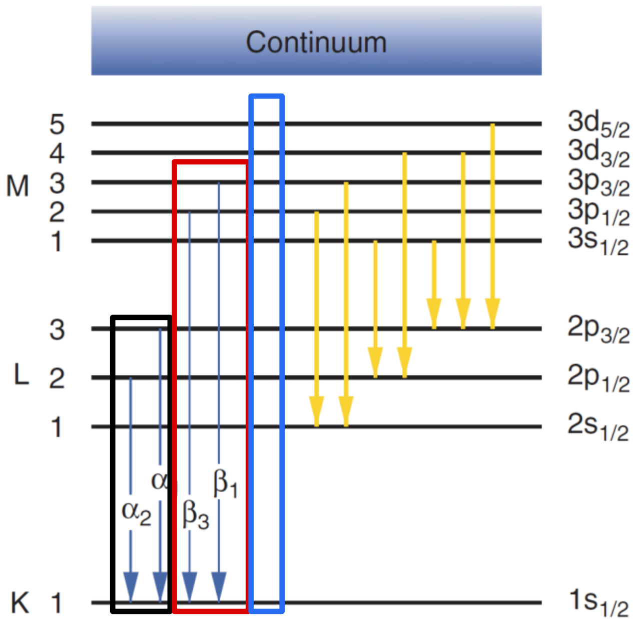
Line intensity *proportional to:*
- *concentration of the element*
- *absorption cross section*
- *transition probability*

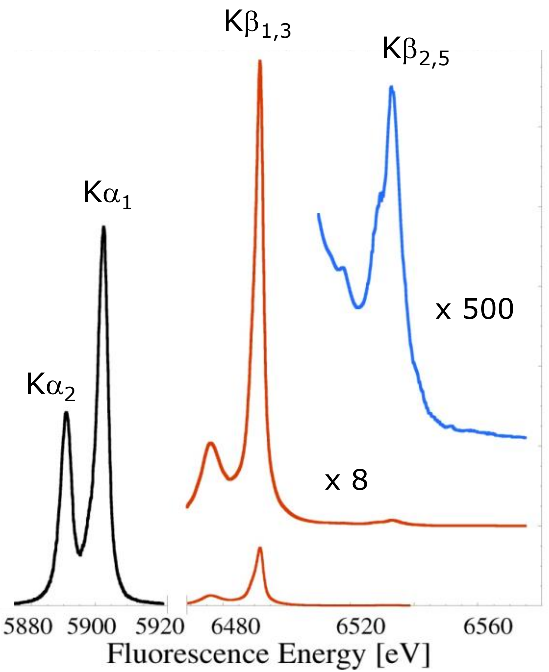
Line energy *characteristic to:*
- *atomic number (Z)*

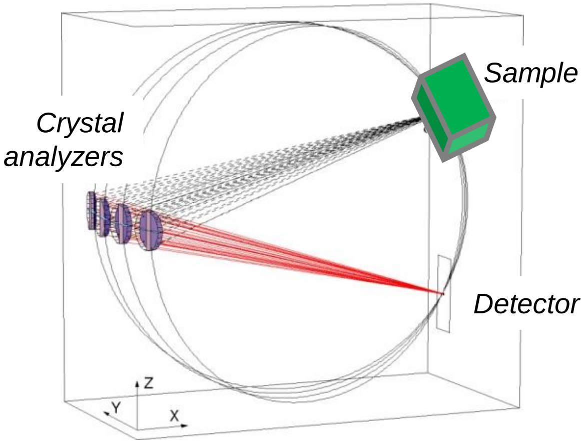
Non-destructive probe of ***chemical composition***

X-ray emission spectroscopy

High Energy Resolution X-ray Fluorescence detection







Energy resolution

XRF (silicon detector): ~120eV

XES (crystal analyzer): ~1eV

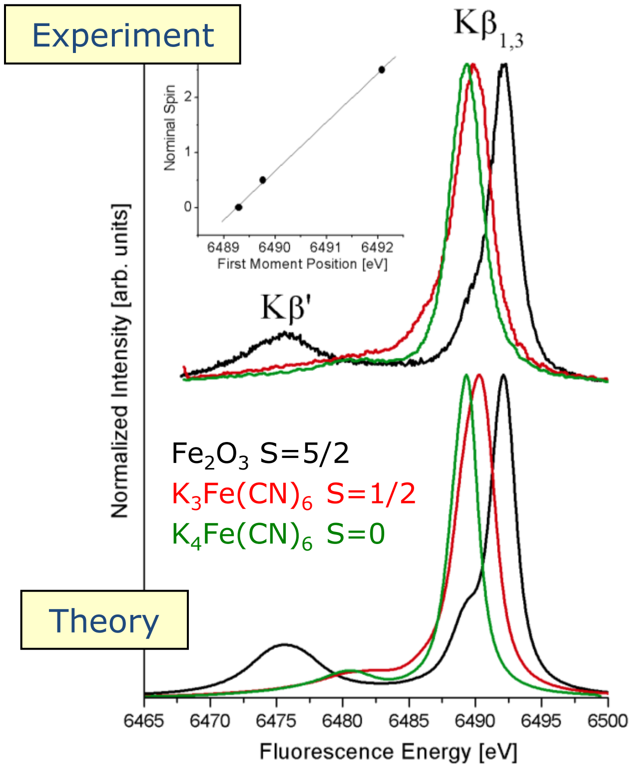
background free

Non-destructive probe of ***chemical composition, effective spin****, and* ***valence band structure***

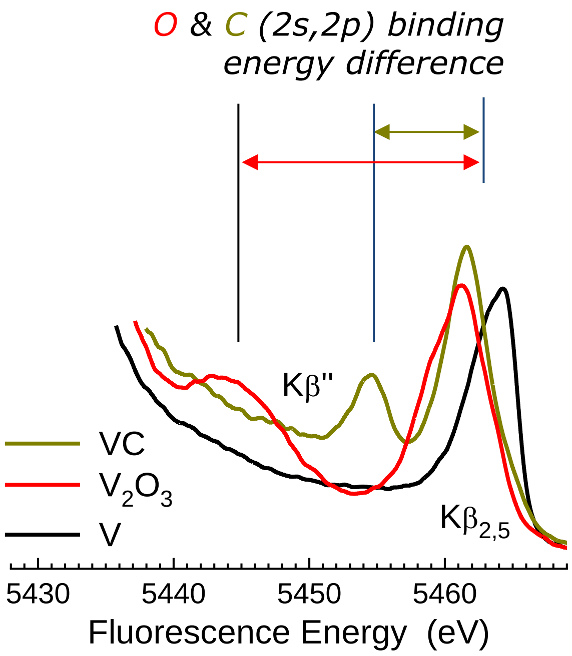
Kβ emission spectroscopy

P.Glatzel & U.Bergmann, Coord. Chem. Rev. 249, 65 (2005)

Element selective probe of spin state and ligand structure



X-ray emission spectra probed with 1 eV resolution show a splitting of Kβ resonance (left) and allow to probe valence band structure (right). The former is sensitive to spin state of the probed element in the sample, while the latter to the next neighbour type and distance



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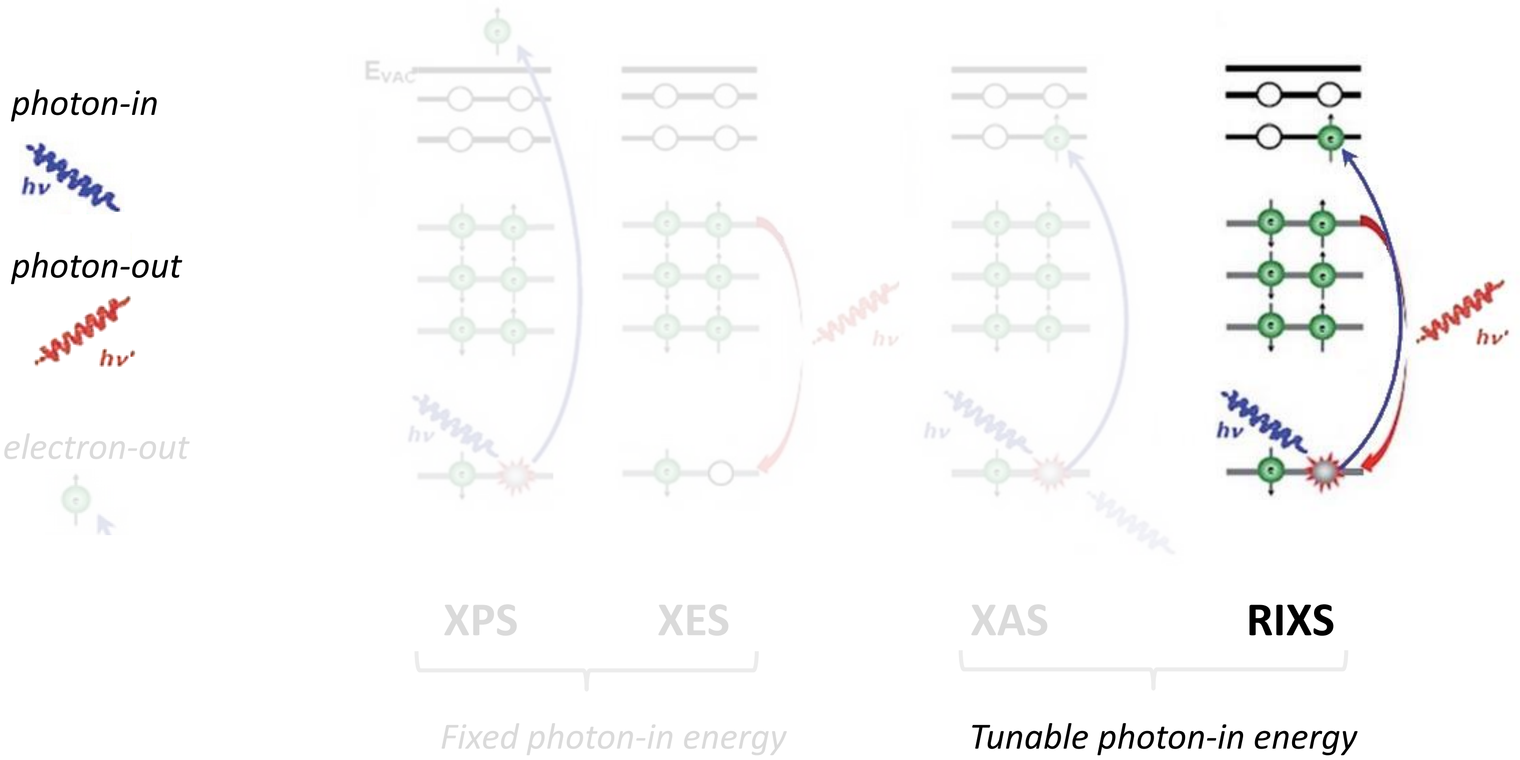
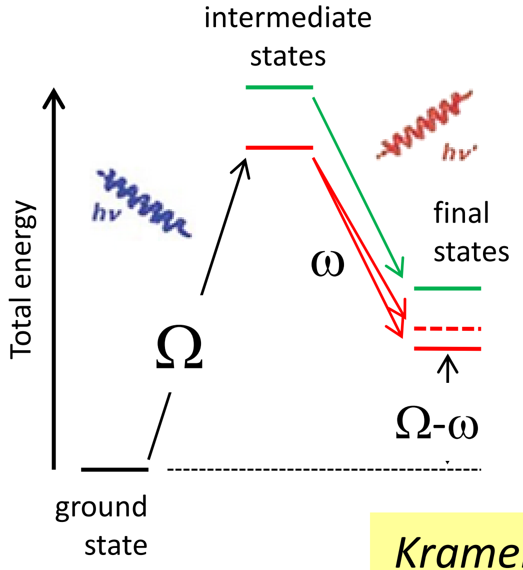
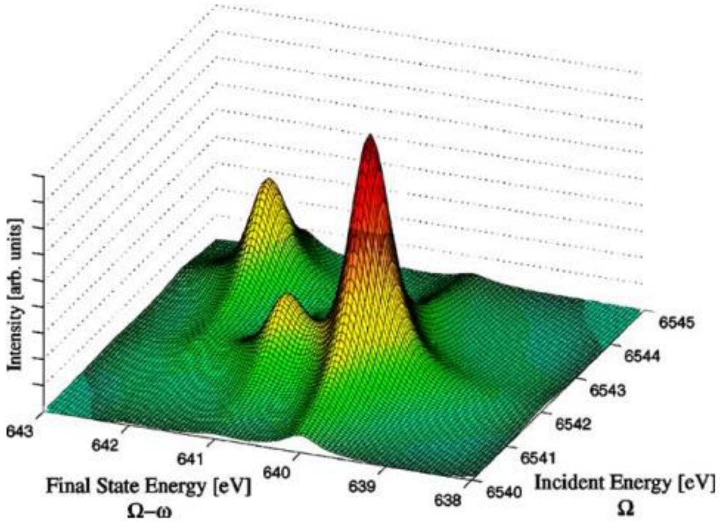
Resonant inelastic X-ray scattering



RIXS plane

P.Glatzel & U.Bergmann, Coord. Chem. Rev. 249, 65 (2005)





RIXS probes how X-ray emission intensity dependes on incident X-ray energy. A typical 2D spectrum is pletted as a function of Energy transfer (or final state energy), which is the difference between Energy of incident and emitted photon

RIXS is especially usefull to probe resonant excitations in strongly correlated materials

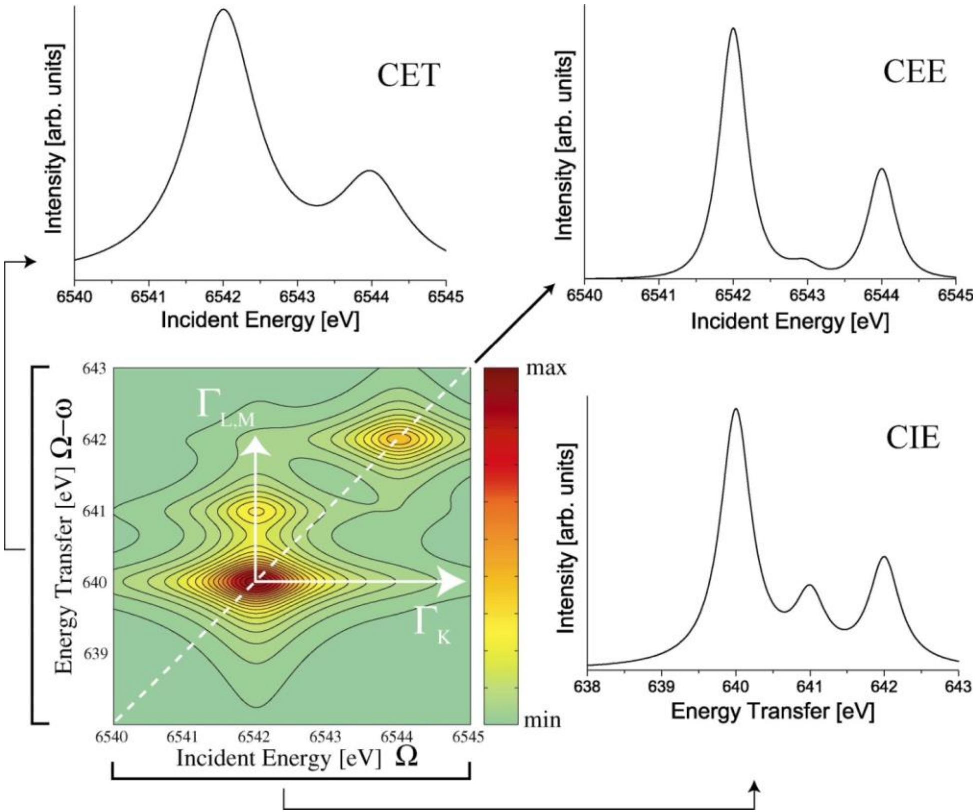
Kramers – Heisenberg formula

$$F(\Omega,\omega)=\sum_{\mathrm{f}}\left|\sum_n \frac{\langle f|T_2|n\rangle\langle n|T_1|g\rangle}{E_g-E_n+\Omega-i\,\Gamma_K/2}\right|^2\times\frac{\Gamma_{\mathrm{f}}/2\pi}{(E_g-E_f+\Omega-\omega)^2+\Gamma_{\mathrm{f}}^2/4}$$

P.Glatzel & U.Bergmann, Coord. Chem. Rev. 249, 65 (2005)

RIXS plane

Fluorescence detected absorption, i.e. constant energy transfer (CET)



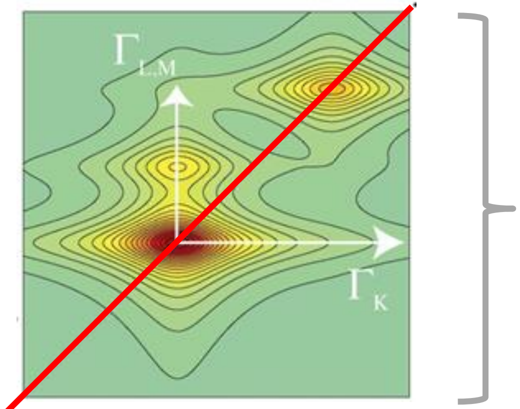
High energy resolution fluorescence detected X-ray absorption (HERFD-XAS), i.e. constant emission energy (CEE)

Final states of emission or resonant scattering (X-ray Raman), i.e. constant incydent energy (CIE)

Three distinct types of line-scans (spectra) may be extracted from 2D RIXS plane

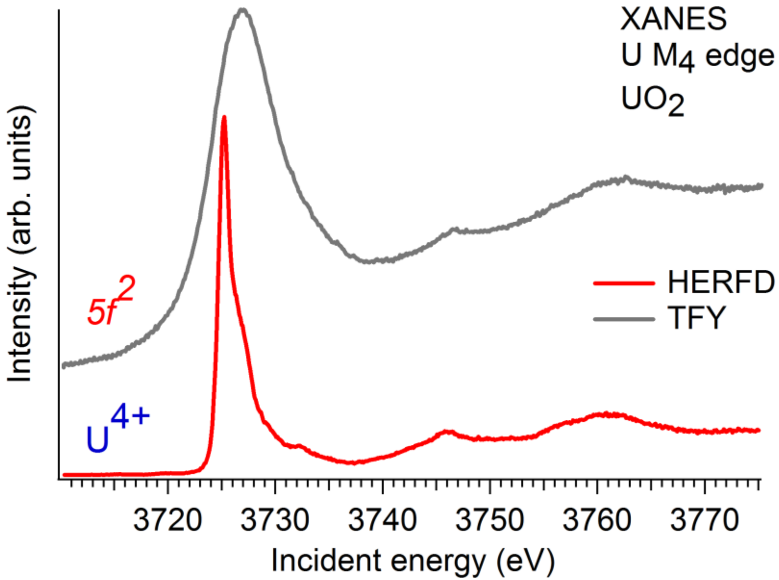
K. Kvashnina et al., Phys. Rev. Lett. 111, 253002 (2013)

HERFD-XAS



HERFD at the *U* M_4 edge

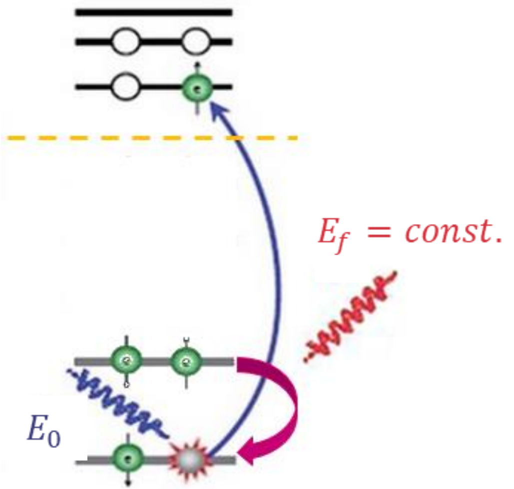
Dipole: 3d → 5f

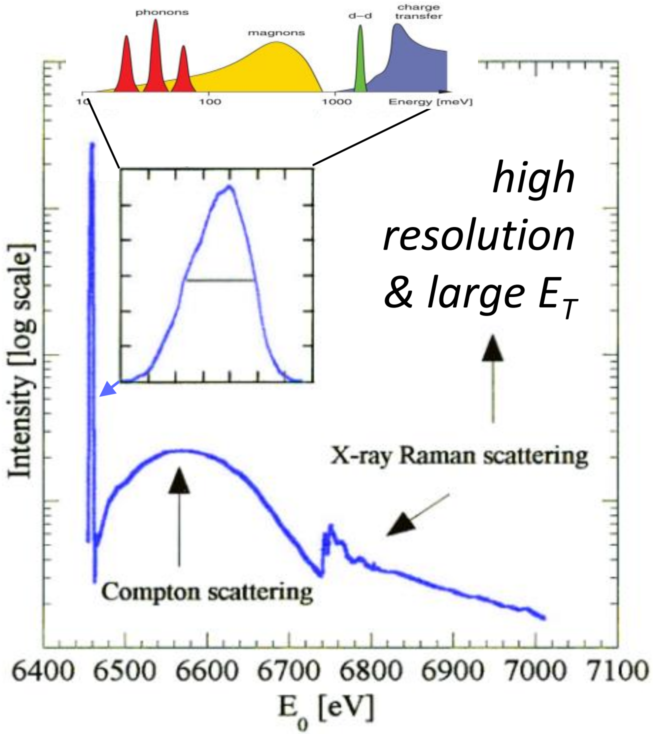


Background free detection
and sharpening of absorption spectra (beyond that of life-time broadening)

X-ray Raman scattering (XRS)

$$E_T = E_0 - E_f$$





***high energy** transfer features provide access to binding energies in the range of soft X-rays, but probed with (two) hard X-ray photons*

→ XAS-like bulk sensitive probe of soft matter

Application of XRS

Z. Sun et al., Phys. Rev. Lett. 121, 137401 (2018)

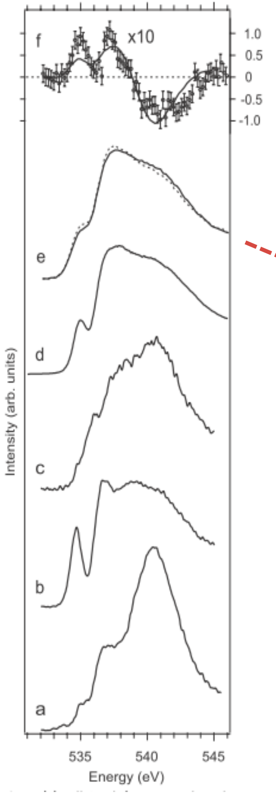
Liquid bulk 25°C & 90°C

Liquid bulk at ambient

Ice I_h NH_3^- term. surface

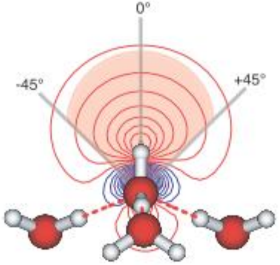
Ice I_h surface

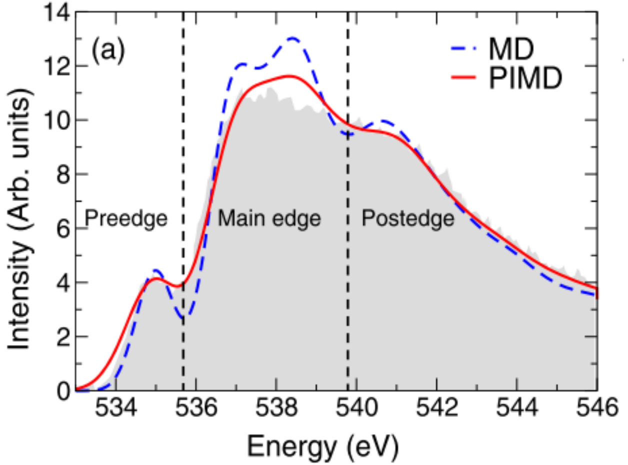
Ice I_h bulk



Ph. Wernet et al., Science 304, 995 (2004)

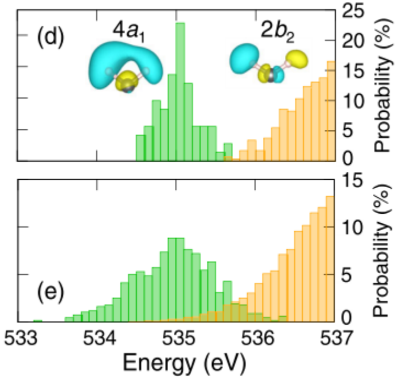
Local coordination of oxygen in water





Classical MD

Including proton delocalization (variation of covalent bond length)



Summary

SOLARIS
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RADIATION CENTRE

What kind of questions can be answered using X-ray spectroscopy:

- What is the chemical composition of the sample?
- What is the local atomic structure of the absorbing element (symmetry, type and distance of next neighbor, distortions)?
- What is the spin and valence state of the probed element?
- What is the valence band structure (dispersion, DOS, bandgap)?

Depending on the type of particles detected (electrons or photons) it provides surface or bulk sensitive information