HESEB Helmholtz-SESAME
Soft X-Ray Beamline
für SESAME

SESAME

DESY. JÜLICH FORSCHUNGSZENTRUM HZB Helmholtz Zentrum Berlin HZDR KIT

Soft X-Ray Spectroscopy at HESEB

Wolfgang Eberhardt
DESY

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

SESAME

X-Ray spectroscopy at HESEB

Introduction---synchrotron radiation properties

Photon-matter interactions

Absorption (yield) spectroscopy

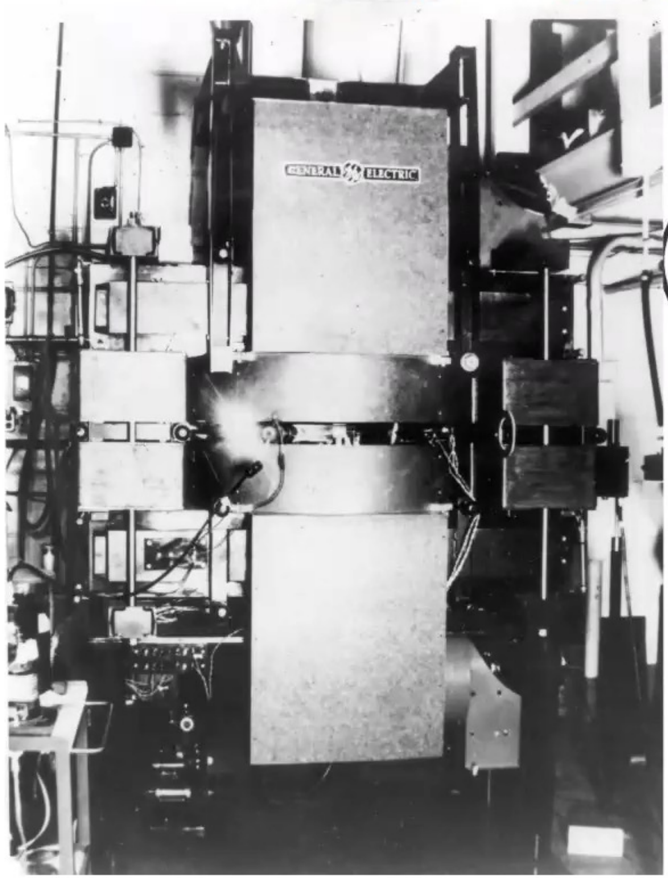
X-ray-Magnetic-Circular-Dichroism   XMCD

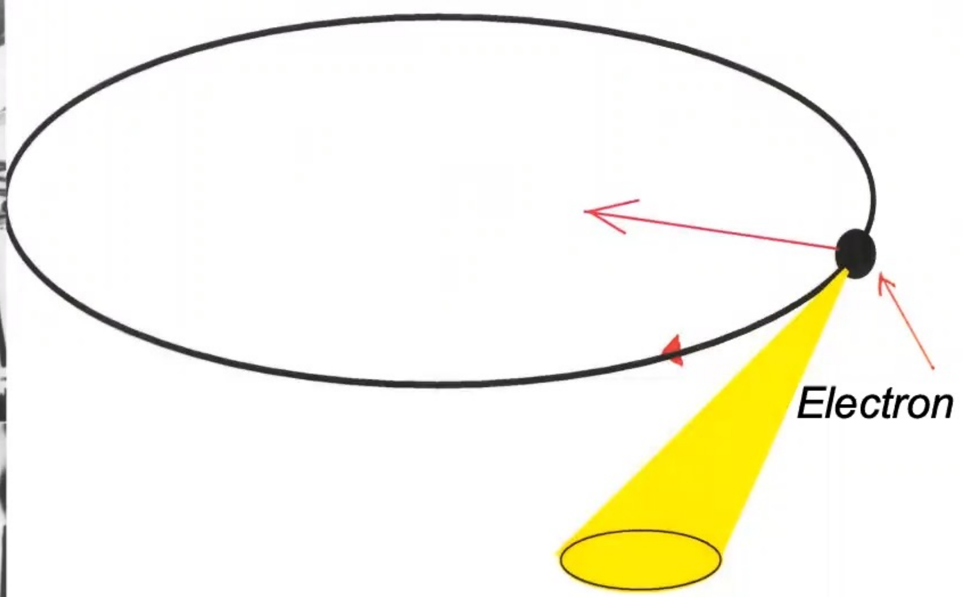
Photoemission and RIXS (short)

Coherent scattering

SYNCHROTRON-RADIATION

Electrons moving at nearly the speed of light on a circular path



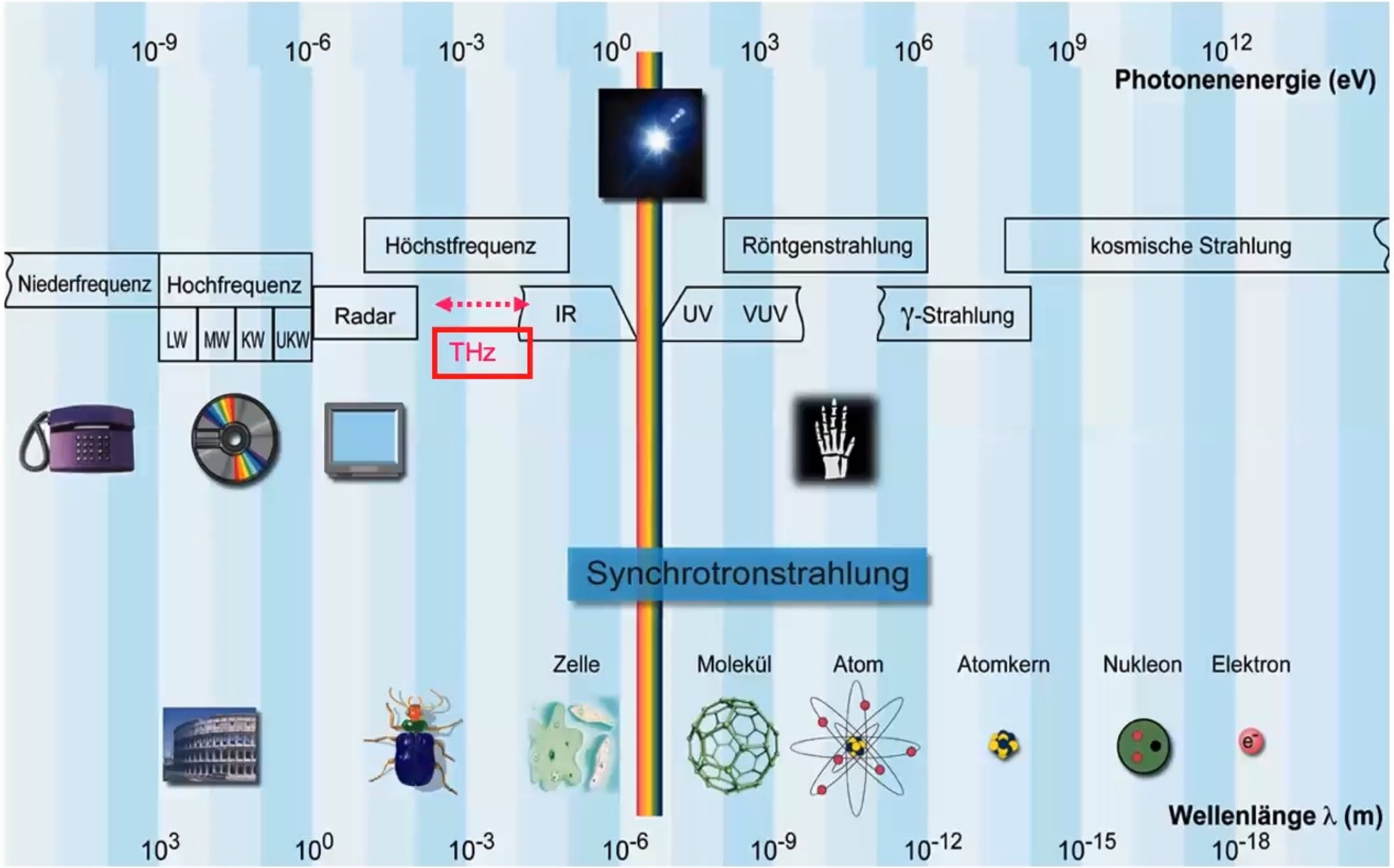


…. radiate a special light

Synchrotron-Radiation

in

Spectral Range of Synchrotron-Radiation



Hand illuminated by X-Rays

Josef Albert impr. Ohne Retusche.

Hand des Anatomen Geheimrath von Kölliker in Würzburg.
Im Physikalischen Institut der Universität Würzburg
am 23. Januar 1896 mit X-Strahlen aufgenommen
von
Professor Dr. W. C. Röntgen.

Verlag der Stahel'schen k. Hof- und Universitäts-Buch- und Kunsthandlung in Würzburg.

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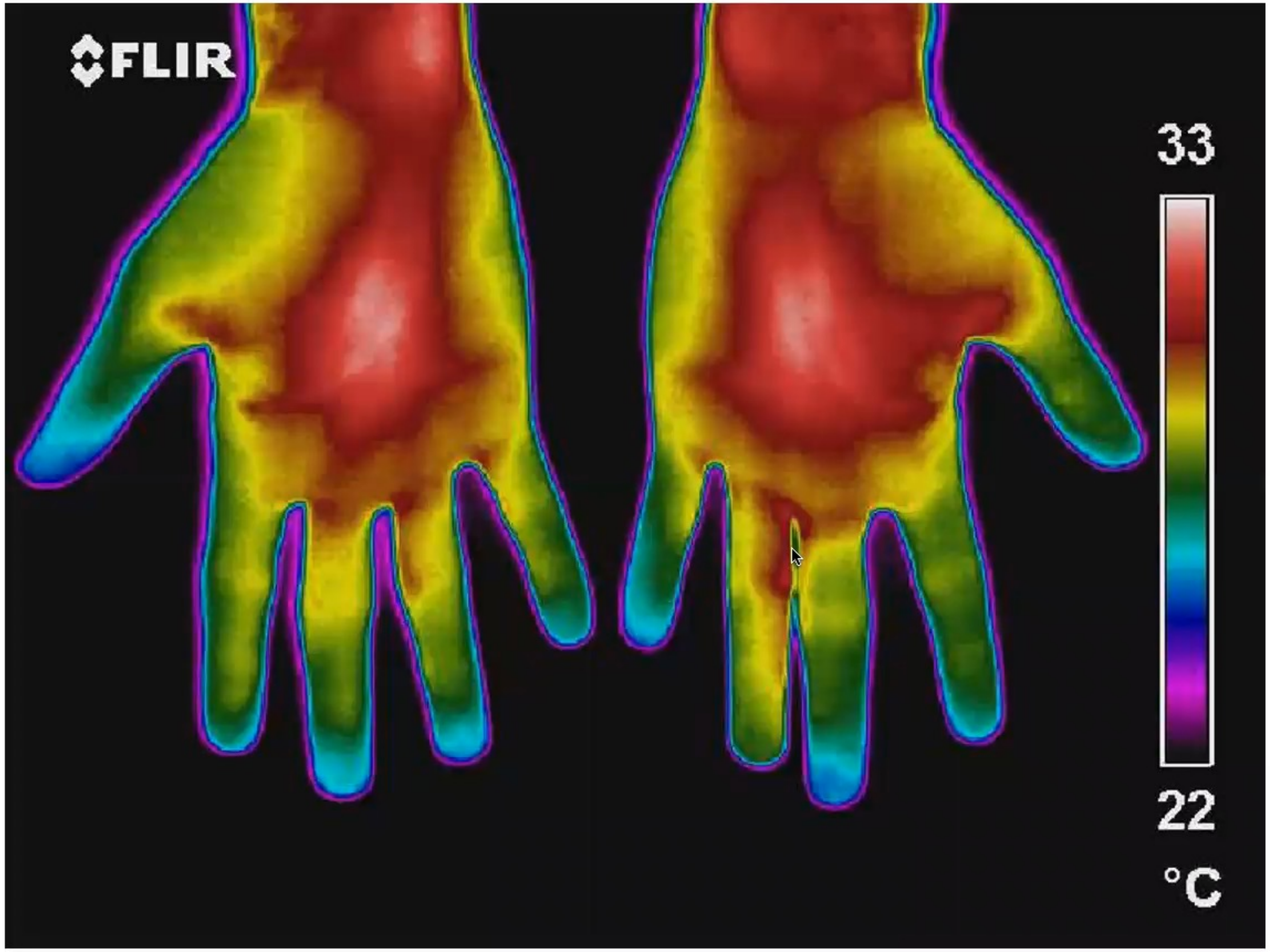
Hand----IR emission Spectrum



Synchrotron Radiation: Brightness -- the quality factor

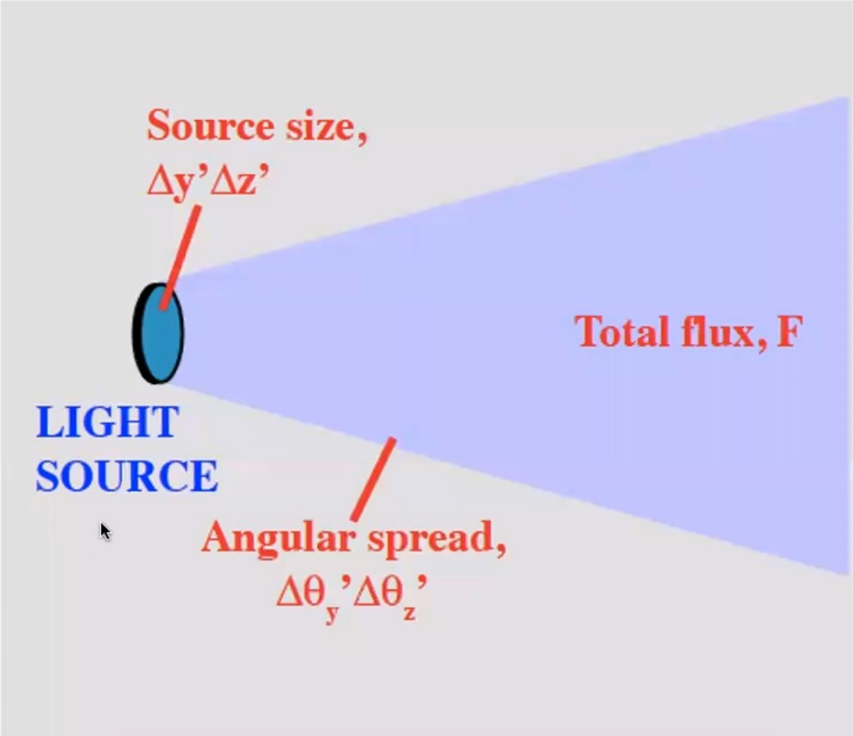


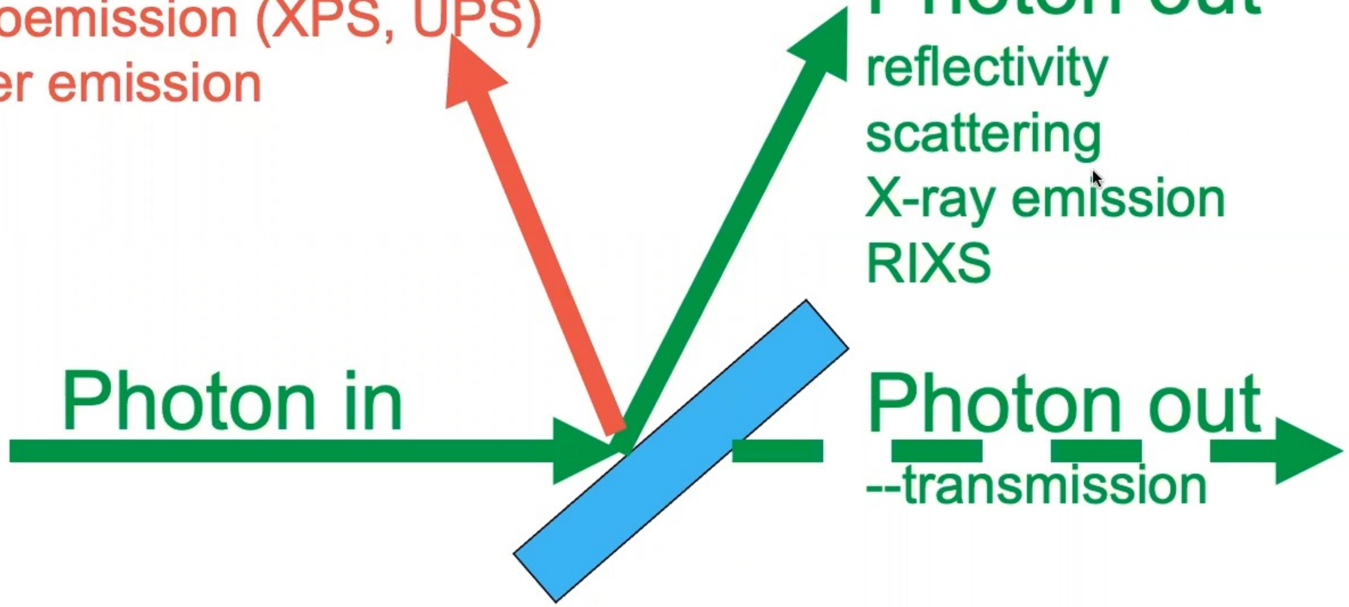
Fig. 8 - The source parameters which determine the brightness or brilliance.

Brightness

B = photons per
    source size
    angular spread
    energy interval
    time

The Brightness is conserved
(Liouville Theorem)

Interactions of photons with matter



Electron out

electron yield

photoemission (XPS, UPS)

Auger emission

Photon out

reflectivity

scattering

X-ray emission

RIXS

Photon in

Photon out

--transmission

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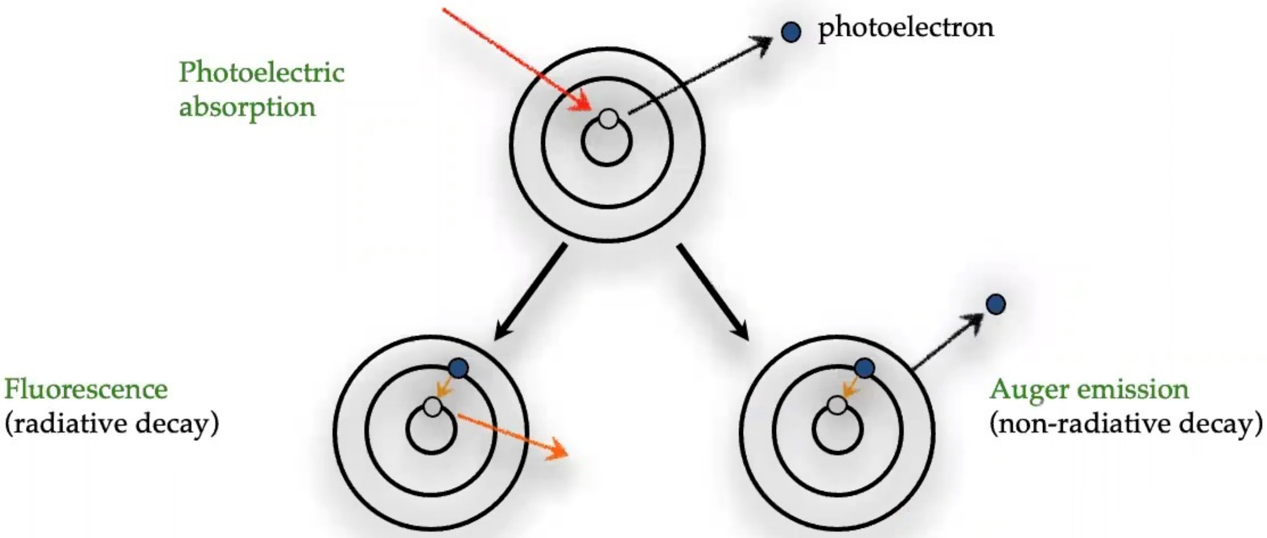
Secondary Processes following the X-ray Absorption Process

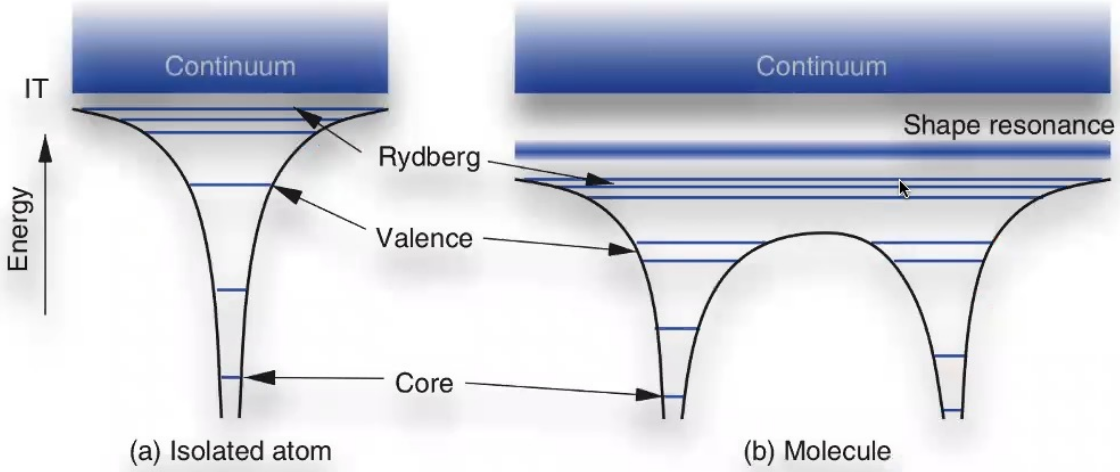
- X-rays are absorbed by matter through the photoelectric effect
- The incident X-ray photon promotes a core level electron to an unoccupied valence state level above the **ionization threshold**
- The electron ejected from the atom is called **photoelectron**
- The atom is left in an excited state with a core hole
- Two decay channels: **X-ray fluorescence** and **Auger emission**



Energy Level Schemes of atoms, molecules and solids

Atoms and Molecules

Chemical bonds primarily involve **valence electrons**:
charge redistribution, formation of bonding/antibonding states (molecular orbitals)



From: P. Willmott, *An Introduction to Synchrotron Radiation*, *Wiley* (2011)

Core levels: weakly affected by chemical bonds through so-called **chemical shifts**

- small BE changes due to differences in the distribution of valence electrons caused by chemical bonding

Shape resonances: quasi-bound electron states physically close to the molecule in the ionization continuum

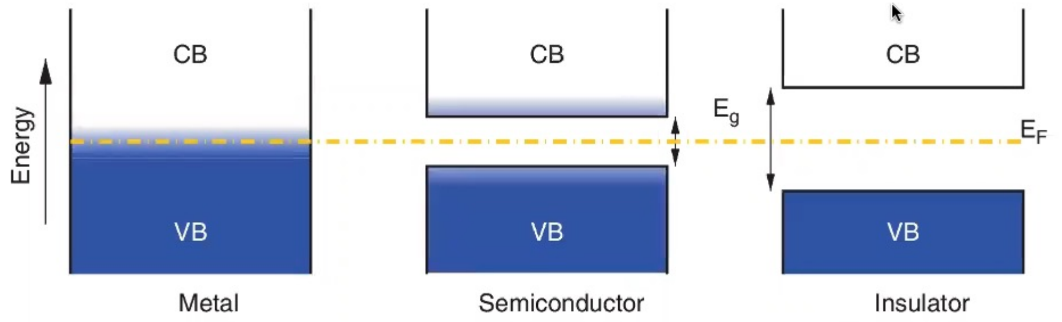
- they still 'feel' the influence of the electrostatic field of the molecule

Energy Level Schemes of solids

Solids

When a large number of atoms (N) is brought together into a solid, the number of orbitals that are formed is $2N$ and the energy differences among successive electron states become exceedingly small → **quasi-continuous bands of electron states**

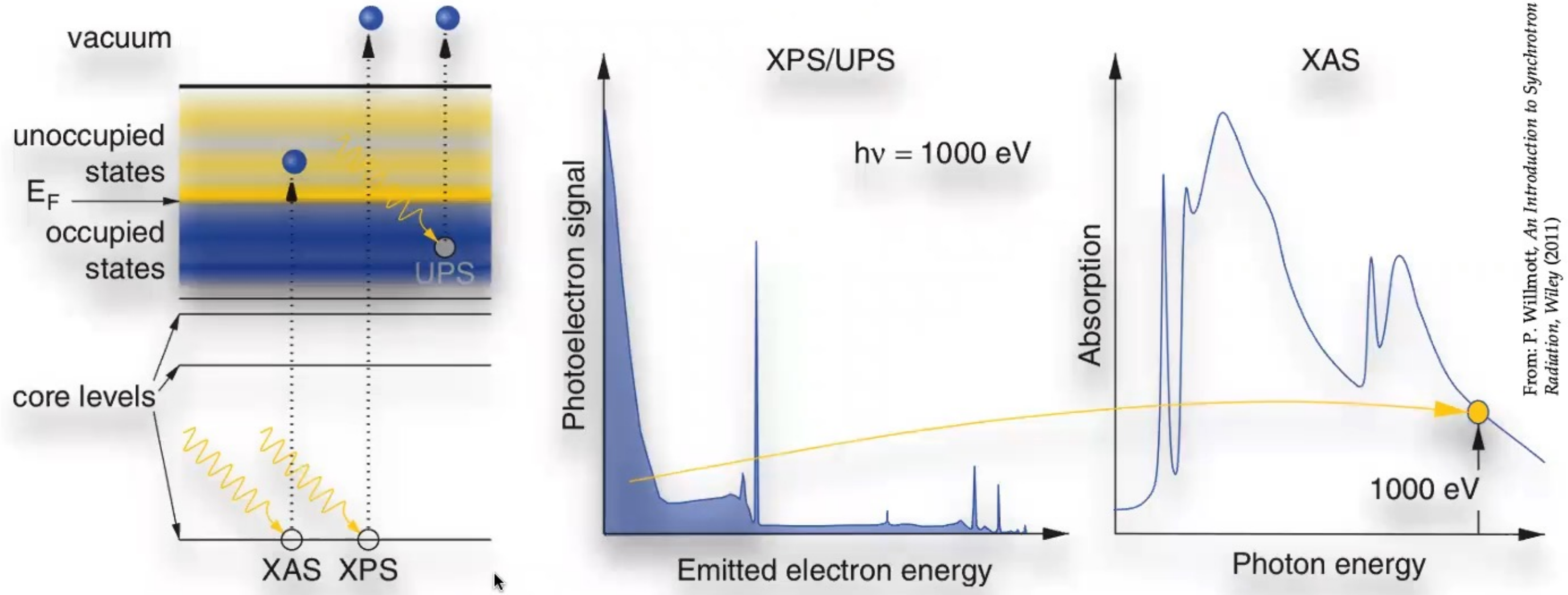
Simplified diagram of the electronic band structure of different solids:



From: P. Willmott, *An Introduction to Synchrotron Radiation*, *Wiley* (2011)

Metals:	highest occupied band is partly empty and partly filled regardless of temperature → gas of delocalized and nearly free valence electrons
Semiconductors:	narrow energy gap (<3 eV), a small fraction of valence electrons can be thermally promoted into the conduction band
Insulators:	wide gap, melting (or decomposition) takes place before a detectable fraction of valence electrons is promoted into the conduction band

X-ray absorption and photoemission



From: P. Willmott, *An Introduction to Synchrotron Radiation*, *Wiley* (2011)

- promotes core-level electrons to unoccupied valence-state levels and thereby probes these upper states by varying the incident photon energy

→ requirement: energy tunability + monochromatic radiation

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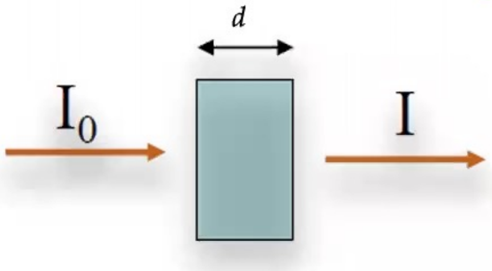
Description of the X-ray Absorption Process

- Absorbing power of a material expressed through the **linear absorption coefficient μ**, which depends on the photon energy $E = \hbar\omega$

Beer-Lambert equation



$$\boxed{I(z) = I_0 e^{-\mu d}}$$

μ - attenuation/absorption coefficient

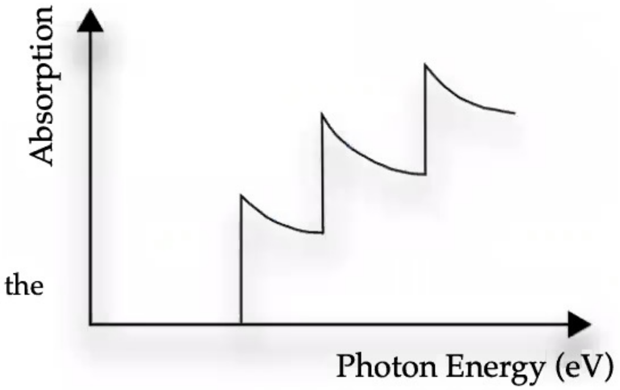
μ describes the probability that an X-ray beam travelling a distance *d* in a medium is absorbed

$\mu(E)$: element-specific and strongly dependent on the atomic number Z

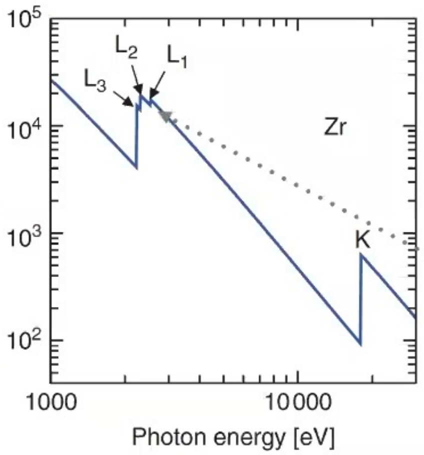
$$\boxed{\mu(E) \propto Z^4/E^3}$$

discontinuous jumps of $\mu(E)$ → absorption edges

→ photon energy equals the minimum energy needed to ionize the atom by ejection of an electron from a given energy level



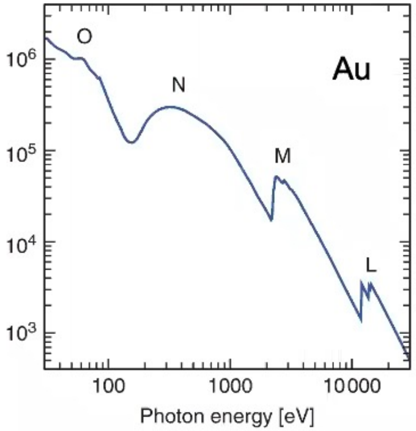
Absorption features and spectral regions



μ varies appr. as the inverse third power of the photon energy

interrupted by steplike increases in absorption as the photon energy matches the ionization potential of an occupied electron state in a atom

L-edge has three components, corresponding to ionization from the $2s$, $2p_{1/2}$ and $2p_{3/2}$ levels



From: P. Willmott, *An Introduction to Synchrotron Radiation*, Wiley (2011)

The shape of the absorption edges depends on the initial state excited in the transition

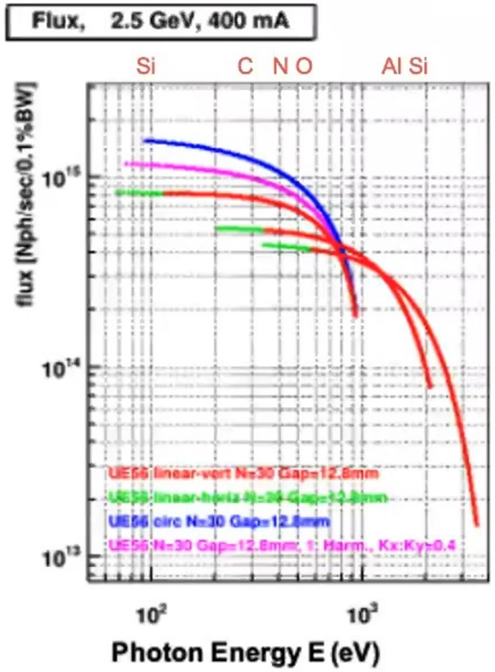
→ states with $l = 0$ or $l = 1$: sharp rising edges
→ states with larger l values: broader appearance "delayed onset" (by some tens of eV)

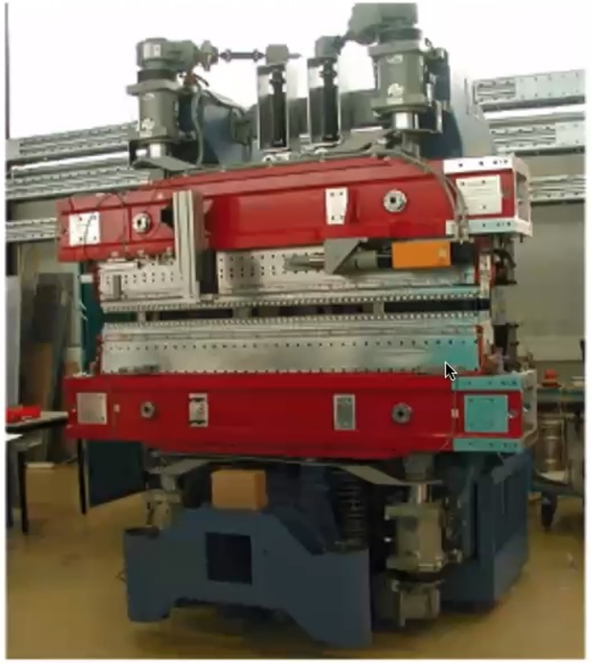
(l - angular-momentum quantum number)

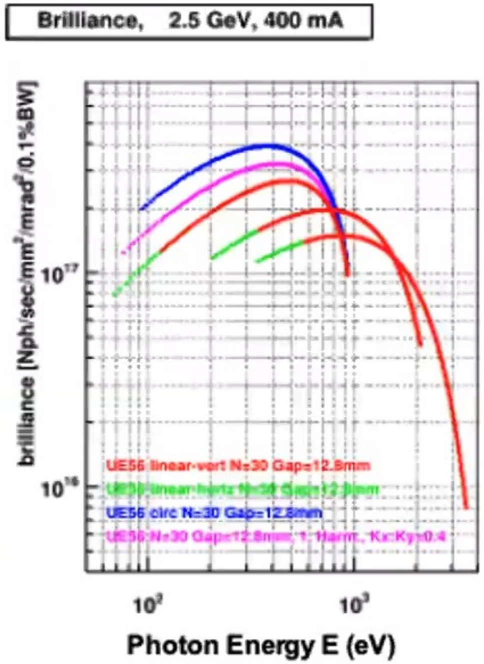
Quantum states with high principal quantum number tend to remain away from the nucleus - classically, one would expect them to have a large circular orbit

HESEB Beamline

Undulator UE56 (APPLE II) with variable polarization



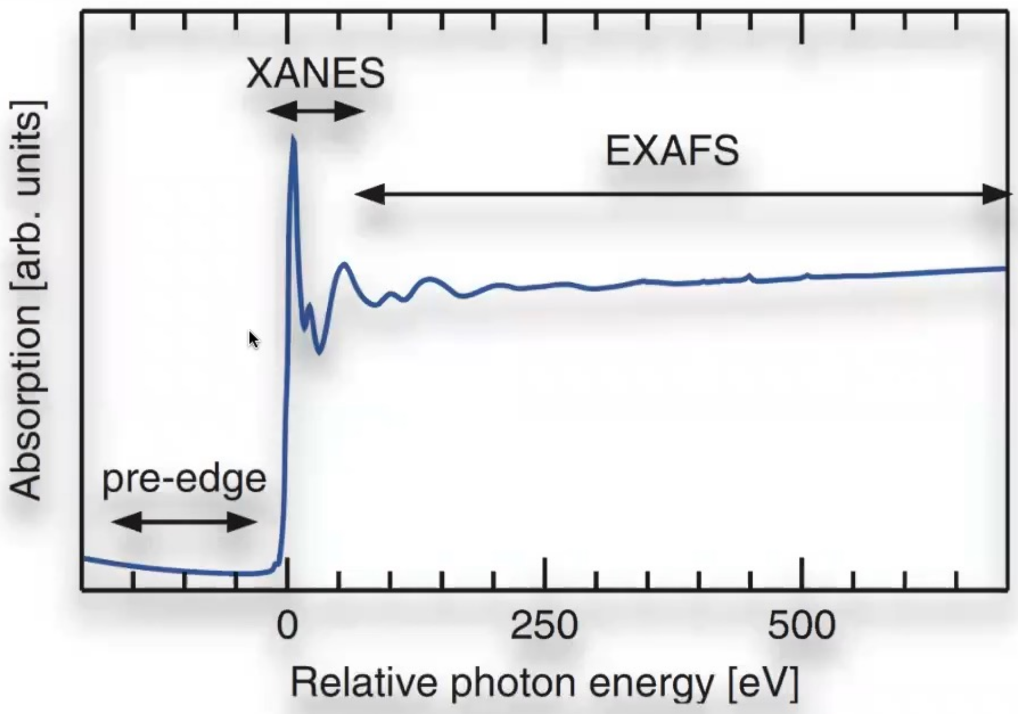




Covers the core edges:

- Si L-edge—semiconductors
- C-, N-, O- Kedge - Organics catalysis
- TM-L-edges magnetics
- RE 3d edges magnetics
- Al- K-edge, Si-K-edge

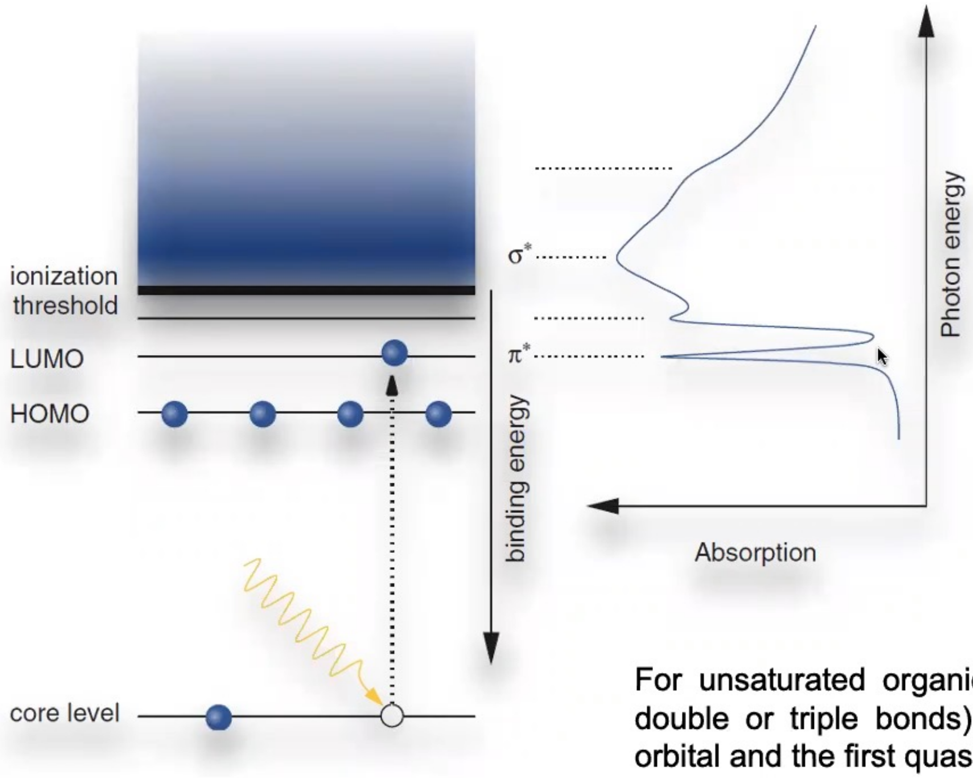
Absorption features and spectral regions



1. XANES (= X-ray Absorption Near-Edge Structure) or NEXAFS (= Near-Edge X-ray Absorption Fine Structure)*
2. EXAFS (= Extended X-ray Absorption Fine Structure)**

NEXAFS: application to molecular adsorbates in surface scienc

Interactions with the substrates are often "weak", in the sense that the excited electronic states immediately above the highest occupied state are found to display to a large degree a structure very similar to the one they display in the isolated molecules



From: P. Willmott, *An Introduction to Synchrotron Radiation*, *Wiley* (2011)

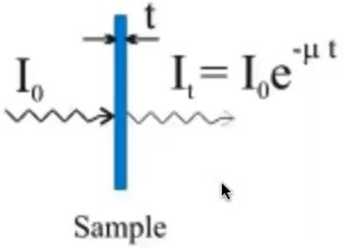
HOMO = highest occupied molecular orbital

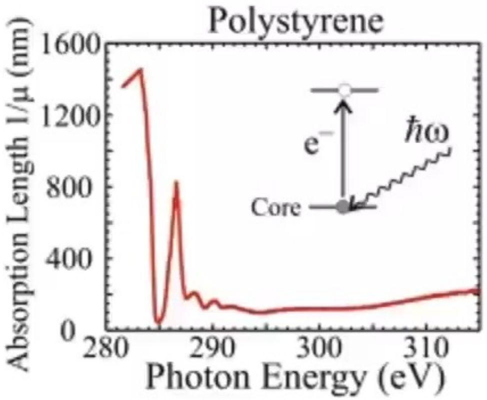
LUMO = lowest unoccupied molecular orbital

For unsaturated organic compounds (i.e., those with double or triple bonds) the LUMO is invariably a π* orbital and the first quasi-unbound state above IT a σ*

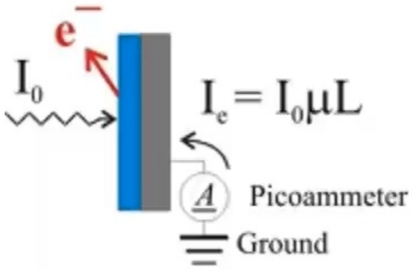
X-Ray Absorption Spectroscopy

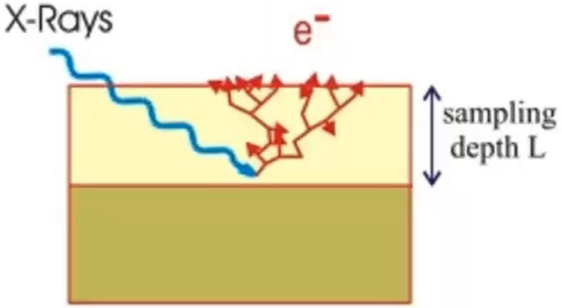
Transmission

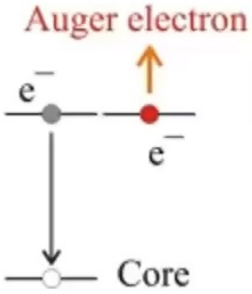




Electron Yield

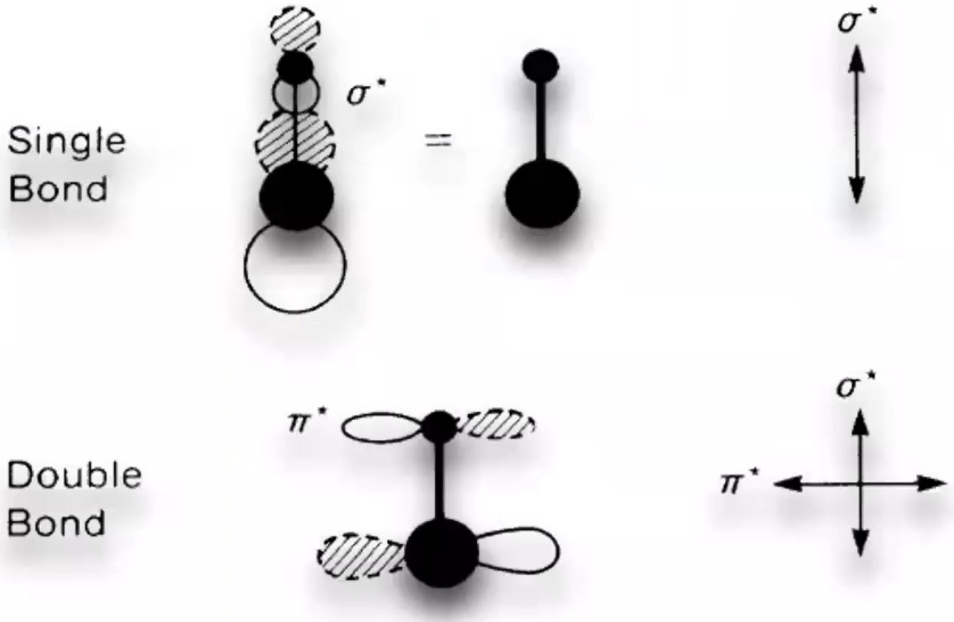




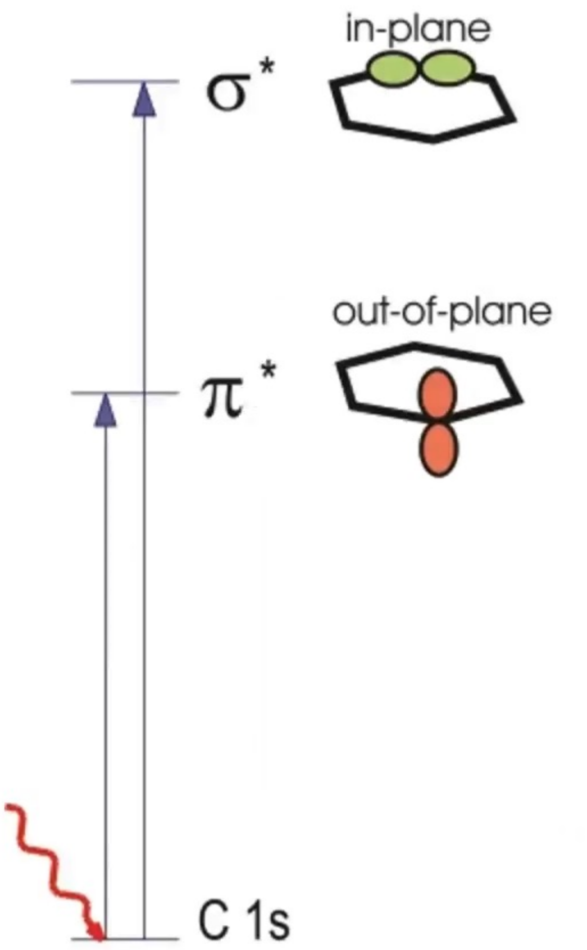


Polarization-dependent NEXAFS

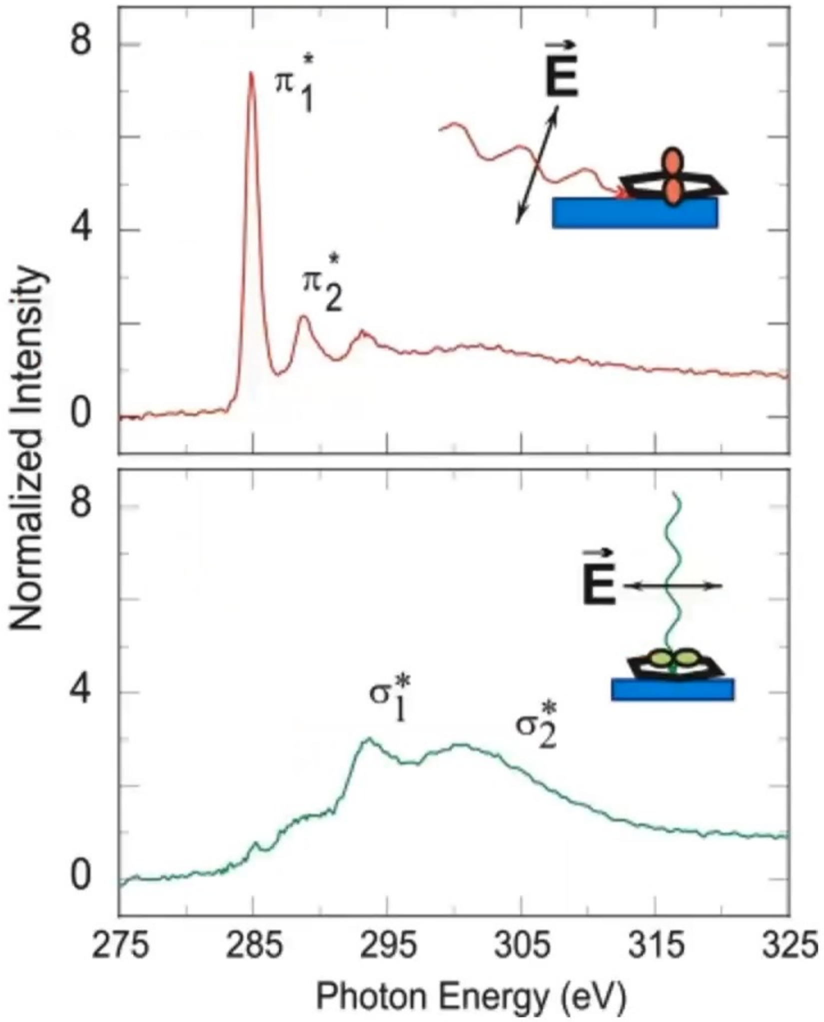
- linearly polarized radiation used
- initial state: very often a K shell [e.g., of C, N or O; at higher energy: S]
- the probability of a photon being absorbed depends on the orientation of the electric field vector of the X-ray beam relative to the polarization direction of the orbital to which the excitation takes place*



The Search Light Effect

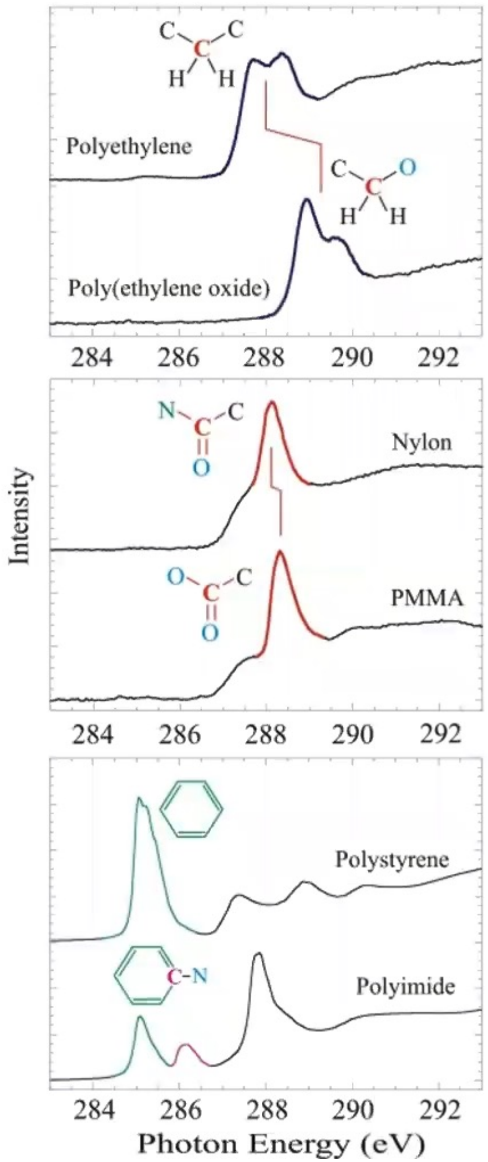


Benzene Molecular Orbitals

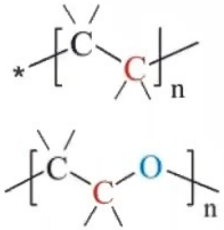


Lying-down benzene on Ag (110)

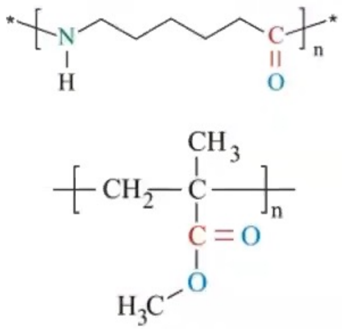
Basic Building Blocks of Polymers



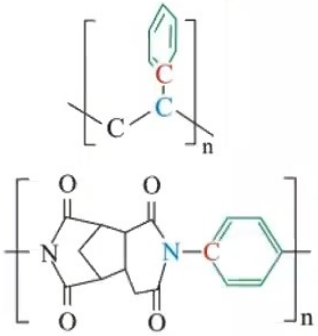
Carbon-Hydrogen Bonds



Unsaturated Bonds



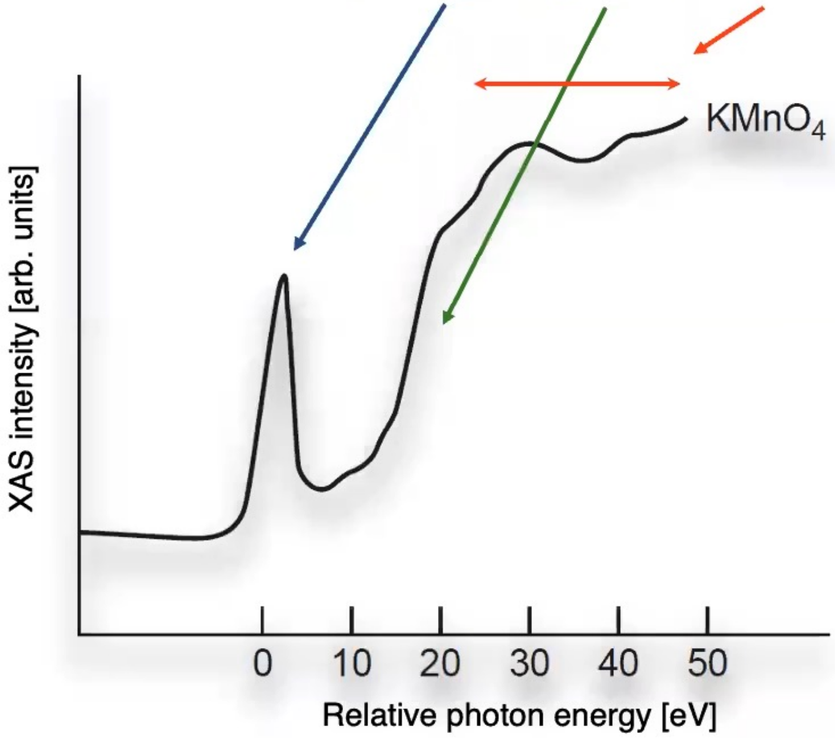
Aromatic Rings



X-ray Absorption Near-Edge Structure (XANES or NEXAFS) of sol

What is XANES?

XANES = pre-edge + edge + XANES



XANES is very sensitive to the chemistry of the absorbing atom:

→ formal oxidation state

→ coordination environment

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XANES

The intensity of transitions to bound-state unoccupied orbitals depends not only on the dipole selection rules (and the symmetry) but also on the **unoccupied DOS**

Re: [Xe] $6s^2\ 4f^{14}\ 5d^5$

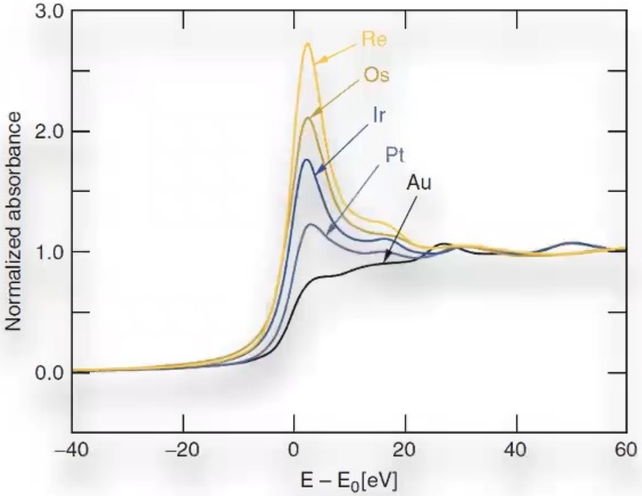
⋮

Ir: [Xe] $6s^2\ 4f^{14}\ 5d^7$

⋮

Au: [Xe] $6s^1\ 4f^{14}\ 5d^{10}$

L_3 absorption edges of five 5*d*-metals



G. Meitzner *et al*., J. Phys. Chem. **96**, 4960-4964 (1992)

- from Re to Pt: strong white lines* of bound unoccupied 5*d*-states below IT
- Au has no such states, excitation is directly into the unbound *continuum*

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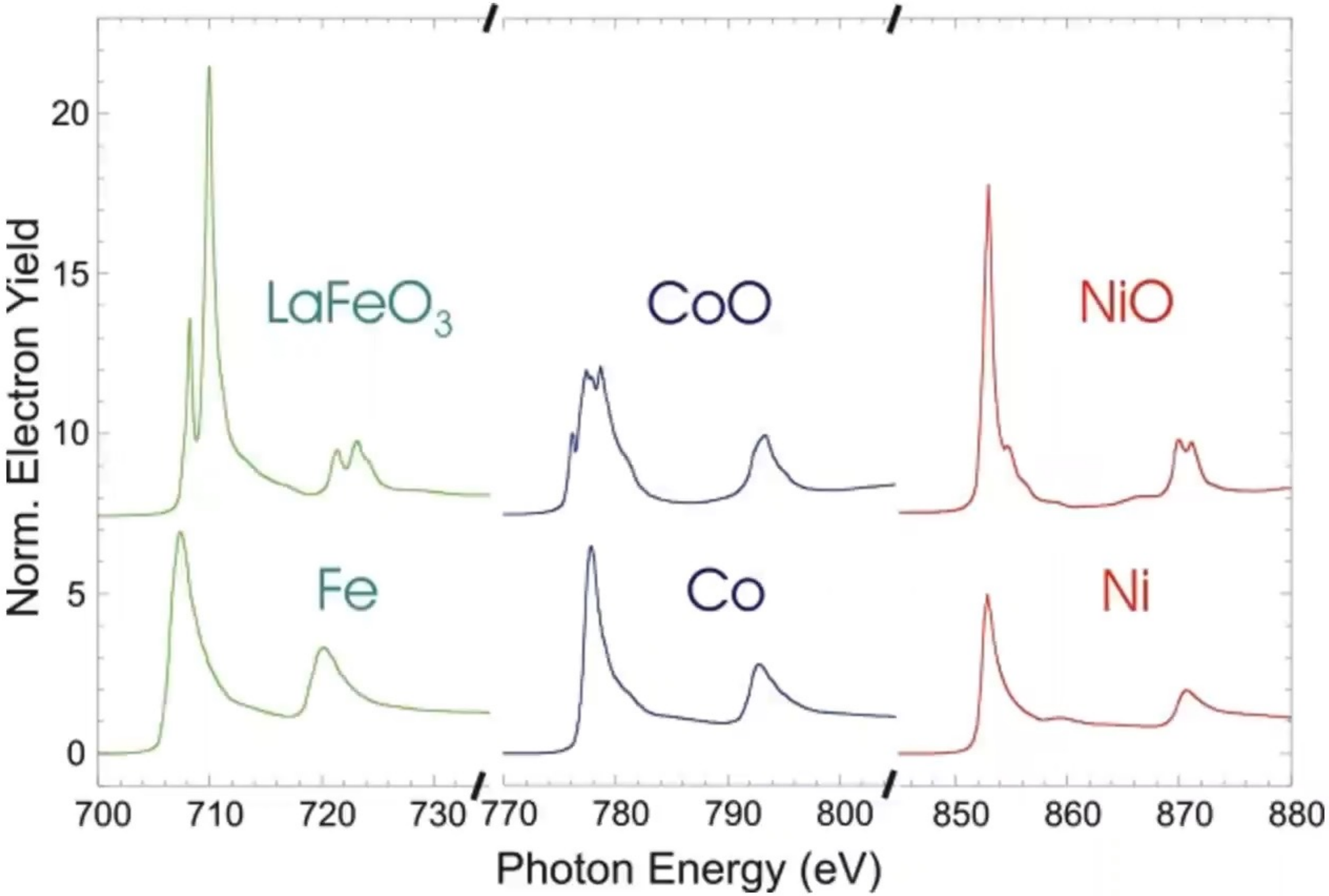
Norm. Electron Yield
0
5
10
15
20
LaFeO$_3$
CoO
NiO
Fe
Co
Ni
700
710
720
730
770
780
790
800
850
860
870
880
Photon Energy (eV)

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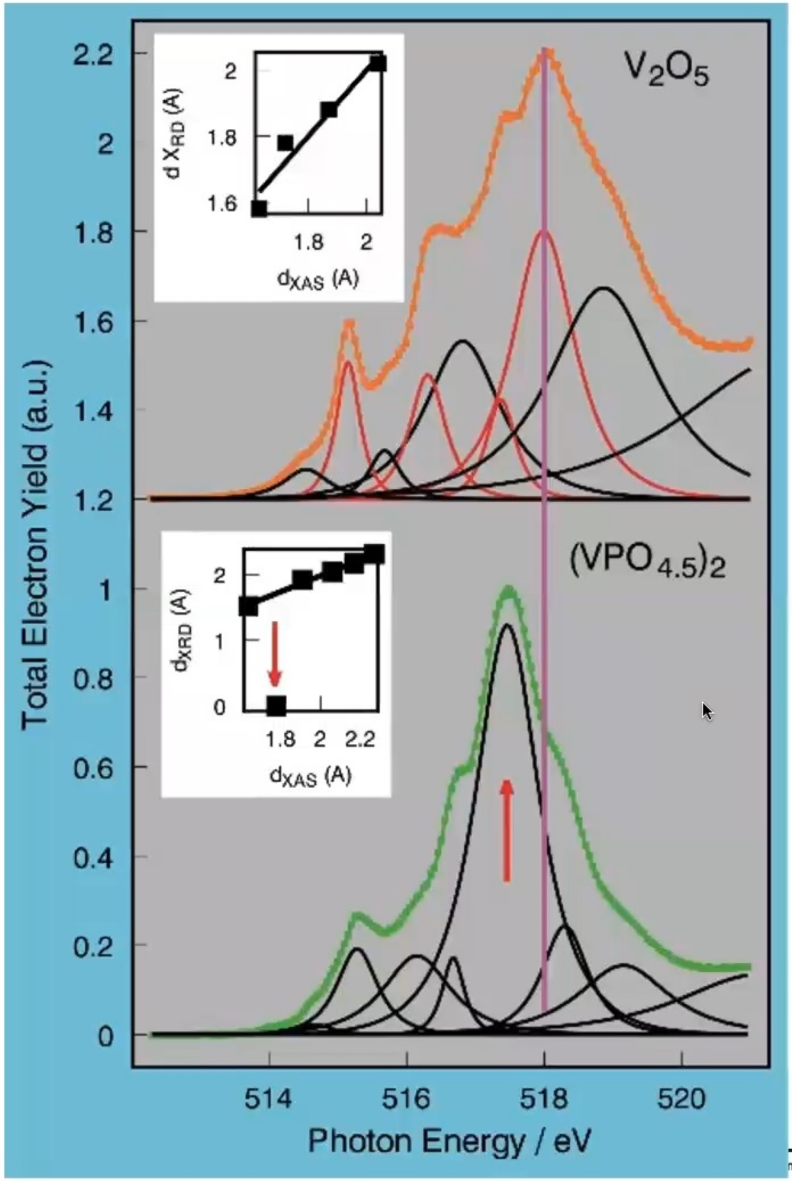
Spectroscopy of catalysts under process conditions



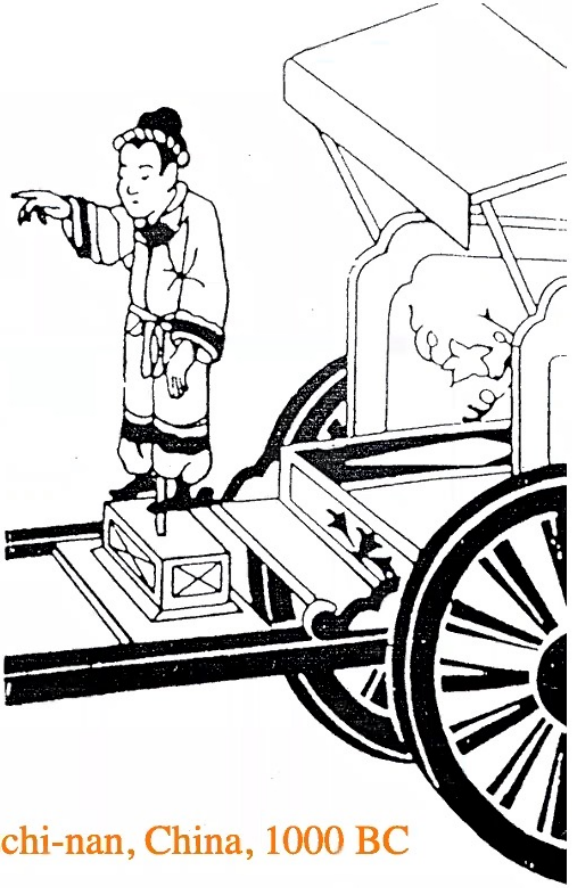
Methane oxidation using a vanadium oxide catalyst reveals an intermediate state which is only present under reaction conditions

NEXAFS spectra of catalysts during chemical reactions

M. Hävecker, R.W. Mayer, A. Knop-Gericke, R. Schlögl (FHI Berlin)

Magnetism and Magnetic Materials in the Light of Synchrotron Radiation

W. Eberhardt BESSY



Tschi-nan, China, 1000 BC

It is not possible to understand
the magnetic effects of materials
in any honest way from the point
of view of classical physics.
Magnetic phenomena are completely a
quantum mechanical phenomenon.

R.P. Feynman
The Feynman Lectures Vol.II, 34-2

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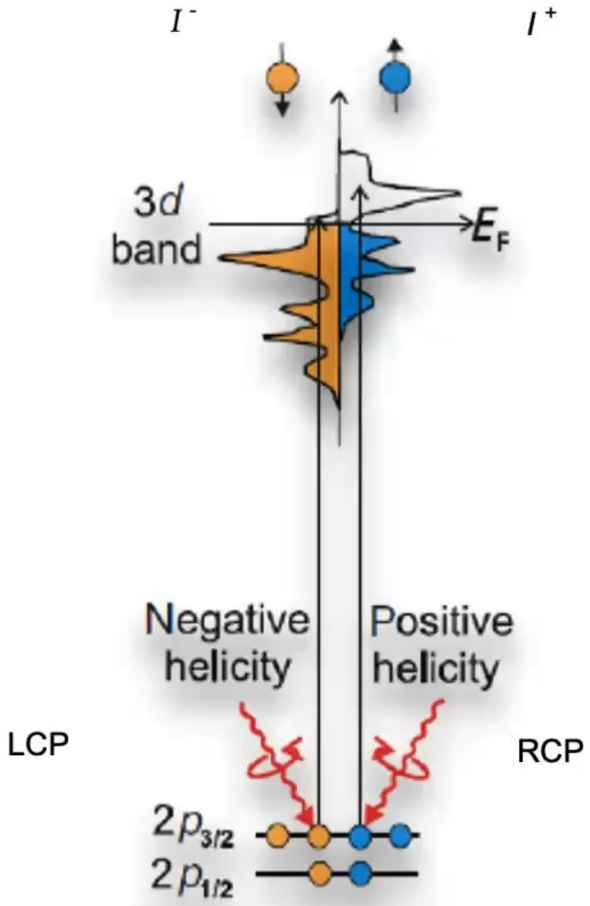
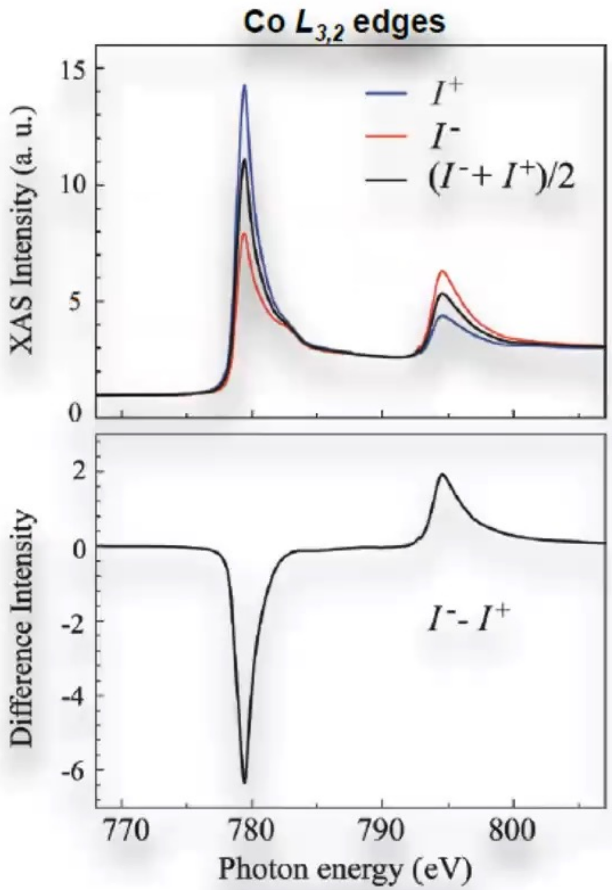
Principle of XMCD (X-Ray Magnetic Circular Dichroism)





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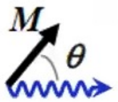
Quantitative analysis of XMCD spectra: sum rules

- The size of the dichroism effect scales as cos θ

  θ = angle between photon spin and magnetization direction
- Sum rules: relate A, B, I_{L_3}, I_{L_2} with the spin & orbital magnetic moments of the probed atom

$I_{XMCD} \; \alpha \; M\cos\theta$



1st sum rule: $I_{L_3} + I_{L_2}$ is ∝ to the number of 3*d* holes

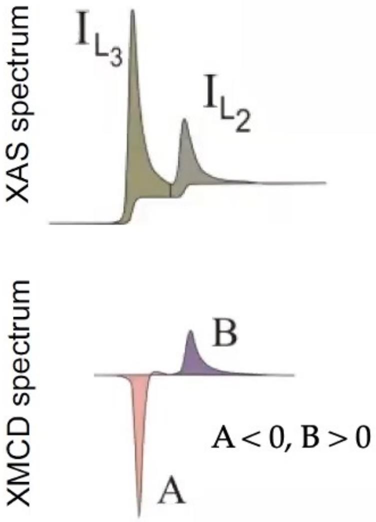
2nd sum rule: the spin magnetic moment is related to [2B-A]

3rd sum rule: the orbital magnetic moment is ∝ to -[A+B]

See, e.g.: J. Stöhr, Journal of Magnetism and Magnetic Materials **200**, 470-497 (1999)

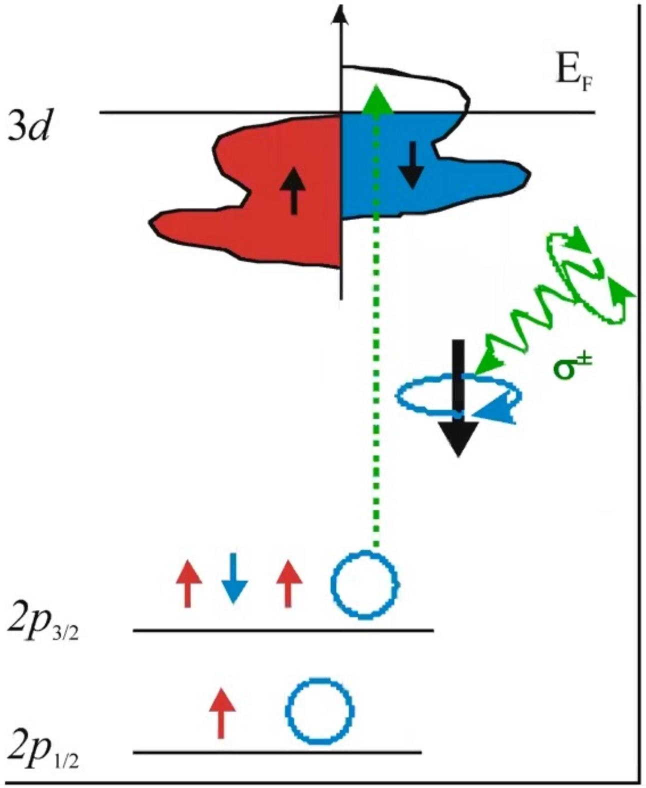
↓

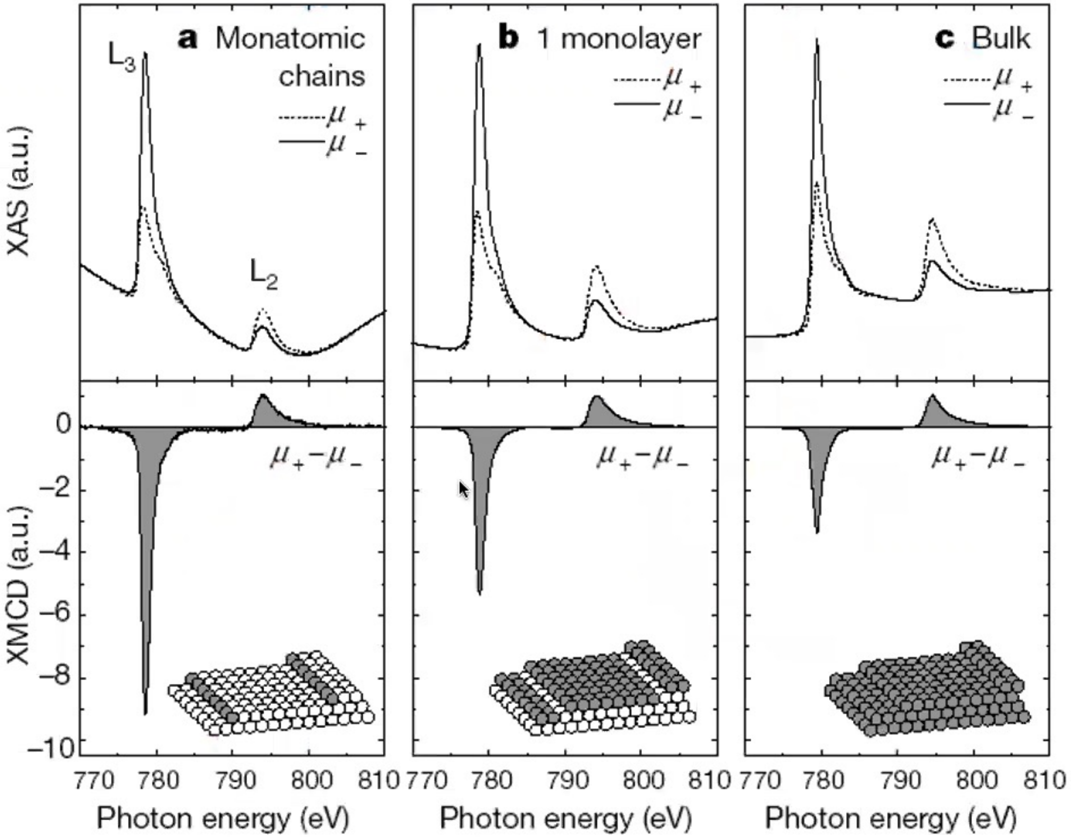
quantitative determination of the spin & orbital magnetic moments with element specificity



measurements: by reversing (1) photon's helicity or (2) the direction of the magnetization

Magnetic Systems → CMXD





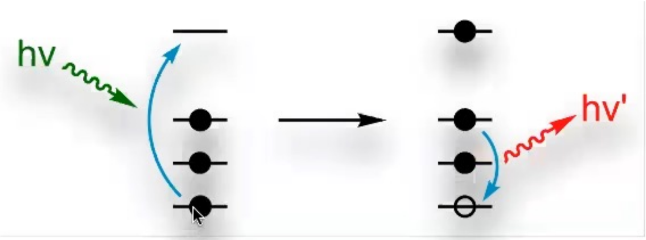
P. Gambardella, A. Dallmeyer, K. Maiti, M. C. Malagoli, W. Eberhardt, K. Kern, C. Carbone, **Nature 416**, 301 (2002)

X-Ray Fluorescence Spectroscopy

photon-in — photon-out technique

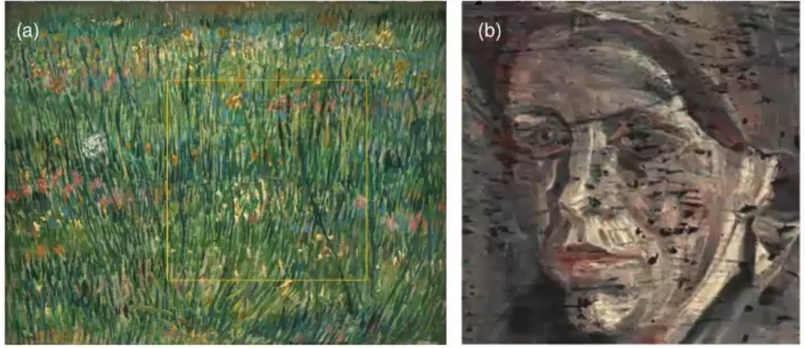
→ can be used also for isolating samples as well as under ambient or in-vivo environments

X-ray fluorescence (XRF)



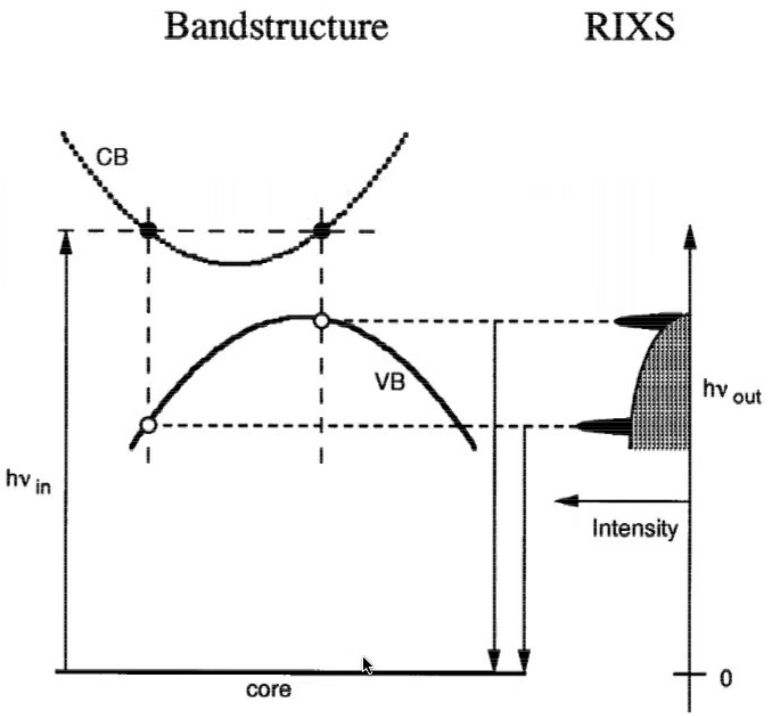
- emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by being bombarded with high-energy X-rays
- widely used for elemental analysis and chemical analysis
- non-destructive analytical technique

Visualization of a Lost Painting by Vincent van Gogh



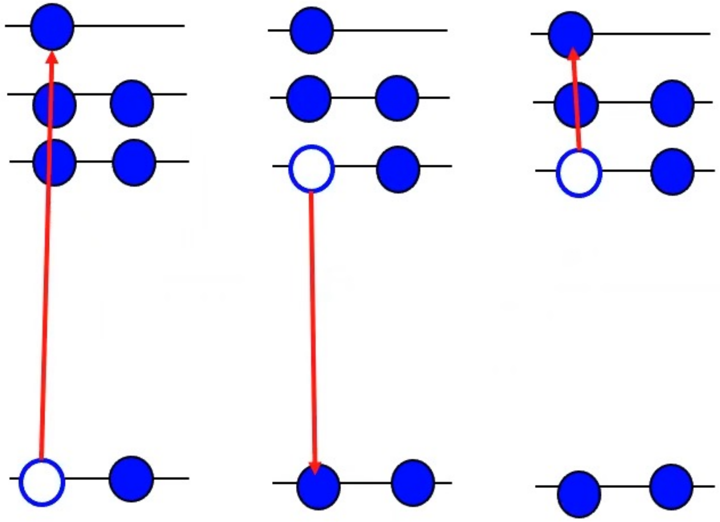
J. Dik et al, Anal. Chem. **80**, 6436 (2008)

RIXS as a bandstructure tool



S. Eisebitt, W. Eberhardt, RIXS-REVIEW
J. Electr. Spectr. 110, 335 (2000)

RIXS process



The relevant time is the dephasing time – not the lifetime

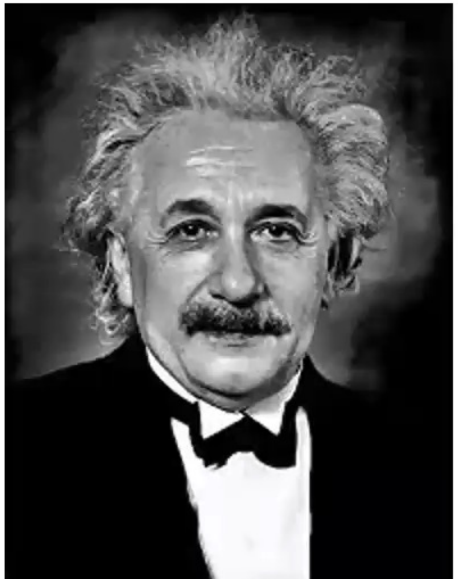
Energy Conservation in Photoemission (Einstein)

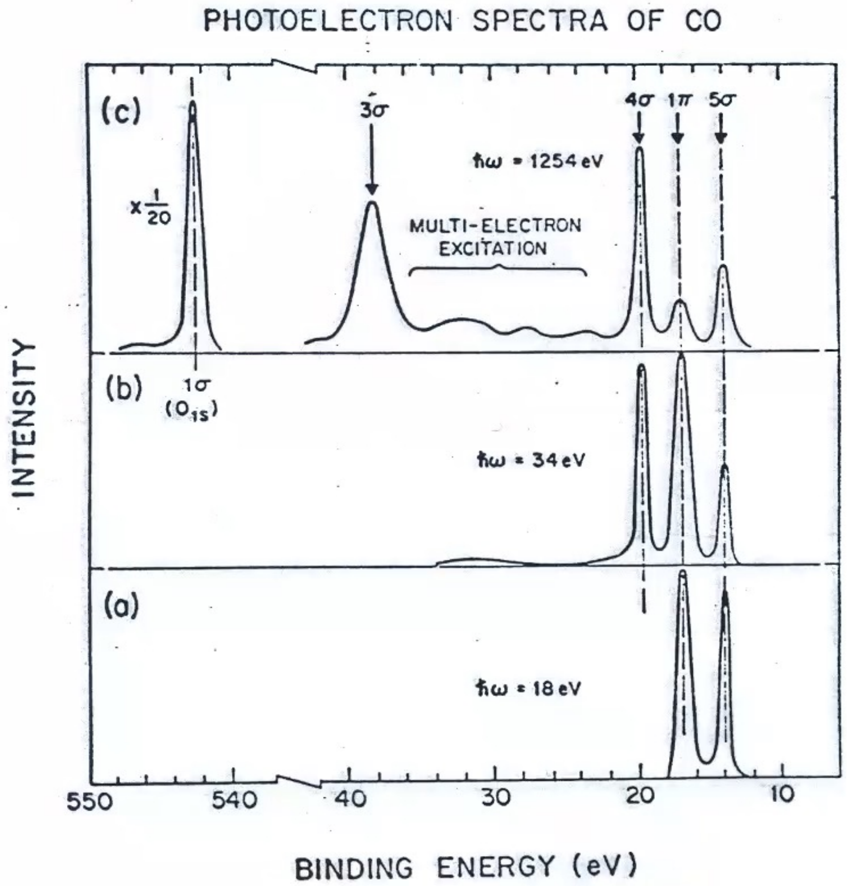
$$\boxed{E_{kin} = h\nu - E_B}$$

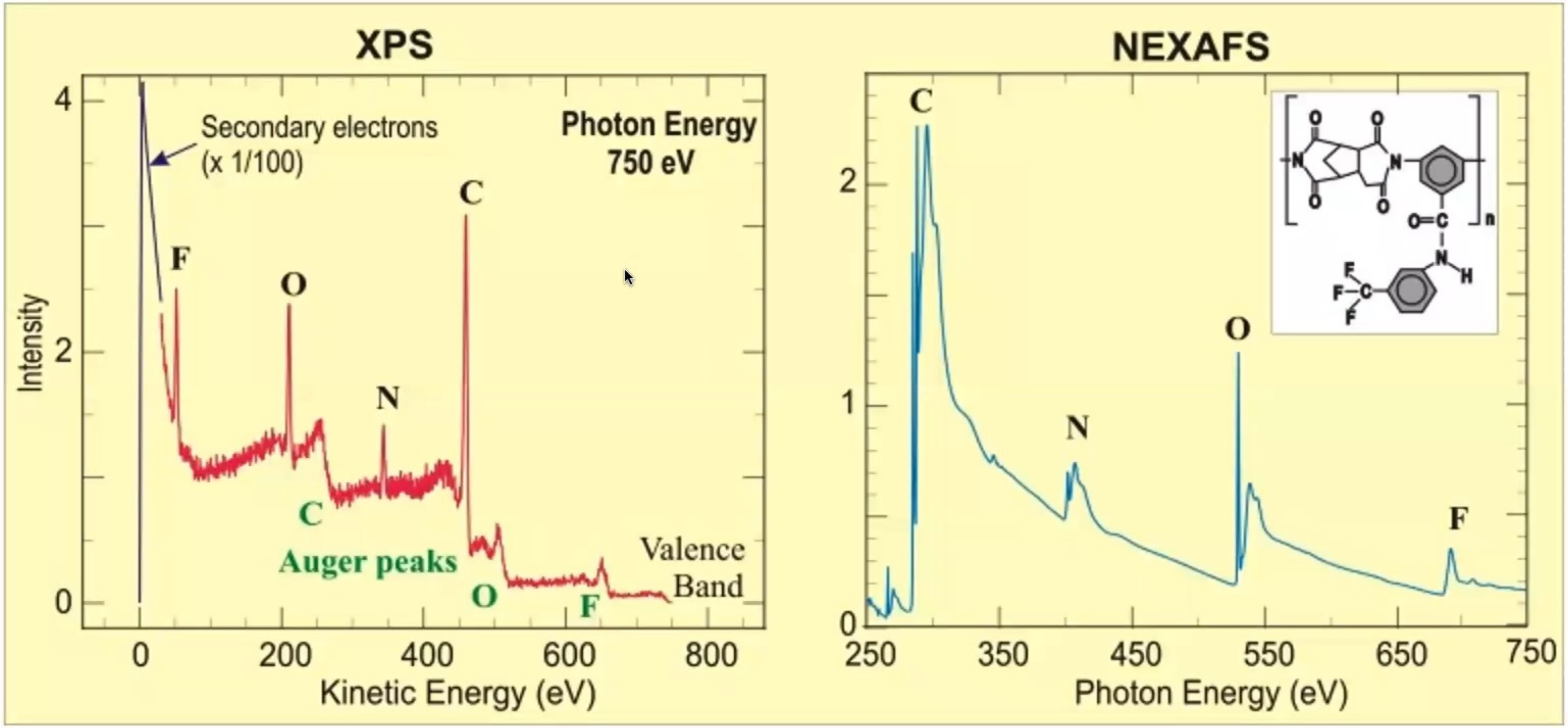
kinetic energy

photon energy

binding energy





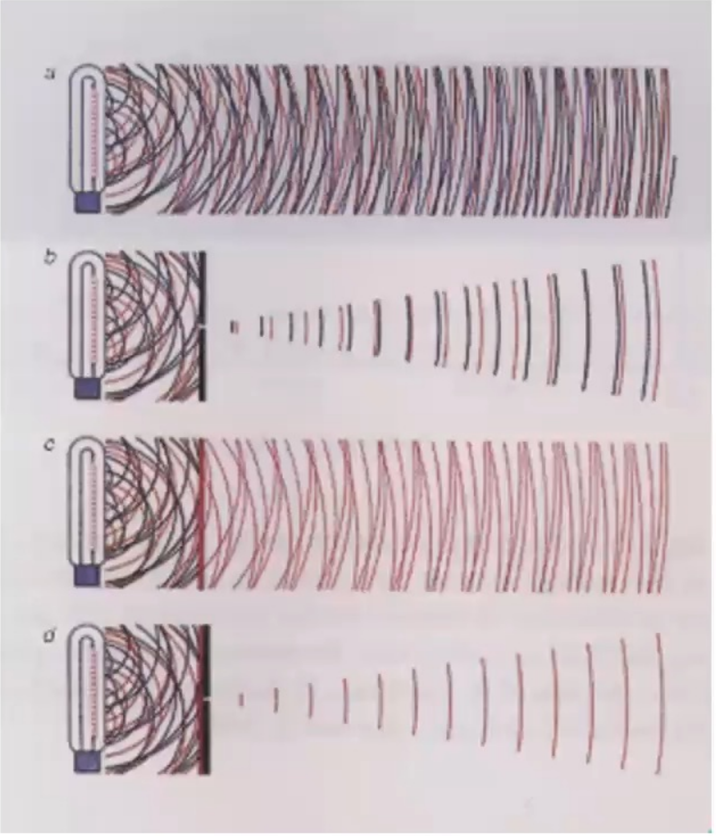


XPS

NEXAFS

Intensity
4
2
0
Secondary electrons
(x 1/100)
Photon Energy
750 eV
F
O
N
C
C
Auger peaks
O
F
Valence
Band
0
200
400
600
800
Kinetic Energy (eV)
C
2
1
0
N
O
F
250
350
450
550
650
750
Photon Energy (eV)
O
N
O
N
O
O
O=C
N
H
F
F–C
F
n

Coherent Light Scattering



A. Schawlow, Sci. Am. **219**, 120 (Sept 1968)

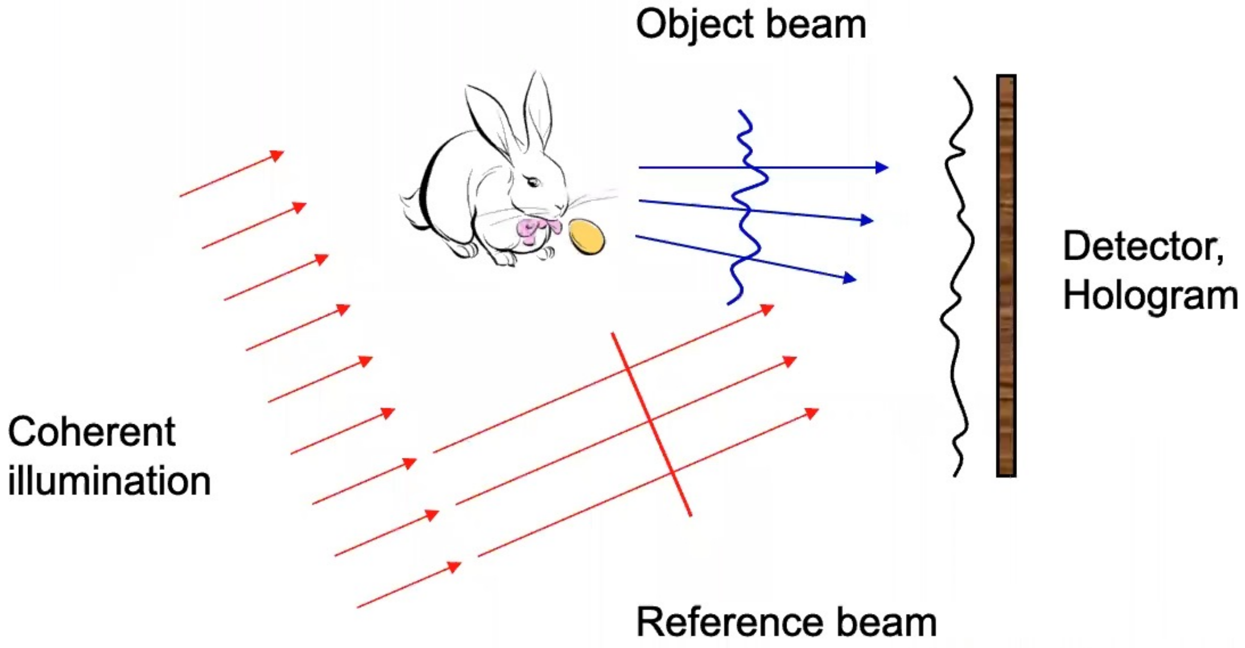
incoherent source

spatial filtering

spectral filtering

spatial & spectral filtering

Holography Principle
--- in-line holografy



Coherence --- a New Tool in X-Ray Science

Sensitive to the individual configuration

beyond statistical information

Spatial Domain

Reconstruction with nm feature resolution
chemical sensitivity

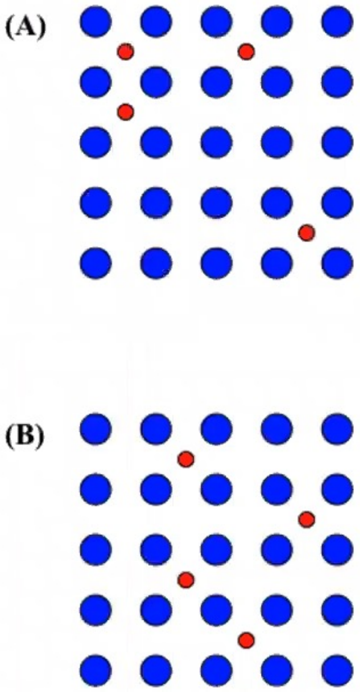
Temporal Domain

- Fingerprinting fluctuations -> Dynamics

➔XPCS

General Features

resonant → element specific
photon-in photon-out
combines spectroscopy and scattering
chemical and structural information

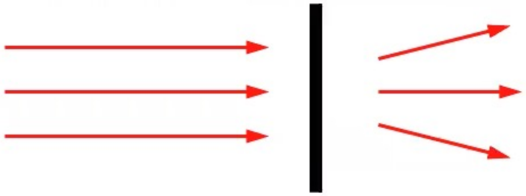


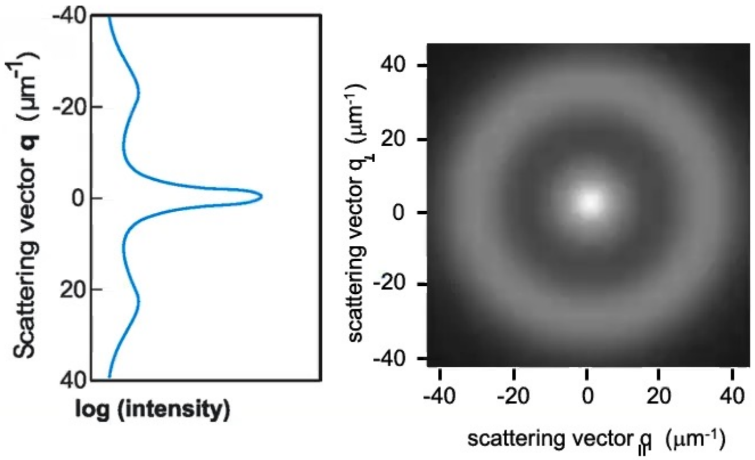
Identical periodic lattice
Identical mean deviation
But different individual configuration

Incoherent vs. *Coherent* X-Ray Scattering

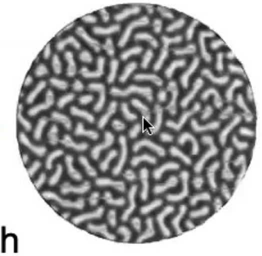
Small Angle Scattering

Incoherent scattering



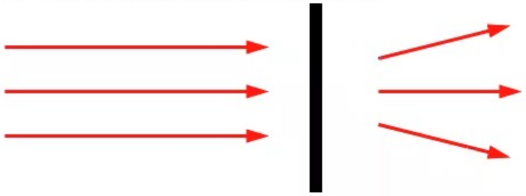


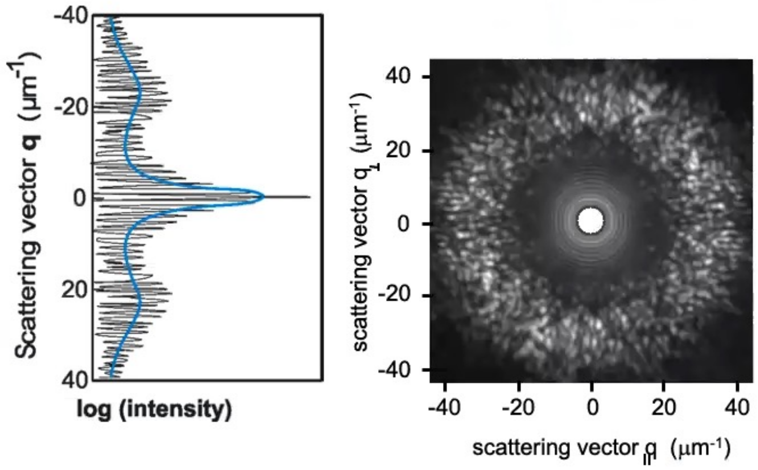
information
about
domain
statistics



Speckle

Coherence length
larger than illuminated area

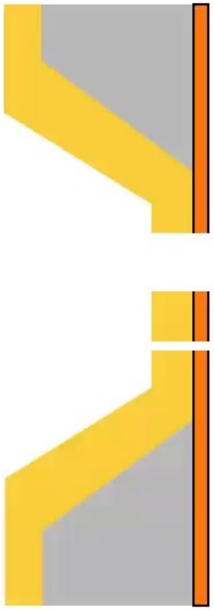




information
about
individual
domain
structure

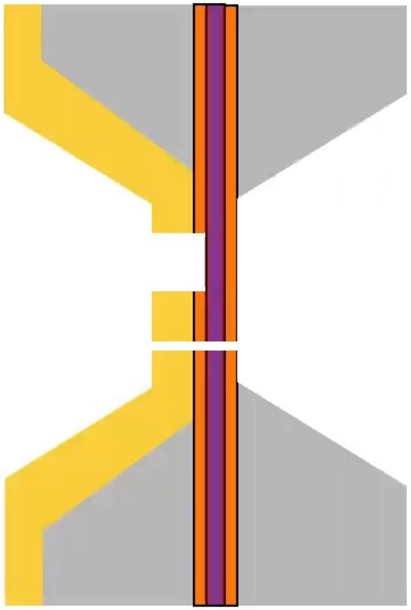
HESEB

Fourier Transform Holography at λ=1.6 nm



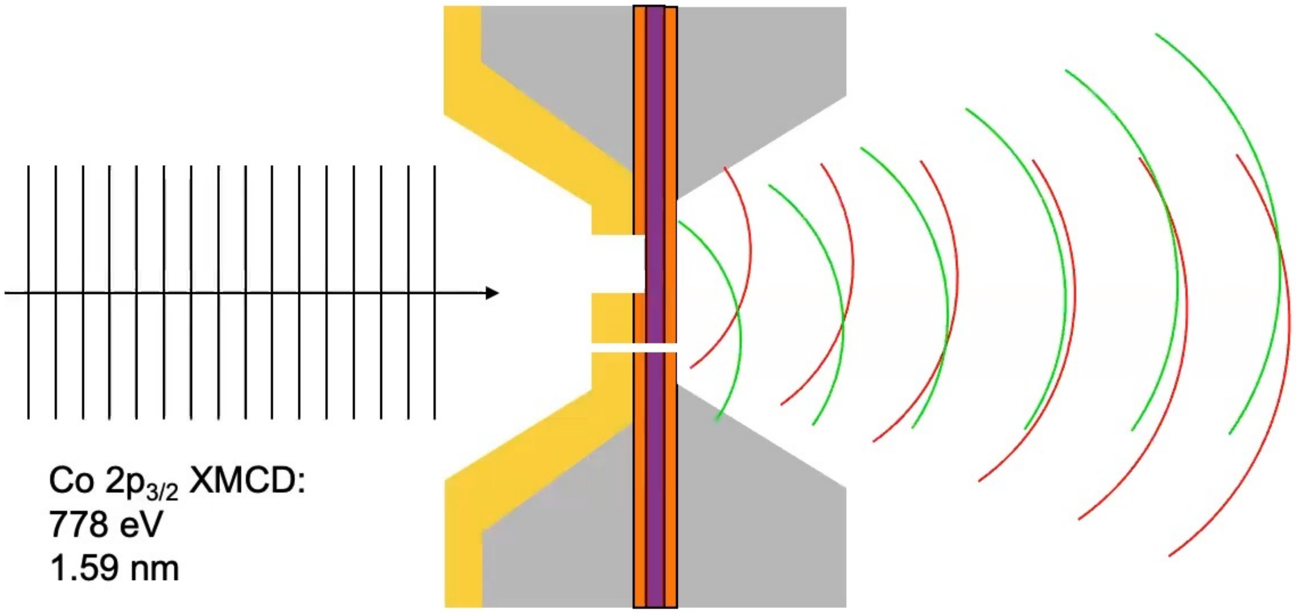
Co $2p_{3/2}$ XMCD:
778 eV
1.59 nm

Fourier Transform Holography at λ=1.6 nm



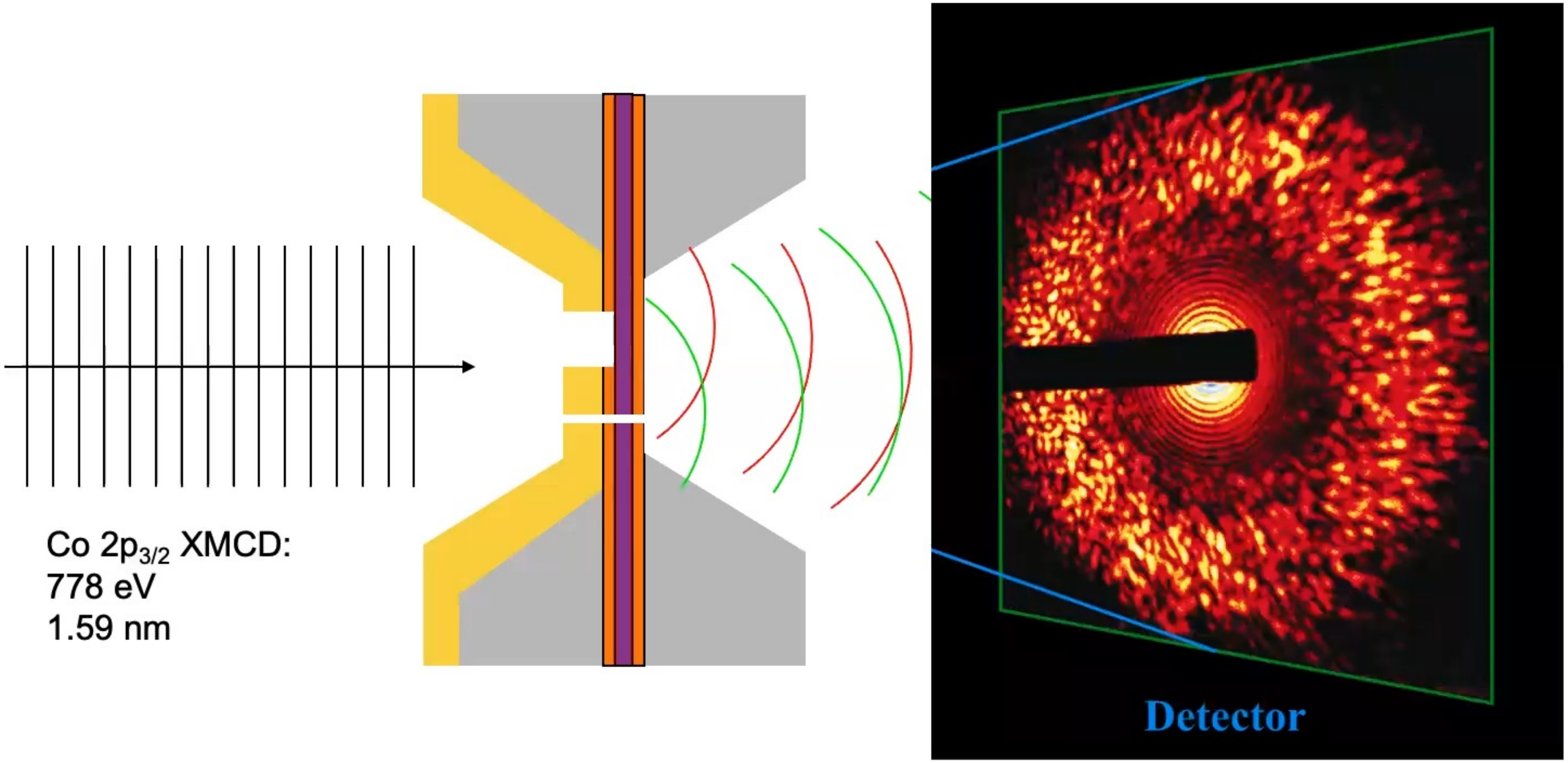
Co $2p_{3/2}$ XMCD:
778 eV
1.59 nm

Fourier Transform Holography at λ=1.6 nm



Co $2p_{3/2}$ XMCD:
778 eV
1.59 nm

Fourier Transform Holography at λ=1.6 nm

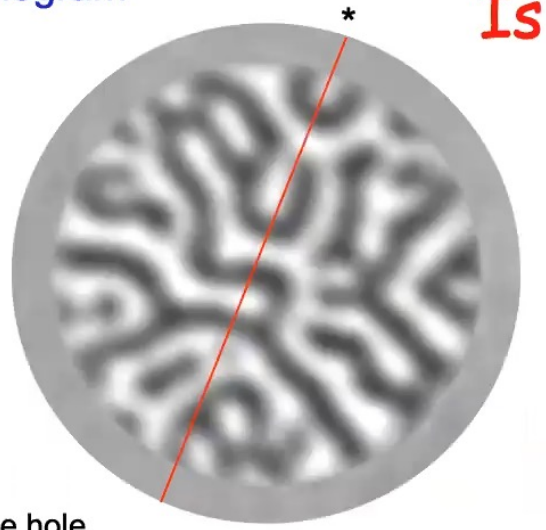


Co $2p_{3/2}$ XMCD:
778 eV
1.59 nm

Is it real?

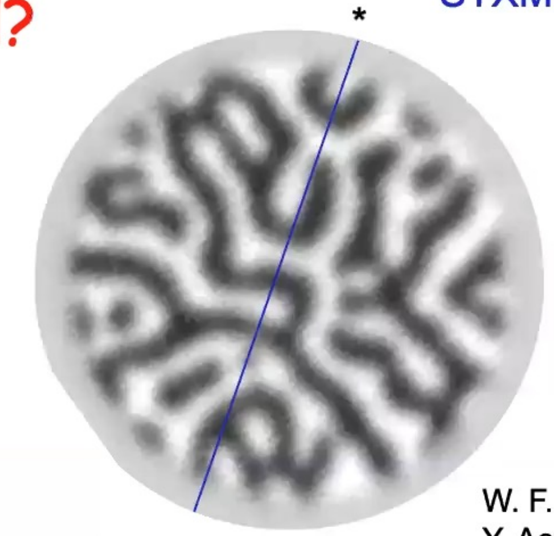
Is it good?

FT Hologram



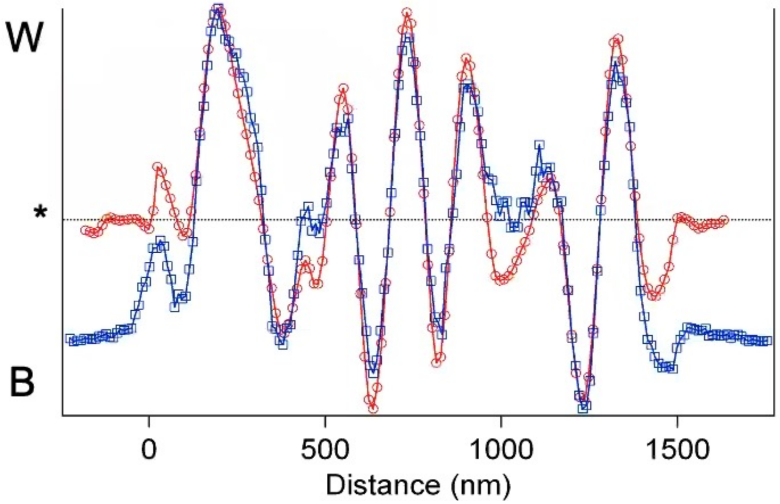
Reference hole
∅ 100 nm

STXM



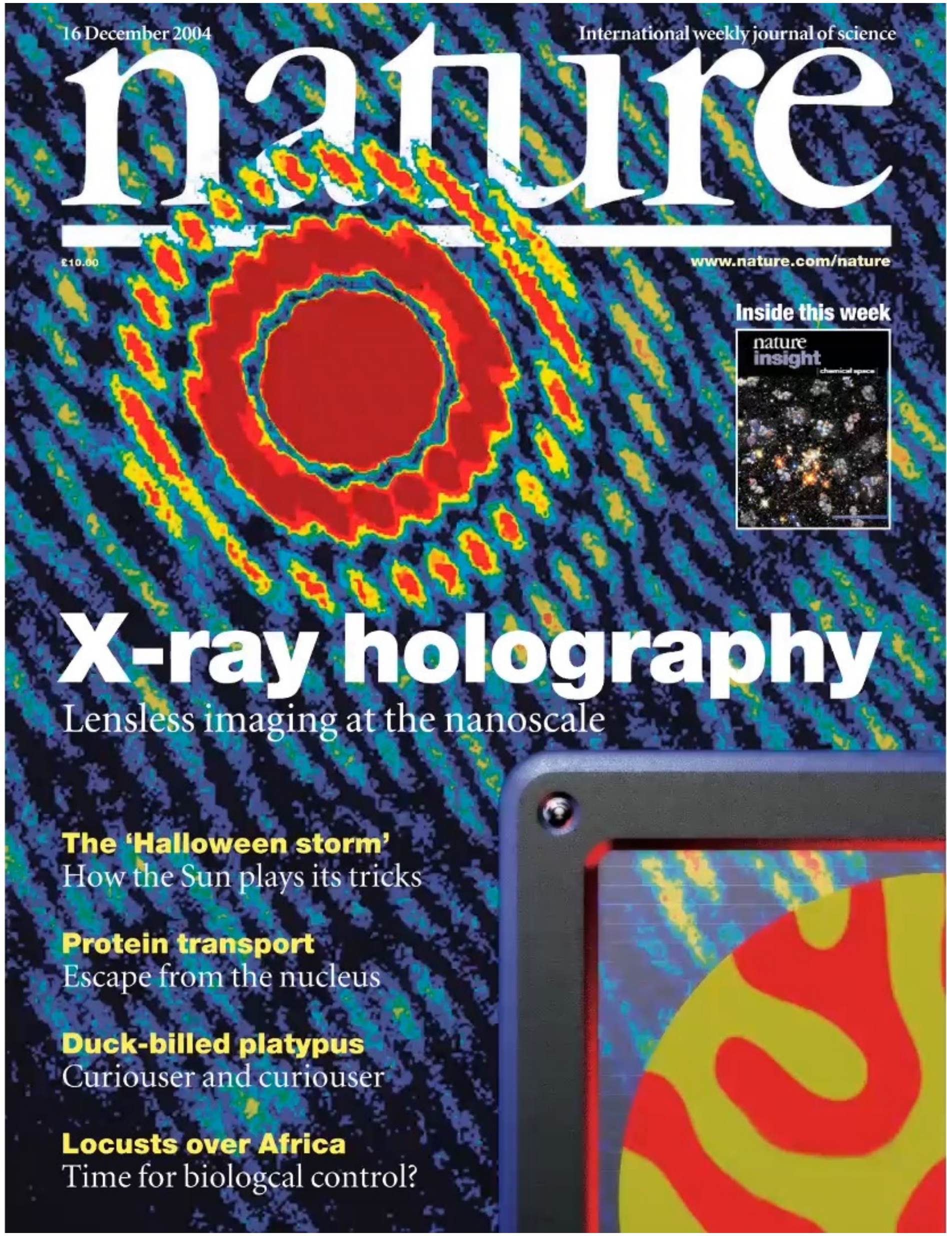
W. F. Schlotter
Y. Acremann

Resolution
30 - 40 nm



S. Eisebitt
J. Lüning
W.F. Schlotter
M. Lörgen
O. Hellwig
W. Eberhardt
J. Stöhr

NATURE **432**, 885 (2004)



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Locusts over Africa
Time for biologcal control?

BESSY

LELAND STANFORD JUNIOR UNIVERSITY
ORGANIZED 1891

SSRL

IBM
Almaden Research Center

HESEB

Summary

HESEB soft x-ray beamline

HESEB Helmholtz-SESAME Soft X-Ray Beamline for SESAME

- HESEB project is progressing well; BL has been installed in Jan 2022 (undulator in April 2022)
- First beam on June 8, 2022
- Alignment, Characterization and Commissioning
- User community building activities will increase – also in synergy with BEATS