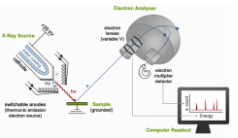
Why x-ray spectroscopy?

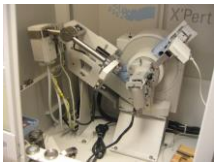
- local excitations > element specific
- sensitive to low concentrations
- applicable under extreme conditions
- Space-Time-Energy (combination with x-ray microscopy, time-resolution and high-resolution x-ray emission)

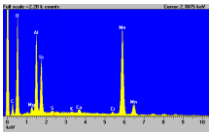
X-ray experiments (small scale)



X-ray photoemission
X-ray diffraction
X-ray fluorescence (in a TEM)

→ Fixed x-ray energy source





X-ray experiments (large scale)

Synchrotron
→ Tunable energy source
→ More flux & brilliance
→ Polarized & focused

Free electron laser
→ Time resolution (fs)
→ Coherence
→ More peak brilliance

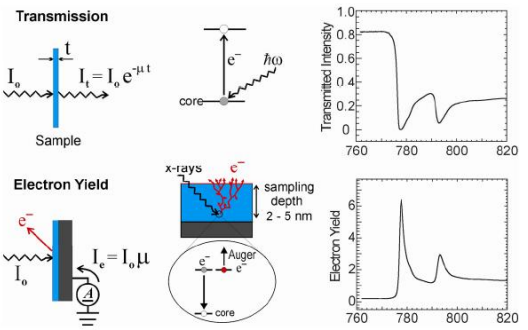
Why a synchrotron?

- **Energy**: tunable source
- **Intensity**: 10^6-10^{12} higher than x-ray tube
- **Space**: spot-size 1x1 mm (unfocussed)
  down to 20x20 nm (focussed)
- **Time**: pulse 50 ps
- **Polarization:** Circular dichroism:
- NOT coherent

Why a X-FEL?

- **Energy**: tunable source [less tunable]
- **Intensity**: 10^{12} higher than x-ray tube [10^{22}]
- **Space**: spot-size 1x1 mm (unfocussed)
  down to 20x20 nm (focussed)
- **Time**: pulse 50 ps [10 fs]
- **Polarization:** Circular dichroism:
- NOT coherent >> COHERENT

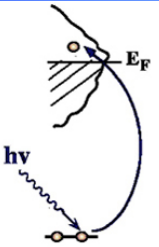
XAS experimental techniques



X-ray Absorption Spectroscopy

Excitations of core electrons to empty states

The XAS spectrum is given by the Fermi Golden Rule

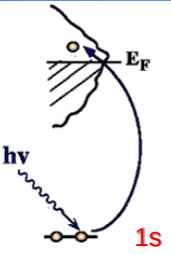


$$I_{XAS} \sim \Sigma_f \left| \langle \Phi_f | \hat{e} \cdot r | \Phi_i \rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray Absorption Spectroscopy

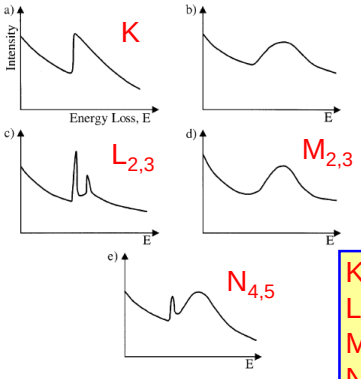
Excitations of core electrons to empty states

The XAS spectrum is given by the Fermi Golden Rule



$$I_{XAS} \sim M^2 \rho \approx \rho_{site,symmetry}$$

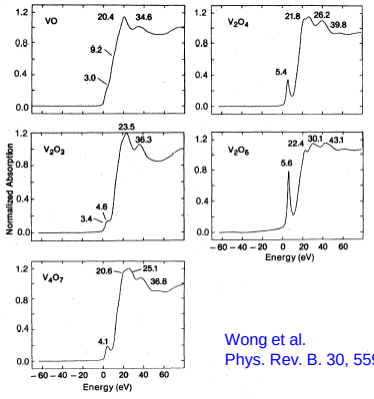
XAS edges



Selection rules:
ΔS=0
ΔL = +1 or -1

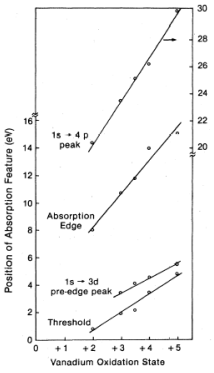
K	1s→p
$L_{2,3}$	2p→3d
$M_{2,3}$	3p→3d
$N_{4,5}$	4d→4f

XAS qualitative analysis of metal K edges



Wong et al.
Phys. Rev. B. 30, 5596 (1984)

XAS qualitative analysis



Edge position gives valence

Pre-edge gives valence

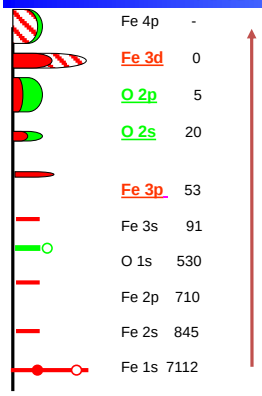
Different slopes

XAS: iron K edge

Fe 4p	-
Fe 3d	0
O 2p	5
O 2s	20
Fe 3p	53
Fe 3s	91
O 1s	530
Fe 2p	710
Fe 2s	845
Fe 1s	7112

Fe_2O_3 $3d^5$

XAS: iron K edge

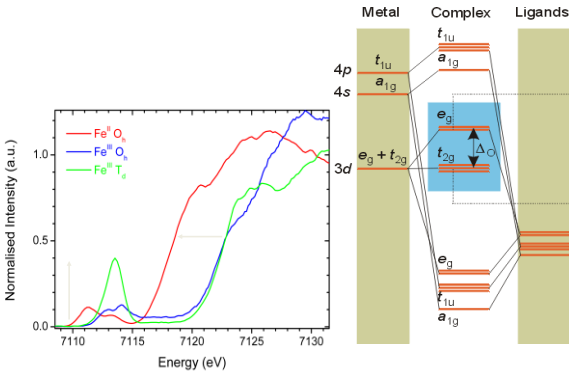


Fe_2O_3 $3d^5$

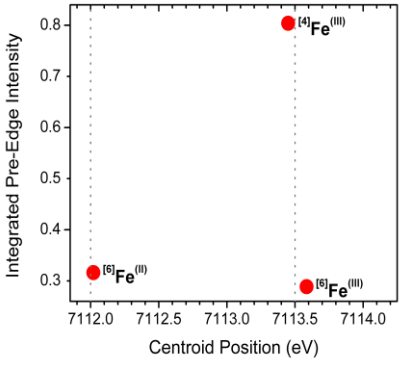
Edge:
1s>4p dipole

Pre-edge:
1s> 3d quadrupole

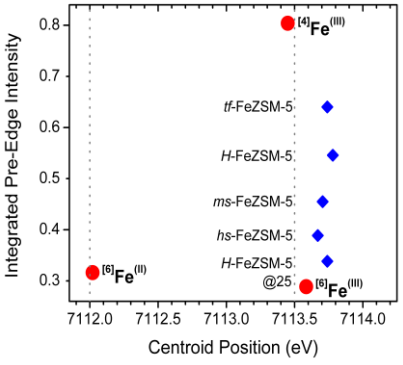
X-ray absorption



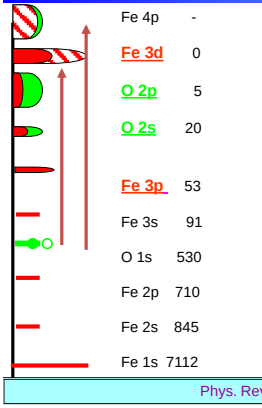
Sharpened pre-edge analysis

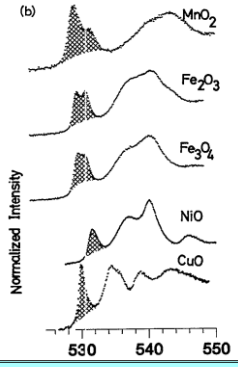


Sharpened pre-edge analysis



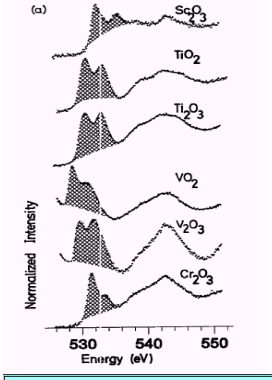
XAS: oxygen K edge

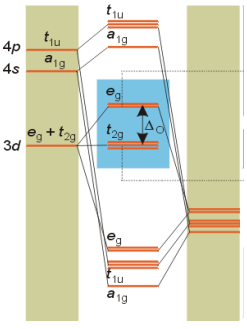




Phys. Rev. B.40, 5715 (1989)

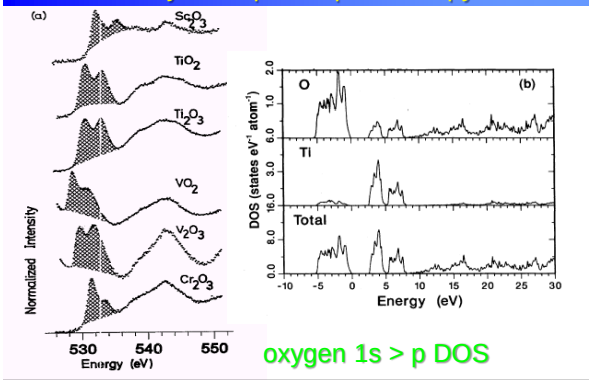
X-ray Absorption Spectroscopy





Phys. Rev. B.40, 5715 (1989)

X-ray Absorption Spectroscopy



oxygen 1s > p DOS

Phys. Rev. B.40, 5715 (1989); 48, 2074 (1993)

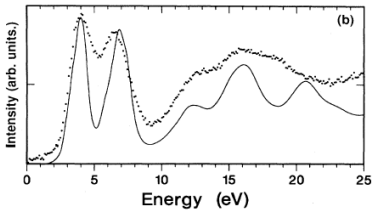
X-ray Absorption Spectroscopy

— Constant matrix element approximation

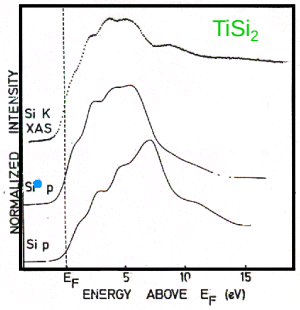
X-ray Absorption Cross-section

$$\sigma(\omega) \sim 4\pi^2 \alpha_0 \hbar\omega M_i \sum_f \delta(E_f - E_i - \hbar\omega)$$

$D_i(\hbar\omega - E_i)$ local Density of States



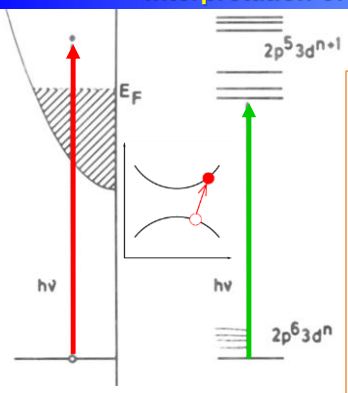
XAS: Final state Rule



- **Final State Rule:** Spectral shape of XAS looks like final state DOS

Phys. Rev. B.41, 11899 (1991)

Interpretation of XAS



1-particle:
1s edges
(DFT + core hole +U)

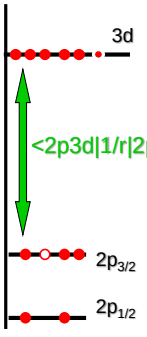
2-particle:
+ all edges of closed shell systems
(TDDFT, BSE)

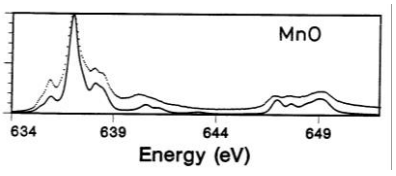
many-particle:
open shell systems
(CTM4XAS)

XAS: multiplet effects

Overlap of core and valence wave functions

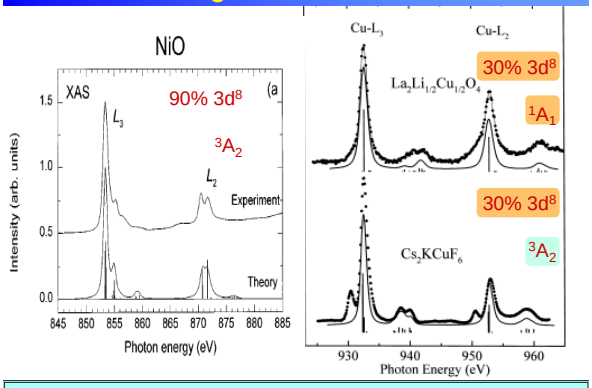
→ Single Particle model breaks down





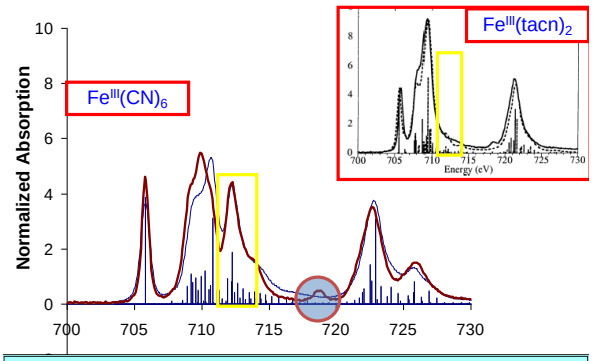
Phys. Rev. B. 42, 5459 (1990)

Charge Transfer effects



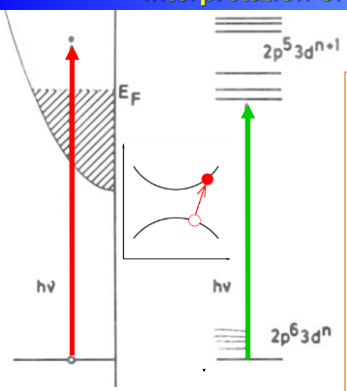
Chem. Phys. Lett. 297, 321 (1998)

LMCT and MLCT: π - bonding



with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

Interpretation of XAS



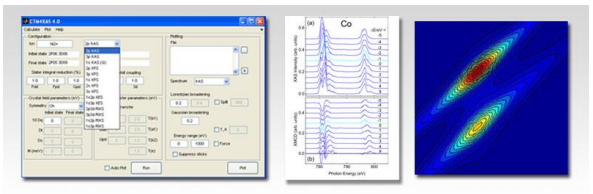
1-particle:
1s edges
(DFT + core hole +U)

2-particle:
+ all edges of closed shell systems
(TDDFT, BSE)

many-particle:
open shell systems
(CTM4XAS)

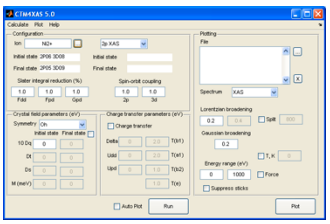
Charge Transfer Multiplet program

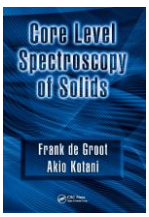
Used for the analysis of XAS, EELS, Photoemission, Auger, XES,



http://www.anorg.chem.uu.nl/CTM4XAS/

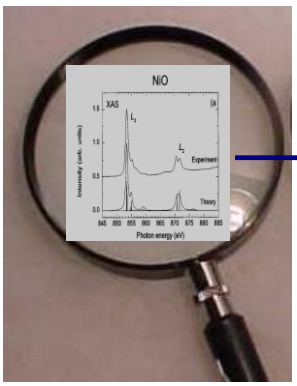
Charge Transfer Multiplet program





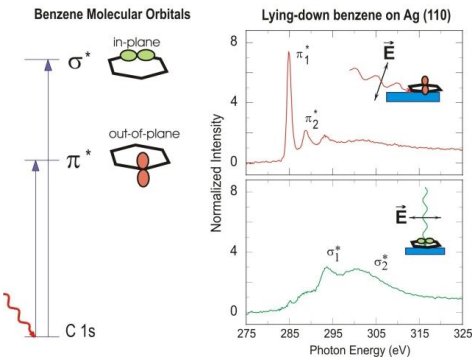
http://www.anorg.chem.uu.nl/CTM4XAS/

Ground states of TM Ions

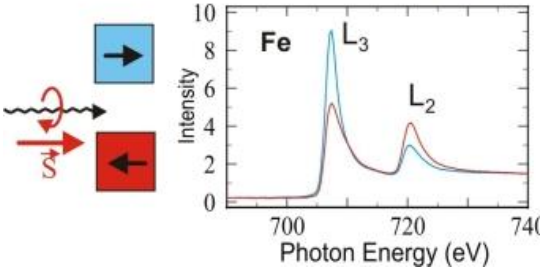


Ground State

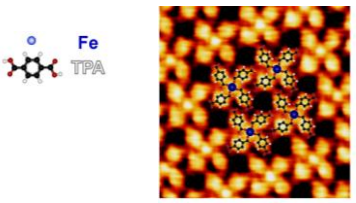
Angular dependence (linear dichroism)



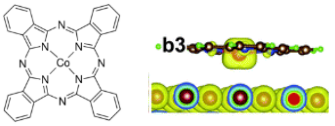
Circular Dichroism - Ferromagnets



Example: XAS in surface science

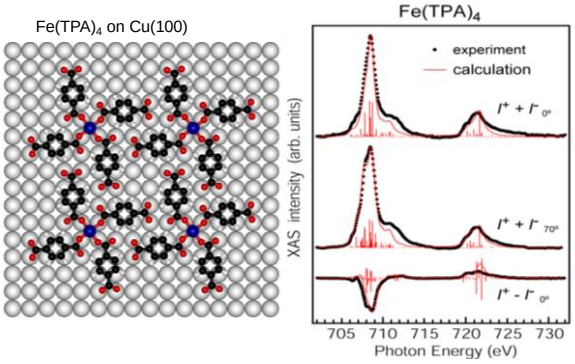


Fe TPA on Cu



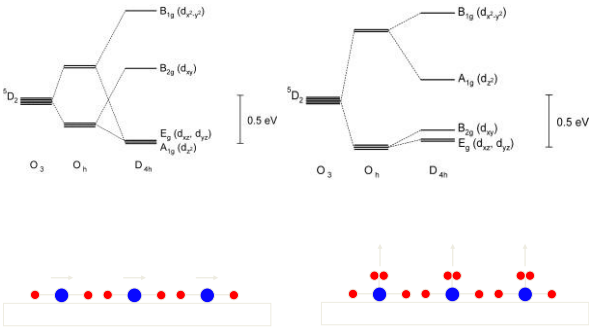
Co Pc on Au

Iron 2p XAS of Fe arrays



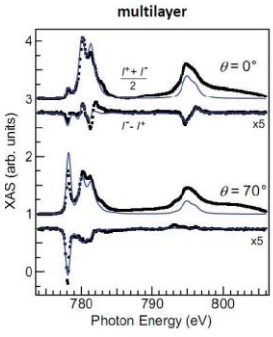
Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

Iron 2p XAS of Fe arrays



Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

Co Phtallocyanine on gold

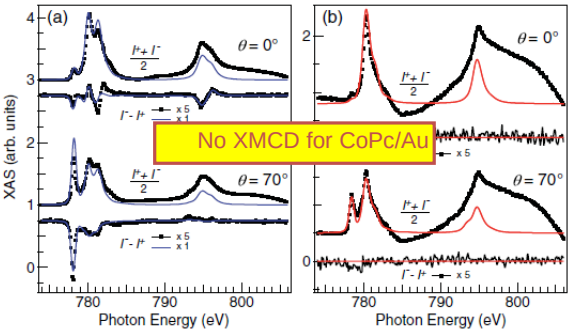


Ligand field multiplet calculations

- Model: d^7, T = 8 K, B = 5 T
- CF: $10D_q$ = 2.3, D_s = 0.55, D_t = 0.20 eV
- Ground state: $^2A_{1g}$
- Low spin S = ½
- Occupancy: $(e_g)^{3.8}(b_{2g})^2(a_{1g})^{1.2}$

Stepanow et al. Phys. Rev. B. 83, 220401 (2011)

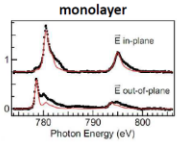
Co Phtallocyanine on gold



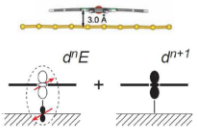
Stepanow et al. Phys. Rev. B. 83, 220401 (2011)

Co Phtallocyanine on gold

monolayer



XAS lineshape and XMCD signal cannot satisfactorily simulated with either d^7 or d^8 configuration



Charge transfer multiplet calculations

- Mixing of two configurations: $\psi = \alpha\, d^8(d^0) + \beta\, d^7(d^1)$
- Charge transfer via d_{z2}
- Hopping parameter t = 1 eV, ΔE = 0.8 eV between configurations
- Similar crystal field to powder samples

- Formation of singlet state with <S> = 0 and 61% d^7 and 39% d^8 character
- Charge fluctuation induced moment quenching

Stepanow et al. Phys. Rev. B. 83, 220401 (2011)

Why x-ray spectroscopy?

- local excitations > element specific
- sensitive to low concentrations
- applicable under extreme conditions
- Space-Time-Energy (combination with x-ray microscopy, time-resolution and high-resolution x-ray emission)