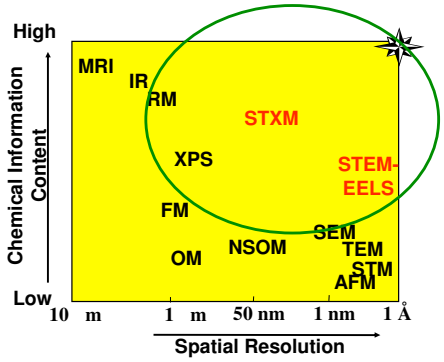
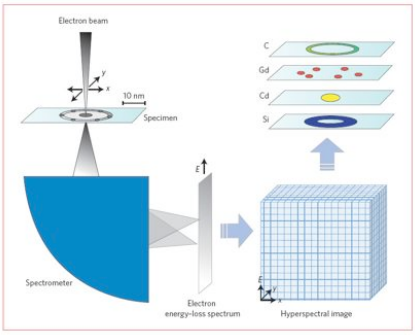
Chemical Microspectroscopy



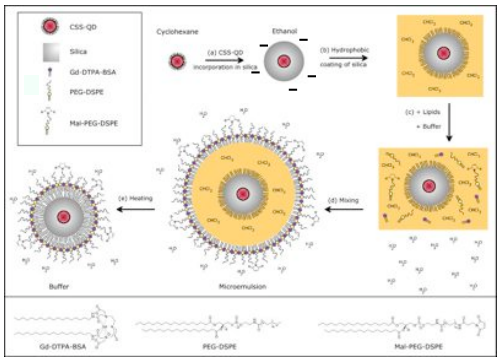
Review: ChemPhysChem 11, 951 (2010)

STEM-EELS chemical imaging



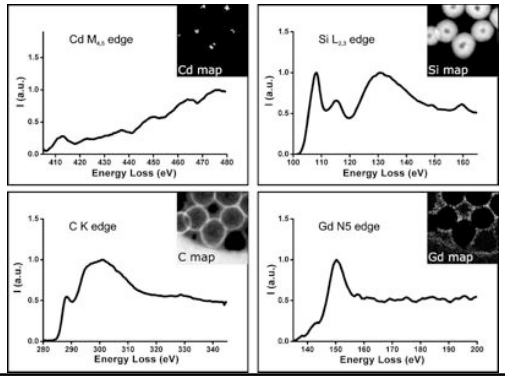
Nature Nanotechnology 5, 538 (2010) & News & Views 5, 480 (2010)

Lipid-coated nanocrystal@silica particles

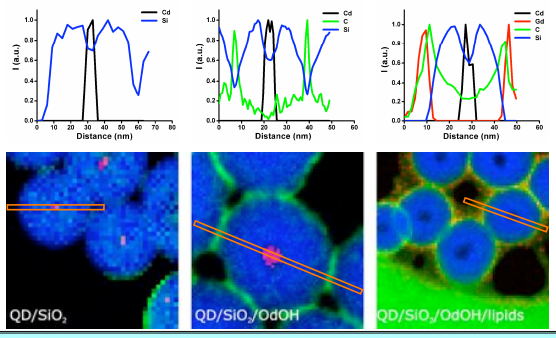


Koole *et al.* Bioconjugate Chem. **2008**

STEM-EELS chemical imaging



STEM-EELS chemical imaging



Nature nanotechnology (June 6 online)

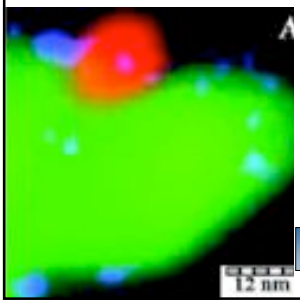
Fischer-Tropsch Synthesis

-The Fischer-Tropsch GTL process produces an extremely clean synthetic fraction of gasoil
- GTL fuel is virtually free of sulphur and aromatics.

STEM-EELS of Mn-doped Co/TiO2

STEM-EELS

Catalysis



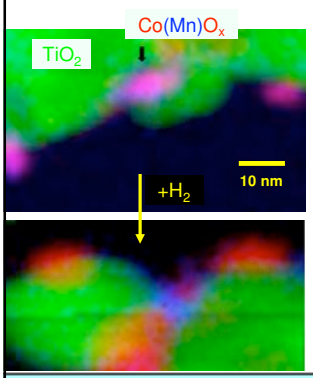
CO
$+H_2$

Fuels

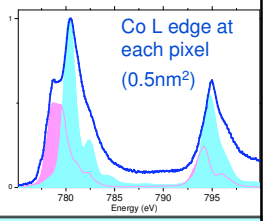
Co

TiO_2

SPACE: Electron Energy Loss in a TEM



Mn-doped Co on TiO_2

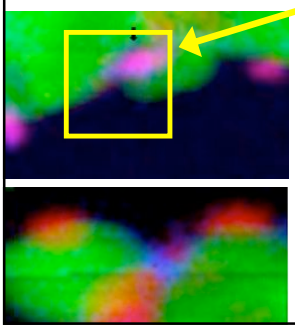


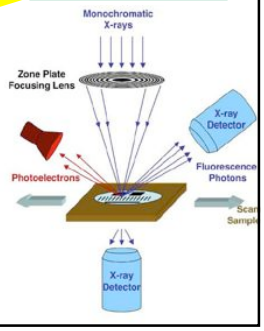
Fernando Morales et al., PCCP 7, 568 (2005); J. Catal. 230, 310 (2005)

SPACE: STEM-EELS versus STXM-XAS

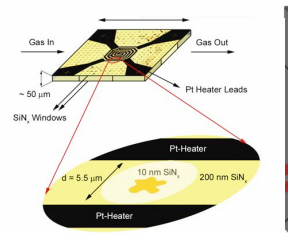
STEM-EELS
UHV, 0.5 nm

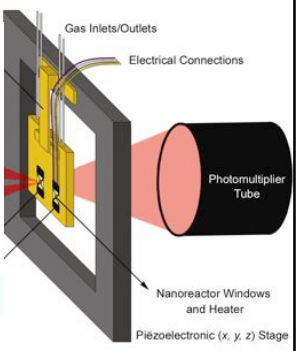
STXM-XAS
1 bar, 500ºC, 30 nm





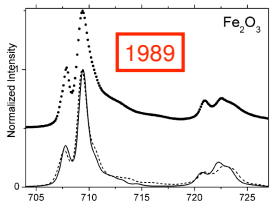
Nanoscale chemical imaging of a working catalyst

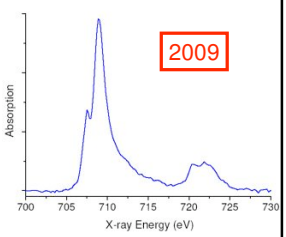




Emiel de Smit et al. **Nature** 456, 222 (2008); Angew. Chem. 48, 3632 (2009)

Metal L edges in 1989 and 2009

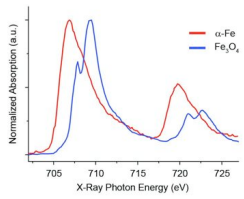


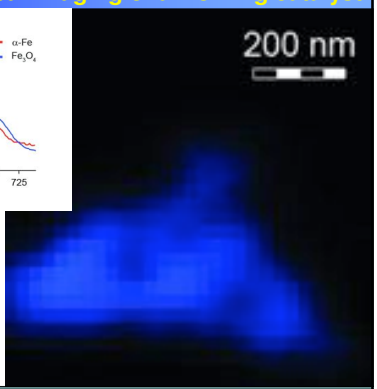


- UHV
- RT
- bulk

- 2 bar flowing gas
- up to 750K
- 20 nm resolution

Nanoscale chemical imaging of a working catalyst



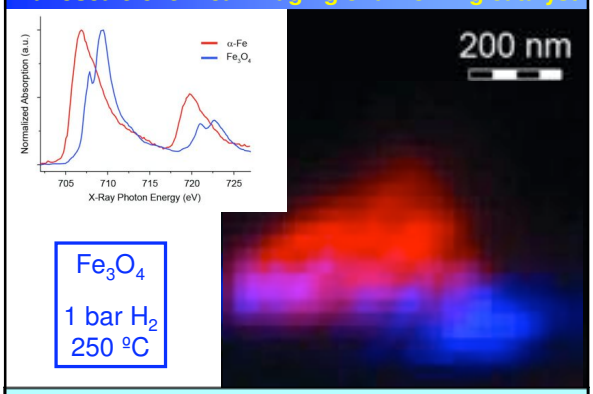


Fe_3O_4

1 bar H_2
150 ºC

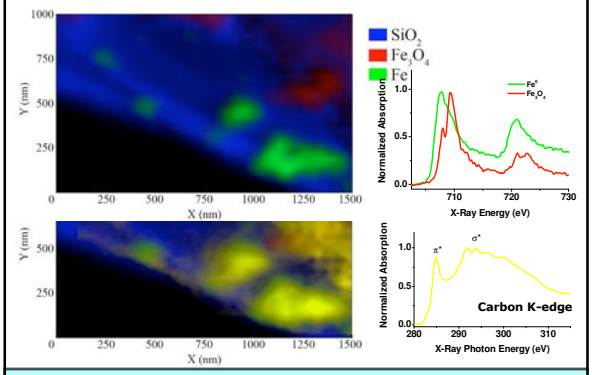
Emiel de Smit et al. **Nature** 456, 222 (2008); Angew. Chem. 48, 3632 (2009)

Nanoscale chemical imaging of a working catalyst



Emiel de Smit et al. **Nature** 456, 222 (2008); Angew. Chem. 48, 3632 (2009)

Nanoscale chemical imaging of a working catalyst



Emiel de Smit et al. **Nature** 456, 222 (2008); Angew. Chem. [early view] (2009); **poster 138**

Why X-ray Absorption?

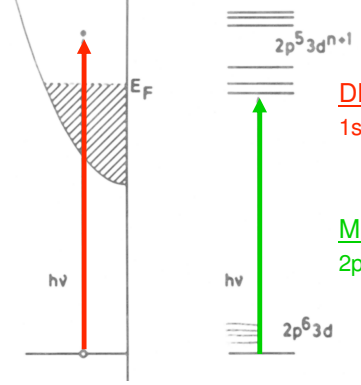
- Element specific
- Low concentrations (0.01-0.1 wt%)

- Valence, Spin-state, Crystal field energies
- Hybridization, MO energies / Density of states

- **Time:** excited states (mainly) in ps range
- **Pressure**: 1 bar/500 ºC flowing gas
- **Space**: 0.5 nm (STEM), 20 nm (STXM)

www.anorg.chem.uu.nl/people/staff/FrankdeGroot/

X-ray Absorption Spectroscopy



DFT:
1s edges

Multiplets:
2p, 3s, 3p edges

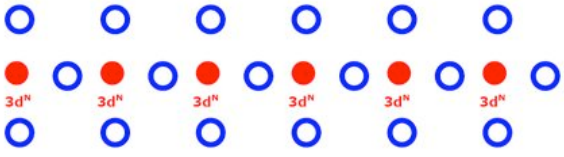
Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

ATOMIC PHYSICS
⇓
GROUP THEORY
⇓
MODEL HAMILTONIANS

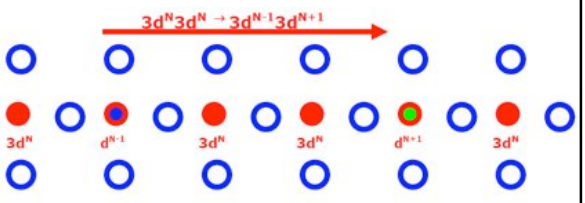
Charge Transfer Effects



Ground state of a transition metal system
$3d^N$ at every site

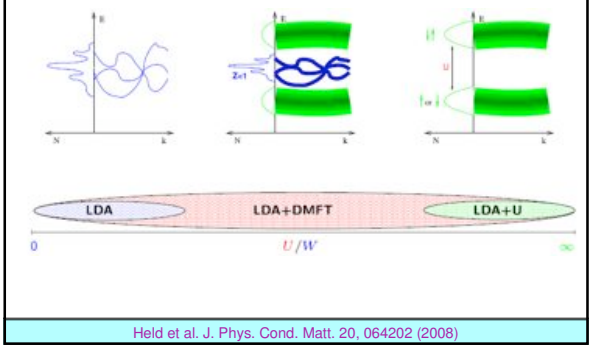
Charge fluctations

Charge Transfer Effects



Hubbard U for a $3d^8$ ground state:
U= $E(3d^7) + E(3d^9) - E(3d^8) - E(3d^8)$

Ligand-to-Metal Charge Transfer (LMCT):
Δ= $E(3d^9\underline{L}) - E(3d^8)$



Held et al. J. Phys. Cond. Matt. 20, 064202 (2008)

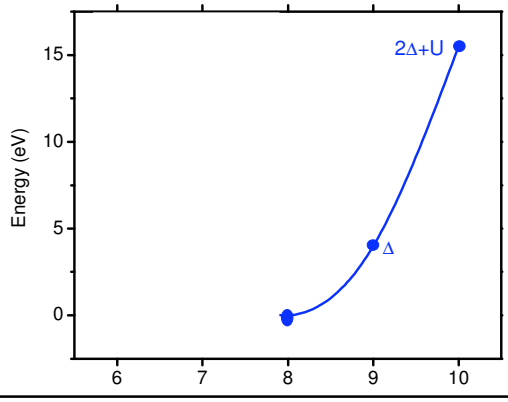
Charge Transfer Effects

Δ= $E(3d^9\underline{L}) - E(3d^8)$

$E(3d^{10}\underline{LL}') - E(3d^8)$
Two times charge transfer: 2**Δ**
Extra 3d3d interaction: U

2**Δ** +U

Charge Transfer Effects



Charge Transfer Effects in XAS

$E(3d^9\underline{L}) - E(3d^8)$ = **Δ**
$E(3d^{10}\underline{LL}') - E(3d^8)$ = 2**Δ** +U

2p XAS: $3d^8 \rightarrow 2p^5\ 3d^9$

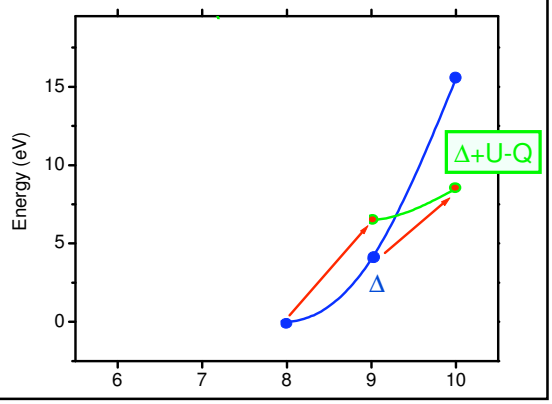
$E(2p^53d^9)$ = E_{2p}+ **Δ**

2p XAS: $3d^9\underline{L} \rightarrow 2p^5\ 3d^{10}\underline{L}$

$E(2p^53d^{10}\underline{L})$ = E_{2p}- Q +2Δ+U

Energy difference: E_{2p}- Q +2Δ+U- E_{2p} -Δ = **Δ+U-Q**
Q ≅ U+2 eV

Charge Transfer Effects in XAS



Charge Transfer Effects

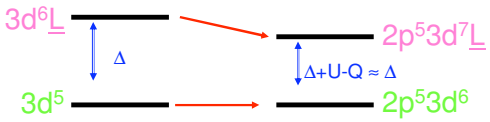
MnO: Ground state: $3d^5$ + $3d^6\underline{L}$

Energy of $3d^6\underline{L}$: Charge transfer energy Δ

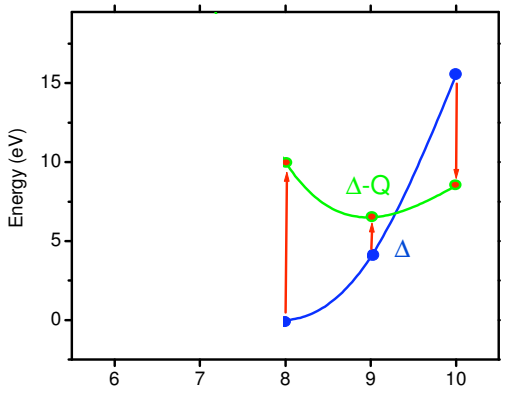
Charge Transfer Effects

MnO: Ground state: $3d^5$ + $3d^6\underline{L}$

Energy of $3d^6\underline{L}$: Charge transfer energy Δ

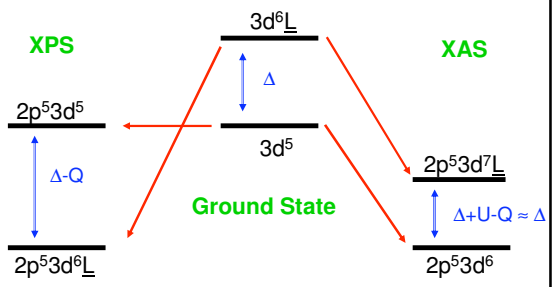


Charge Transfer Effects in XPS



Charge transfer effects in XAS and XPS

- Transition metal oxide: Ground state: $3d^5$ + $3d^6\underline{L}$
- Energy of $3d^6\underline{L}$: Charge transfer energy Δ

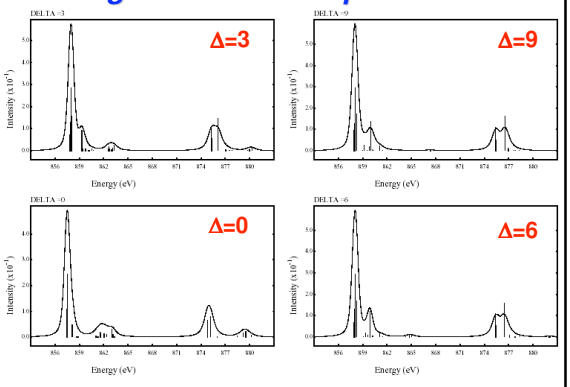


Charge Transfer Effects

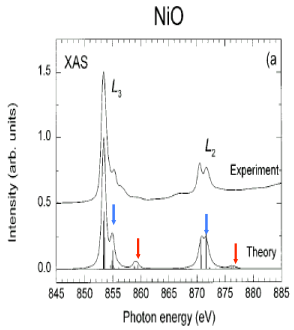
NiO: Ground state: $3d^8$ ($3d^8$)

+ $3d^9\underline{L}$ Charge transfer energy Δ
+ $3d^93d^7$ Hubbard U
+ $3d^{10}\underline{L}^2$ 2Δ+U
+ $3d^7\underline{L}$ Metal-ligand CT Δ_{MLCT}

Charge Transfer Multiplets of Ni^{2+}



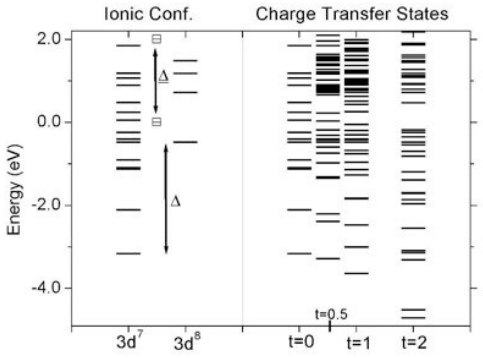
X-ray Absorption Spectroscopy



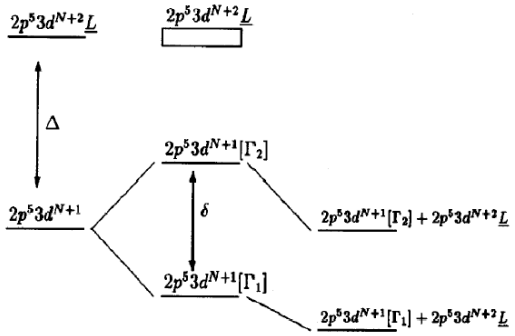
Spectral shape:
(1) Multiplet effects
(2) Charge Transfer

J. Elec. Spec. 67, 529 (1994)

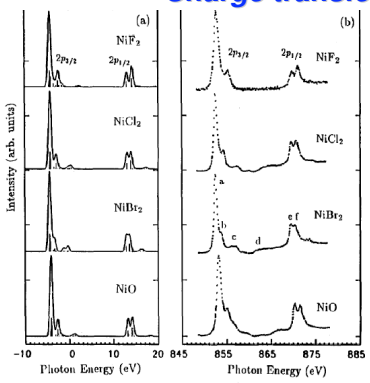
Charge transfer



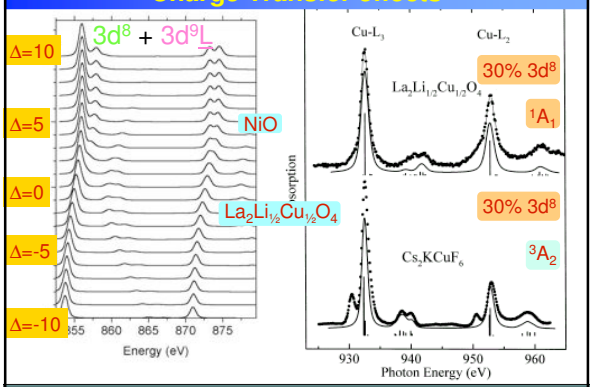
Charge transfer



Charge transfer



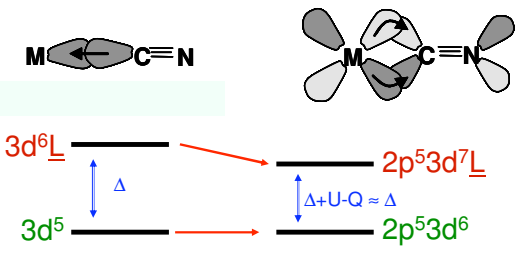
Charge Transfer effects



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

LMCT and MLCT: π - bonding

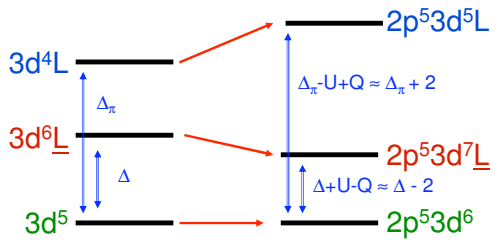
Fe^{III}: Ground state: $3d^5 + 3d^6\underline{L}$



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

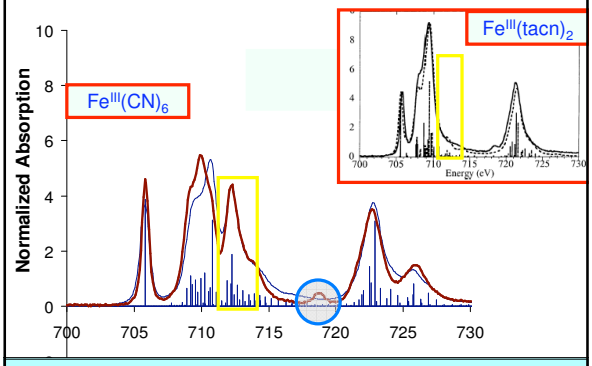
LMCT and MLCT: π - bonding

Fe^{III}: Ground state: $3d^5$ + $3d^6\underline{L}$ + $3d^4L$



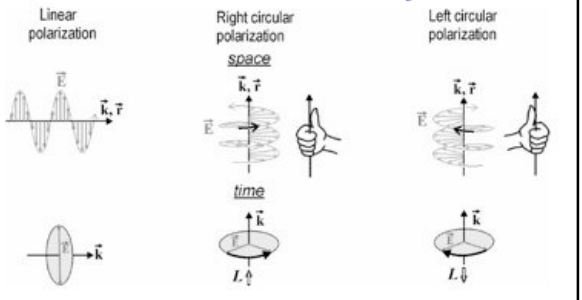
with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

LMCT and MLCT: π - bonding

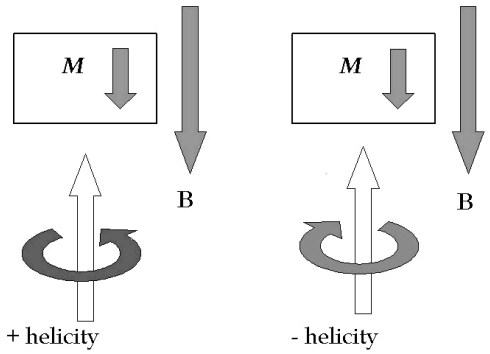


with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

Polarization of X-rays



X-MCD



X-MCD

Cu^{2+}: $3d^9$ → $2p^53d^{10}$

$[\underline{l_1},\underline{s_1}]=[-2,-1/2]$
L=2, S=1/2 → ^2D
J=5/2 or 3/2
More than half-full
→$^2D_{5/2}$

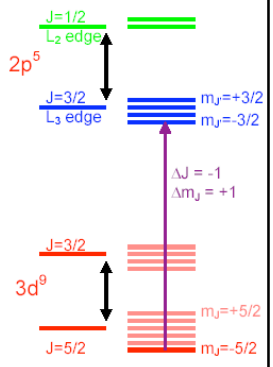
$[\underline{l_2},\underline{s_2}]=[-1,-1/2]$
L=1, S=1/2 → ^2P
J=3/2 or 1/2

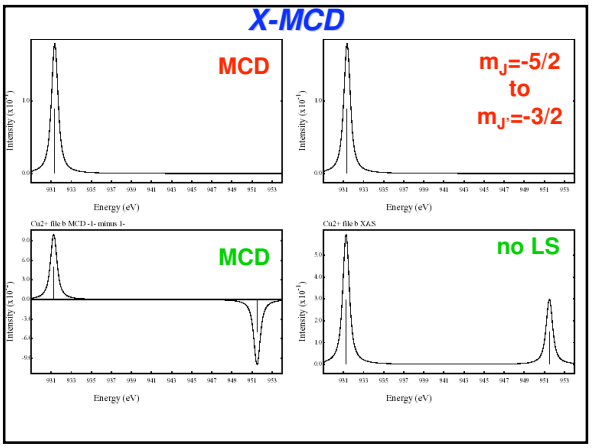
→ $^2P_{3/2}$ or $^2P_{1/2}$

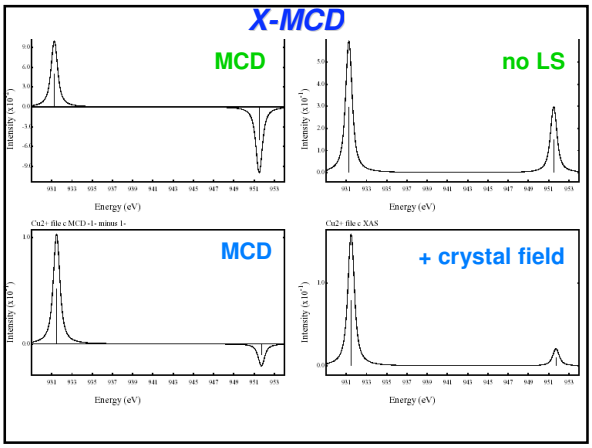
ΔJ= +1 or 0 or -1
light polarization q = m_J

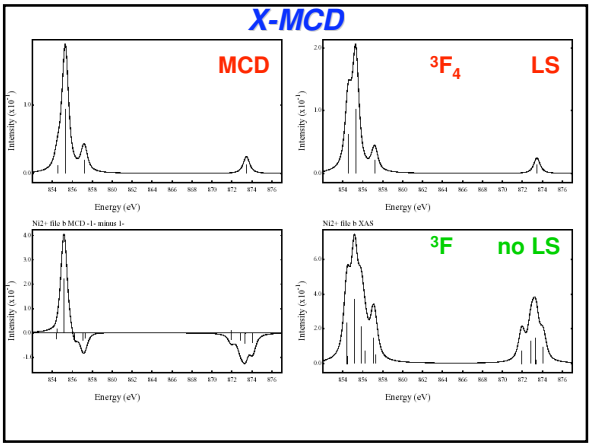
X-MCD

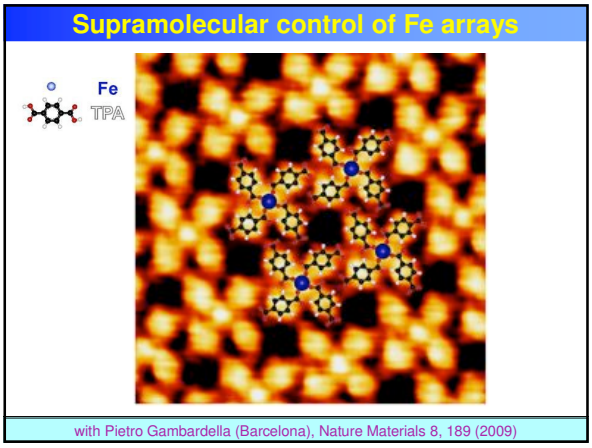
Cu^{2+}: $3d^9$

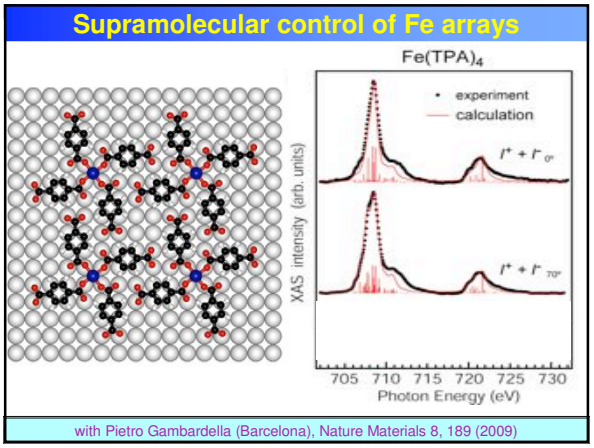


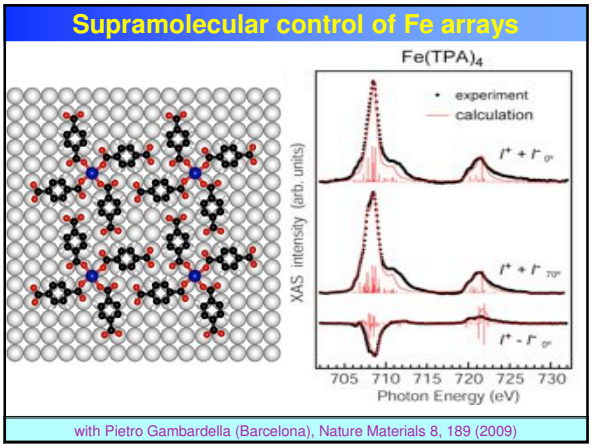

X-MCD
MCD
m_J=-5/2
to
$m_{J'}$=-3/2
MCD
no LS
Energy (eV)


X-MCD
MCD
no LS
MCD
+ crystal field
Energy (eV)

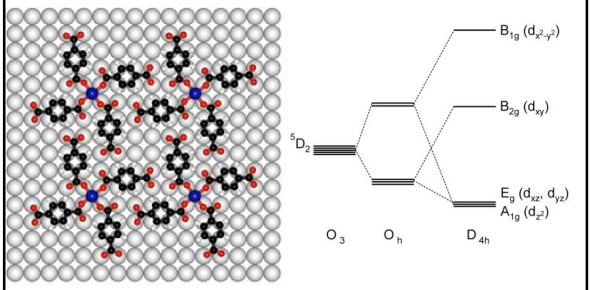

X-MCD
MCD
$^3F_4$
LS
^3F
no LS
Energy (eV)


Supramolecular control of Fe arrays
Fe
TPA
with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)


Supramolecular control of Fe arrays
$Fe(TPA)_4$
experiment
calculation
XAS intensity (arb. units)
705 710 715 720 725 730
Photon Energy (eV)
with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

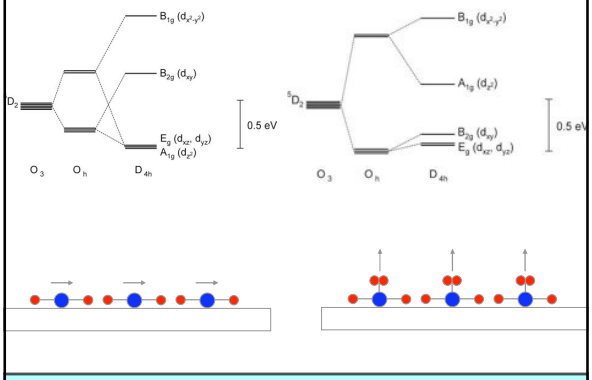

Supramolecular control of Fe arrays
$Fe(TPA)_4$
experiment
calculation
XAS intensity (arb. units)
705 710 715 720 725 730
Photon Energy (eV)
with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

Supramolecular control of Fe arrays



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

Supramolecular control of Fe arrays



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

Resonant Inelastic X-ray Scattering

(RIXS)

RIXS

Resonant Inelastic X-ray Scattering

or

Resonant Inelastic X-ray Spectroscopy

or

Resonant X-ray Emission Spectroscopy (RXES)

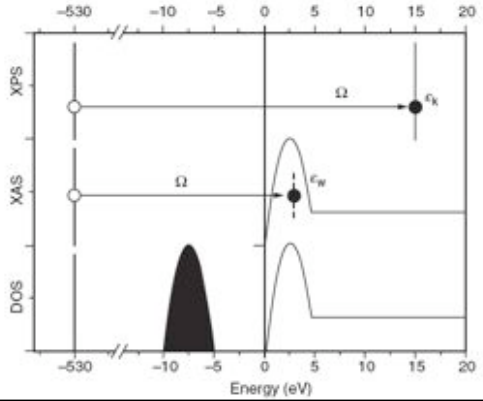
or

Resonant X-ray Raman Scattering (RXRS)

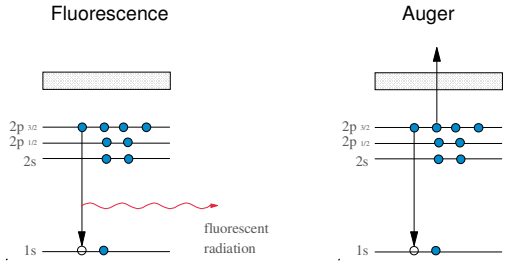
or

X-ray Energy Loss Spectroscopy (XELS)

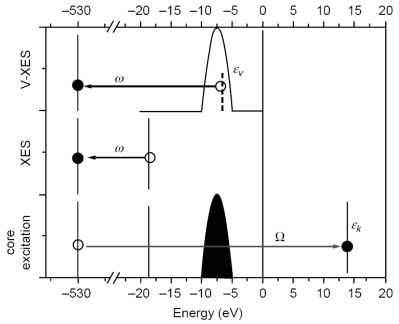
X-ray absorption and X-ray photoemission



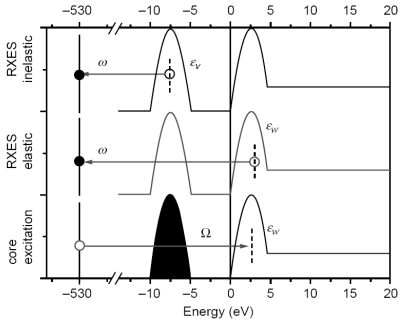
Core Hole Decay



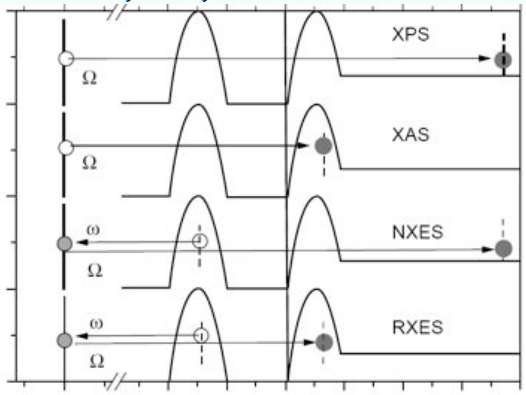
X-ray emission



Resonant X-ray emission spectroscopy



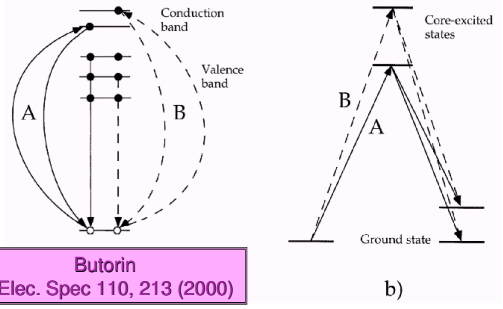
XPS, XAS, NXES and RXES



RIXS

Single-particle approach

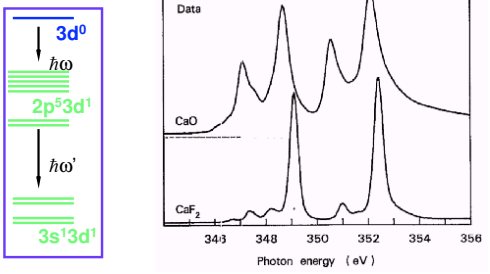
Many-body approach



Butorin
J. Elec. Spec 110, 213 (2000)

Resonant Inelastic X-ray Spectroscopy

2p XAS of CaF_2



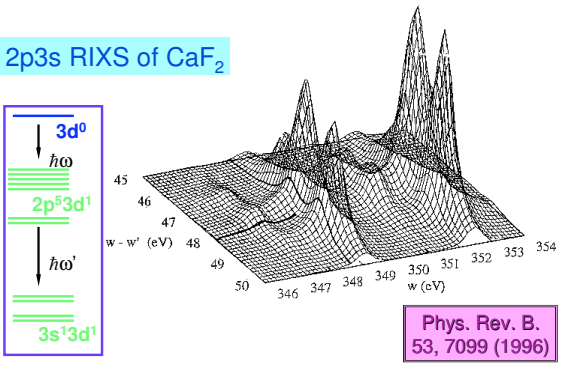
2p3s RIXS of ScF_3

- Ground state is $3d^0$
- Excitation (i_0) $3d^0 \rightarrow$ (x) $2p^53d^1$
- Decay (x) $2p^53d^1 \rightarrow$ (f) $3s^13d^1$

$$I(\omega,\omega') = \sum_f \left| \sum_x \frac{\langle f|r_q|x\rangle\langle x|r_q|i_0\rangle}{E_{i_0}+\omega-E_x-i\Gamma_x} \right|^2 L_f(\omega-\omega')G_E$$

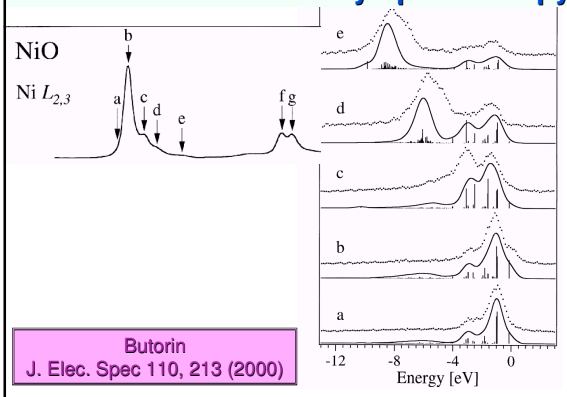
Resonant Inelastic X-ray Scattering

2p3s RIXS of CaF_2



Phys. Rev. B. 53, 7099 (1996)

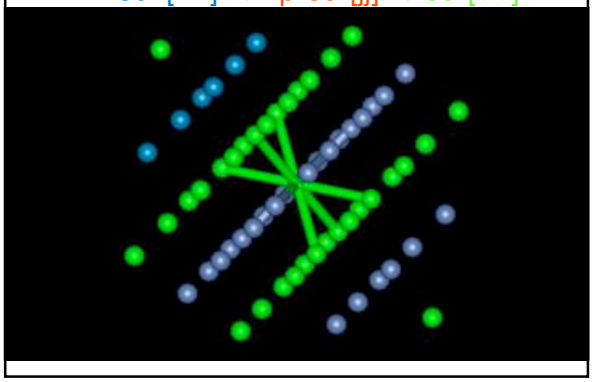
Resonant Inelastic X-ray Spectroscopy



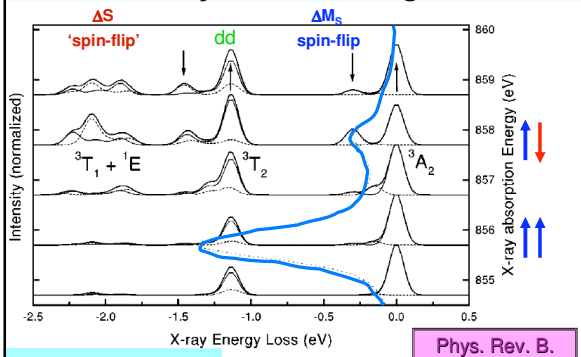
Butorin J. Elec. Spec 110, 213 (2000)

Soft x-ray RIXS and magnetism

Ni^{II} $3d^8$ [↑↑] → $2p^5 3d^9$[jj] → $3d^8$[↓↓]



Soft x-ray RIXS and magnetism

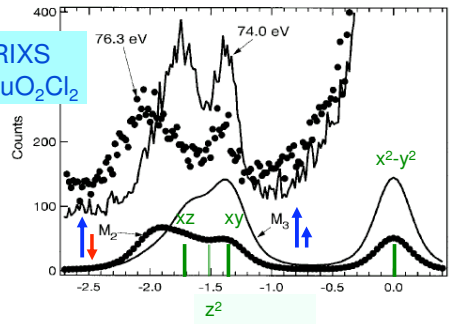


2p3d RIXS of NiO

Phys. Rev. B. 57, 14584 (1998)

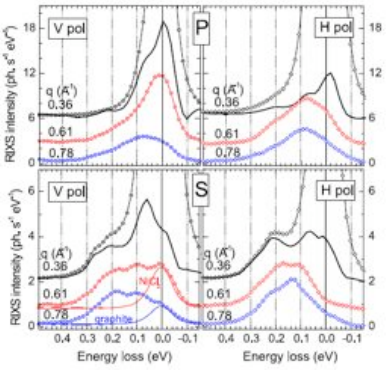
Soft x-ray RIXS and magnetism

3p3d RIXS of $Sr_2CuO_2Cl_2$



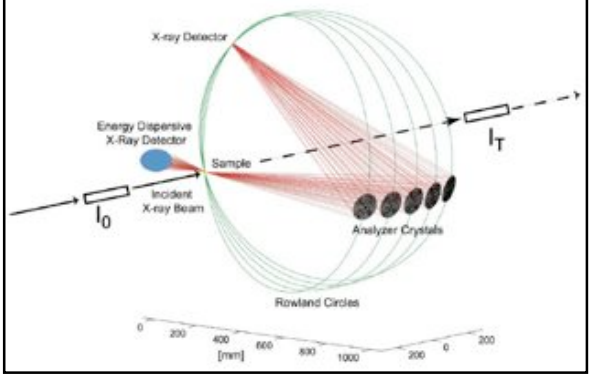
$\Phi_0 \rightarrow \underline{3p} \rightarrow \Phi_0$ + dd + spin-flip

Phys. Rev. Lett. 80, 5204 (1998)

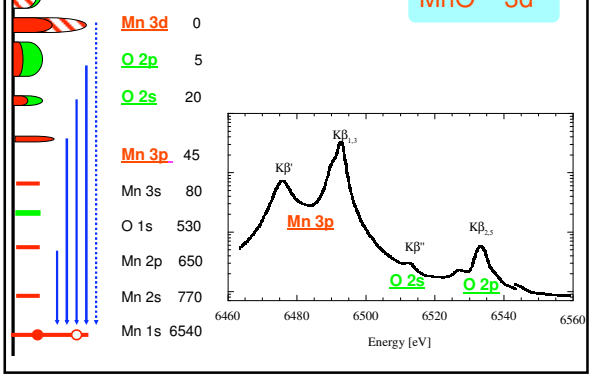


Ghiringhelli et al. Phys. Rev. Lett. 102, 027401 (2009)

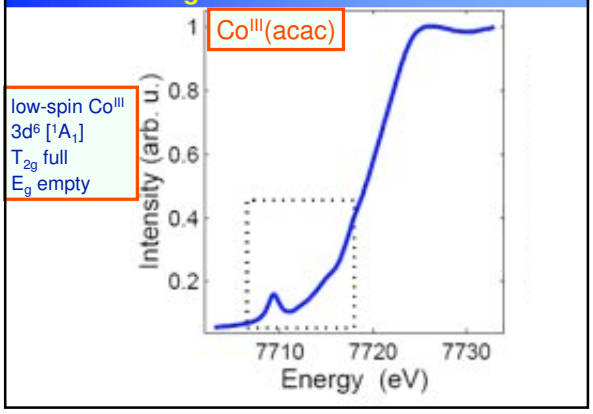
Pre-edges structures in 1s XAS



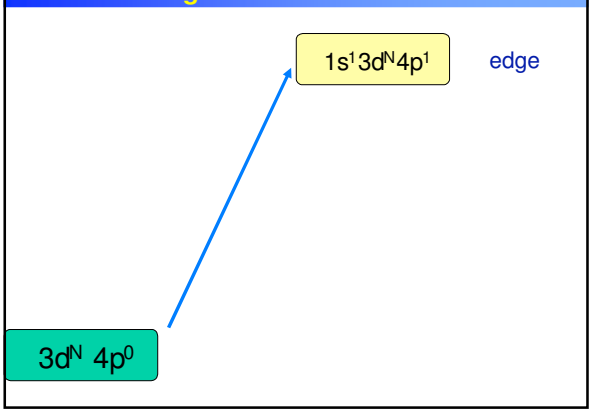
Selective XAFS



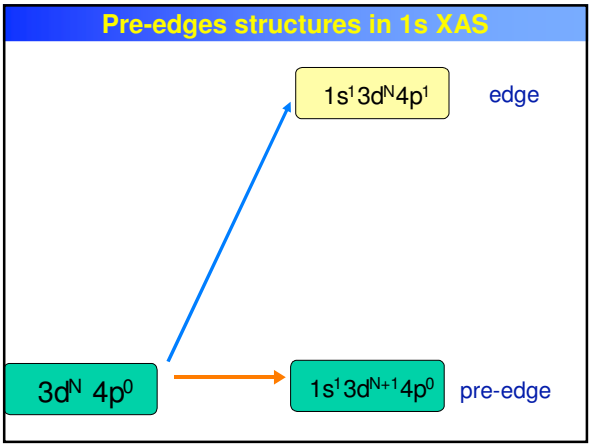
Pre-edges structures in 1s XAS



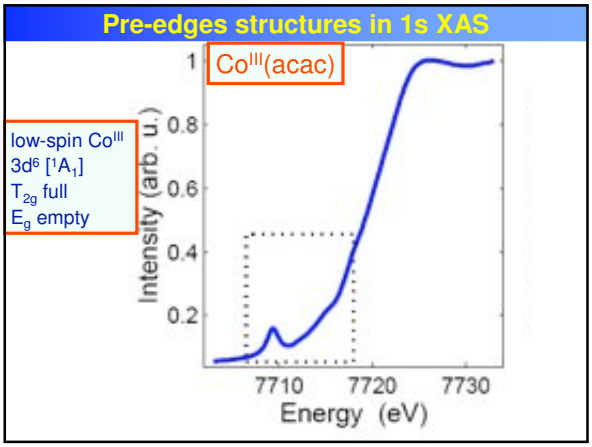
Pre-edges structures in 1s XAS



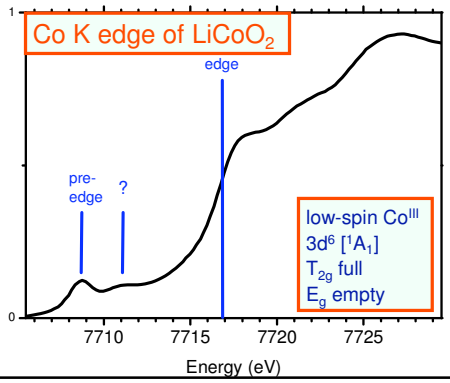
Pre-edges structures in 1s XAS



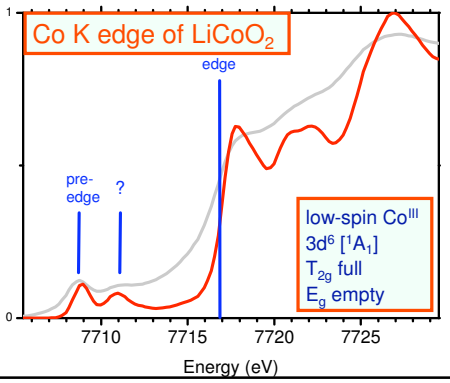
Pre-edges structures in 1s XAS



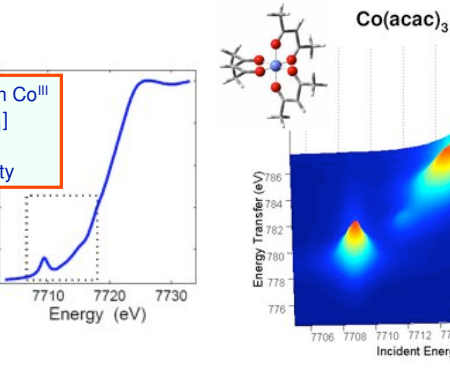
Pre-edges structures in 1s XAS



Pre-edges structures in 1s XAS

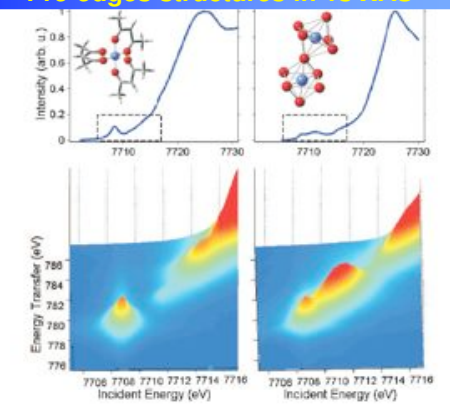


Pre-edges structures in 1s XAS

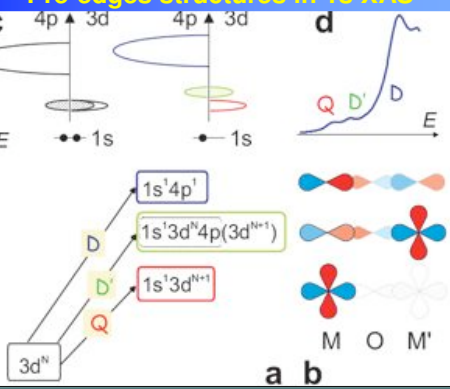


Vanko et al. (submitted)

Pre-edges structures in 1s XAS

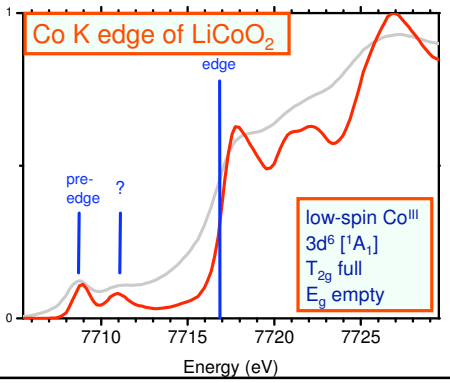


Pre-edges structures in 1s XAS

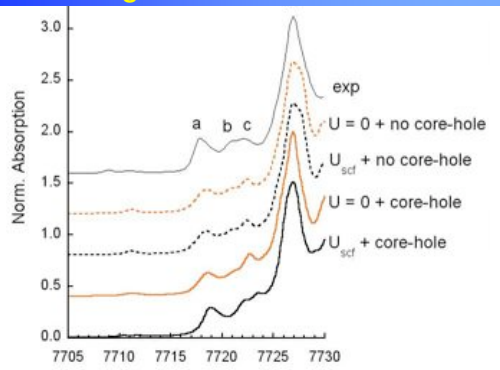


J. Phys. Cond. Matt. 21, 104207 (2009)

Pre-edges structures in 1s XAS

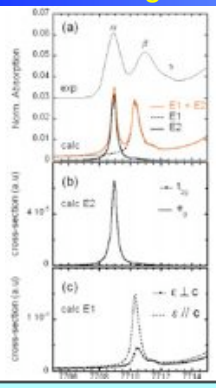


Pre-edges structures in 1s XAS



Juhin Phys. Rev. B. 81, 115115 (2010)

Pre-edges structures in 1s XAS

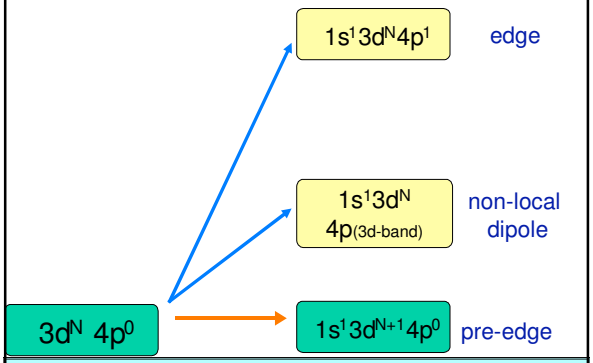


LDA+U
+ core hole
with PWSCF

$LiCoO_2$

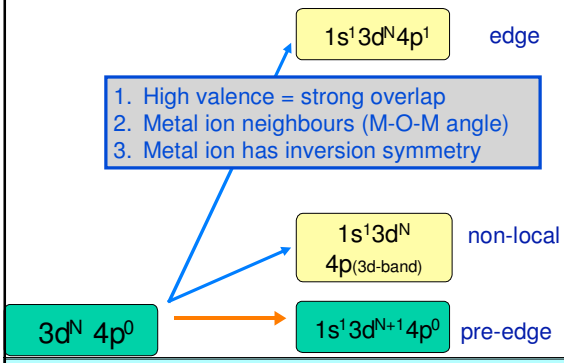
Juhin Phys. Rev. B. 81, 115115 (2010)

Pre-edges structures in 1s XAS



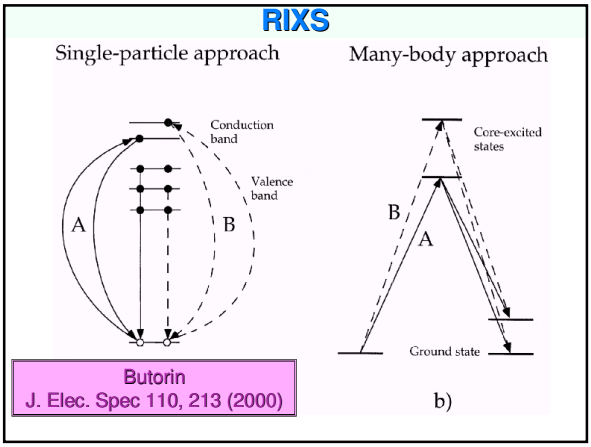
J. Phys. Cond. Matt. 21, 104207 (2009)

Pre-edges structures in 1s XAS



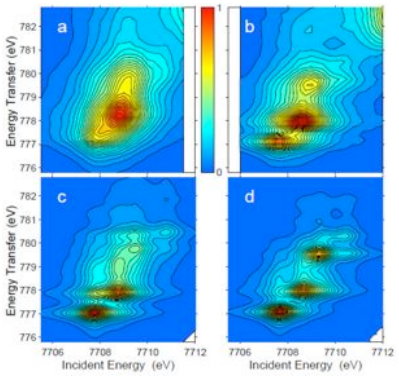
J. Phys. Cond. Matt. 21, 104207 (2009)

RIXS

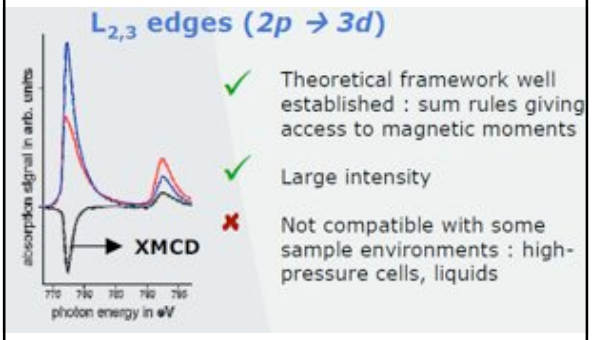


Butorin
J. Elec. Spec 110, 213 (2000)

RIXS of CoO



RIXS-MCD at the K pre-edge



✓ Theoretical framework well established : sum rules giving access to magnetic moments

✓ Large intensity

✘ Not compatible with some sample environments : high-pressure cells, liquids

RIXS-MCD at the K pre-edge

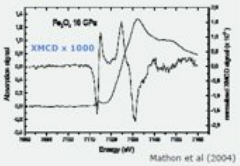
K pre-edge ($1s \rightarrow 3d$)

✓ Compatible with high-pressure cells

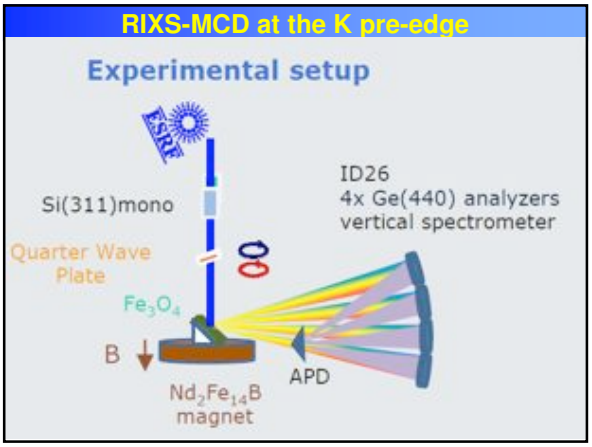
✘ Difficult to interpret (no SO coupling on *1s* orbital)

✘ XMCD at K pre-edge obscured by broadening and edge tail

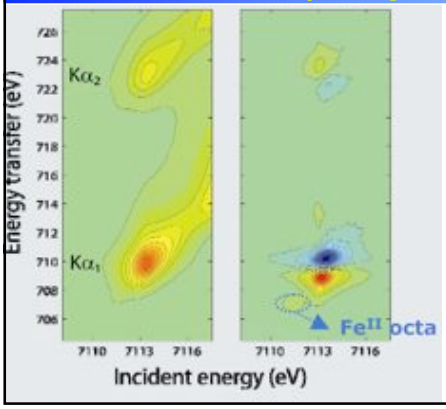
✘ Very small intensity (a few 0.1 %)



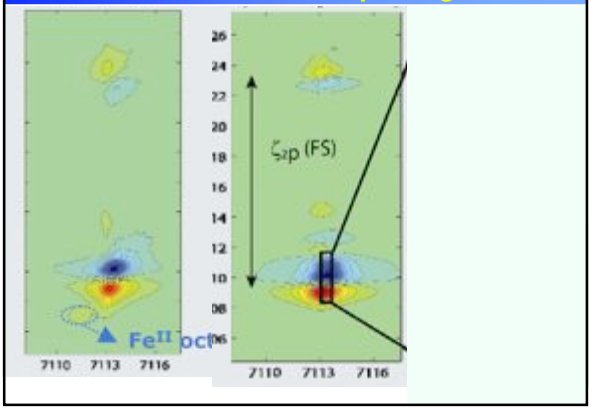
RIXS-MCD at the K pre-edge



RIXS-MCD at the K pre-edge of Fe_3O_4

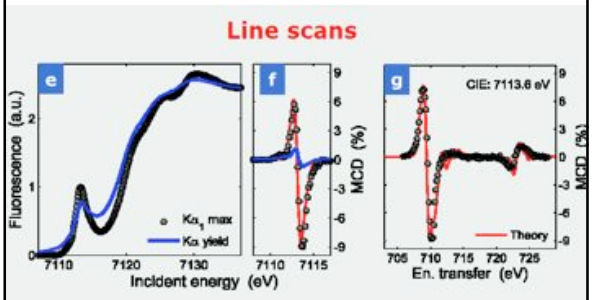


RIXS-MCD at the K pre-edge



RIXS-MCD at the K pre-edge

Line scans



XMCD at high-pressure

Phys. Rev. Lett. (soon)