The Abdus Salam
International Centre for Theoretical Physics

United Nations
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2139-15

School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

26 April - 7 May, 2010

X-ray absorption spectroscopy

F. De Groot
Utrecht University
Netherlands

X-ray Absorption Spectroscopy

(K edges)

- Interaction of X-rays with matter
- XANES and EXAFS
- XANES analysis
- Pre-edge analysis
- Resonant Inelastic X-ray Spectroscopy (RIXS)

Frank de Groot

Studie: scheikunde in **Nijmegen** (1982-1986)
Promotie: vaste stof chemie **Nijmegen** (1991)

Post-doc: Laboratoire pour l' utilisation du rayonnement électromagnétique in **Parijs** (93-94)
Post-doc: vaste stof natuurkunde in **Groningen** (95-98)

Universitair hoofddocent: anorganische chemie **Utrecht**

- Theorie van röntgenspectroscopie
- Ontwikkelen nieuwe röntgenspectroscopieën
- Onderzoek aan heterogene katalysatoren
- Onderzoek aan vaste stoffen

Why X-ray Absorption?

- Element specific
- Sensitive to low concentrations
  (0.01-0.1 %)
- Applicable under extreme conditions
  (high-pressure, high temperature, in-situ)
- Applicable to gasses, liquids and solids
- Combination with microscopy

What do we learn from XAS?

- Metal valence during synthesis and reaction
- Metal coordination
  (very small) nanoparticles/clusters
- Metal site symmetry
- d-band occupation
  (3d, 4d or 5d; metal versus oxide, valence)
- Energy positions of empty bands of adsorbates
  (CO, H_2 on Pt, nature of adsorption site)
- **20 nm spatial-resolved, 50 ps time-resolved**

Interaction of x-rays with matter 1

The photon moves towards the atom

Interaction of x-rays with matter 1

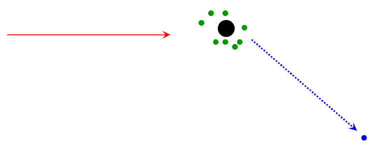
The photon meets an electron and is annihilated

Interaction of x-rays with matter 1

The electron gains the energy of the photon
and is turned into a **blue electron**.

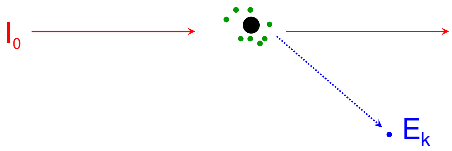
Interaction of x-rays with matter 1

The blue electron (feeling lonely) leaves the atom
and scatters of neighbors
or escapes from the sample



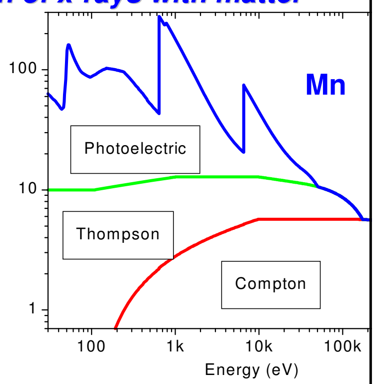
Interaction of x-rays with matter 1

The probability of photon annihilation determines
the intensity of the transmitted photon beam



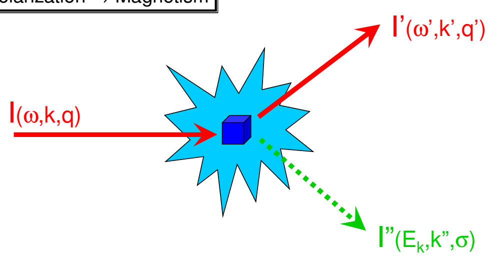
Interaction of x-rays with matter

- XAFS studies photoelectric absorption
- Elastic scattering (Thompson)
- Inelastic scattering
- (Compton)



Interaction of x-rays with matter

Energy → Spectroscopy
Direction → Structure
Polarization → Magnetism



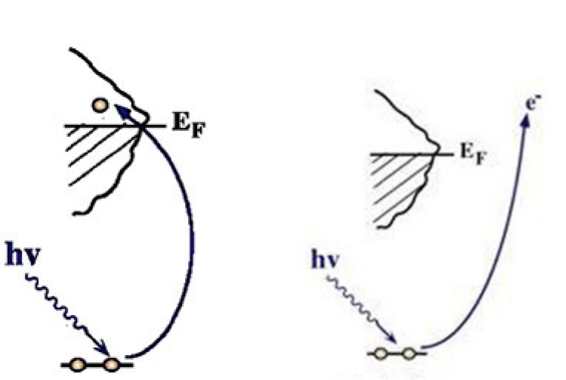
X-ray absorption and X-ray photoemission

Excitation of core electrons to empty states.

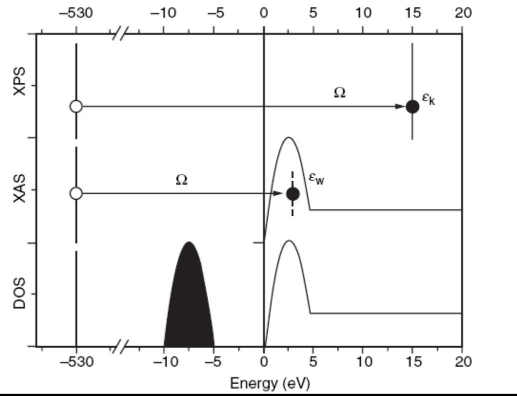
Spectrum given by the **Fermi Golden Rule**

$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \middle| T_1 \middle| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

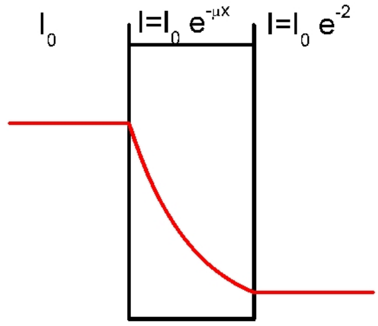
X-ray absorption and X-ray photoemission



X-ray absorption and X-ray photoemission



X-ray absorption



X-ray absorption

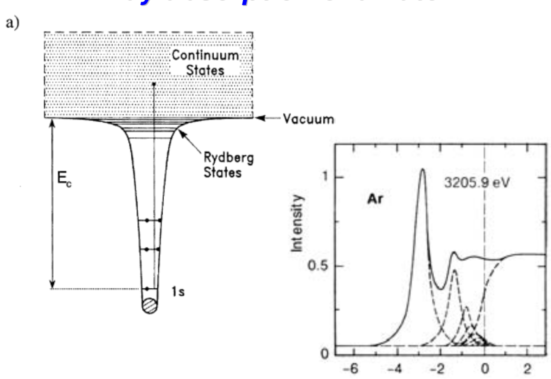
$$\ln \frac{I_0}{I_t} = \varepsilon \cdot c \cdot l$$

- Lambert-Beer

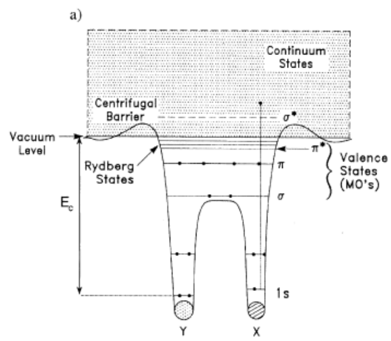
$$\mu = \frac{1}{x} \ln \frac{I_0}{I_t}$$

- μ = absorption coefficient
- x = sample thickness
- Measure x-ray intensity before and after sample

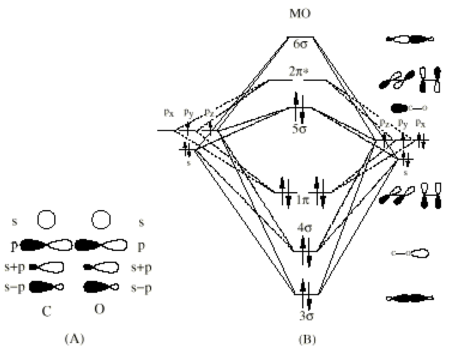
X-ray absorption of an atom



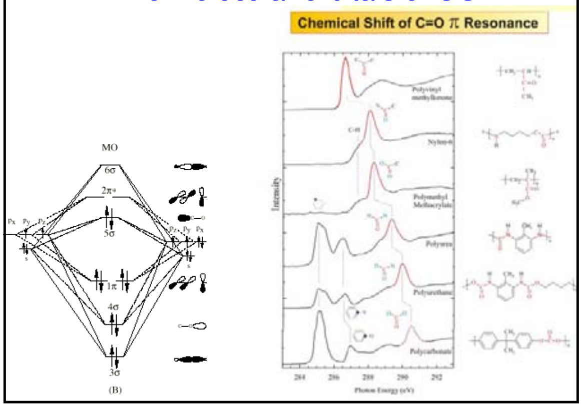
X-ray absorption of a molecule



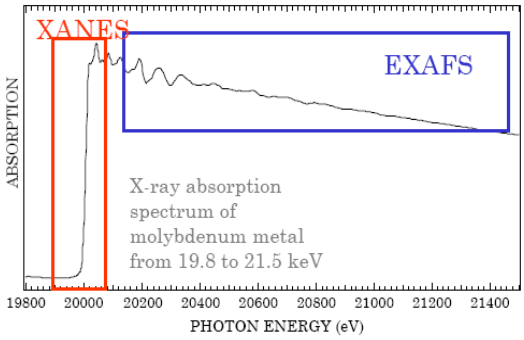
The molecular orbitals of CO



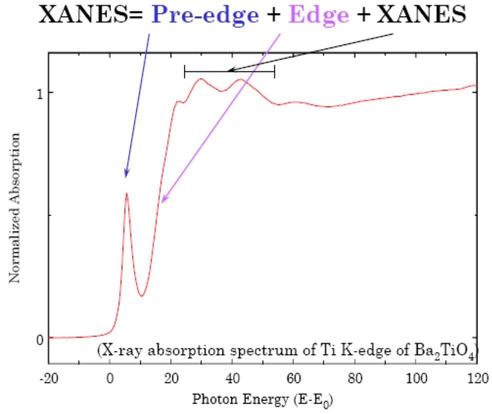
The molecular orbitals of CO



X-ray absorption



XANES= Pre-edge + Edge + XANES



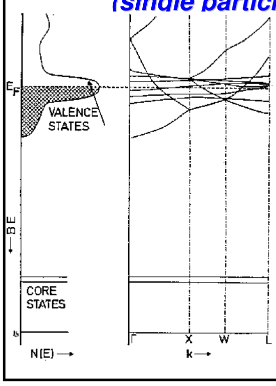
X-ray absorption

Excitation of core electrons to empty states.

Spectrum given by the **Fermi Golden Rule**
(name Golden Rule given by Fermi; rule itself given by Dirac)

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

X-ray absorption
(single particle interpretation)

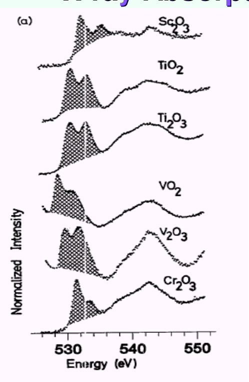


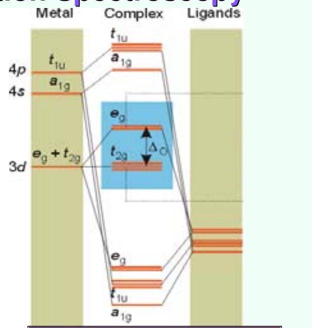
)ensity of States (DOS) is the
ıtegral over k-space of the
ıand structure.

)ore states have no dispersion.

(AS preserves momentum (k)

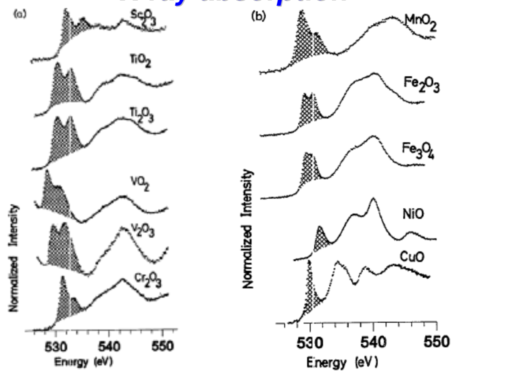
X-ray Absorption Spectroscopy



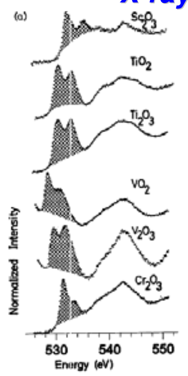


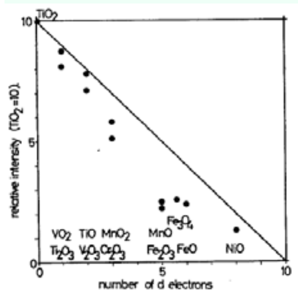
Phys. Rev. B.
40, 5715 (1989) / 48, 2074 (1993)

X-ray absorption



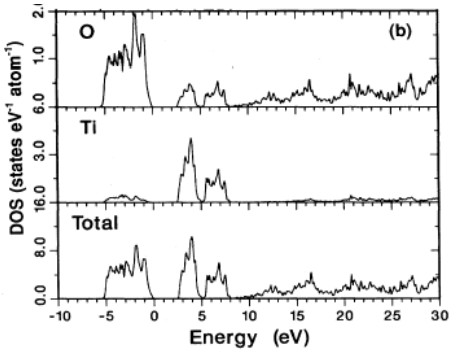
X-ray absorption



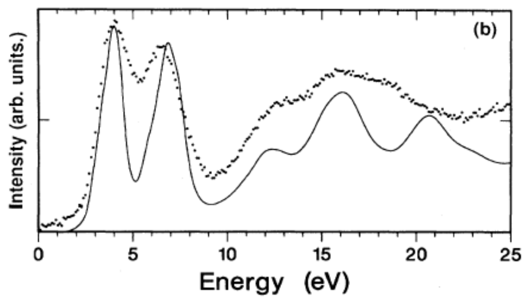


Phys. Rev. B.
40, 5715 (1989)

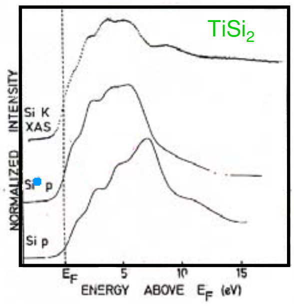
Electronic Structure



Electronic Structure

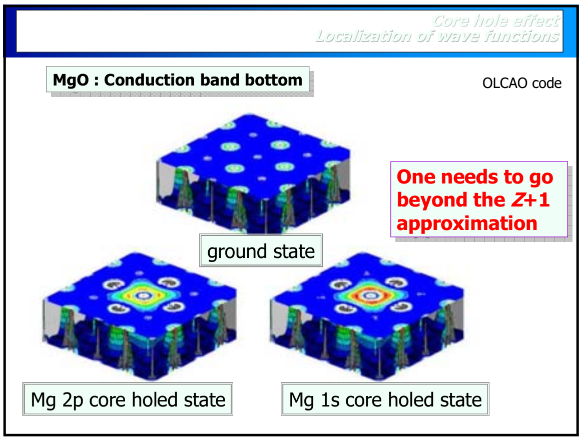


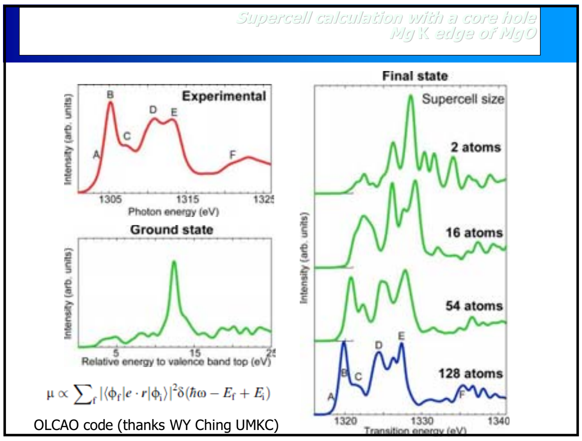
X-ray absorption: core hole effect

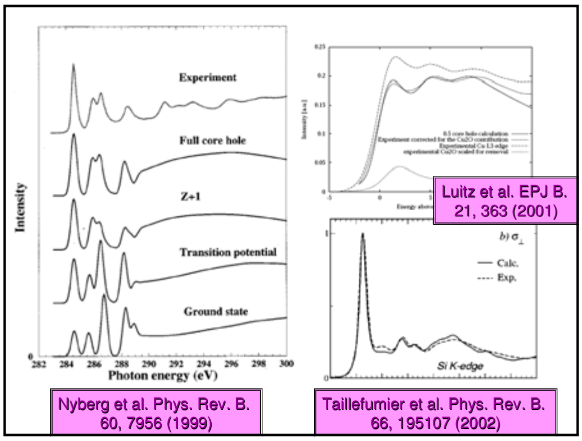


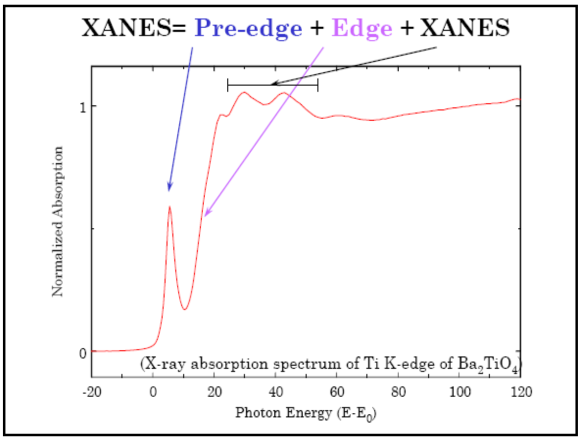
- **Final State Rule:** Spectral shape of XAS looks like final state DOS
- **Initial State Rule:** Intensity of XAS is given by the initial state

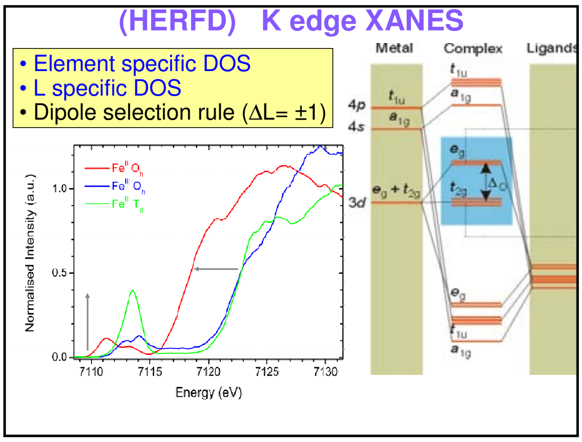
Phys. Rev. B.
41, 11899 (1991)

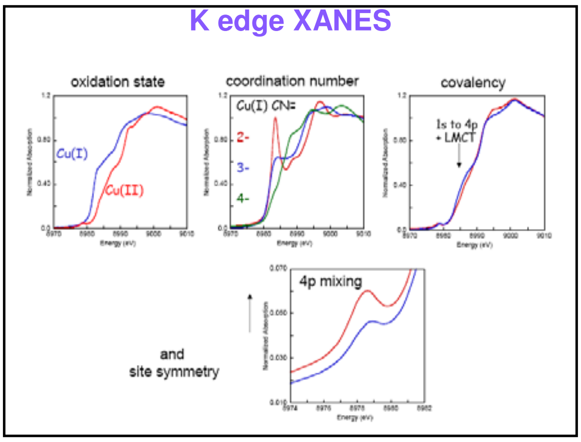

Core hole effect
Localization of wave functions
MgO : Conduction band bottom
OLCAO code
One needs to go beyond the Z+1 approximation
ground state
Mg 2p core holed state
Mg 1s core holed state


Supercell calculation with a core hole
Mg K edge of MgO
Experimental
Photon energy (eV)
Ground state
Relative energy to valence band top (eV)
Final state
Supercell size
2 atoms
16 atoms
54 atoms
128 atoms
Transition energy (eV)
OLCAO code (thanks WY Ching UMKC)

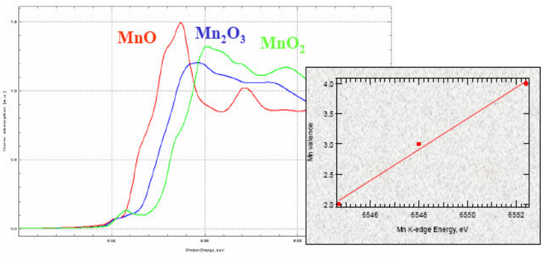

Experiment
Full core hole
Z+1
Transition potential
Ground state
Intensity
Photon energy (eV)
Luitz et al. EPJ B. 21, 363 (2001)
Calc.
Exp.
Si K-edge
Nyberg et al. Phys. Rev. B. 60, 7956 (1999)
Taillefumier et al. Phys. Rev. B. 66, 195107 (2002)


XANES= Pre-edge + Edge + XANES
Normalized Absorption
(X-ray absorption spectrum of Ti K-edge of Ba2TiO4)
Photon Energy (E-E0)


(HERFD) K edge XANES
• Element specific DOS
• L specific DOS
• Dipole selection rule (ΔL= ±1)
Metal
Complex
Ligands
Normalised Intensity (a.u.)
Energy (eV)


K edge XANES
oxidation state
coordination number
covalency
Cu(I)
Cu(II)
Cu(I) CN=
1s to 4p + LMCT
4p mixing
and
site symmetry

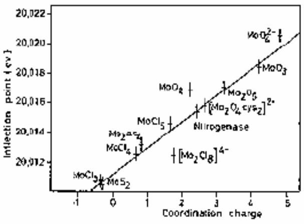
XANES: qualitative analysis



Edge position gives valence

XANES: qualitative analysis

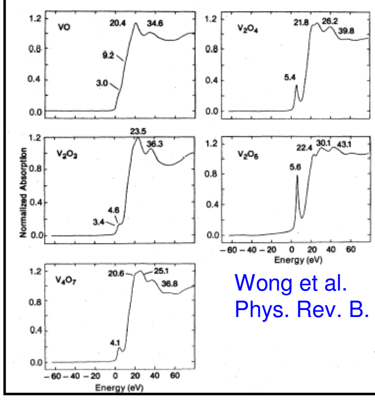
Mo K-edge



Ref: Cramer et al., JACS, 98 (1976) 1287

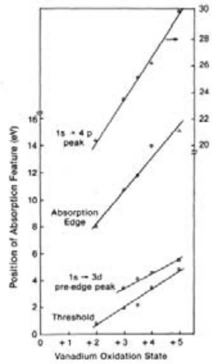
Edge position gives valence

XANES: qualitative analysis



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

XANES: qualitative analysis

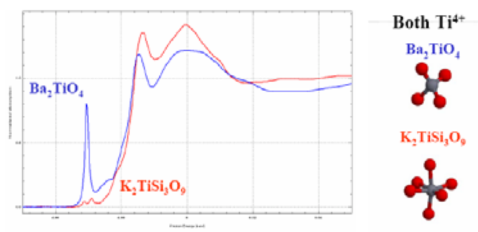


Edge position gives valence

Pre-edge gives valence

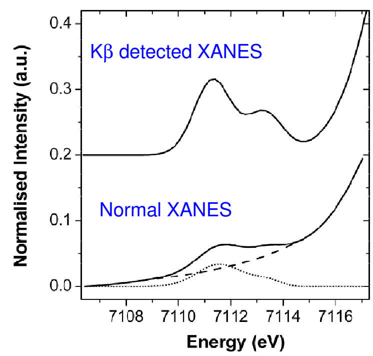
Different slopes

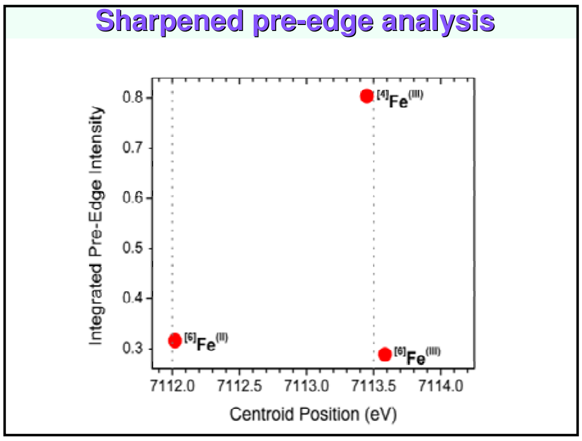
XANES: qualitative analysis

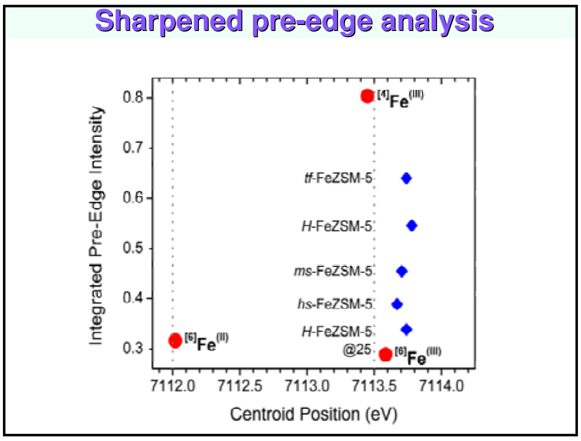


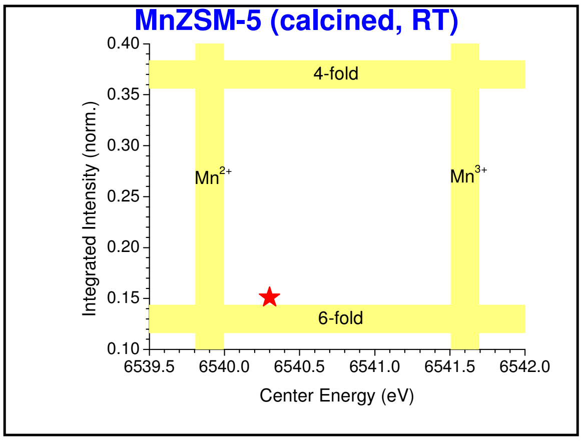
Pre-edge intensity gives site symmetry

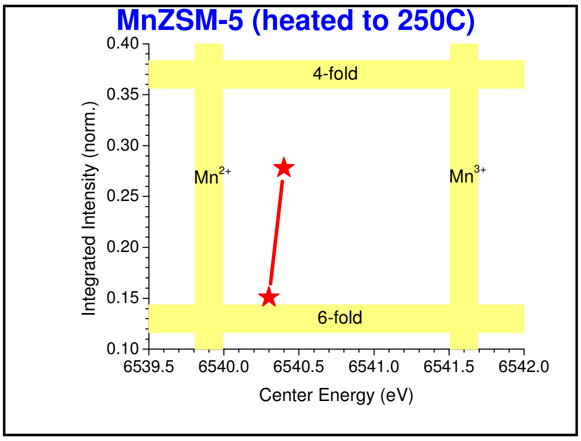
Spectral Sharpening

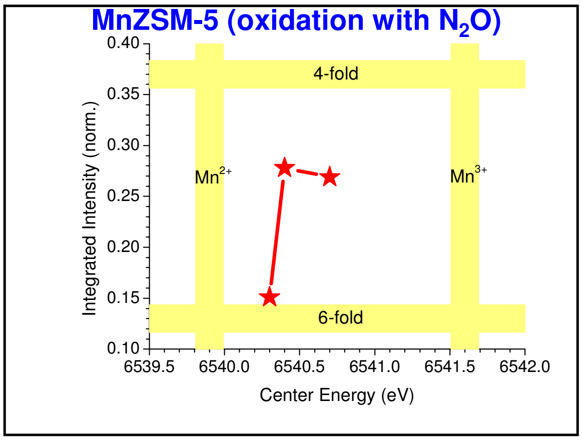


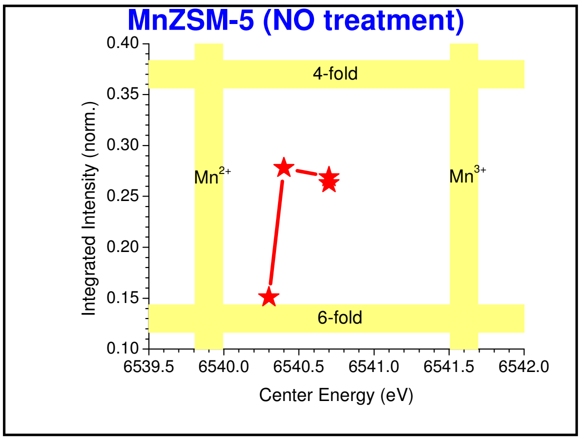

Sharpened pre-edge analysis
Integrated Pre-Edge Intensity
0.8
0.7
0.6
0.5
0.4
0.3
[4]Fe(III)
[6]Fe(II)
[6]Fe(III)
7112.0
7112.5
7113.0
7113.5
7114.0
Centroid Position (eV)


Sharpened pre-edge analysis
Integrated Pre-Edge Intensity
0.8
0.7
0.6
0.5
0.4
0.3
[4]Fe(III)
tf-FeZSM-5
H-FeZSM-5
ms-FeZSM-5
hs-FeZSM-5
H-FeZSM-5
@25
[6]Fe(II)
[6]Fe(III)
7112.0
7112.5
7113.0
7113.5
7114.0
Centroid Position (eV)

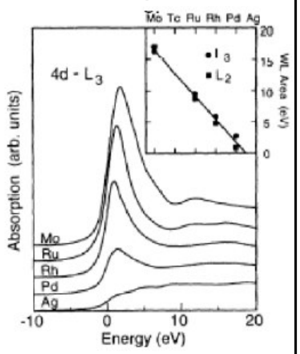

MnZSM-5 (calcined, RT)
Integrated Intensity (norm.)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
4-fold
6-fold
Mn2+
Mn3+
6539.5
6540.0
6540.5
6541.0
6541.5
6542.0
Center Energy (eV)


MnZSM-5 (heated to 250C)
Integrated Intensity (norm.)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
4-fold
6-fold
Mn2+
Mn3+
6539.5
6540.0
6540.5
6541.0
6541.5
6542.0
Center Energy (eV)


MnZSM-5 (oxidation with N2O)
Integrated Intensity (norm.)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
4-fold
6-fold
Mn2+
Mn3+
6539.5
6540.0
6540.5
6541.0
6541.5
6542.0
Center Energy (eV)

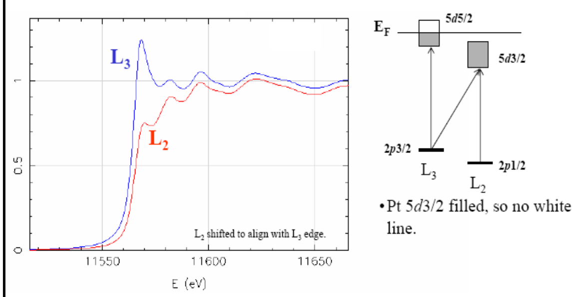

MnZSM-5 (NO treatment)
Integrated Intensity (norm.)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
4-fold
6-fold
Mn2+
Mn3+
6539.5
6540.0
6540.5
6541.0
6541.5
6542.0
Center Energy (eV)

XANES: qualitative analysis



L edge of 4d-systems > number of empty 4d states

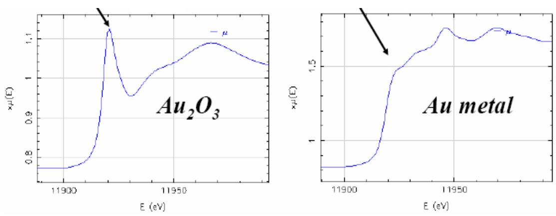
XANES: qualitative analysis



L edge of 5d-systems > number of empty 5d states

Difference between $5d^{3/2}$ and $5d^{5/2}$

XANES: qualitative analysis



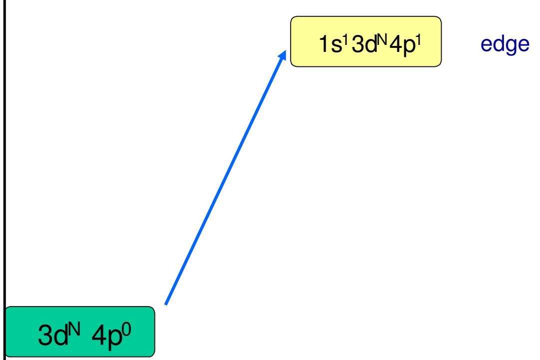
L edge of 5d-systems > number of empty 5d states

Difference between metal and oxide

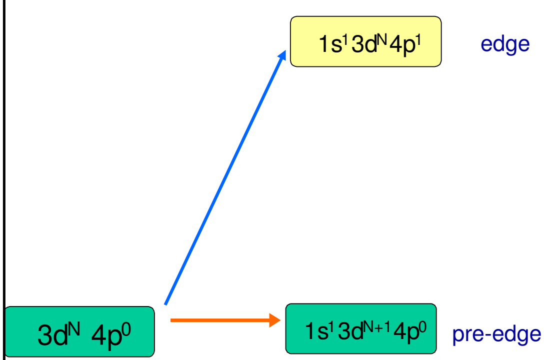
What do we learn from XANES?

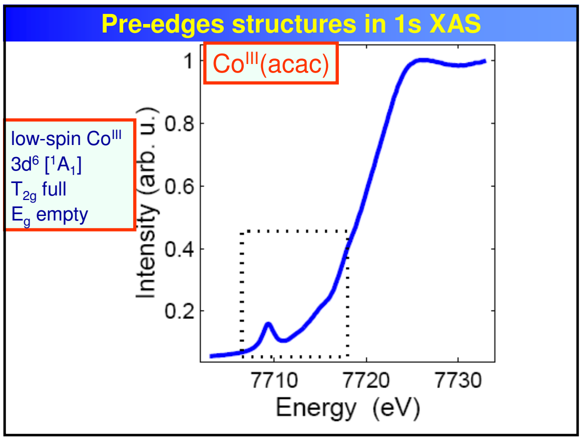
- Edge position gives valence
- K pre-edge center gives valence
- K pre-edge intensity gives site symmetry
- L edge intensity gives empty d-states
- HERFD-XANES gives details anti-bonding bands of adsorbates

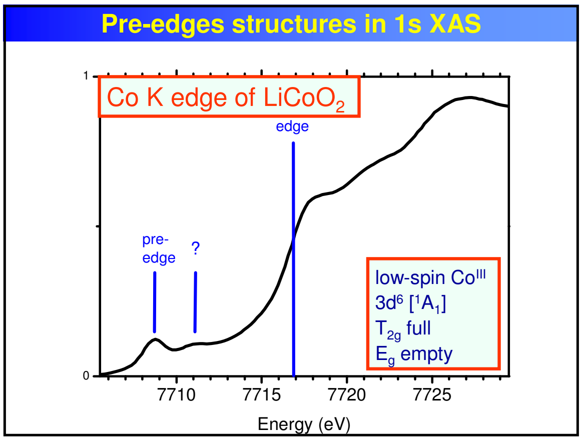
Pre-edges structures in 1s XAS

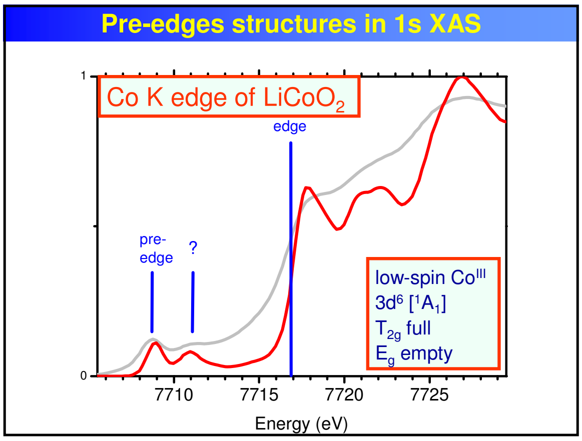


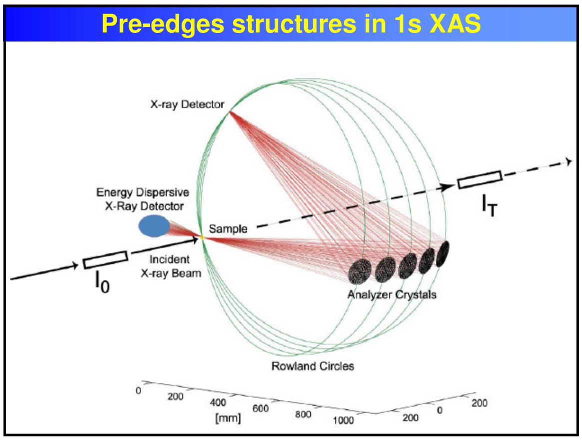
Pre-edges structures in 1s XAS

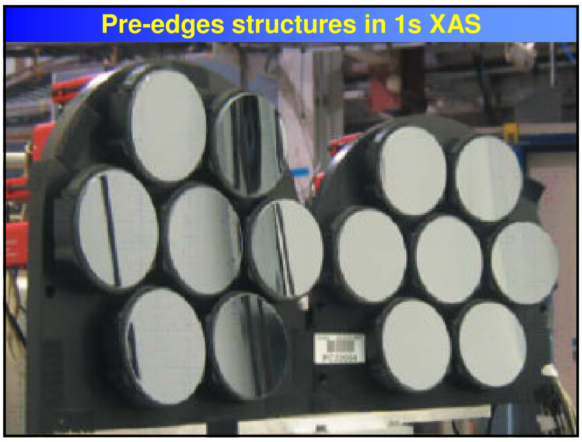


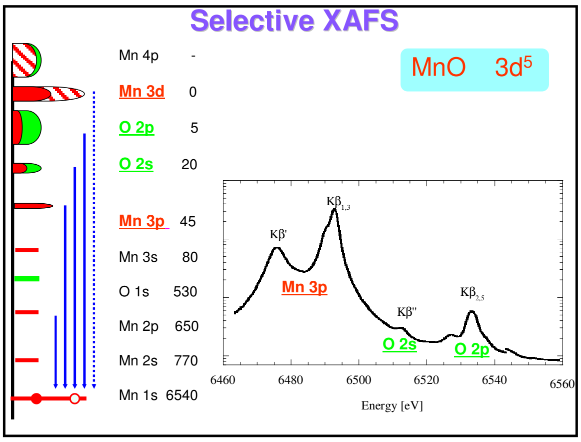

Pre-edges structures in 1s XAS
Co^{III}(acac)
low-spin Co^{III}
3d^6 [$^1A_1$]
T_{2g} full
E_g empty
Intensity (arb. u.)
1
0.8
0.6
0.4
0.2
7710
7720
7730
Energy (eV)

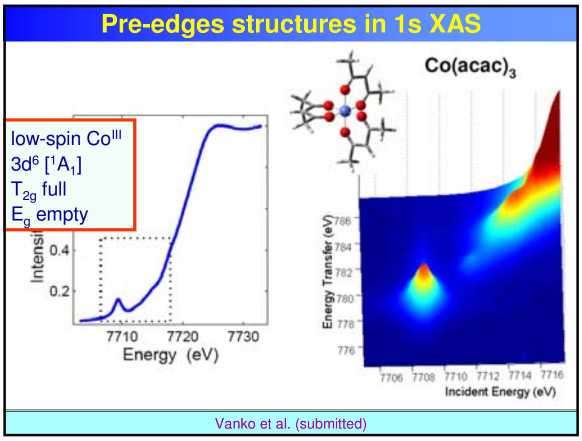

Pre-edges structures in 1s XAS
Co K edge of $LiCoO_2$
edge
pre-edge
?
low-spin Co^{III}
3d^6 [$^1A_1$]
T_{2g} full
E_g empty
1
0
7710
7715
7720
7725
Energy (eV)

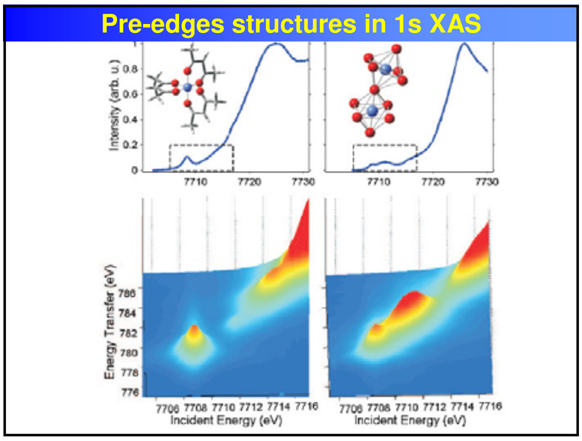

Pre-edges structures in 1s XAS
Co K edge of $LiCoO_2$
edge
pre-edge
?
low-spin Co^{III}
3d^6 [$^1A_1$]
T_{2g} full
E_g empty
1
0
7710
7715
7720
7725
Energy (eV)

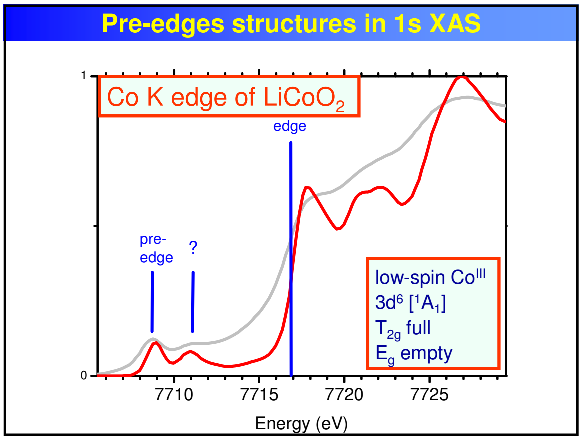

Pre-edges structures in 1s XAS
X-ray Detector
Energy Dispersive X-Ray Detector
Sample
I_T
I_0
Incident X-ray Beam
Analyzer Crystals
Rowland Circles
0
200
400
600
800
1000
[mm]
200
0
200

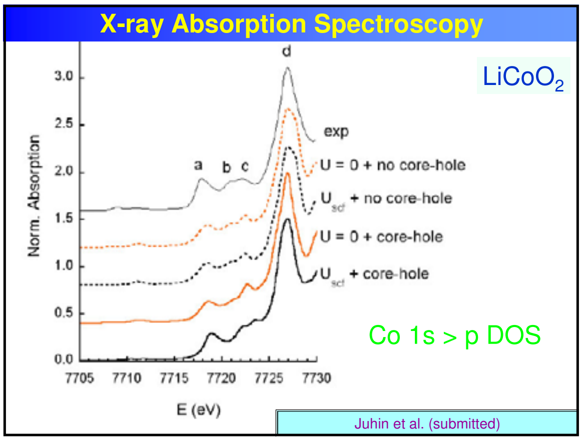

Pre-edges structures in 1s XAS

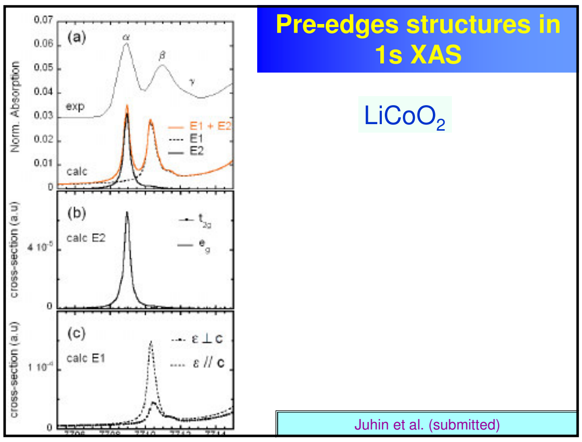

Selective XAFS
MnO 3d^5
Mn 4p -
Mn 3d 0
O 2p 5
O 2s 20
Mn 3p 45
Mn 3s 80
O 1s 530
Mn 2p 650
Mn 2s 770
Mn 1s 6540
Kβ'
$K\beta_{1,3}$
Mn 3p
Kβ''
$K\beta_{2,5}$
O 2s
O 2p
6460
6480
6500
6520
6540
6560
Energy [eV]

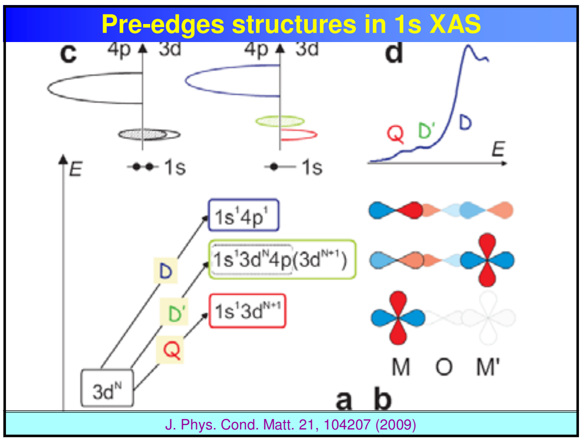

Pre-edges structures in 1s XAS
low-spin Co^{III}
3d^6 [$^1A_1$]
T_{2g} full
E_g empty
Co(acac)$_3$
Energy (eV)
Energy Transfer (eV)
Incident Energy (eV)
Vanko et al. (submitted)

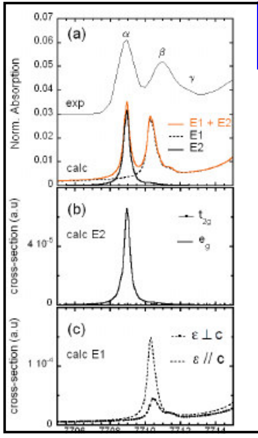

Pre-edges structures in 1s XAS
Intensity (arb. u.)
Energy Transfer (eV)
Incident Energy (eV)
Incident Energy (eV)


Pre-edges structures in 1s XAS
Co K edge of $LiCoO_2$
edge
pre-edge
?
low-spin Co^{III}
3d^6 [$^1A_1$]
T_{2g} full
E_g empty
Energy (eV)


X-ray Absorption Spectroscopy
$LiCoO_2$
exp
U = 0 + no core-hole
U_{scf} + no core-hole
U = 0 + core-hole
U_{scf} + core-hole
Norm. Absorption
E (eV)
Co 1s > p DOS
Juhin et al. (submitted)


Pre-edges structures in 1s XAS
$LiCoO_2$
Norm. Absorption
exp
calc
E1 + E2
E1
E2
calc E2
cross-section (a.u)
calc E1
Juhin et al. (submitted)


Pre-edges structures in 1s XAS
c
4p
3d
1s
d
Q
D'
D
E
$1s^14p^1$
$1s^13d^N4p(3d^{N+1})$
$1s^13d^{N+1}$
$3d^N$
M
O
M'
a
b
J. Phys. Cond. Matt. 21, 104207 (2009)

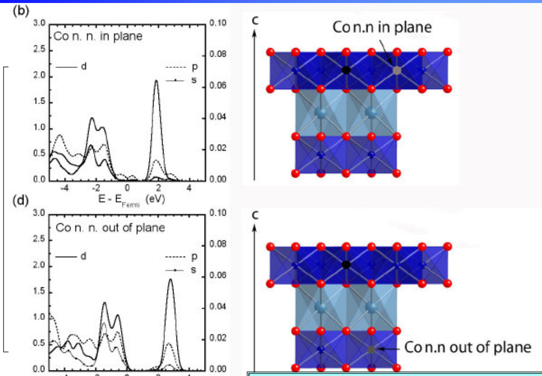


Pre-edges structures in 1s XAS

$LiCoO_2$

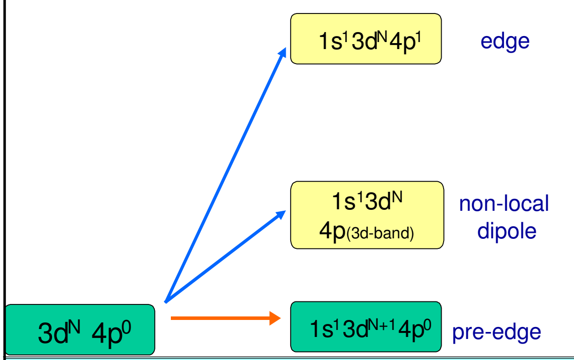
Juhin et al. (submitted)

Pre-edges structures in 1s XAS



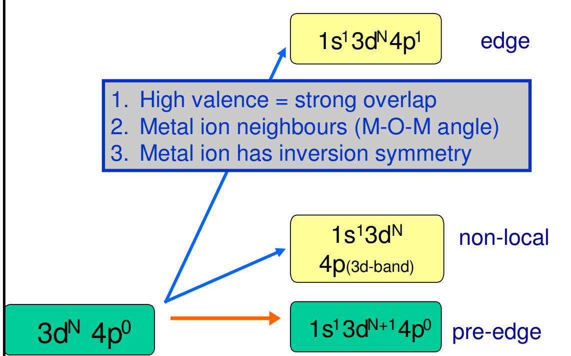
Juhin et al. (submitted)

Pre-edges structures in 1s XAS



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

Pre-edges structures in 1s XAS



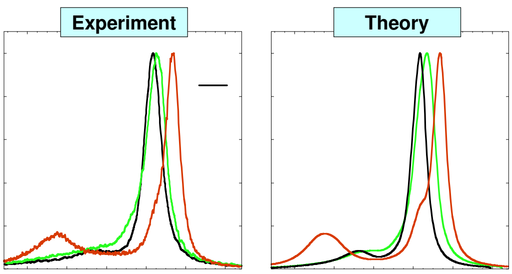
J. Phys. Cond. Matt. 21, 104207 (2009)

Valence selective XAFS

- Independent XANES and EXAFS spectra for different valences in the same system.
- Use chemical shift in the XES emission line with <1 eV resolution.
- 1s3p decay gives clearest chemical shifts due to changing 3p3d exchange with 3d-count.
- Note: the center-of-gravity does not shift with valence because the energy difference between 1s and 3p core levels is constant

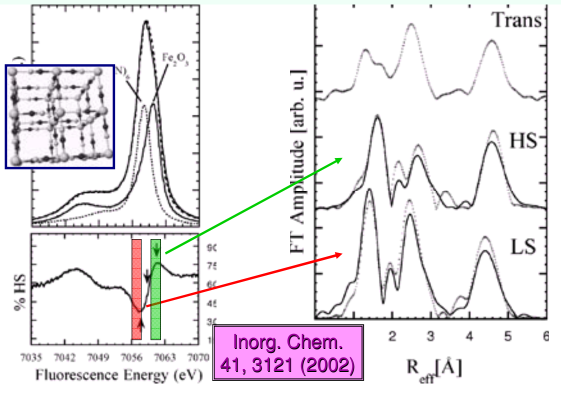
Valence selective XAFS

Chemical Dependence of Kβ Emission



Equal center-of-gravity energies used in calculations!

Valence selective XAFS

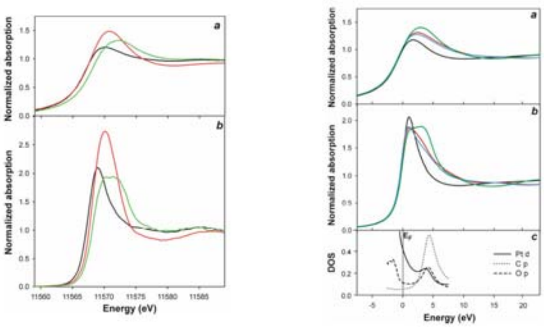


HERFD-XANES

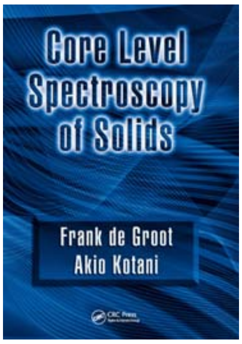
- measure deep core hole XANES with the resolution of a shallow core hole
- For example 3d metal K edges, 5d metal L edges and rare earth L edges.
  - (1) detect adsorbates on Pt or Au,
  - (2) separate pre-edges from edges
  - (3) make quadrupole peaks visible.
- The overall resolution should be as good as the shallow core hole, ~0.3 eV.

(HERFD = High-Energy Resolution Fluorescence Detection)

HERFD-XANES

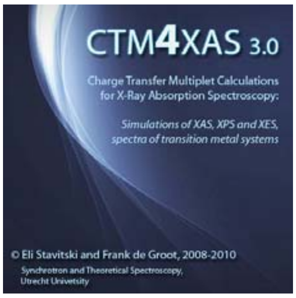


Recent data on Pt catalyst with and without CO
(Olga Sofanova, Moniek Tromp et al, Southampton, subm.)



X-ray Absorption Spectroscopy

(L edges)



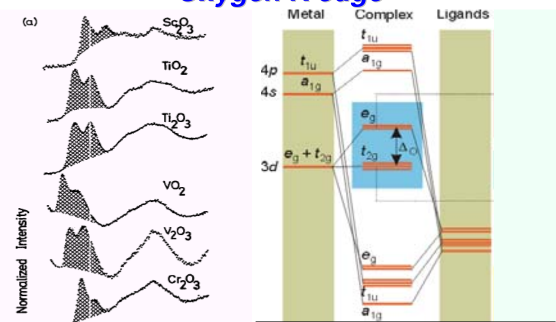
X-ray absorption

Excitation of core electrons to empty states.

Spectrum given by the **Fermi Golden Rule**

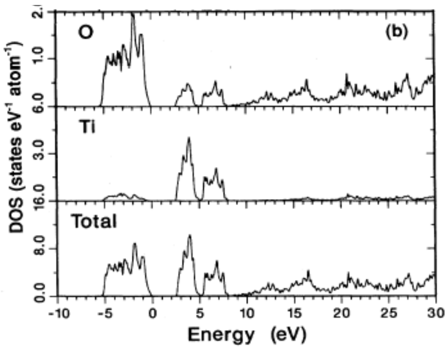
$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \middle| \hat{e} \cdot r \middle| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

Oxygen K edge

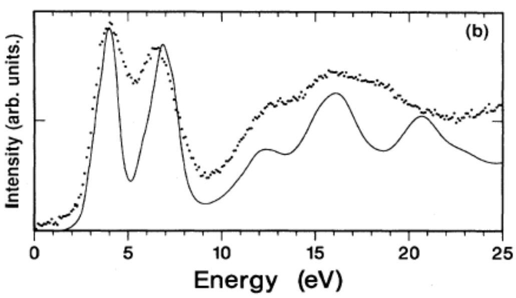


Phys. Rev. B.
40, 5715 (1989) / 48, 2074 (1993)

Electronic Structure



Oxygen K edge



X-ray Absorption Spectroscopy

Fermi Golden Rule:

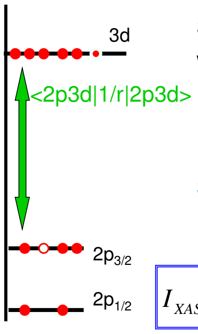
$I_{XAS} = |\langle\Phi_f|\text{dipole}|\ \Phi_i\rangle|^2\ \delta_{[\Delta E=0]}$

Single electron (excitation) approximation:

$I_{XAS} = |\langle\Phi_{empty}|\text{dipole}|\ \Phi_{core}\rangle|^2\ \rho$

1. Neglect <vv'|1/r|vv'> ('many body effects')
2. Neglect <cv|1/r|cv> ('multiplet effects')

multiplet effects

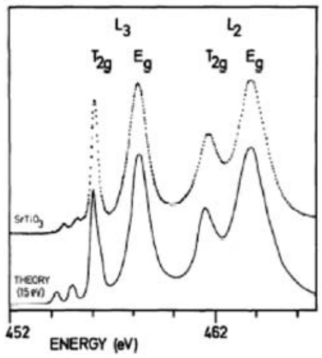


Strong overlap of core and valence wave functions

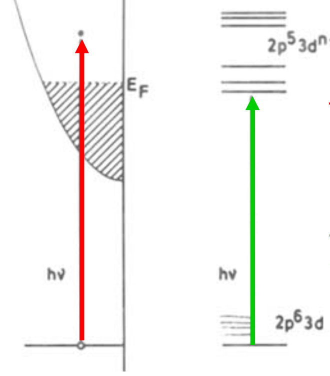
Single Particle model breaks down

$$I_{XAS} \sim \left|\left\langle 2p^5 3d^6 \middle| \hat{e}\cdot r \middle| 3d^5 \right\rangle\right|^2 \delta_{E_f - E_i - \hbar\omega}$$

2p X-ray absorption



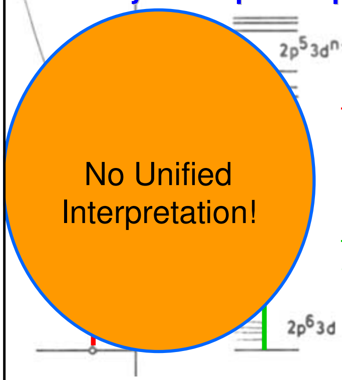
X-ray Absorption Spectroscopy



DFT:
1s edges

Multiplets:
2p, 3s, 3p edges

X-ray Absorption Spectroscopy



Single Particle:
1s edges
(WIEN, FEFF, GN-XAS .....)

Multiplets:
2p, 3s, 3p edges
(TT-MULTIPLETS)

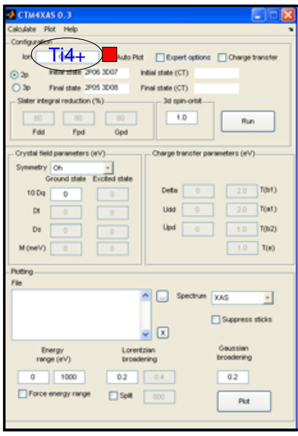
Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

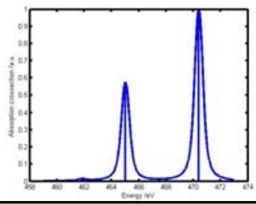
Photoemission, Auger, XES,

ATOMIC PHYSICS
⇓
GROUP THEORY
⇓
MODEL HAMILTONIANS

2p XAS of TiO_2



Put Ti4+ in Ion
Set Autoplot ON
Press Run

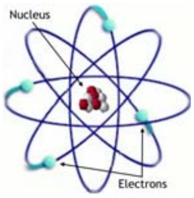


Atomic Multiplet Theory

HΨ=EΨ

$$H = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling



Atomic Multiplet Theory

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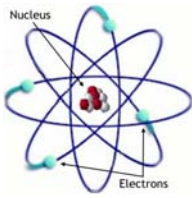
- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling



Atomic Multiplet Theory (ground state)

$$\left\langle {}^{2S+1}L_J \,|\, \frac{e^2}{r_{12}} \,|\, {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k$$

Electron Correlation of Valence States

$$H_{ATOM} = \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

Valence Spin-orbit coupling

Atomic Multiplet Theory (core hole)

$$\left\langle {}^{2S+1}L_J \,|\, \frac{e^2}{r_{12}} \,|\, {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

Core Valence Overlap

$$H_{ATOM} = \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

Core Spin-orbit coupling

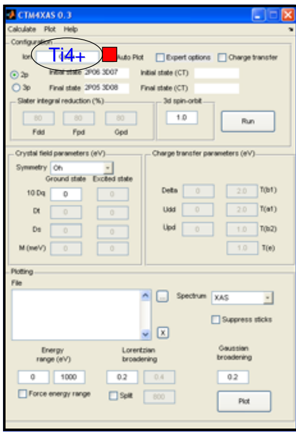
Multiplet Effects

1s	2s	2p	3s	3p
0.07	5	8	13	17
0	0	17	0	2

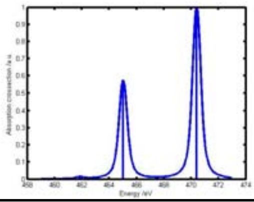
Core Valence Overlap

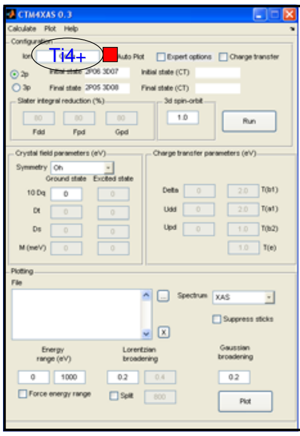
Core Spin-orbit coupling

2p XAS of TiO_2



Put Ti4+ in Ion
Set Autoplot ON
Press Run



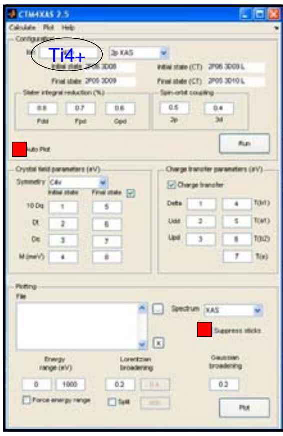


2p XAS of TiO_2

CTM4XAS:
Error for $3d^0$ systems in version 3

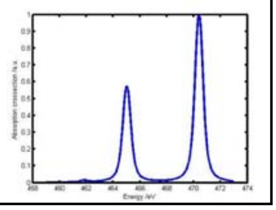
Use version 2.5 for $3d^0$ systems

(Will be solved in version 3.1)



2p XAS of TiO_2

Put Ti4+ in Ion
Set Autoplot ON
Suppress Sticks ON



Term Symbols

- **Term symbols of a $2p^53d^1$ configuration**

→ $^3P_0$ $^1P_1$ $^3P_1$ $^3P_2$

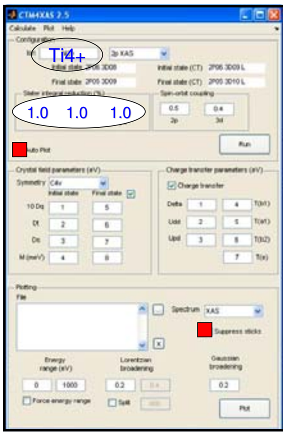
→ $^3D_1$ $^1D_2$ $^3D_2$ $^3D_3$

→ $^3F_2$ $^1F_3$ $^3F_3$ $^3F_4$

[1   3   4   3   1]

1   3x3   4x5   3x7   1x9

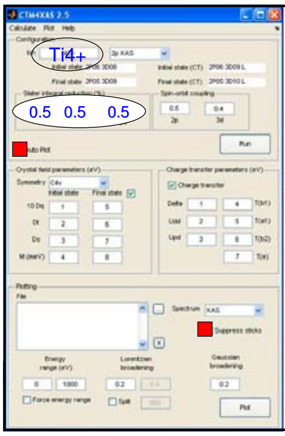
Ground state: $3d^0$: L=S=J=0 $^1S_0$
Selection rule: Final state must have J'=1



Atomic multiplets

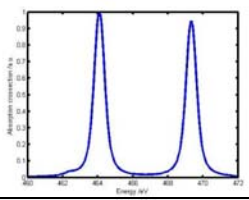
Slater integral reduction:

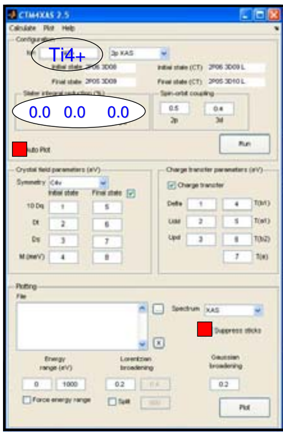
The F_{dd}, F_{pd} and G_{pd} Slater integrals can be reduced to any other value. The default value is 1.0 which implies atomic values.



2p XAS of TiO_2

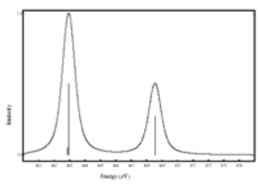
Put Ti4+ in Ion
Set Autoplot ON
Set Expert options ON



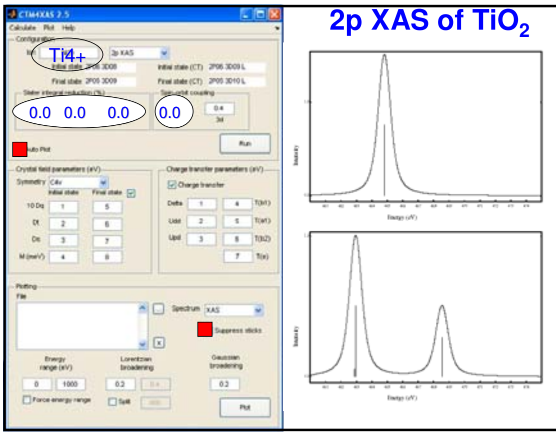


2p XAS of TiO_2

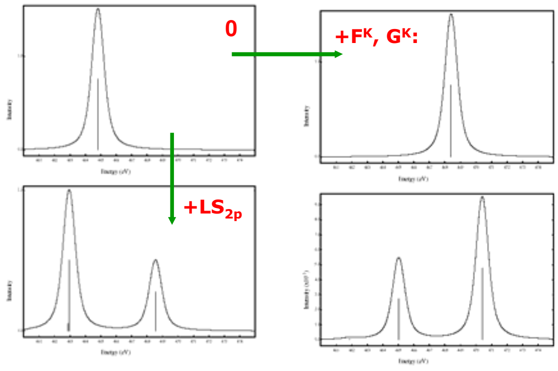
Put Ti4+ in Ion
Set Autoplot ON
Set Slater integral reduction to 0.0



2p XAS of TiO_2



$3d^0$ XAS calculation



Hunds rules

- Term symbols with **maximum spin** S are lowest in energy,
- Among these terms:

Term symbols with **maximum L** are lowest in energy

- In the presence of spin-orbit coupling, the lowest term has
- J = |L-S| if the shell is less than half full
- **J = L+S** if the shell is more than half full

$3d^1$ has $^2D_{3/2}$ ground state
$3d^9$ has $^2D_{5/2}$ ground state

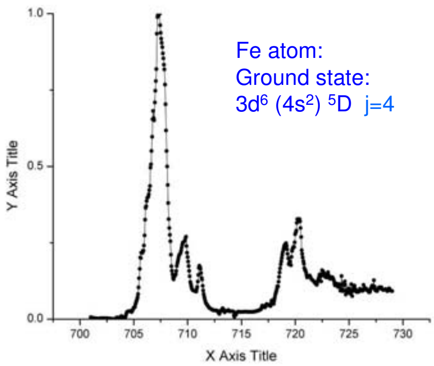
$3d^2$ has $^3F_2$ ground state
$3d^8$ has $^3F_4$ ground state

Give the Hund's rule ground states for $3d^1$ to $3d^9$

$3d^N$ XAS calculation

Transition	Ground	Transitions	Term Symbols
$3d^0 \rightarrow 2p^53d^1$	$^1S_0$	3	12
$3d^1 \rightarrow 2p^53d^2$	$^2D_{3/2}$	29	45
$3d^2 \rightarrow 2p^53d^3$	$^3F_2$	68	110
$3d^3 \rightarrow 2p^53d^4$	$^4F_{3/2}$	95	180
$3d^4 \rightarrow 2p^53d^5$	$^5D_0$	32	205
$3d^5 \rightarrow 2p^53d^6$	$^6S_{5/2}$	110	180
$3d^6 \rightarrow 2p^53d^7$	$^5D_4$	68	110
$3d^7 \rightarrow 2p^53d^8$	$^4F_{9/2}$	16	45
$3d^8 \rightarrow 2p^53d^9$	$^3F_4$	4	12
$3d^9 \rightarrow 2p^53d^{10}$	$^2D_{5/2}$	1	2

Term Symbols and XAS



Fe atom:
Ground state:
$3d^6$ ($4s^2$) ^5D j=4

Term Symbols and XAS

Fe atom:

Ground state:	$3d^6$ ($4s^2$)	
Final state:	$2p^53d^7$	
Dipole transition:	p-symmetry	
$3d^6$-configuration:	^5D, etc.	j=4
$2p^53d^7$-configuration:	110 states	j'= 3,4, 5
p-transition:	^1P	Δj=+1,0,-1
ground state symmetry:	^5D	$^5D_4$
transition:	$^5D \otimes ^1P = ^5PDF$	
possible final states:		68 states

Exercise

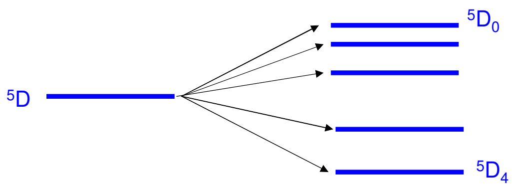
Calculate the atomic multiplet spectrum of the 2p XAS spectrum of an iron atom (use Fe^{2+})

Run CTM4XAS with Autoplot ON.
Do a second calculation with the 3d spin-orbit coupling set to zero.

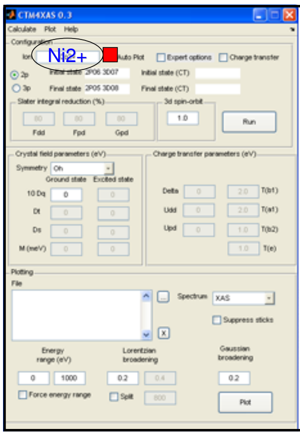
Choose an appropriate name;
the program saves the rcn, rcg, rac, ban, plo and xy files with this name.

Term Symbols and XAS

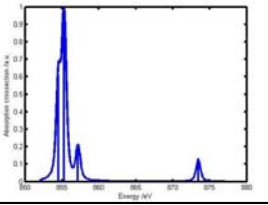
Fe atom:
Ground state: $3d^6$ $(4s^2)$ ^5D j=4



2p XAS of NiO



Put Ni2+ in Ion
Set Autoplot ON



Term Symbols and XAS

Ni^{II} ion in NiO:
Ground state: $3d^8$
Final state: $2p^5 3d^9$
Dipole transition: p-symmetry

$3d^8$-configuration: ^1S, ^1D, ^3P, ^1G, ^3F j=4
$2p^5 3d^9$-configuration: $^2P \otimes ^2D$ = $^{1,3}PDF$ j'=0,1,2,3,4
p-transition: ^1P Δj=+1,0,-1

ground state symmetry: ^3F $^3F_4$
transition: $^3F \otimes ^1P$ = ^3DFG
two possible final states: ^3D, ^3F $^3D_3$, $^3F_3$, $^3F_4$, $^1F_3$

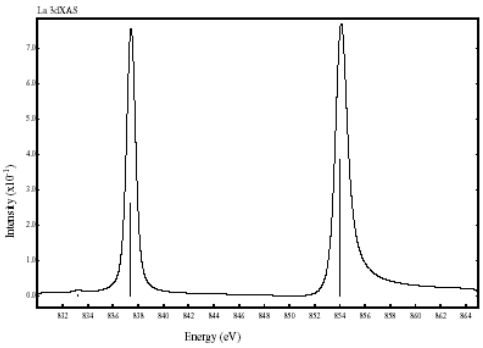
3d XAS of La_2O_3

- La in La_2O_3 can be described as La^{3+} ions:
- Ground state is $4f^0$
- Dipole transition $4f^0 \rightarrow 3d^9 4f^1$
- Ground state symmetry: $^1S_0$
- Final state symmetry: $^2P \otimes ^2D$ gives
- ^1P, ^1D, ^1F, ^1G, ^1H and ^3P, ^3D, ^3F, ^3G, ^3H.

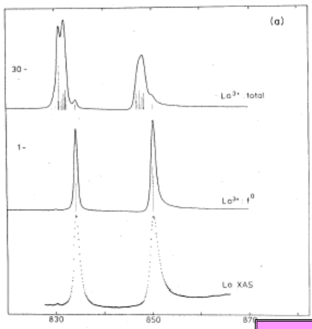
3d XAS of La_2O_3

- Final state symmetries:
  ^1P, ^1D, ^1F, ^1G, ^1H and ^3P, ^3D, ^3F, ^3G, ^3H.
- Transition $<^1S_0|\Delta J=+1|\ ^1P_1,\ ^3P_1,\ ^3D_1>$
- 3 peaks in the spectrum

3d XAS of La_2O_3



3d XAS of La_2O_3



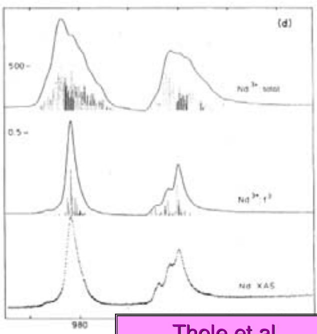
Thole et al.
PRB 32, 5107 (1985)

3d XAS of Nd

Nd^{III} ion in Nd metal

Ground state: $4f^3$

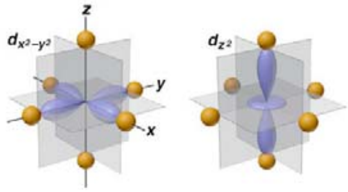
Final state: $3d^9 4f^4$



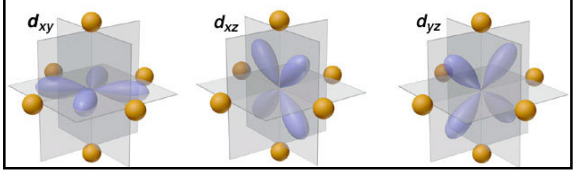
Thole et al.
PRB 32, 5107 (1985)

Crystal Field Effects

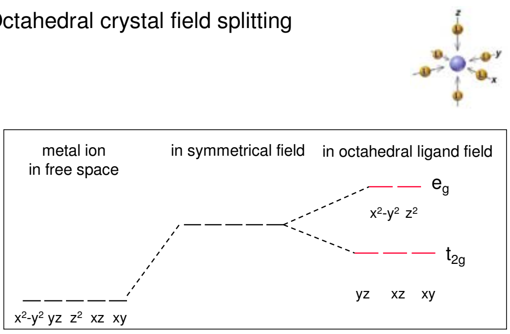
e_g states



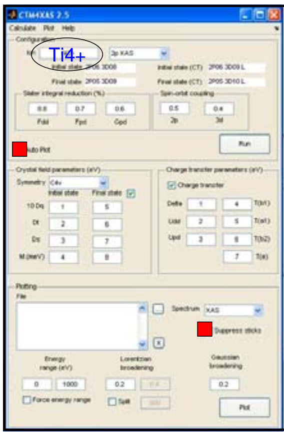
t_{2g} states



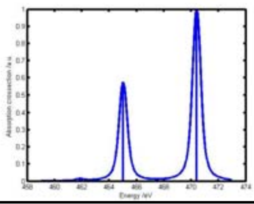
Octahedral crystal field splitting



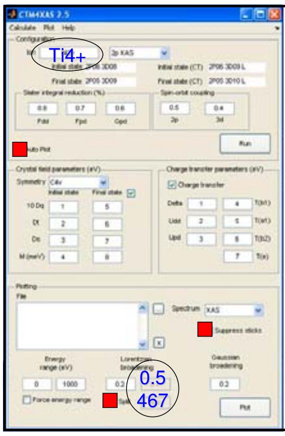
2p XAS of TiO_2



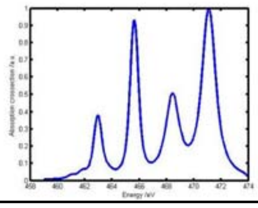
Put Ti4+ in Ion
Set Autoplot ON
Press Run



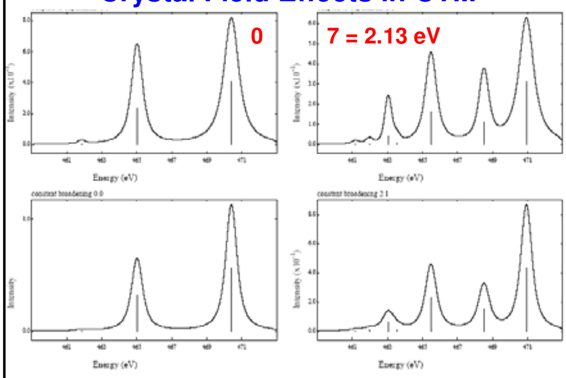
2p XAS of TiO_2



Crystal field effect:
+ 2.5 for 10Dq
+ Split ON
+ 0.5 Lorentzian L2
+ 467 split energy



Crystal Field Effects in CTM



Crystal Field Effects

SO_3			O_h (Mulliken)
S	0		A_1
P	1		T_1
D	2		$E+T_2$
F	3		$A_2+T_1+T_2$
G	4		$A_1+E+T_1+T_2$

Crystal Field Effect on XAS

J in SO_3	Deg.	Branchings		
0	1	A_1		
1	3	$3\times T_1$		
2	4	$4\times E$, $4\times T_2$		
3	3	$3\times A_2$, $3\times T_1$, $3\times T_2$		
4	1	A_1, E, T_1, T_2		
Σ	12			

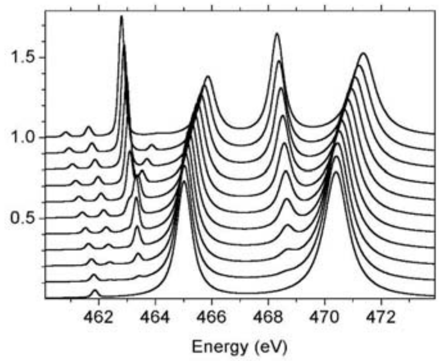
<$^1S_0$|dipole|$^1P_1$> goes to <A_1|T_1|T_1>

Crystal Field Effect on XAS

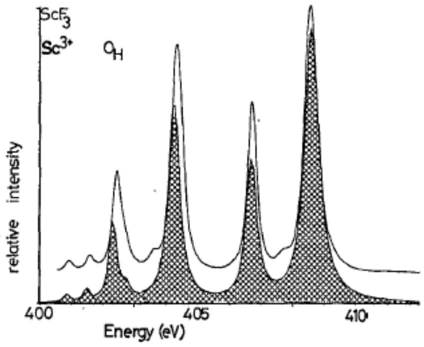
J in SO_3	Deg.	Branchings	Γ in O_h	Deg.
0	1	A_1	A_1	2
1	3	$3\times T_1$	A_2	3
2	4	$4\times E$, $4\times T_2$	T_1	7
3	3	$3\times A_2$, $3\times T_1$, $3\times T_2$	T_2	8
4	1	A_1, E, T_1, T_2	E	5
Σ	12			25

<$^1S_0$|dipole|$^1P_1$> goes to <A_1|T_1|T_1>

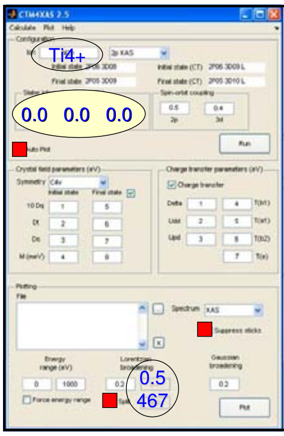
Effect of 10Dq on XAS:$3d^0$

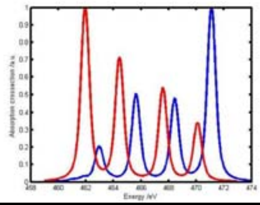


Comparison with Experiment

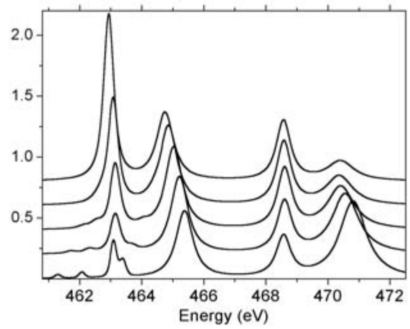


2p XAS of TiO_2

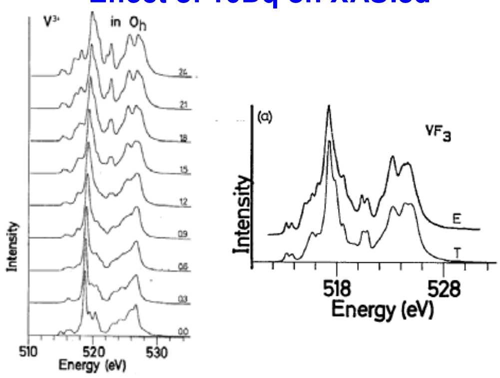


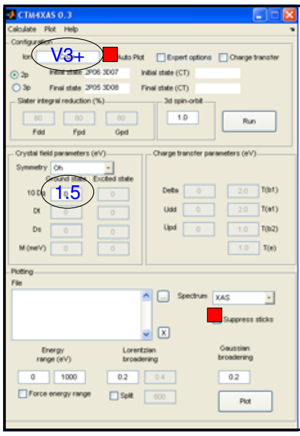


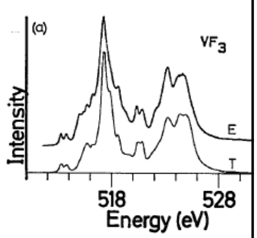
Turning multiplet effects off



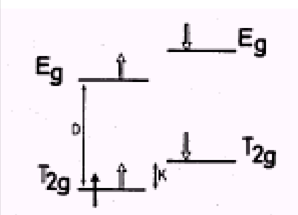
Effect of 10Dq on XAS:$3d^N$







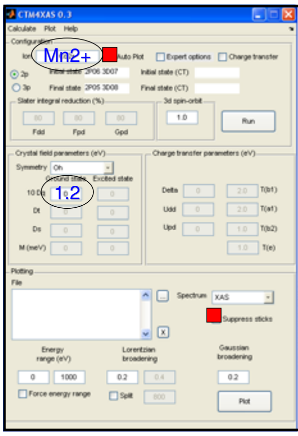
High-spin or Low-spin



10Dq > 3J
(d^4 and d^5)

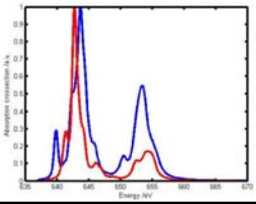
10Dq > 2J
(d^6 and d^7)

2p XAS of Mn2+

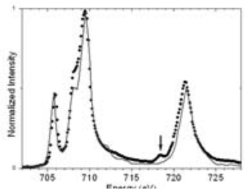


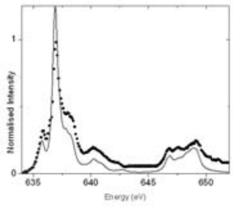
High-spin: 10Dq = 1.2

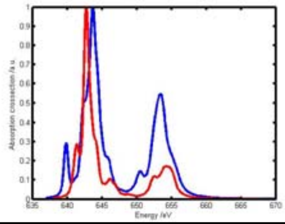
Low-spin: 10Dq = 3.0



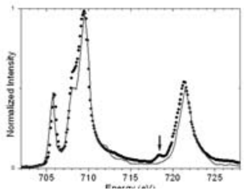
2p XAS of Mn2+

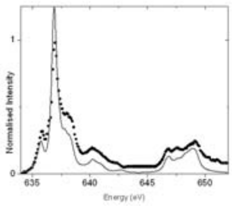


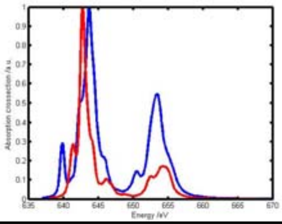




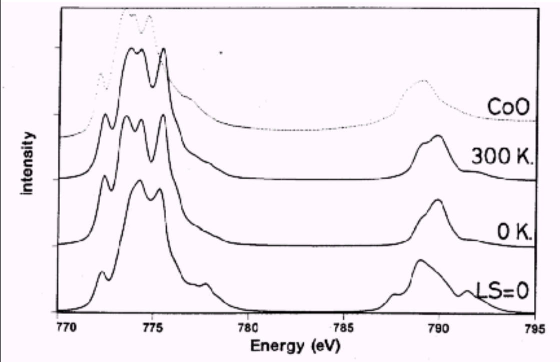
2p XAS of Mn2+



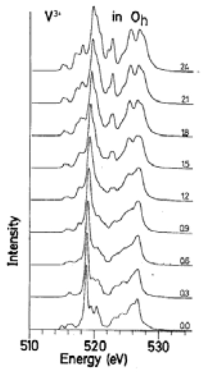


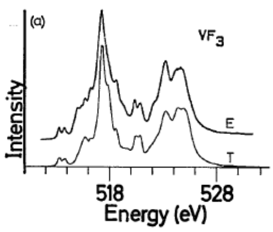


3d spin-orbit coupling

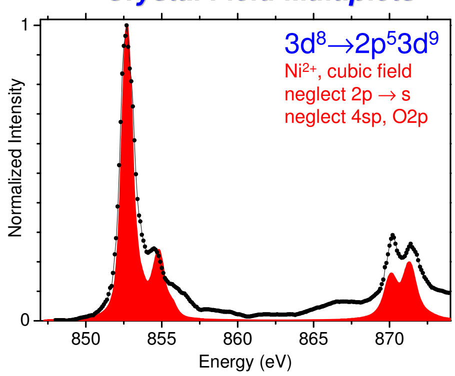


Effect of 10Dq on XAS:3d^N

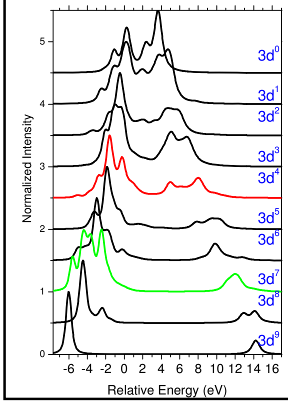




Crystal Field Multiplets



Metal L edges



Calculated L-edges
$3d^N \rightarrow 2p^5 3d^{N+1}$

- Single configuration
- Atomic values for intra-atomic interactions
- Cubic crystal field of 1.2 eV

Exercise

Calculate the crystal field multiplet spectrum of the 2p XAS spectrum of all divalent transition metal ions from Ca to Cu. Use 10Dq=1.2 eV.

Run CTM4XAS with Autoplot ON.
Do a calculation with and without the 3d spin-orbit coupling set to zero.

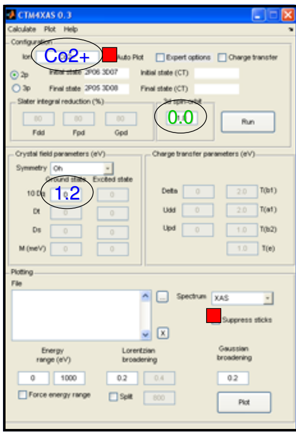
Which TM^{2+} ions are sensitive to 3d spin-orbit coupling? Explain

Exercise

Calculate the crystal field multiplet spectrum of the 2p XAS spectrum of all divalent transition metal ions from Ca to Cu.

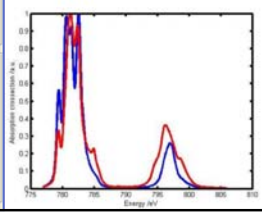
Use 10Dq=1.0, 2.0 and 3.0 eV.

Which TM^{2+} ions are very sensitive to the crystal field strength? Explain



2p XAS of CoO

+ with and without 3d spin-orbit (1.0 and 0.0)

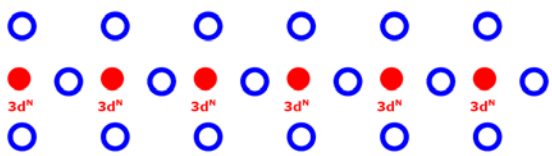


Charge Transfer Effects

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

$3d^5$ ——→—— $2p^5 3d^6$

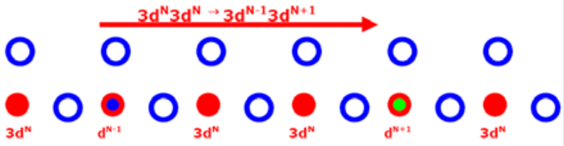
Charge Transfer Effects



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

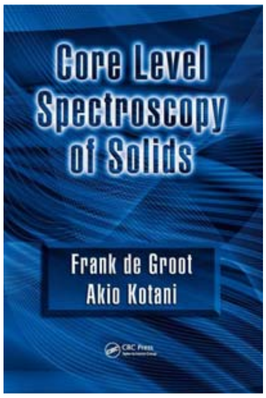
Charge fluctuations

Charge Transfer Effects

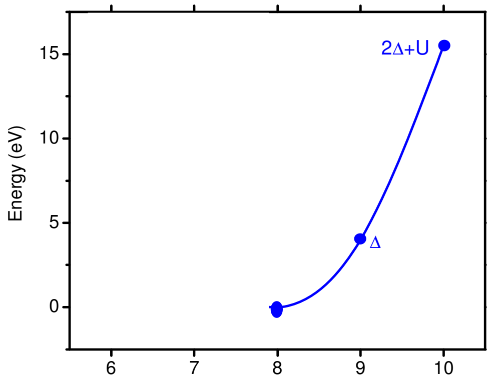


Hubbard U for a $3d^8$ ground state:
U= $E(3d^7) + E(3d^9) - E(3d^8) - E(3d^8)$

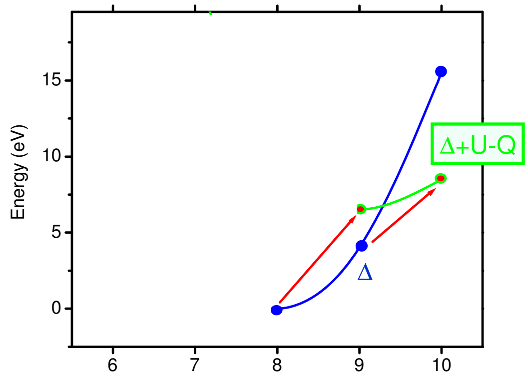
Ligand-to-Metal Charge Transfer (LMCT):
Δ= $E(3d^9\underline{L}) - E(3d^8)$



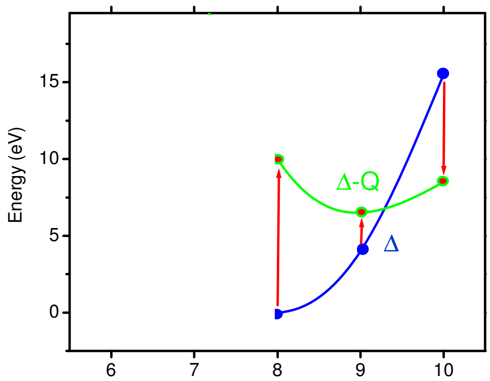
Charge Transfer Effects



Charge Transfer Effects in XAS

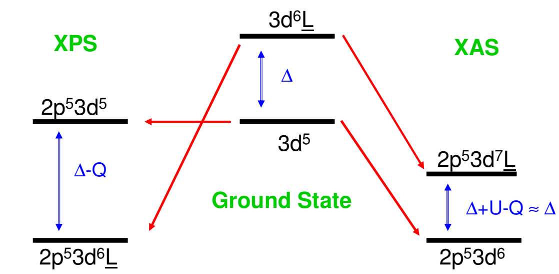


Charge Transfer Effects in XPS

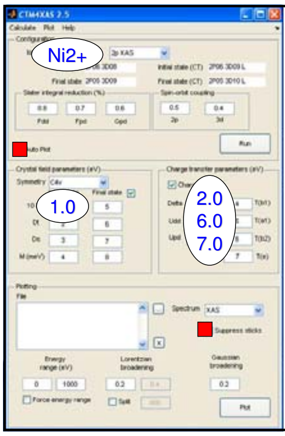


Charge transfer effects in XAS and XPS

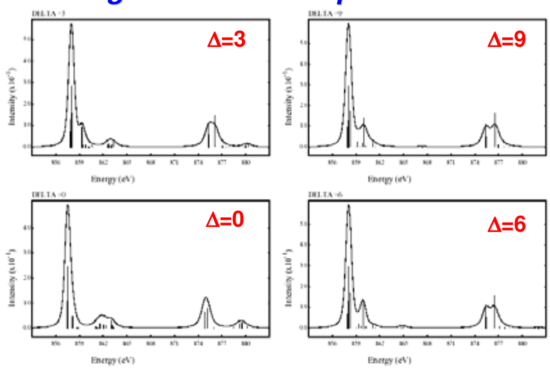
- Transition metal oxide: Ground state: $3d^5 + 3d^6\underline{L}$
- Energy of $3d^6\underline{L}$: Charge transfer energy Δ



2p XAS of Ni^{2+}



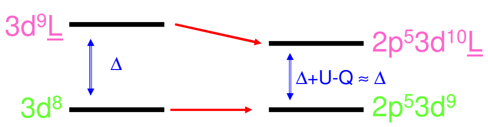
Charge Transfer Multiplets of Ni^{2+}



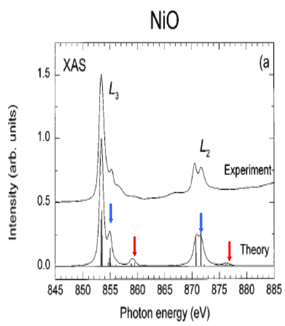
Charge Transfer Effects in XAS

NiO: Ground state: $3d^8$ + $3d^9\underline{L}$

Energy of $3d^9\underline{L}$: Charge transfer energy Δ



X-ray Absorption Spectroscopy



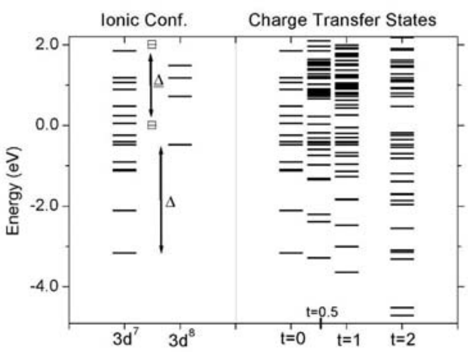
Spectral shape:

(1) Multiplet effects

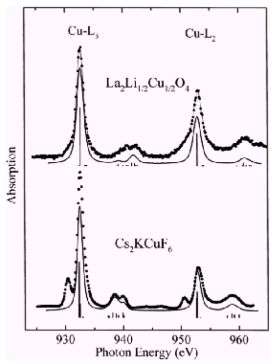
(2) Charge Transfer

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

Charge transfer



Exercise



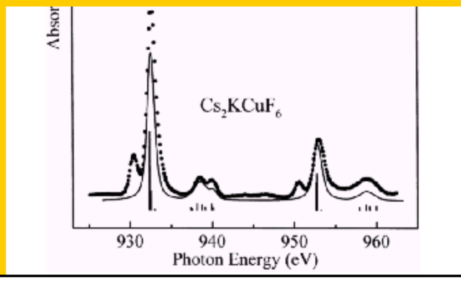
Exercise

Try to reproduce the Cu 2p XAS spectrum of Cs_2KCuF_6
The symmetry is octahedral;
Use T(eg) = 2.0, $T(e_g)=2^* T(t_{2g})$ and U_{dd}-U_{pd}=-1.0 eV.
Optimize 10Dq and Δ.

Try to reproduce the Cu 2p XAS spectrum of $La_2Li_{1/2}Cu_{1/2}O_4$
The symmetry is square planar;
Use Ds=0.3, $T(b_1)$ = 3.0, $T(a_1)$ = 1.73, $T(b_2)$ = 1.5, T(e) = 1.05* and U_{dd}-U_{pd}=-1.0 eV.
Optimize 10Dq and Δ.

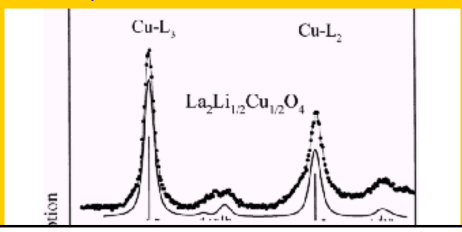
Exercise

Try to reproduce the Cu 2p XAS spectrum of Cs_2KCuF_6
The symmetry is octahedral;
Use T(eg) = 2.0, $T(e_g)=2^* T(t_{2g})$ and U_{dd}-U_{pd}=-1.0 eV.
Optimize 10Dq and Δ.



Exercise

Try to reproduce the Cu 2p XAS spectrum of $La_2Li_{1/2}Cu_{1/2}O_4$
The symmetry is square planar;
Use Ds=0.3, $T(b_1)$ = 3.0, $T(a_1)$ = 1.73, $T(b_2)$ = 1.5, T(e) = 1.05* and U_{dd}-U_{pd}=-1.0 eV.
Optimize 10Dq and Δ.



Exercise

Calculate all spectra for NiO

2p XAS, 3p XAS, 1s (pre-edge) XAS

1s, 2s and 3s XPS

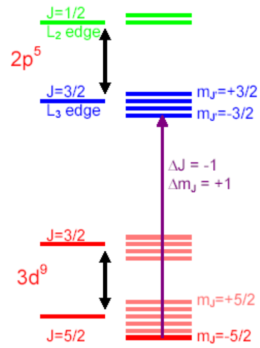
2p and 3p XPS

1s2p and 1s3p XES

X-MCD

X-MCD

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

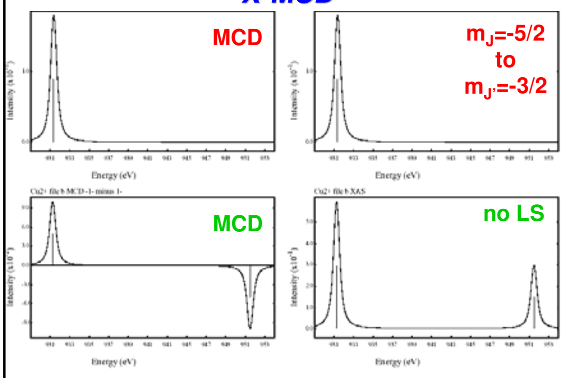


Exercise

Run CTM4XAS for Cu^{2+} in C4 symmetry, with a magnetic field (M) of 1 meV; Plot the XAS spectrum and the MCD spectrum;

Run CTM4XAS for Cu_2^+ in C4 symmetry, with a magnetic field (M) of 1 meV and with the 3d spin-orbit coupling set to 0.0; Plot the XAS spectrum and the MCD spectrum;

X-MCD



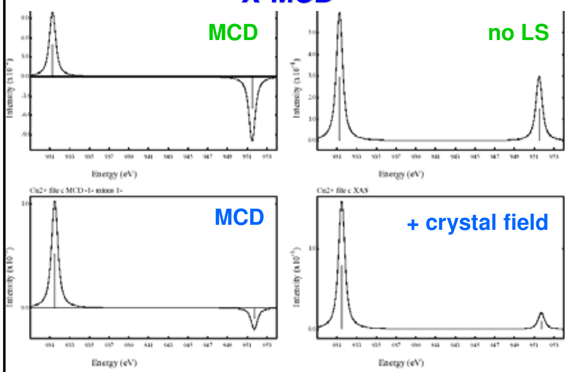
Exercise

Run CTM4XAS for Cu2+ in C4v symmetry, with a magnetic field (M) of 1 meV, adding a crystal field value 10Dq of 0.3 eV.; Plot the XAS spectrum and the MCD spectrum;

Perform a number of calculations for varying values of 10Dq, in steps of 0.3 eV from 0.0 to 1.5 eV. What does one observe for the XAS and MCD spectra?

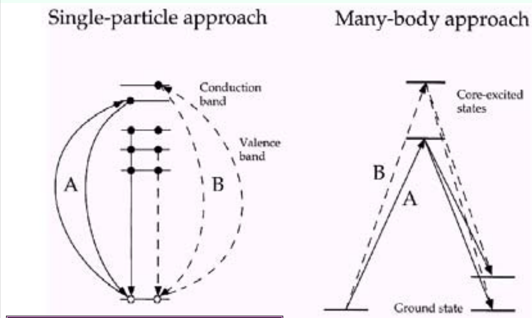
Perform a calculation for negative values of 10Dq, for example -0.3, -0.5 and -0.9 eV. What does one observe? Explain.

X-MCD

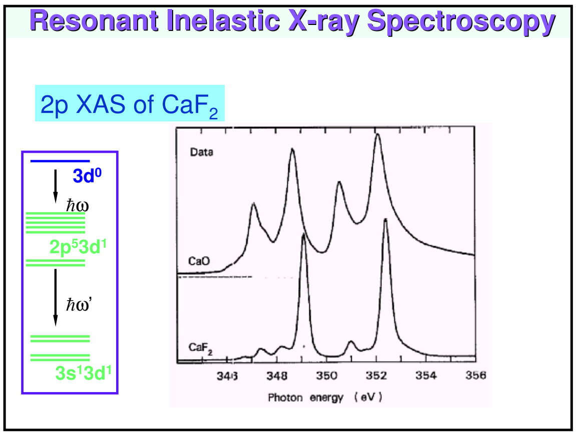


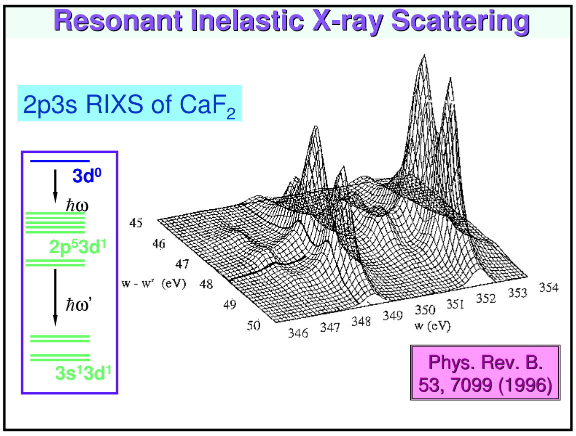
RIXS

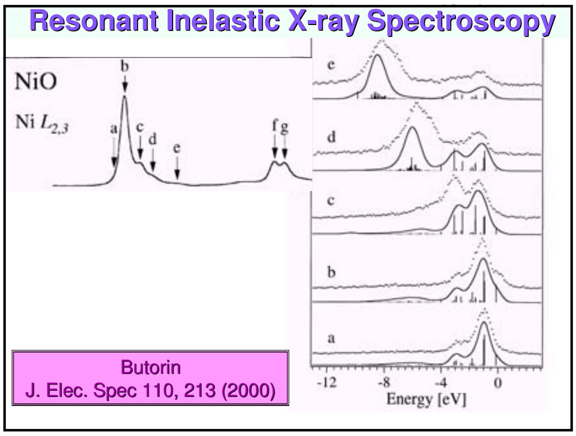
RIXS

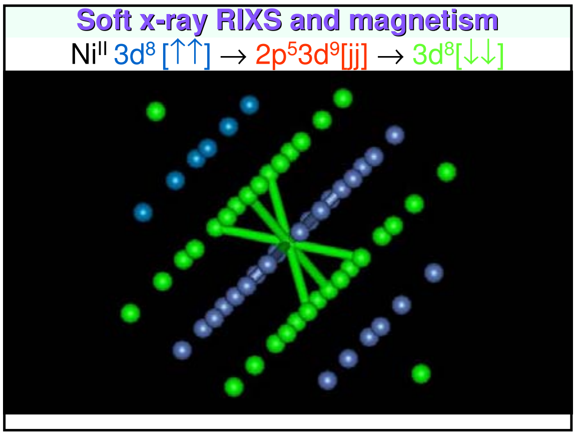


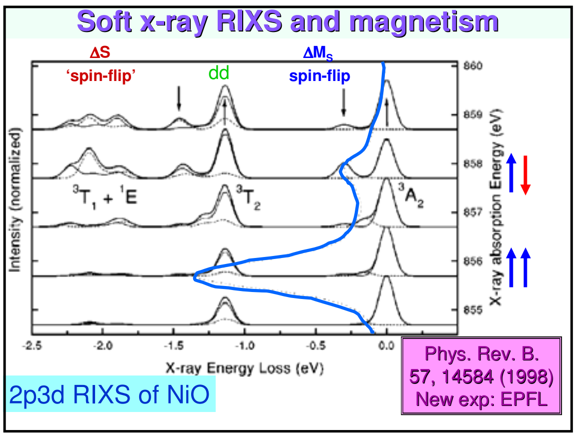
Butorin
J. Elec. Spec 110, 213 (2000)

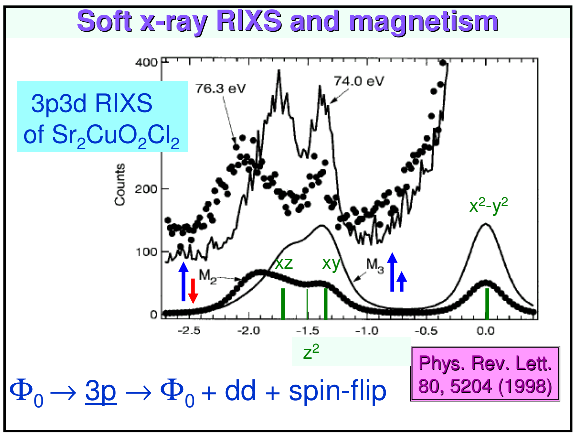

Resonant Inelastic X-ray Spectroscopy
2p XAS of CaF2
3d0
ħω
2p53d1
ħω'
3s13d1
Data
CaO
CaF2
346 348 350 352 354 356
Photon energy (eV)

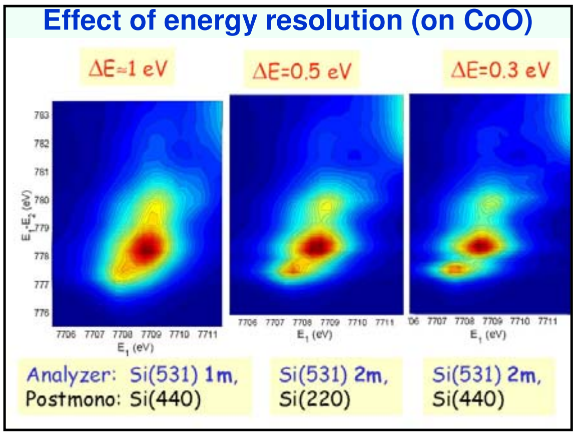

Resonant Inelastic X-ray Scattering
2p3s RIXS of CaF2
3d0
ħω
2p53d1
ħω'
3s13d1
w - w' (eV)
45 46 47 48 49 50
346 347 348 349 350 351 352 353 354
w (eV)
Phys. Rev. B. 53, 7099 (1996)

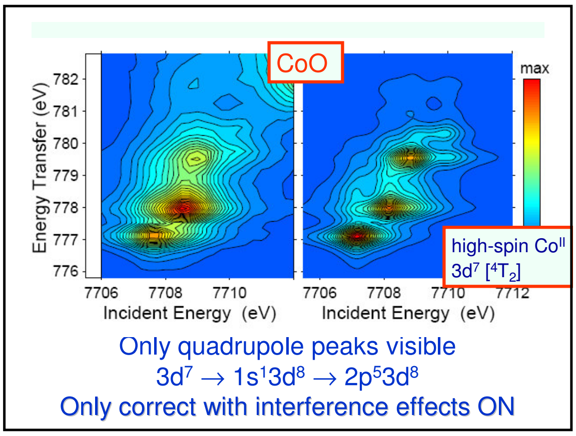

Resonant Inelastic X-ray Spectroscopy
NiO
Ni L2,3
a b c d e f g
-12 -8 -4 0
Energy [eV]
Butorin
J. Elec. Spec 110, 213 (2000)

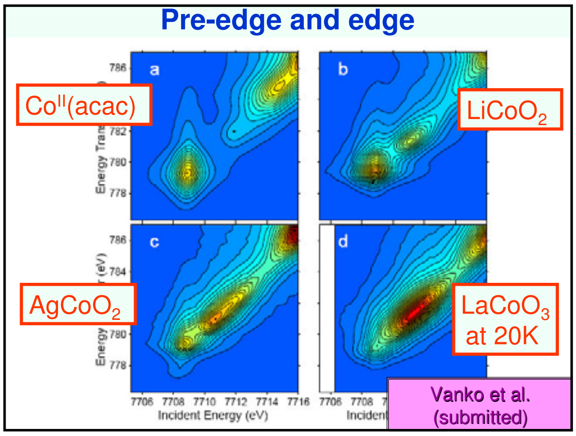

Soft x-ray RIXS and magnetism
NiII 3d8 [↑↑] → 2p53d9[jj] → 3d8[↓↓]

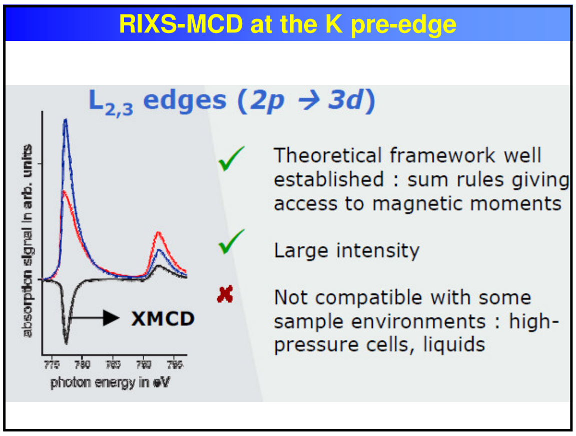

Soft x-ray RIXS and magnetism
ΔS
'spin-flip'
dd
ΔMS
spin-flip
3T1 + 1E
3T2
3A2
Intensity (normalized)
X-ray absorption Energy (eV)
860 859 858 857 856 855
-2.5 -2.0 -1.5 -1.0 -0.5 0.0
X-ray Energy Loss (eV)
2p3d RIXS of NiO
Phys. Rev. B. 57, 14584 (1998)
New exp: EPFL

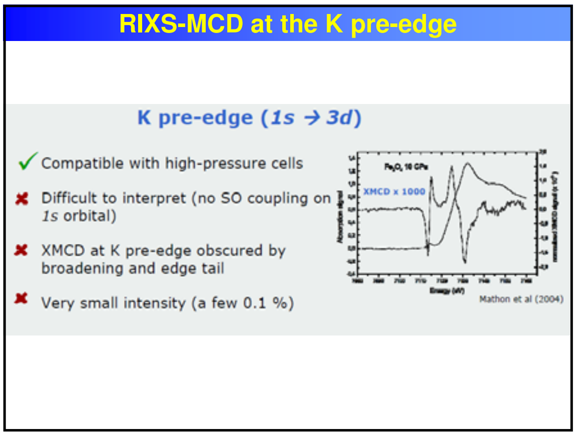

Soft x-ray RIXS and magnetism
3p3d RIXS of Sr2CuO2Cl2
76.3 eV
74.0 eV
Counts
400 200 100 0
M2
xz
xy
M3
x2-y2
z2
-2.5 -2.0 -1.5 -1.0 -0.5 0.0
Φ0 → 3p → Φ0 + dd + spin-flip
Phys. Rev. Lett. 80, 5204 (1998)

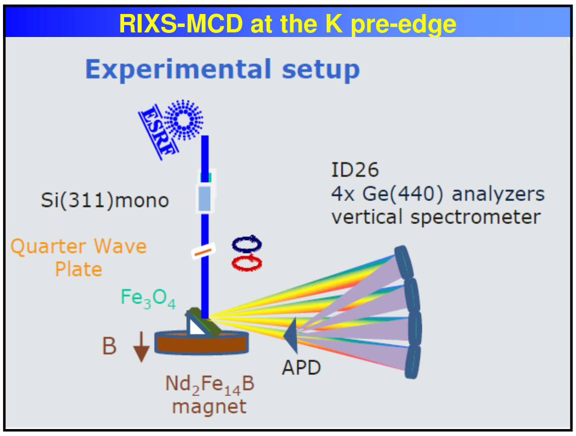

Effect of energy resolution (on CoO)
ΔE≈1 eV
ΔE=0.5 eV
ΔE=0.3 eV
Analyzer: Si(531) 1m,
Postmono: Si(440)
Si(531) 2m,
Si(220)
Si(531) 2m,
Si(440)


CoO
max
Energy Transfer (eV)
Incident Energy (eV)
Incident Energy (eV)
high-spin Co^II
3d^7 [^4T_2]
Only quadrupole peaks visible
3d^7 → 1s^1 3d^8 → 2p^5 3d^8
Only correct with interference effects ON

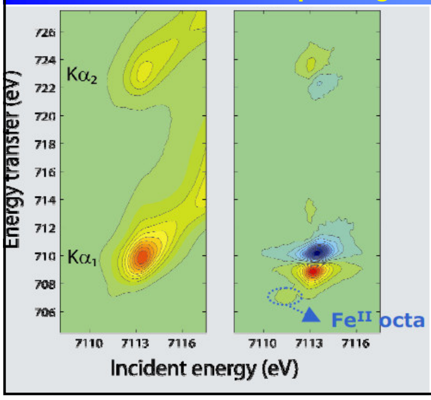

Pre-edge and edge
Co^II(acac)
LiCoO_2
AgCoO_2
LaCoO_3
at 20K
Incident Energy (eV)
Vanko et al.
(submitted)


RIXS-MCD at the K pre-edge
L_2,3 edges (2p → 3d)
Theoretical framework well established : sum rules giving access to magnetic moments
Large intensity
Not compatible with some sample environments : high-pressure cells, liquids
absorption signal in arb. units
XMCD
photon energy in eV

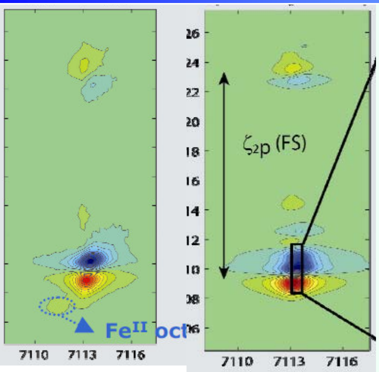

RIXS-MCD at the K pre-edge
K pre-edge (1s → 3d)
Compatible with high-pressure cells
Difficult to interpret (no SO coupling on 1s orbital)
XMCD at K pre-edge obscured by broadening and edge tail
Very small intensity (a few 0.1 %)
XMCD x 1000
Mathon et al (2004)


RIXS-MCD at the K pre-edge
Experimental setup
ESRF
Si(311)mono
ID26
4x Ge(440) analyzers
vertical spectrometer
Quarter Wave
Plate
Fe_3O_4
B
APD
Nd_2Fe_14B
magnet

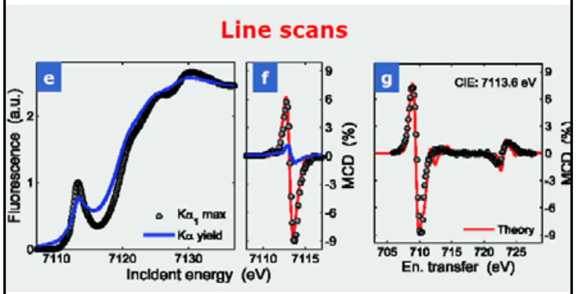
RIXS-MCD at the K pre-edge of Fe_3O_4



RIXS-MCD at the K pre-edge

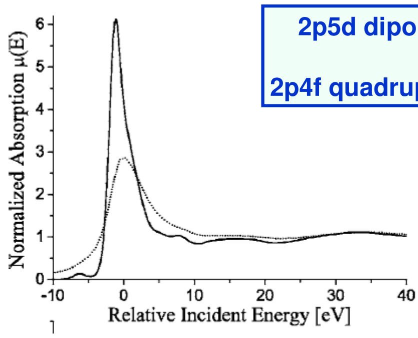


RIXS-MCD at the K pre-edge



XMCD at high-pressure

La 2p XAS: effects of HERFD



2p5d dipole

2p4f quadrupole

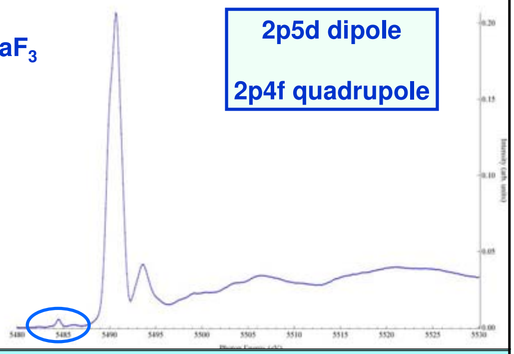
Glatzel et al. PRB 72, 014117 (2005)

La 2p XAS: effects of HERFD

- HERFD makes pre-edge 2p4f transition visible

La 2p XAS: effects of HERFD

LaF_3



2p5d dipole

2p4f quadrupole

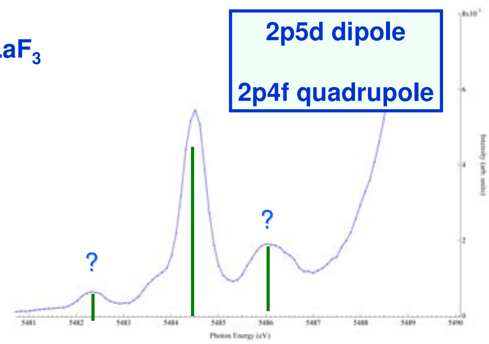
Suljoti et al. (new data from ID26)

Does FY does measure X-ray Absorption?

LaF$_3$

2p5d dipole

2p4f quadrupole



Suljoti et al. (new data from ID26)

La 2p XAS: effects of HERFD

- HERFD makes pre-edge 2p4f transition visible
- Why has the 2p4f pre-edge 3 peaks?

Does HERFD measure X-ray Absorption?

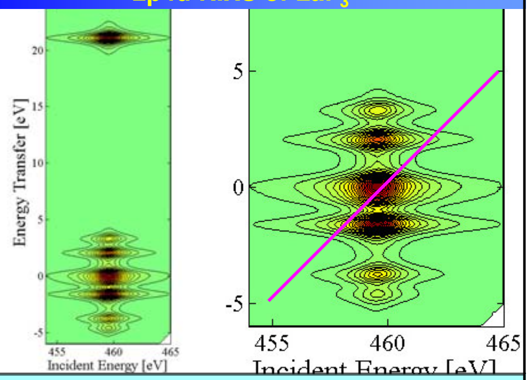
2p4f quadrupole

$4f^0 \rightarrow 2p^5\ 4f^1$

$4f^0 + 4f^1\underline{L} \rightarrow 2p^5\ 4f^1 + 2p^5\ 4f^2\underline{L}$

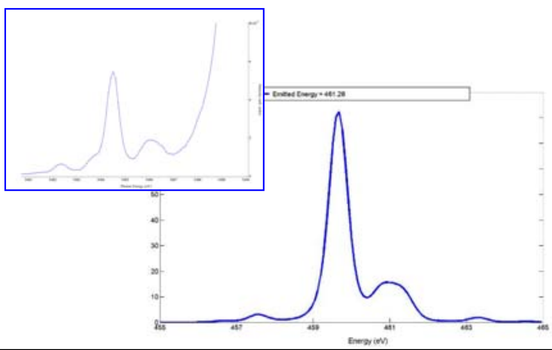
$4f^05d^0 + 4f^0\ 5d^1\underline{L} \rightarrow 2p^5\ 4f^1 + 2p^54f^15d^1\underline{L}$

2p4d RIXS of LaF$_3$



Suljoti et al. (new data from ID26)

HERFD-XANES of LaF$_3$



Suljoti et al. (new data from ID26)

2p4d RIXS of LaF$_3$

measured with 2p4d XES

$4f^0 \rightarrow 2p^5\ 4f^1 \rightarrow 4d^9\ 4f^1$

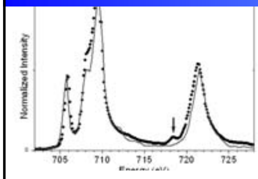
one peak

multiplet structure

Applications

- Systems with pi-bonds
- X-MCD of Fe-complexes on metal surfaces
- In-situ STXM chemical imaging

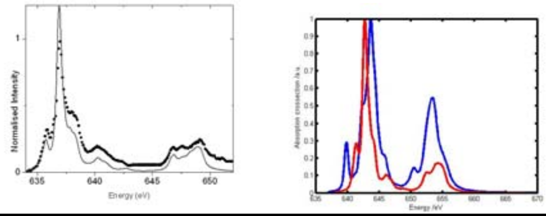
CTM4XAS simulations



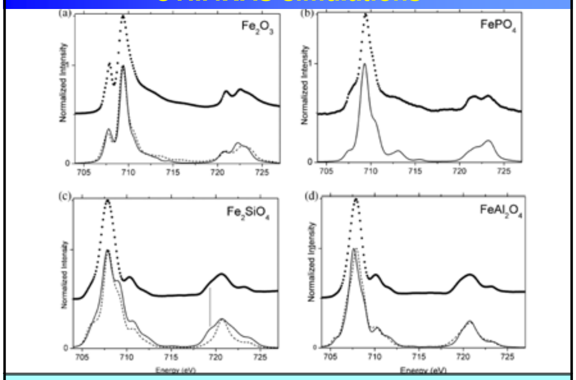
2p XAS of Mn^{2+} and Fe^{3+}

High-spin: 10Dq = 1.2
→ MnO

Low-spin: 10Dq = 3.0
→ Fe^{III}(tacn)



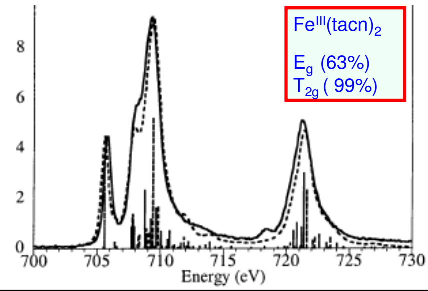
CTM4XAS simulations



J. Phys. Chem. B. 109, 20751 (2005)

XAS and Differential Orbital Covalence

- Derive DOC from CTM4XAS simulation
- Comparison to DOC from DFT (ADF) calculation



XAS and Differential Orbital Covalence

- Derive DOC from CTM4XAS simulation
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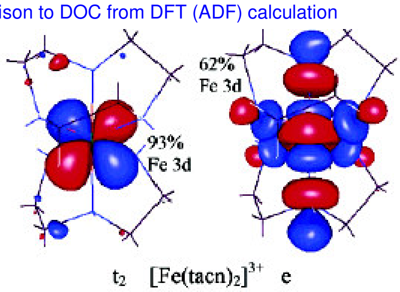
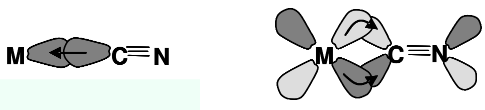
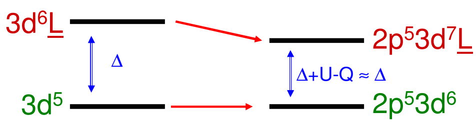


with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

LMCT and MLCT: π - bonding

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

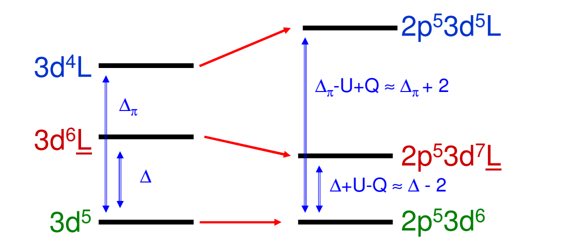




with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

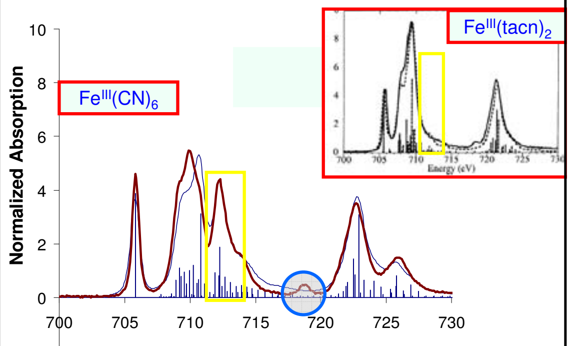
LMCT and MLCT: π - bonding

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



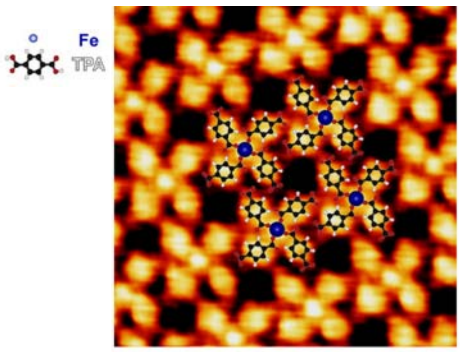
with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

LMCT and MLCT: π - bonding



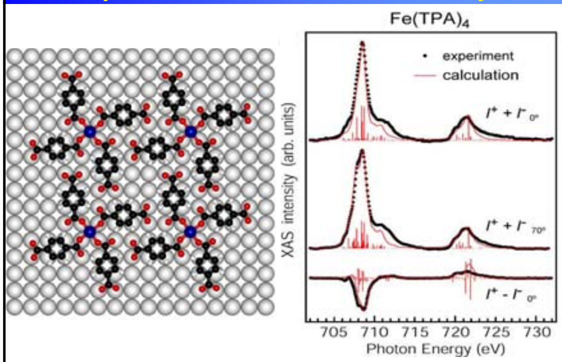
with Ed Solomon (Stanford) JACS 125, 12894 (2003), JACS 128, 10442 (2006), JACS 129, 113 (2007)

Supramolecular control of Fe arrays



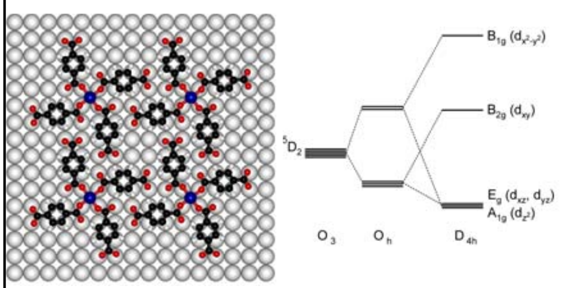
with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

Supramolecular control of Fe arrays



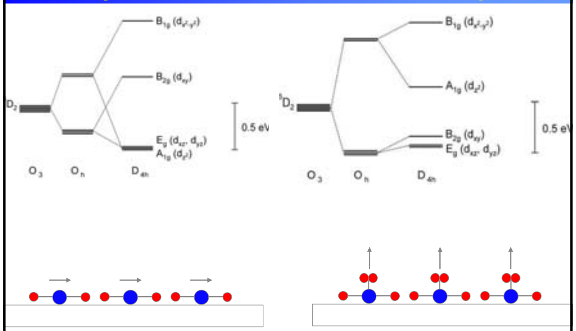
with Pietro Gambardella (Barcelona), Nature Materials 8, 189 (2009)

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)

Why X-ray absorption?

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

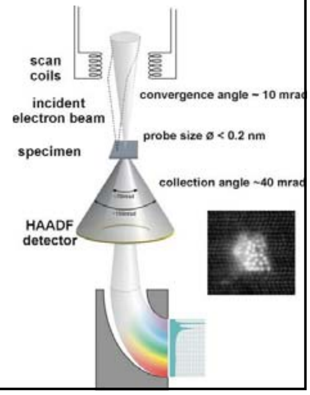
- Valence, Spin-state,
- Crystal field energies, dd-excitations
- Hybridization (differential orbital covalence)
- MO energies / Density of states

UHV

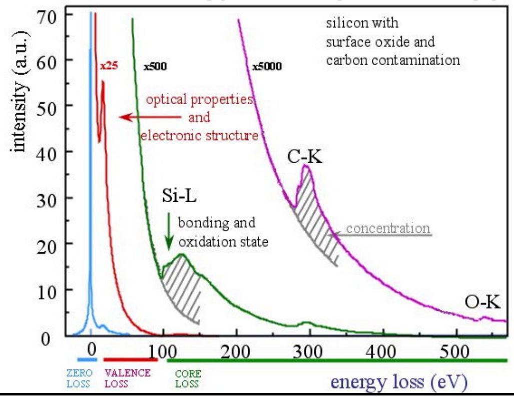
Space?, Time?, Pressure?

Electron Energy Loss Spectroscopy

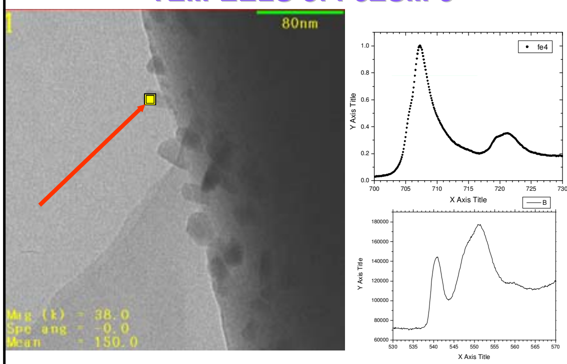
- Identical spectral shape
- XAS at Synchrotron
- EELS with Electron Microscope
- XAS: 0.2 eV/20nm
- EELS: 0.2 eV/0.5 nm
- XAS: extreme conditions
- EELS: vacuum



Electron Energy Loss Spectroscopy

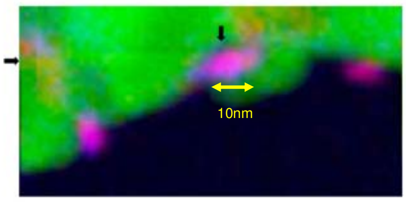


TEM-EELS of FeZSM-5



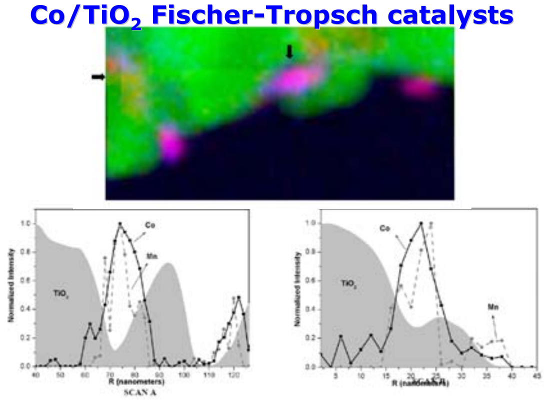
Co/TiO_2 Fischer-Tropsch catalysts

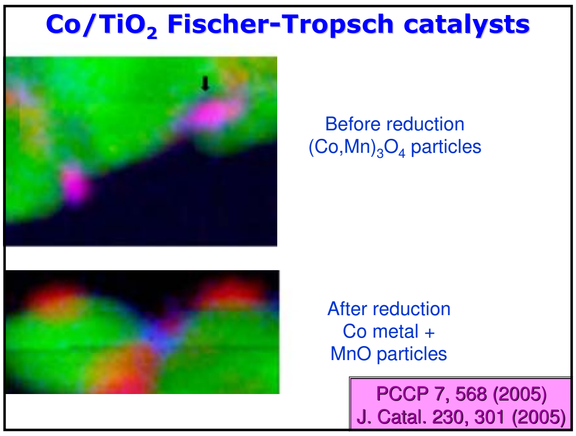
Quantify EELS spectra of Ti, Mn and Co

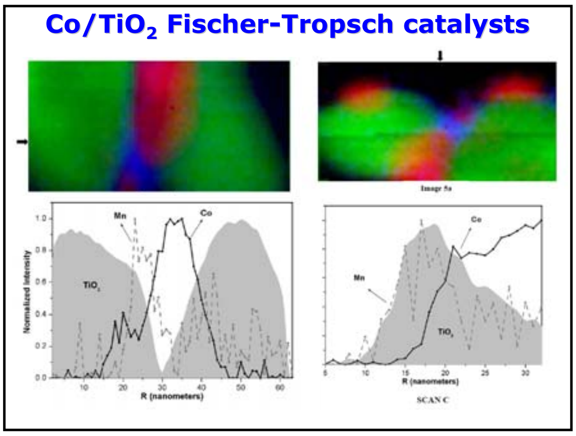


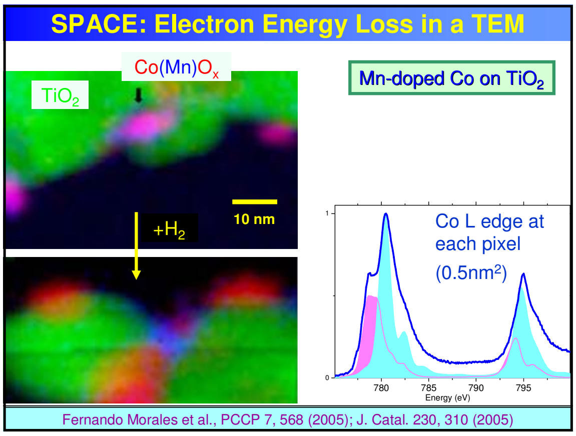
J. Catal. 230, 301 (2005)

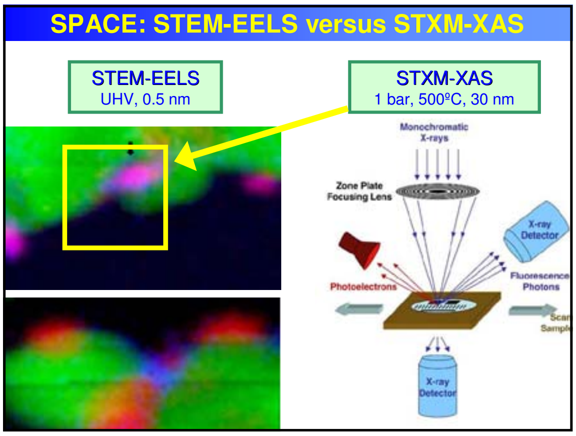
Co/TiO_2 Fischer-Tropsch catalysts

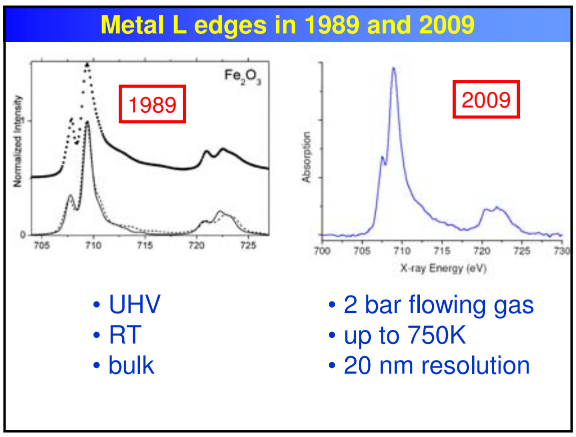


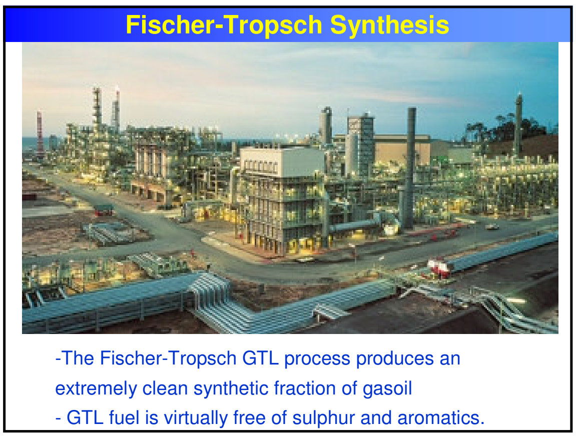

Co/TiO2 Fischer-Tropsch catalysts
Before reduction
(Co,Mn)3O4 particles
After reduction
Co metal +
MnO particles
PCCP 7, 568 (2005)
J. Catal. 230, 301 (2005)


Co/TiO2 Fischer-Tropsch catalysts
Mn
Co
TiO2
R (nanometers)
SCAN C

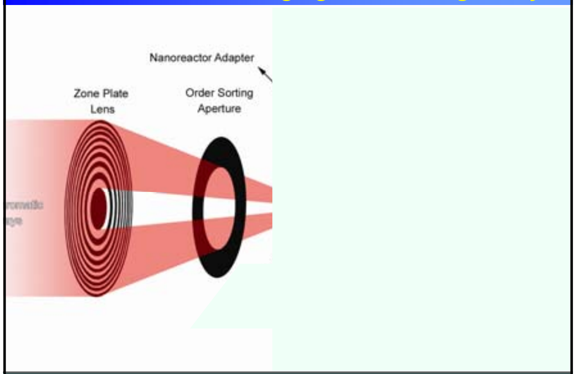

SPACE: Electron Energy Loss in a TEM
Co(Mn)Ox
TiO2
Mn-doped Co on TiO2
10 nm
+H2
Co L edge at
each pixel
(0.5nm2)
780
785
790
795
Energy (eV)
Fernando Morales et al., PCCP 7, 568 (2005); J. Catal. 230, 310 (2005)


SPACE: STEM-EELS versus STXM-XAS
STEM-EELS
UHV, 0.5 nm
STXM-XAS
1 bar, 500ºC, 30 nm
Monochromatic
X-rays
Zone Plate
Focusing Lens
X-ray
Detector
Photoelectrons
Fluorescence
Photons
X-ray
Detector


Metal L edges in 1989 and 2009
1989
Fe2O3
Normalized Intensity
705
710
715
720
725
2009
Absorption
700
705
710
715
720
725
730
X-ray Energy (eV)
• UHV
• RT
• bulk
• 2 bar flowing gas
• up to 750K
• 20 nm resolution

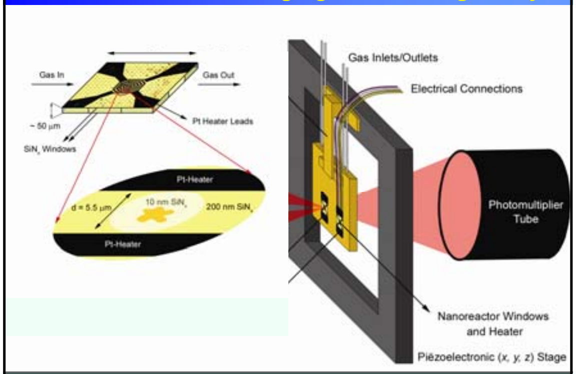

Fischer-Tropsch Synthesis
-The Fischer-Tropsch GTL process produces an
extremely clean synthetic fraction of gasoil
- GTL fuel is virtually free of sulphur and aromatics.

Nanoscale chemical imaging of a working catalyst

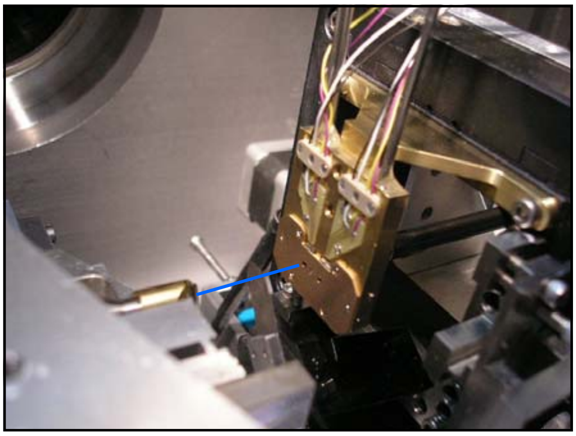


On reactor cell: Fredrik Creemer et al. Ultramicroscopy 108, 993 (2008)

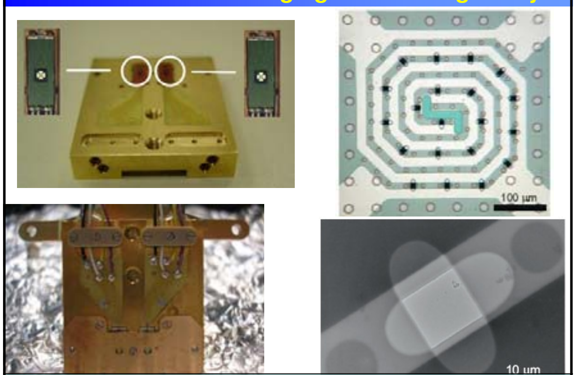
Nanoscale chemical imaging of a working catalyst



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



Nanoscale chemical imaging of a working catalyst



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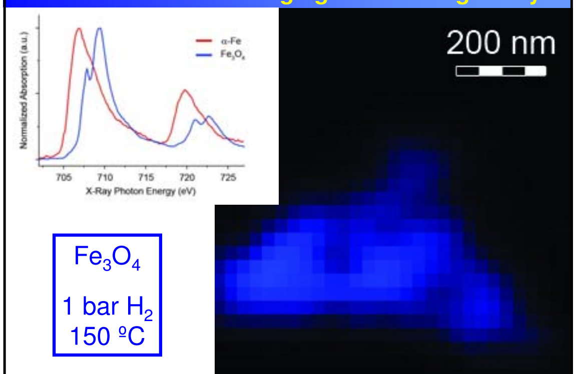
Nanoscale chemical imaging of a working catalyst



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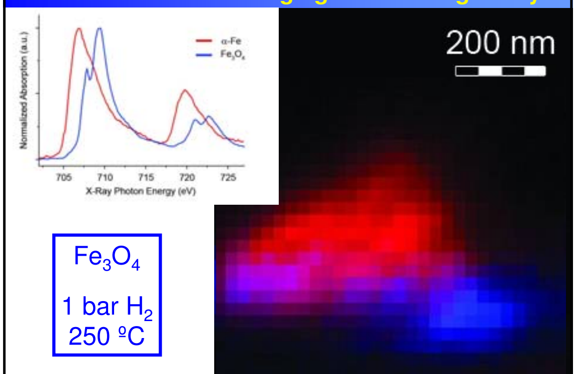
Nanoscale chemical imaging of a working catalyst



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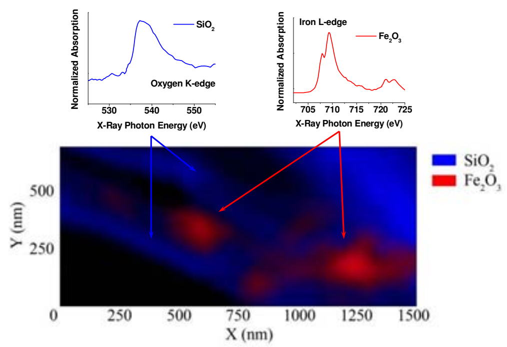
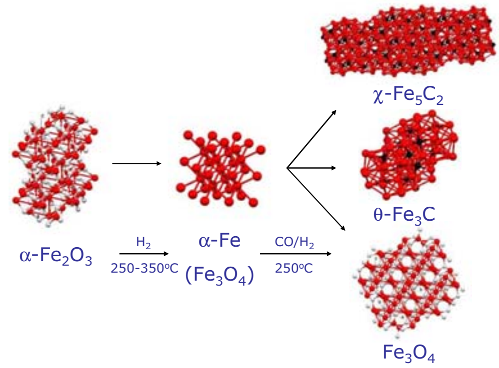
Nanoscale chemical imaging of Fe_2O_3 [K, Cu]/SiO_2

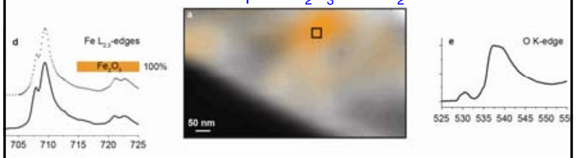


Nanoscale chemical imaging of a working catalyst



Nanoscale chemical imaging of a working catalyst

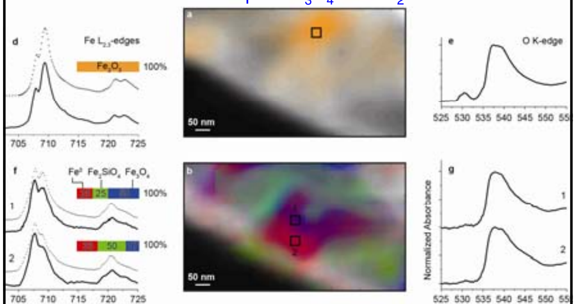
K+Cu doped Fe_2O_3 on SiO_2



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

Nanoscale chemical imaging of a working catalyst

K+Cu doped Fe_3O_4 on SiO_2



Before and after reduction

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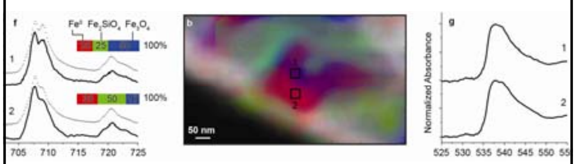
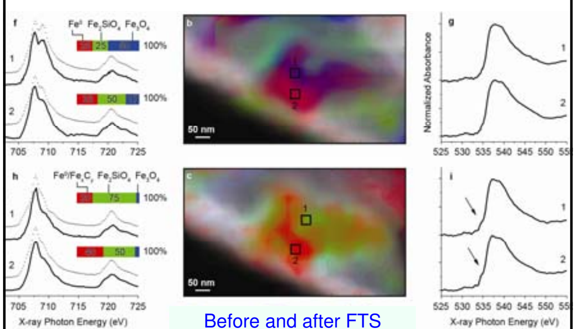
Nanoscale chemical imaging of a working catalyst



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

Nanoscale chemical imaging of a working catalyst



Before and after FTS

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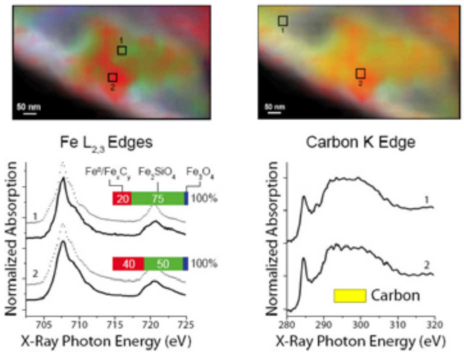
Nanoscale chemical imaging of a working catalyst



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

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)

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