X-ray absorption spectroscopy

X-ray absorption spectroscopy

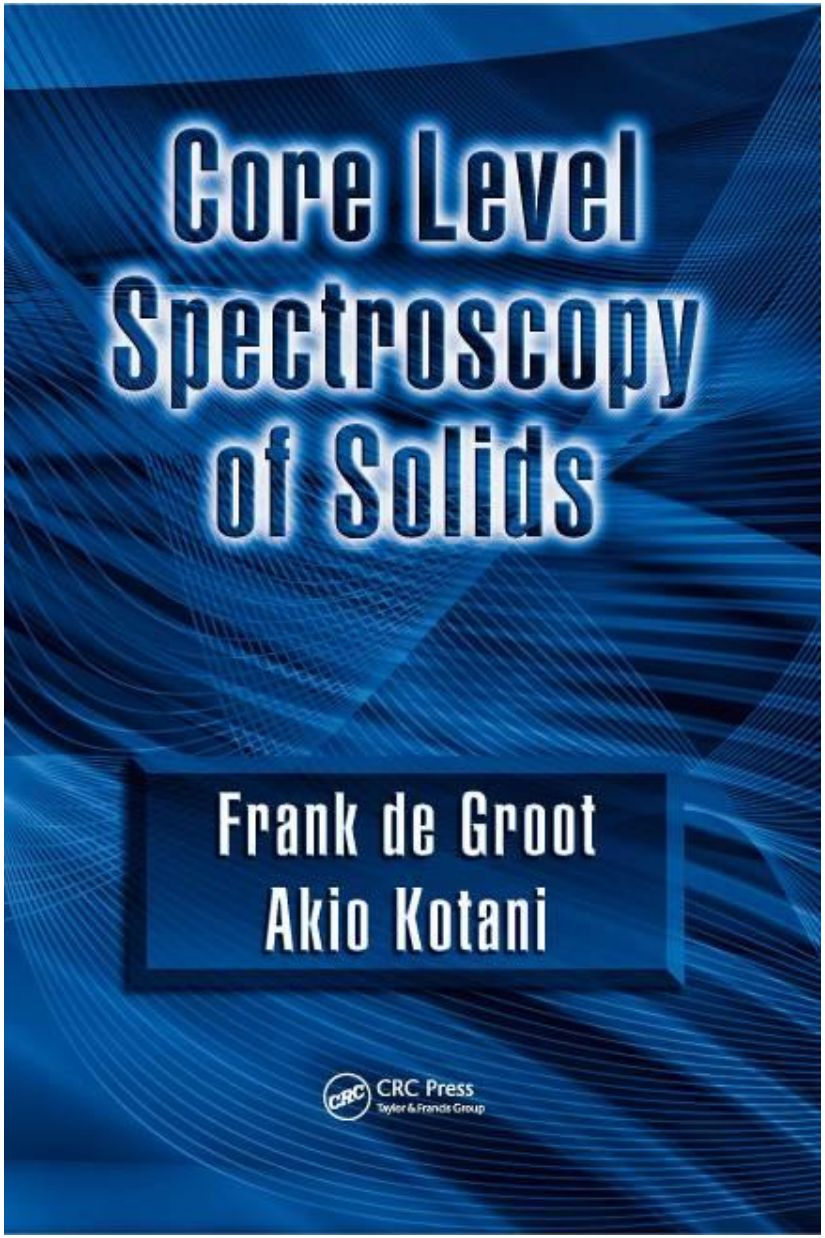
Frank de Groot

PhD: solid state chemistry	**U Nijmegen** (91)
Post-doc:	**LURE, Orsay** (93-94)
Post-doc: solid state physics	**U Groningen** (95-98)

U Utrecht since 1999

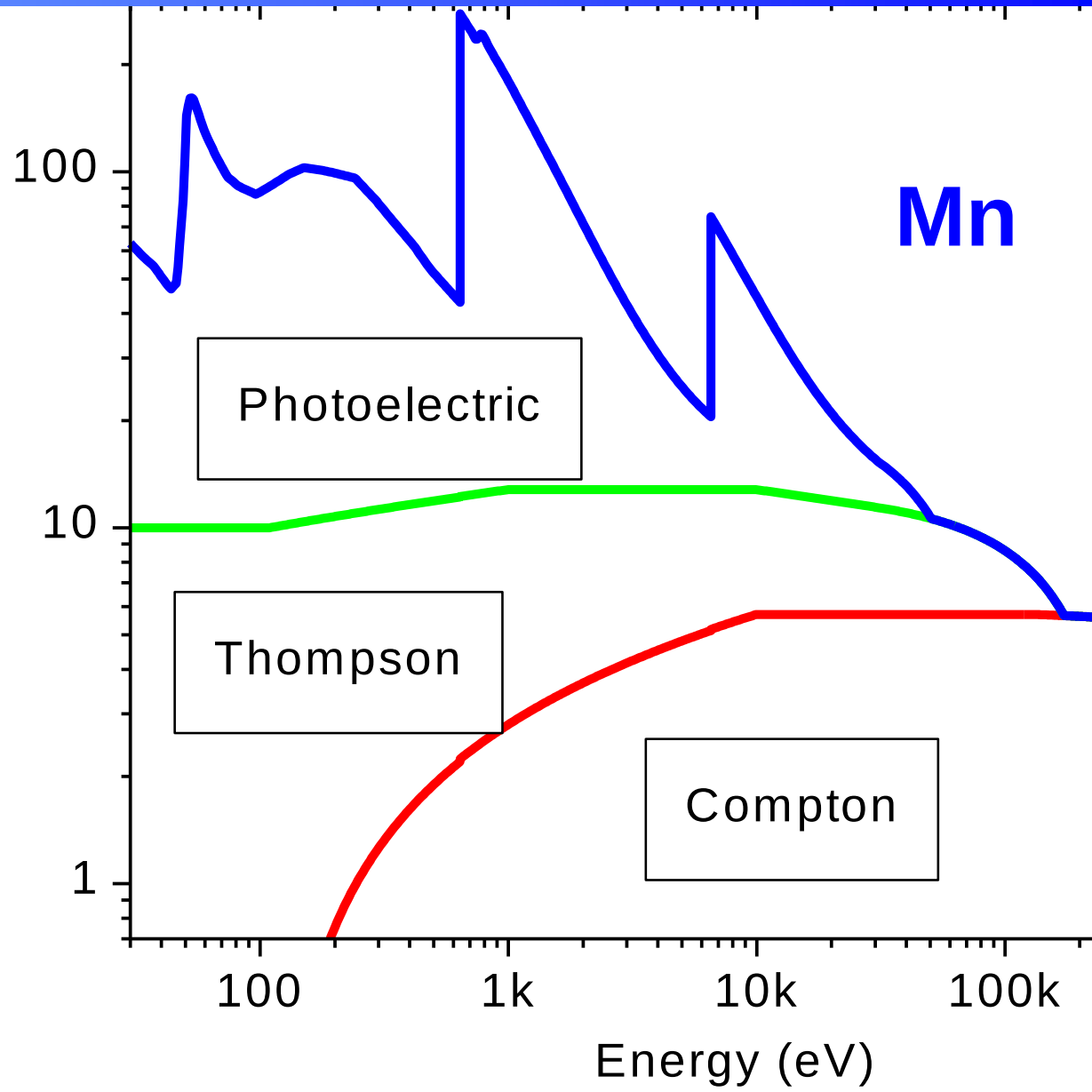
Synchrotron and theoretical spectroscopy of catalytic nanomaterials

(inorganic chemistry and catalysis)

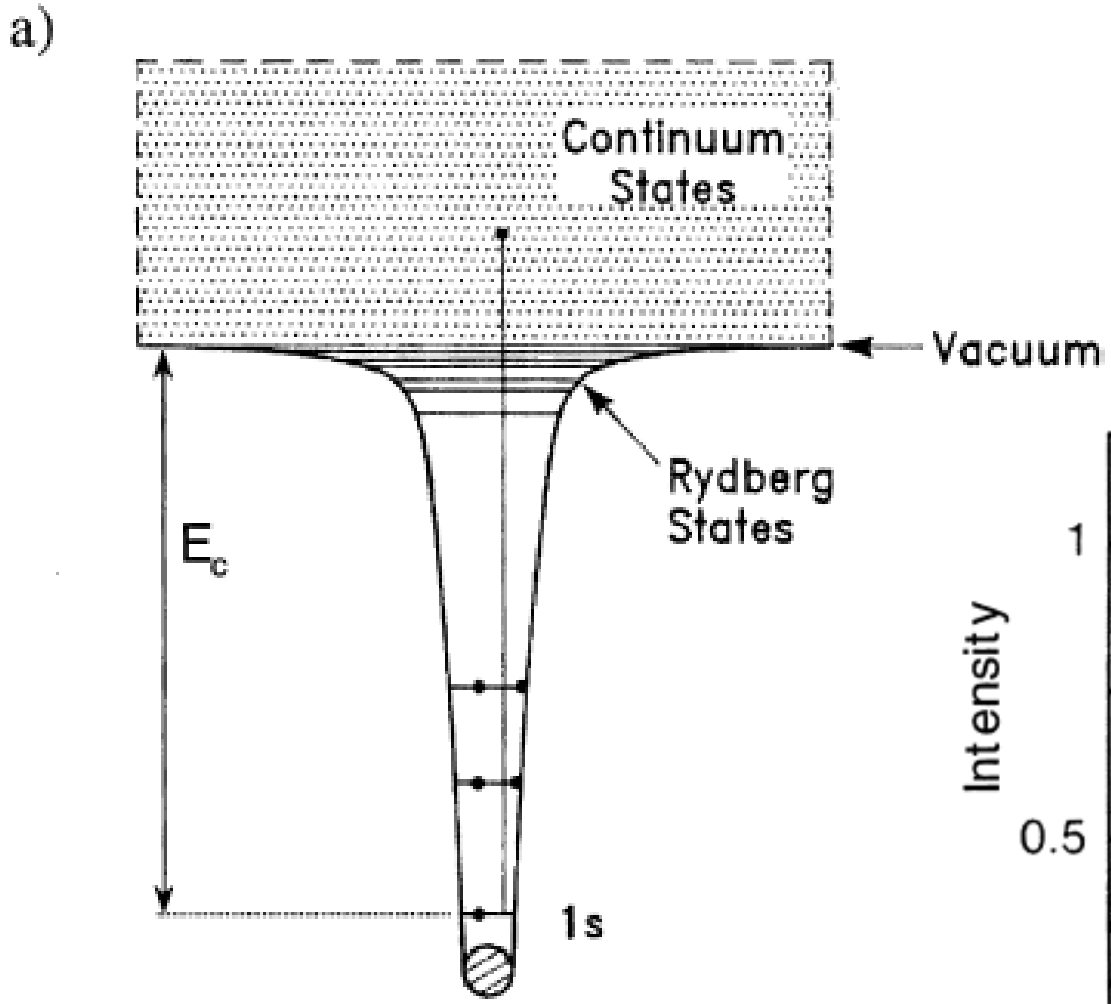

Core Level
Spectroscopy
of Solids
Frank de Groot
Akio Kotani
CRC Press
Taylor & Francis Group

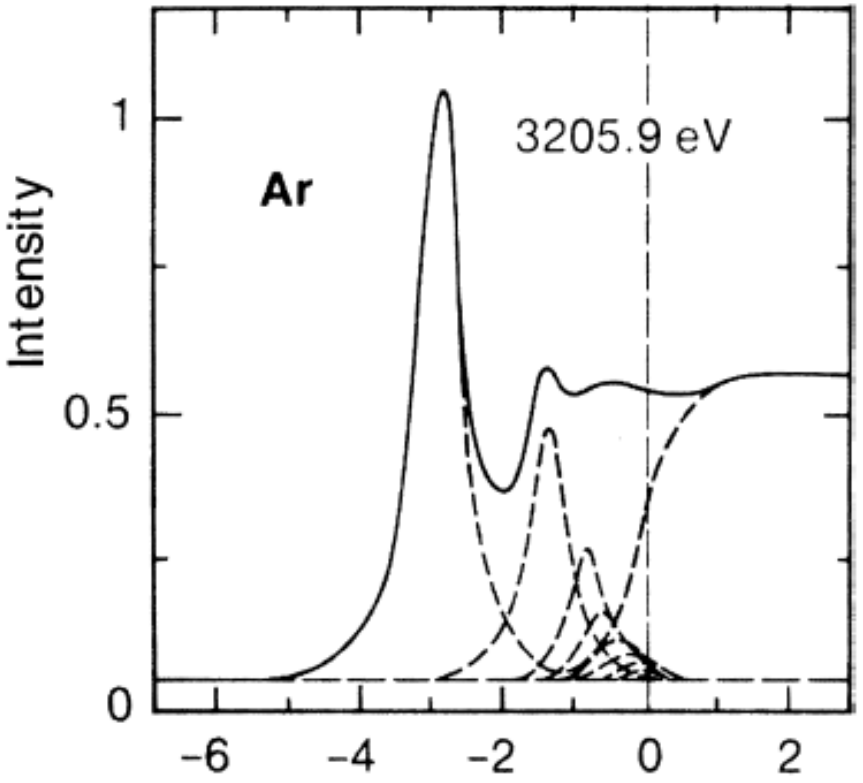
Interaction of x-rays with matter

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



XAS of an atom





XAS of a solid

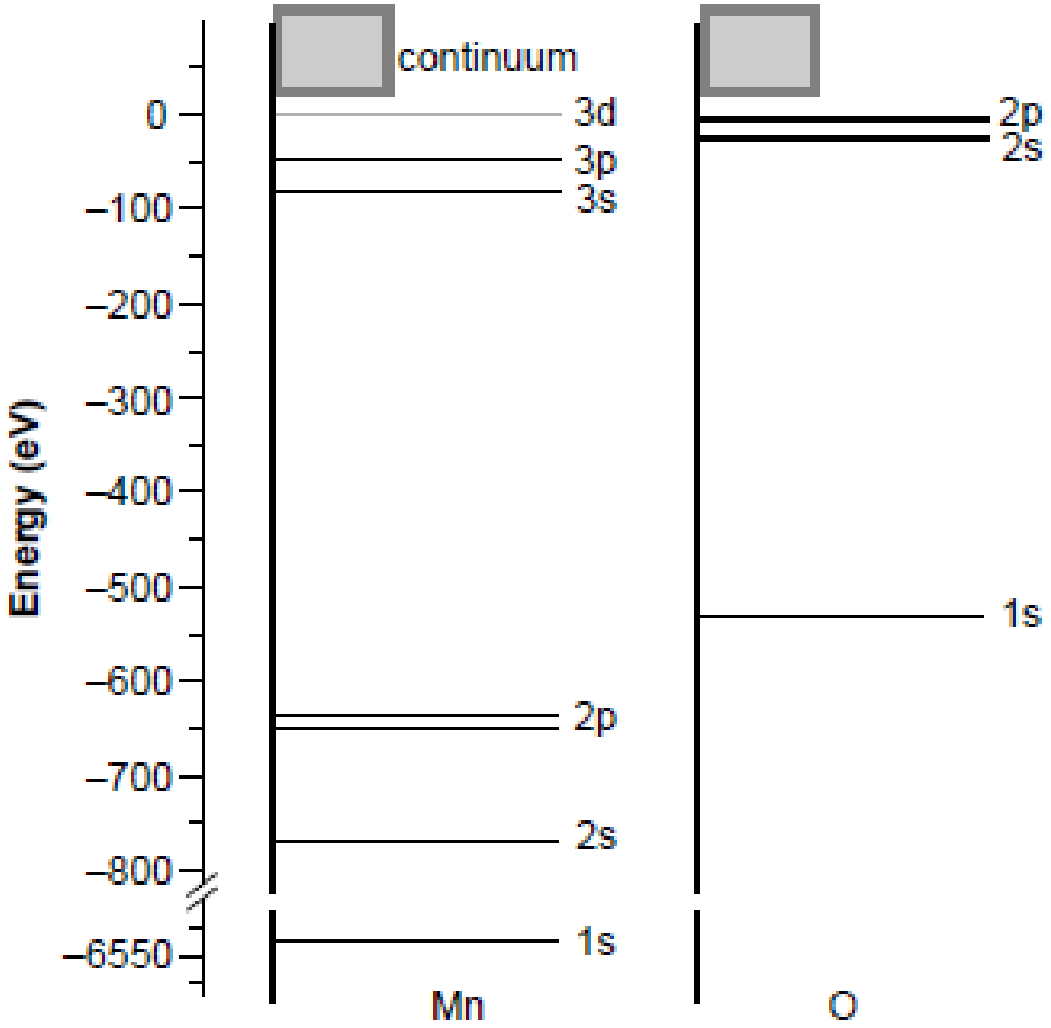


FIGURE 1.1 Energies of the core levels and VES of Mn and O in MnO.

XAS of a solid

TABLE 2.1
Nomenclature for Core Level Spectra

Orbital*	Label†	E‡ (Ni)	E‡ (O)
1s	K	8333	543
2s	L_1	1008	42
$2p_{1/2}$	L_2	870	V§
$2p_{3/2}$	L_3	853	V§
3s	M_1	111	
$3p_{1/2}$	M_2	68	
$3p_{3/2}$	M_3	66	
$3d_{3/2}$	M_4	V	
$3d_{5/2}$	M_5	V	

* Orbital notation.

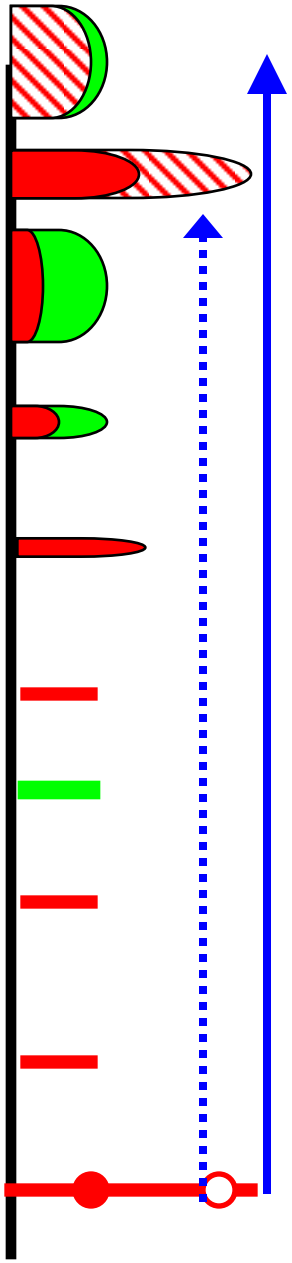
† Spectroscopic names (Barkla notation).

‡ Binding energies.

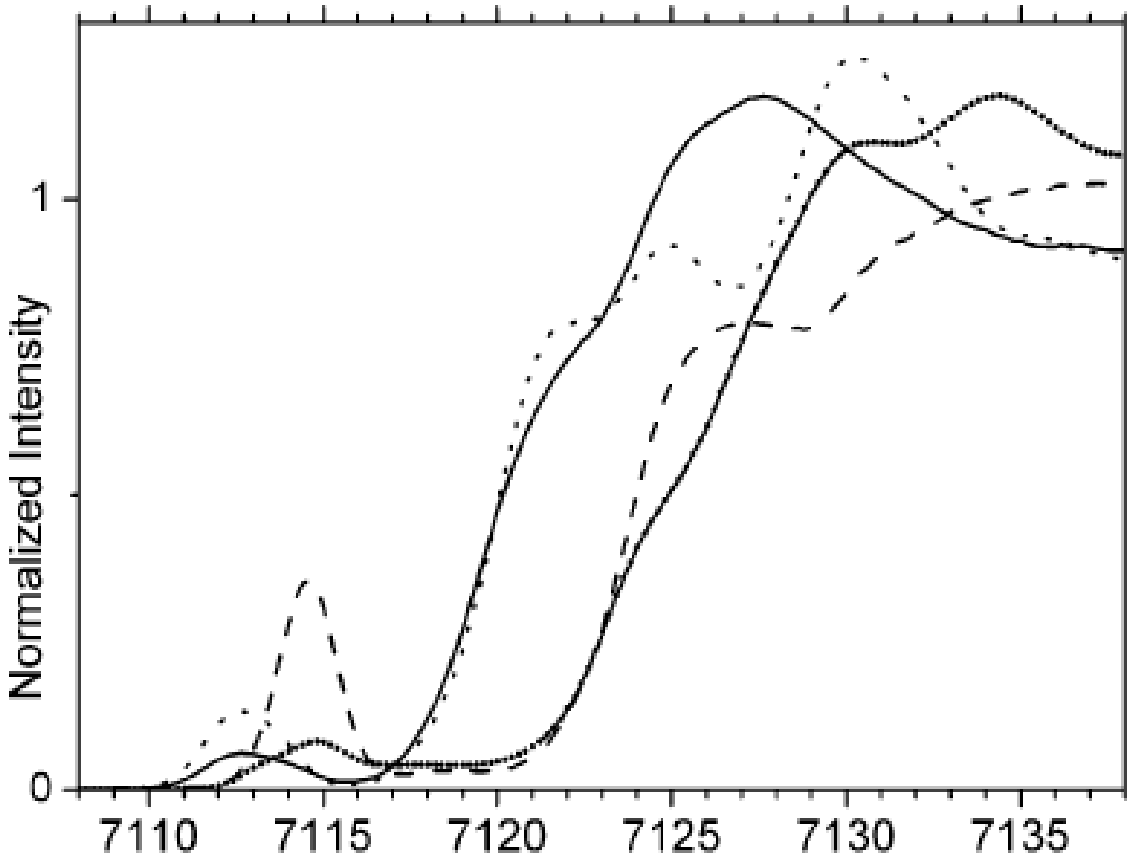
§ Valence state with a binding energy of a few eV.

Source: X-ray Data Booklet (2001) (LBNL, Berkeley).

XAS of a solid



Fe 4p	-
Fe 3d	0
O 2p	5
O 2s	20
Fe 3p	50
Fe 3s	85
O 1s	530
Fe 2p	700
Fe 2s	800
Fe 1s	7115



XAS of a solid

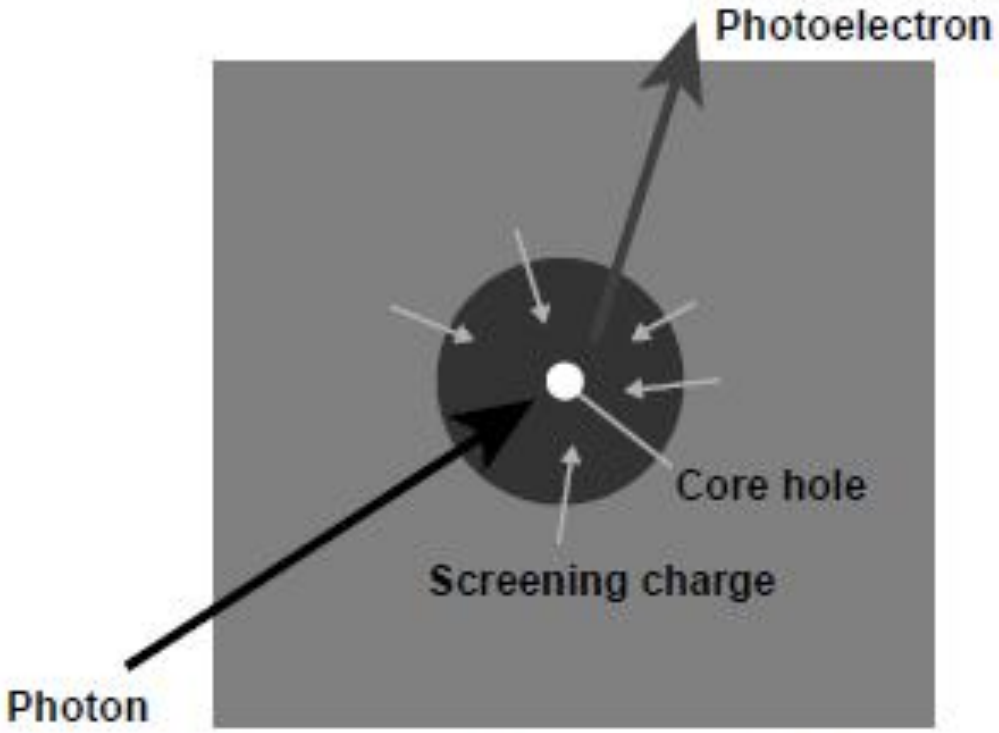


FIGURE 1.3 Excitation of a photoelectron by an x-ray photon creates a core hole that is screened by the surroundings.

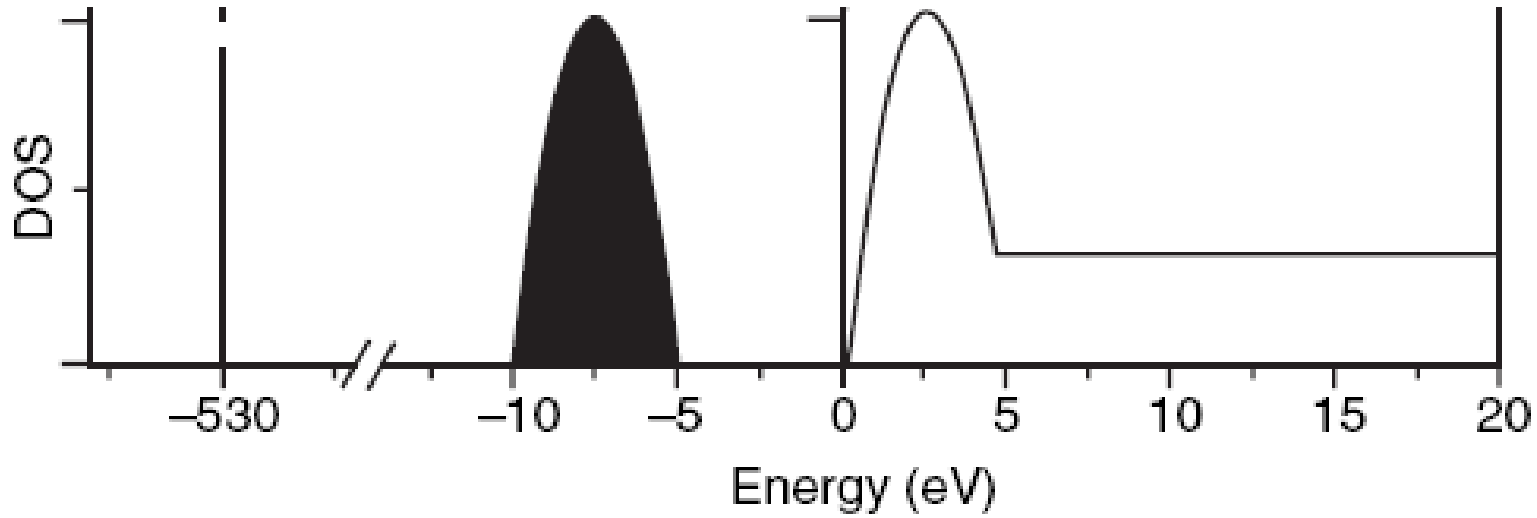
XAS and XPS

Excitation of core electrons to empty states.

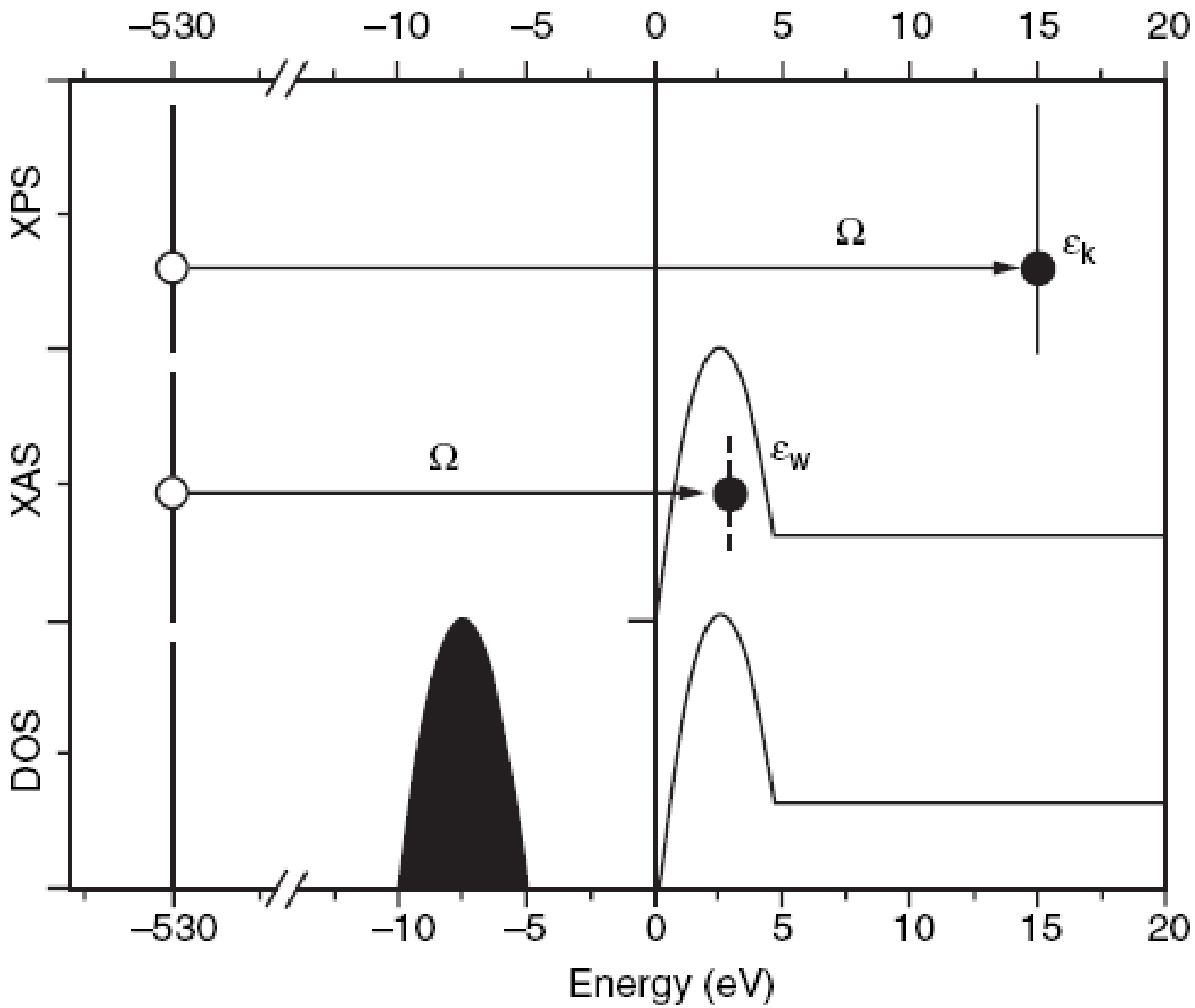
Spectrum given by the **Fermi Golden Rule**

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

XAS and XPS



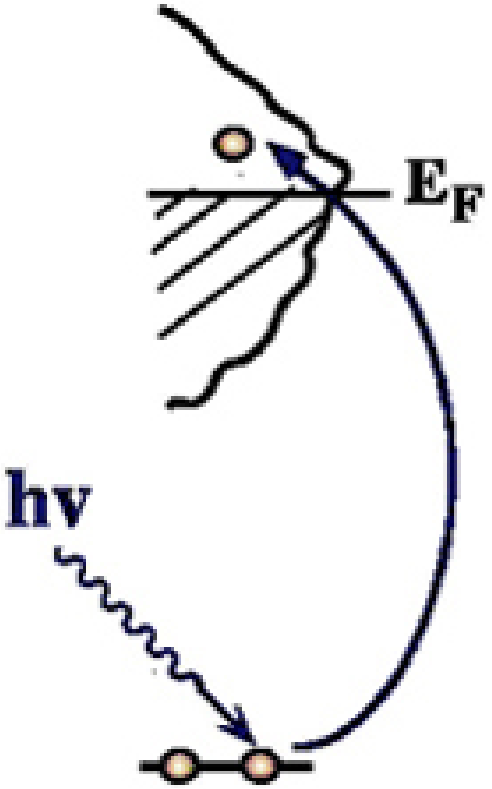
XAS and XPS


–530
–10
–5
0
5
10
15
20
XPS
XAS
DOS
Ω
ε_k
Ω
ε_w
–530
–10
–5
0
5
10
15
20
Energy (eV)

X-ray absorption spectroscopy

Excitations of
core electrons
to empty states

The XAS spectrum
is given by the
Fermi Golden Rule

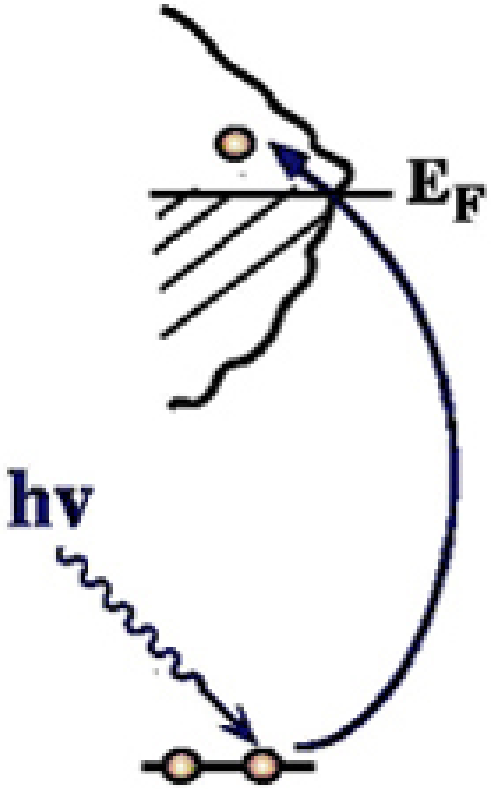


$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \left| \hat{e} \cdot r \right| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray Absorption Spectroscopy

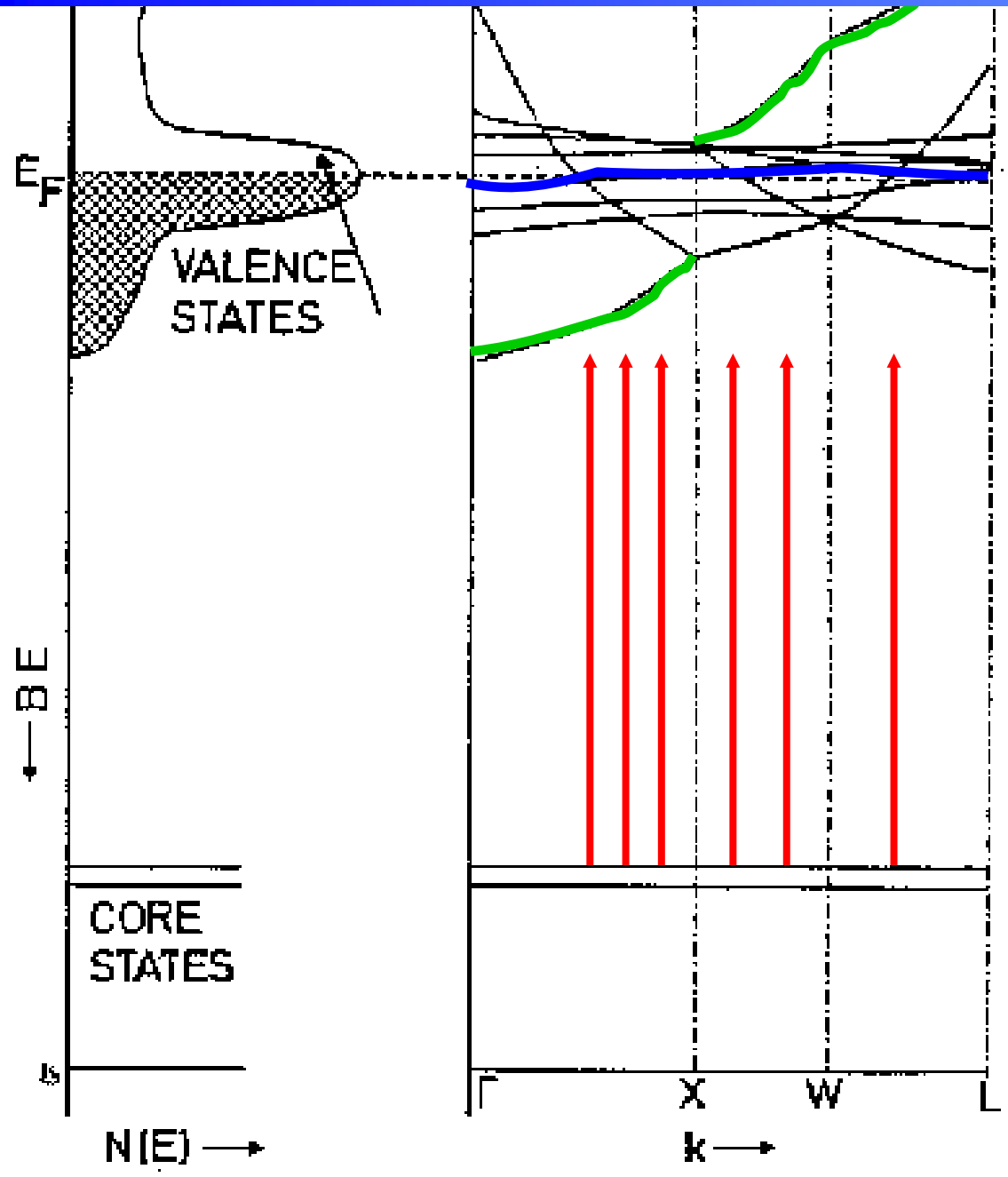
Excitations of
core electrons
to empty states

The XAS spectrum
is given by the
Fermi Golden Rule



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

X-ray Absorption Spectroscopy

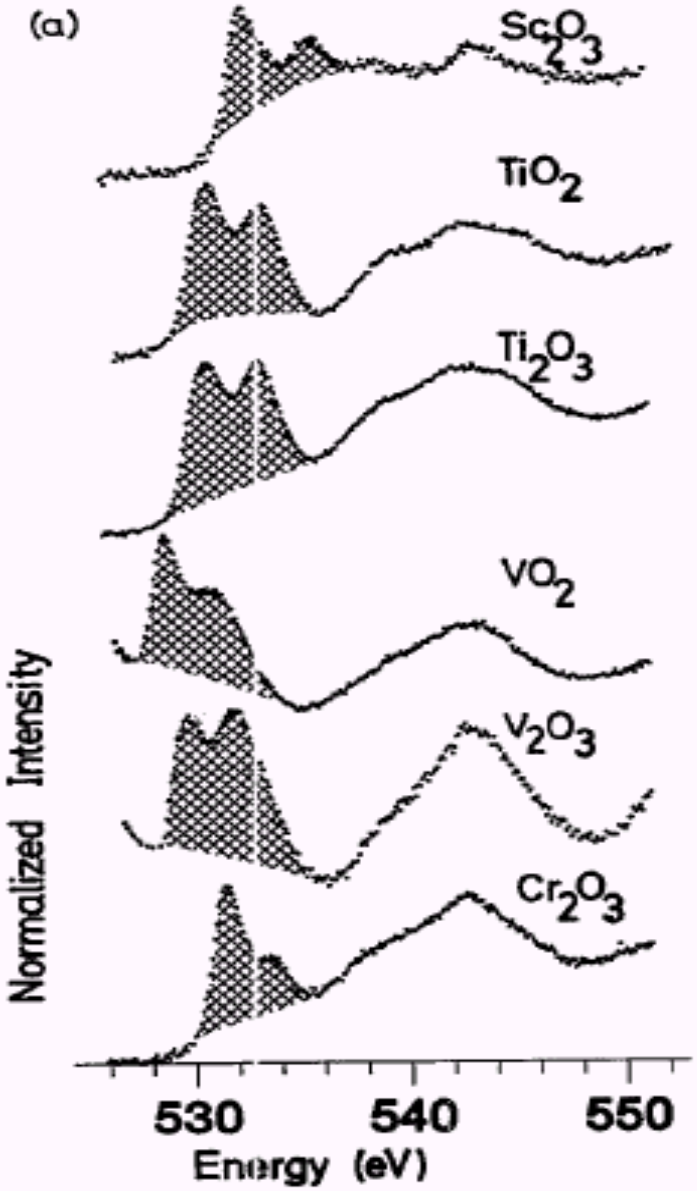


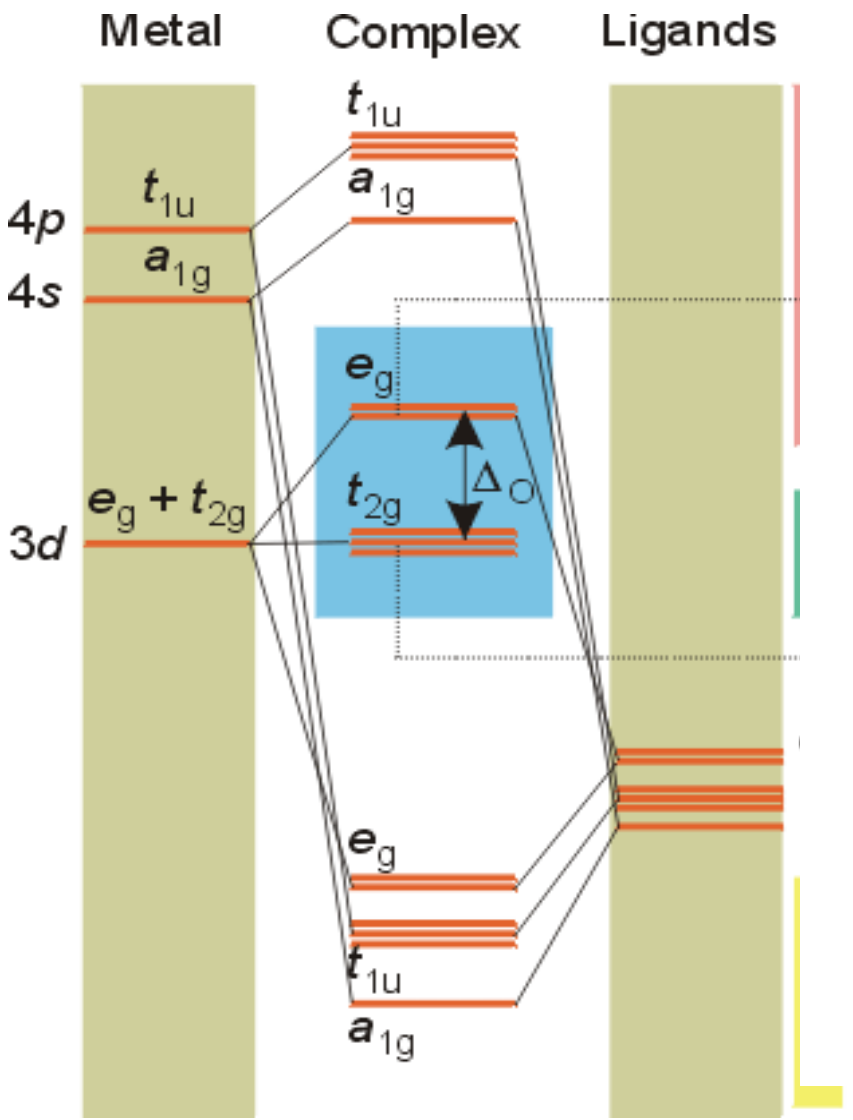
Density of States (DOS) is the integral over k-space of the band structure.

Core states have no dispersion.

XAS preserves momentum (k)

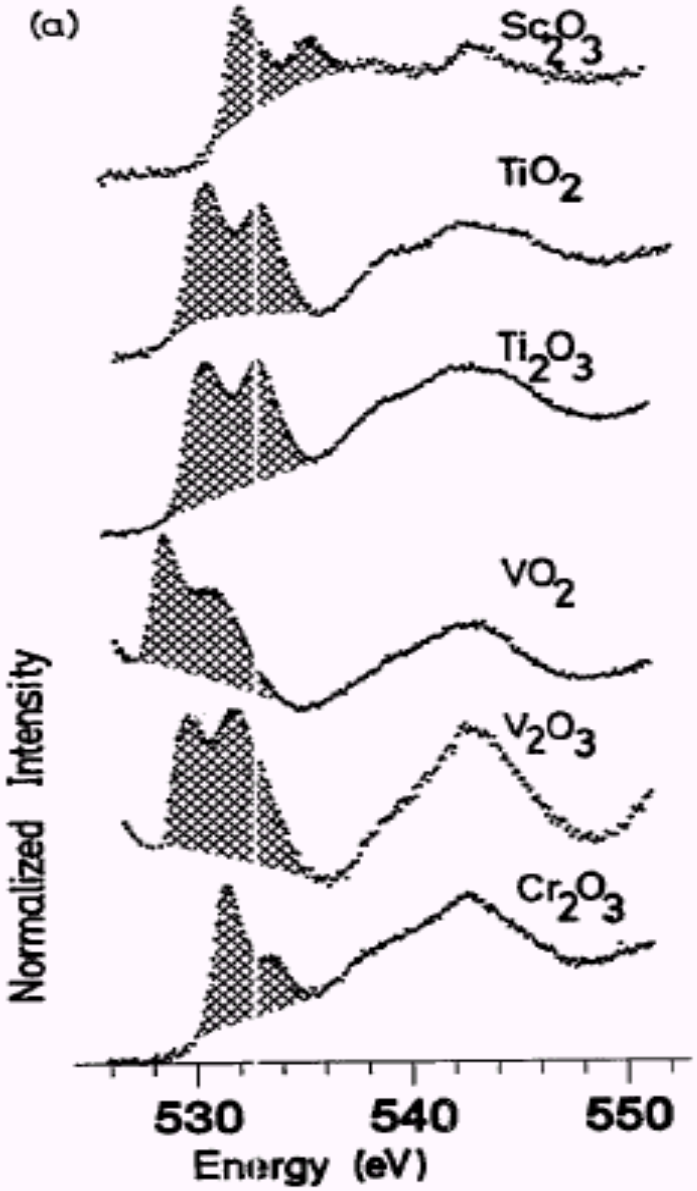
X-ray Absorption Spectroscopy





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

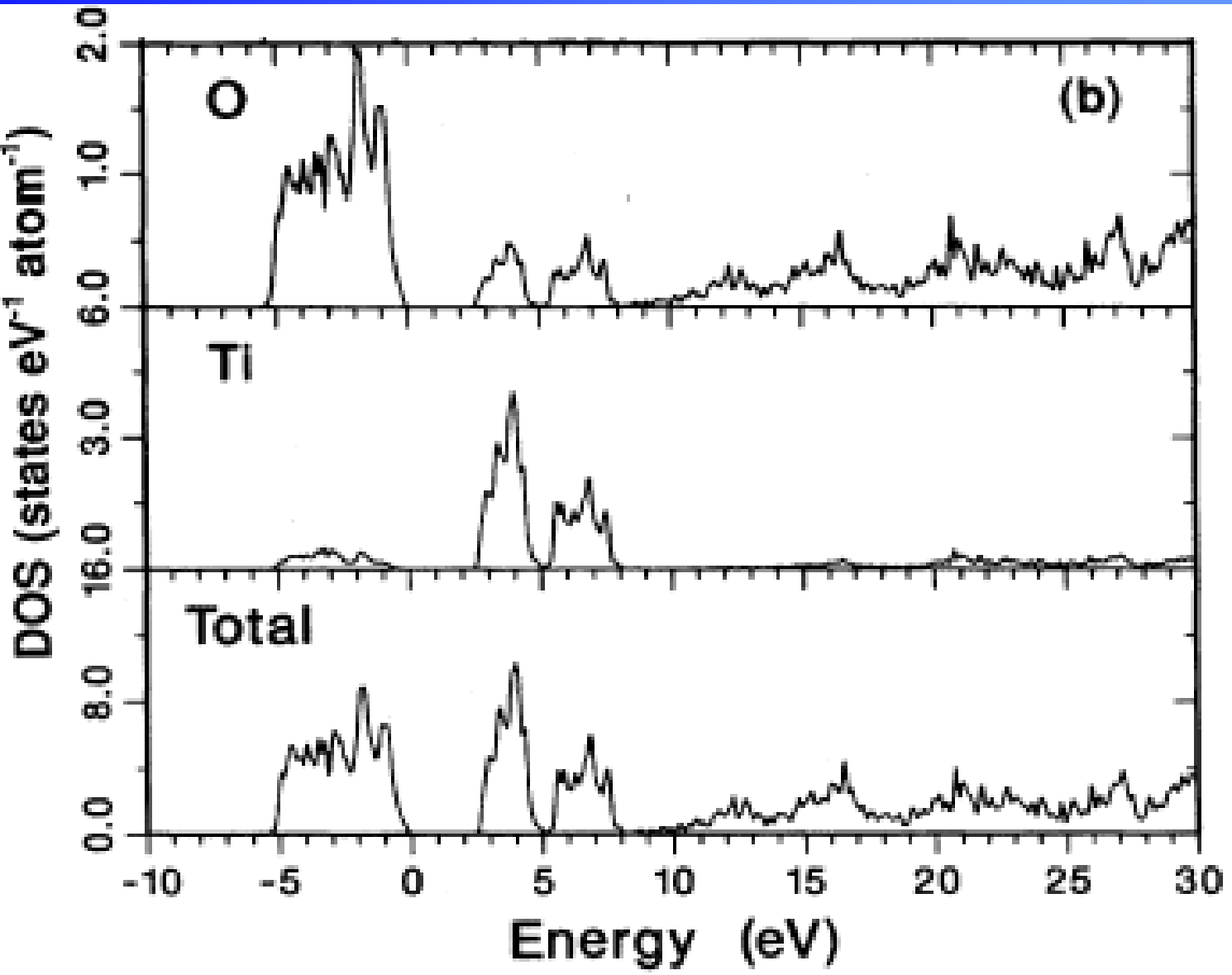
X-ray Absorption Spectroscopy



oxygen 1s > p DOS

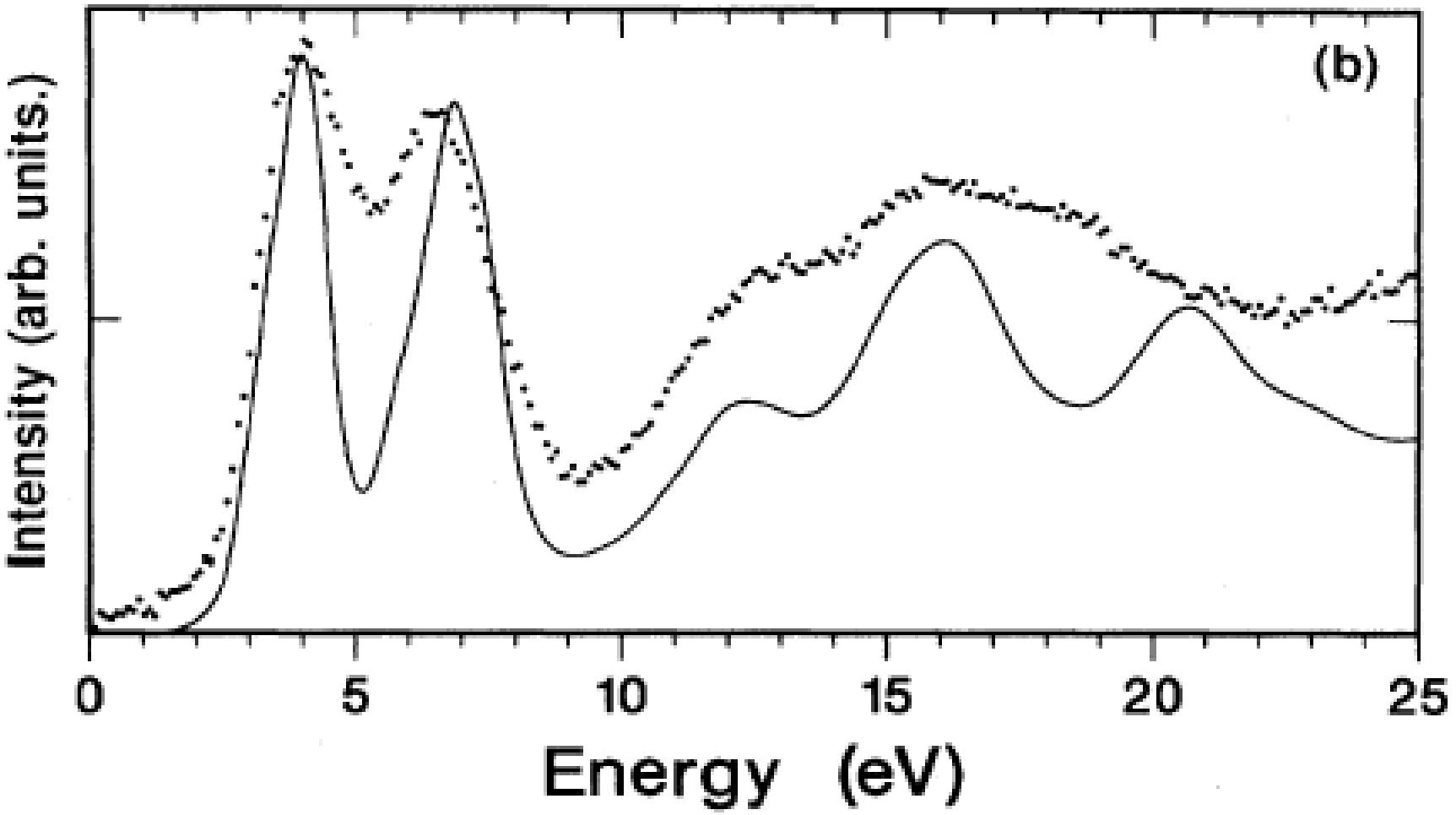
Phys. Rev. B.40, 5715 (1989); 48, 2074 (1993)

Density of States of TiO_2



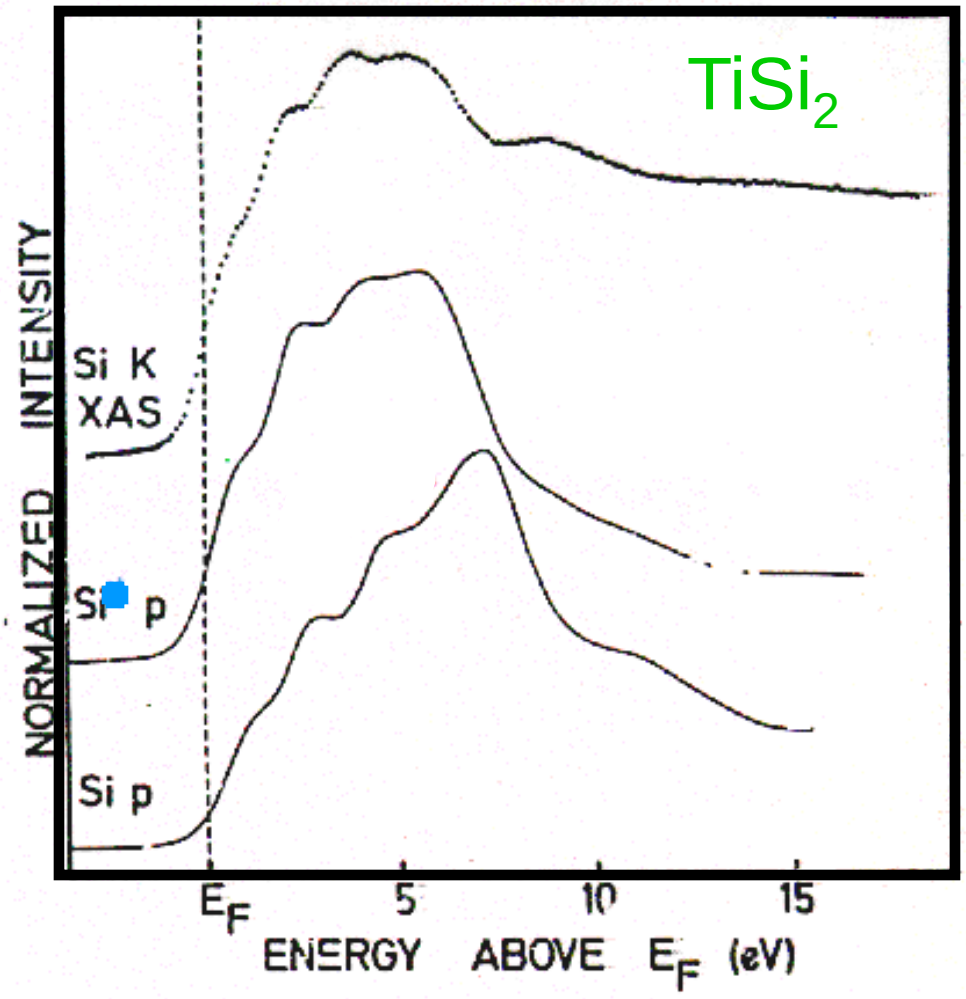
Phys. Rev. B. 40, 5715 (1989); 48, 2074 (1993)

Density of States of TiO_2



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

XAS: 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)

X-ray Absorption Spectroscopy

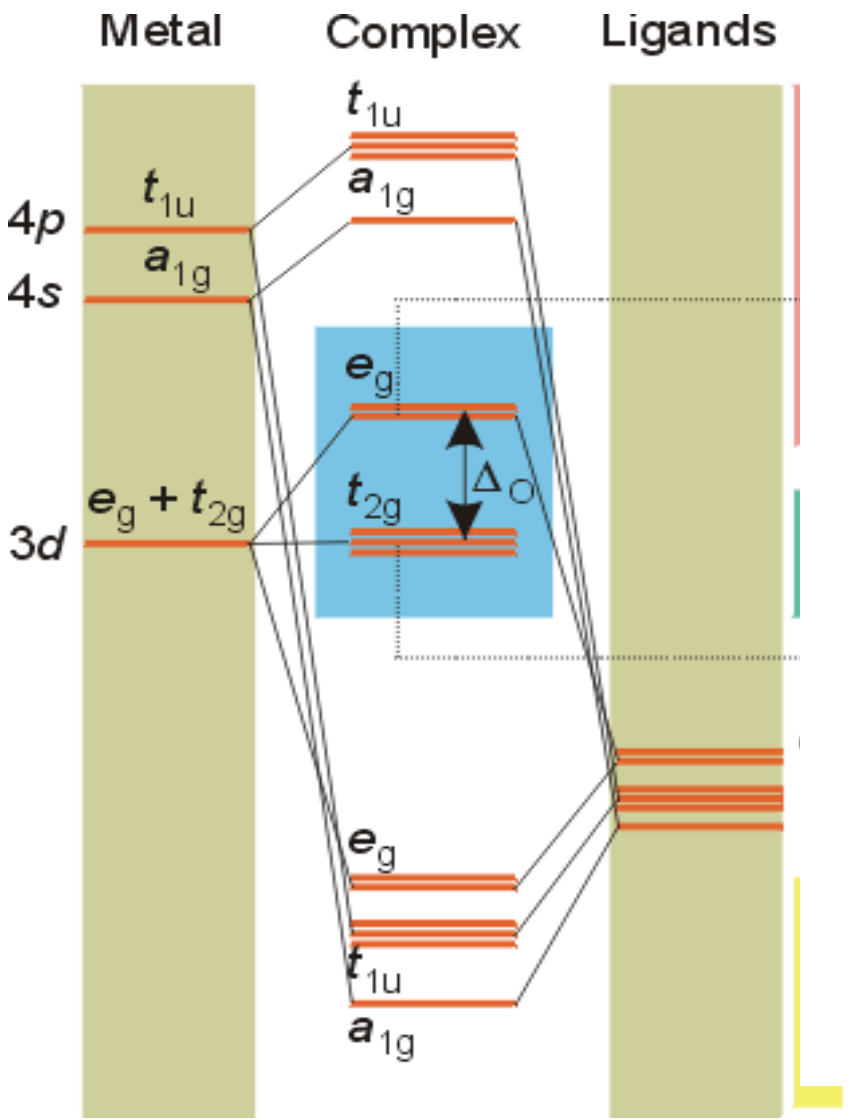
Excitation of core electrons to empty states.

Spectrum identifies with the
empty Density of States

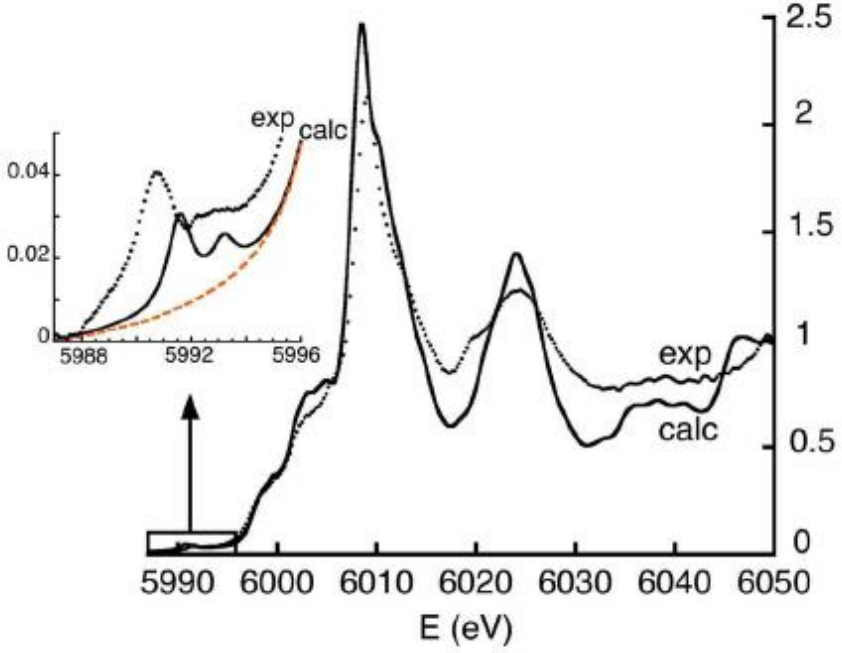
Works well for K edges (1s)

Calculate with DFT
(LDA+U, DMFT, BSE)

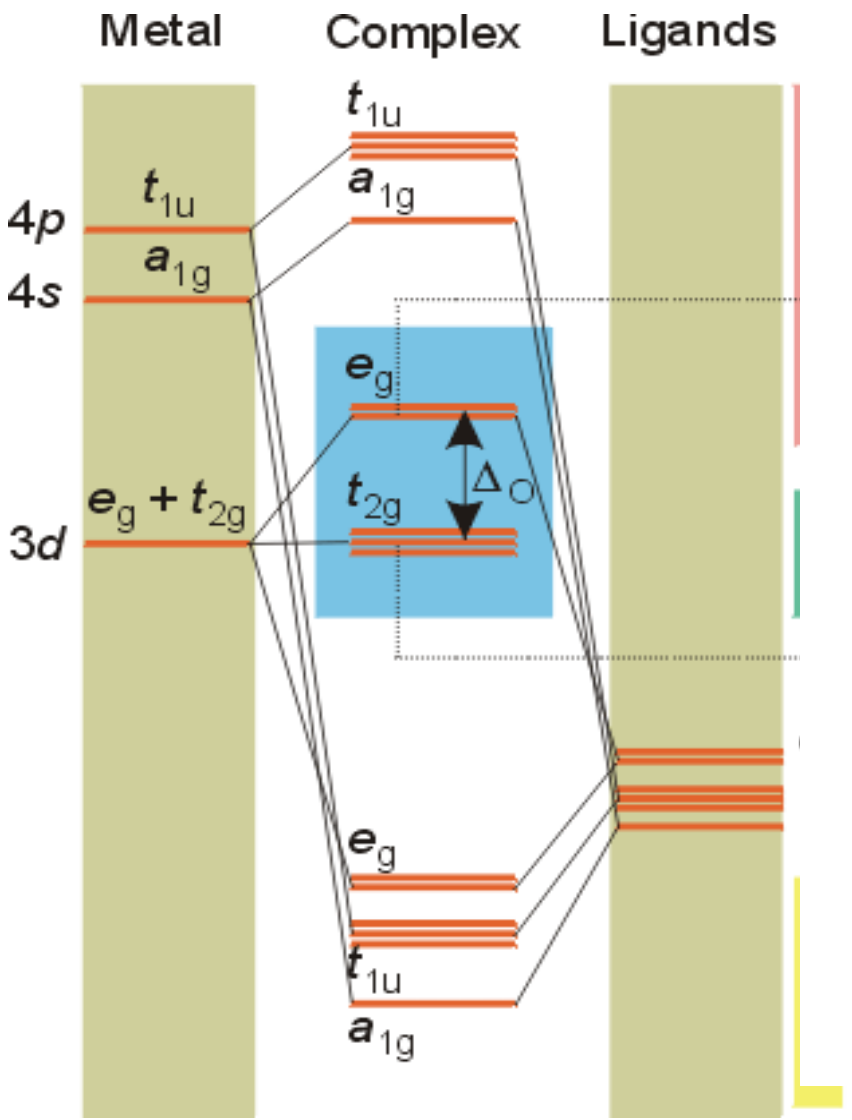
Metal 1s XAS


Metal
Complex
Ligands
4p
4s
3d
t_{1u}
a_{1g}
$e_g + t_{2g}$
t_{1u}
a_{1g}
e_g
t_{2g}
Δ_O
e_g
t_{1u}
a_{1g}

Metal 1s XAS

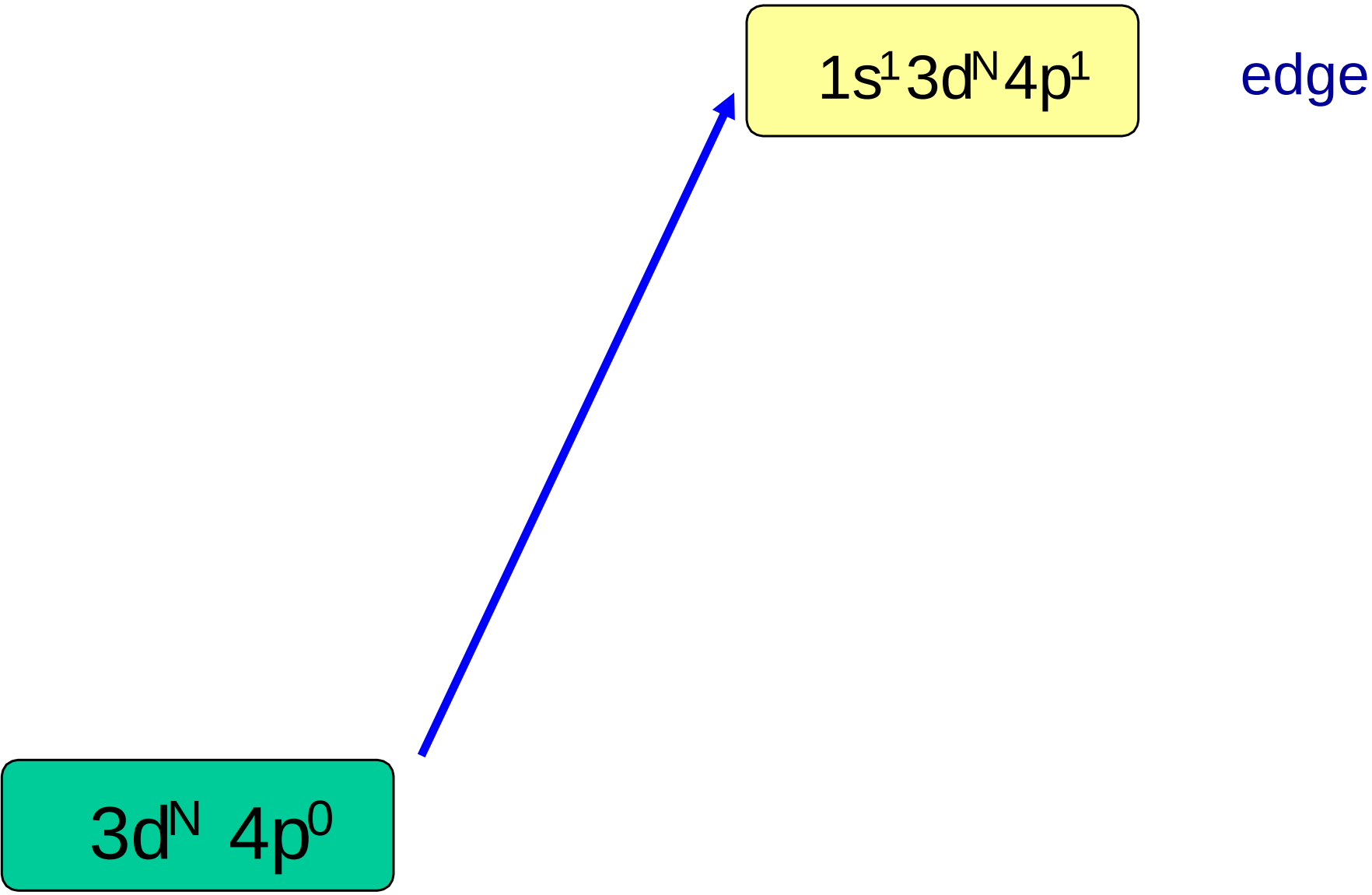


Cr^{3+} in $MgAl_2O_4$

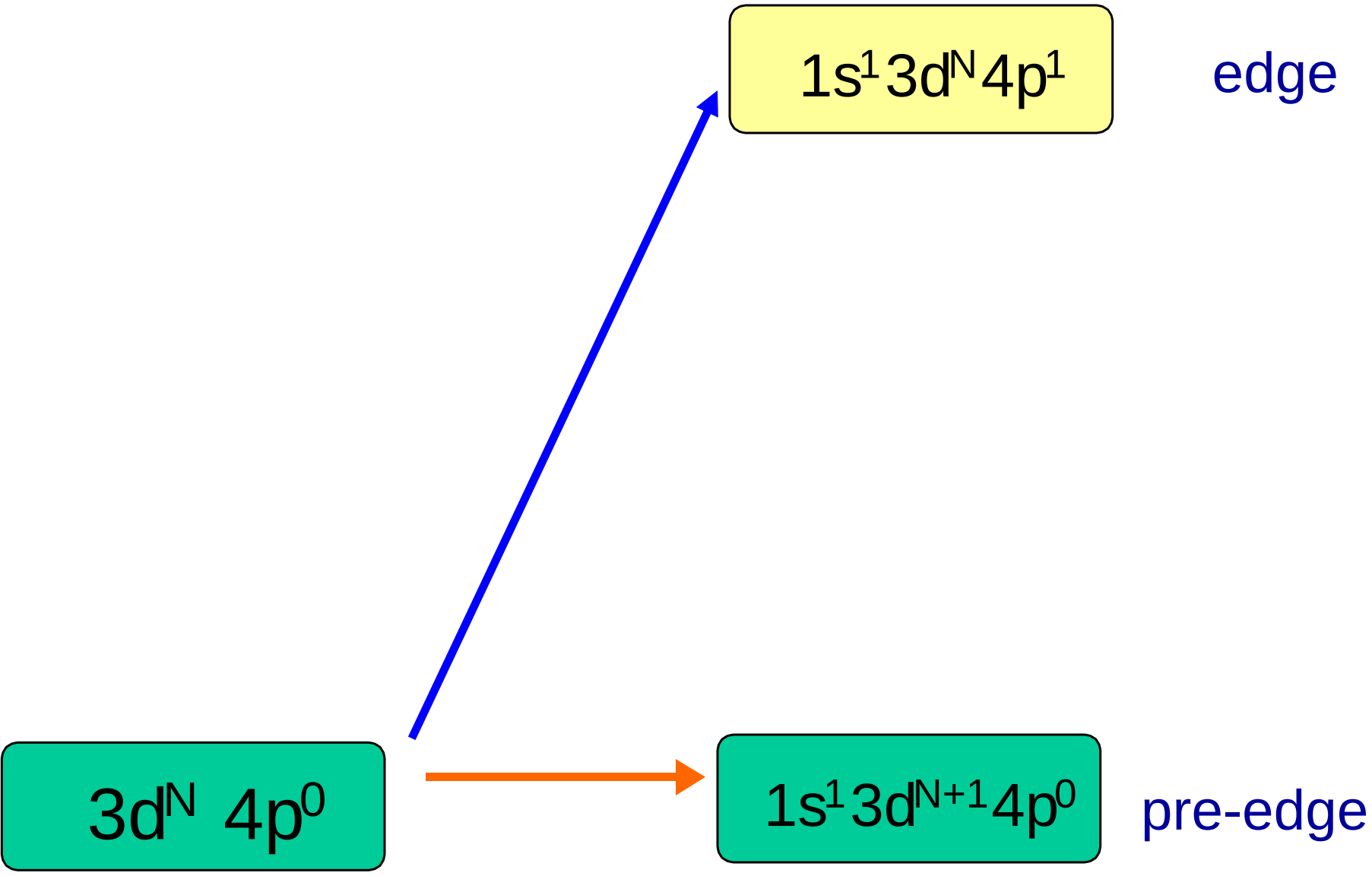


Juhin et al., Phys. Rev. B. 78, 195103 (2008)

Pre-edges structures in 1s XAS

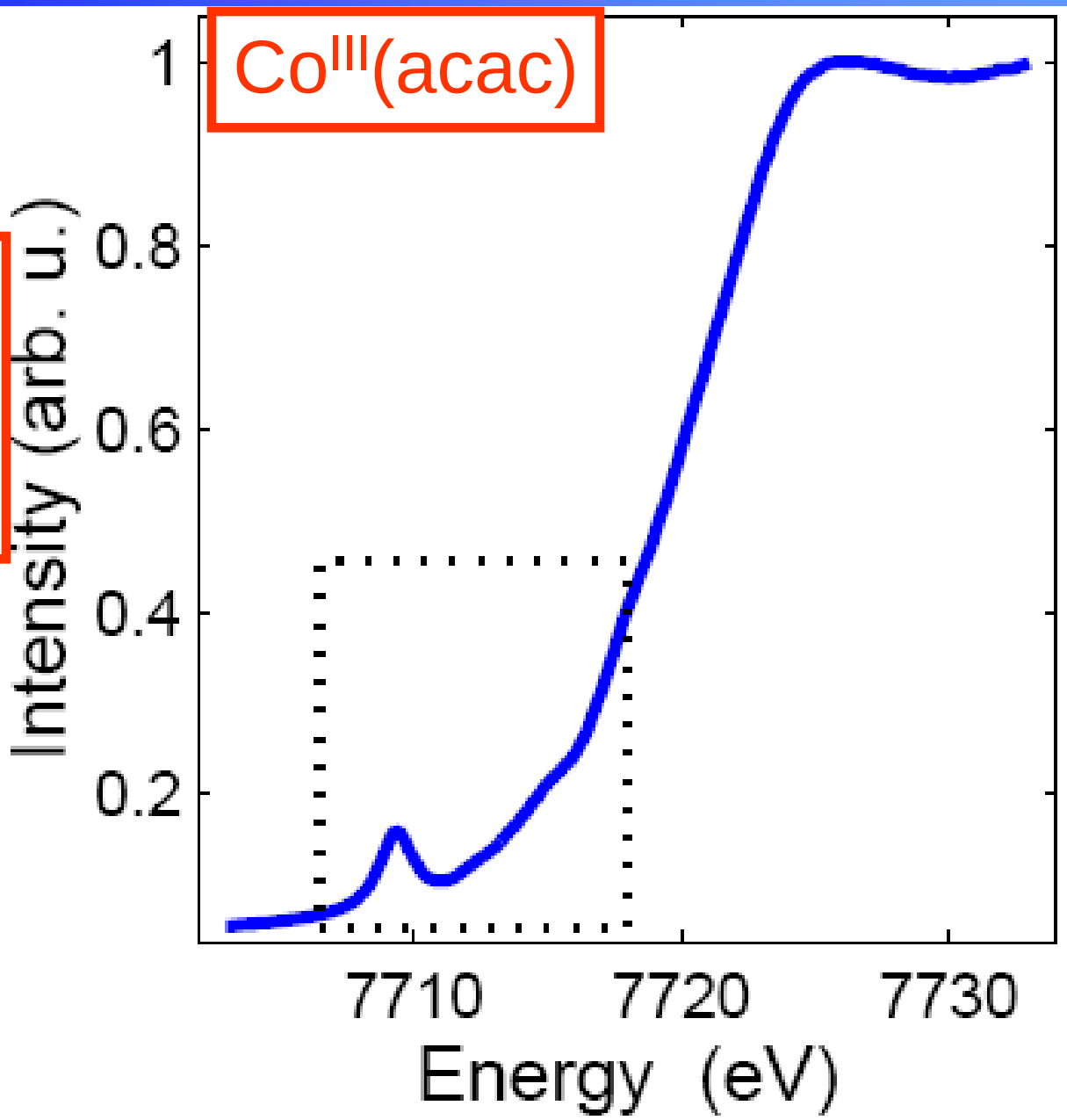


Pre-edges structures in 1s XAS

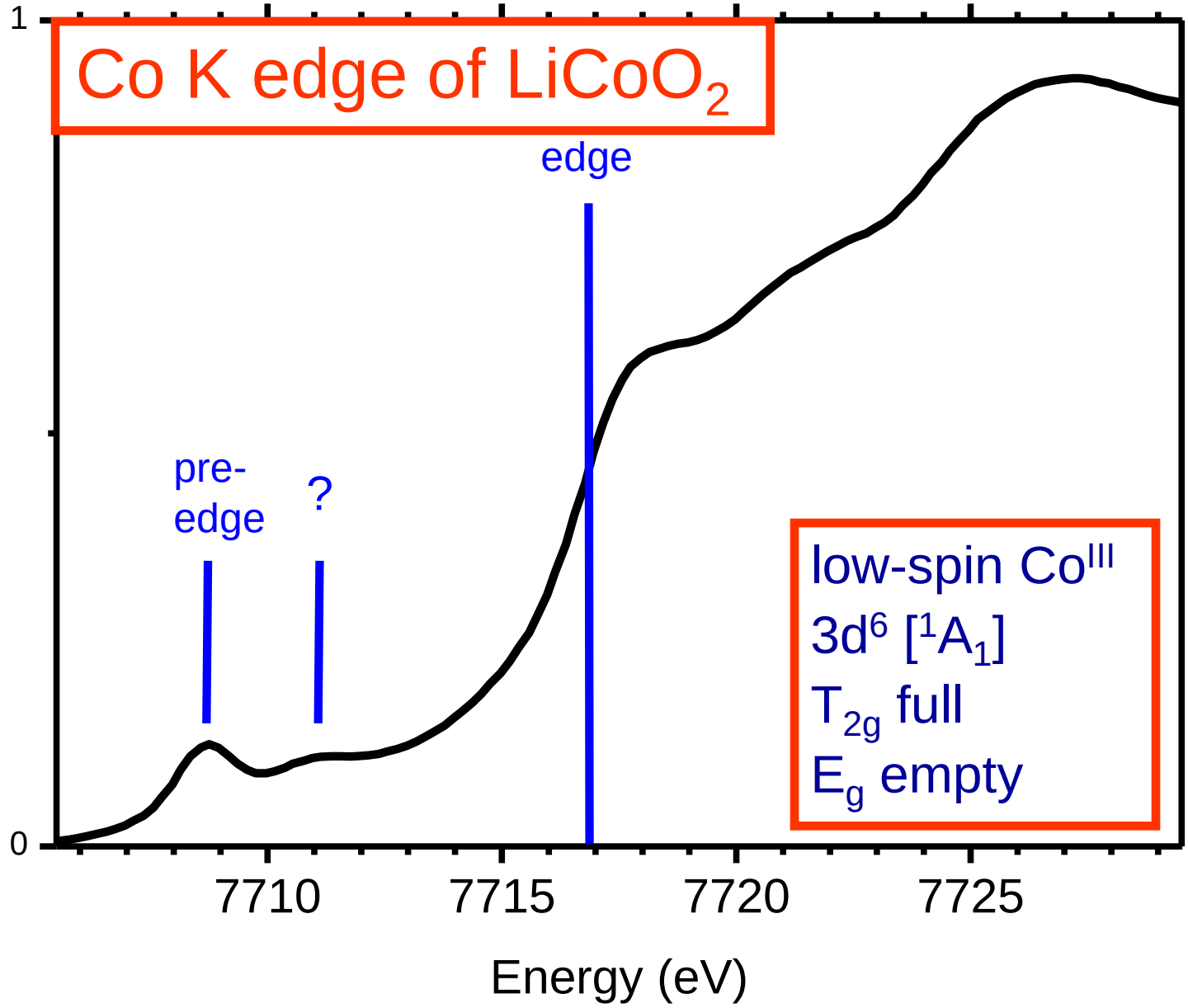


Pre-edges structures in 1s XAS

low-spin Co^{III}
$3d^6$ [$^1A_1$]
T_{2g} full
E_g empty



Pre-edges structures in 1s XAS



X-ray absorption spectroscopy

Excitation of core electrons to empty states.

Spectrum identifies with the
empty Density of States

Works well for K edges

Metal K edges: quadrupole 1s3d transitions

X-ray absorption spectroscopy

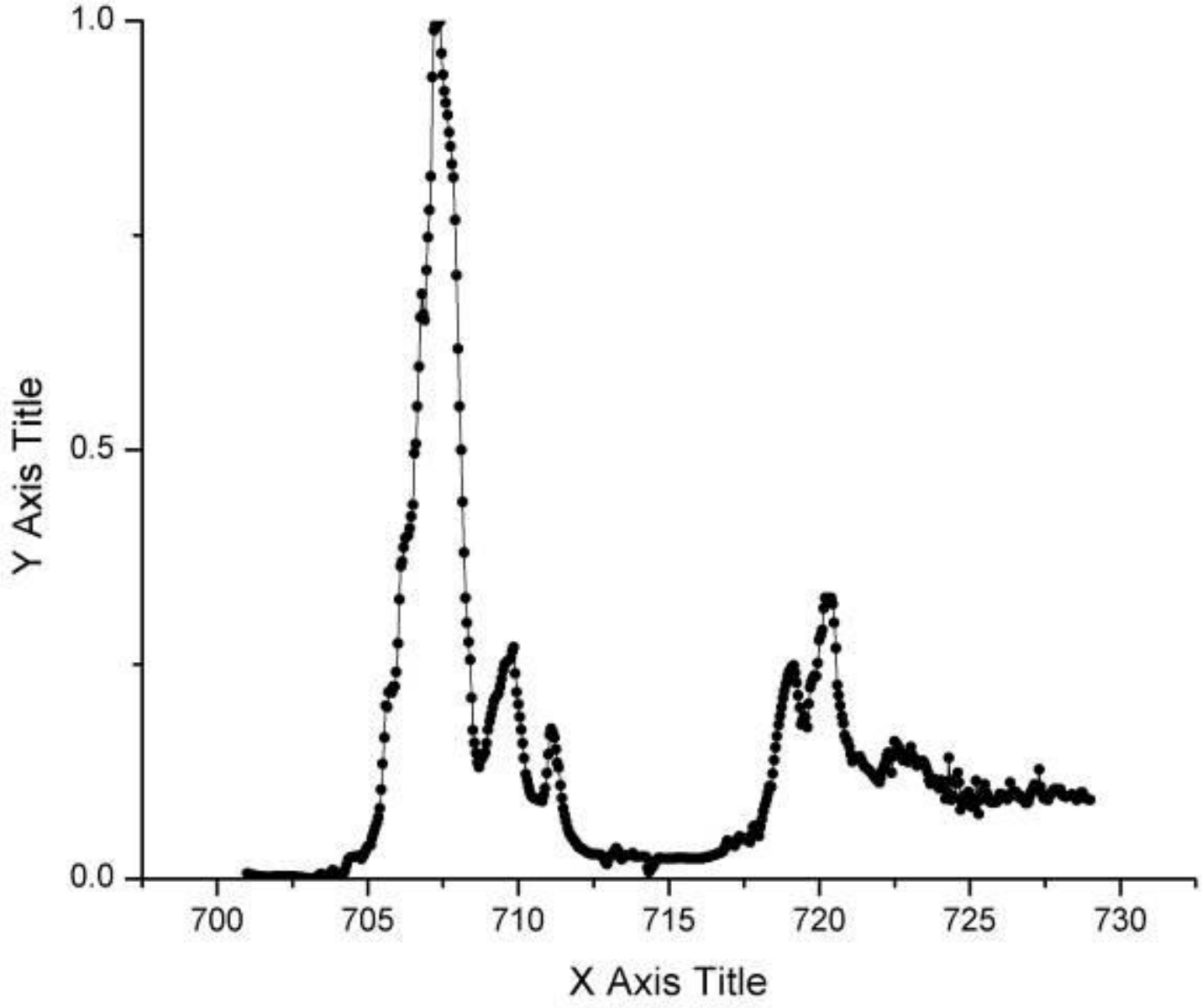
Fermi Golden Rule:

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

Single electron (excitation) approximation:

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

Quiz: Calculate the 2p XAS spectrum of Fe atom



XAS of an iron atom

Fermi Golden Rule:

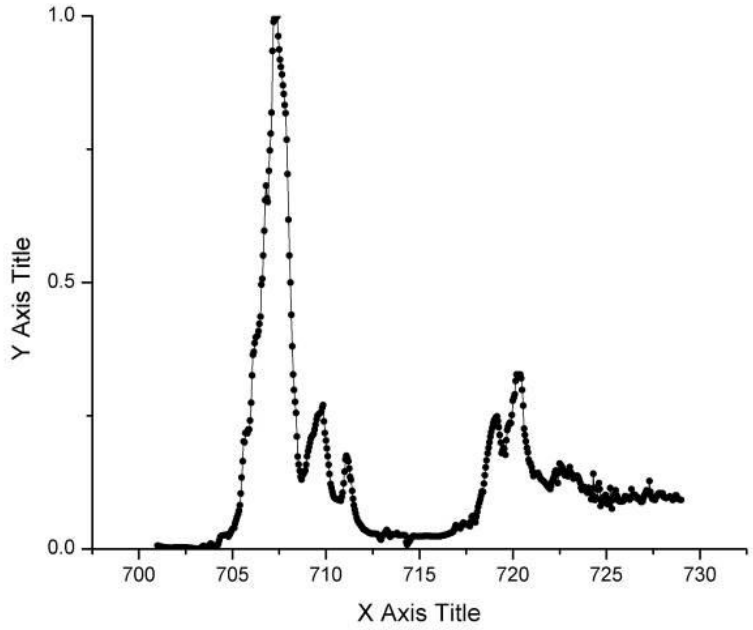
$I_{XAS} = |\langle \Phi_f | \text{dipole} | \Phi_i \rangle|^2 \ \delta_{[\Delta E=0]}$

$\Phi_i = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

$\Phi_f = 1s^2\ 2s^2\ 2p^5\ 3s^2\ 3p^6\ 4s^2\ 3d^7$

$\Phi_i = 2p^6\ 3d^6$

$\Phi_f = 2p^5\ 3d^7$



XAS of an iron atom

Fermi Golden Rule:

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

$\Phi_i = 2p^6\ 3d^6$

$\Phi_f = 2p^5\ 3d^7$

Single electron (excitation) approximation:

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

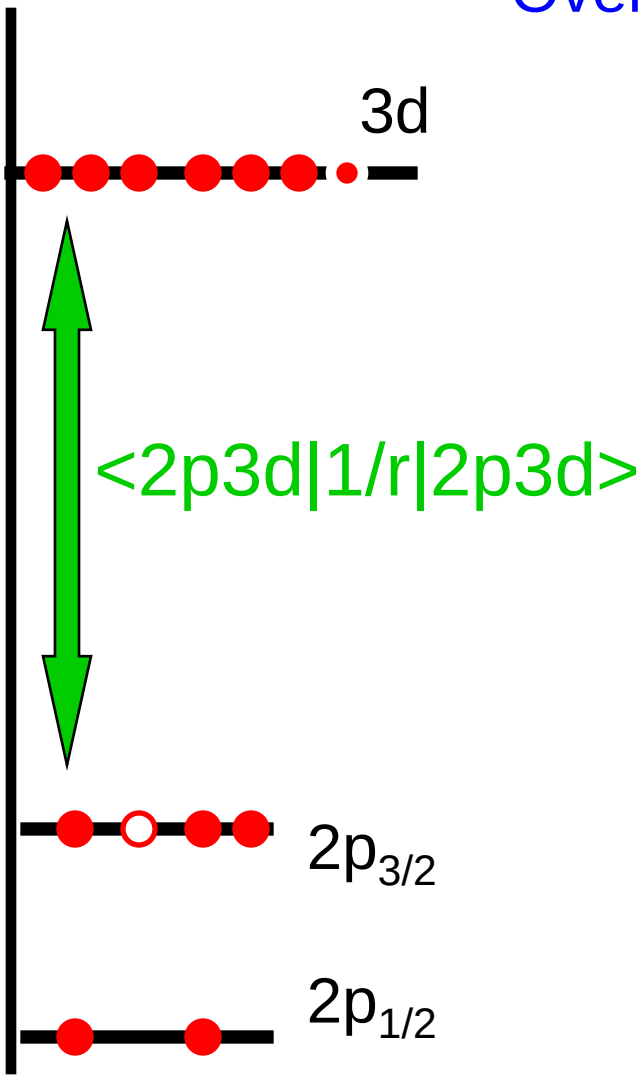
$\Phi_{core} = 2p$

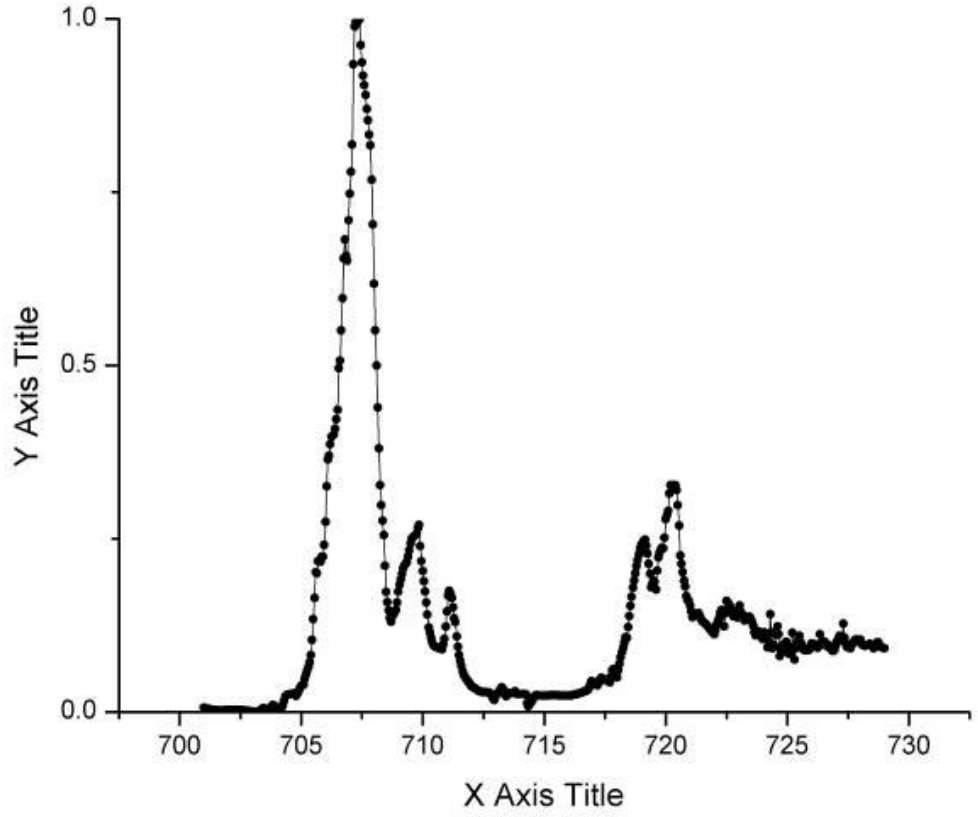
$\Phi_{empty} = 3d$

Neglect 2p-3d interactions (in the final state)

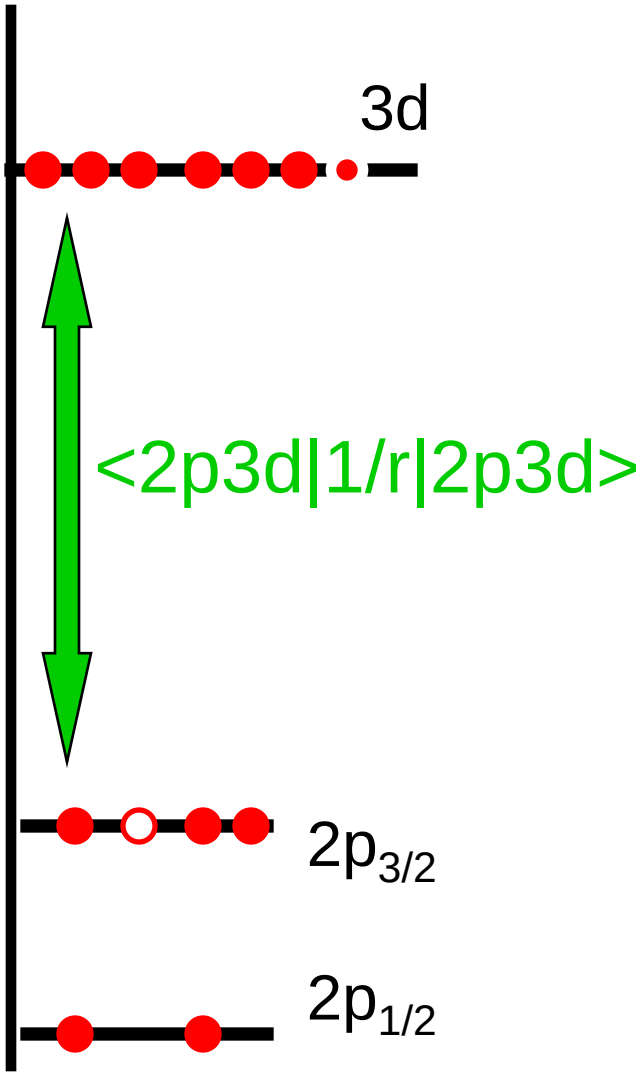
XAS of an iron atom

Overlap of core and valence wave functions





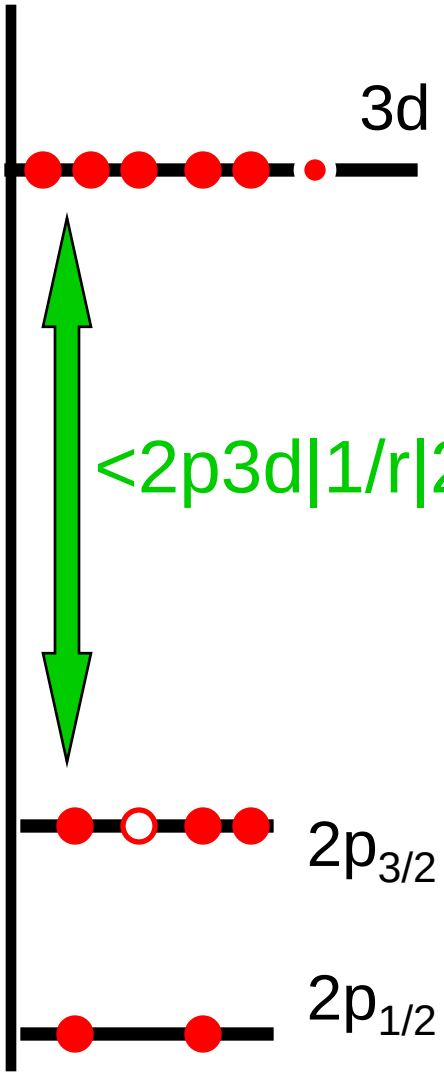
XAS of atoms and solids



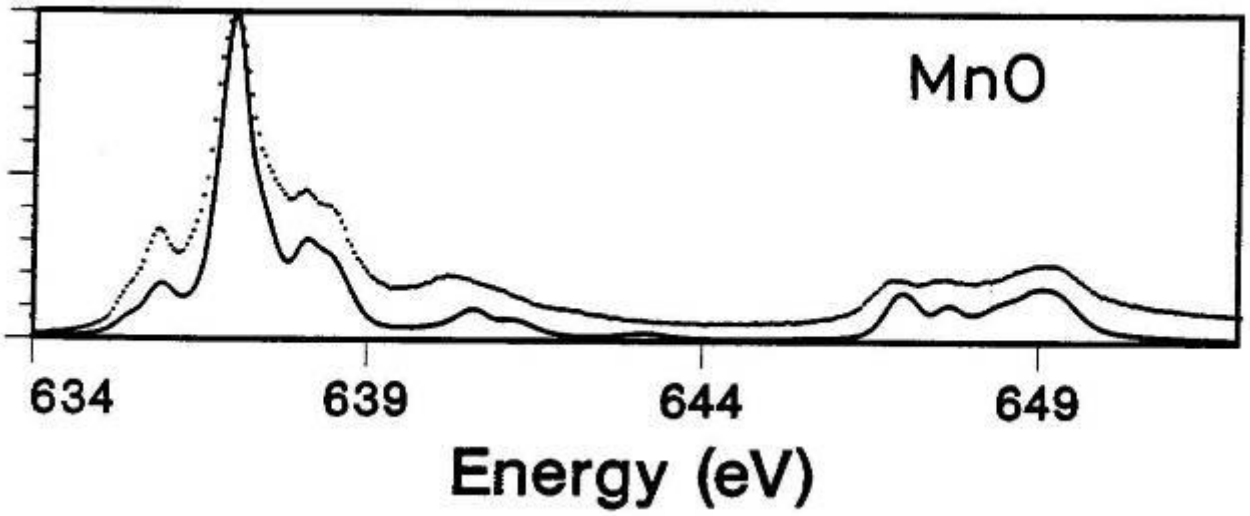
Direct 2p3d Coulomb interaction (= core hole potential) is screened in molecules and solids.

Higher order terms (Coulomb and exchange) are **NOT** screened in molecules and solids

XAS of atoms and solids

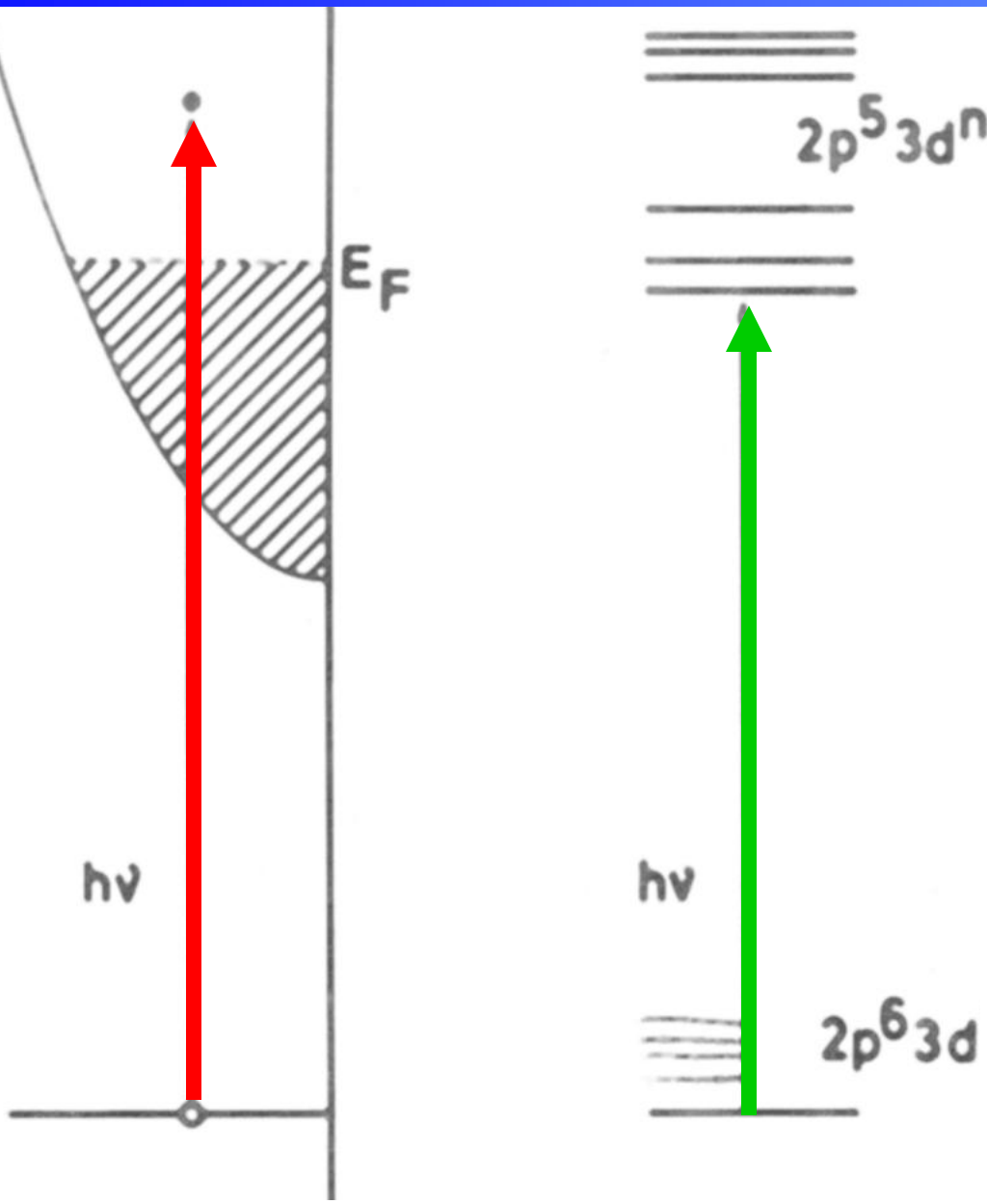


→ Single Particle model breaks down



PRB 42, 5459 (1990)

XAS of molecules and solids



Single Particle:

1s edges

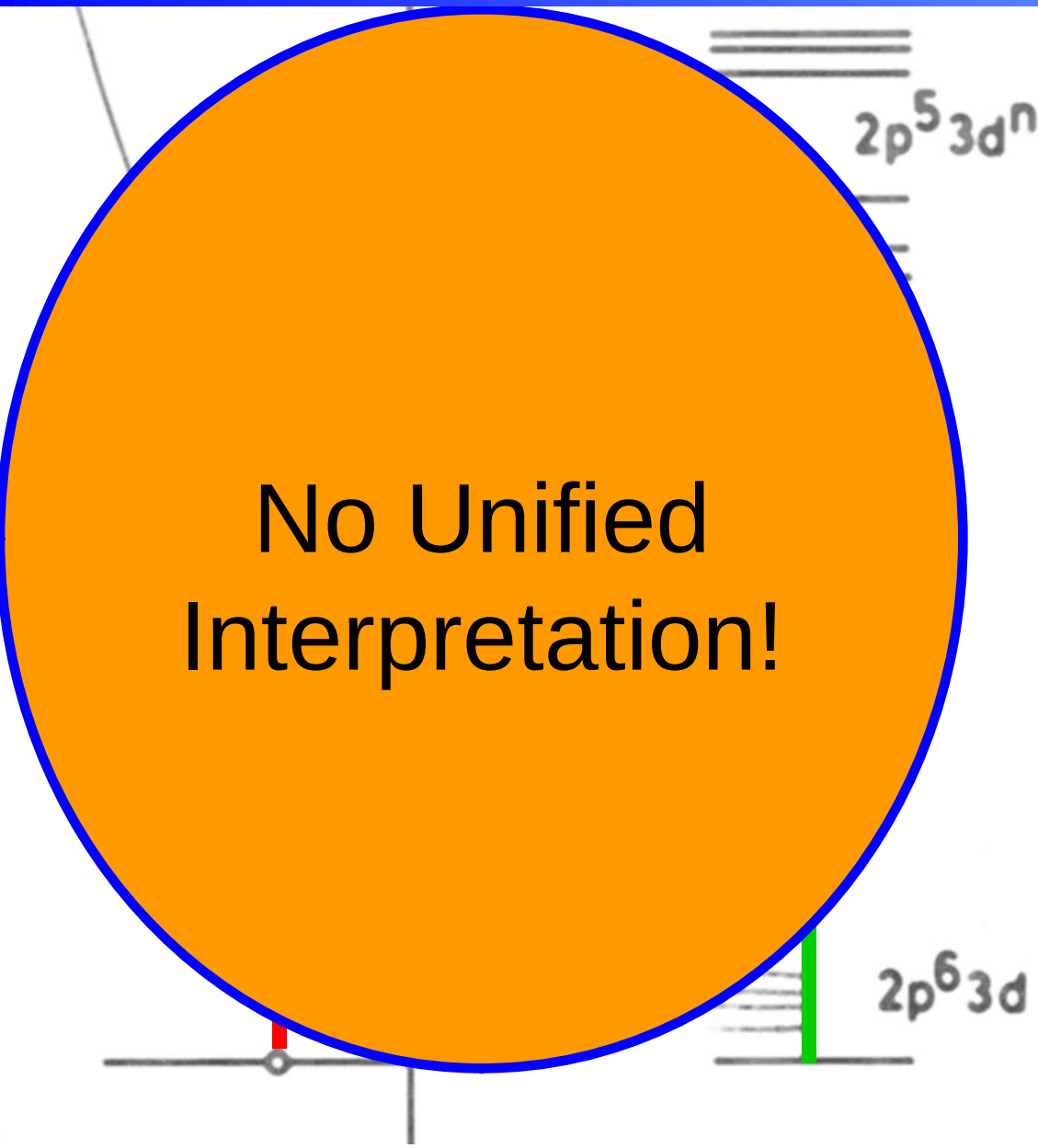
(WIEN, FEFF, PARATEC, ...)

Multiplets:

2p, 3s, 3p edges

(TT-MULTIPLETS)

XAS of molecules and solids



No Unified Interpretation!

Single Particle:

1s edges

(WIEN, FEFF, ORCA, PWSCF, etc.)

Multiplets:

2p, 3s, 3p edges

(TT-MULTIPLETS)

Charge transfer multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

ATOMIC PHYSICS

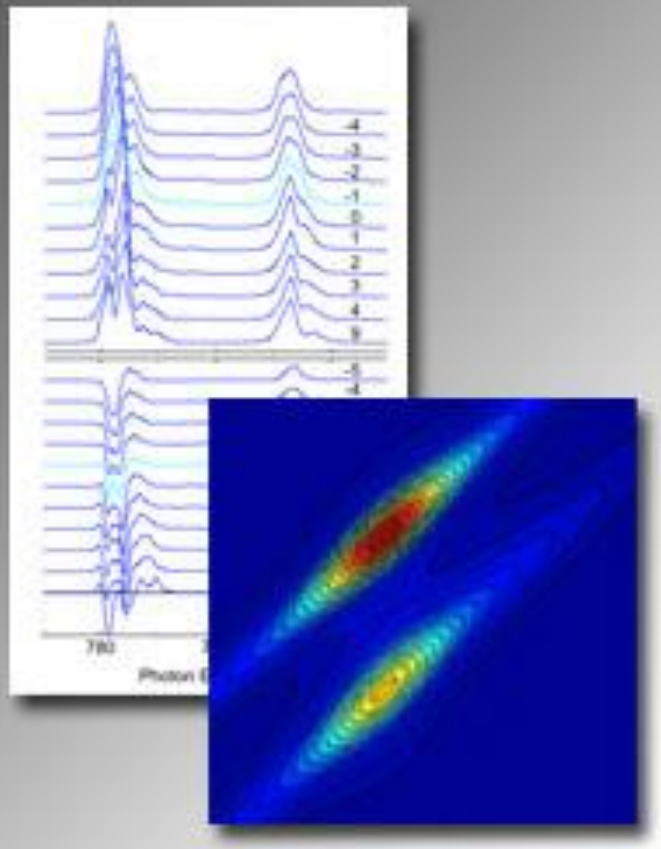
⇓

GROUP THEORY

⇓

MODEL HAMILTONIANS

CTM4XAS program

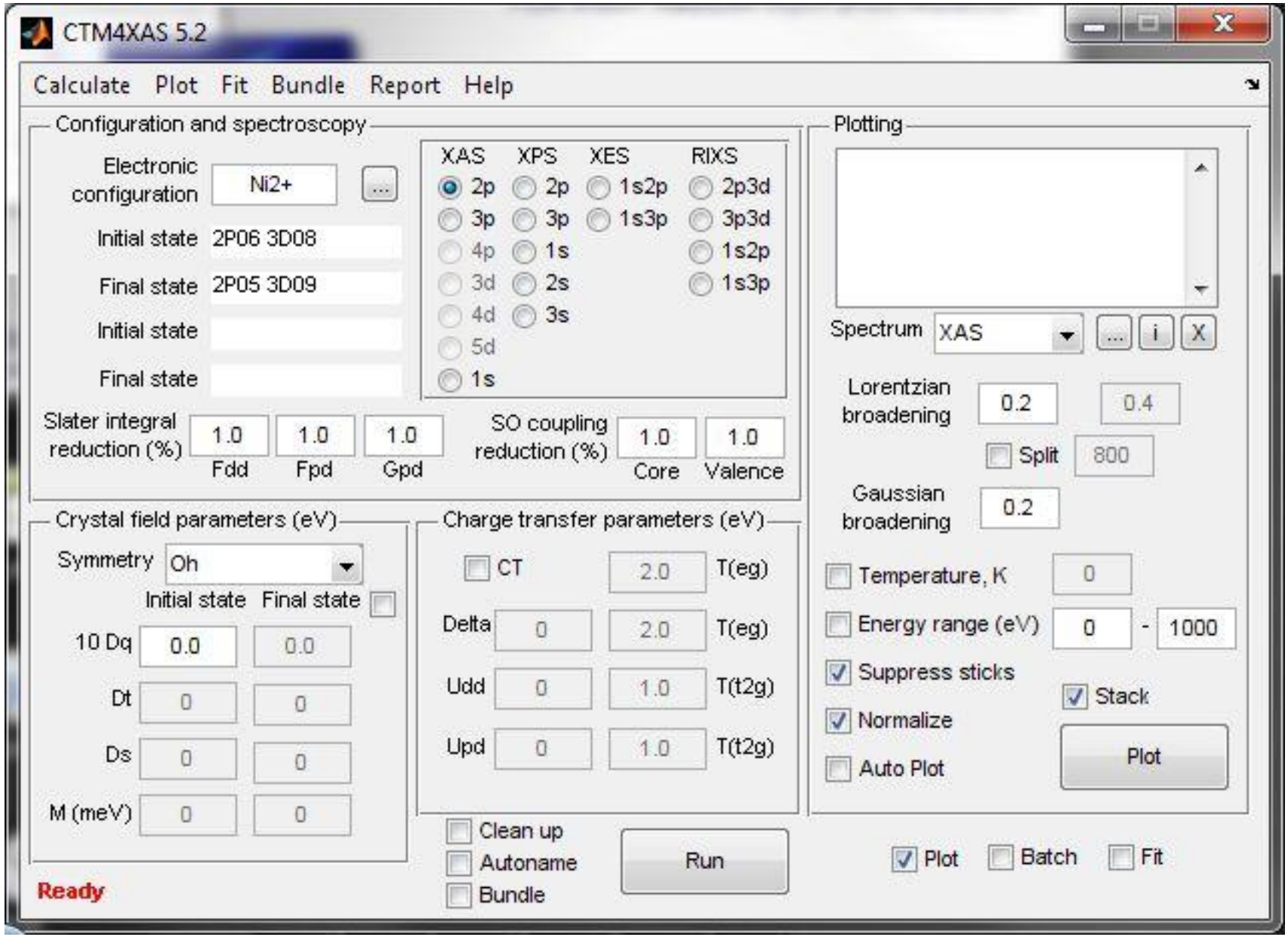


CTM4XAS 5.1

CHARGE TRANSFER MULTIPLET CALCULATIONS
FOR X-RAY ABSORPTION SPECTROSCOPY

Synchrotron and Theoretical Spectroscopy, Utrecht University/ National Synchrotron Light Source

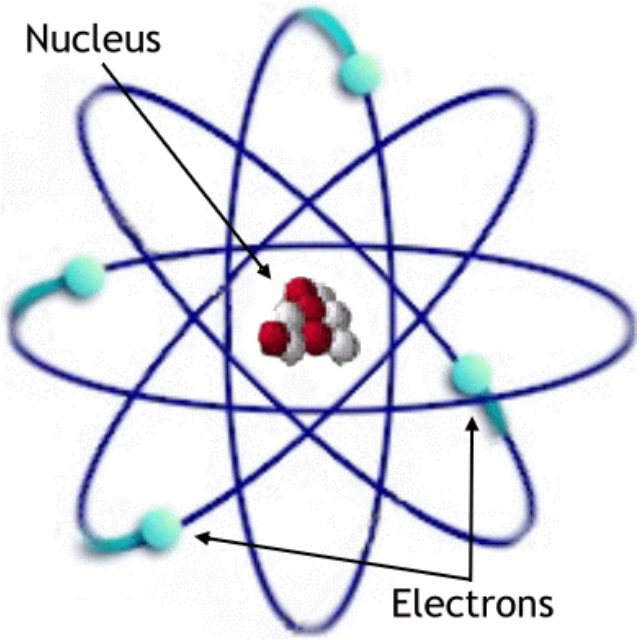
CTM4XAS program



Atomic Multiplet Theory

$$H\Psi=E\Psi$$

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

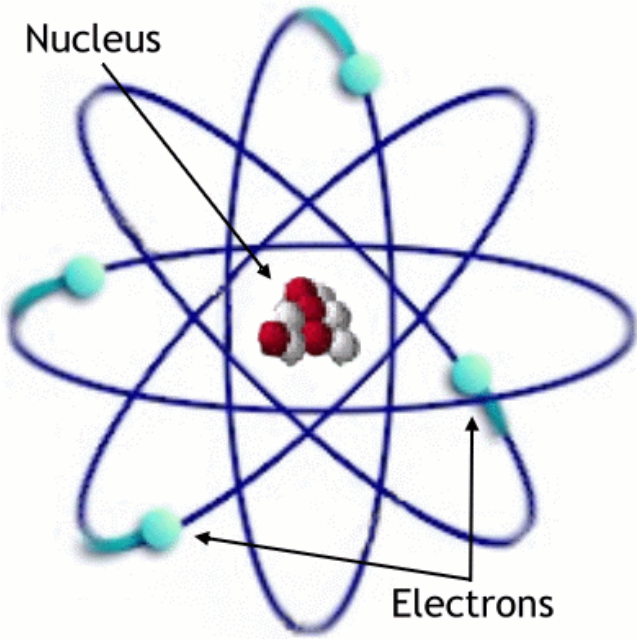


- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling

Atomic Multiplet Theory

$$H\Psi=E\Psi$$

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



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

Atomic Multiplet Theory (ground state)

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

Electron Correlation of Valence States [5 eV]

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

Valence Spin-orbit coupling [0.1 eV]

Atomic Multiplet Theory (core hole)

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

Core Valence Overlap [5 eV]

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

Core Spin-orbit coupling [15 eV]

2p XAS of a Ca atom

- Ground state is $3d^0$
- Dipole transition $3d^0 \rightarrow 2p^5 3d^1$
- Dipole selection rules:

~~$\Delta S=1$ and $\Delta L=\pm 1$~~

- Core hole spin-orbit coupling large
- L and S are no good quantum numbers

$\Delta J=\pm 1$ or 0

$(J=J\neq 0)$

Term symbols

- Term Symbol $^{2S+1}L_J$

- L=0,1,2,3,4 > S, P, D, F, G
- LS quantum numbers not useful for XAS due to large spin-orbit coupling of the core hole.
- Use only J quantum numbers
- Degeneracy of each J-state: 2J+1

Term symbols

Term symbols of a 1s electron

- S=1/2, L=0

$$J=1/2 \rightarrow {}^2S_{1/2}$$

Term symbols of a 3d electron

- S=1/2, L=2

$$J=3/2 \text{ or } J=5/2 \rightarrow {}^2D_{3/2} \text{ or } {}^2D_{5/2}$$

Term symbols

2p3d-configuration (6x10 = 60 states)

all combinations are possible:

In short: $^{2}P \otimes {}^{2}D = {}^{1,3}P,D,F$

Add J-quantum numbers:

$^{1}P_{1}$, $^{1}D_{2}$, $^{1}F_{3}$

+ $^{3}P_{0}$, $^{3}P_{1}$, $^{3}P_{2}$

+ $^{3}D_{1}$, $^{3}D_{2}$, $^{3}D_{3}$,

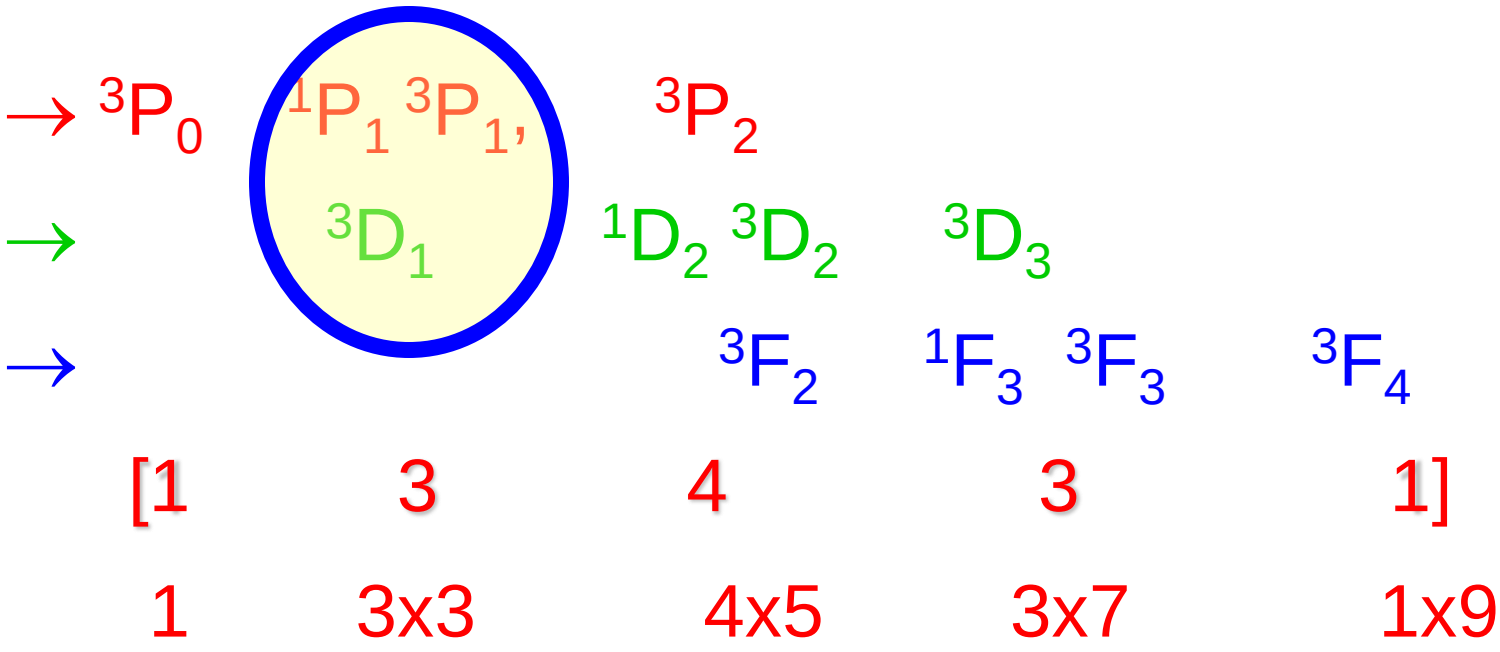
+ $^{3}F_{2}$, $^{3}F_{3}$, $^{3}F_{4}$,

2p XAS of a Ca atom

- Ground state is $3d^0$: symmetry: $^1S_0$
- Dipole transition $3d^0 \rightarrow 2p^5 3d^1$
- Selection rule: $\Delta J = \pm 1$ or 0 (and $J = J' \neq 0$)
- $J' = 1$

2p XAS of a Ca atom

- **Term symbols of a $2p^5 3d^1$ configuration**

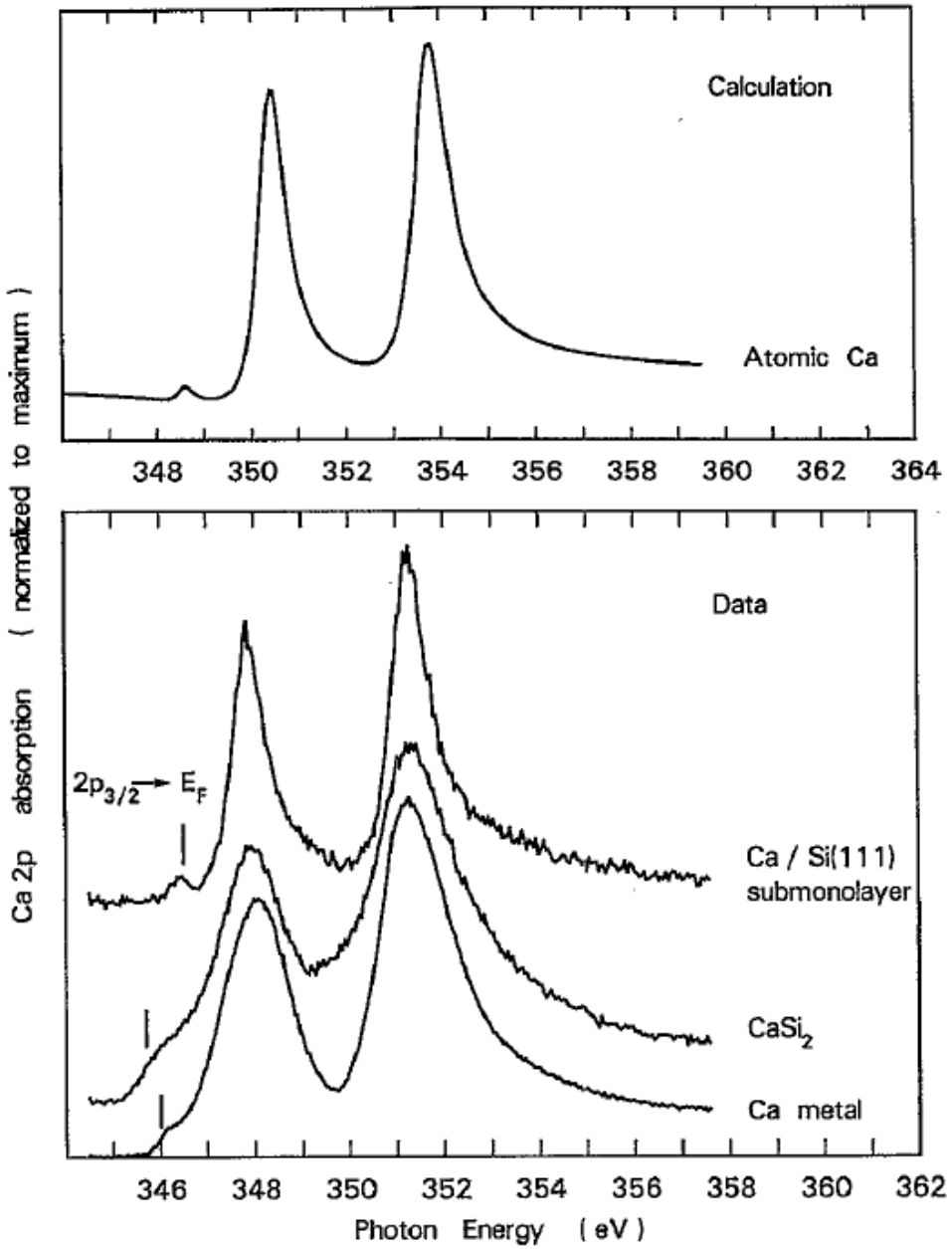


Ground state: $3d^0$: L=S=J=0 $^1S_0$

Selection rule: Final state must have J'=1

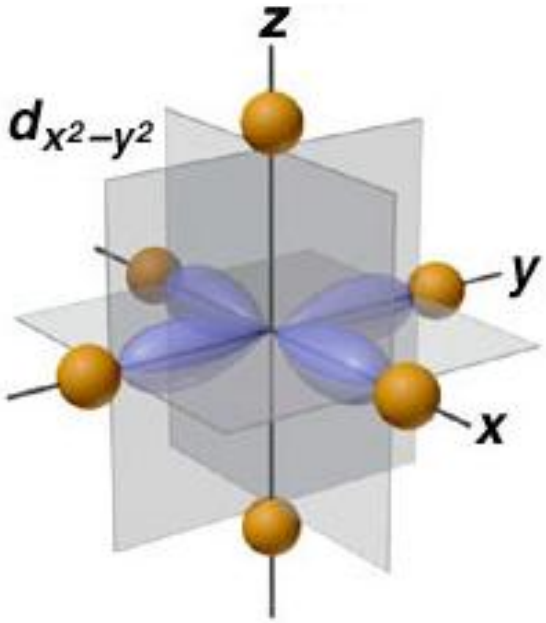
2p XAS of a Ca atom

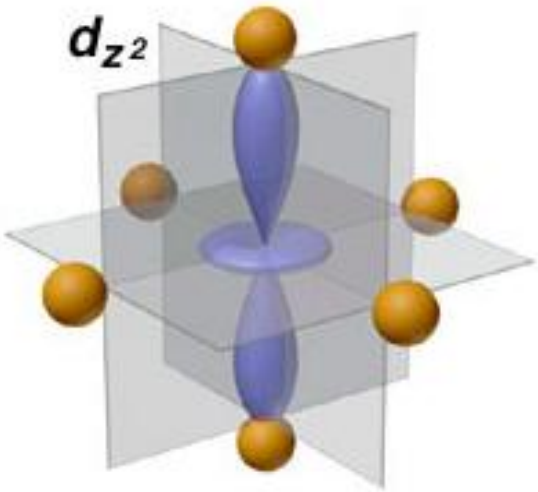
Ground state is $3d^0$



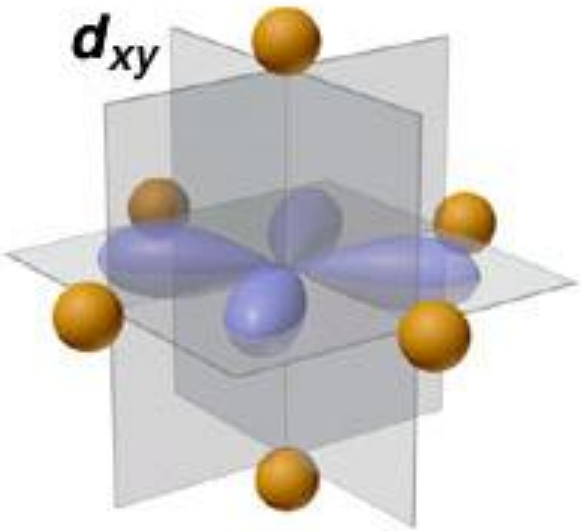
2p XAS of ScF_3: crystal fields

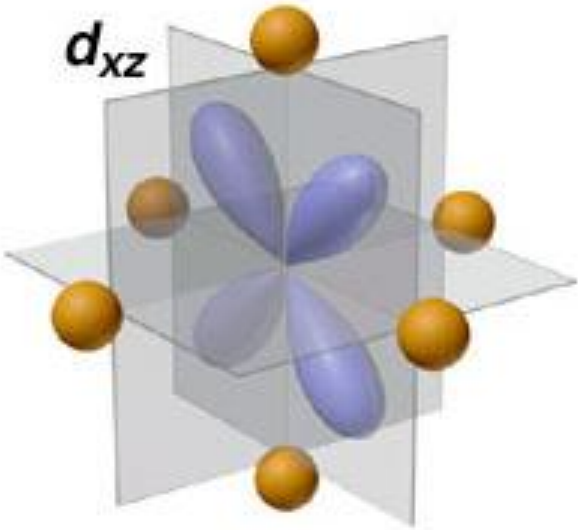
e_g states

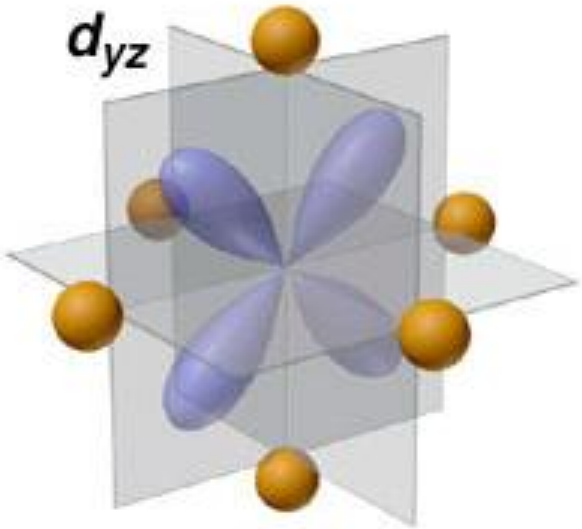




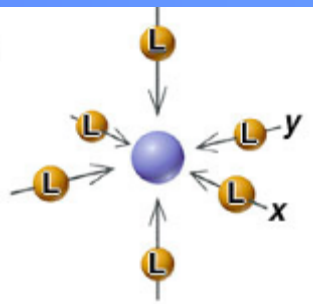
t_{2g} states

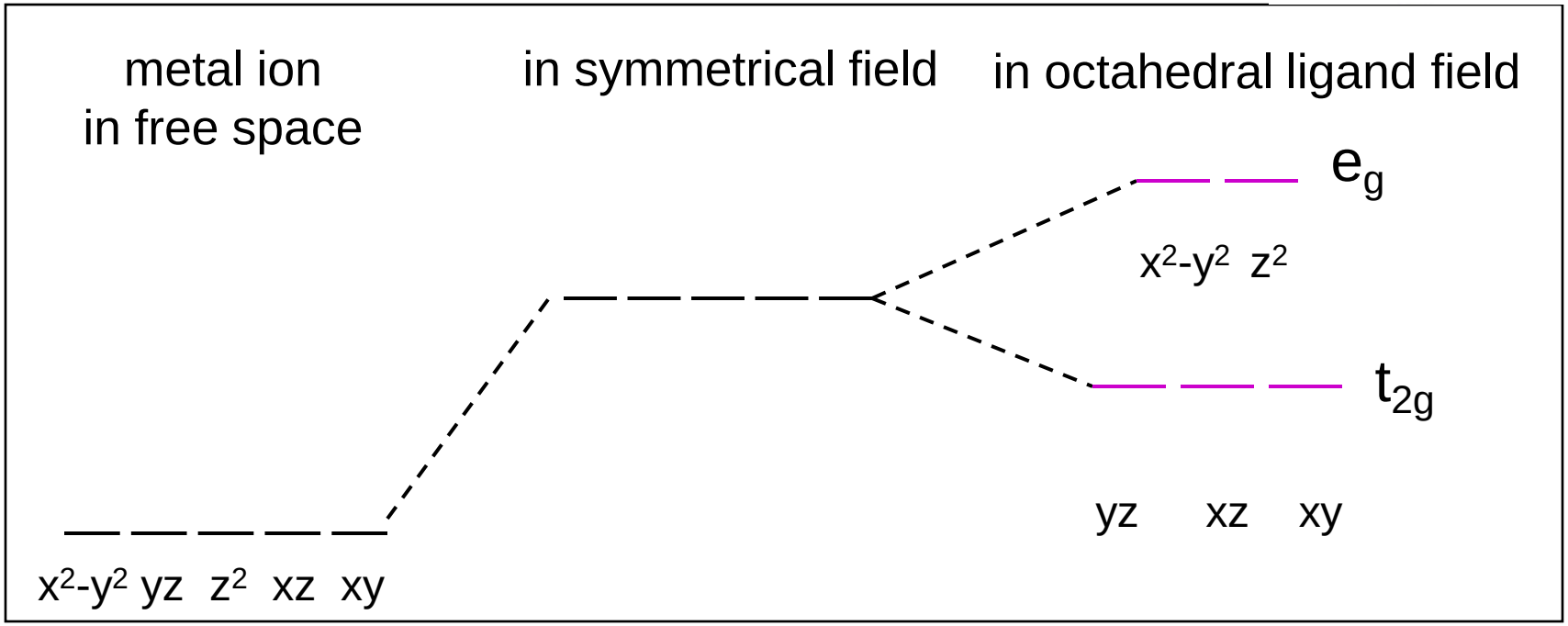




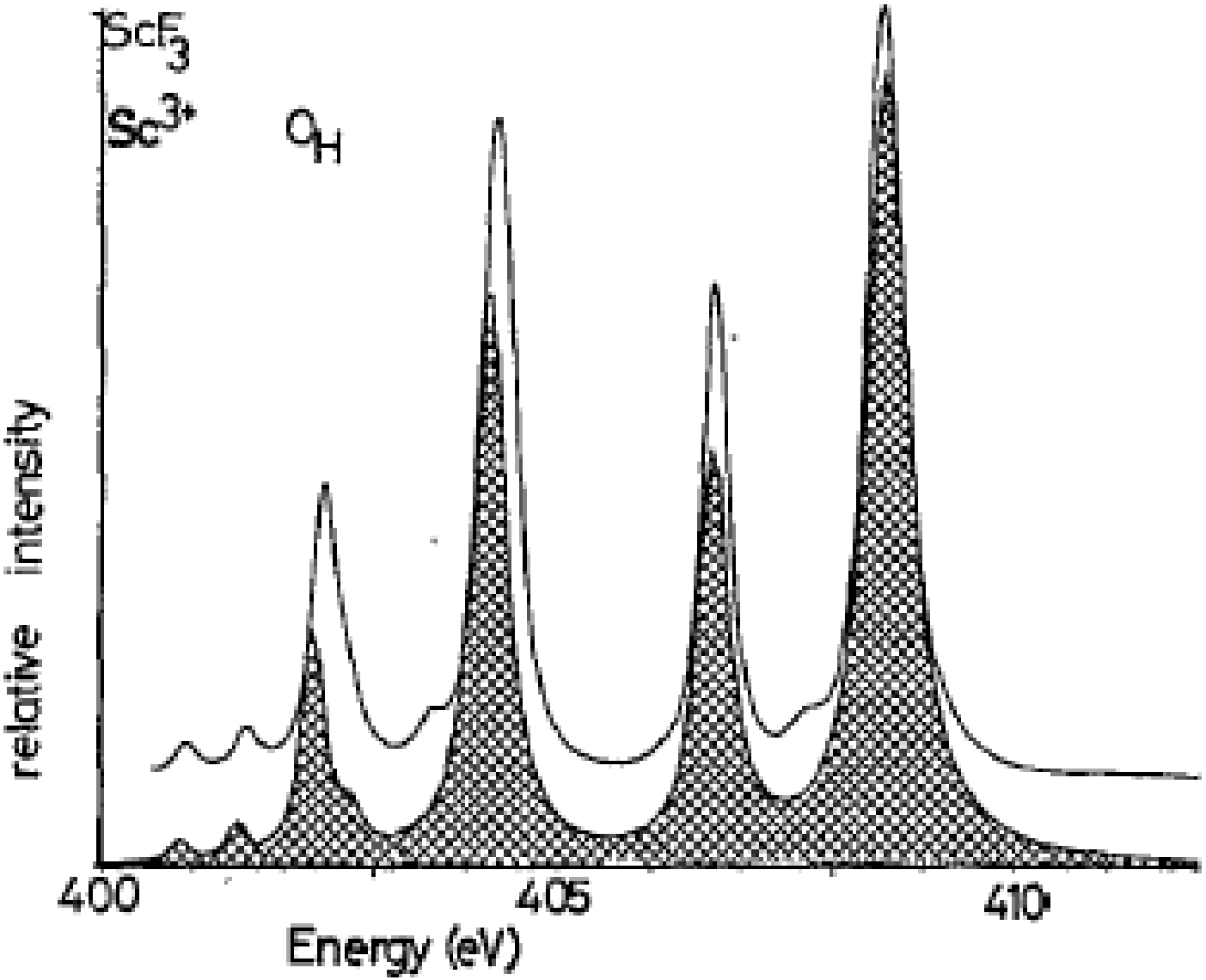


2p XAS of ScF_3: crystal fields

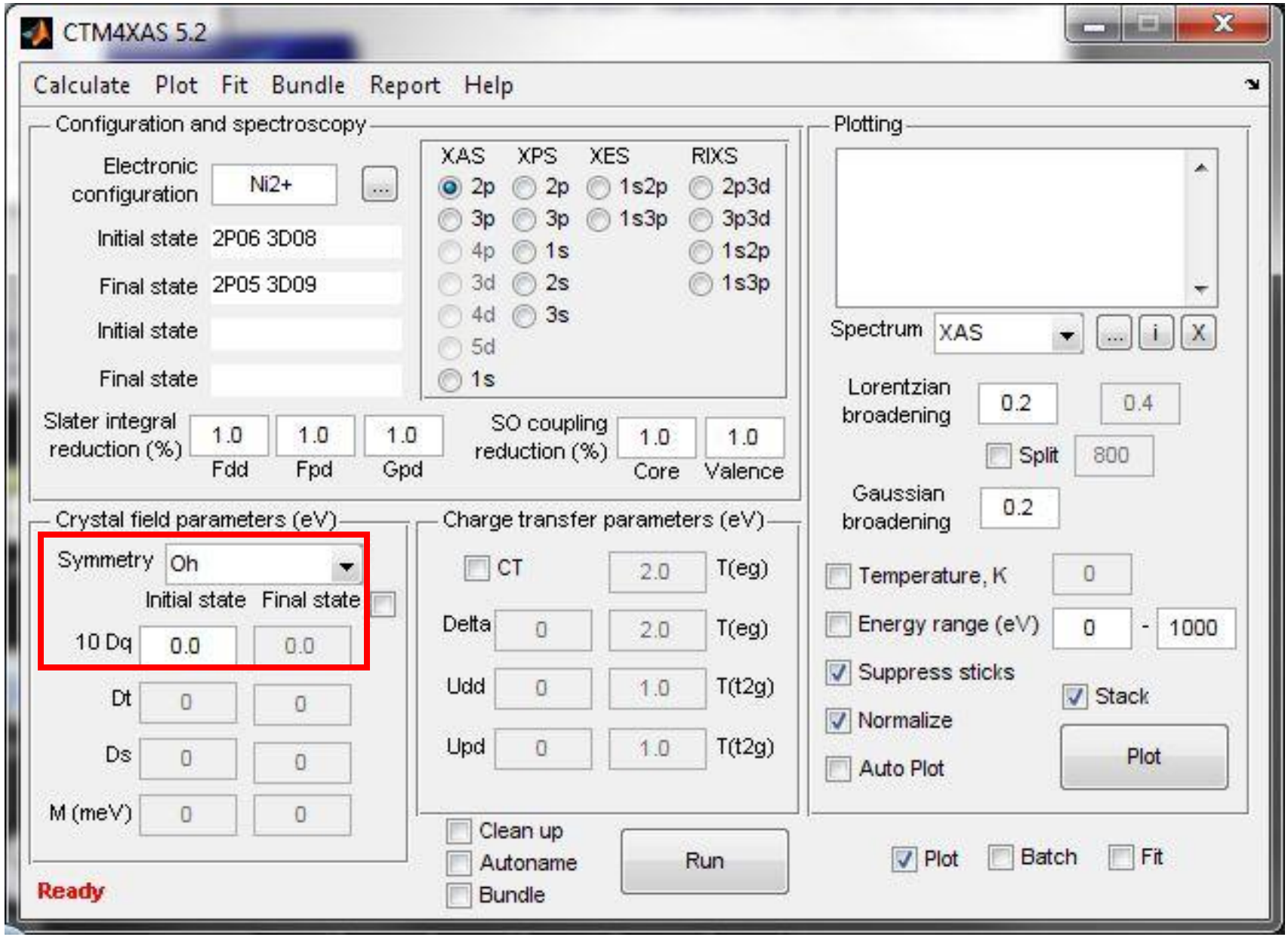




2p XAS of ScF_3



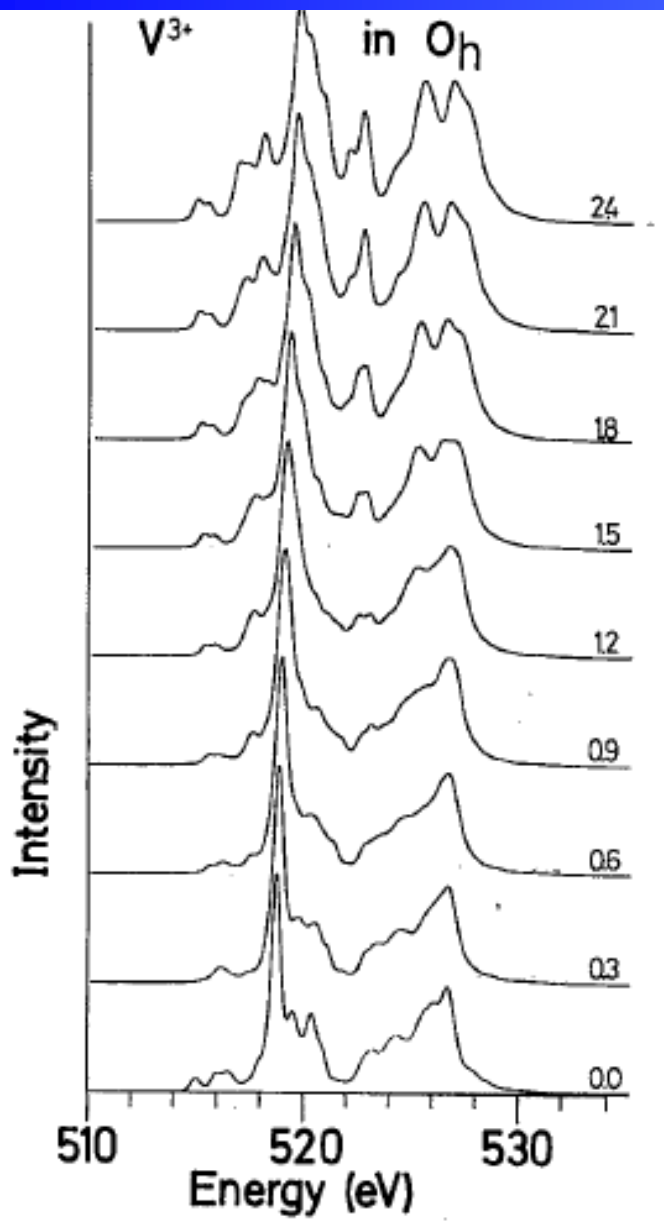
Calculations with CTM4XAS

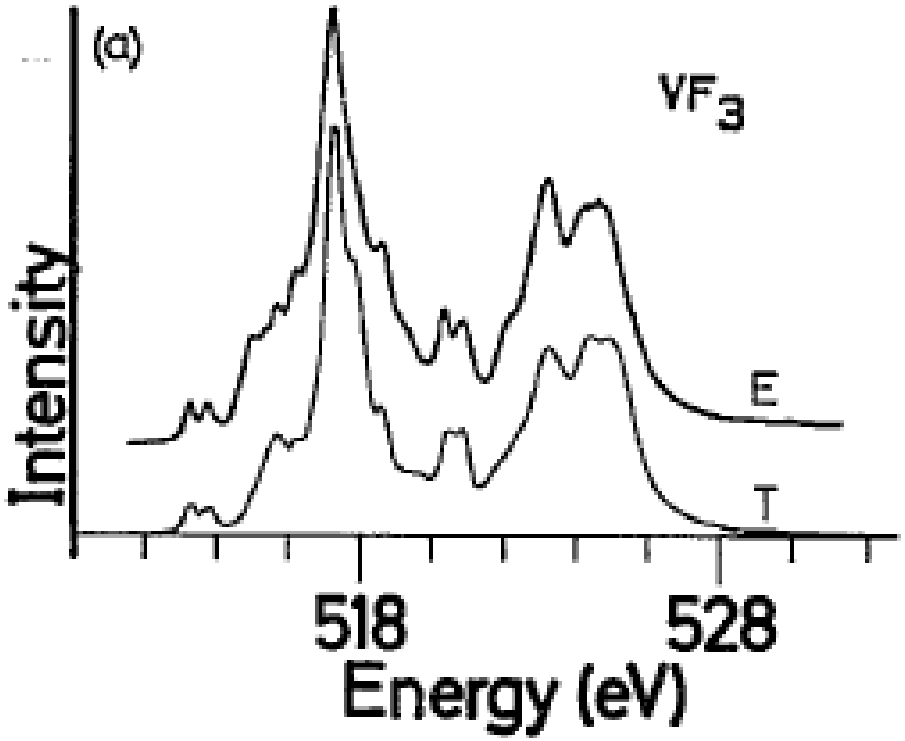


2p XAS of transition metal ions

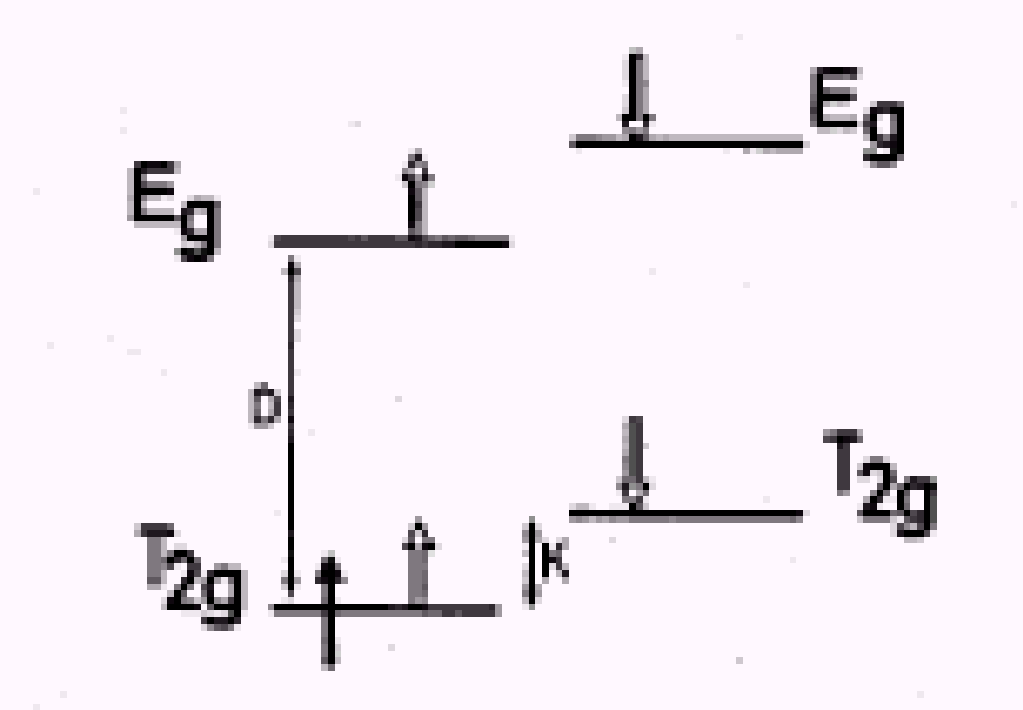
- Ground state is $3d^N$: determine symmetry
- Hunds rule: High-spin ground states
- max S, max L, max J
- Effect of crystal field splitting
- High spin or low spin
- Effect of 3d spin-orbit coupling
- Charge transfer effects

2p XAS of VF_3


V3+ in Oh
24
21
18
15
12
09
06
03
00
Intensity
510
520
530
Energy (eV)


(a)
VF3
E
T
Intensity
518
528
Energy (eV)

High-spin or low-spin



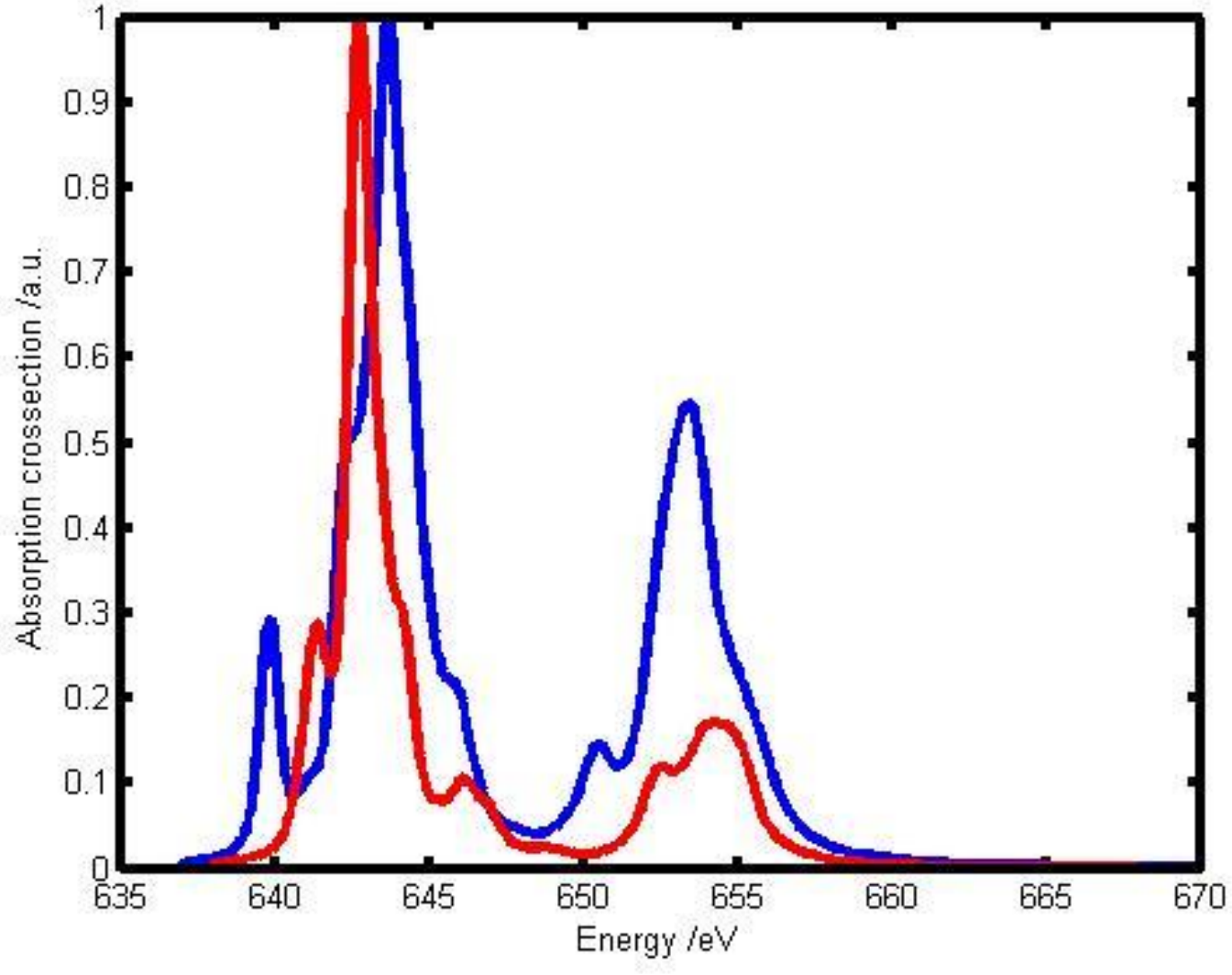
10Dq > 3J
(d^4 and d^5)

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

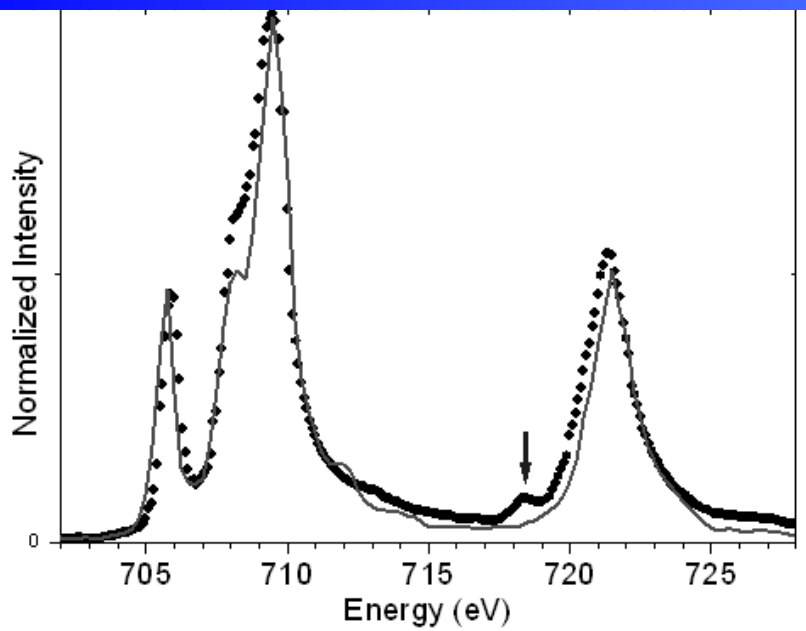
High-spin or low-spin

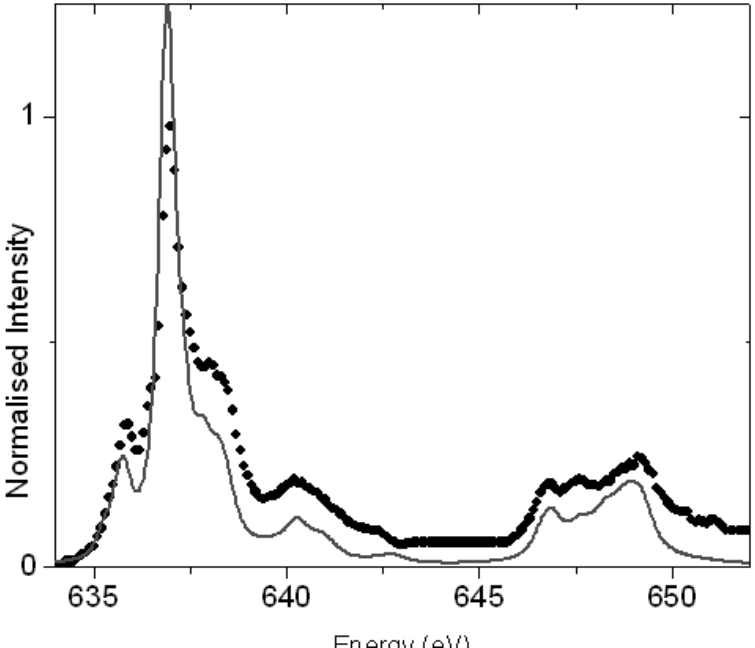
High-spin: 10Dq = 1.2

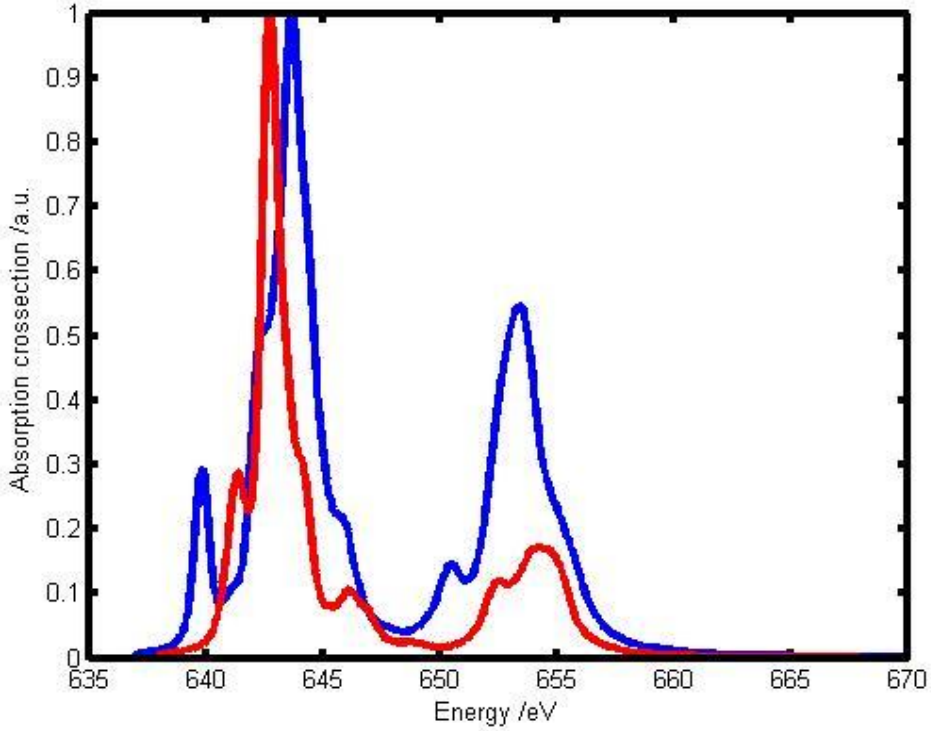
Low-spin: 10Dq = 3.0



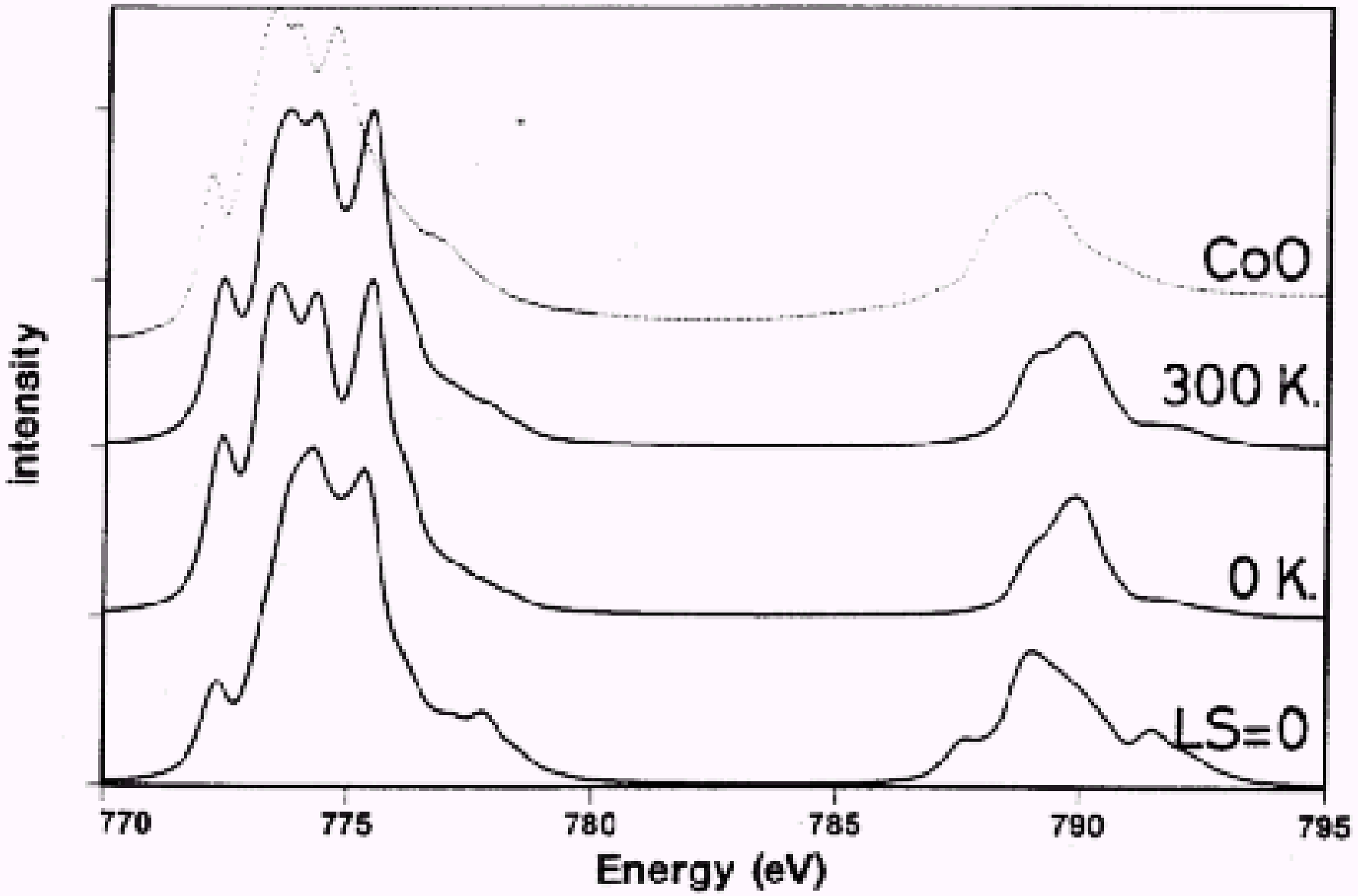
High-spin or low-spin



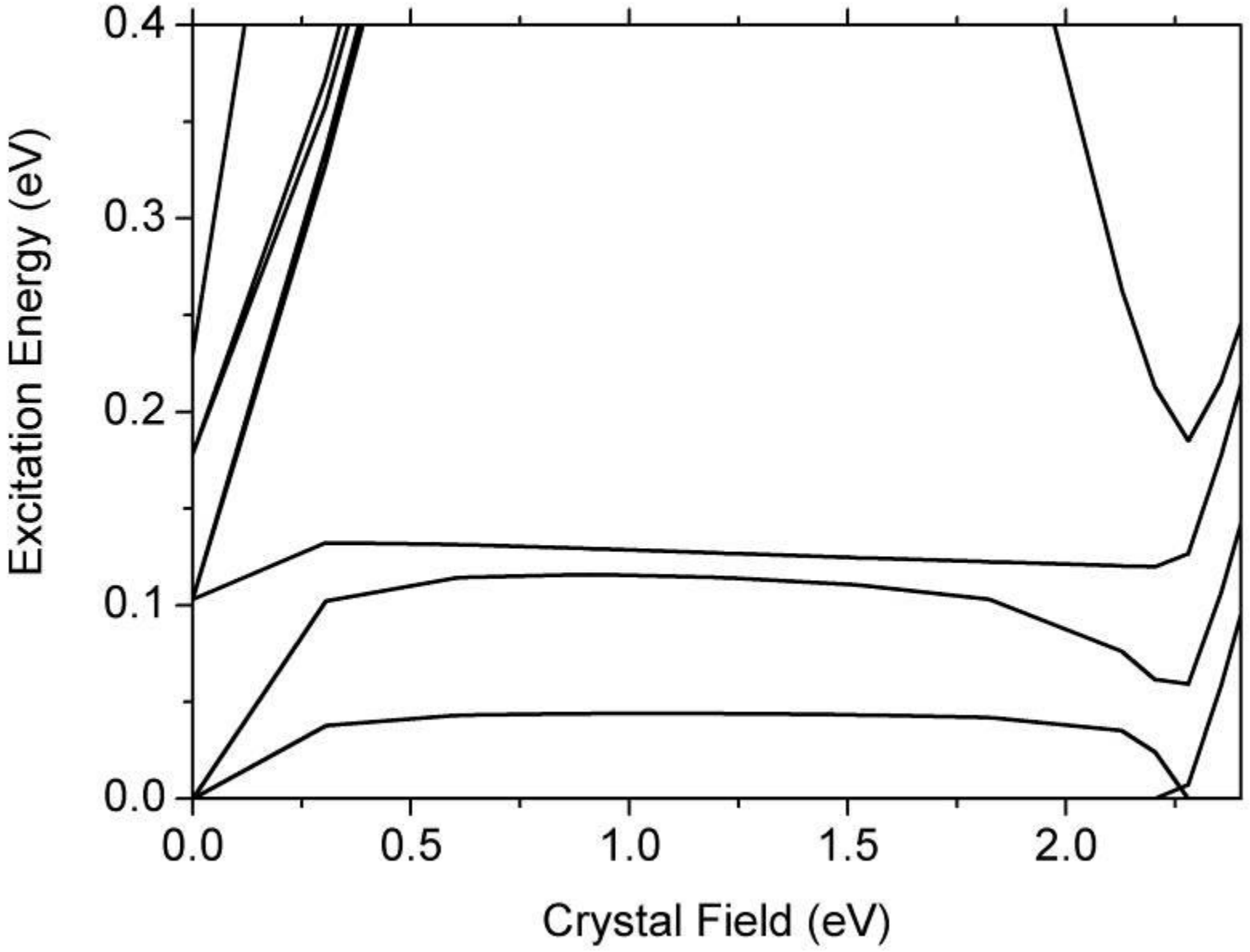




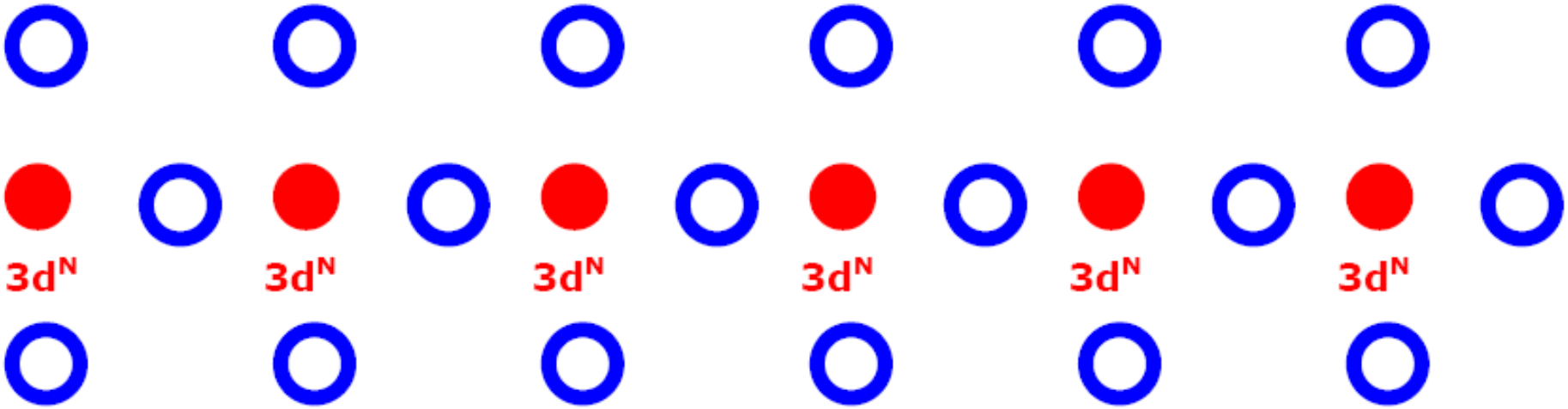
3d spin-orbit coupling



3d spin-orbit coupling



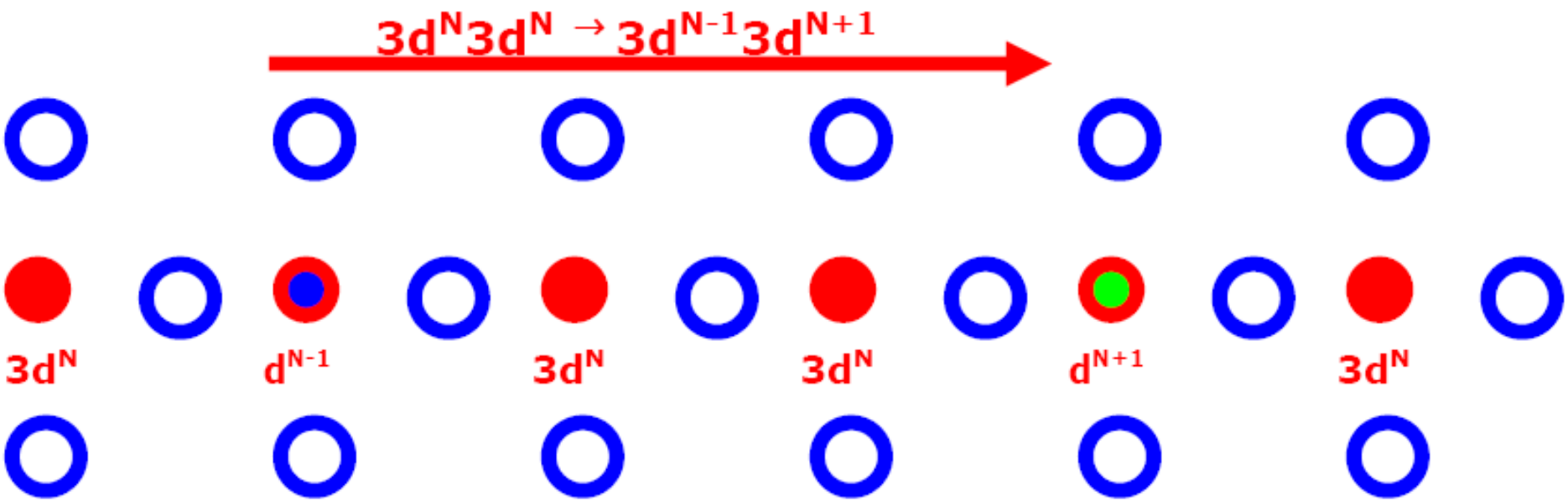
Charge transfer effects



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:

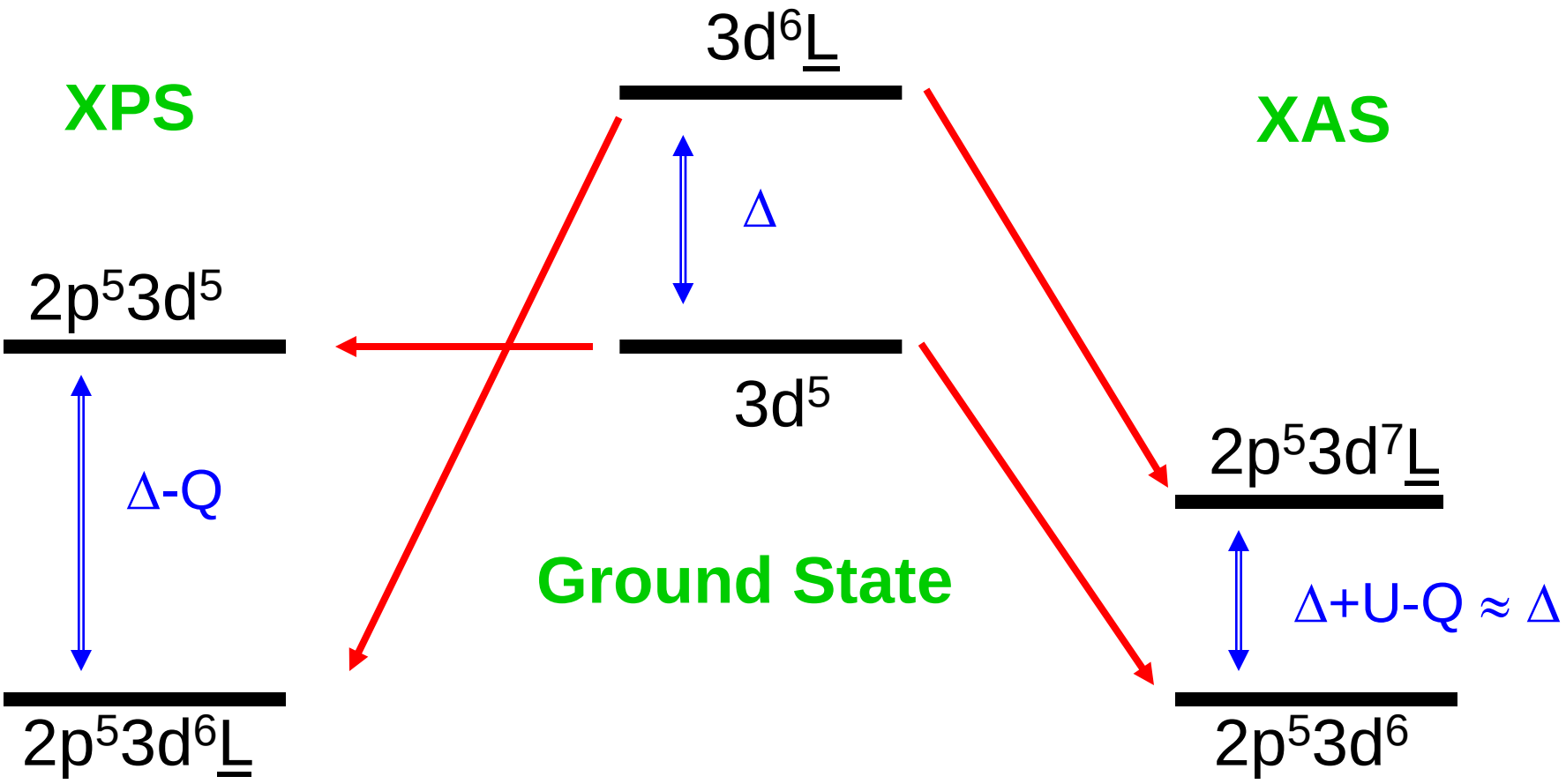
U= $E(3d^7) + E(3d^9) – E(3d^8) – E(3d^8)$

Ligand-to-Metal Charge Transfer (LMCT):

$\Delta = E(3d^9\underline{L}) – E(3d^8)$

Charge transfer effects

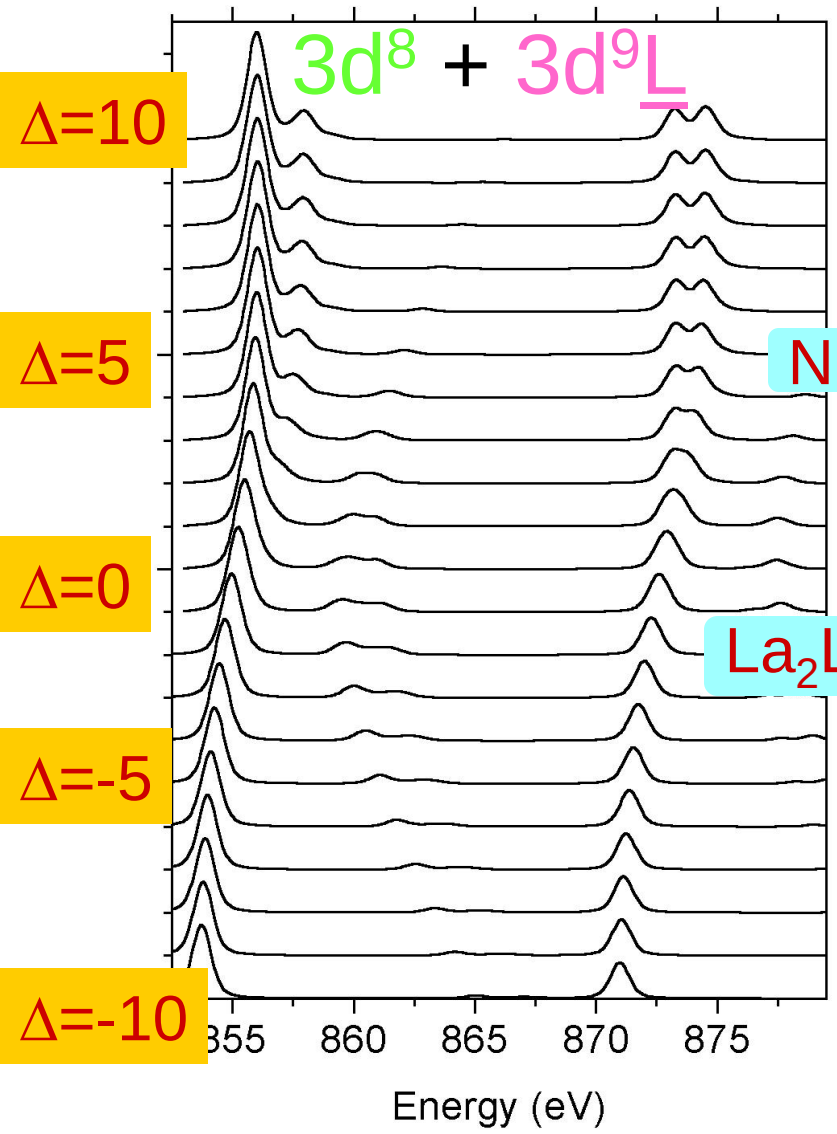
- Transition metal oxide: Ground state: $3d^5 + 3d^6\underline{L}$
- Energy of $3d^6\underline{L}$: Charge transfer energy Δ

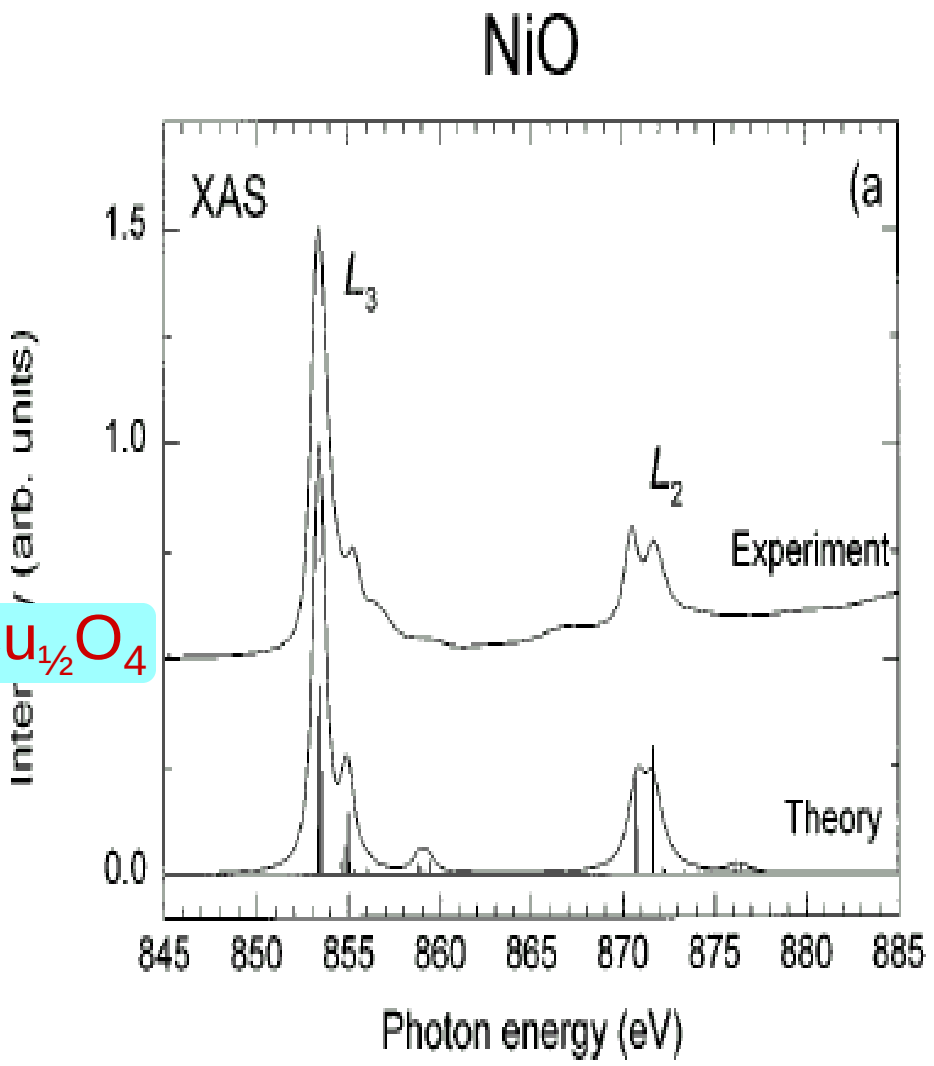


Charge Transfer effects

- High valent oxides (Cu^{3+})
- Systems with π-bonds

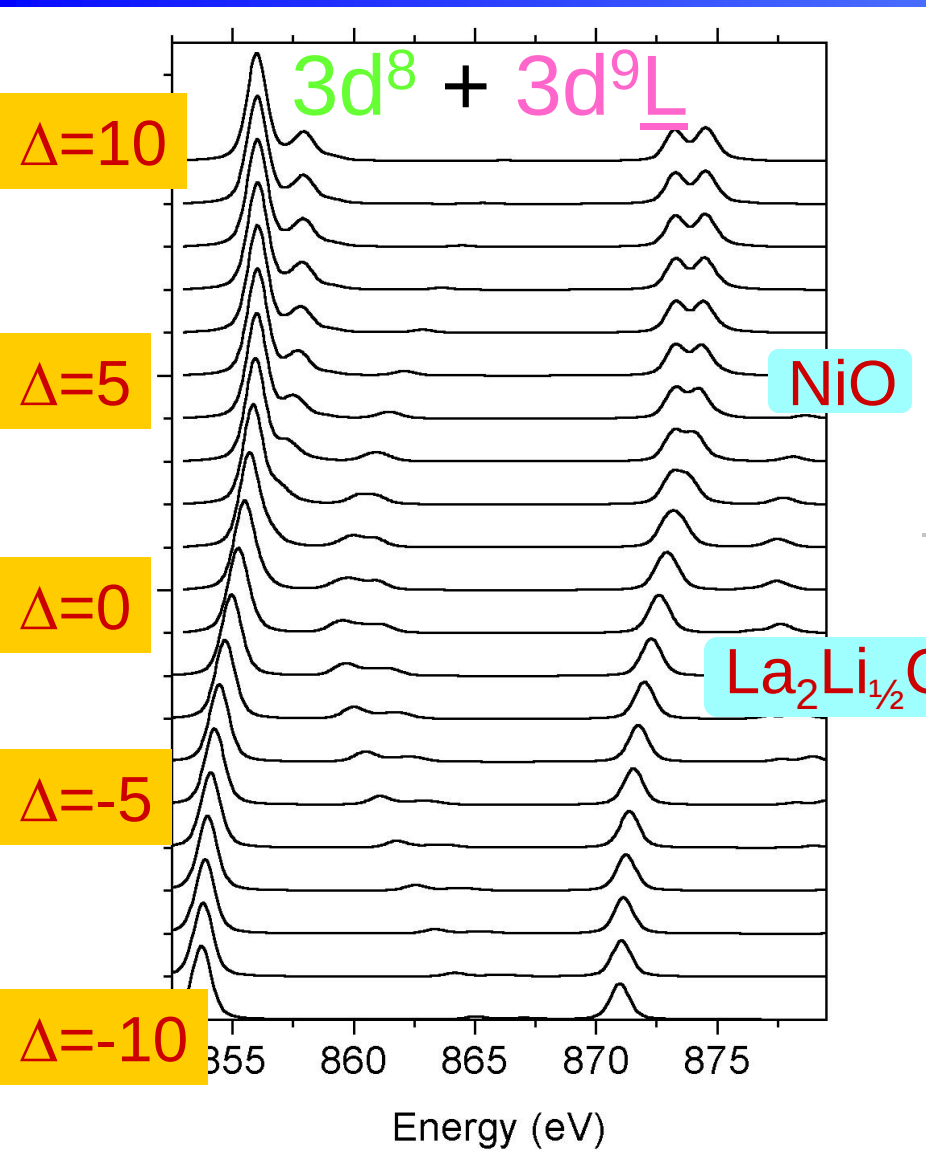
Charge Transfer effects in XAS

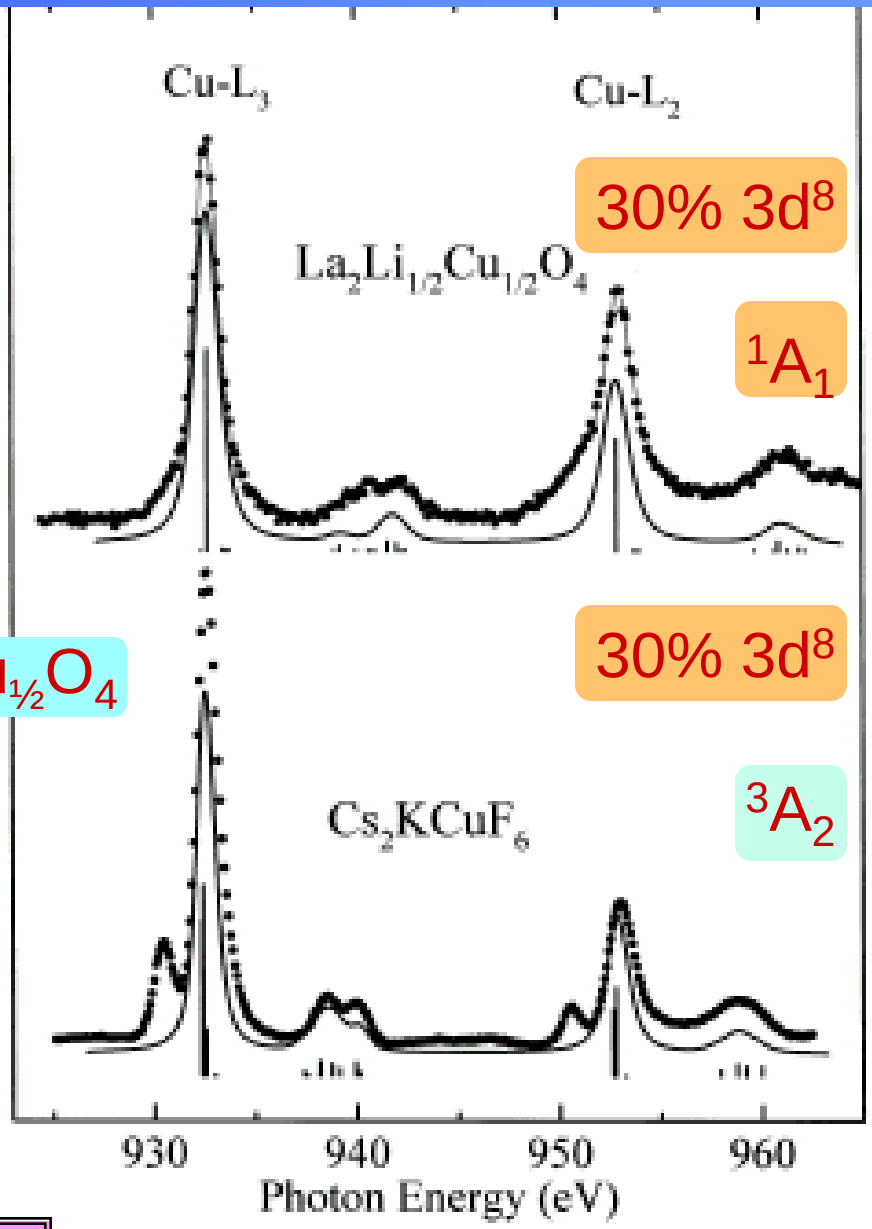




J. Elec. Spec.67, 529 (1994)

Charge Transfer effects in XAS

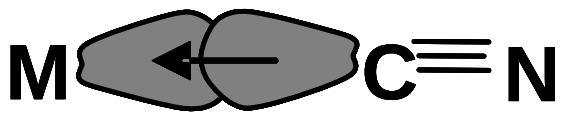


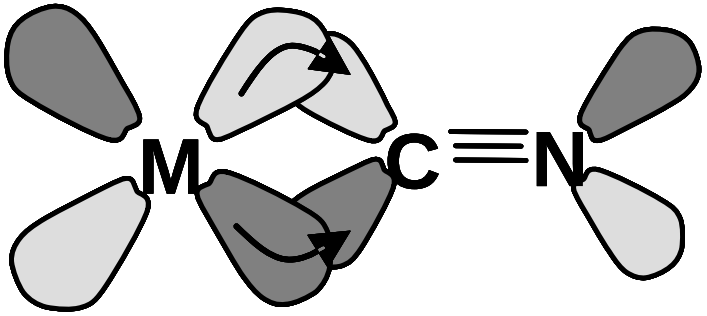


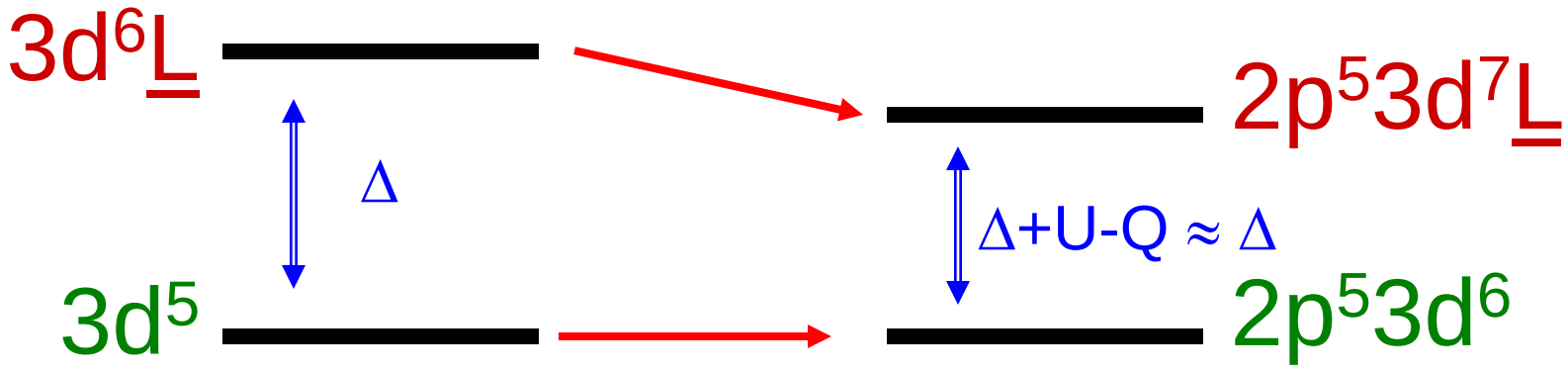
Chem. Phys. Lett. 297, 321 (1998)

LMCT and MLCT: π - bonding

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



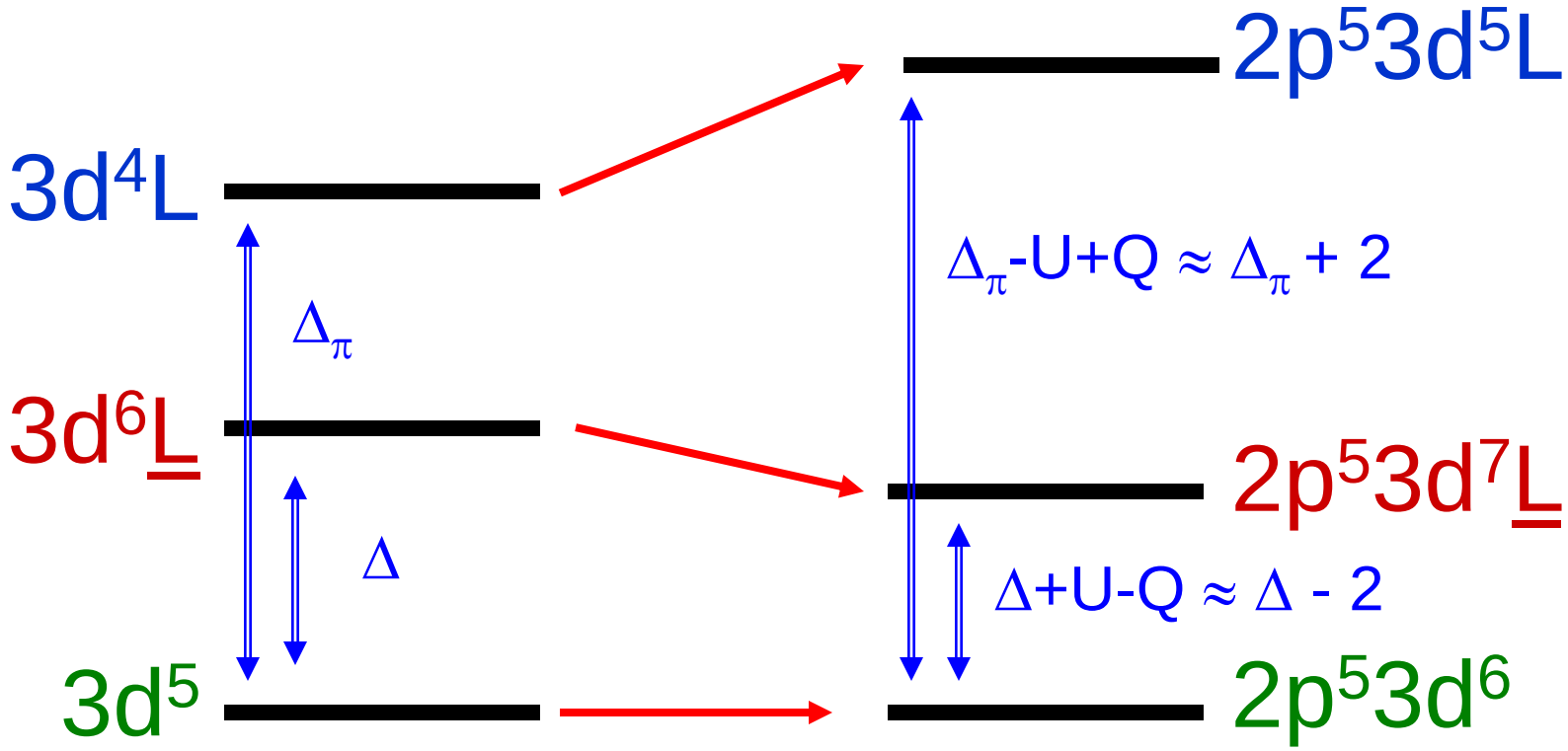




with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

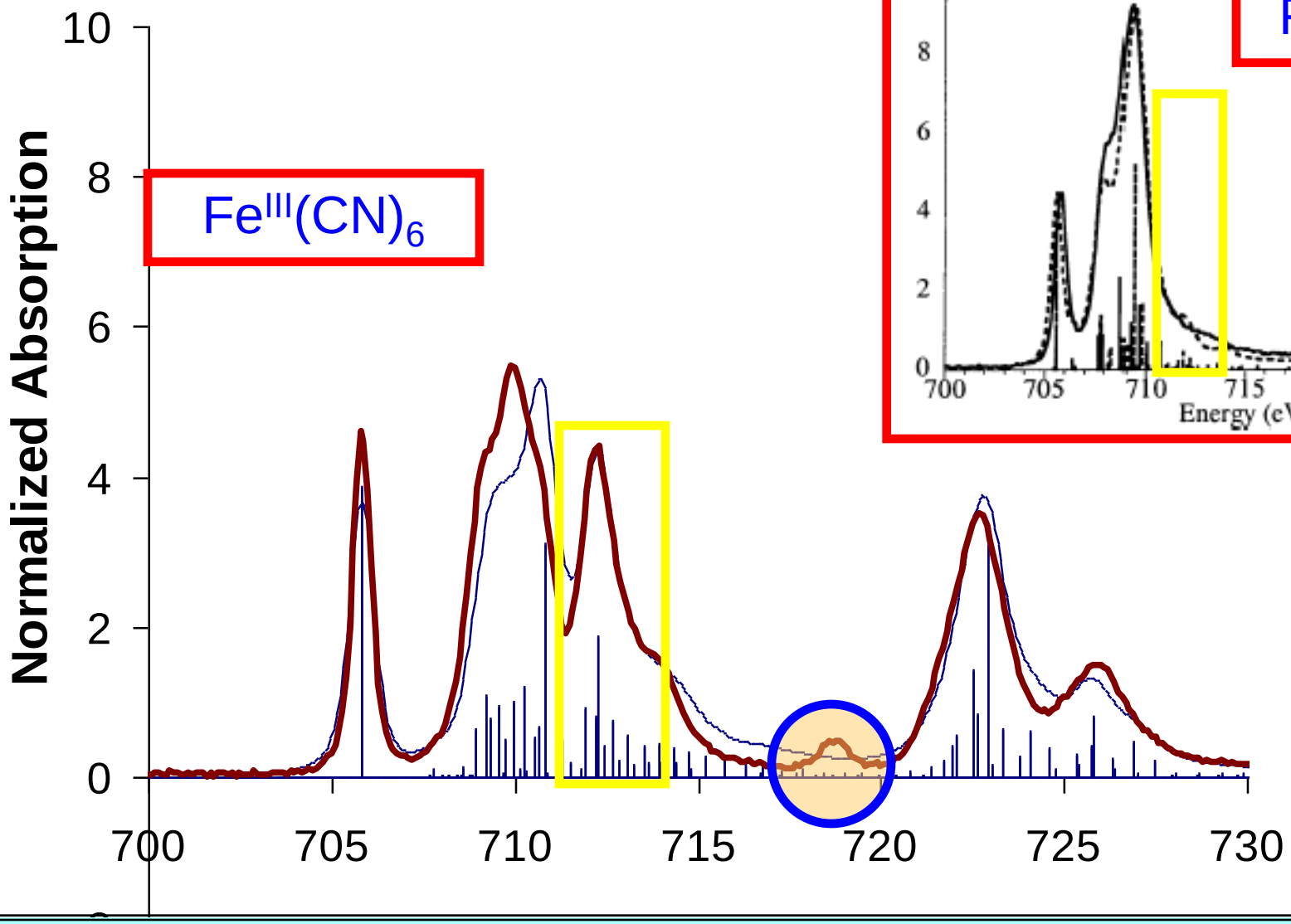
LMCT and MLCT: π - bonding

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



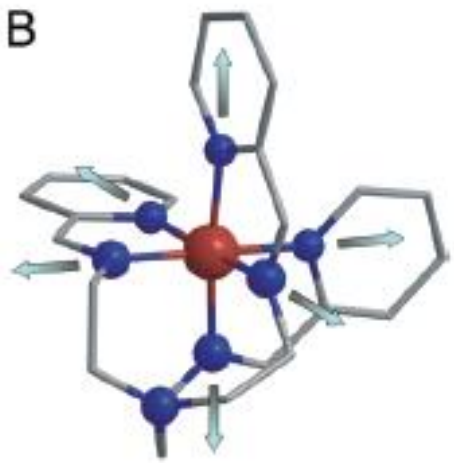
with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

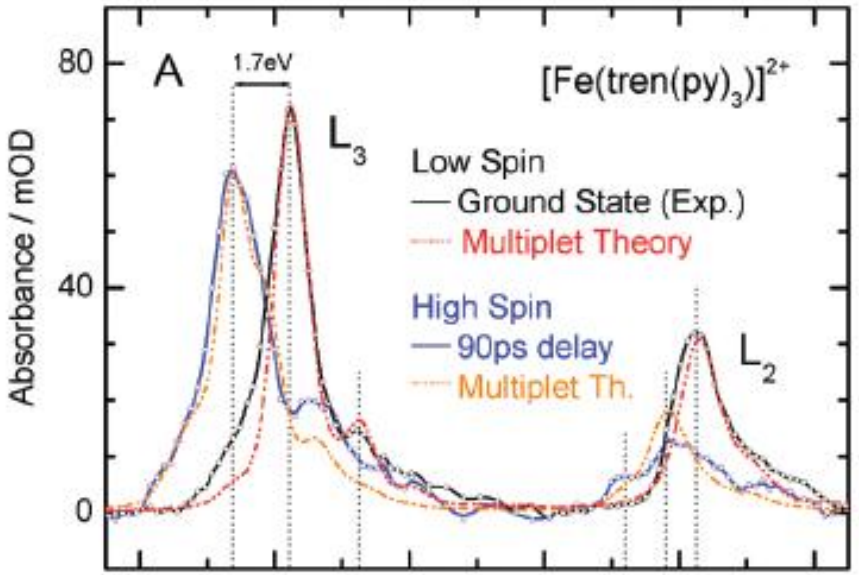
LMCT and MLCT: π - bonding

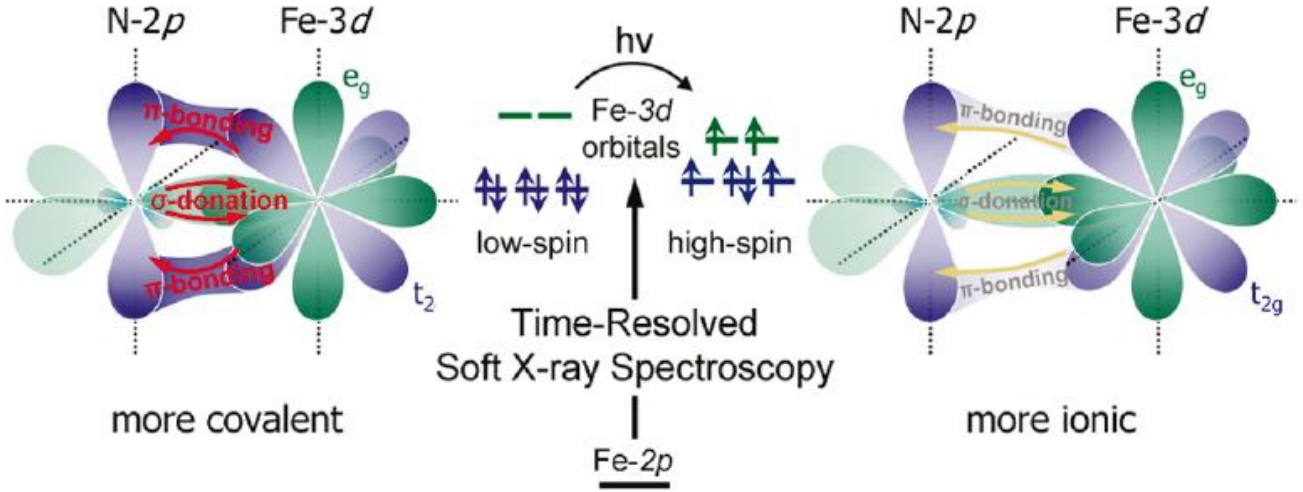


with Ed Solomon (Stanford) JACS 125, 12894 (2003),
JACS 128, 10442 (2006), JACS 129, 113 (2007)

Time resolved XAS

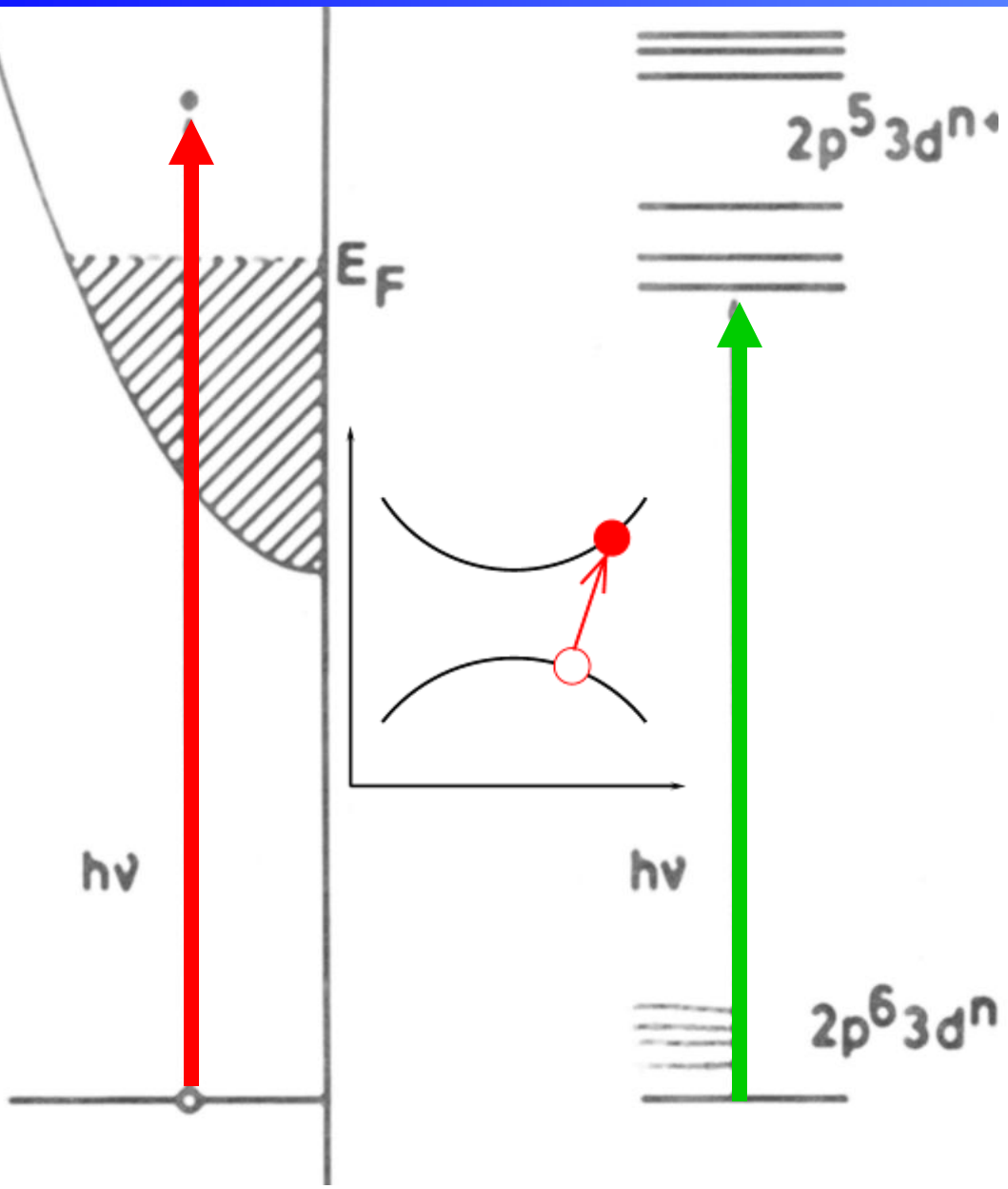






Huse et al. JACS 132, 6809 (2010); JPCL 2, 880 (2011)

XAS: multiplet effects



Single Particle:

1s edges

(DFT + core hole (+U))

2-particle:

(TDDFT, BSE)

+ L edges of $3d^0$

Multiplets:

2p, 3s, 3p edges

(CTM4XAS)

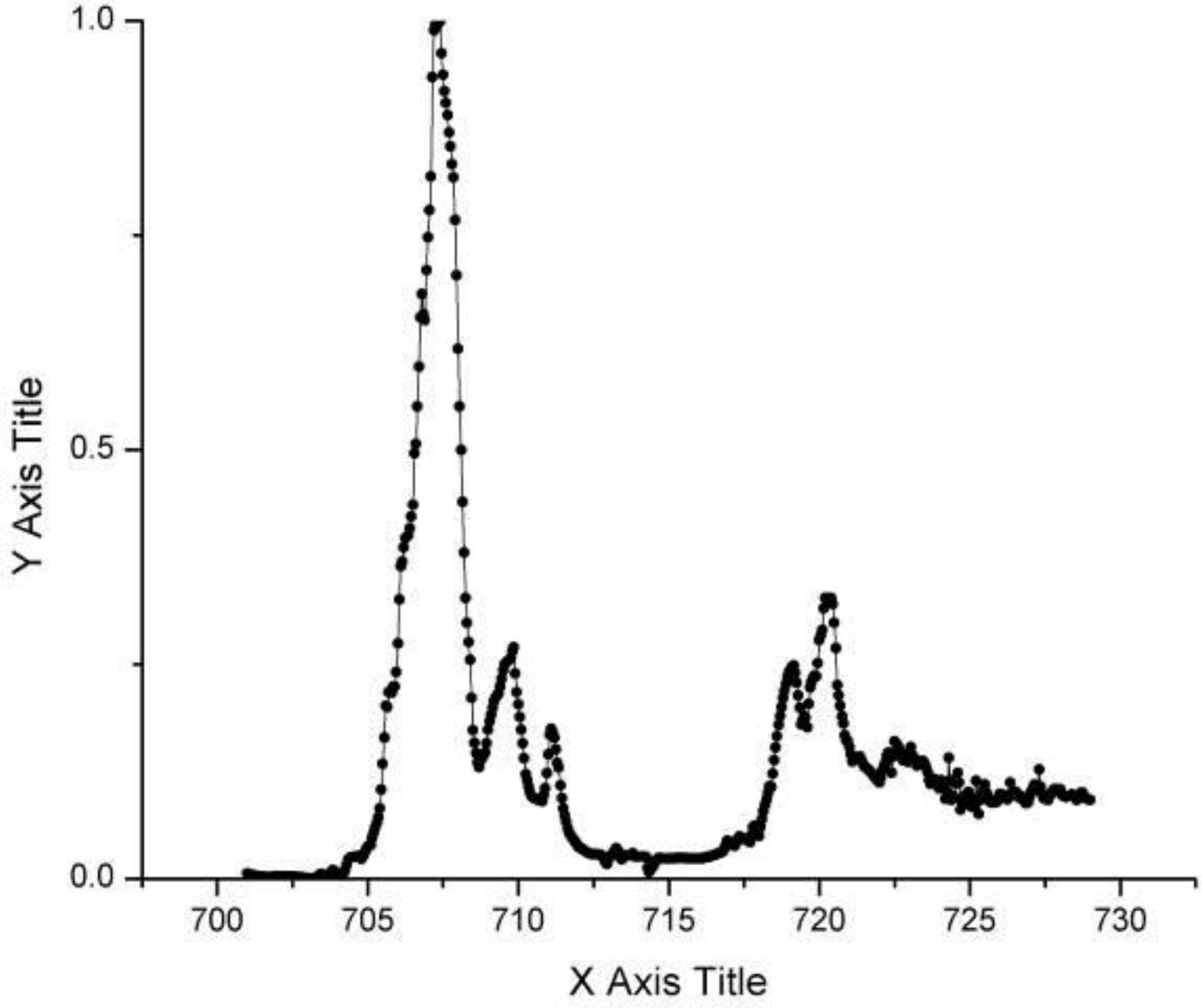
Why X-ray absorption?

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

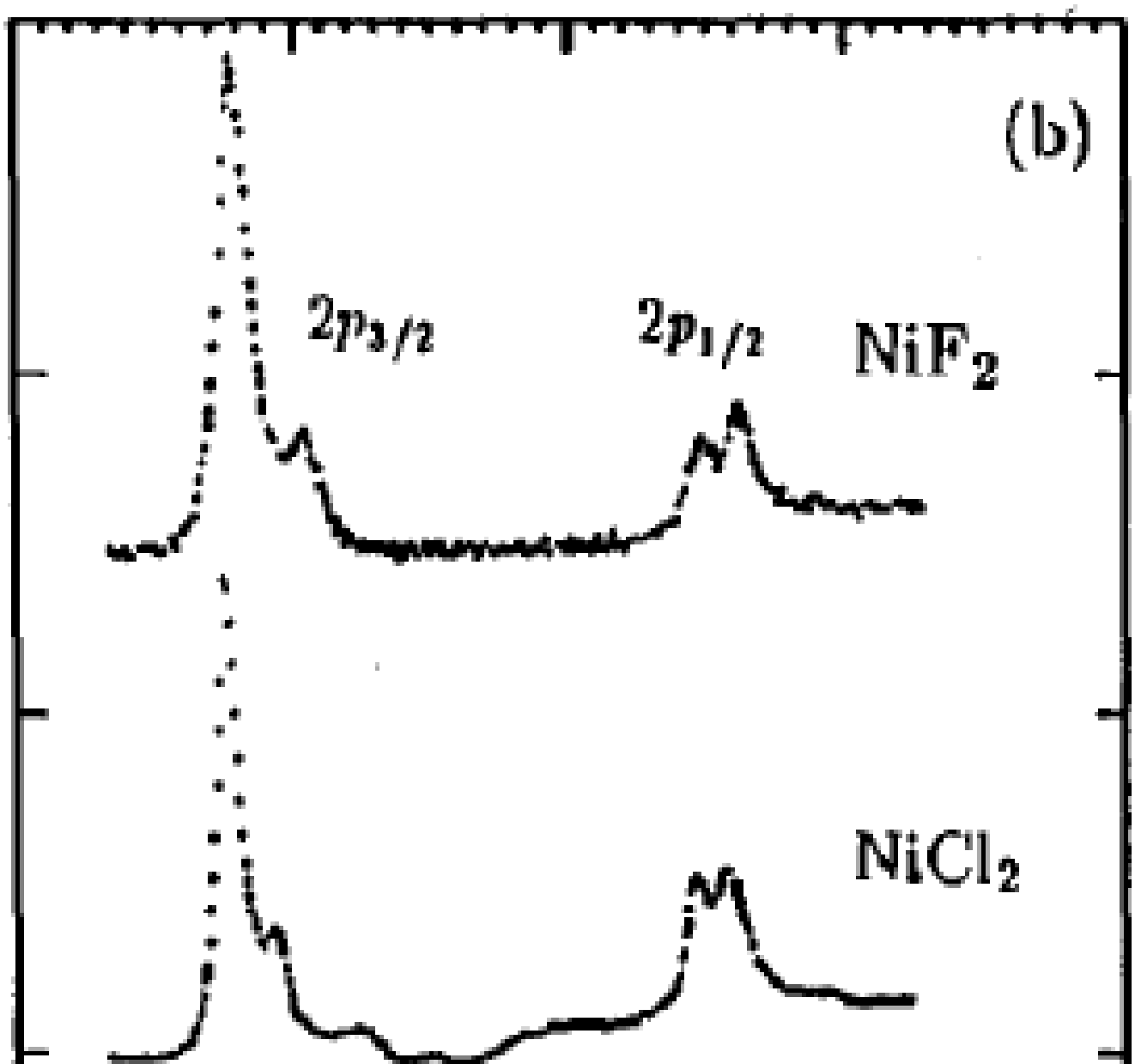
- local electronic & magnetic structure
- valence, spin-state, symmetry
- hybridization, MO energies / density of states
- crystal field, charge transfer, spin-orbit, moments

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

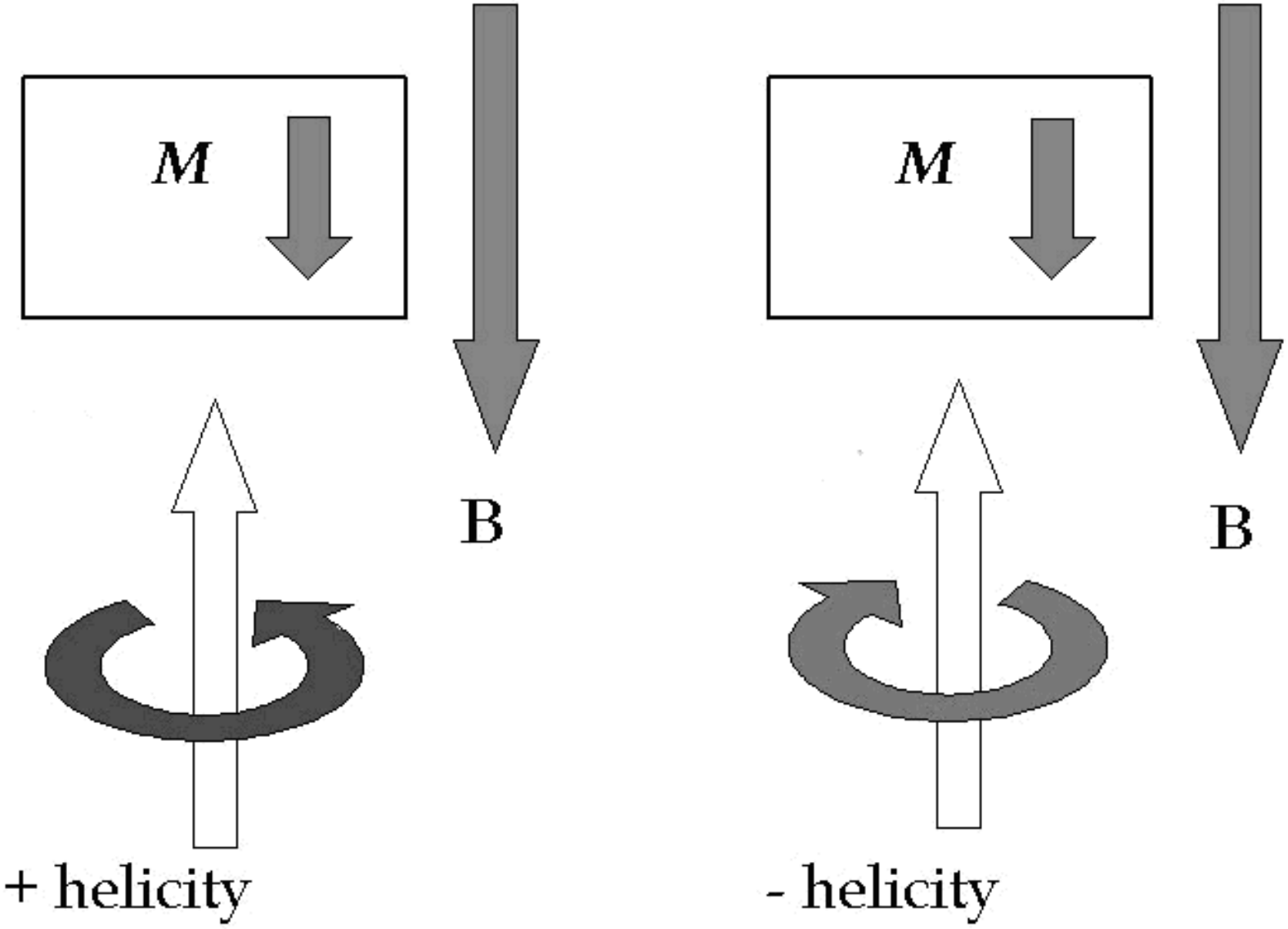
Quiz: Calculate the 2p XAS spectrum of Fe atom



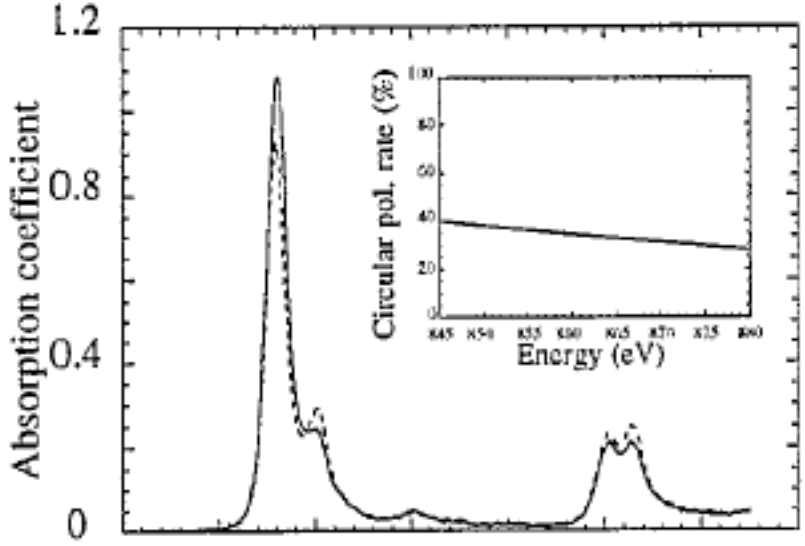
Quiz: Calculate the 2p XAS of NiF_2 and $NiCl_2$

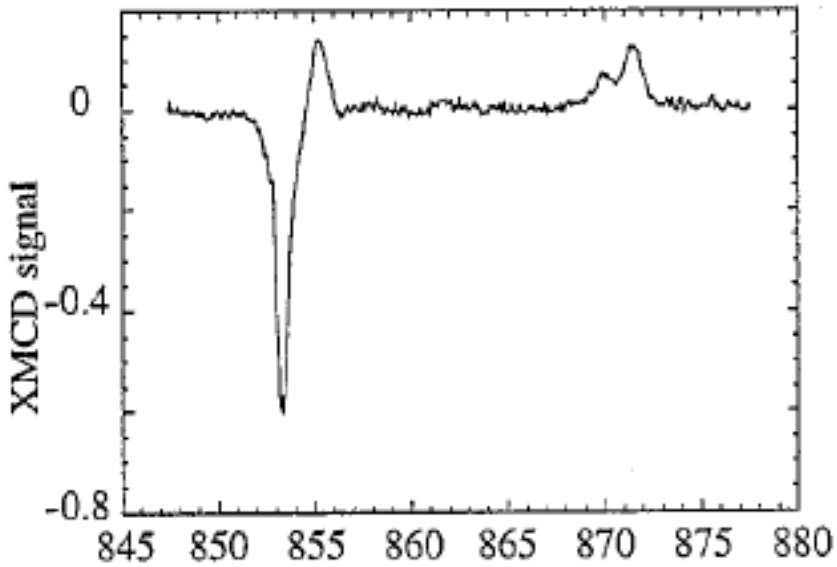


Magnetic circular dichroism



Quiz: Calculate the X-MCD of ferromagnetic Ni^{2+}



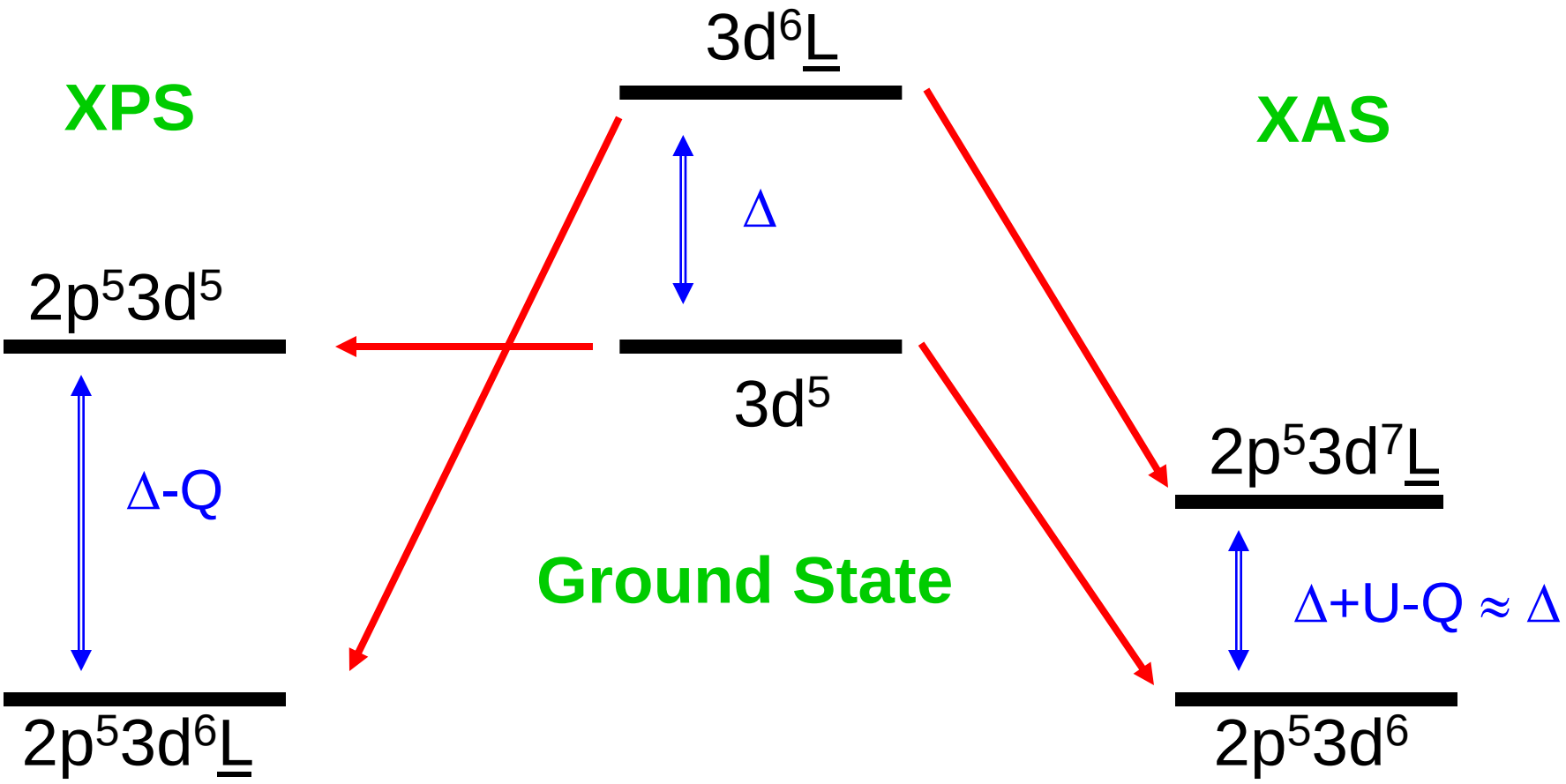


$[Ni^{II}Cr^{III}(CN)_6]^{1-}$

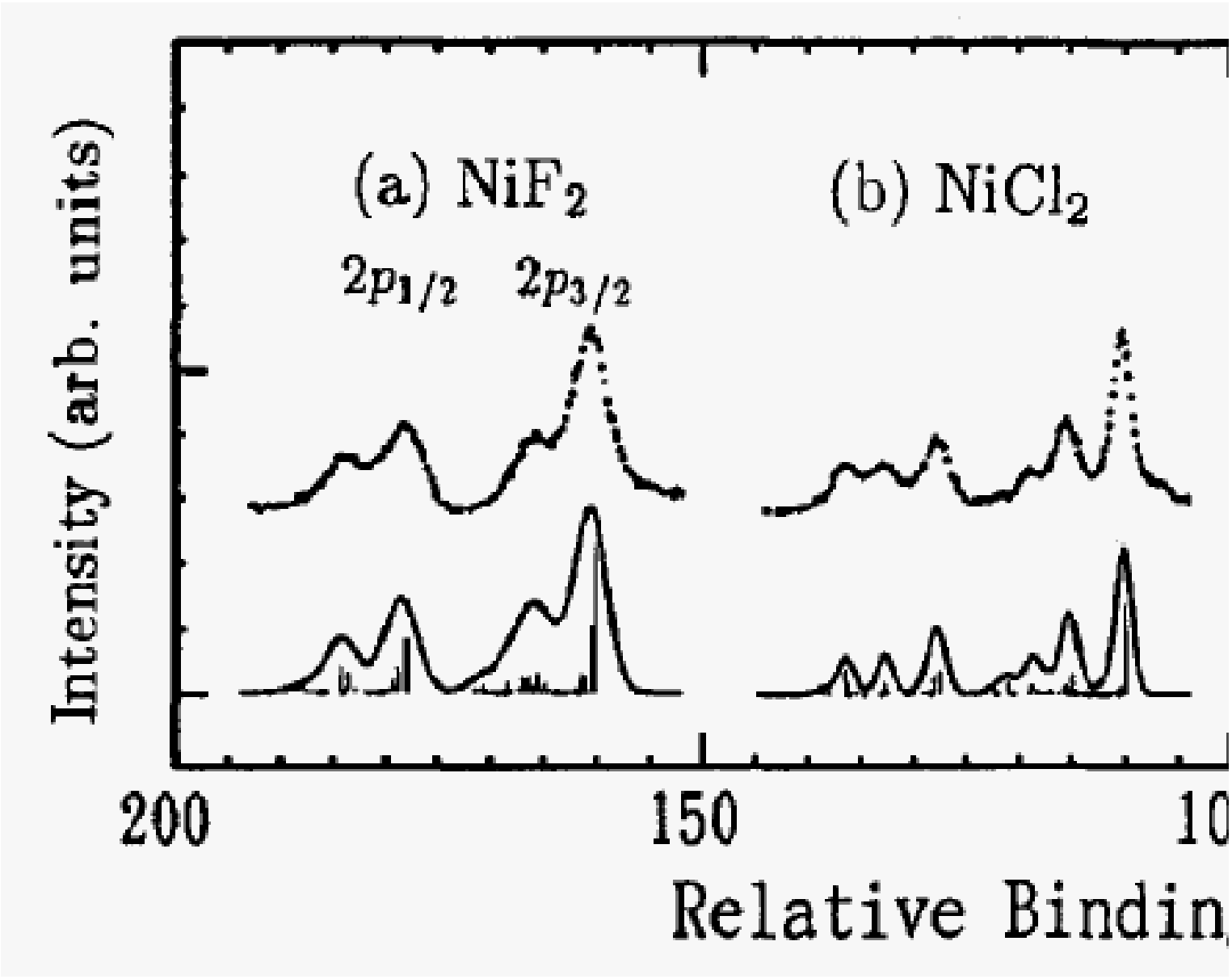
Arrio et al. JPC 100, 4679 (1996)

Charge transfer effects

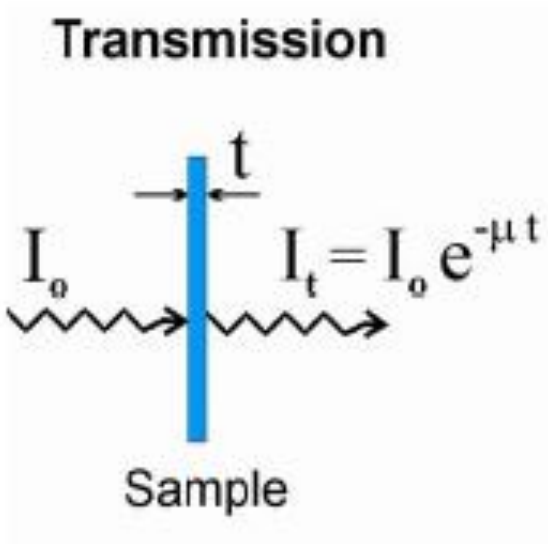
- Transition metal oxide: Ground state: $3d^5 + 3d^6\underline{L}$
- Energy of $3d^6\underline{L}$: Charge transfer energy Δ

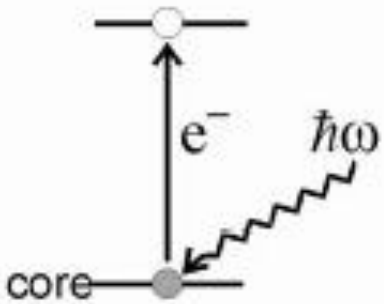


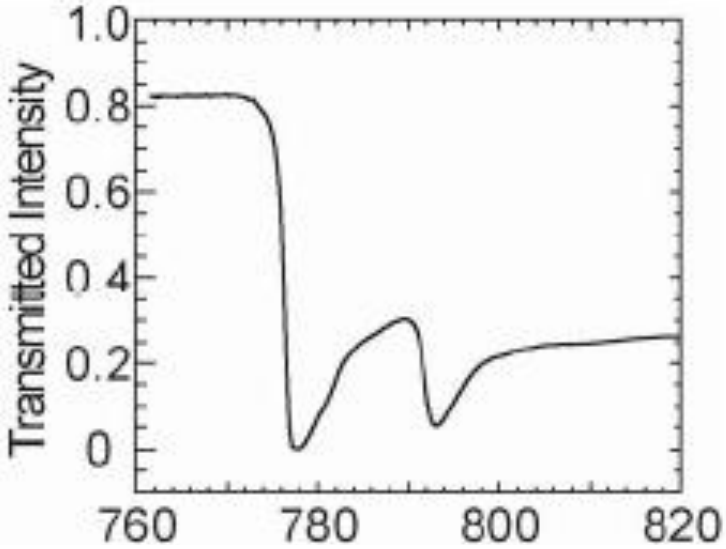
Quiz: Calculate the 2p XPS of NiF_2 and $NiCl_2$



XAS experiments

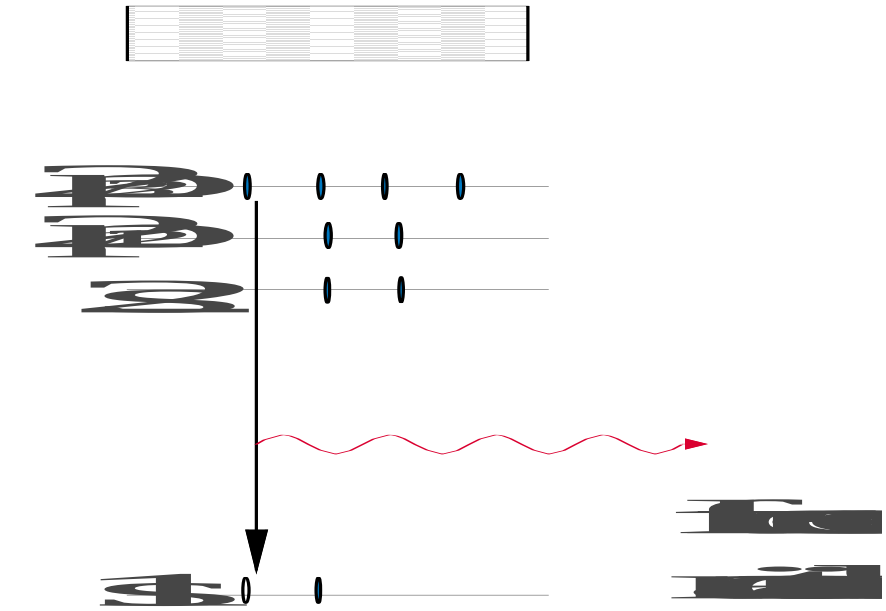




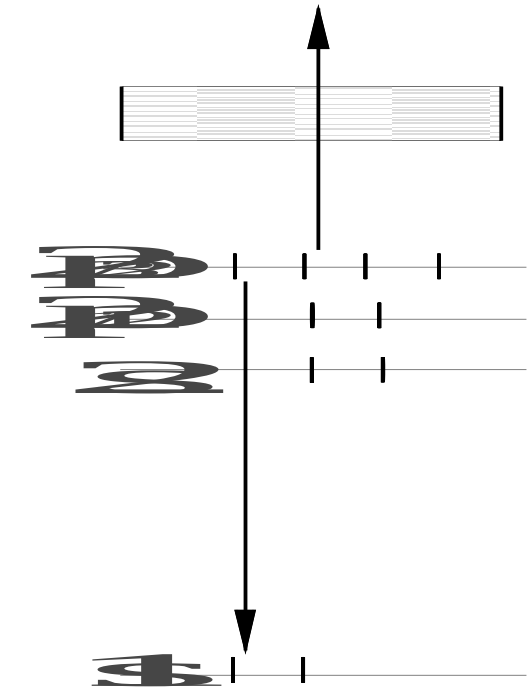


XAS experiments: using the core hole decay

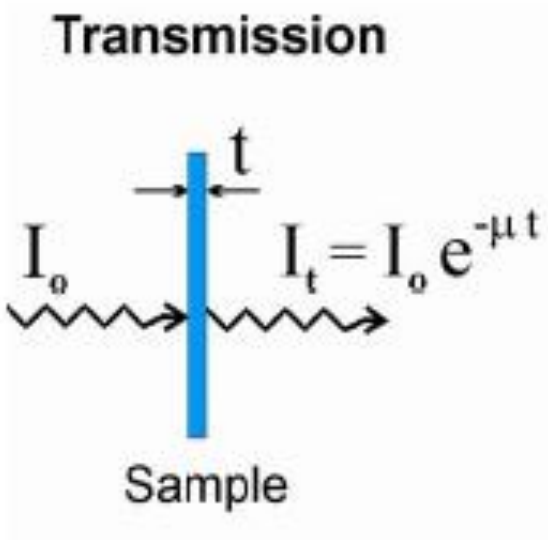
Fluorescence

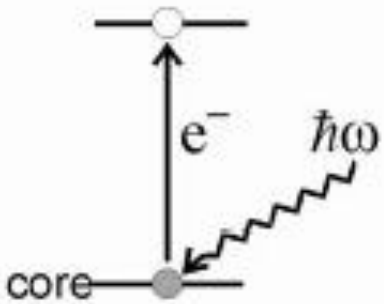


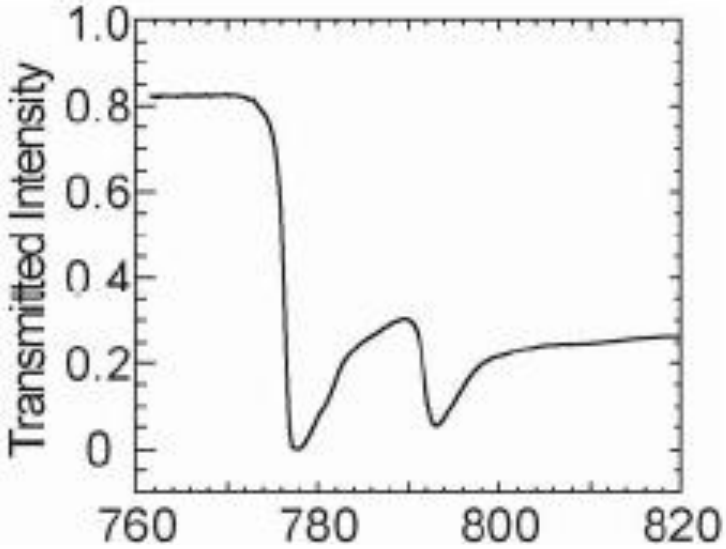
Auger



XAS experiments



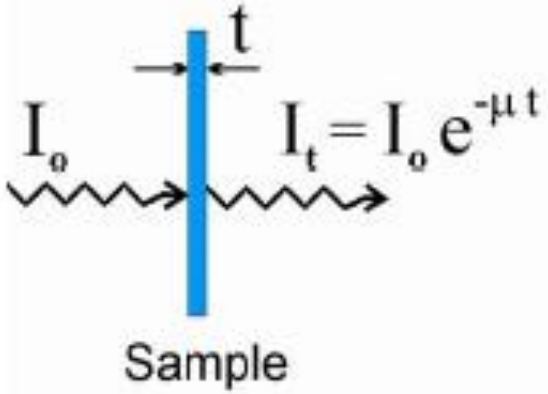


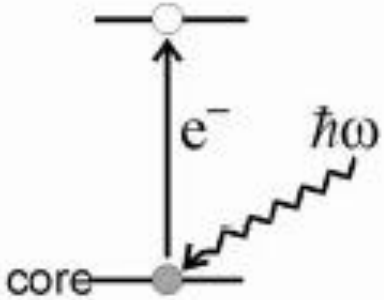


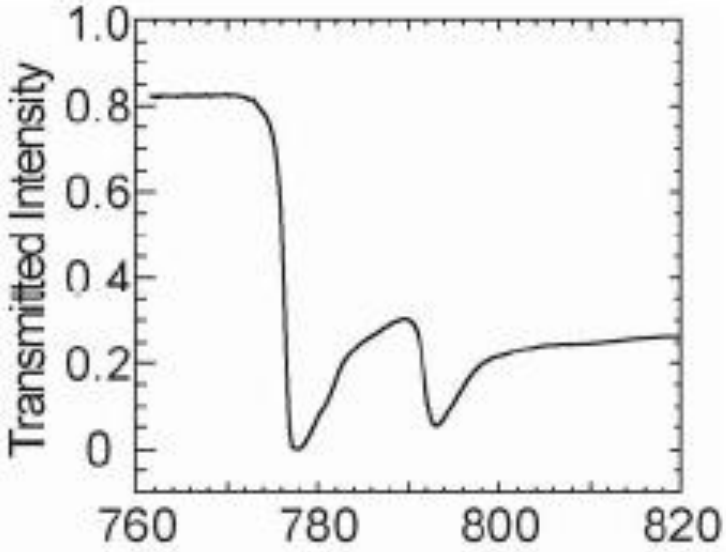
Quiz: How to measure XAS of a solid

XAS experiments

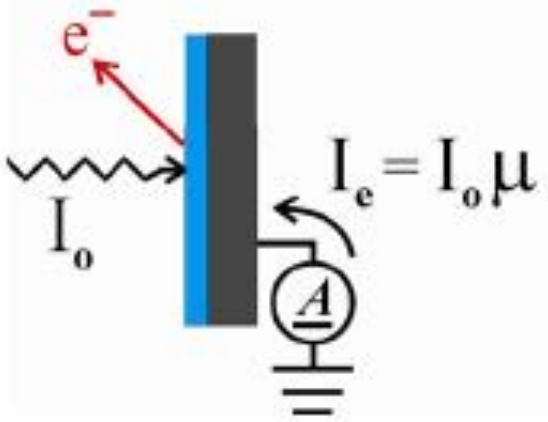
Transmission

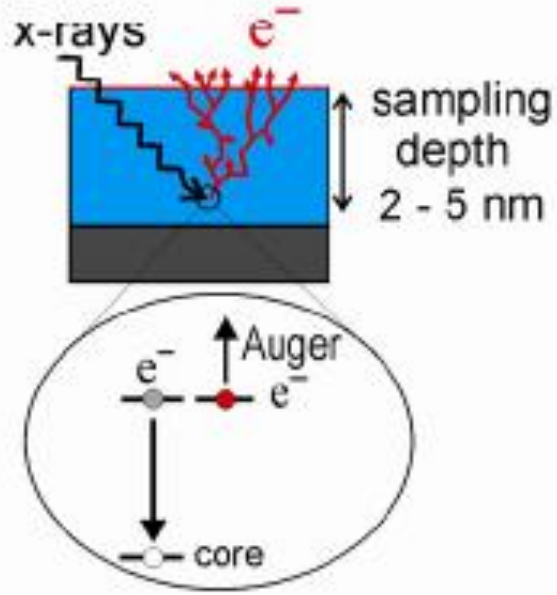


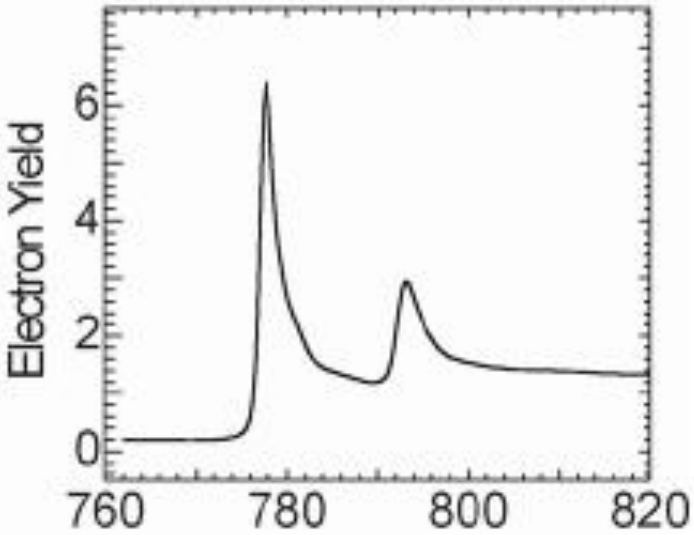


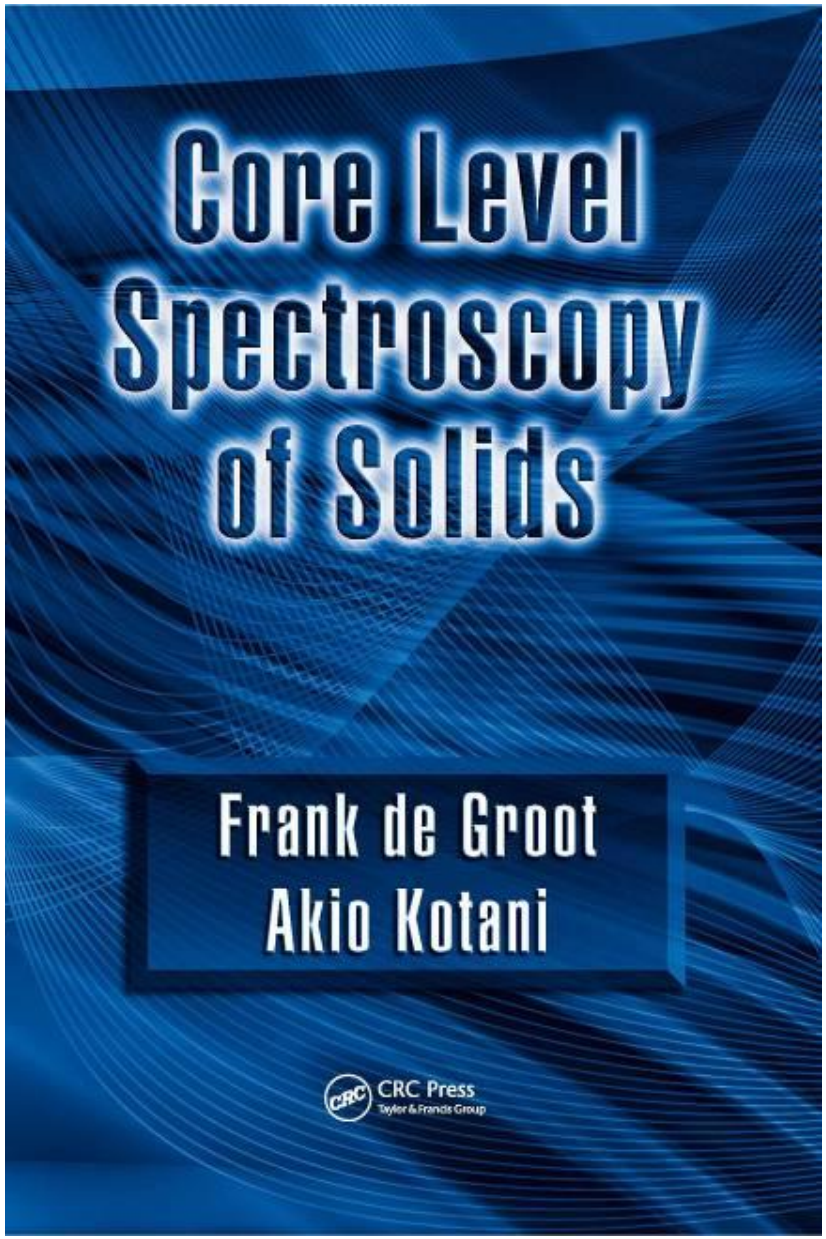


Electron Yield








Core Level
Spectroscopy
of Solids
Frank de Groot
Akio Kotani
CRC Press
Taylor & Francis Group