How well do we understand X-ray absorption spectral shapes?

Department of

Inorganic Chemistry and Catalysis

Utrecht University
Faculty of Chemistry

- Multiplet Analysis

- Resonant inelastic x-ray spectroscopy

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

Oxygen K edge EELS

Oxygen K edge EELS

- Element specific DOS
- L specific DOS

- Core hole effects
- Multiplet effects
- Many body effects

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

EELS

Fermi Golden Rule:

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

Single electron (excitation) approximation:

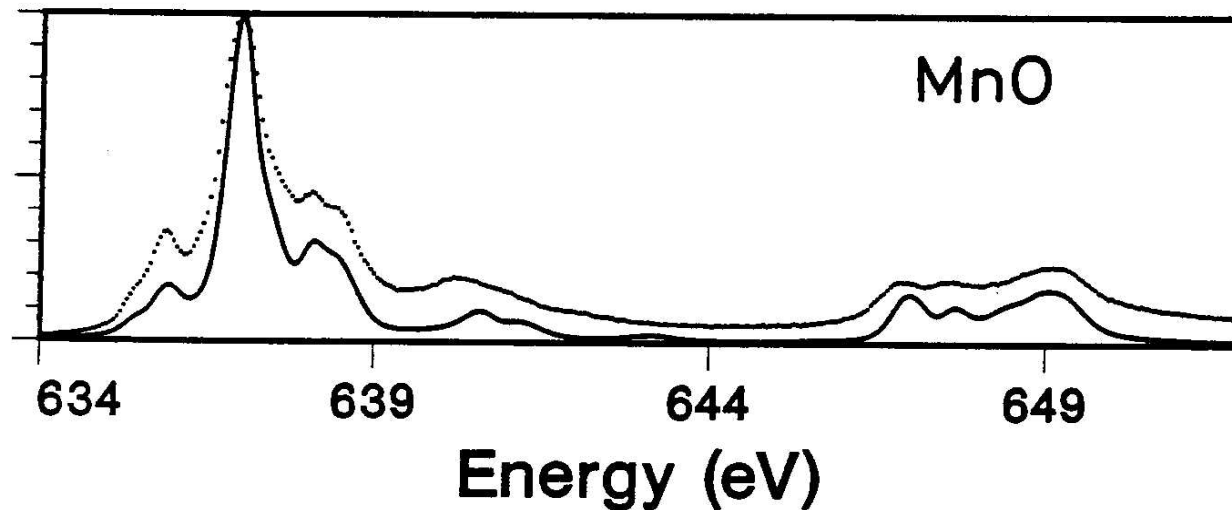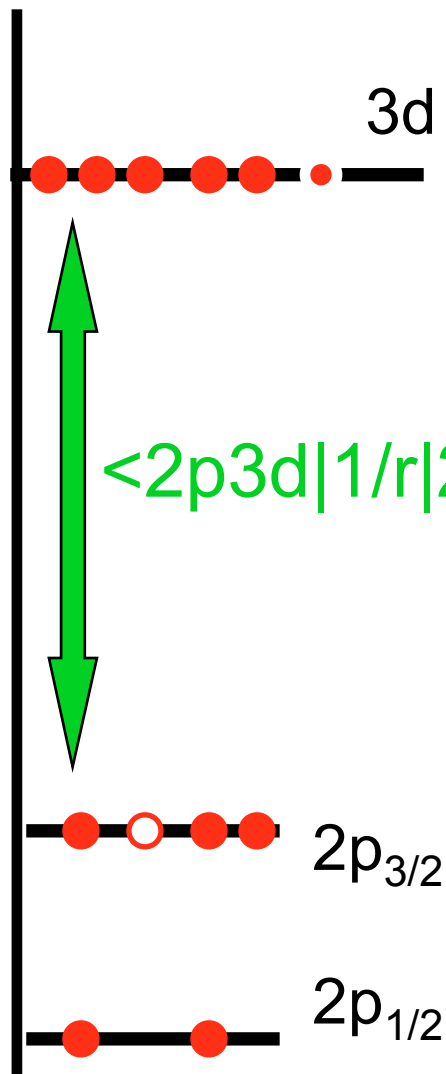$$I_{EELS} = |\langle \Phi_{empty} | dipole | \Phi_{core} \rangle|^2 \, \rho$$

1. Neglect $\langle vv' | 1/r | vv' \rangle$ ('many body effects')

2. Neglect $\langle cv | 1/r | cv \rangle$ ('multiplet effects')
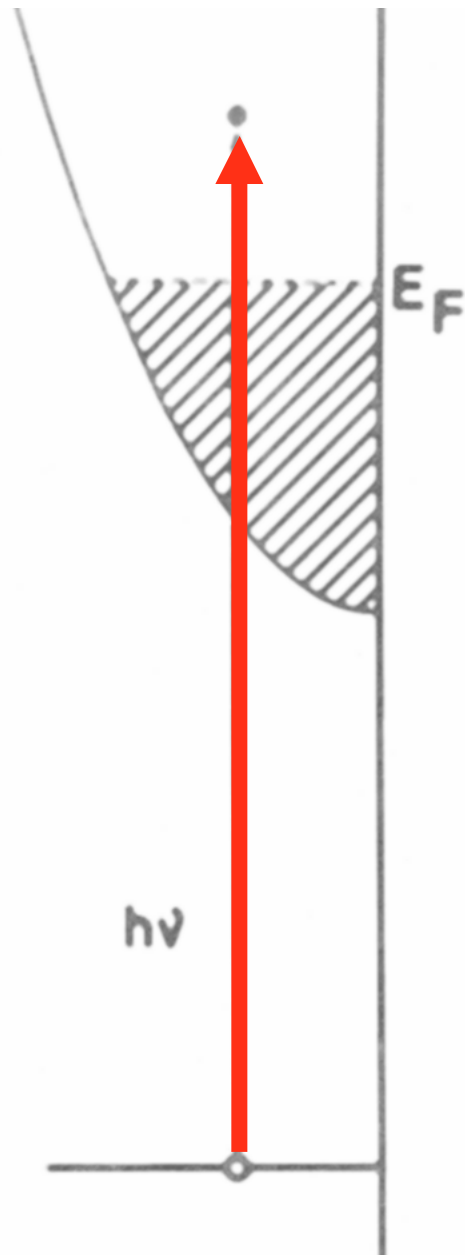
Multiplet Effects in EELS

Overlap of core and valence wave functions

3d

→ Single Particle model breaks down

<2p3d|1/r|2p3d>

2p$_{3/2}$

2p$_{1/2}$

MnO

634   639   644   649

Energy (eV)

EELS

$2p^5 3d^{n+1}$

$2p^6 3d$

$h\nu$

Single Particle:

1s edges

(WIEN, FEFF, PARATEC, …..)

Multiplets:

2p, 3s, 3p edges

(TT-MULTIPLETS)

EELS

$2p^5 3d^{n+1}$

No Unified Interpretation!

$2p^6 3d$

Single Particle:
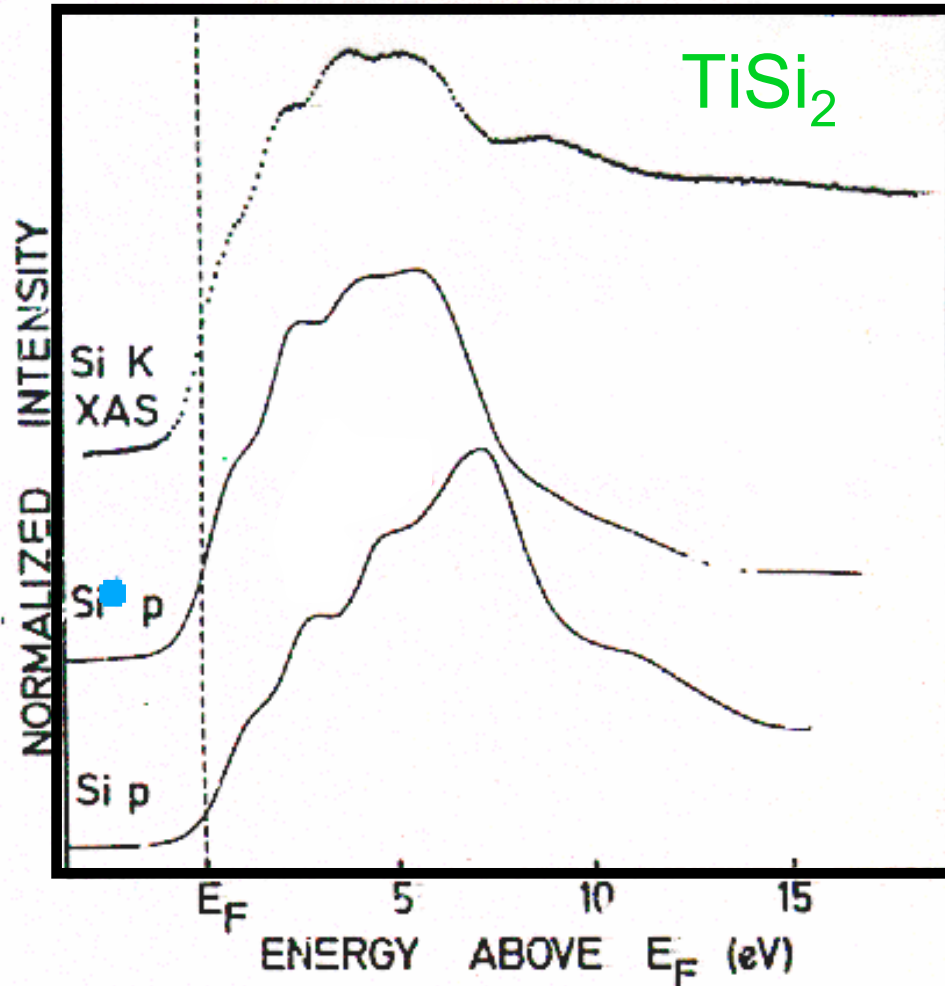
1s edges

(WIEN, FEFF, PARATEC .....)

Multiplets:
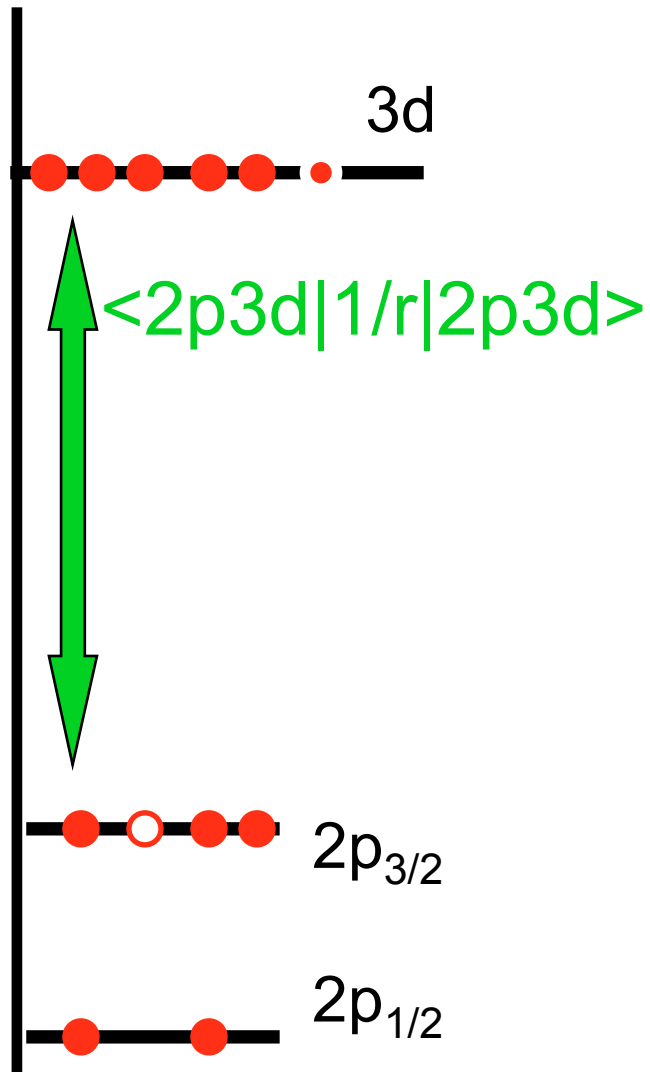
2p, 3s, 3p edges

(TT-MULTIPLETS)

Core Hole Effect in XAS

- **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)

Multiplet Effects in XAS

3d

$\langle 2p3d|1/r|2p3d \rangle$

$2p_{3/2}$

$2p_{1/2}$

Strong overlap of core and valence wave functions

Single Particle model breaks down

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

Multiplet Effects in EELS

Charge Transfer Multiplet program:
Simulation of XAS, EELS, XES, RIXS,
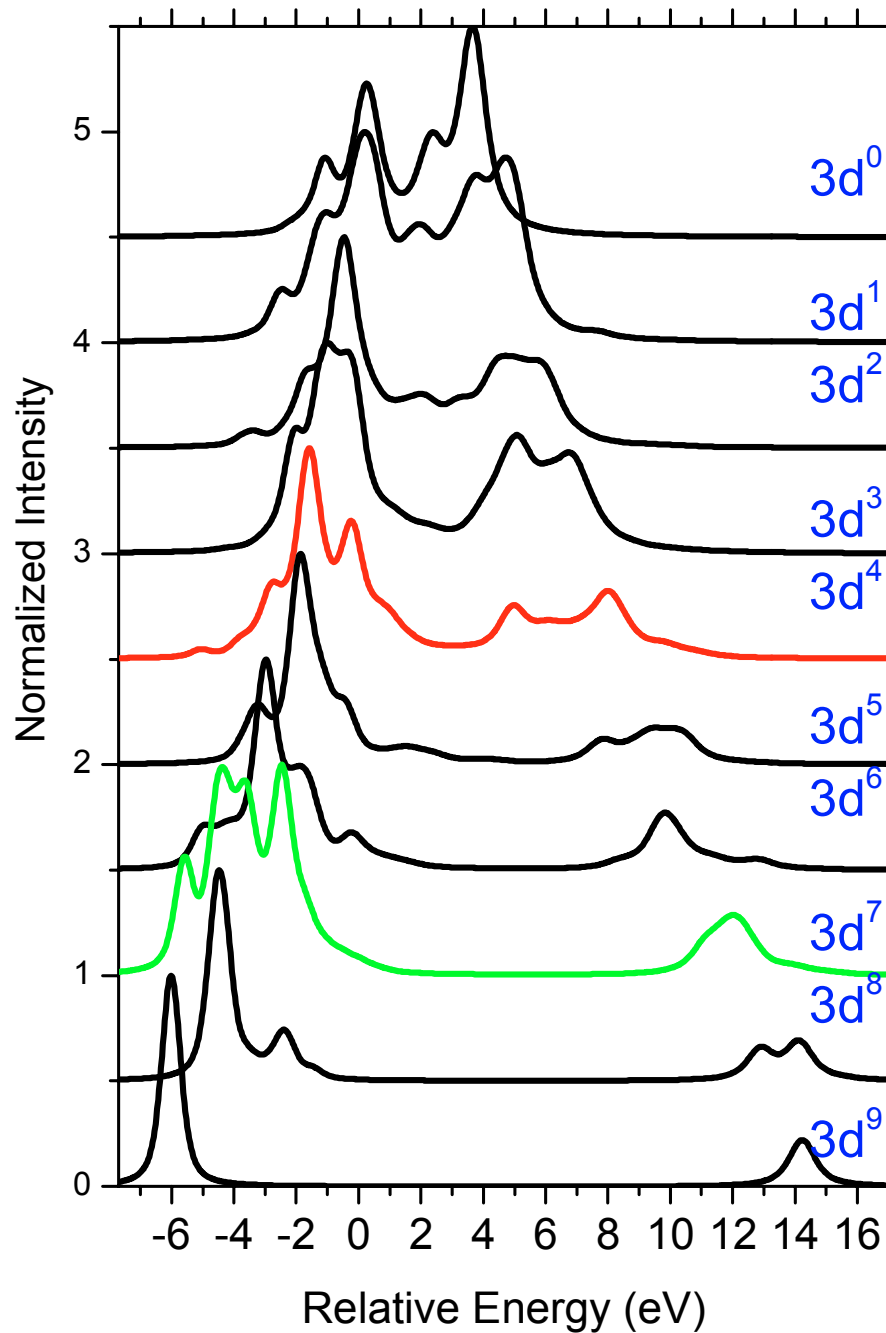(resonant) photoemission, Auger

ATOMIC PHYSICS

⇓

GROUP THEORY

⇓

MODEL HAMILTONIANS

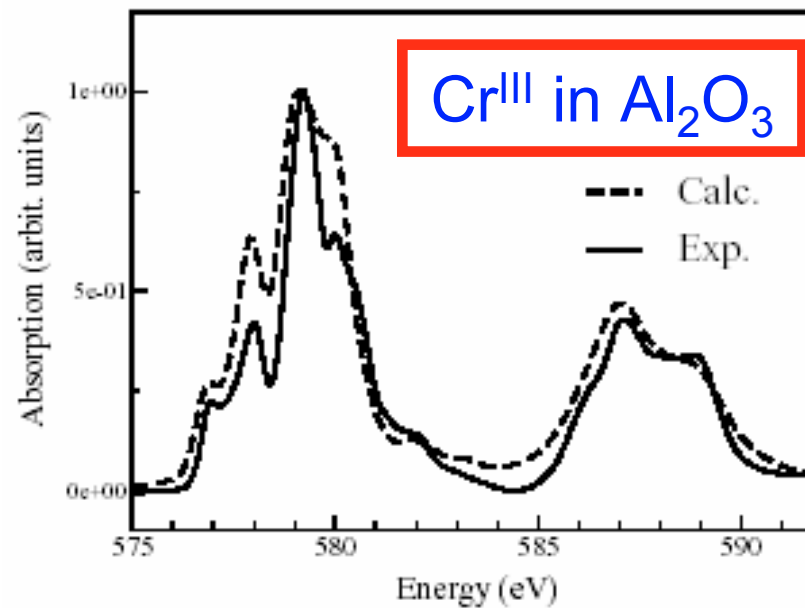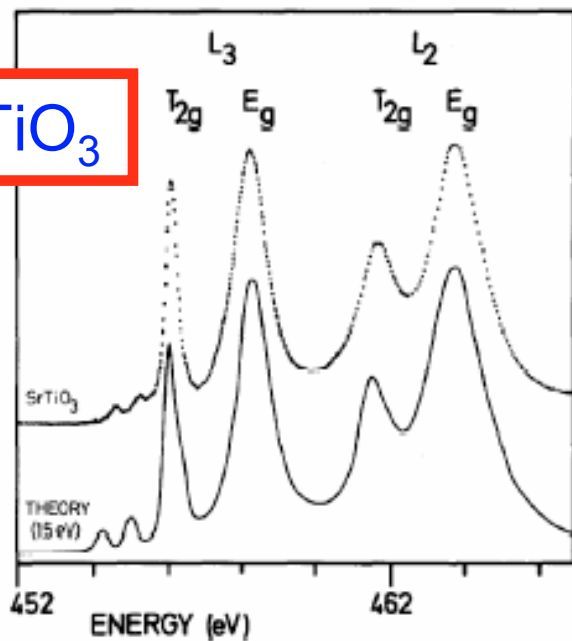www.anorg.chem.uu.nl/people/staff/FrankdeGroot/

Metal L edges

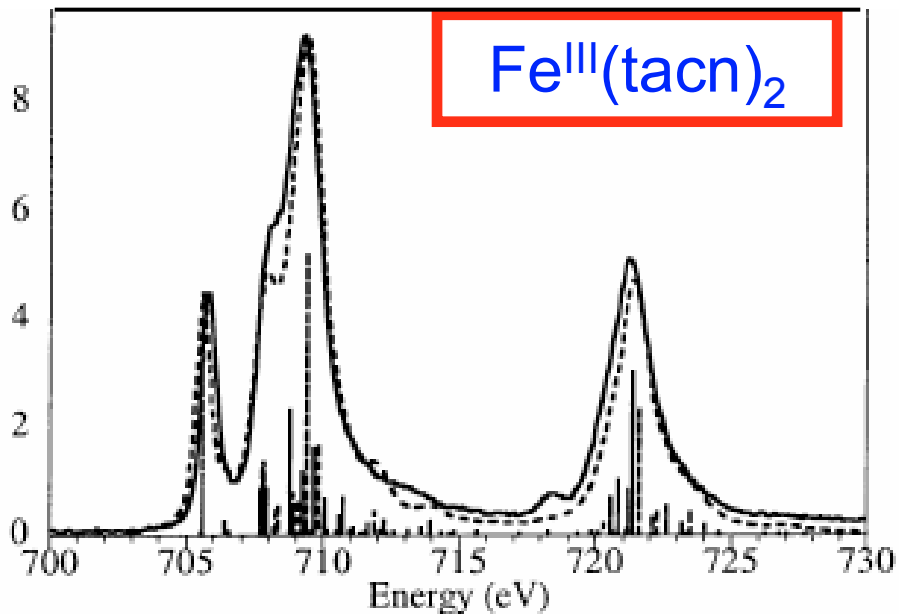Calculated L-edges
$3d^N \rightarrow 2p^5 3d^{N+1}$

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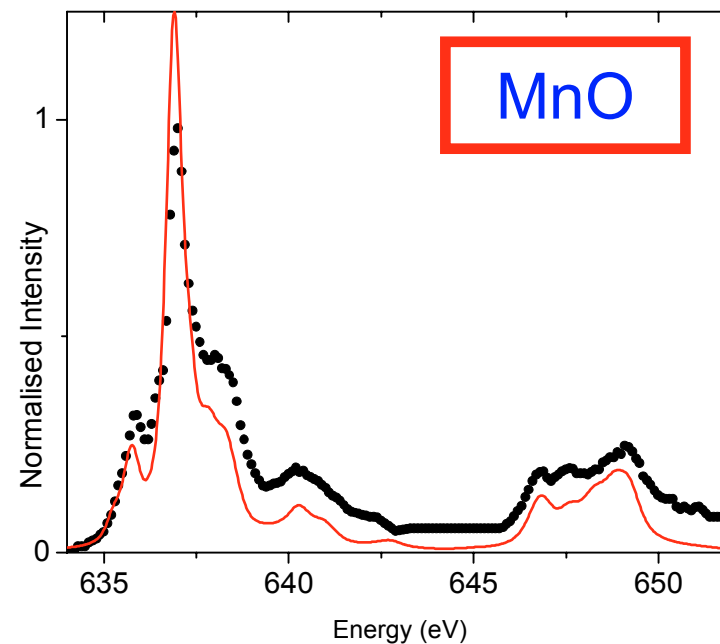- Cubic crystal field of 1.2 eV

Metal L edges

SrTiO$_3$

Cr^{III} in Al$_2$O$_3$

Fe^{III}(tacn)$_2$

MnO

Atomic Multiplet Theory

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

$$H'_{ee} = H_{ee} - \langle H_{ee} \rangle = \sum_{pairs} \frac{e^2}{r_{ij}} - \left\langle \sum_{pairs} \frac{e^2}{r_{ij}} \right\rangle$$
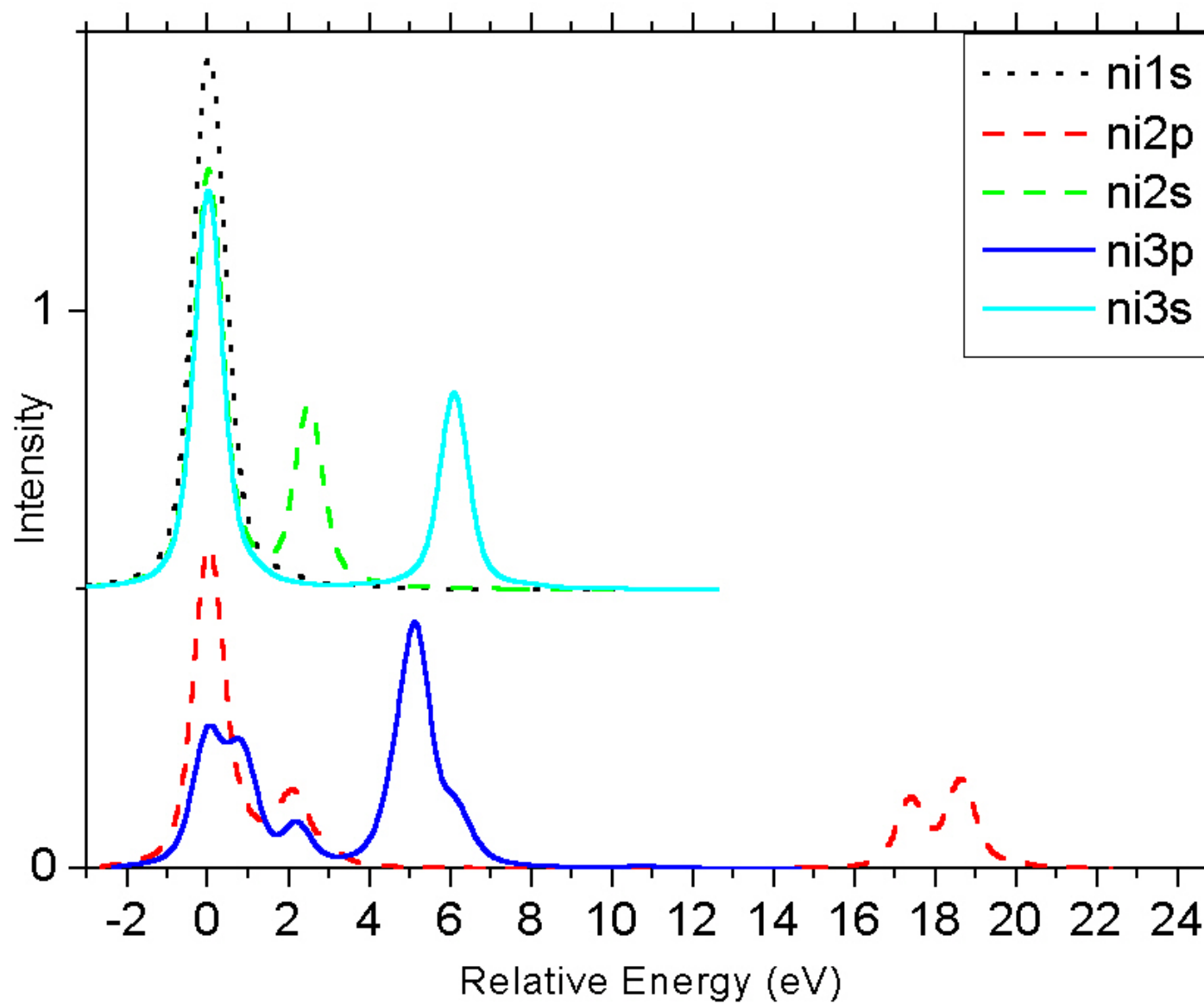
Atomic Multiplet Theory

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

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

Multiplet Effects

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

Core Valence Overlap

1s	2s	2p	3s	3p
0	0	17	0	2

Core Spin-orbit coupling

Multiplet Effects

3d0 XAS calculation

$$H_{eff} = H_{ELECTRO} + H_{LS-2p} + H_{LS-3d}$$

$$H_{ELECTRO} = \left\langle 2p^5 3d^1 \mid \frac{e^2}{r_{12}} \mid 2p^5 3d^1 \right\rangle$$

$$H_{LS-2p} = \left\langle 2p \mid \varsigma_p l_p \cdot s_p \mid 2p \right\rangle$$

$$H_{LS-3d} = \left\langle 3d \mid \varsigma_d l_d \cdot s_d \mid 3d \right\rangle$$

3d⁰ XAS calculation

$H_{electro=0}$ $H_{LS-2p=0}$ $H_{LS-3d=0}$

Energy Matrix				*Eigenvectors*		
$\begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$				$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$		

Energy Levels		Intensities
0.00	^3P	0.00
0.00	^3D	0.00
0.00	^1P	1.00

3d^0 XAS calculation

$H_{electro}$=ATOM H_{LS-2p}=0 H_{LS-3d}=0

Energy Matrix				Eigenvectors		
-1.345	0	0		1	0	0
0	0.671	0		0	1	0
0	0	3.591		0	0	1

| **Energy Levels**		**Intensities**
-1.345	^{3}P	0.00
+0.671	^{3}D	0.00
+3.591	^{1}P	1.00

3d⁰ XAS calculation

$H_{electro=0}$ $H_{LS-2p=ATOM}$ $H_{LS-3d=0}$

Energy Matrix				Eigenvectors		
0.944	1.635	2.312		0.5	-0.5	-0.707
1.635	-0.944	1.335		-0.866	-0.288	-0.408
2.312	1.335	0.000		0.0	0.816	-0.577

Energy Levels		**Intensities**
-1.888	^{3}P	0.00
-1.888	^{3}D	0.666
+3.776	^{1}P	0.333

3d⁰ XAS calculation
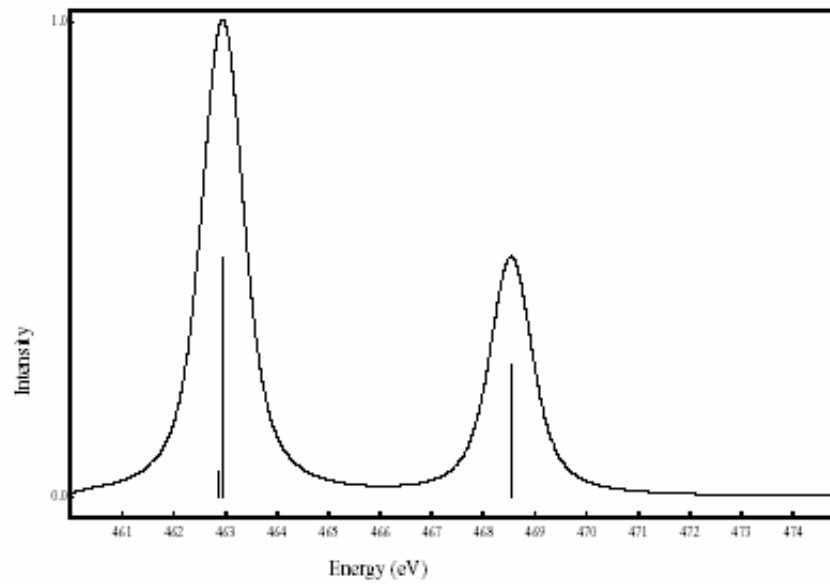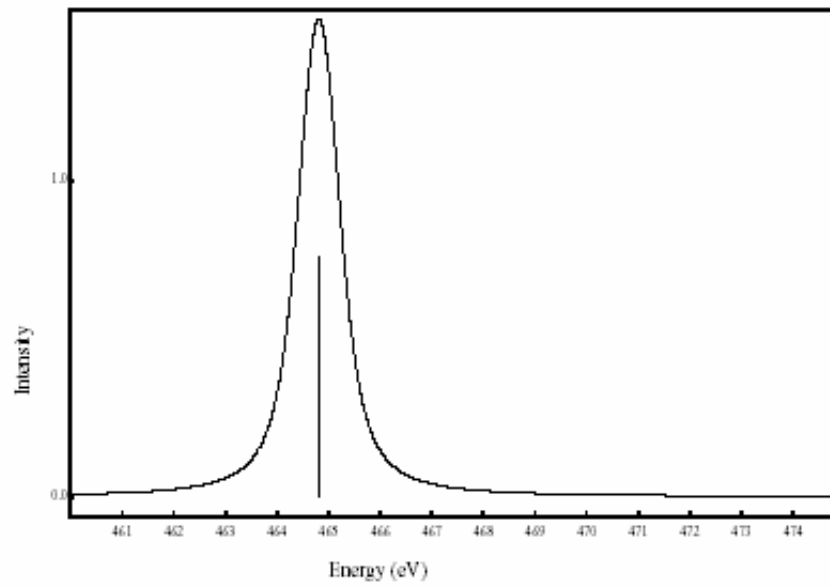
3d⁰ XAS calculation

$H_{\text{electro}}=\text{ATOM}$ $H_{\text{LS-2p}}=\text{ATOM}$ $H_{\text{LS-3d}}=0$

Energy Matrix				*Eigenvectors*		
1.615	1.635	2.312		0.297	-0.776	0.557
1.635	-2.289	1.335		-0.951	-0.185	0.248
2.312	1.335	3.591		0.089	0.603	0.792

Energy Levels		**Intensities**
-2.925	^3P	0.008
+0.207	^3D	0.364
+5.634	^1P	0.628

3d⁰ XAS calculation
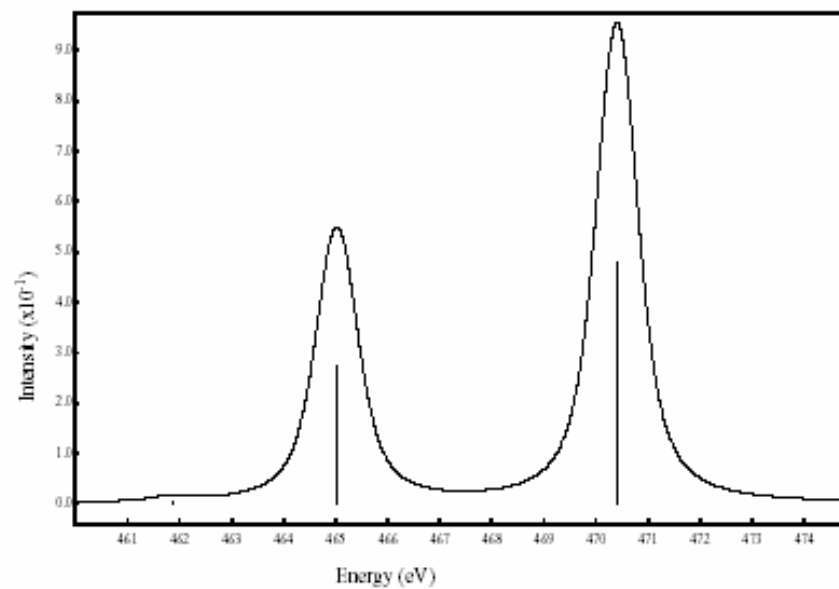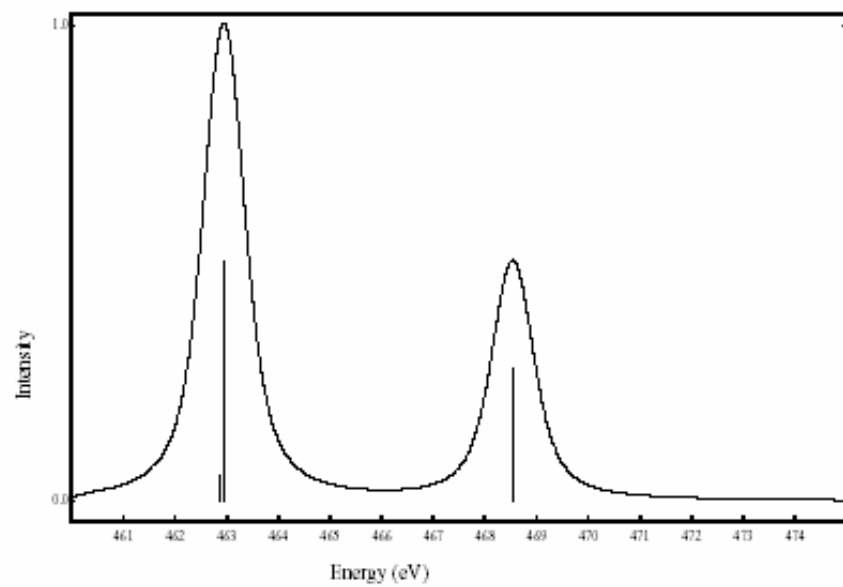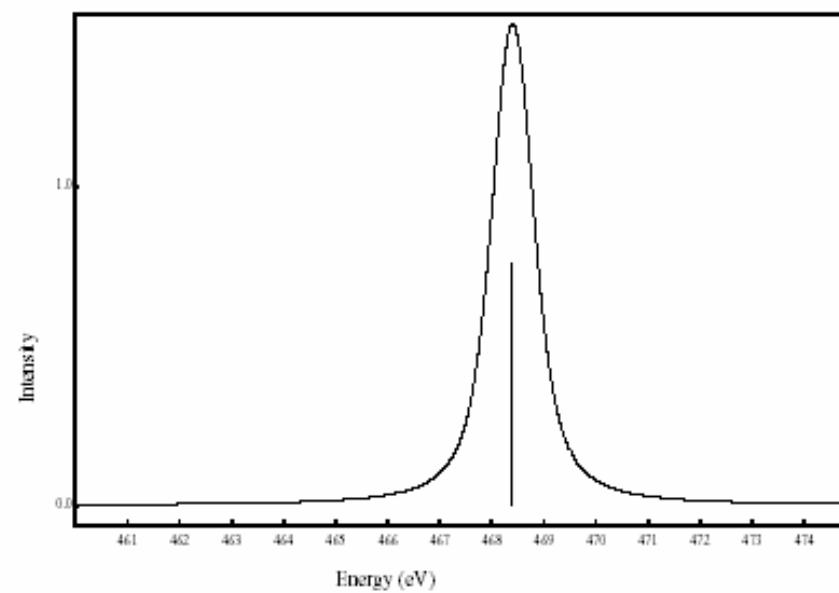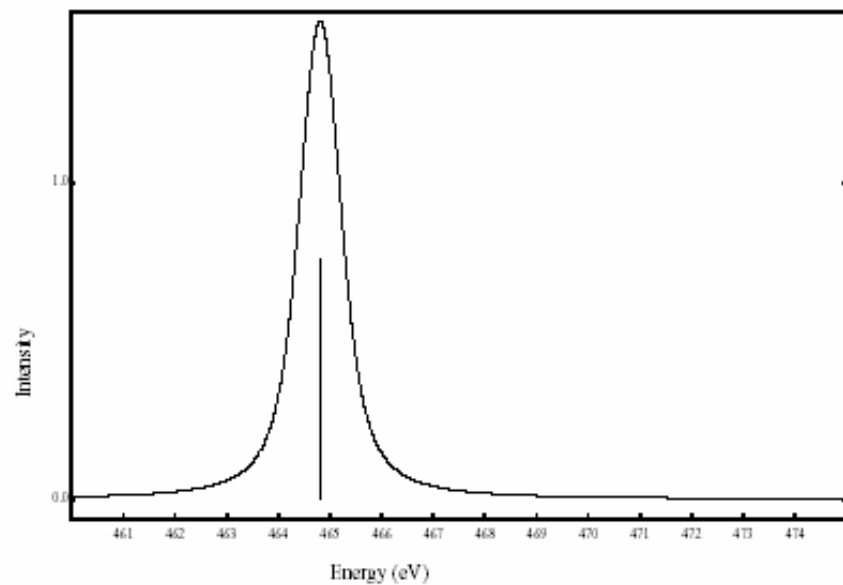
Term Symbols and XAS

Ti^{IV} ion in TiO$_2$:
Ground state: 3d^0
Final state: 2p^{5}3d^1
Dipole transition: p-symmetry

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

ground state symmetry: ^{1}S ^{1}S$_0$
transition: ^{1}S $\otimes^1$P = ^{1}P
two possible final states: ^{1}P ^{1}P$_1$,^{3}P$_1$,^{3}D$_1$,

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	$\Delta j=+1,0,-1$

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

3d⁸ XAS calculation
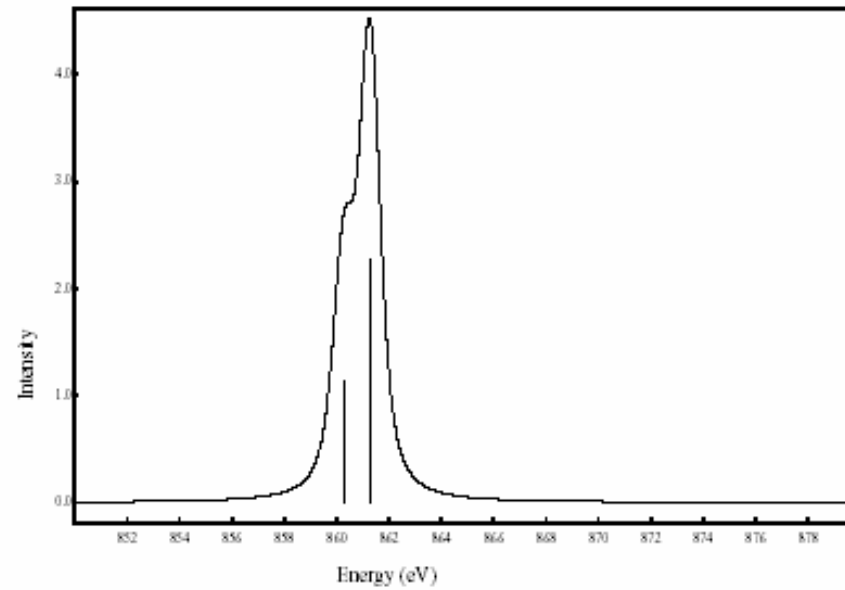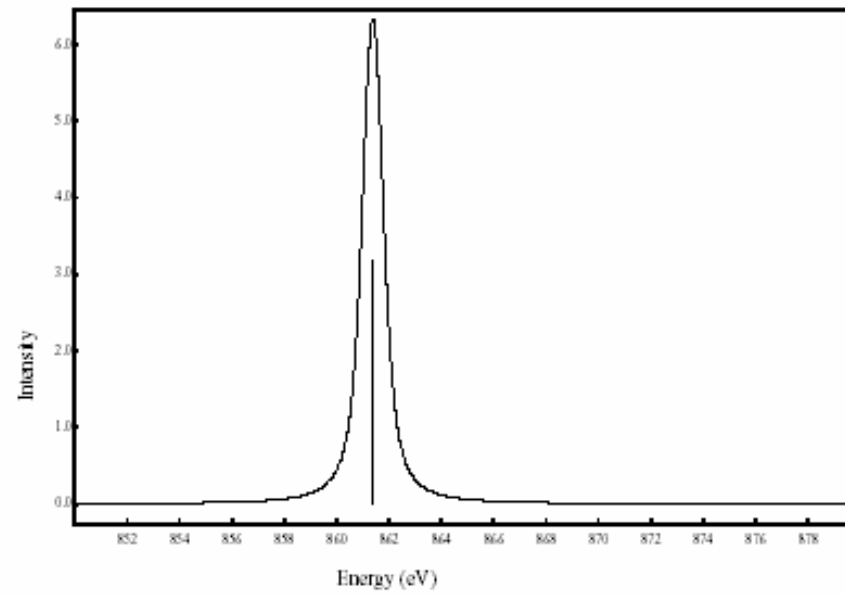
Term Symbols and XAS

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

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

ground state symmetry: ^{3}F ^{3}F$_4$
transition: ^{3}F $\otimes^1$P = ^{3}DFG
two possible final states: ^{3}D, ^{3}F ^{3}D$_3$,^{3}F$_3$,^{3}F$_4$, ^{1}F$_3$

3d⁸ XAS calculation

XAS calculations of rare earths

Nd^{III} ion in Nd metal

Ground state: 4f^3

Final state: 3d^{9}4f^4
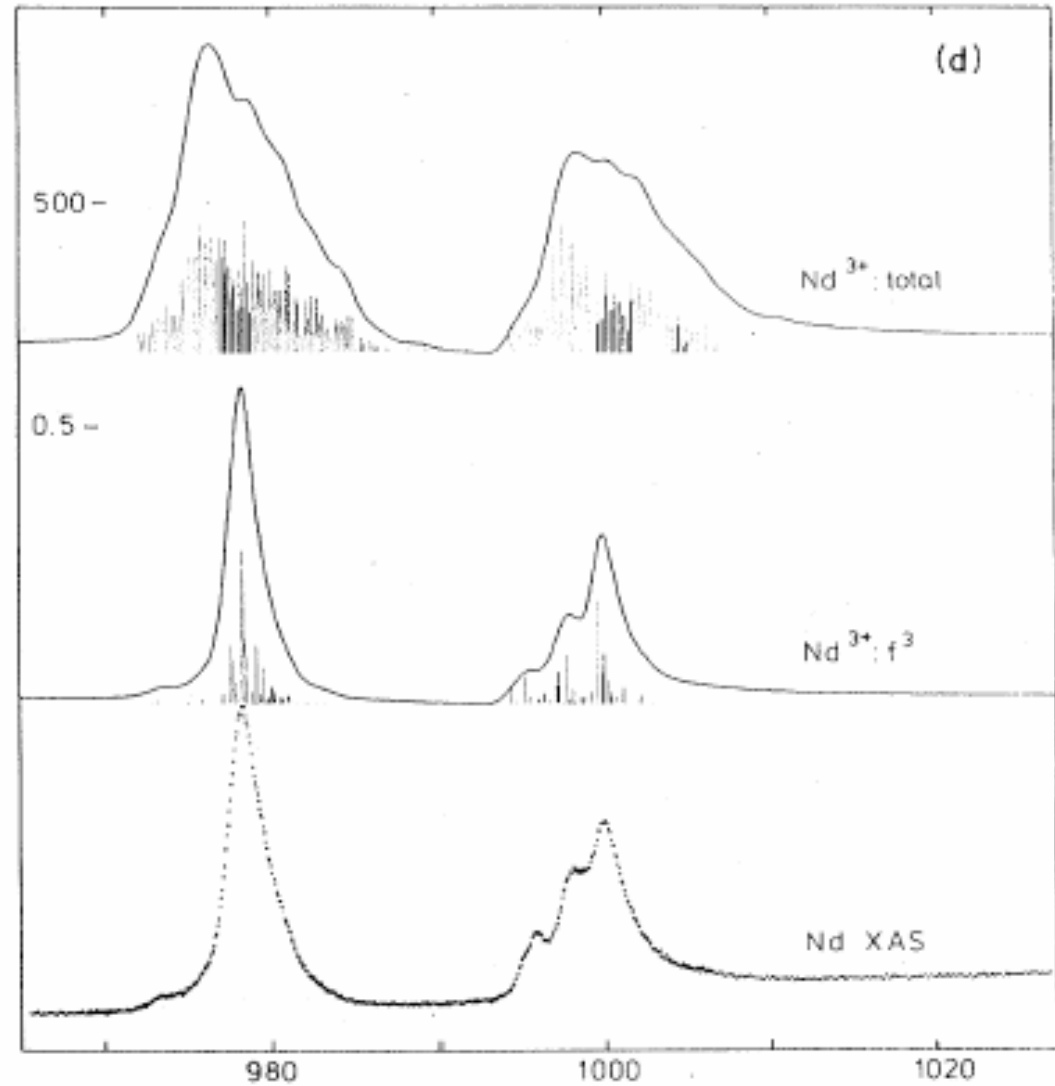
Effect of ligand field on metal d-orbitals

orbitals forming e_g set
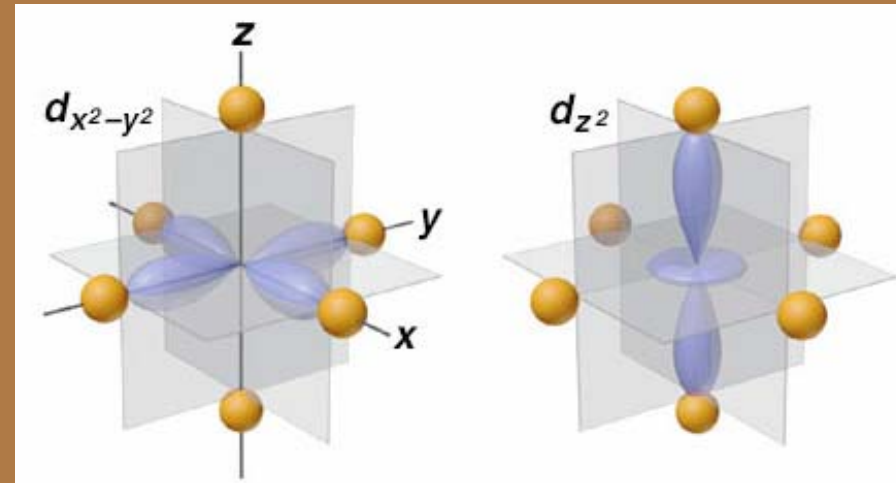
orbitals forming t_{2g} set
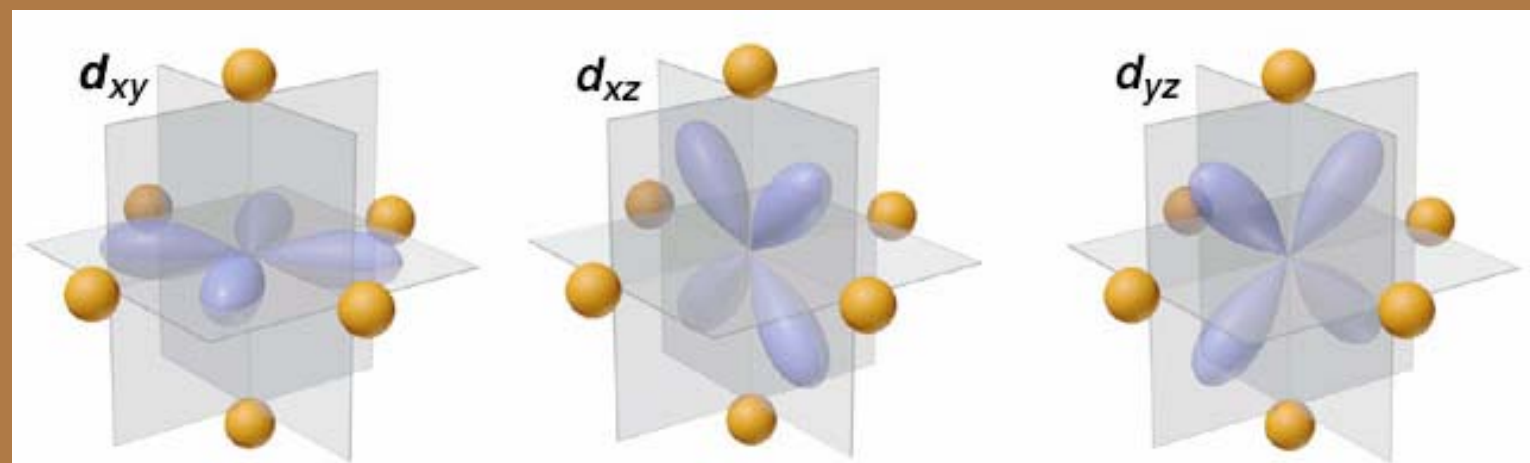
d^4 ions

Two possible arrangements of electrons

High Spin Complex

e_g

$+ 0.6 \Delta_{oct}$

$- 0.4 \Delta_{oct}$

t_{2g}
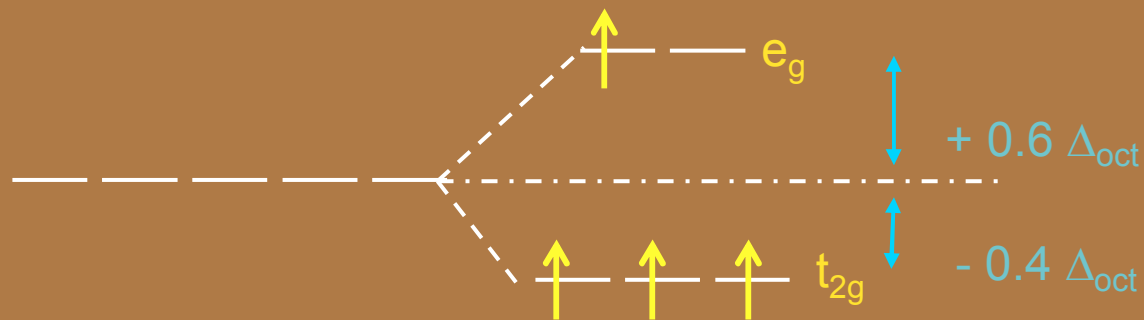
CFSE =

$3 \times - 0.4 \Delta_{oct} + 1 \times 0.6 \Delta_{oct}$

$= - 0.6 \Delta_{oct}$

Low Spin Complex

e_g

$+ 0.6 \Delta_{oct}$

$- 0.4 \Delta_{oct}$

t_{2g}
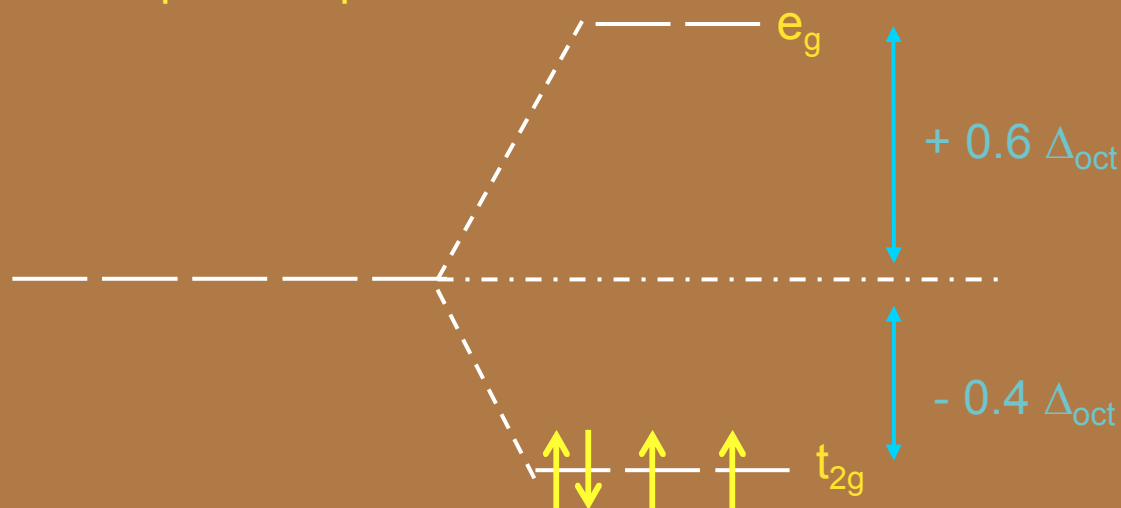
CFSE =

$4 \times - 0.4 \Delta_{oct} + P$

$= - 1.6 \Delta_{oct} + P$

The Pairing Energy P is the energy required to pair two electrons

Effect of 10Dq on XAS:$3d^0$
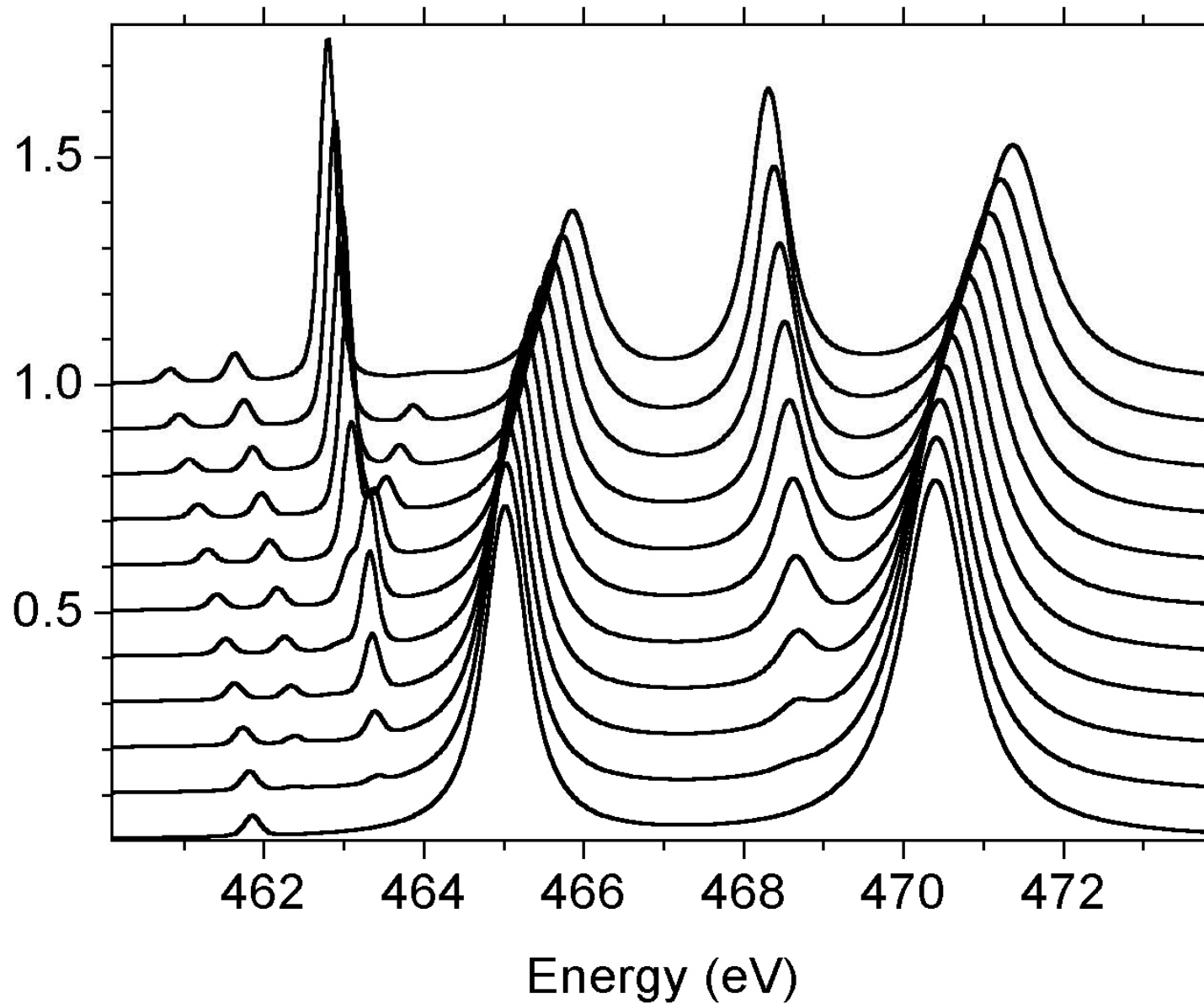
Multiplet Effects in XAS
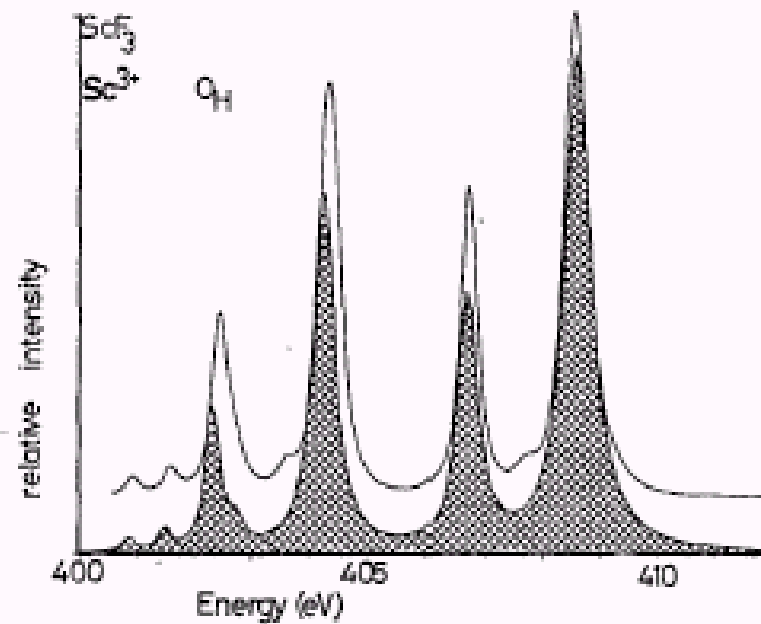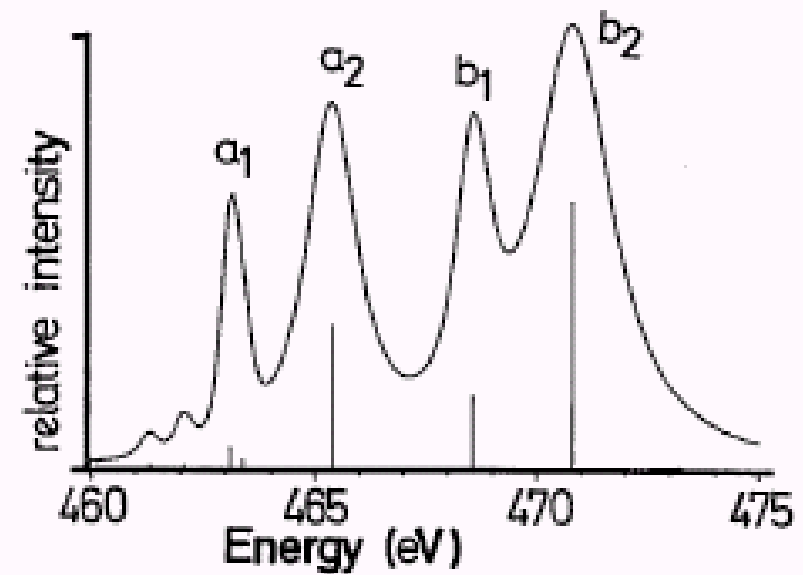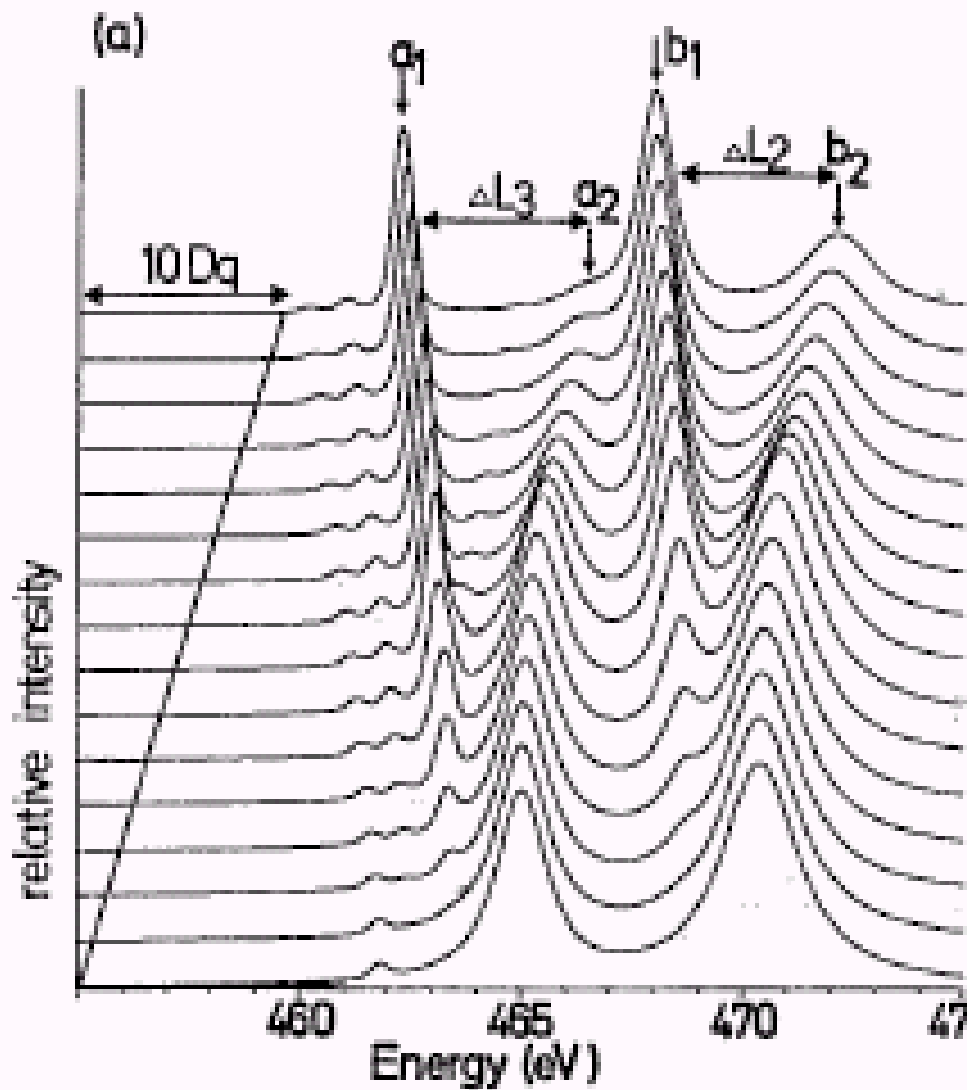
Effect of 10Dq on XAS:3d^N

Charge transfer

Charge transfer

Charge transfer

Ionic Conf.   Charge Transfer States
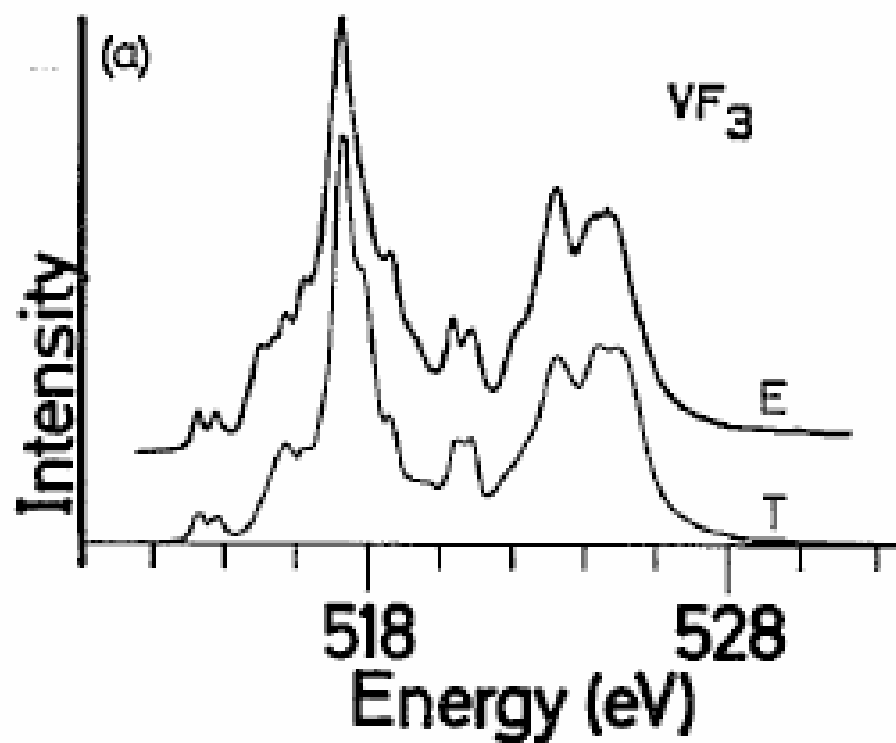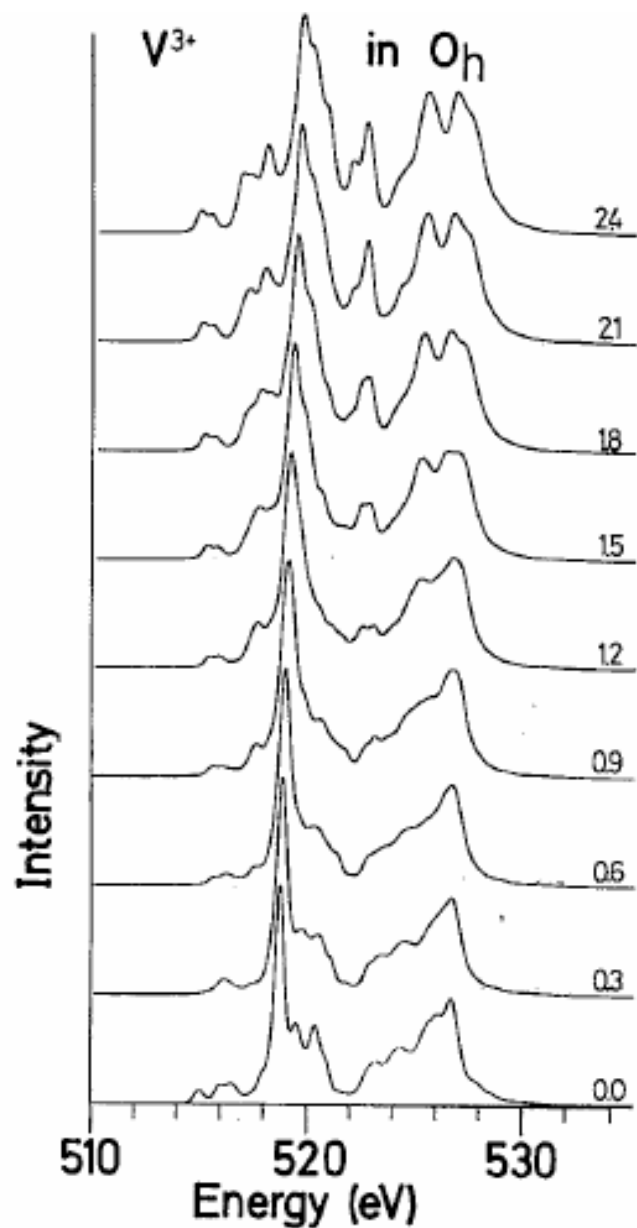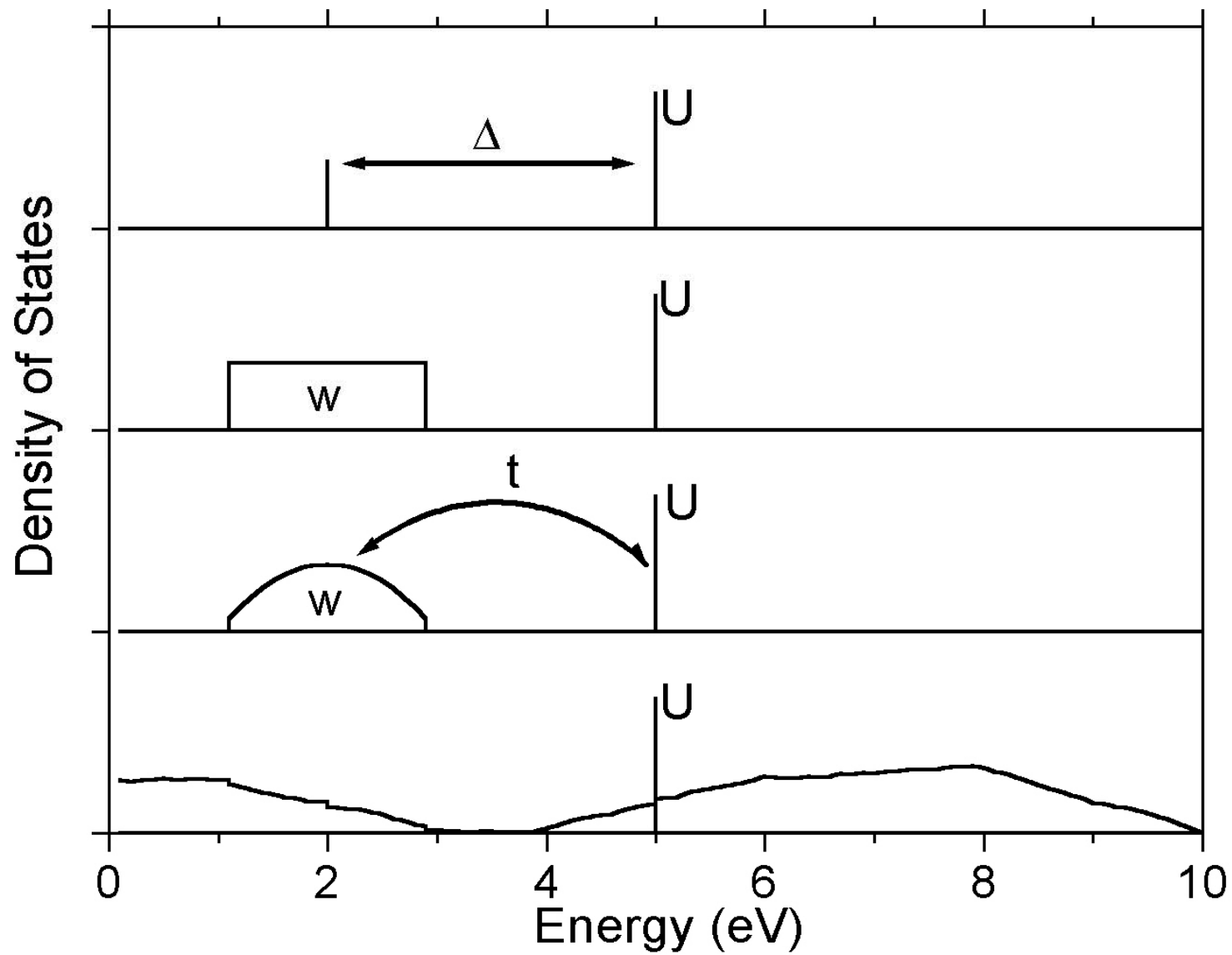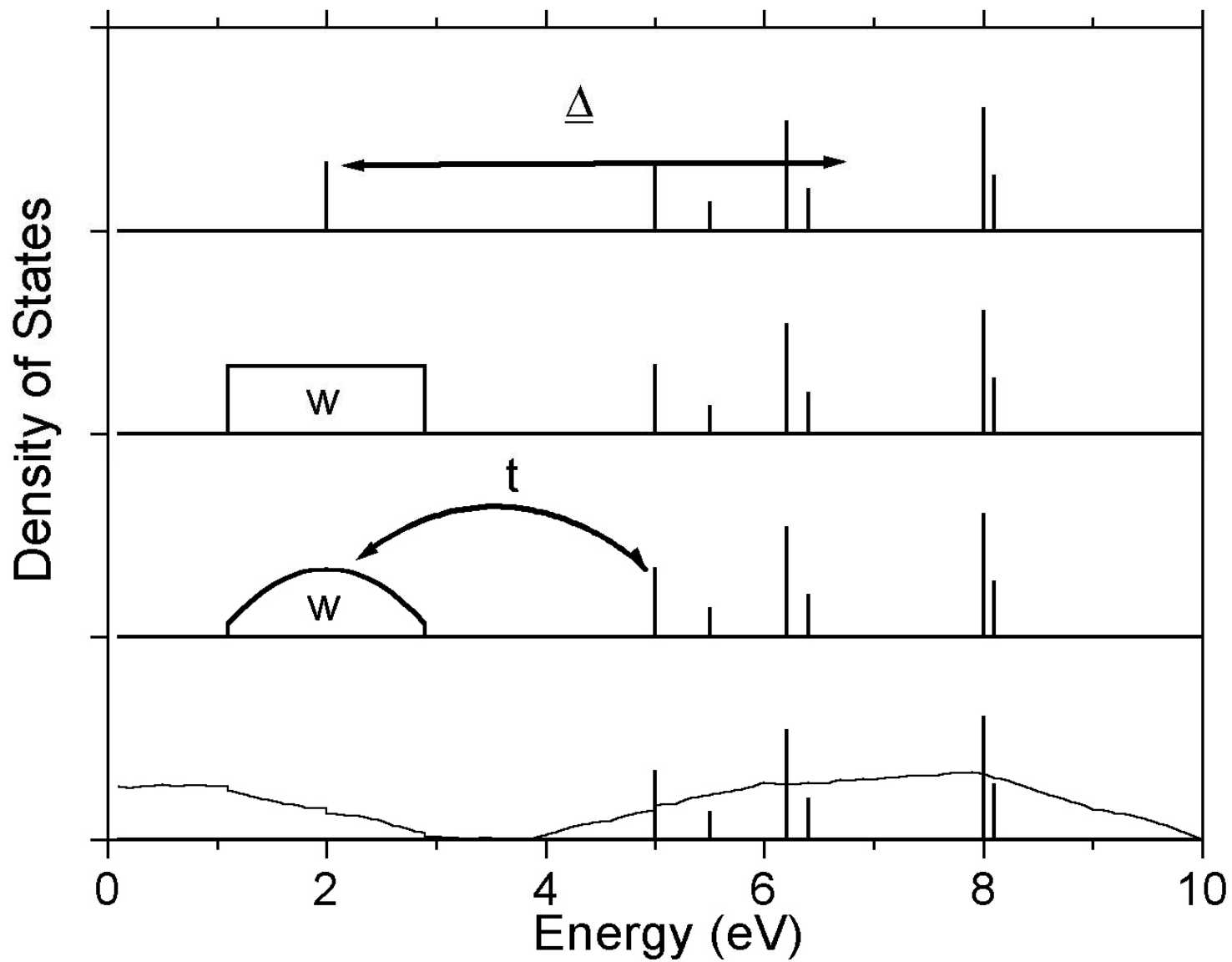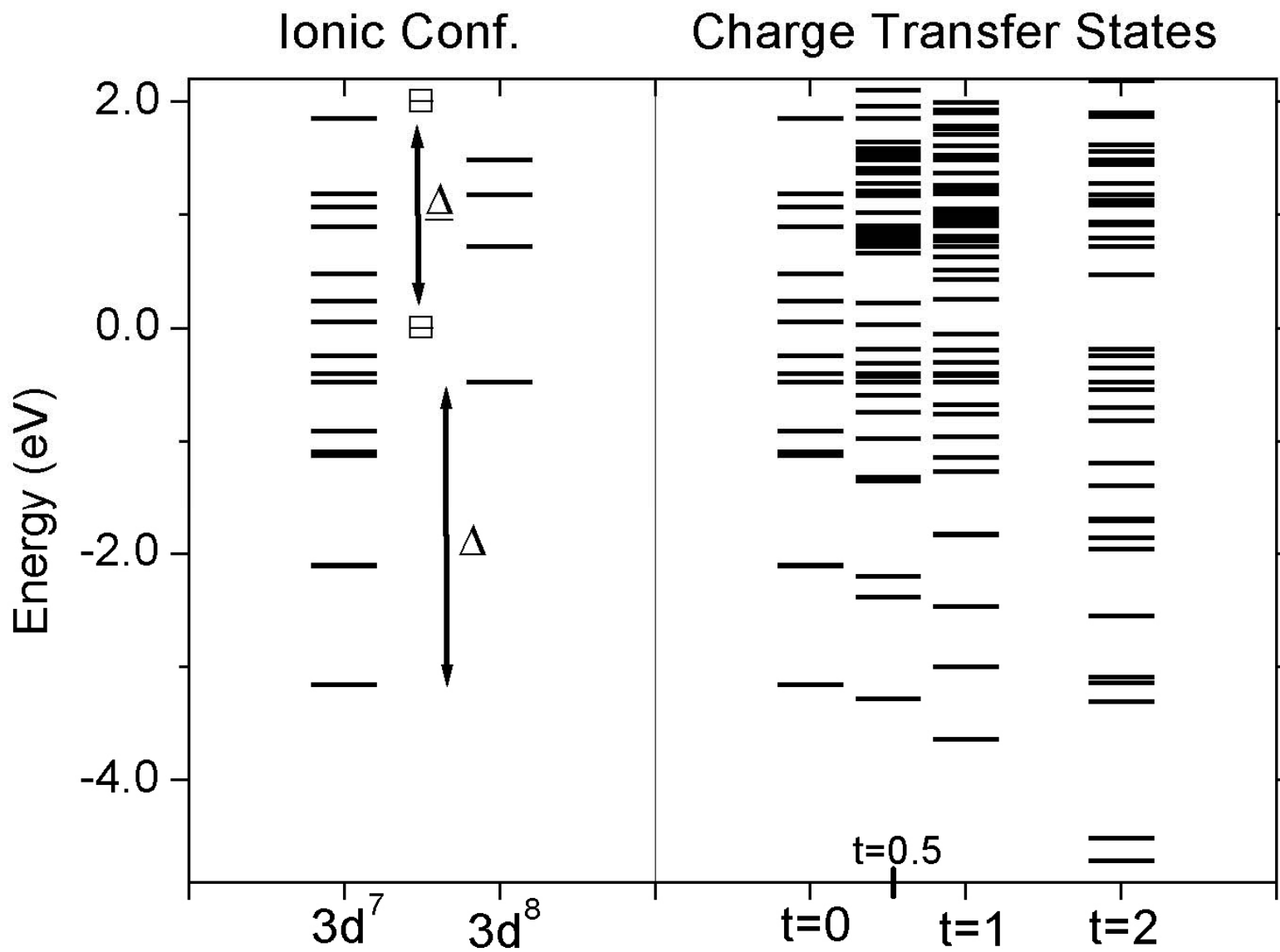
Charge Transfer in EELS

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

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

$3d^5$ ———————— ⟶ ———————— $2p^5 3d^6$

X-ray Absorption Spectroscopy

NiO
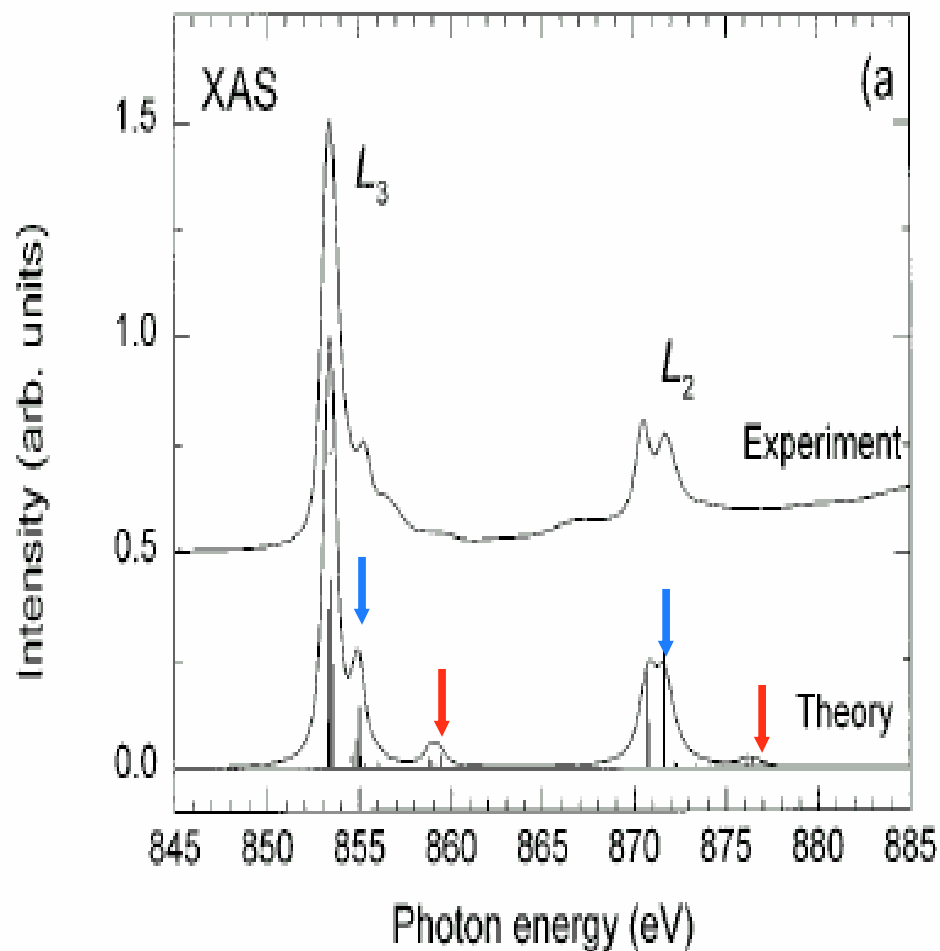
Spectral shape:

(1) Multiplet effects

(2) Charge Transfer

Charge Transfer in XAS

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

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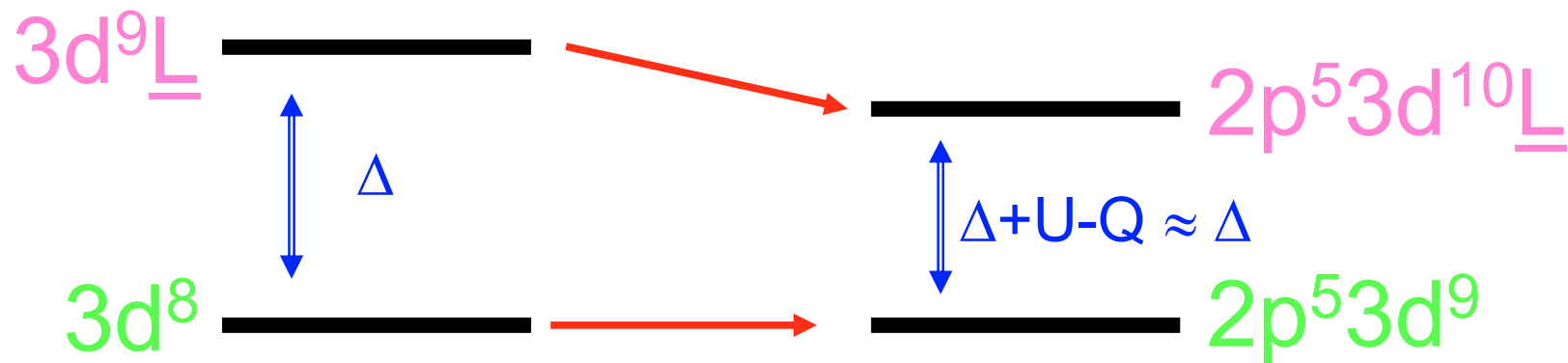
Charge Transfer in XPS

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

Energy of $3d^9\underline{L}$: Charge transfer energy $\Delta = 3.5$

Energy of $3d^{10}\underline{L}^2$: $2\Delta + U = 14$
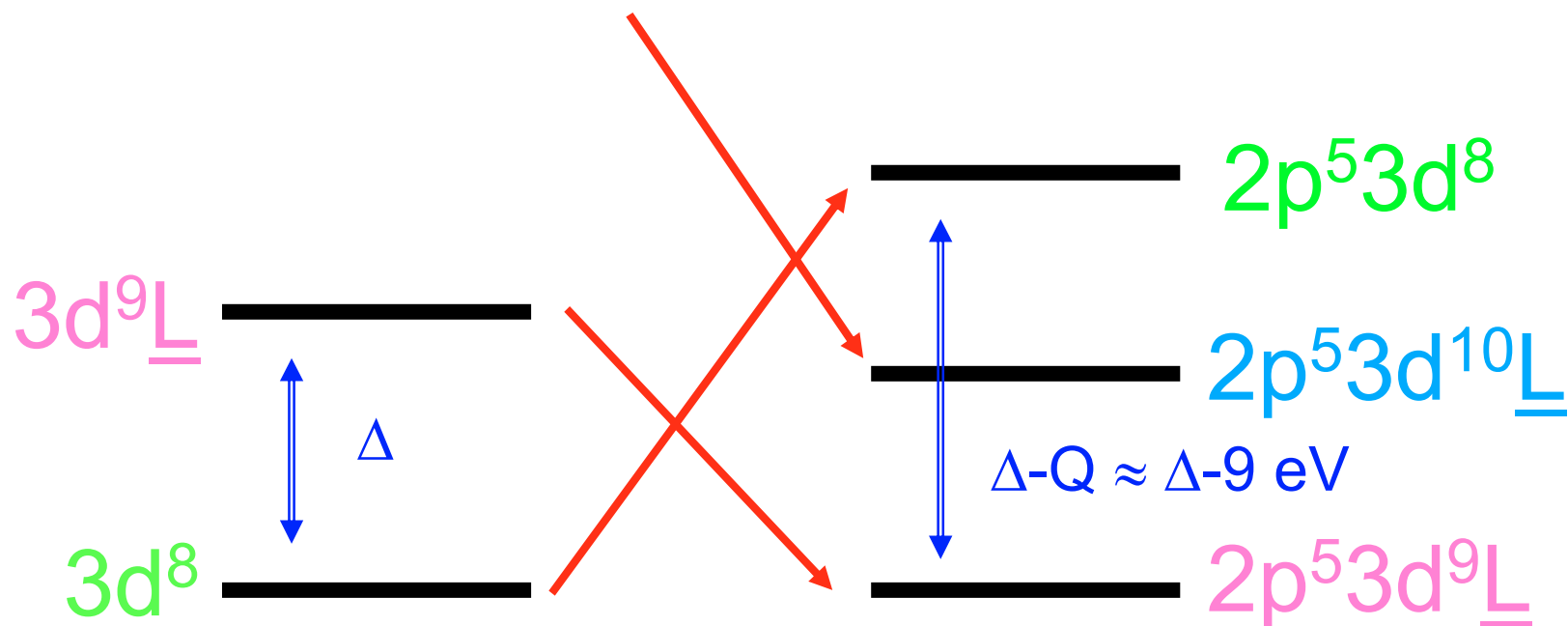
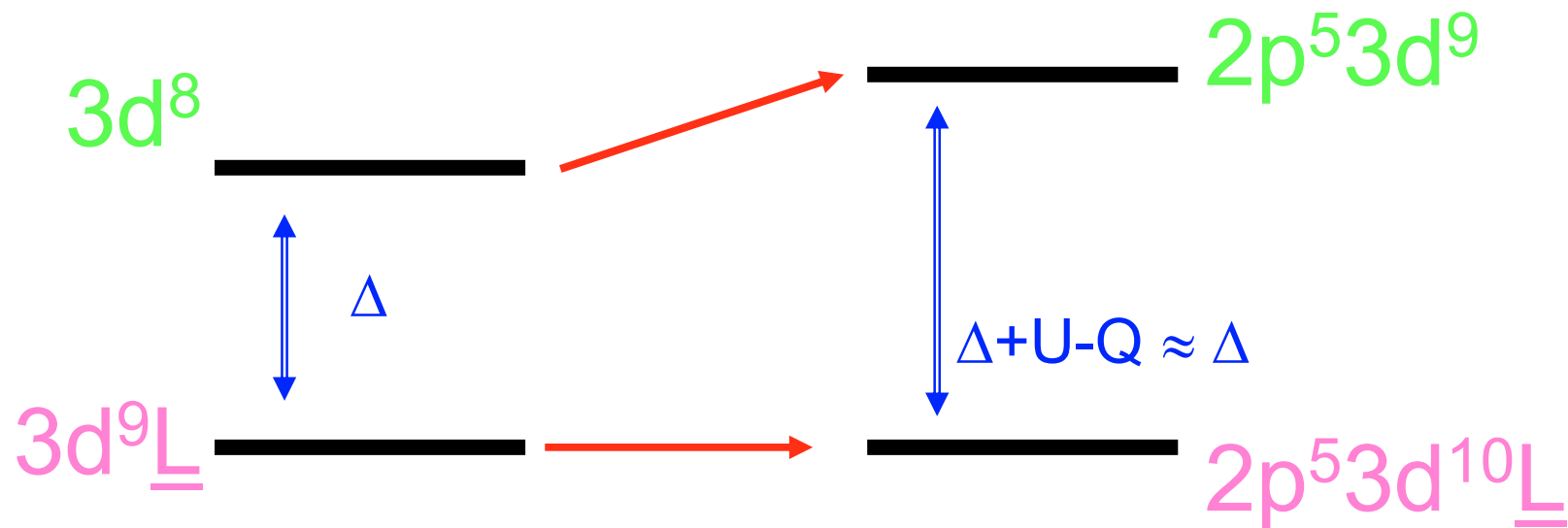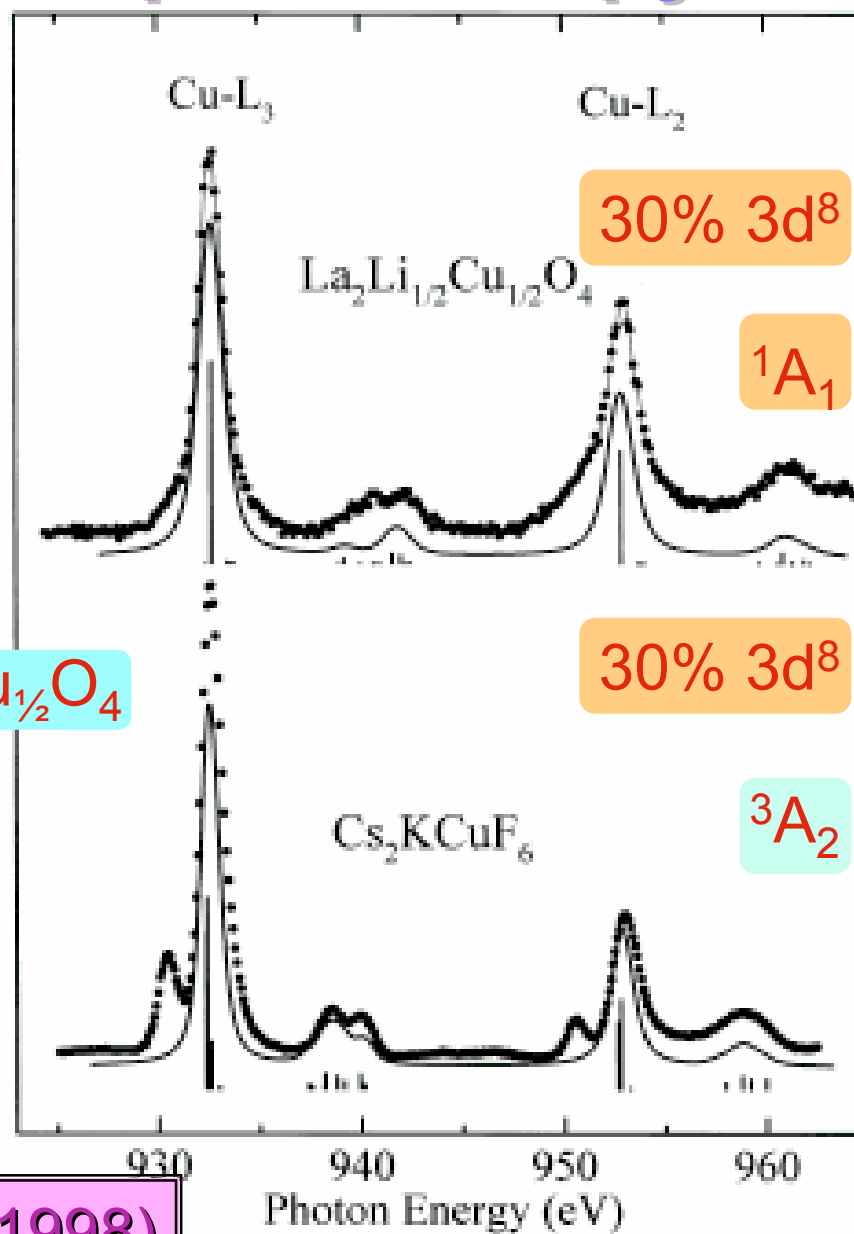# 2p XPS
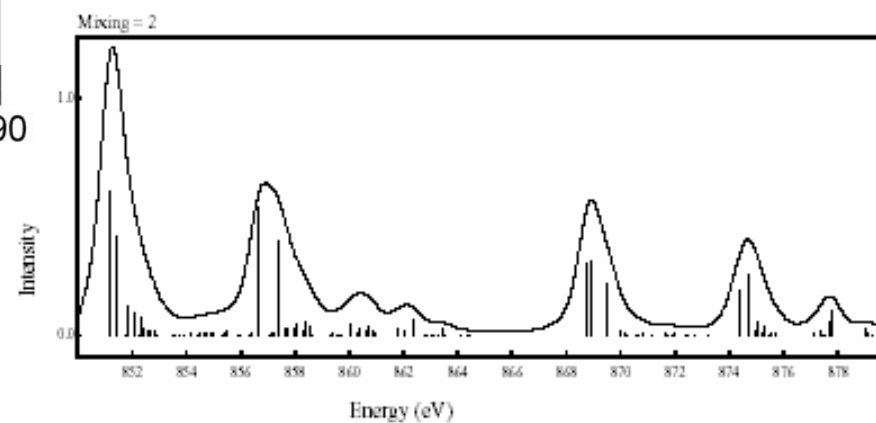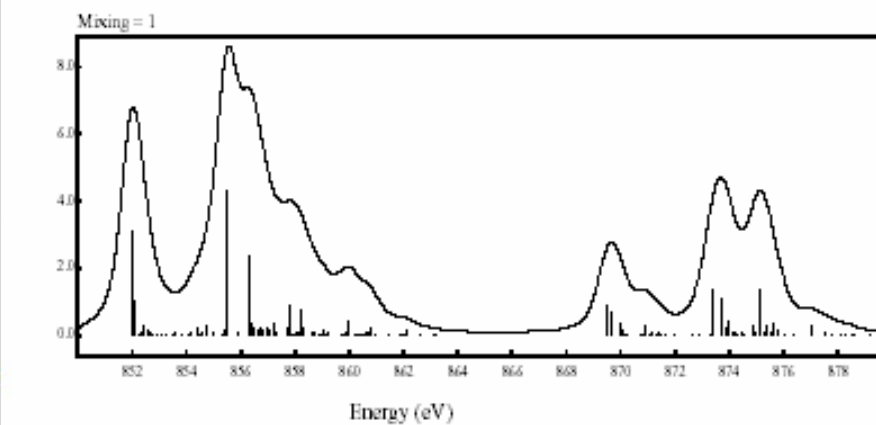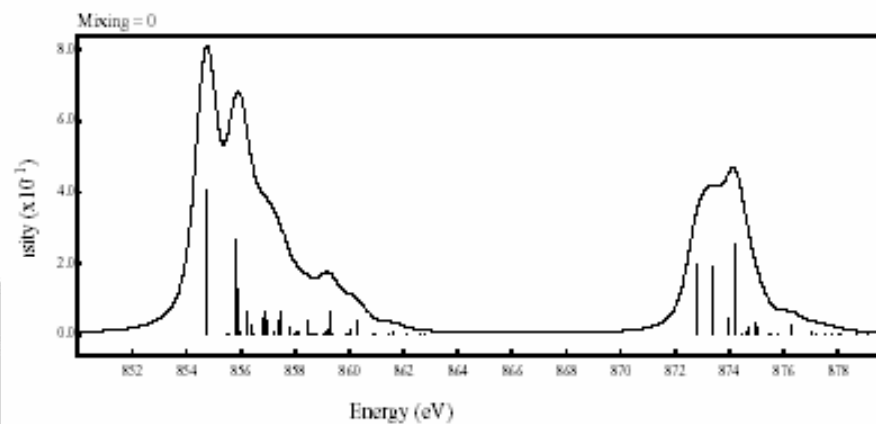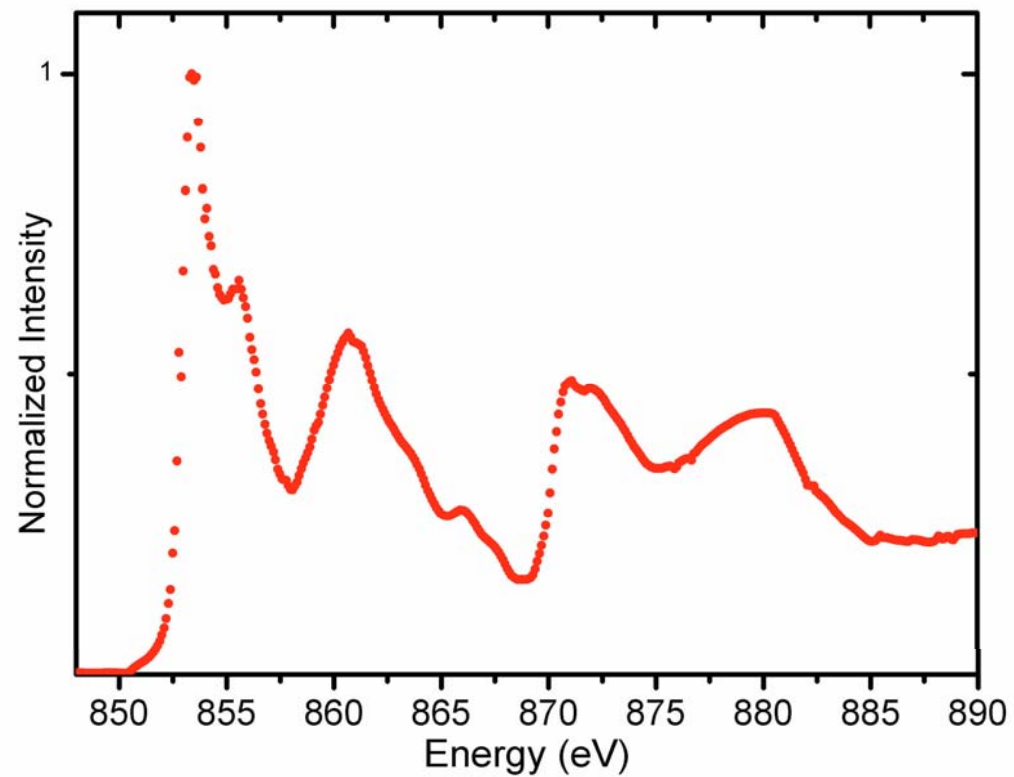
Charge Transfer in XAS

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

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

$3d^9\underline{L}$ —————

Δ

$3d^8$ —————

$2p^5 3d^{10}\underline{L}$ —————
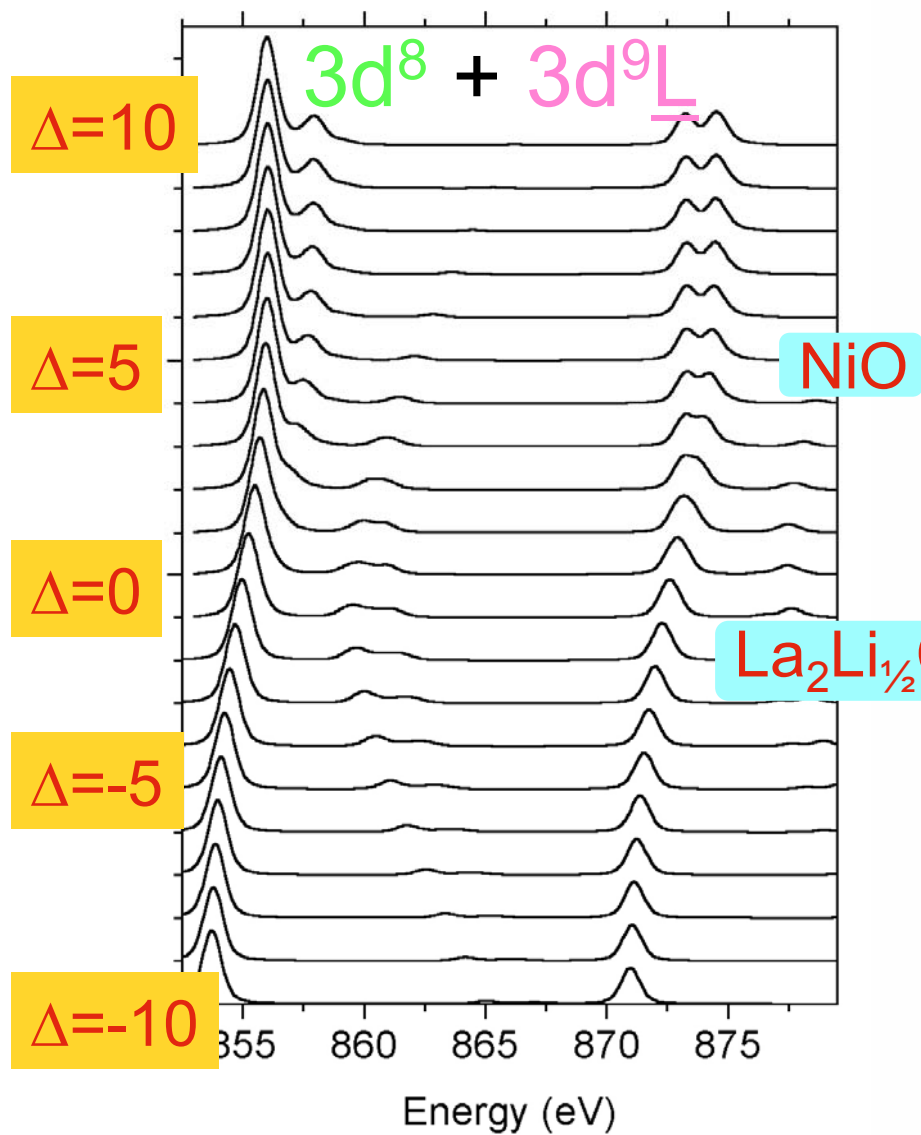
$\Delta + U - Q \approx \Delta$

$2p^5 3d^9$
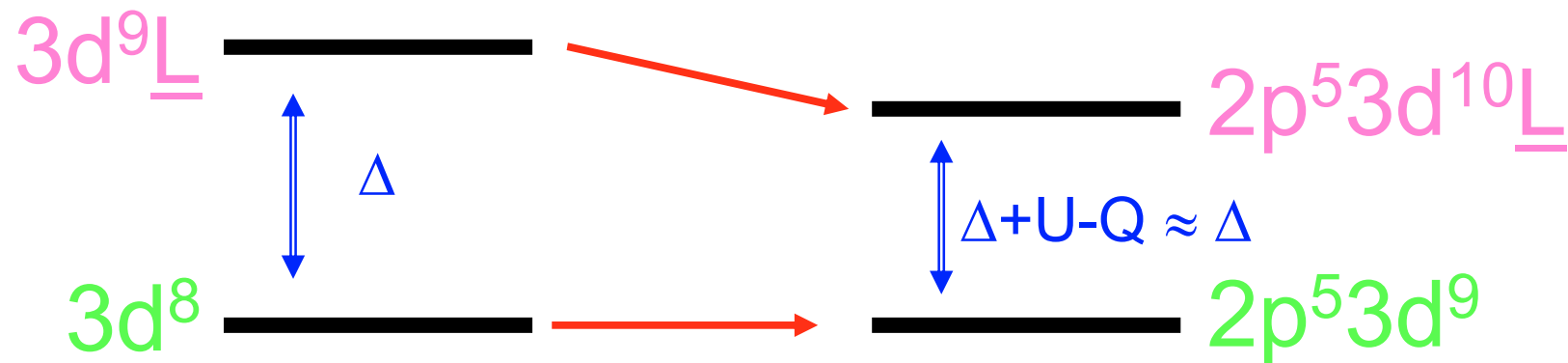
Charge Transfer in XAS

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

Energy of $3d^9\underline{L}$: Charge transfer energy $\Delta < 0$

$3d^8$

$2p^5 3d^9$

Δ

$\Delta + U - Q \approx \Delta$

$3d^9\underline{L}$

$2p^5 3d^{10}\underline{L}$

X-ray Absorption Spectroscopy

$3d^8 + 3d^9\underline{L}$

$\Delta=10$

$\Delta=5$

$\Delta=0$

$\Delta=-5$

$\Delta=-10$

NiO

$La_2Li_{1/2}Cu_{1/2}O_4$

Energy (eV)

Cu-L_3

Cu-L_2

$La_2Li_{1/2}Cu_{1/2}O_4$

30% $3d^8$

$^1A_1$

30% $3d^8$

Cs_2KCuF_6

$^3A_2$

Absorption

Photon Energy (eV)

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

X-ray Absorption Spectroscopy

Charge Transfer Multiplet program:
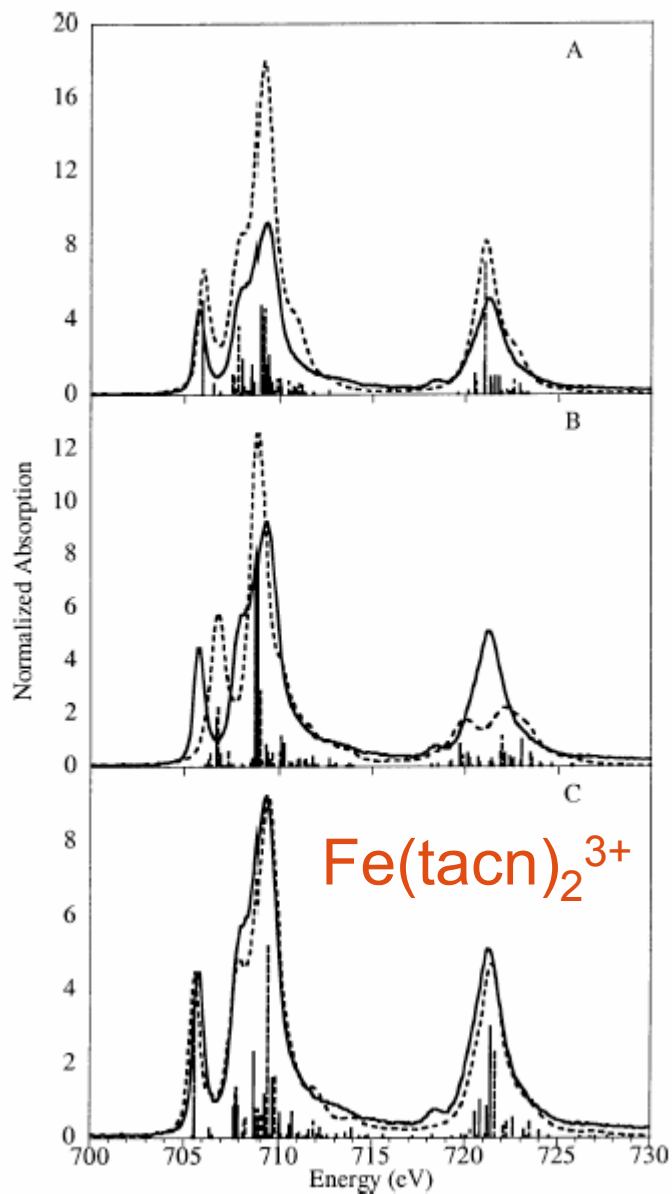Simulation of XAS, EELS, XES, RIXS,
(resonant) photoemission, Auger

ATOMIC PHYSICS

⇓

GROUP THEORY

⇓

MODEL HAMILTONIANS

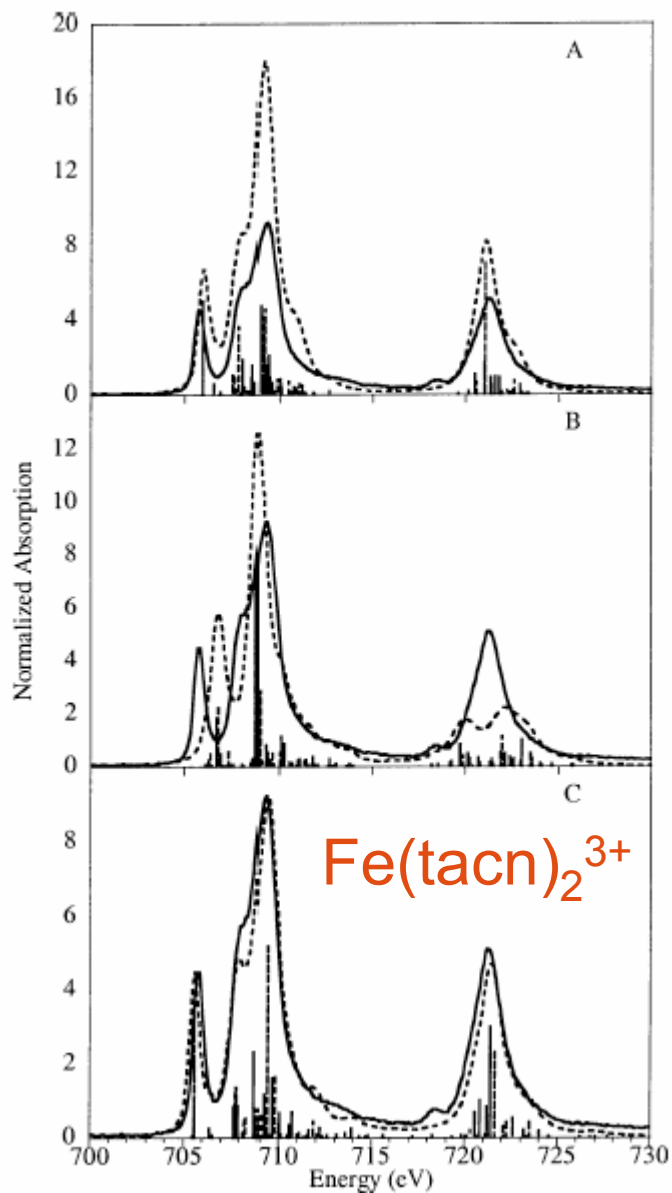www.anorg.chem.uu.nl/people/staff/FrankdeGroot/

Multiplet Theory of XAS

Fe(tacn)₂³⁺

New 'multiplet' developments:

> Erik Wasinger, Ed Solomon (Stanford)

t₂   [Fe(tacn)₂]³⁺   e
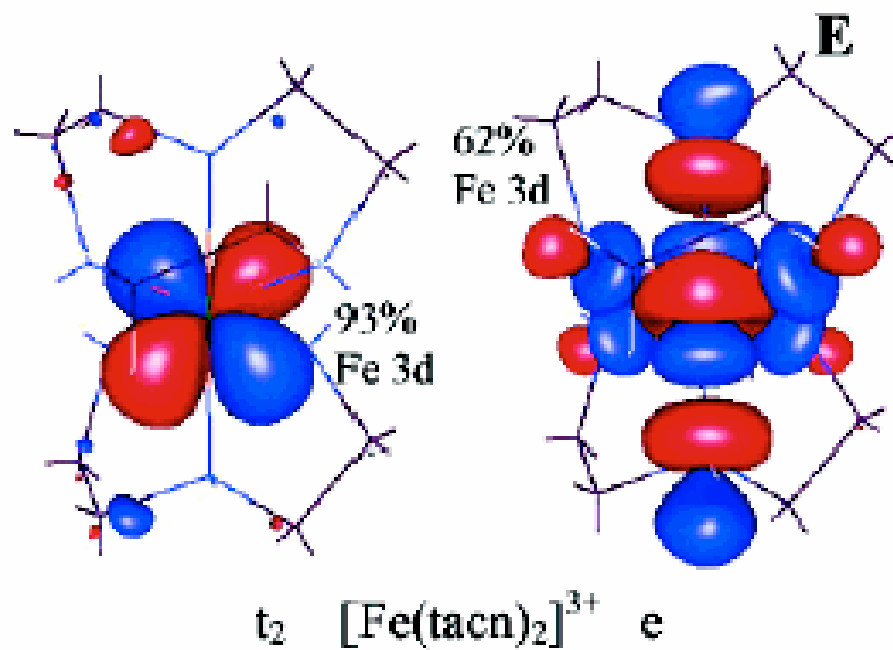
JACS 125, 12894 (2003)

Multiplet Theory of XAS

Fe(tacn)$_2^{3+}$

New 'multiplet' developments:

> Erik Wasinger, Ed Solomon (Stanford)

• Projection of charge transfer simulation
to 'constituents'

➤ Differential Orbital Covalency
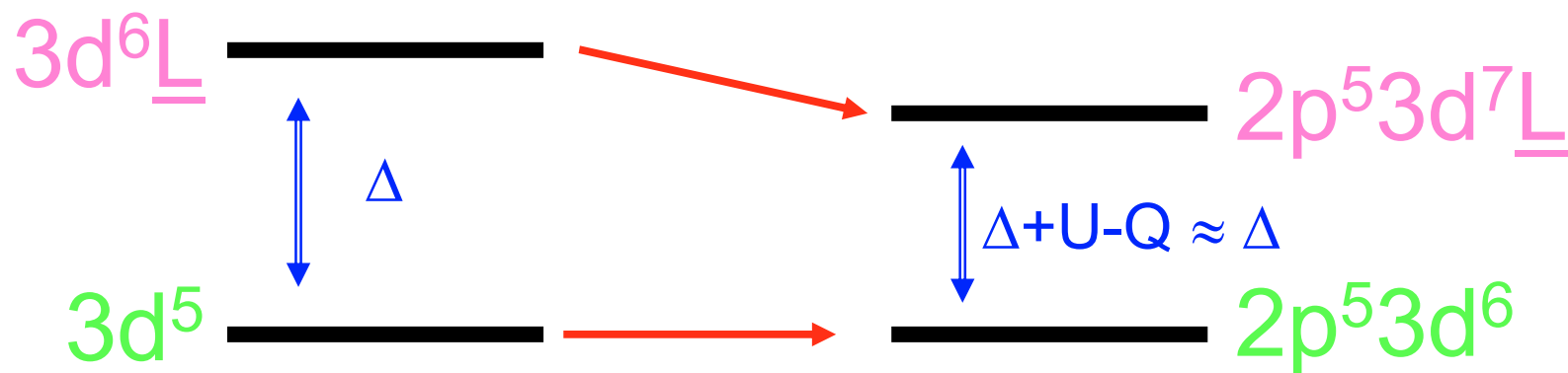
➤ Inclusion π (back)-bonding and MLCT

> Cinthia Piamonteze, Helio Tolentino (Campinas)

➤ Mixed spin ground state in RENiO$_3$

JACS 125, 12894 (2003)

Ligand-metal CT in XAS

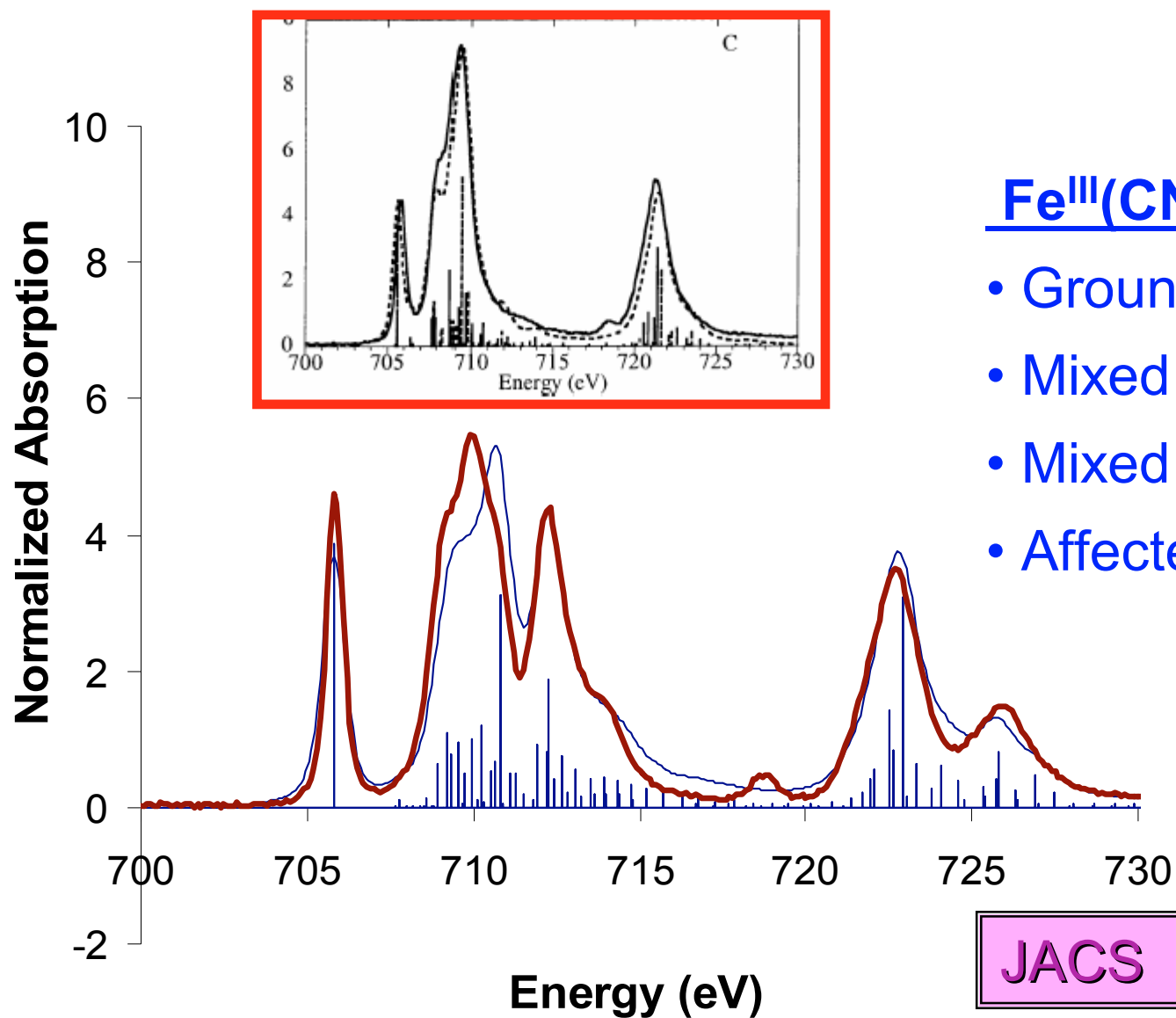Fe^{III}: Ground state: $3d^5$ + $3d^6\underline{L}$

+ Metal-ligand CT in XAS

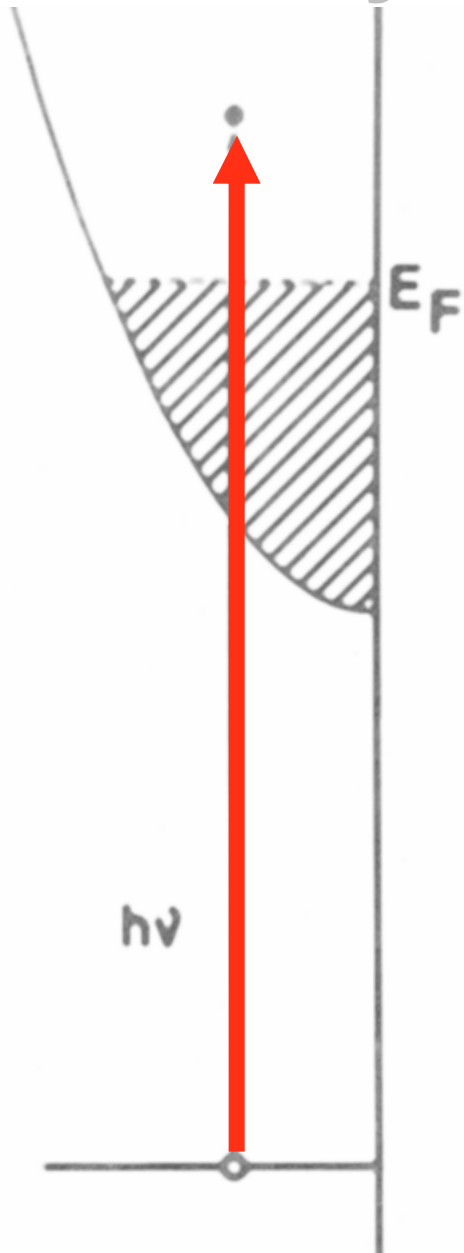Fe^{III}: Ground state: $3d^5$ + $3d^6\underline{L}$ + $3d^4\underline{L}$

$3d^4\underline{L}$

$2p^53d^5\underline{L}$

Δ_π

$\Delta_\pi+U-Q \approx \Delta_\pi + 2$

$3d^6\underline{L}$

$2p^53d^7\underline{L}$

Δ

$\Delta+U-Q \approx \Delta - 2$

$3d^5$

$2p^53d^6$
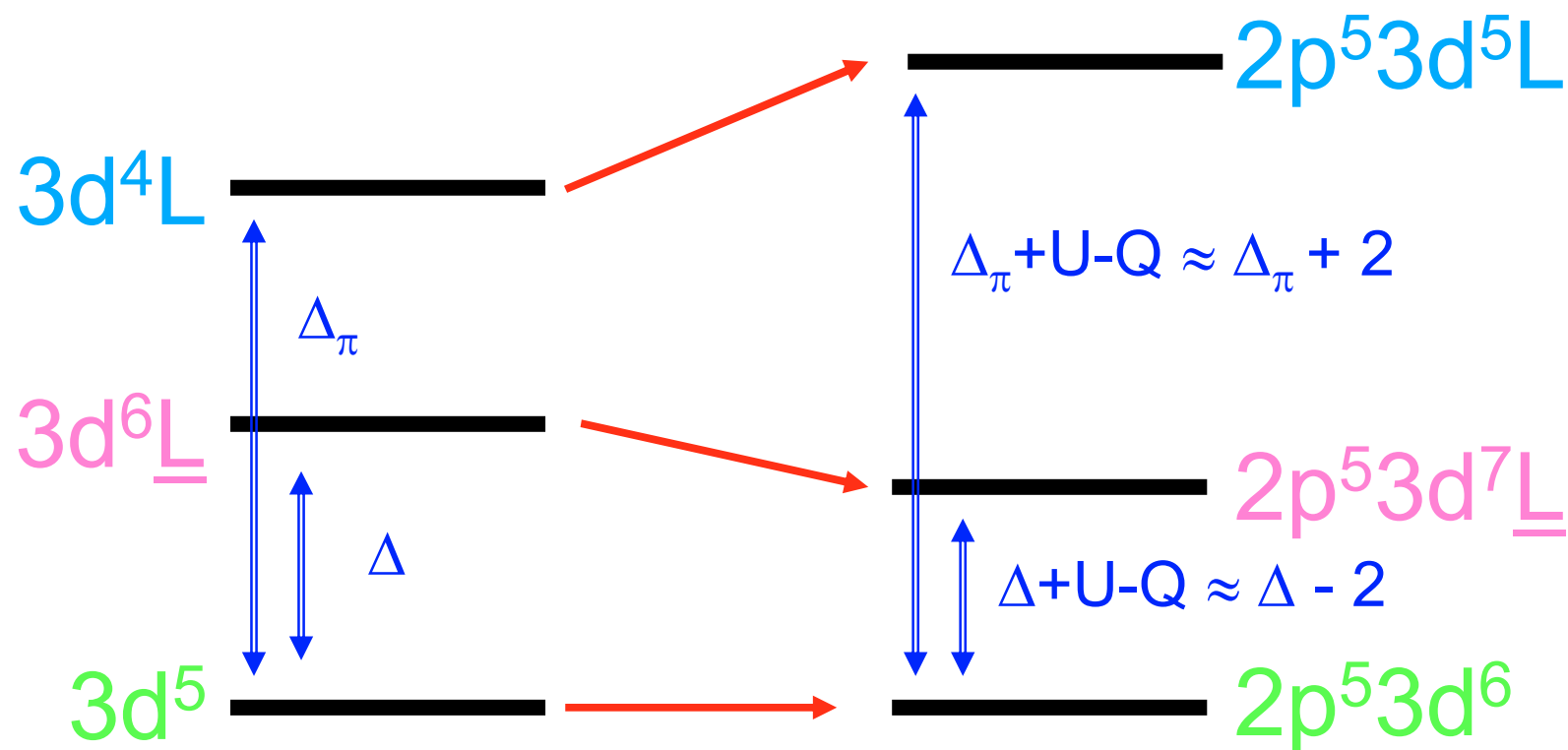
Multiplet Theory of cyanides

Fe^{III}(CN)$_6$

- Ground State 3d^5
- Mixed with 3d^{6}H (LMCT)
- Mixed with 3d^{4}L (MLCT)
- Affected by 3d spin-orbit

JACS (submitted)

X-ray Absorption Spectroscopy

$2p^5 3d^{n+1}$

$2p^6 3d$

hv

E_F

Single Particle:

1s edges

Hard x-rays

Multiplets:

2p, 3s, 3p edges

Soft x-rays

XAS and Electronic Structure

- Directional variations of 3d-electrons:

  symmetry: $^{2S+1}L_J$, crystal field, charge transfer

  interplay spin-orbit, exchange, distortions

  moments: $<S_z>$, $<L_z>$, $<Q_{zz}>$, MCA

- Hybridization of correlated electrons

  superconductivity, magnetism, Kondo

  mixed valence, orbital orderings

X-ray Absorption Spectroscopy

$2p^5 3d^{n+1}$

$2p^6 3d$

E_F

$h\nu$
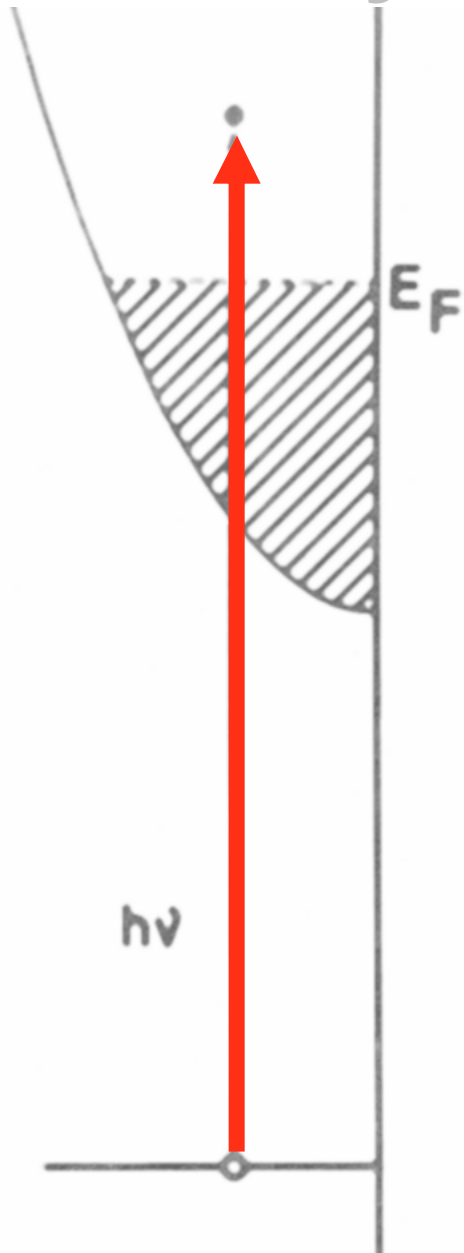
Single Particle:

1s edges

Hard x-rays

Multiplets:

2p, 3s, 3p edges

Soft x-rays

RIXS

Single-particle approach
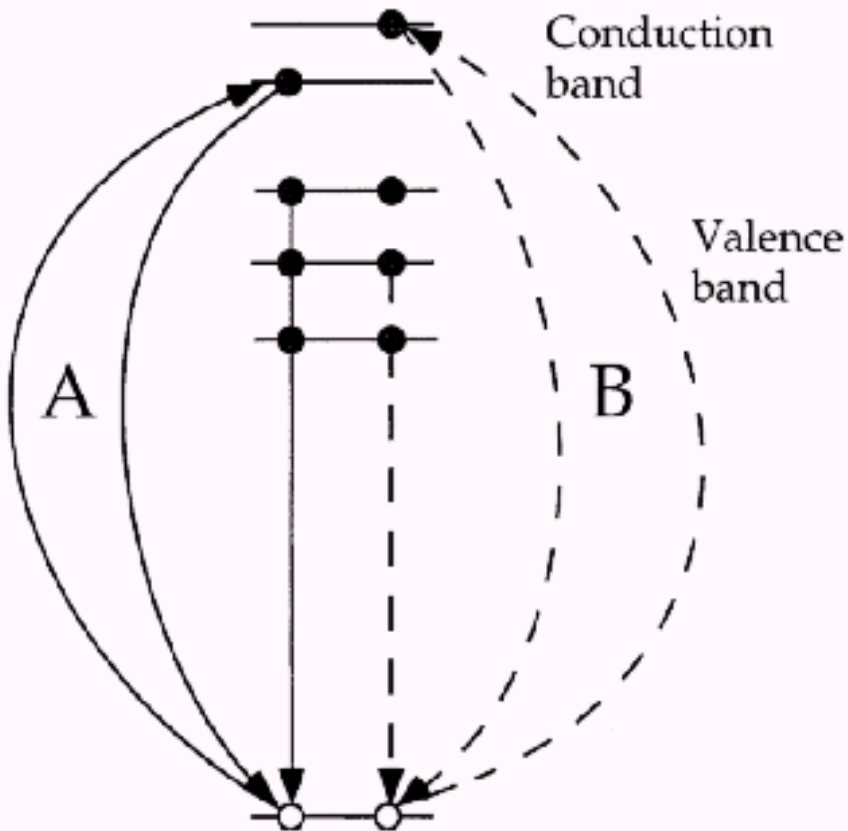
Many-body approach
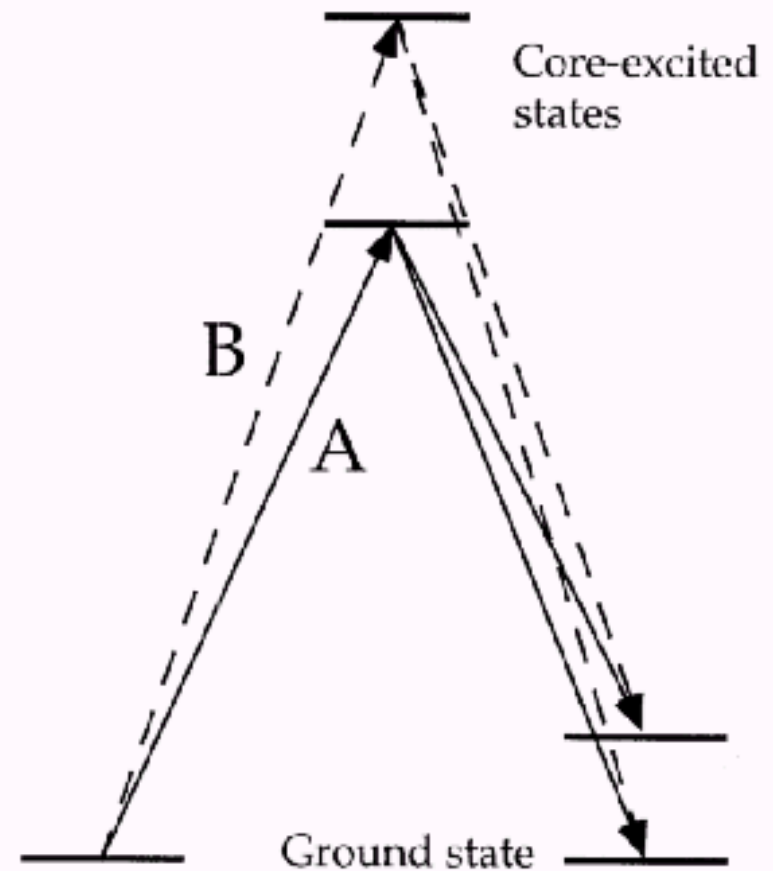
Butorin et al, J. Elec. Spec 110, 213 (2000)

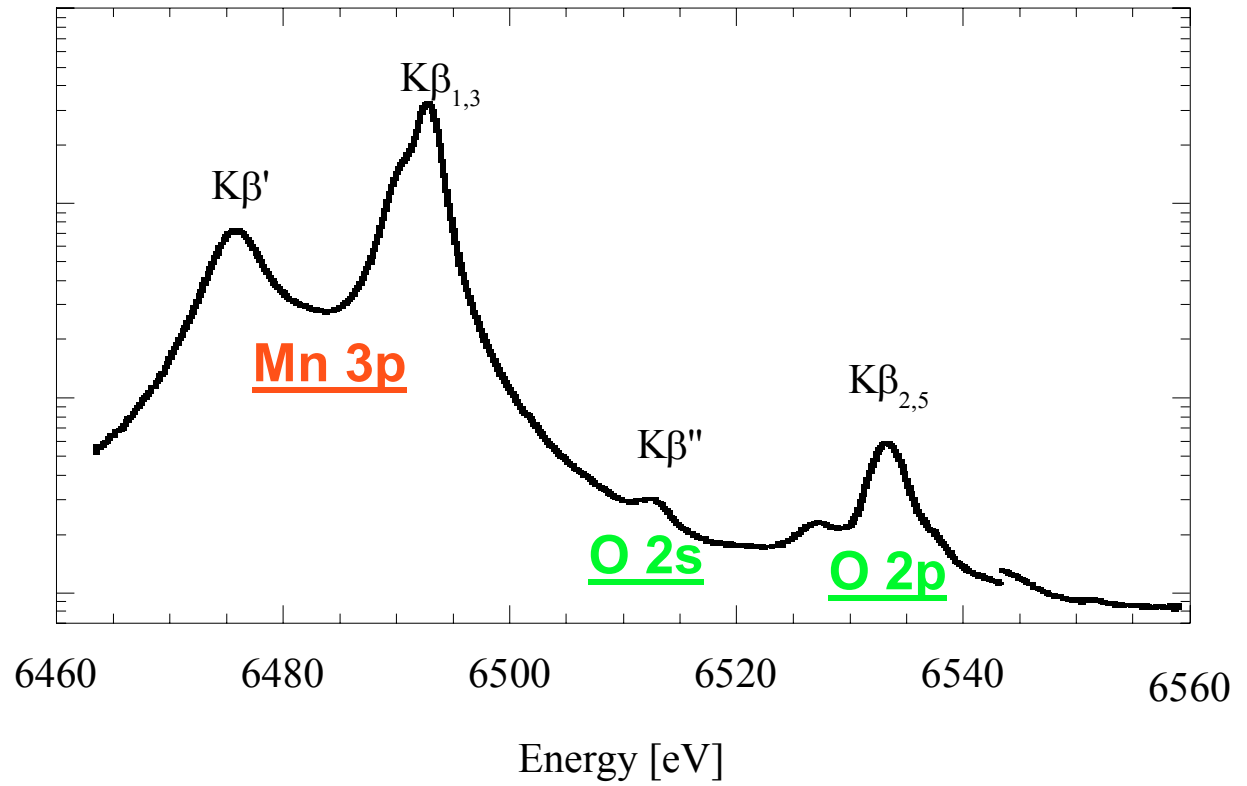# Resonant Inelastic X-ray Scattering
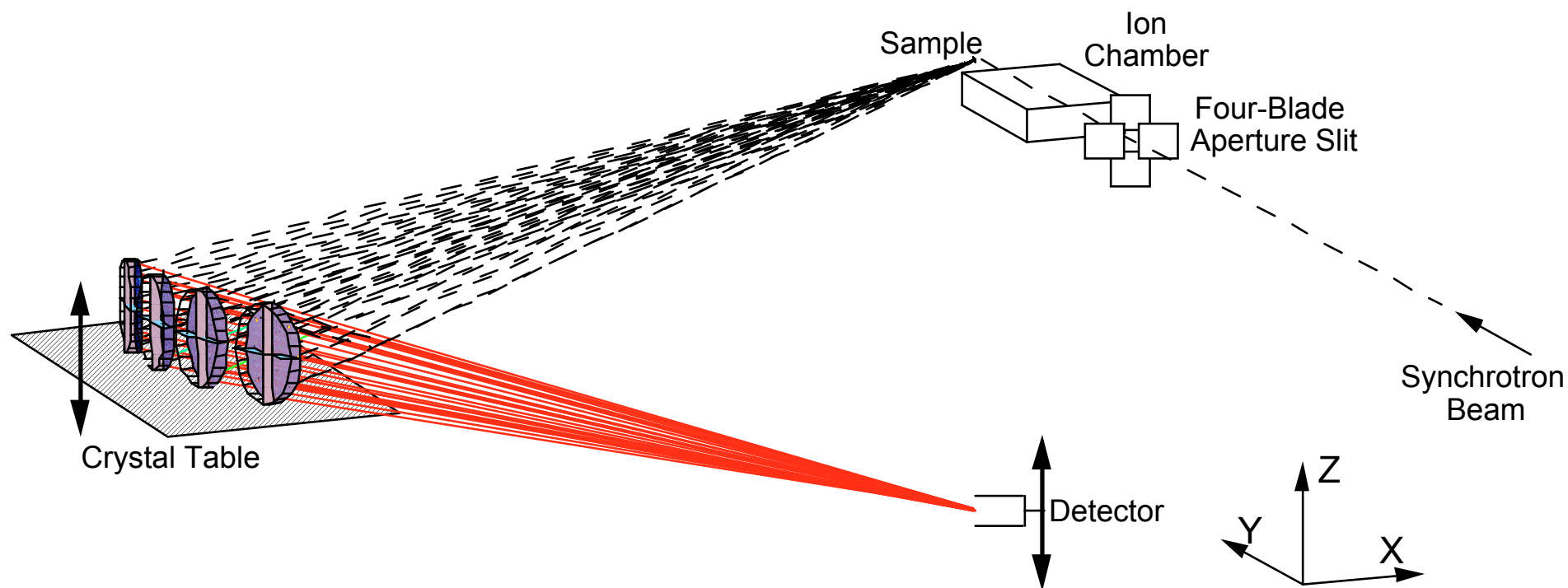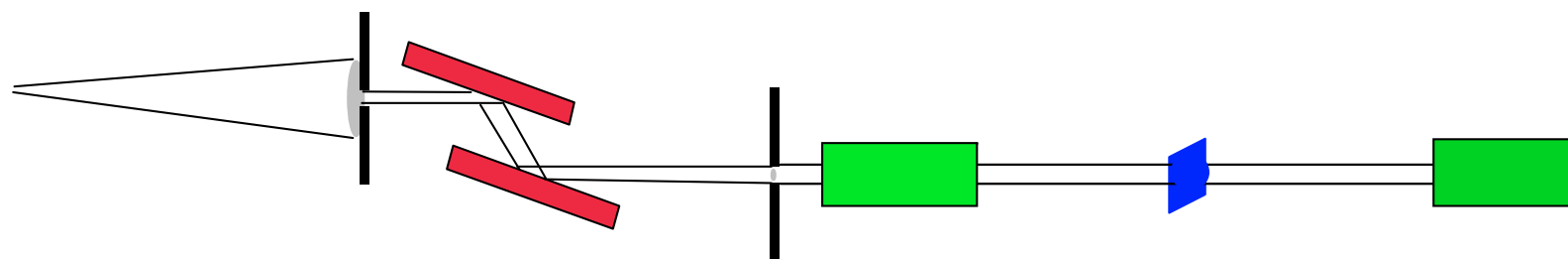
Resonant Inelastic X-ray Scattering
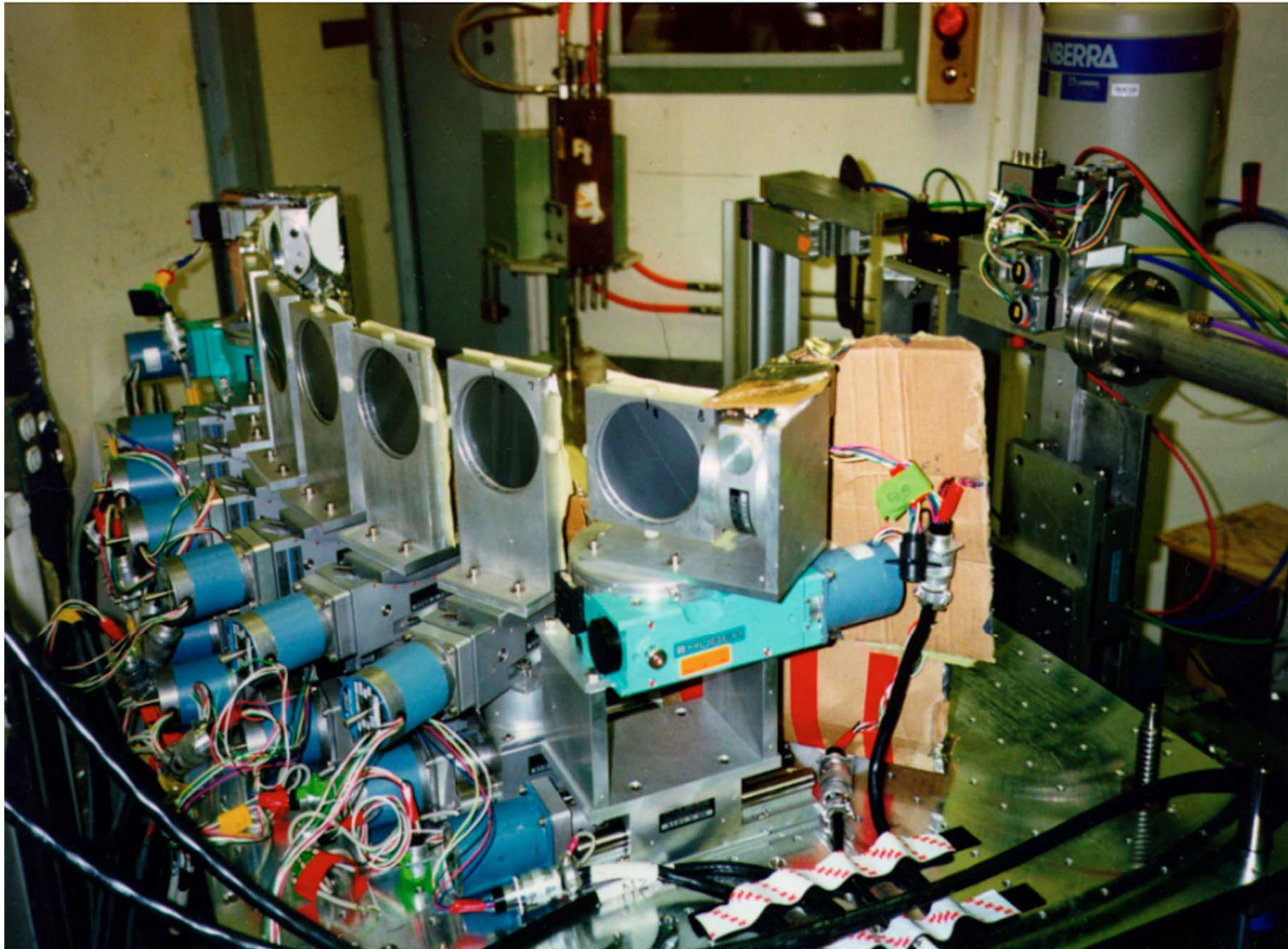
Site selective XAFS
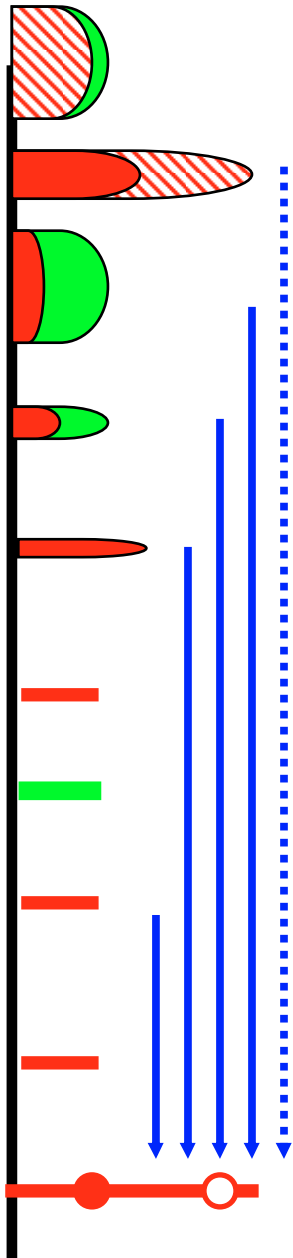
Mn 4p   -

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

MnO $3d^5$

$K\beta_{1,3}$

$K\beta'$

Mn 3p

$K\beta''$

$K\beta_{2,5}$

O 2s   **O 2p**

Energy [eV]

6460   6480   6500   6520   6540   6560

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 exchange.

- Note that the center-of-gravity does not shift with valence because the energy difference between 1s and 3p (or 2p) core levels is constant
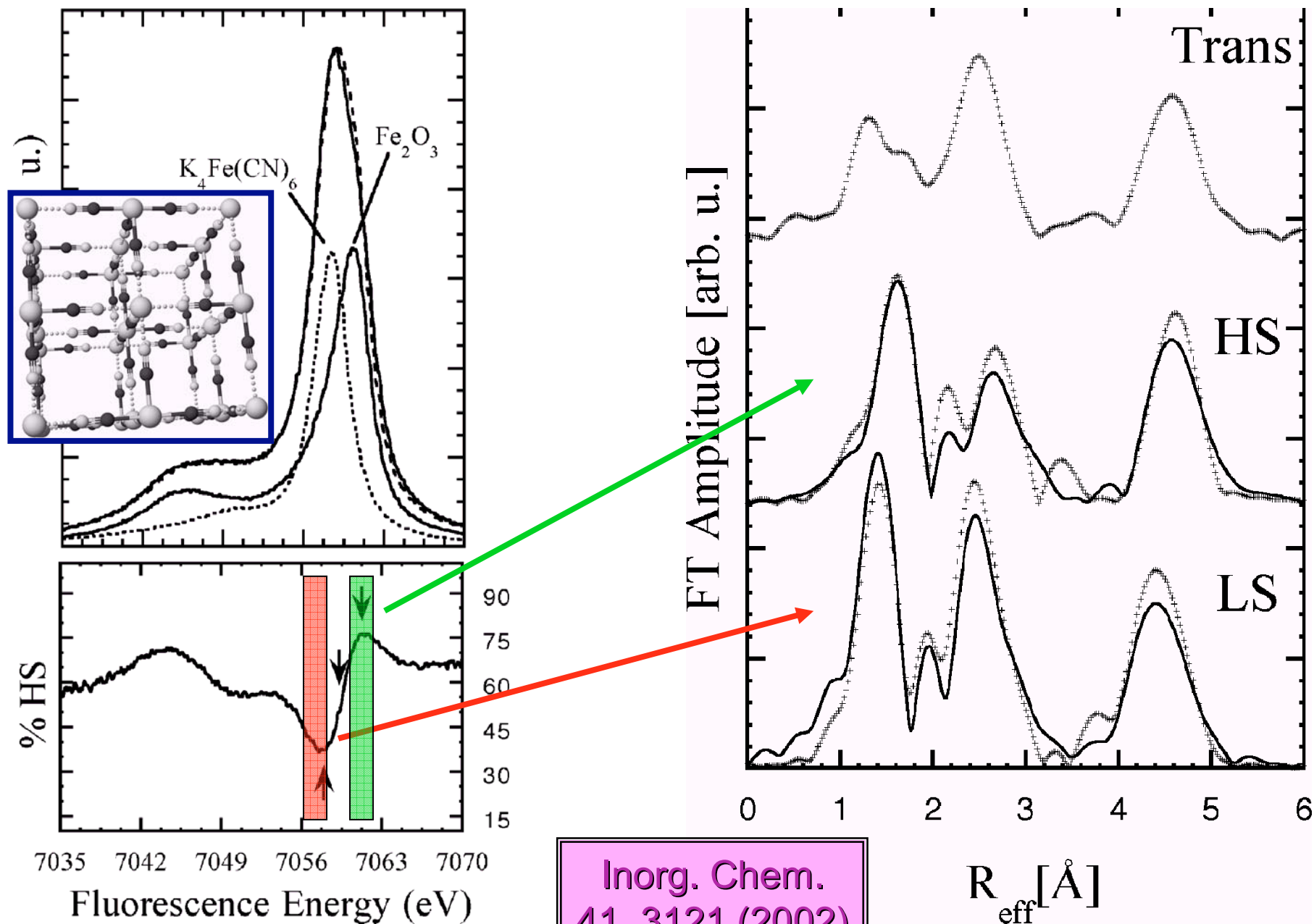
Valence selective XAFS

Chemical Dependence of Kβ Emission
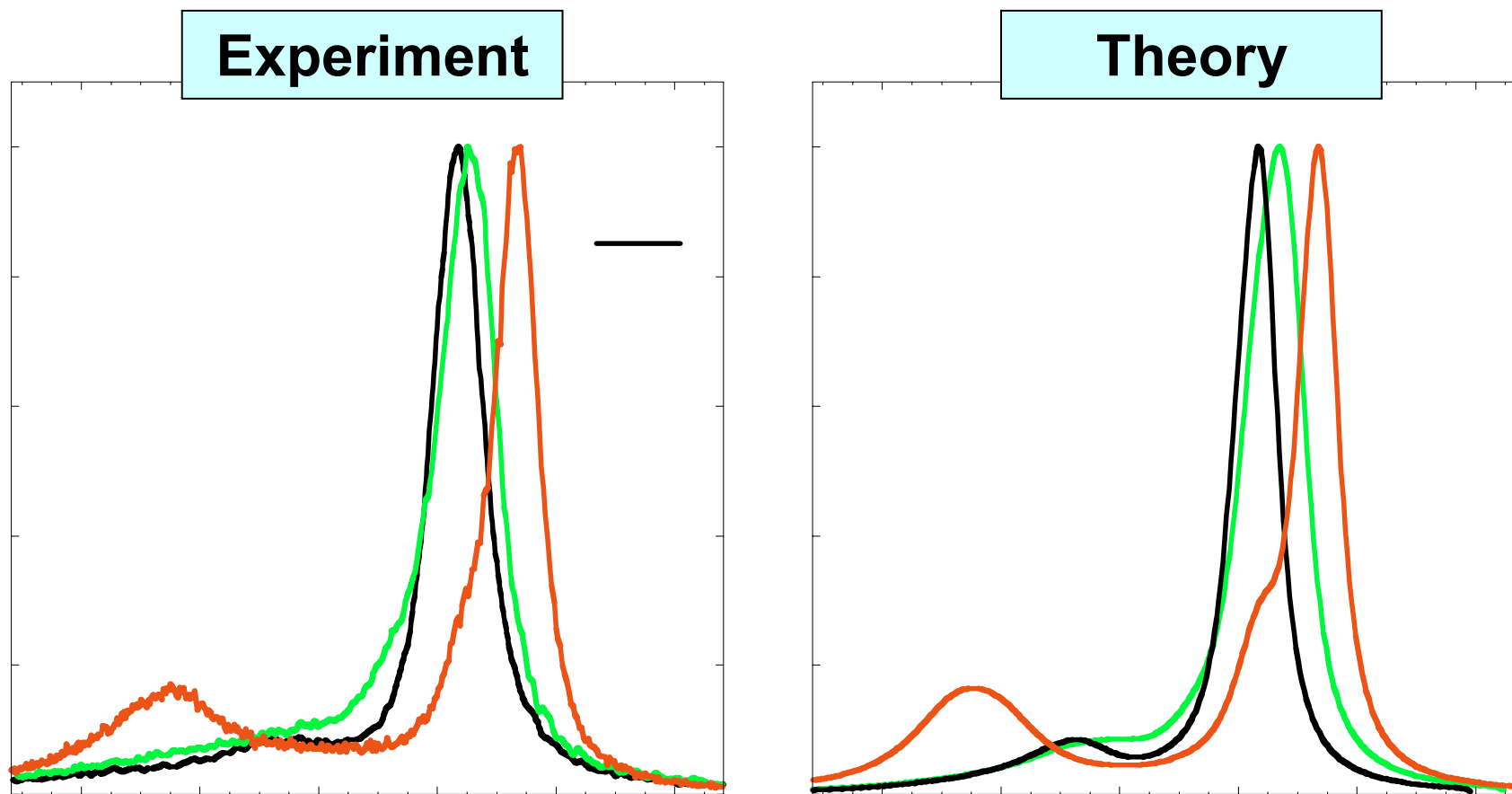
Equal center-of-gravity energies used in calculations!

Valence selective XAFS

Inorg. Chem.
41, 3121 (2002)

Site selective XAFS

- Independent XANES spectra for different neighbours using the cross-over peak.

- Use cross-over peak in the XES with <1 eV resolution.

- The cross-over peak is related to the ligand 2s states that are hybridized with the metal 4p states. The metal 4p states are visible due to 1s4p XES.

- Note that only K edges will have a significant cross-over peak because they have 1s4p XES. L edges create 2p core holes and d metal valence have little overlap with ligand 2s states.

- Only cross-over for 3d metal K edges, not for Pt L edges.

Site selective XAFS
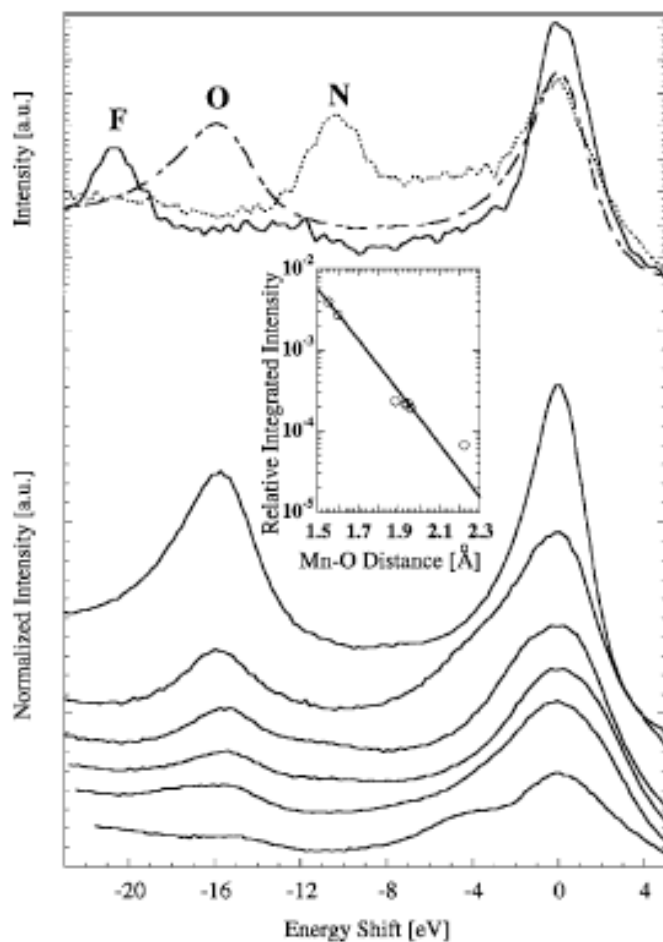
Glatzel and Bergmann
Coord. Chem. Rev.
249, 65 (2005)
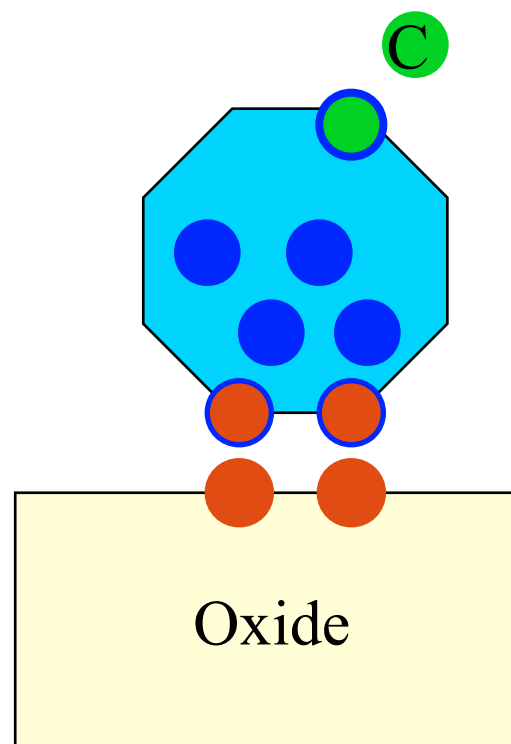
XANES of nanoparticle atoms
bonded to oxygen-bonded
support and to the carbon-
bonded adsorbate

Topics in Catal.10, 179 (2000)

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 for pre-edge analysis,
- (3) make quadrupole peaks visible.
- The overall resolution should ideally be as good as the shallow core hole, say down to 0.4 eV. (1.0 eV experiments are also possible).
- Needs additional monochromator (Si(333) or Si(220))

- (HERFD = High-Energy Resolution Fluorescence detection)

HERFD-XANES

Pt selective XAS

$$\Gamma_{SEL} = 1/\sqrt{\left(1/\Gamma_{2p}^2\right) + \left(1/\Gamma_{3d}^2\right)}$$
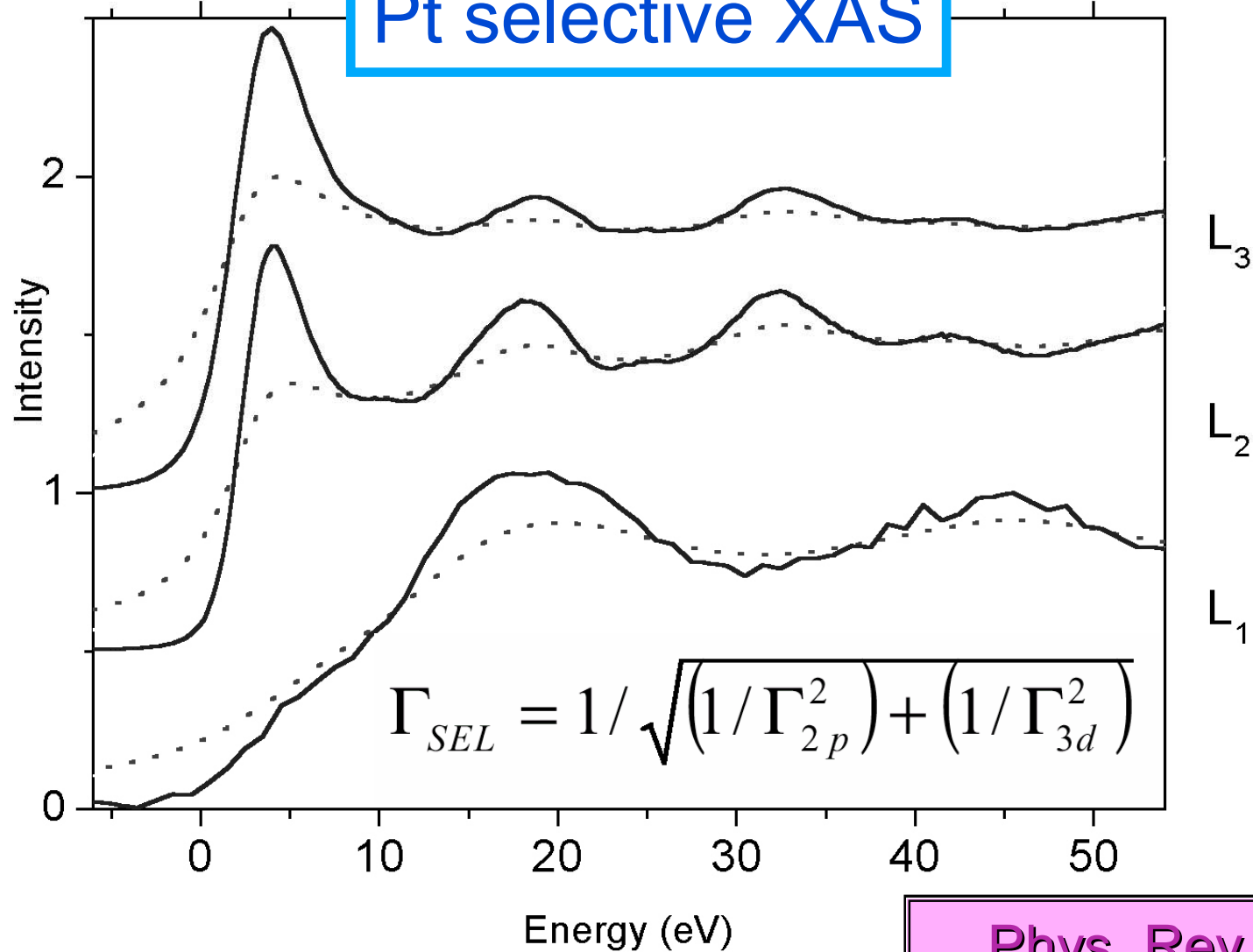
Phys. Rev. B.
66, 195112 (2002)

HERFD-XANES

Kβ detected XANES

Normal XANES

HERFD-XANES

Tracking valence and site symmetry during catalysis

HERFD-XANES

Pt catalyst with and without hydrogen (1999, unpublished)

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

HERFD-XANES and pre-edges

- K Pre-edge structures are due to a combination of 1s3d quadrupole and 1s4p dipole, mixed into the 3d-band.

- HERFD-XANES gives unprecedented high-resolution view on pre-edges.

- A number of 'mysteries' exist:
  1. TiO_2 pre-edge shifts 2.5 eV between dipole and quadrupole, while all Fe-oxide spectra have no shift.
  2. For Mn-oxides normal XANES gives pre-edge shift of 0.3 eV, while HERFD-XANES gives shift of 2.0 eV.
  3. For Fe-oxides exactly the same shifts are found in XANES and HERFD-XANES.

HERFD-XANES and pre-edges

Iron oxides
(3d^5 and 3d^6)

J. Phys. Chem. B.
108, 10002 (2004)
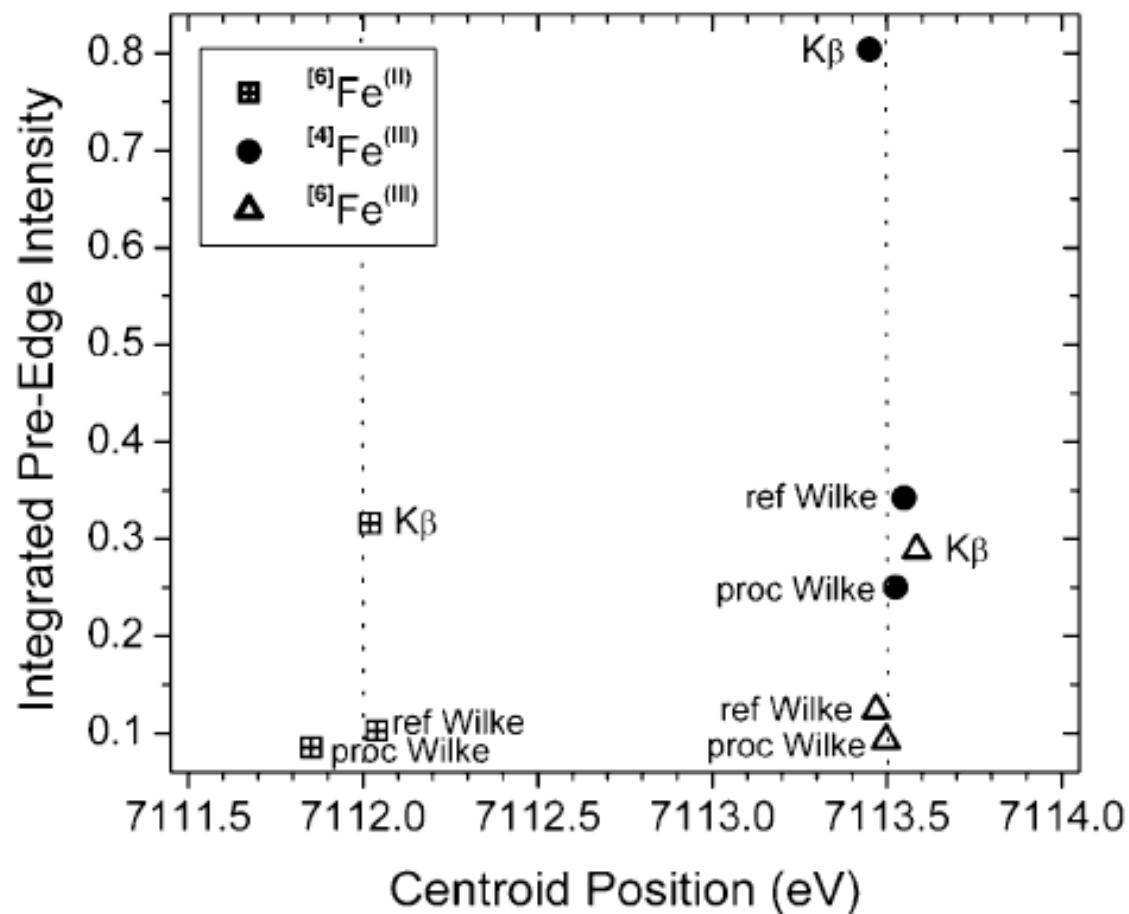
XANES and HERFD-XANES gives identical centroid position

HERFD-XANES yields larger pre-edge intensity (approx. factor 3)

2p X-ray absorption edges
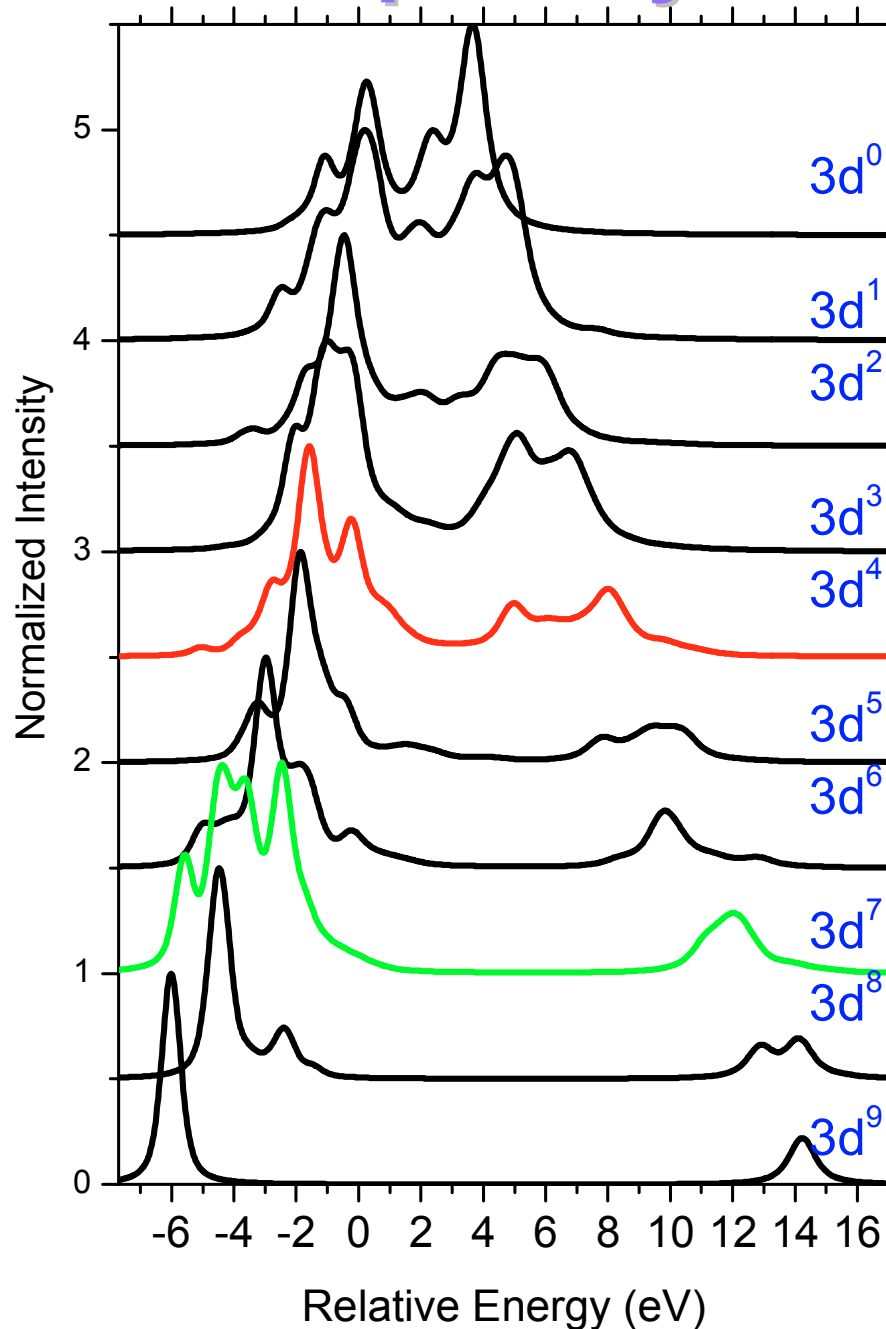
Calculated pre-edges
$3d^N \rightarrow 2p^5 3d^{N+1}$

- Single configuration
- Atomic values for intra-atomic interactions
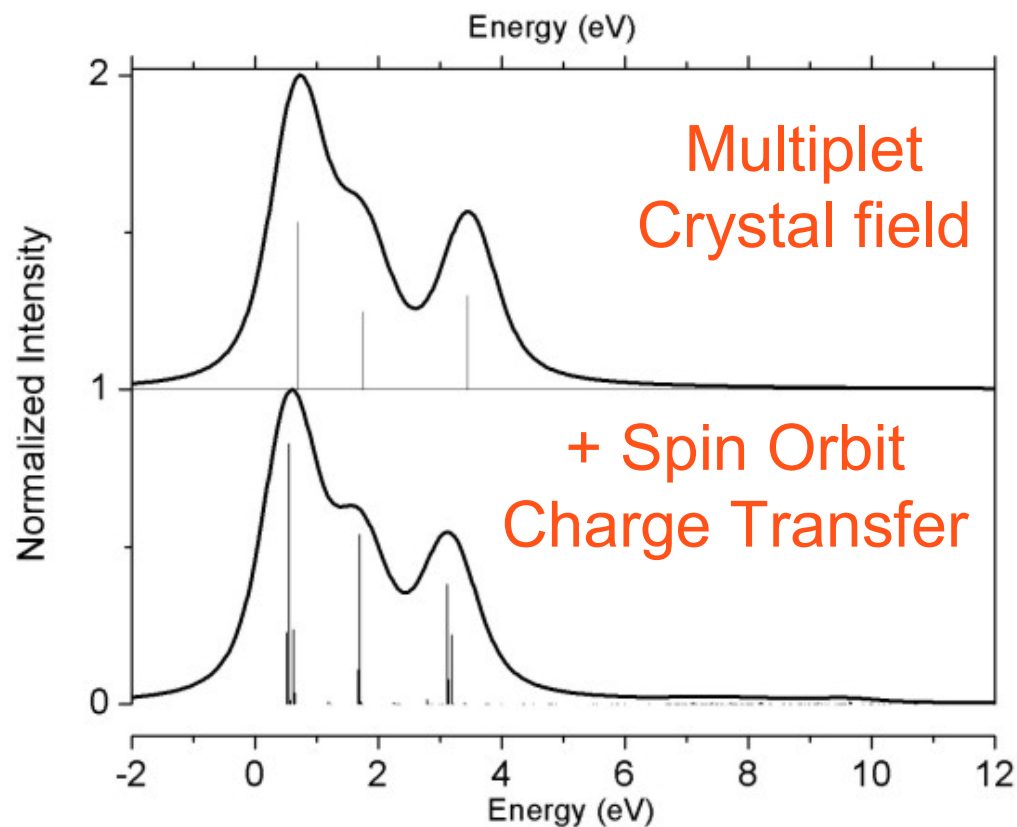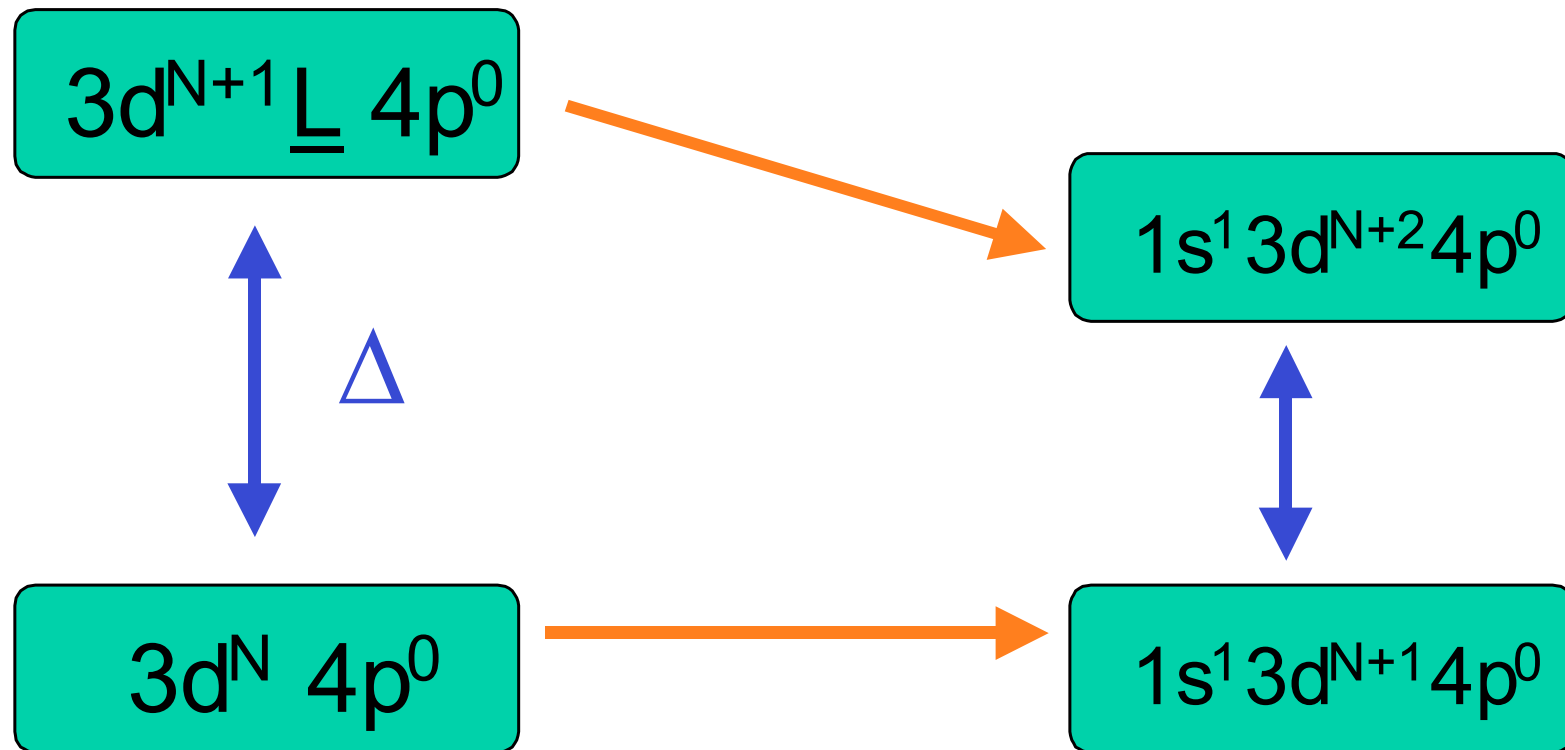- Cubic crystal field of 1.2 eV
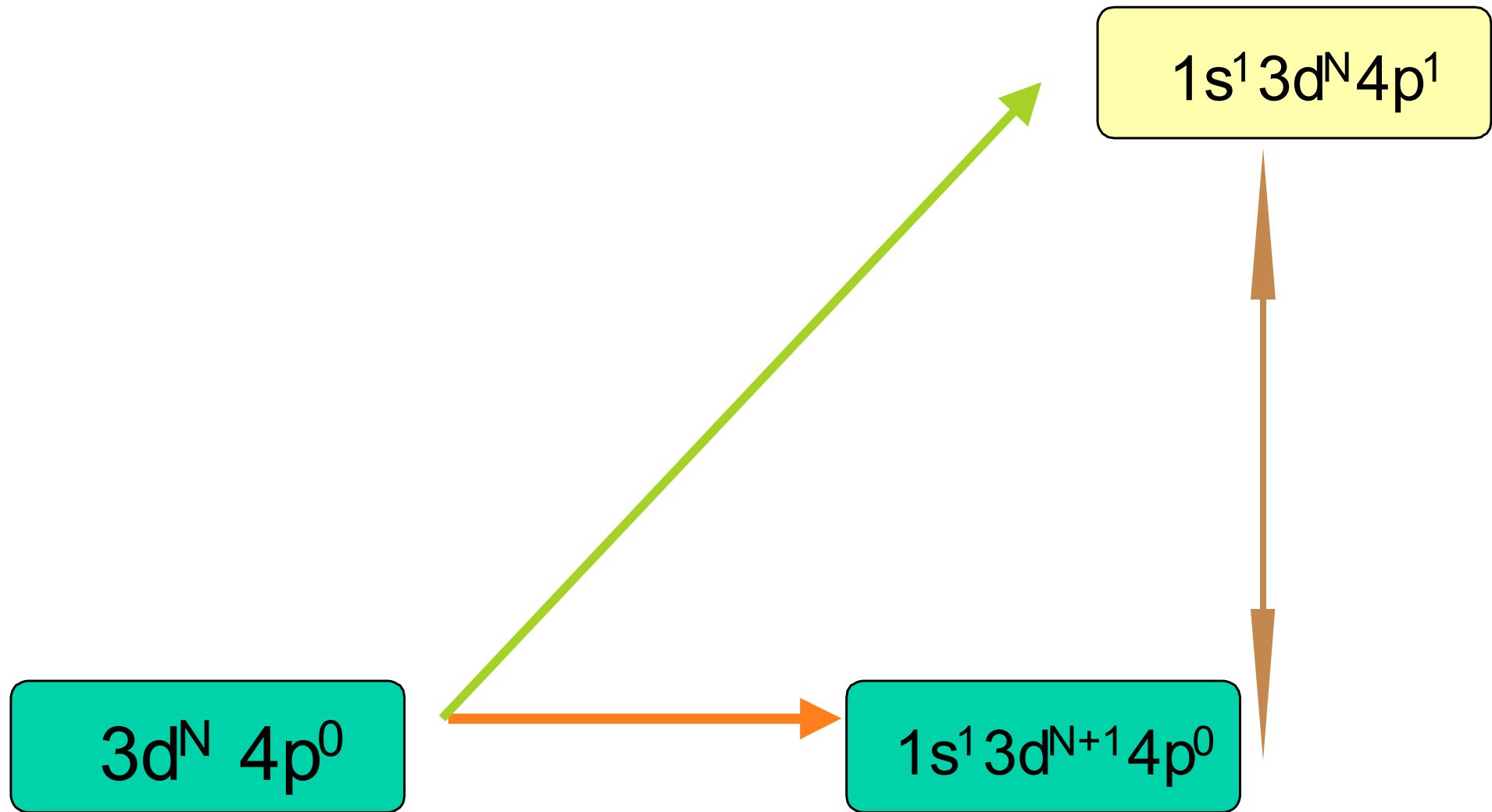- Theoretical relative energy-position

HERFD-XANES and pre-edges
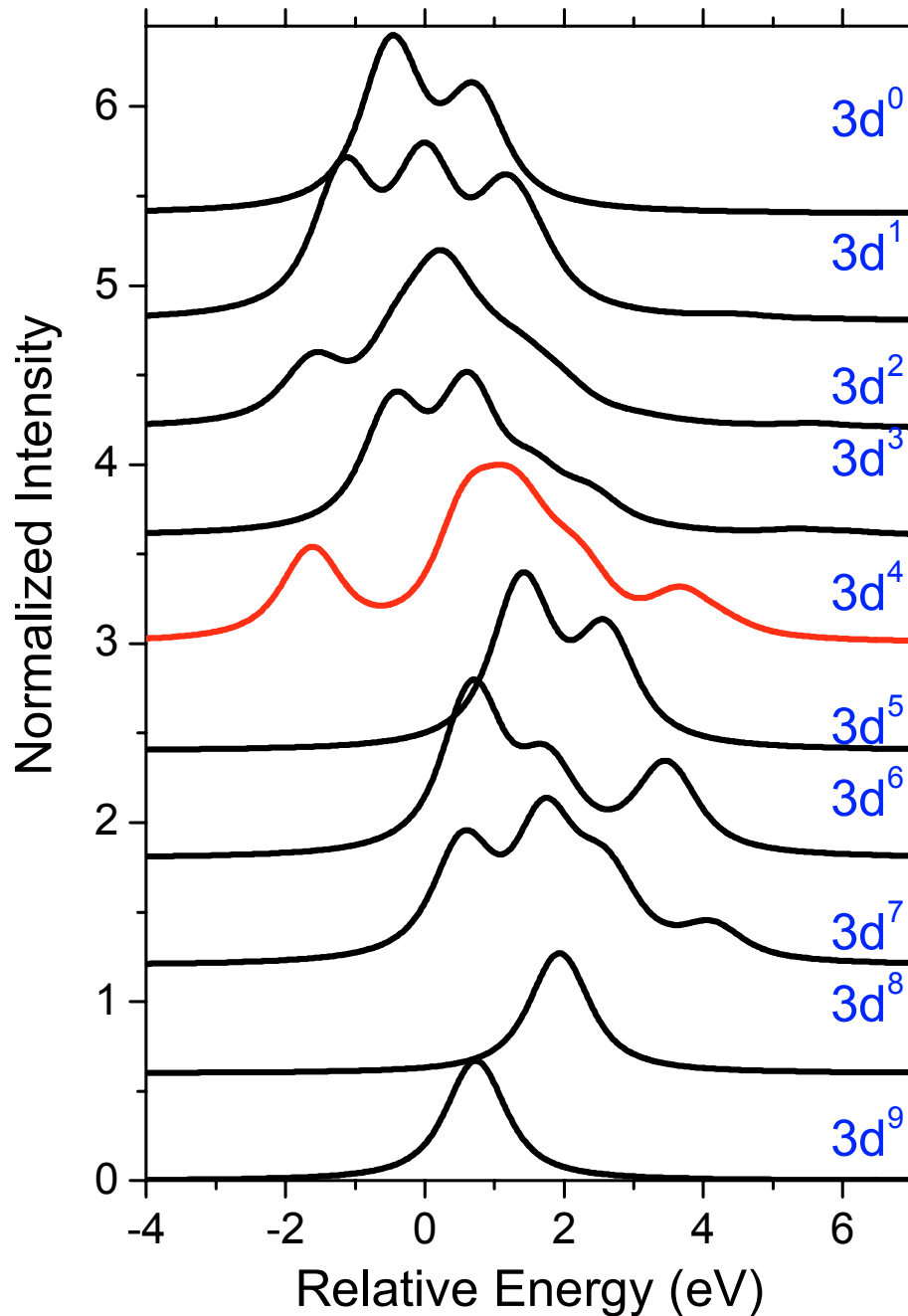
Calculated pre-edges
$3d^N \rightarrow 1s^1 3d^{N+1}$

- Single configuration
- Atomic values for intra-atomic interactions
- Cubic crystal field of 1.2 eV
- Theoretical relative energy-position (= incorrect)

XAS Open Questions: The K pre-edge

Multiplet
Crystal field

+ Spin Orbit
Charge Transfer
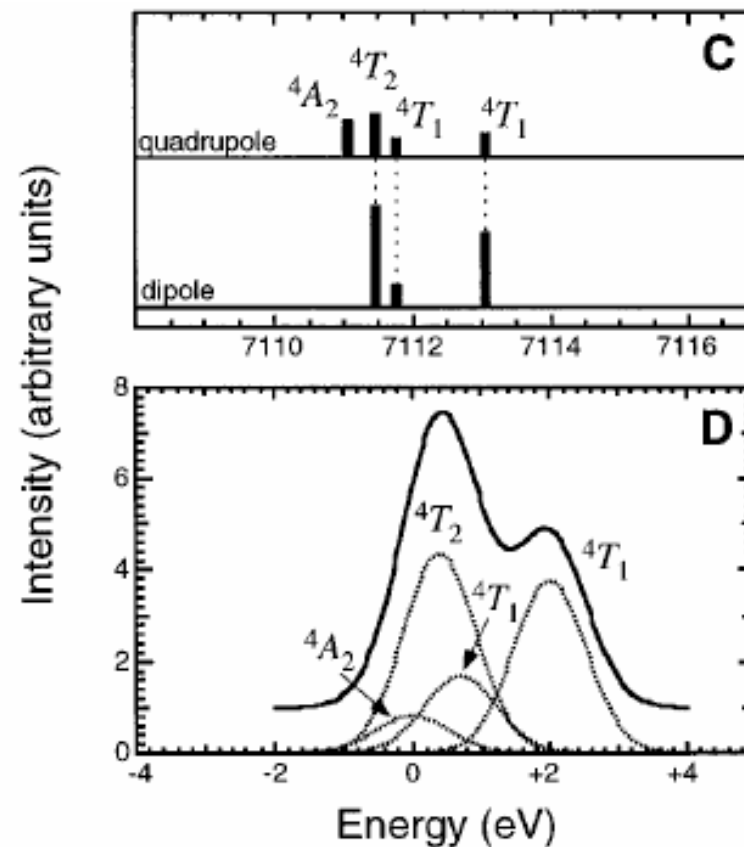
Westre et al., JACS
119, 6297 (1997)

XAS Open Questions: The K pre-edge

$3d^{N+1}\underline{L}\ 4p^0$

$1s^1 3d^{N+2} 4p^0$

Δ

$3d^N\ 4p^0$

$1s^1 3d^{N+1} 4p^0$

XAS Open Questions: The K pre-edge

$1s^1 3d^N 4p^1$

$3d^N 4p^0$

$1s^1 3d^{N+1} 4p^0$

Soft X-ray spectra with hard X-rays

- X-ray Raman (or X-ray energy Loss) gives the carbon and oxygen K edges, for example in H_2O.

- Resonant X-ray Raman (or RIXS) gives the 3d metal L edges at the K pre-edges.

- Only makes sense with a resolution similar to soft x-rays, say 0.4 eV.

- Needs additional monochromator (Si(333) or Si(220))

Resonant Inelastic X-ray Scattering
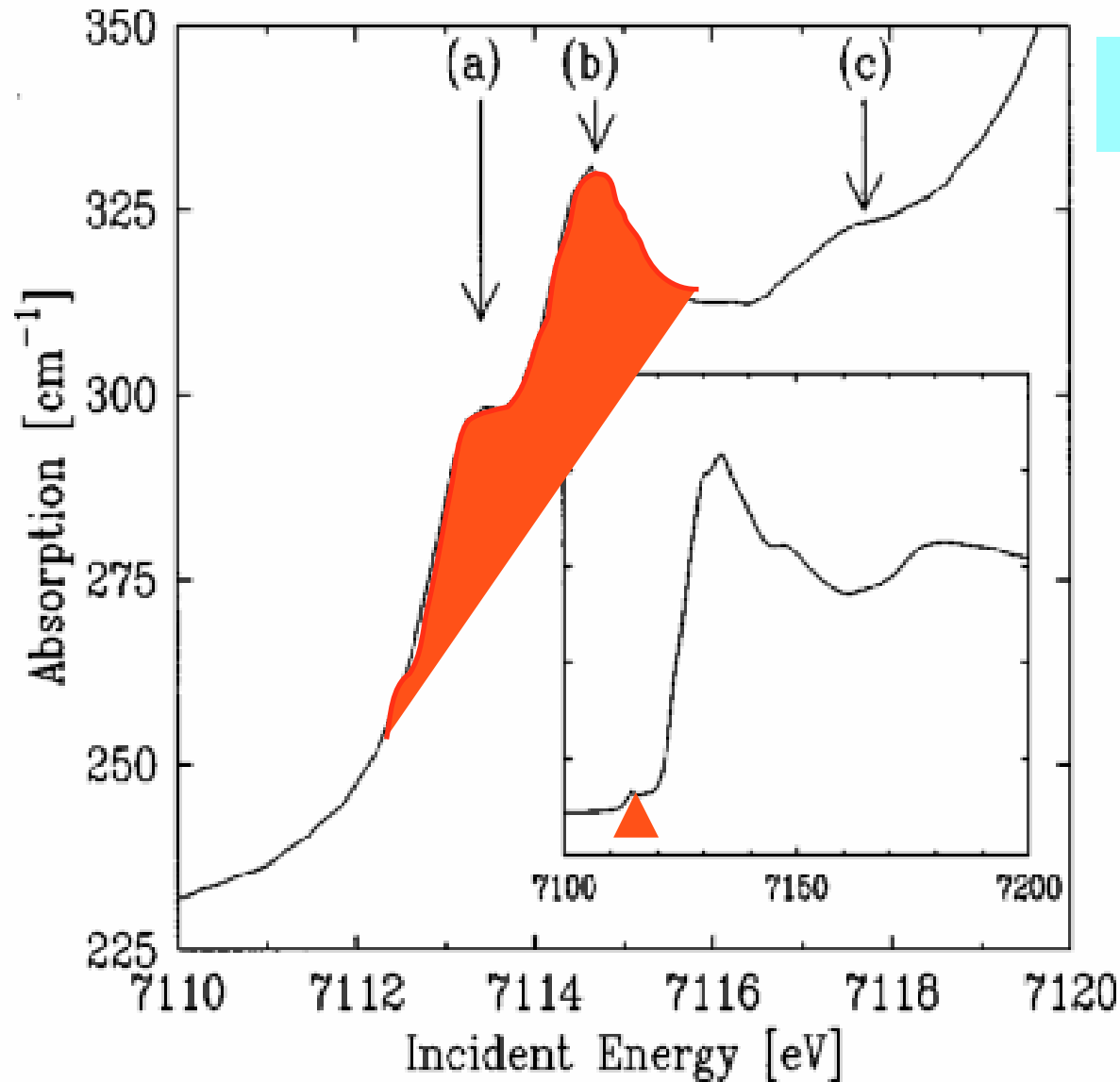
1s XAS of Fe_2O_3

K edge:
1s to 4p

Pre-edge:
1s to 3d

Phys. Rev. B.
58, 13452 (1998)

Resonant Inelastic X-ray Scattering

1s2p RIXS of Fe_2O_3
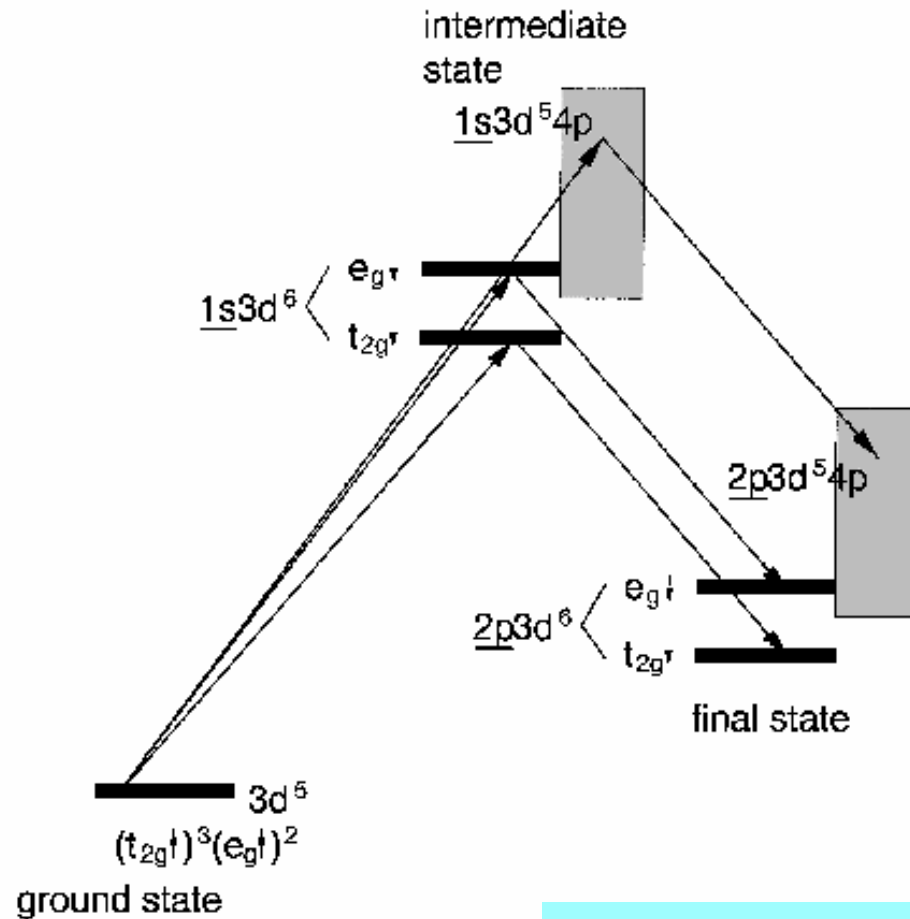
Quadrupole to 3d-states

Dipole to 4p-states

Decay of 2p-electron into 1s-hole

Final state identical to 2p XAS

Resonant Inelastic X-ray Scattering

1s2p RIXS

2p-XAS

Fe $L_{II,III}$

(a)

(b)

(c)

x4

715   730   715   730

Final State Energy [eV]
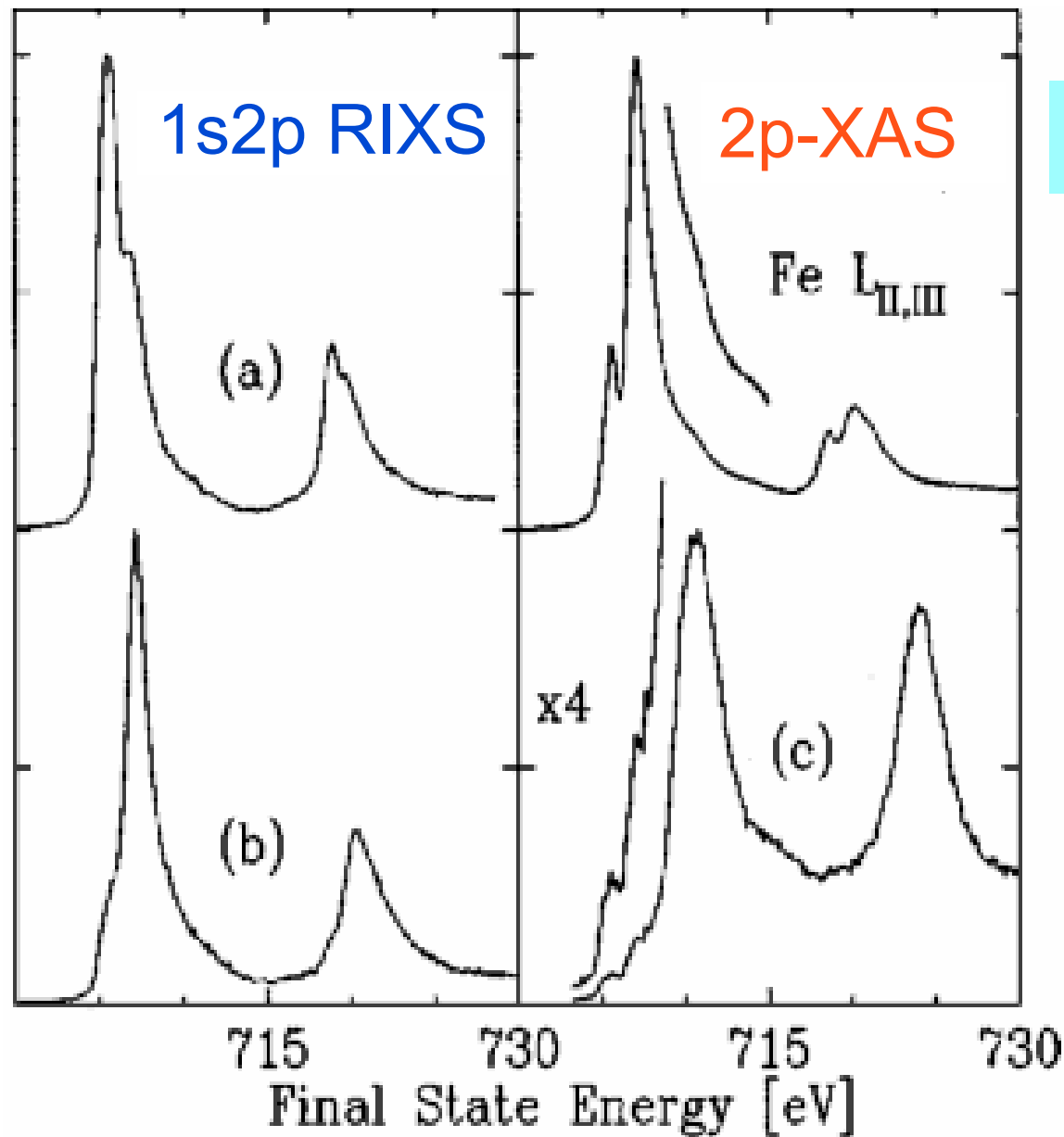
1s2p RIXS of Fe_2O_3

'soft x-ray spectra with hard x-rays'

Phys. Rev. B. 58, 13452 (1998)

Two-dimensional RIXS plots

- Two types of plots:
  - Incident energy versus energy transfer
  - Incident energy versus emitted energy

- Cross-sections
  (different behaviour on- and off-resonance)
  - CIE: constant incident energy
  - CTE: constant transferred energy
  - CEE: constant emitted energy (=used for HERFD-XANES)

- Integrations:
  - IIE: integrated incident energy
  - ITE: integrated transferred energy (=total FY at edge; only the resonances are visible)
  - IEE: integrated emitted energy (=total FY everywhere, if the resonances at the edge fall within the integration area)

  (Away from resonances the XES spectrum has fixed a emission energy)

RIXS of Iron Oxides

RIXS of Iron Oxides

RIXS of Iron Oxides
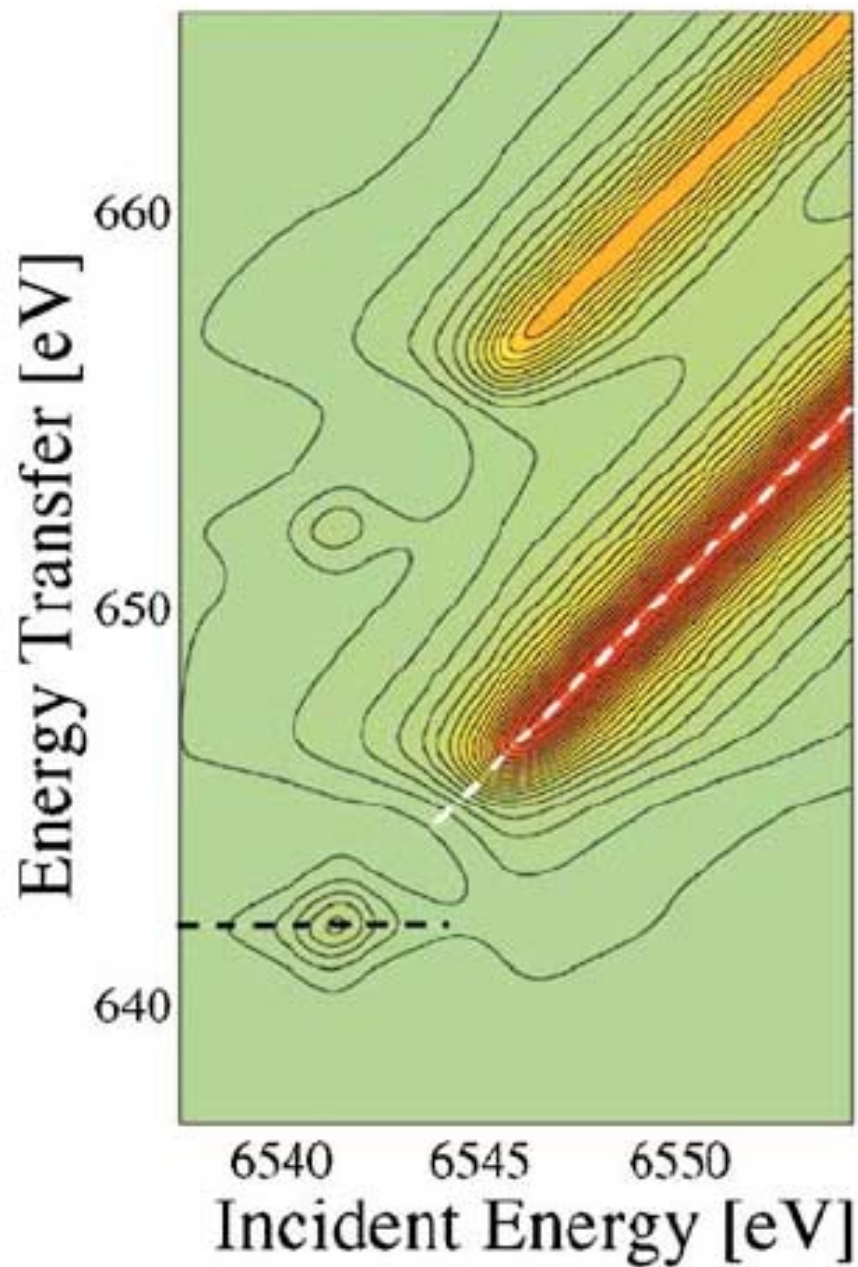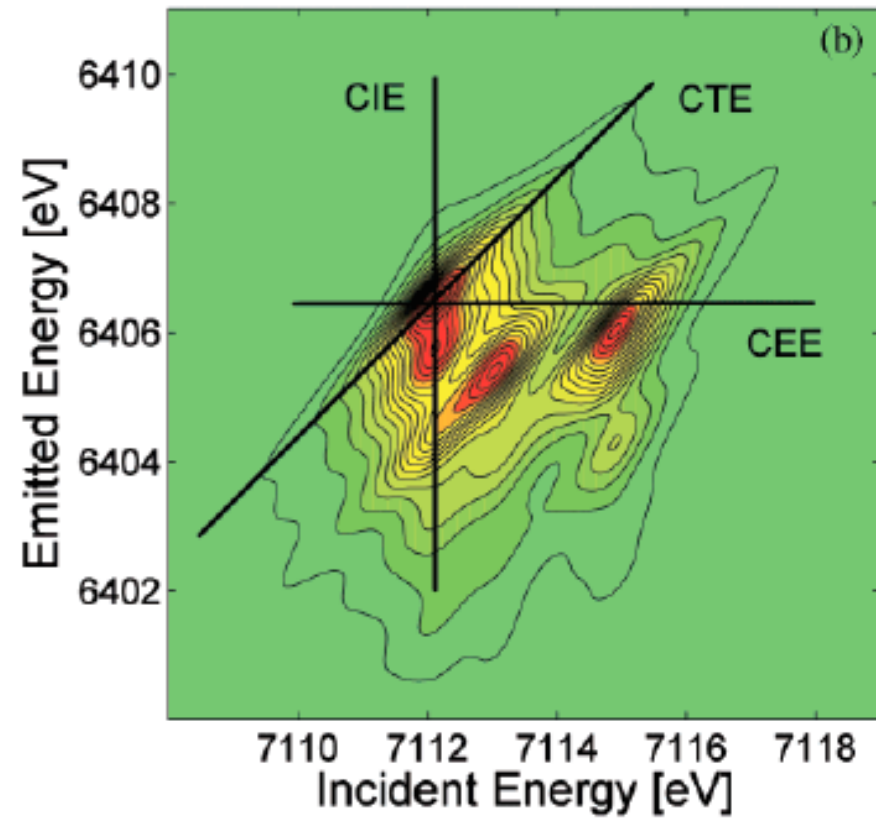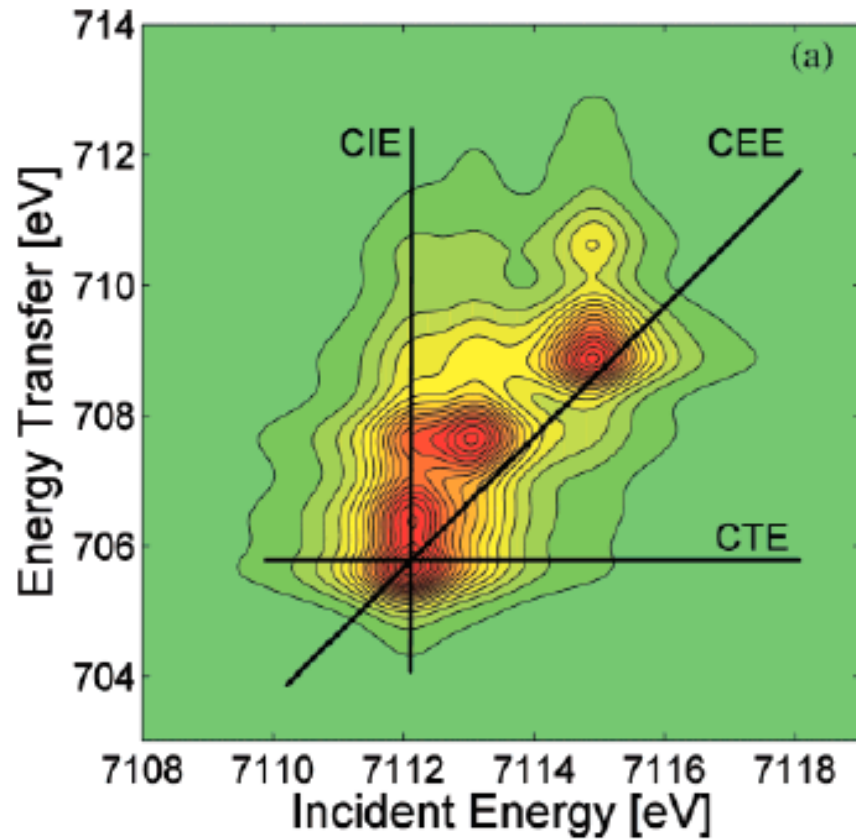
Resonant Inelastic X-ray Scattering

Resonant Inelastic X-ray Scattering

Resonant Inelastic X-ray Scattering