

# X-ray absorption spectroscopy

# X-ray absorption spectroscopy

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PhD: solid state chemistry

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Post-doc:

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Post-doc: solid state physics

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**Synchrotron and theoretical spectroscopy  
of catalytic nanomaterials**  
(inorganic chemistry and catalysis)

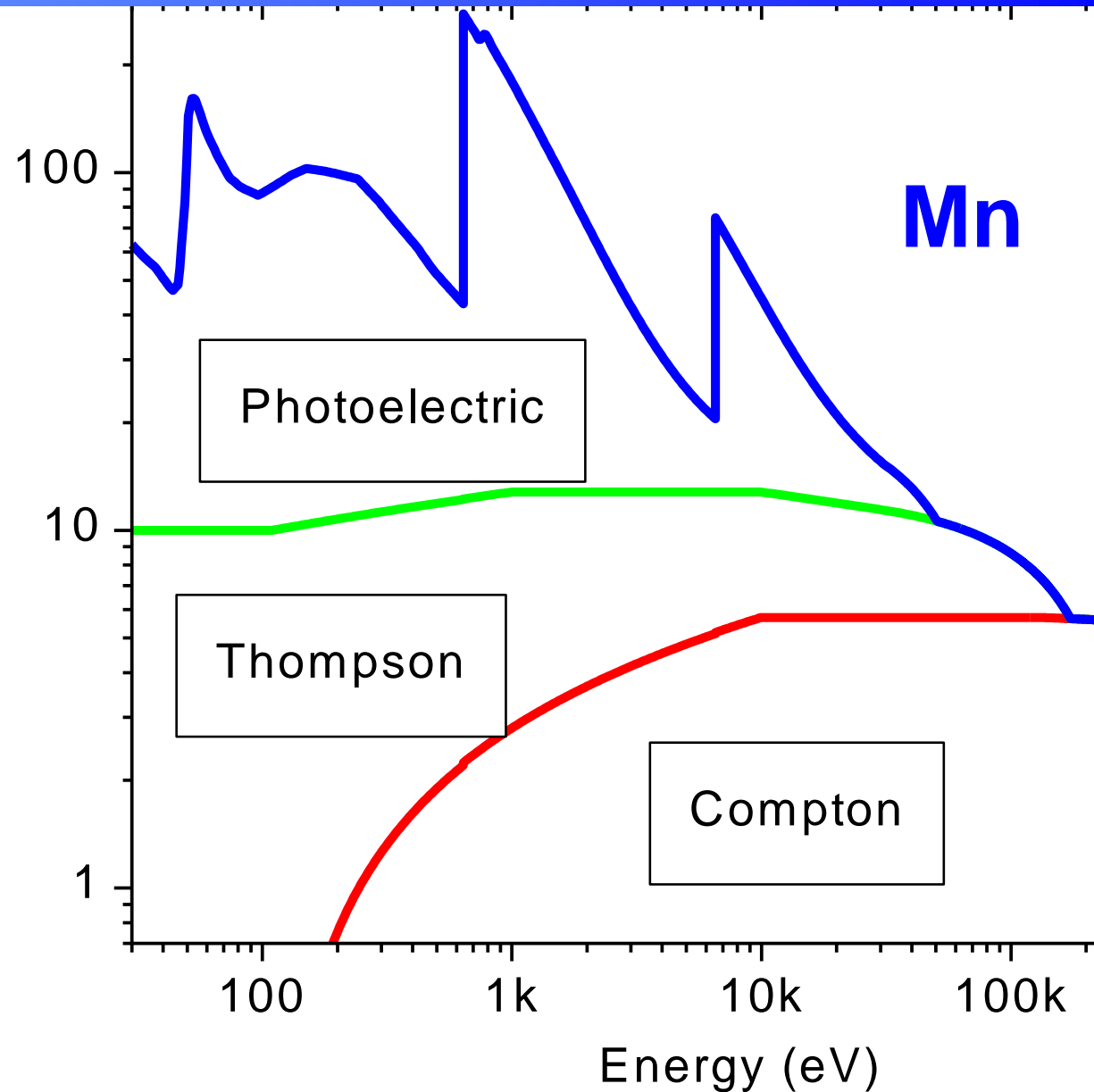
# Core Level Spectroscopy of Solids

Frank de Groot  
Akio Kotani

 CRC Press  
Taylor & Francis Group

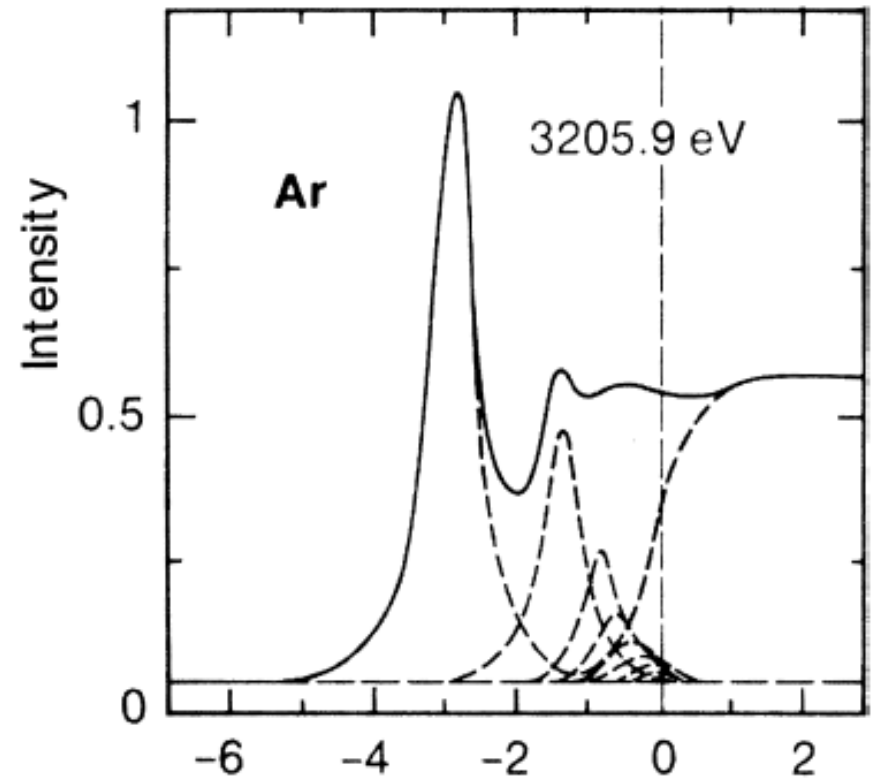
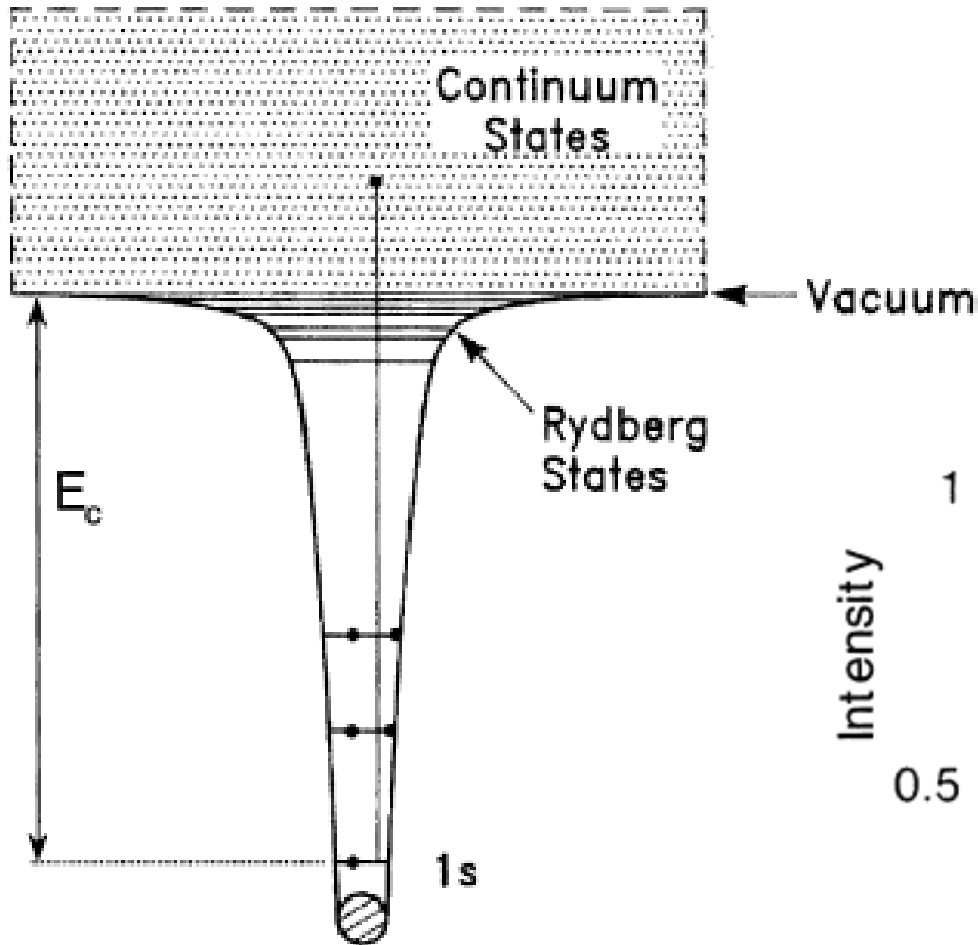
# Interaction of x-rays with matter

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



# XAS of an atom

a)



# XAS of a solid

2

Core Level Spectroscopy of Solids

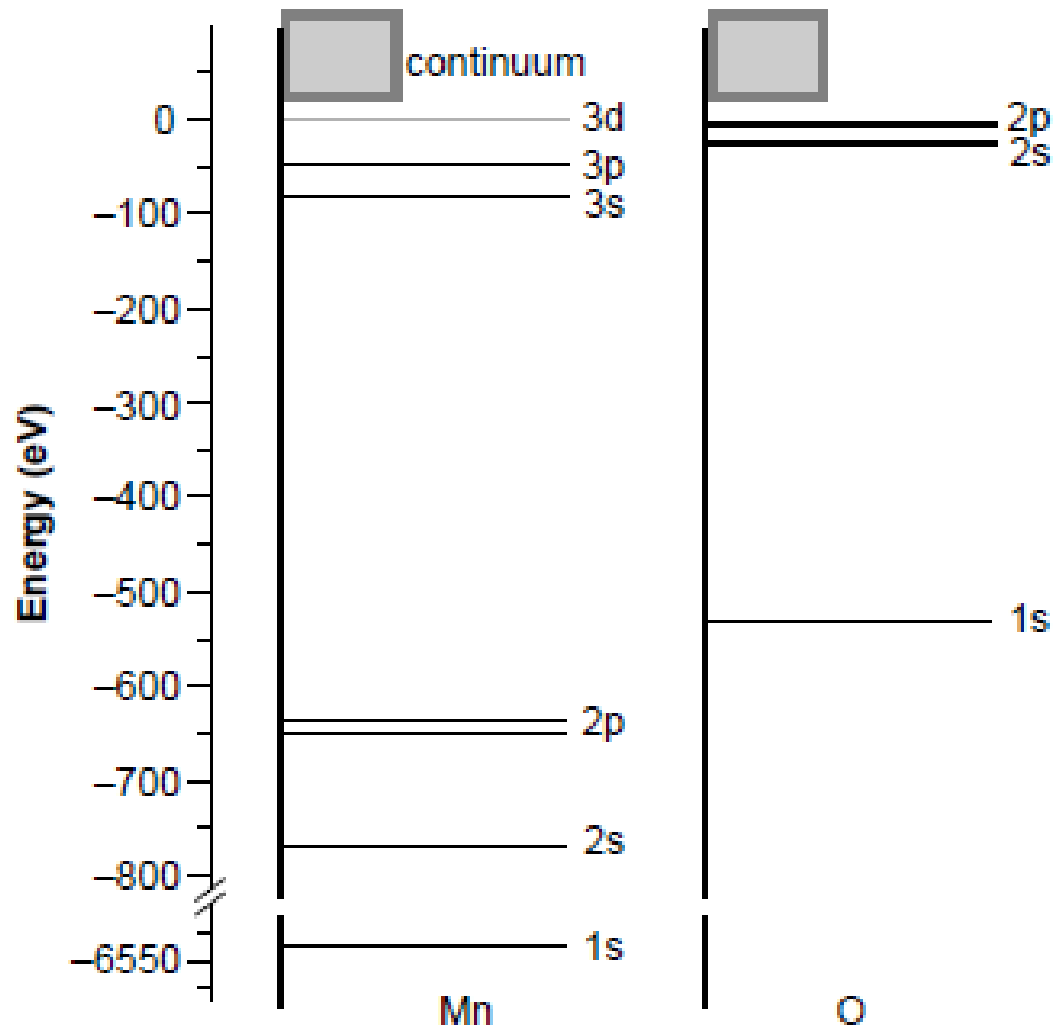


FIGURE 1.1 Energies of the core levels and VES of Mn and O in MnO.

# XAS of a solid

**TABLE 2.1**  
**Nomenclature for Core Level Spectra**

Orbital*	Label <sup>†</sup>	E <sup>‡</sup> (Ni)	E <sup>‡</sup> (O)
1s	K	8333	543
2s	L <sub>1</sub>	1008	42
2p <sub>1/2</sub>	L <sub>2</sub>	870	V <sup>§</sup>
2p <sub>3/2</sub>	L <sub>3</sub>	853	V <sup>§</sup>
3s	M <sub>1</sub>	111	
3p <sub>1/2</sub>	M <sub>2</sub>	68	
3p <sub>3/2</sub>	M <sub>3</sub>	66	
3d <sub>3/2</sub>	M <sub>4</sub>	V	
3d <sub>5/2</sub>	M <sub>5</sub>	V	

\* Orbital notation.

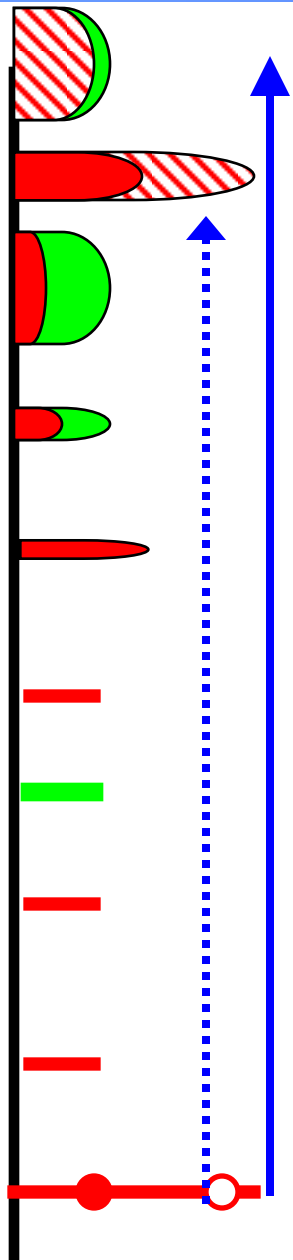
<sup>†</sup> Spectroscopic names (Barkla notation).

<sup>‡</sup> Binding energies.

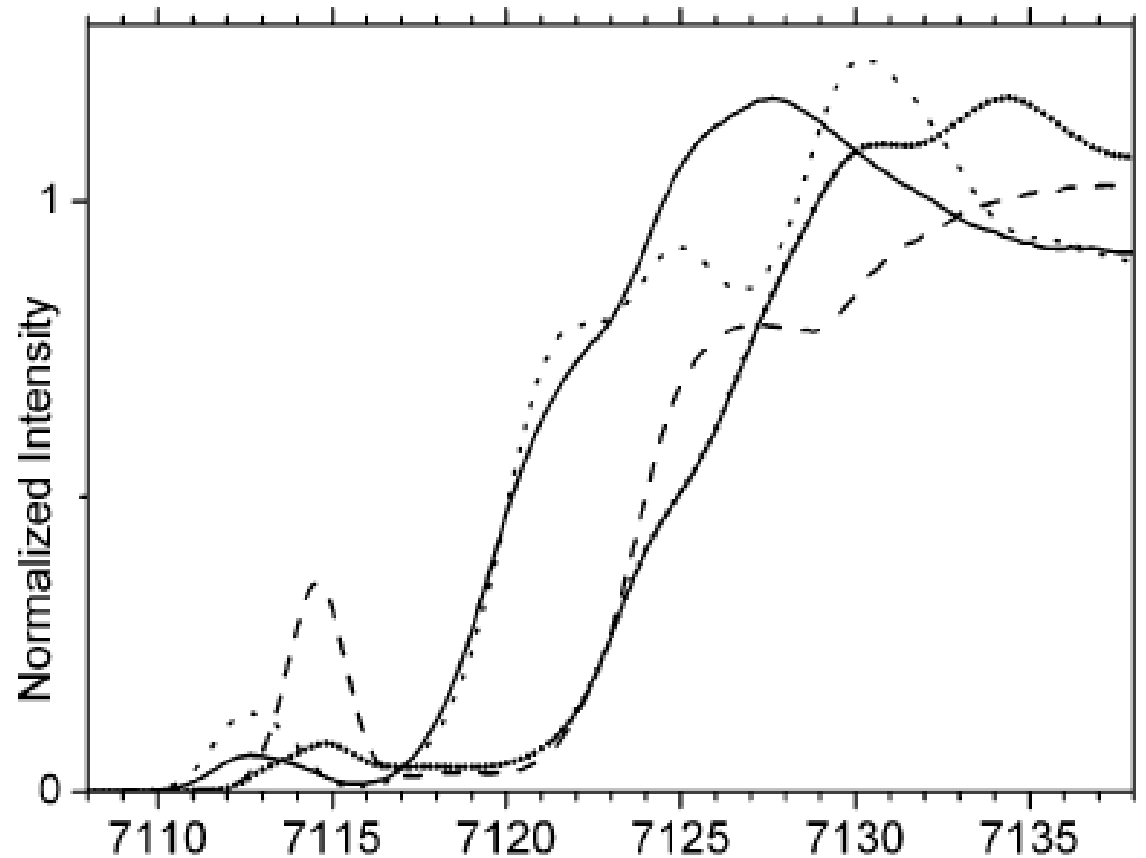
<sup>§</sup> Valence state with a binding energy of a few eV.

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

# XAS of a solid



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

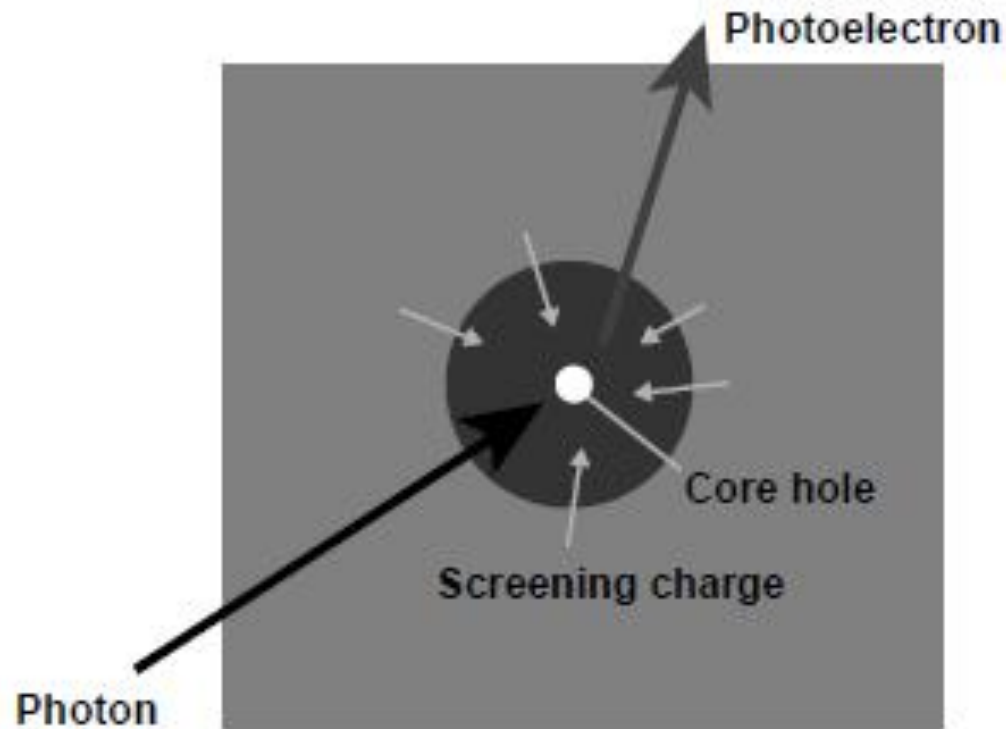




# XAS of a solid

4

Core Level Spectroscopy of Solids



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

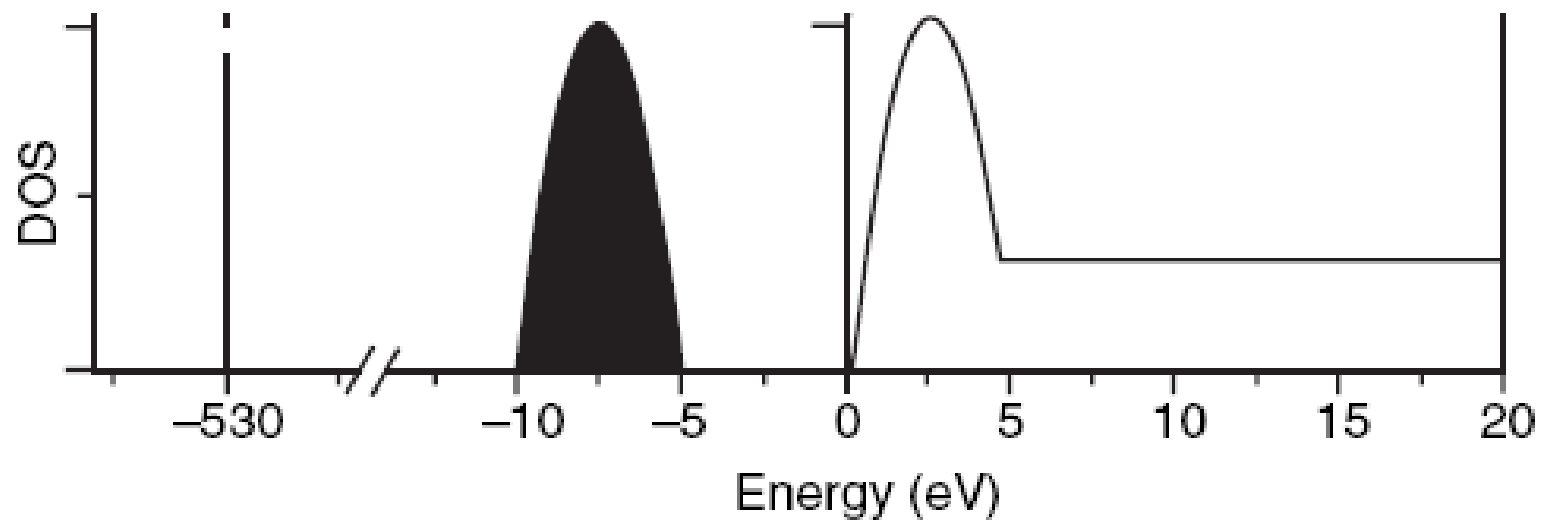
# XAS and XPS

Excitation of core electrons to empty states.

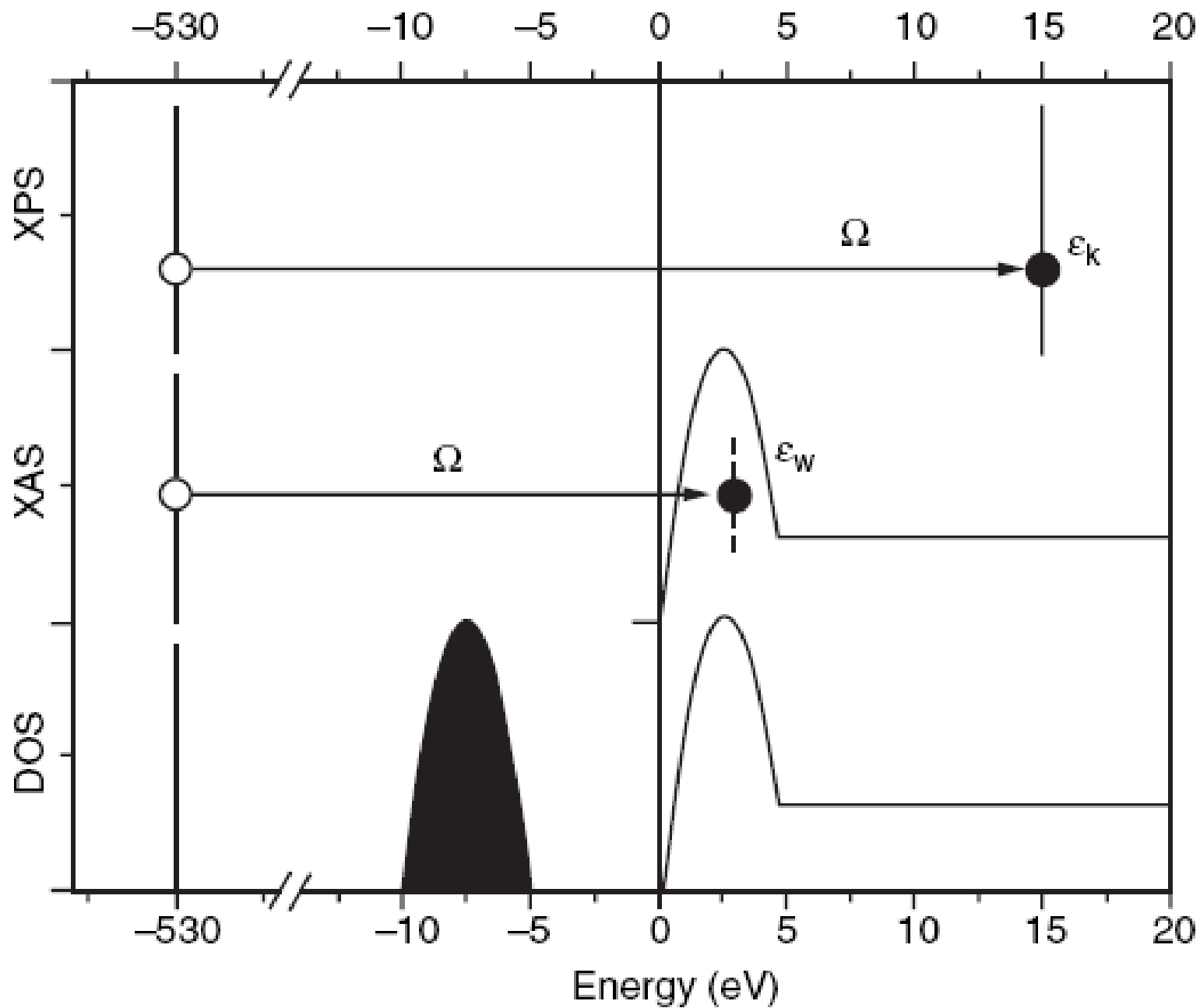
Spectrum given by the **Fermi Golden Rule**

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

# XAS and XPS



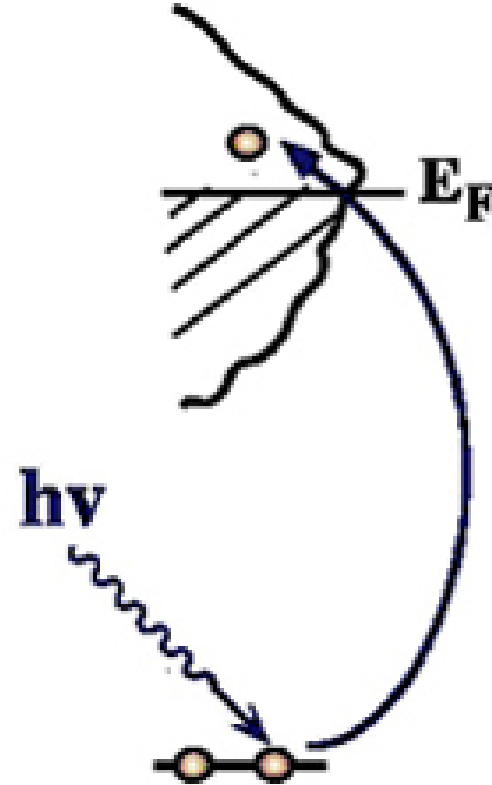
# XAS and XPS



# X-ray absorption spectroscopy

Excitations of  
core electrons  
to empty states

The XAS spectrum  
is given by the  
**Fermi Golden Rule**

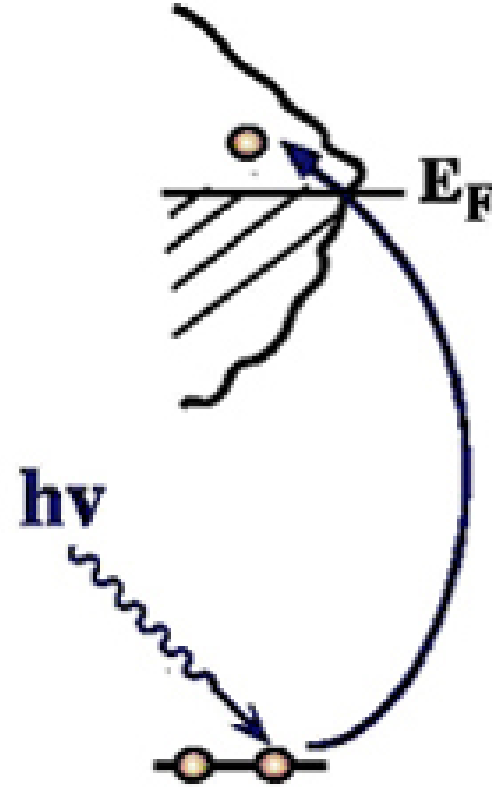


$$I_{XAS} \sim \sum_f \left| \langle \Phi_f | \hat{e} \cdot r | \Phi_i \rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

# X-ray Absorption Spectroscopy

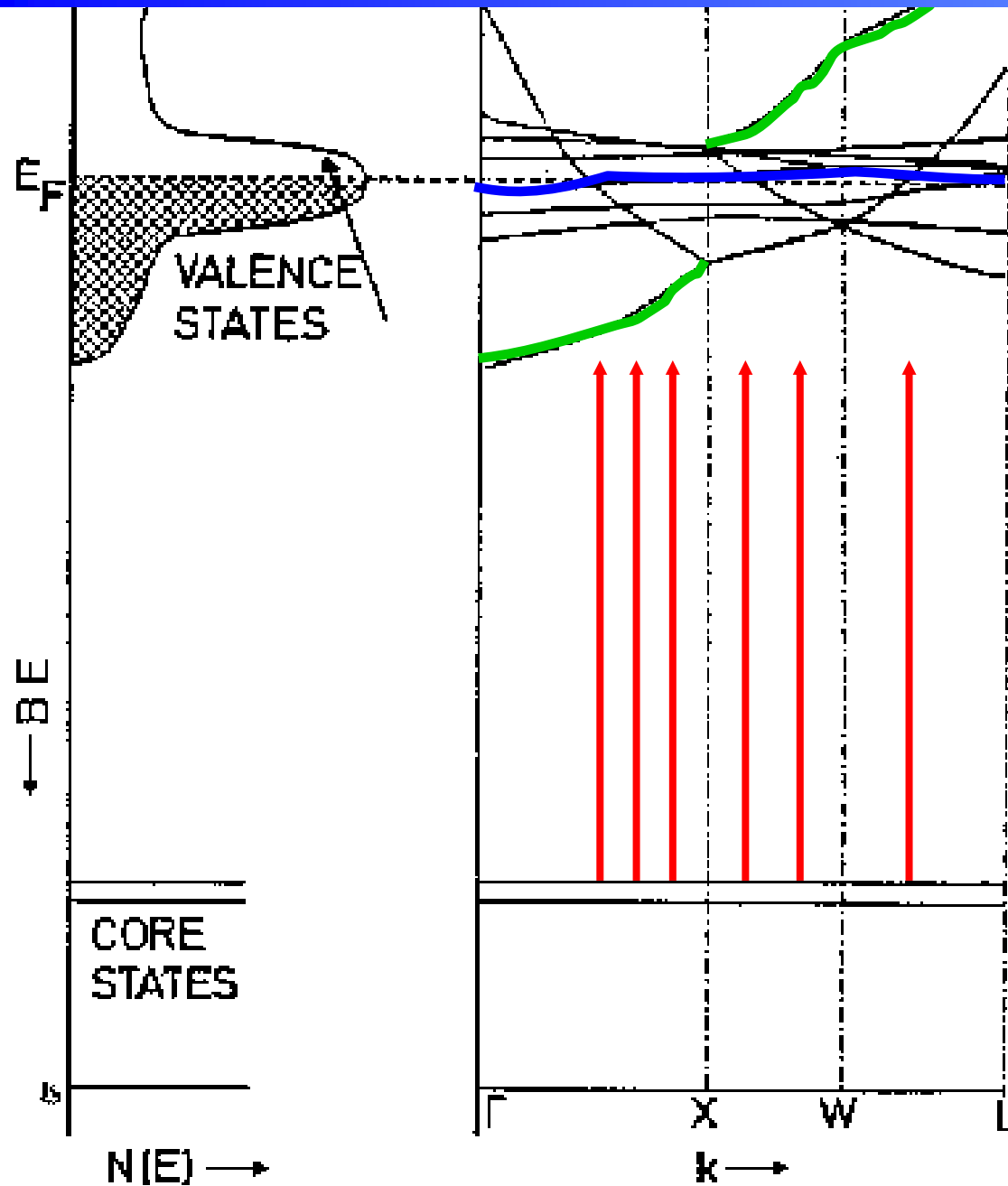
Excitations of  
core electrons  
to empty states

The XAS spectrum  
is given by the  
**Fermi Golden Rule**



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

# X-ray Absorption Spectroscopy

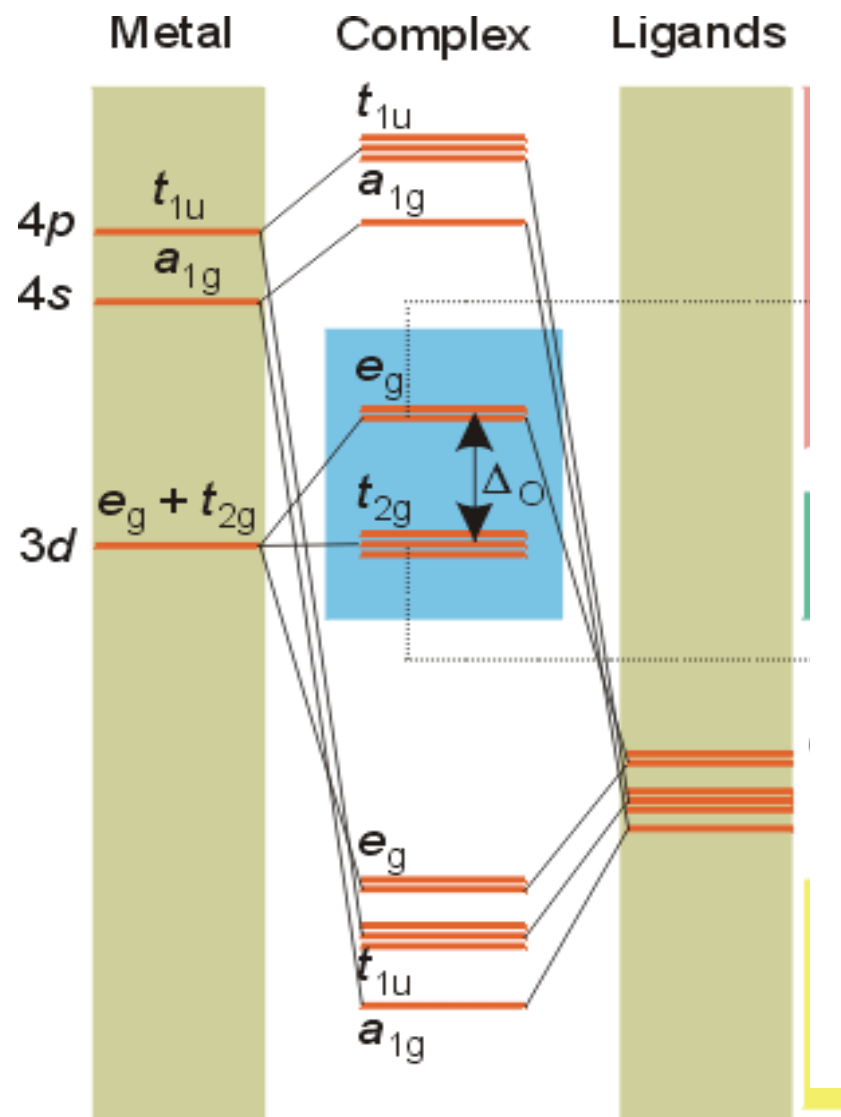
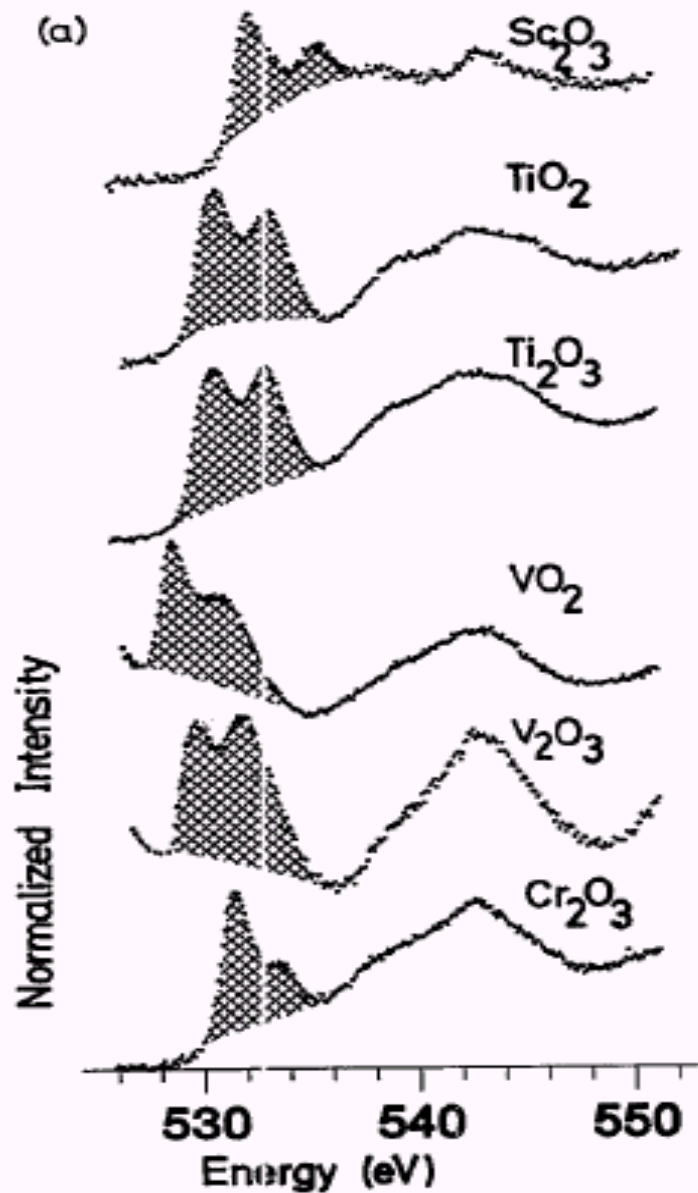


Density of States (DOS) is the integral over  $k$ -space of the band structure.

Core states have no dispersion.

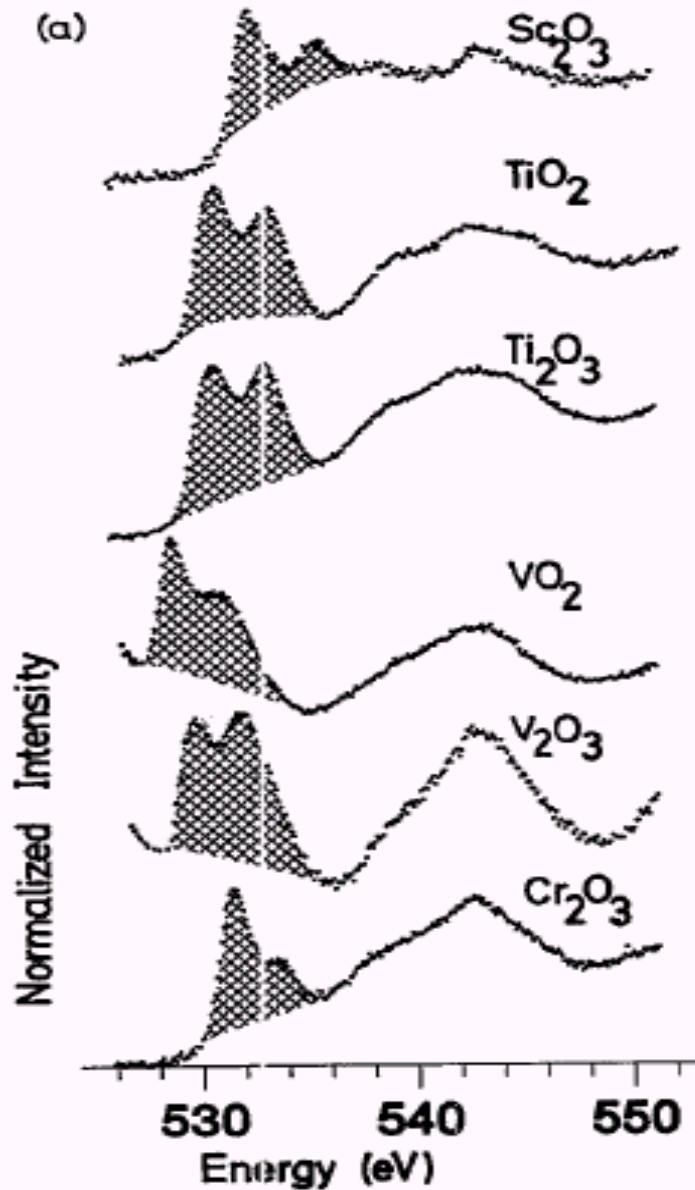
XAS preserves momentum ( $k$ )

# X-ray Absorption Spectroscopy



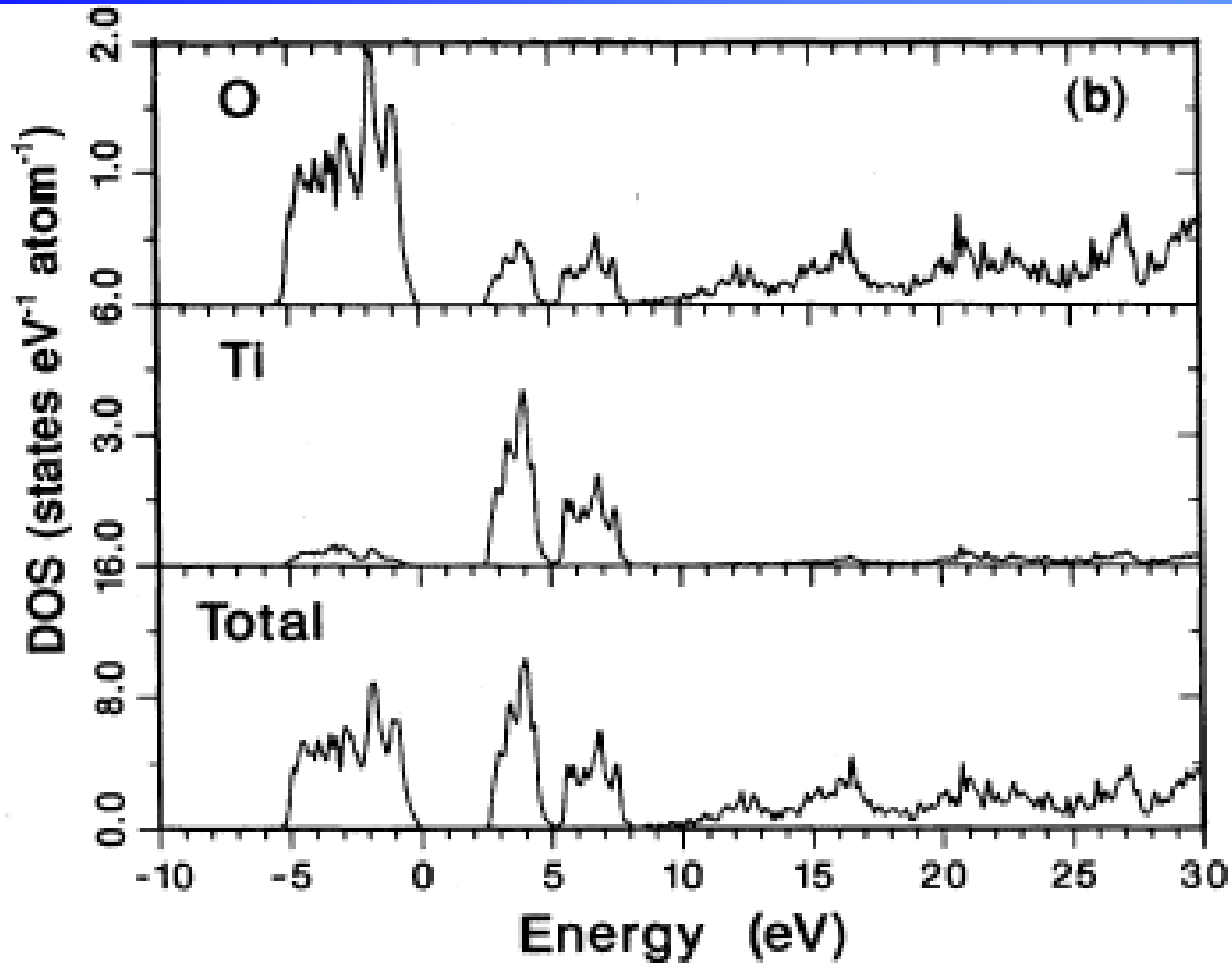


# X-ray Absorption Spectroscopy

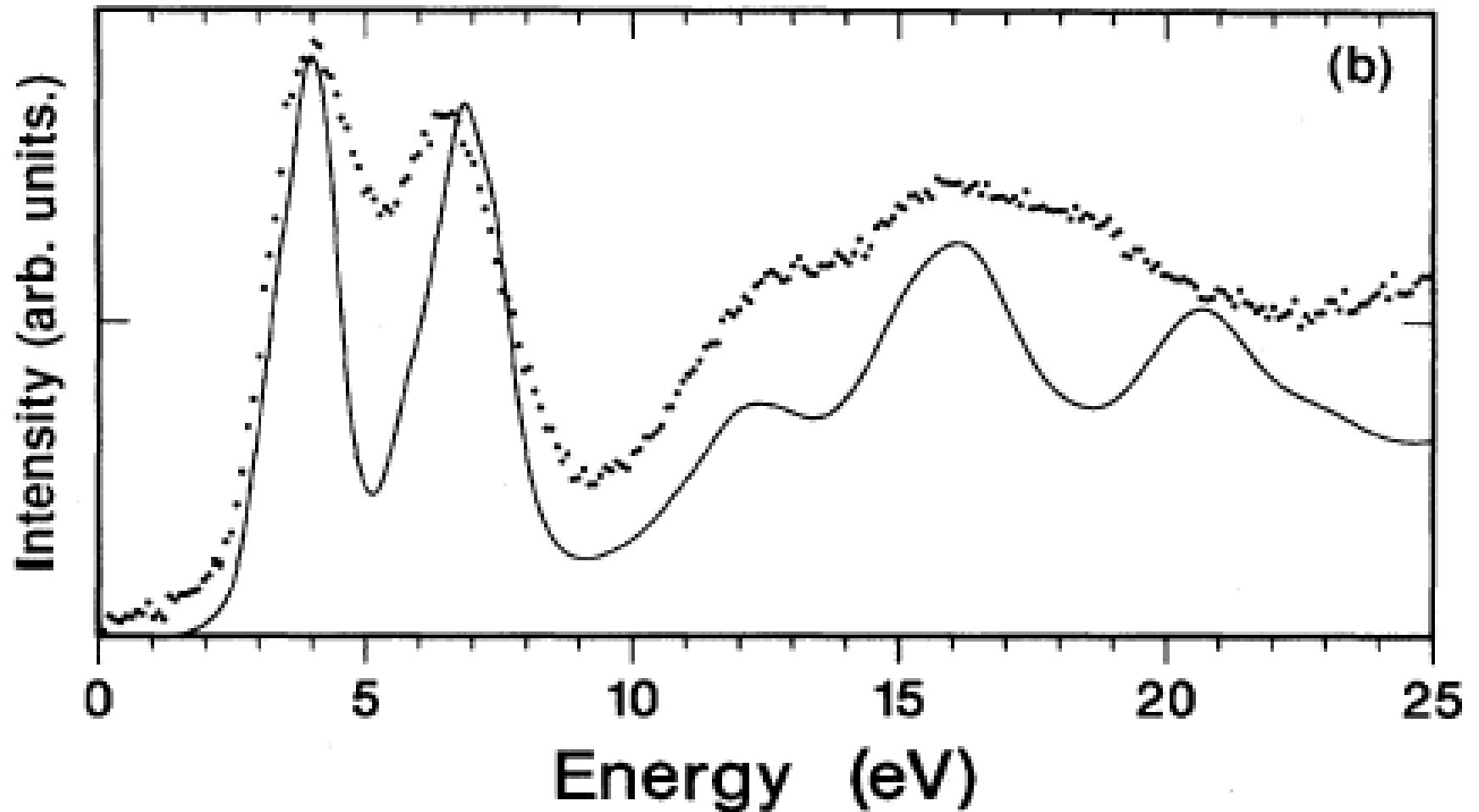


oxygen 1s > p DOS

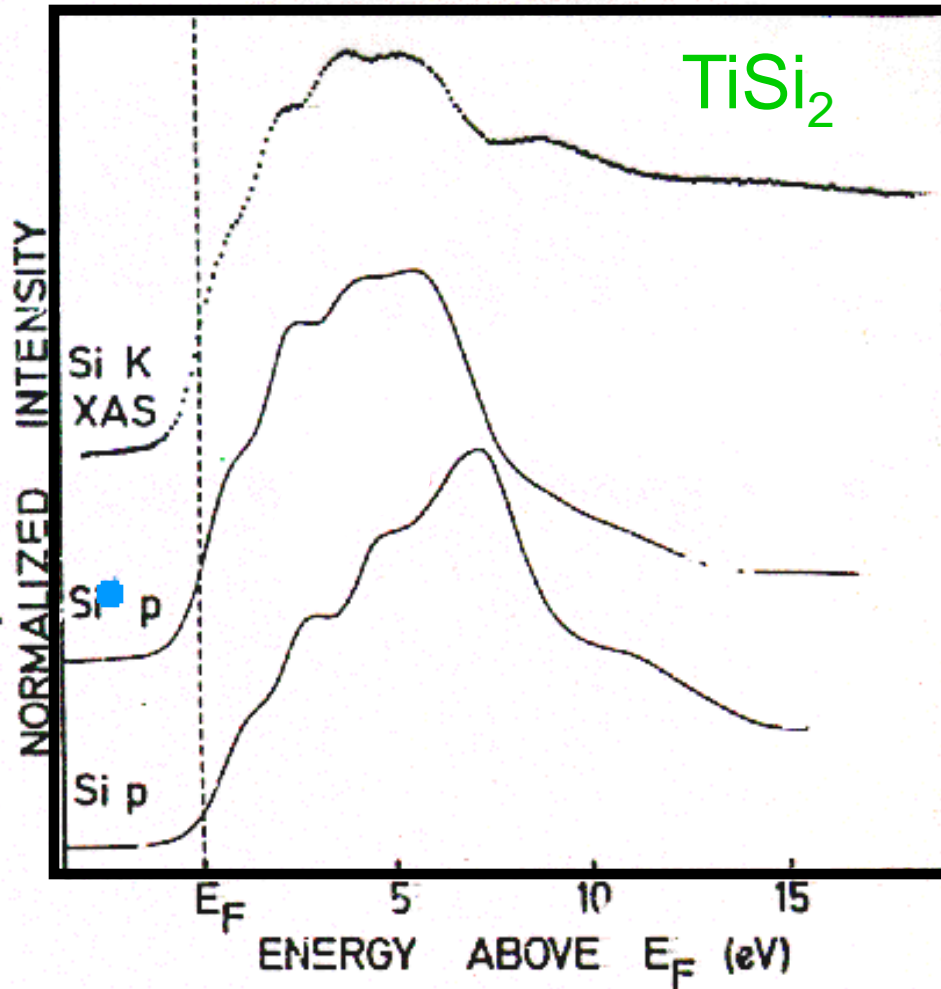
# Density of States of $\text{TiO}_2$



# Density of States of TiO<sub>2</sub>



# 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

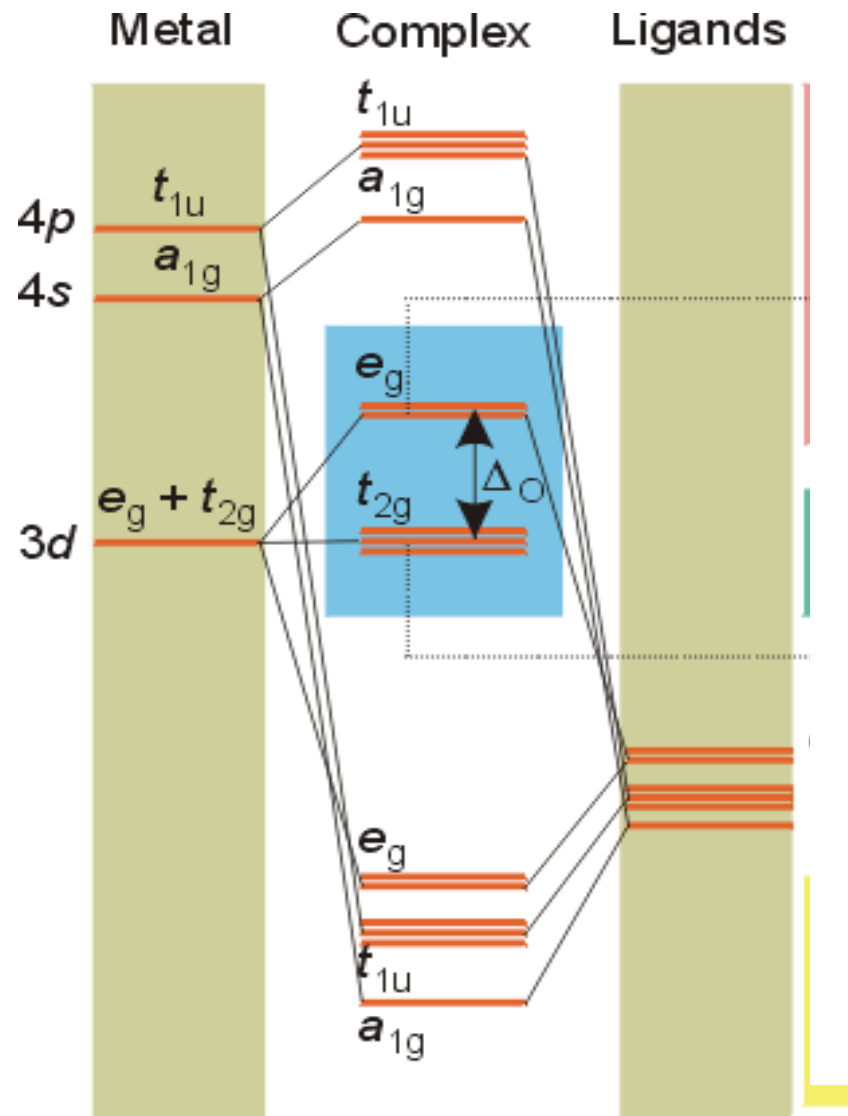
Excitation of core electrons to empty states.

Spectrum identifies with the  
empty Density of States

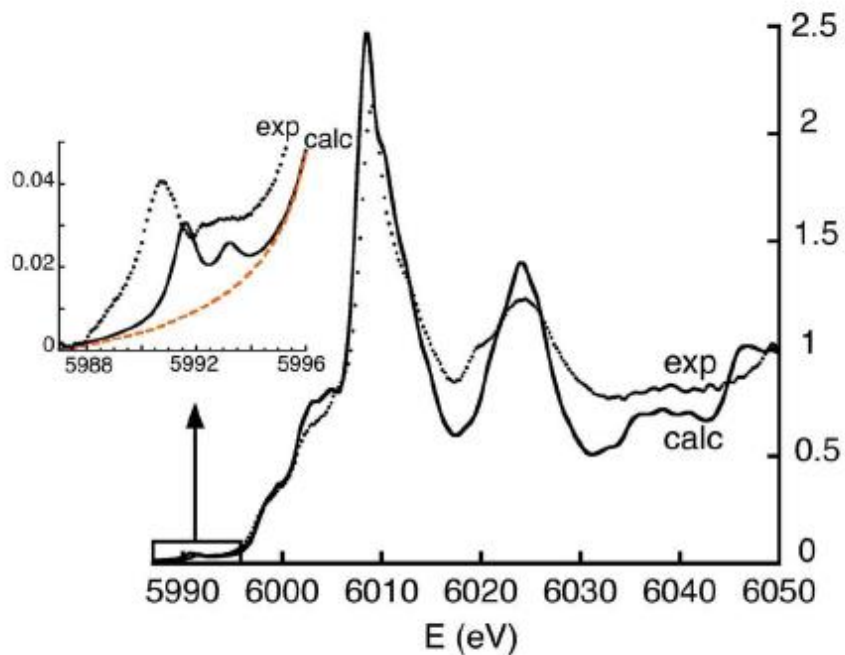
Works well for K edges (1s)

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

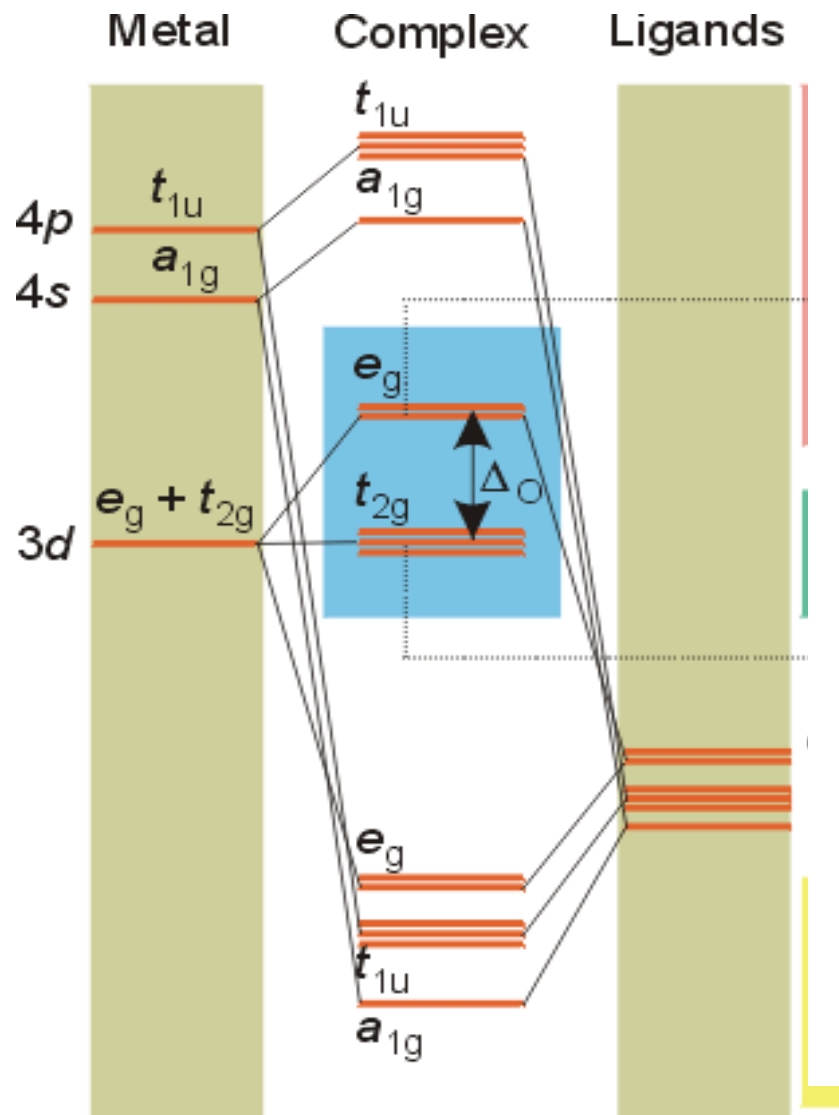
# Metal 1s XAS



# Metal 1s XAS



Cr<sup>3+</sup> in MgAl<sub>2</sub>O<sub>4</sub>



# Pre-edges structures in 1s XAS

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

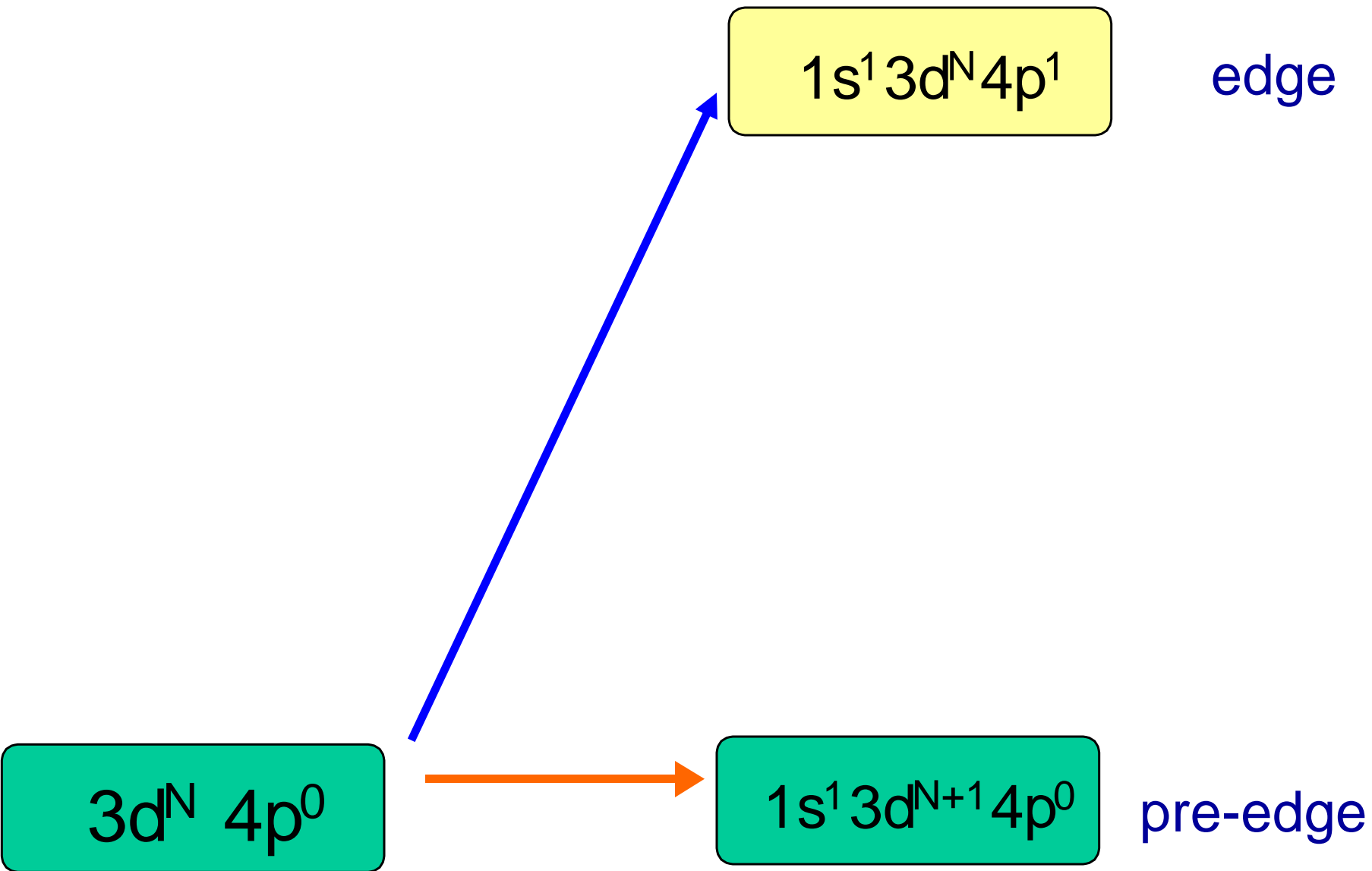
edge

$3d^N 4p^0$

The diagram illustrates the transition of an atom from its ground state to an excited state during a 1s X-ray absorption process. A blue arrow points from the ground state box to the excited state box. The ground state is labeled  $3d^N 4p^0$  and the excited state is labeled  $1s^1 3d^N 4p^1$ . The word "edge" is written to the right of the excited state box.

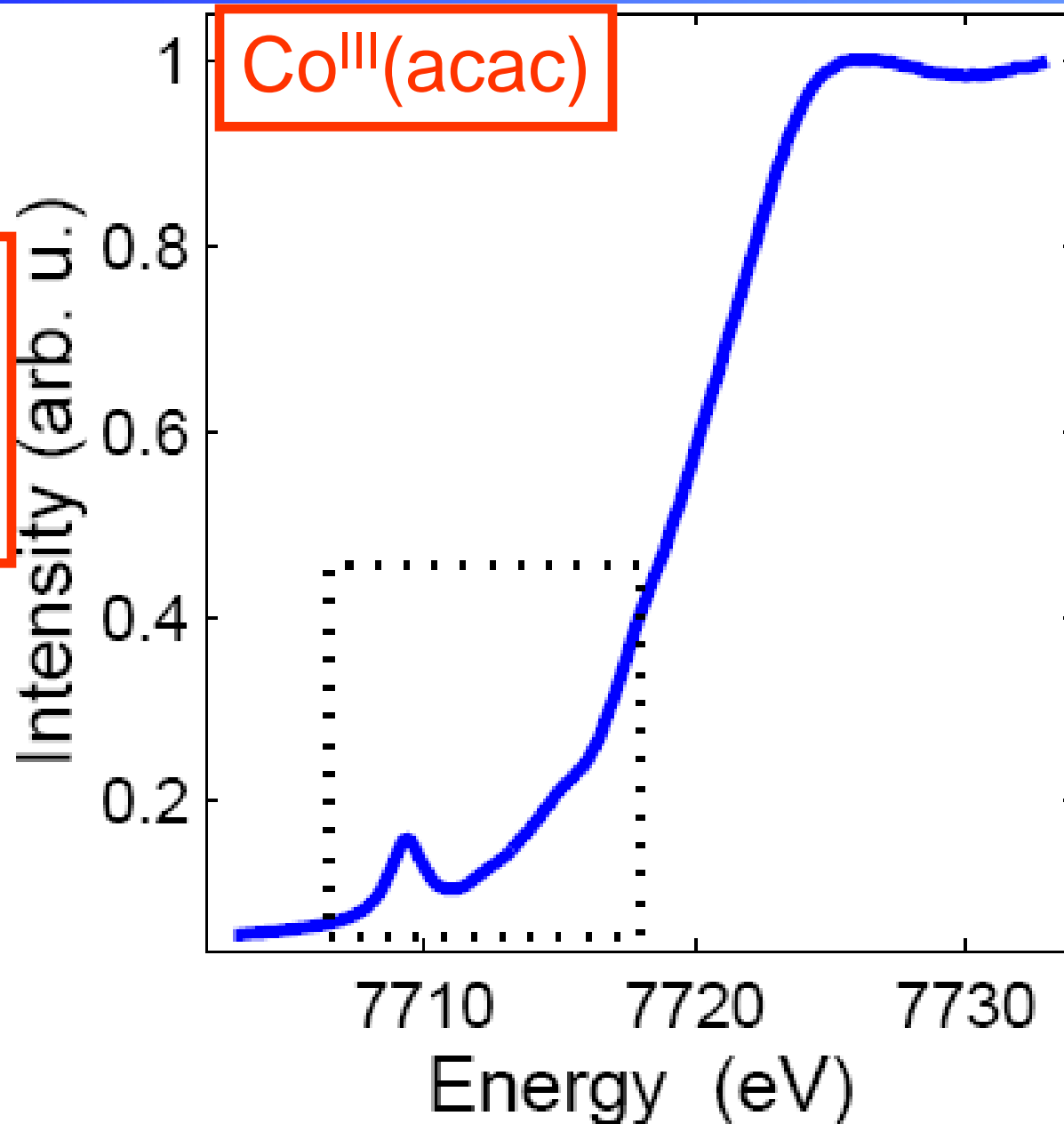


# Pre-edges structures in 1s XAS

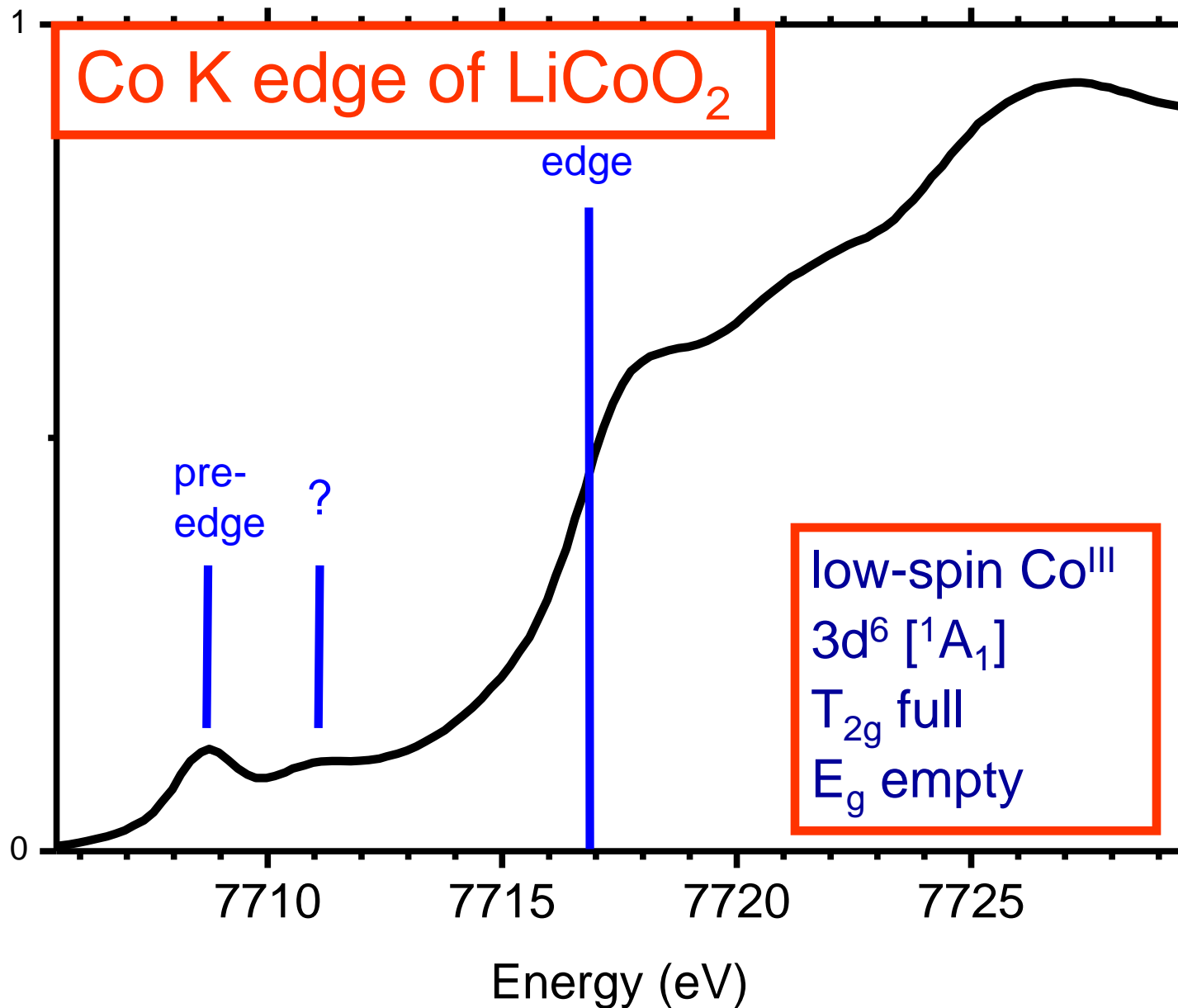


# Pre-edges structures in 1s XAS

low-spin  $\text{Co}^{\text{III}}$   
 $3d^6$  [ $^1A_1$ ]  
 $T_{2g}$  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

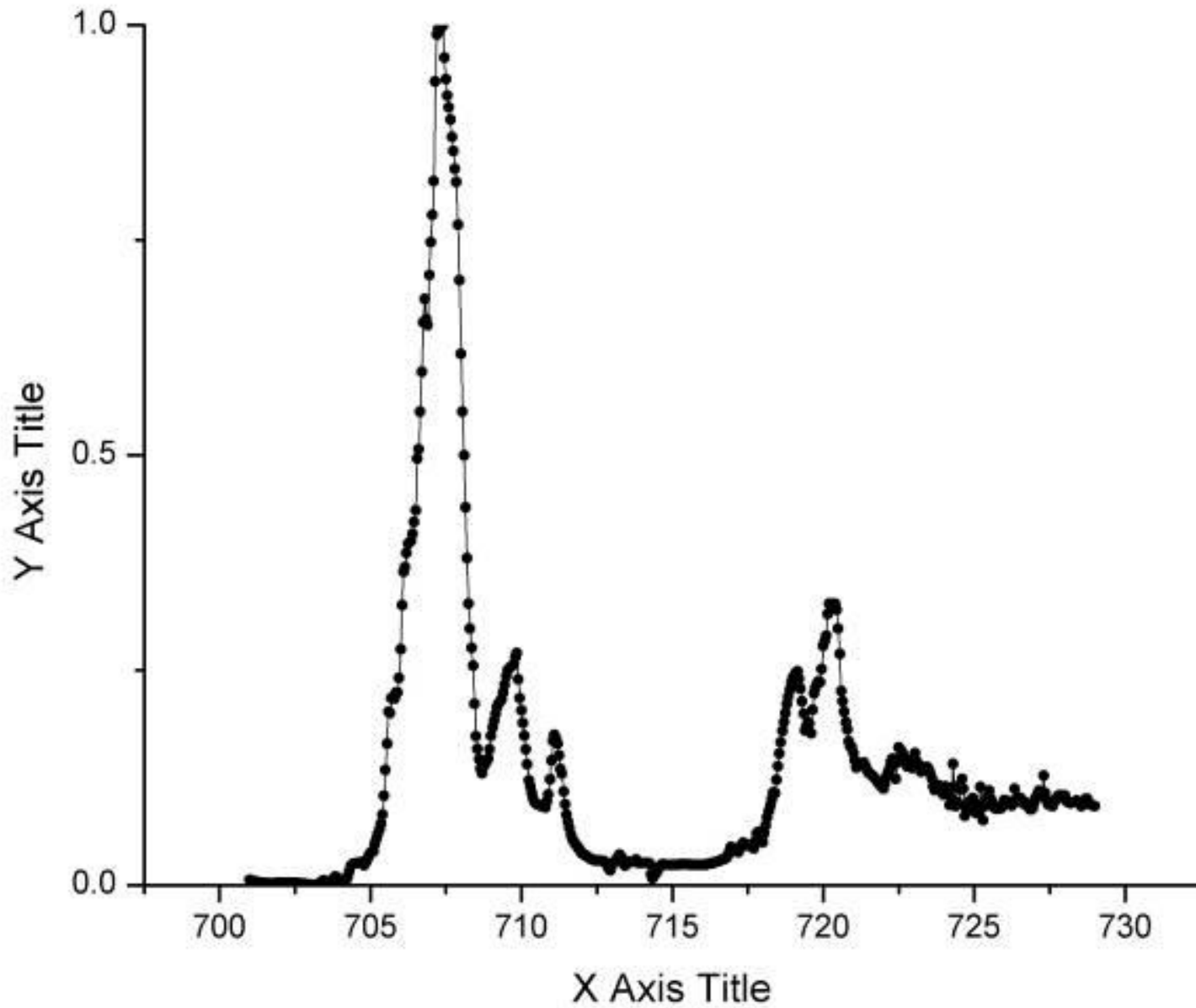
Fermi Golden Rule:

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

Single electron (excitation) approximation:

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

# Quiz: Calculate the 2p XAS spectrum of Fe atom



# XAS of an iron atom

Fermi Golden Rule:

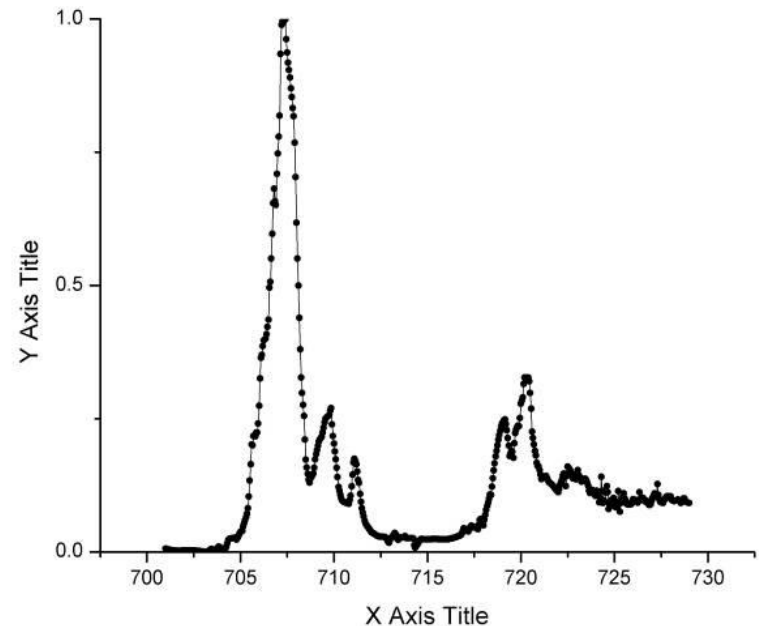
$$I_{\text{XAS}} = |\langle \Phi_f | \text{dipole} | \Phi_i \rangle|^2 \delta_{[\Delta E=0]}$$

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

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

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

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



# XAS of an iron atom

Fermi Golden Rule:

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

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

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

Single electron (excitation) approximation:

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

$$\Phi_{\text{core}} = 2p$$

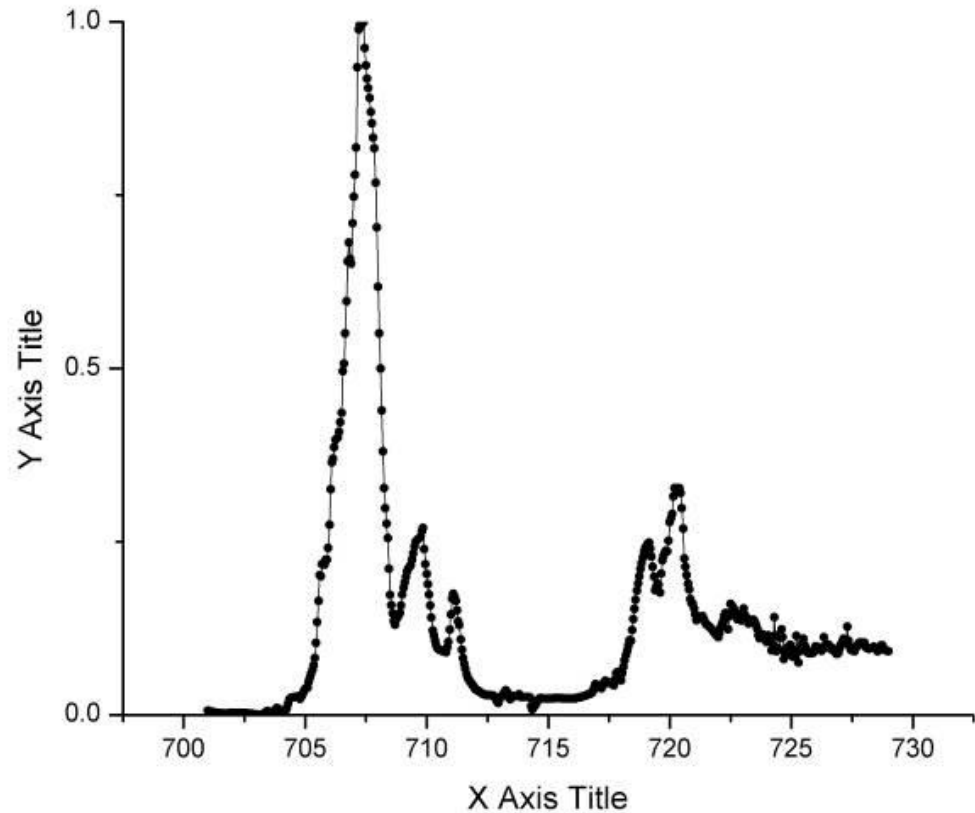
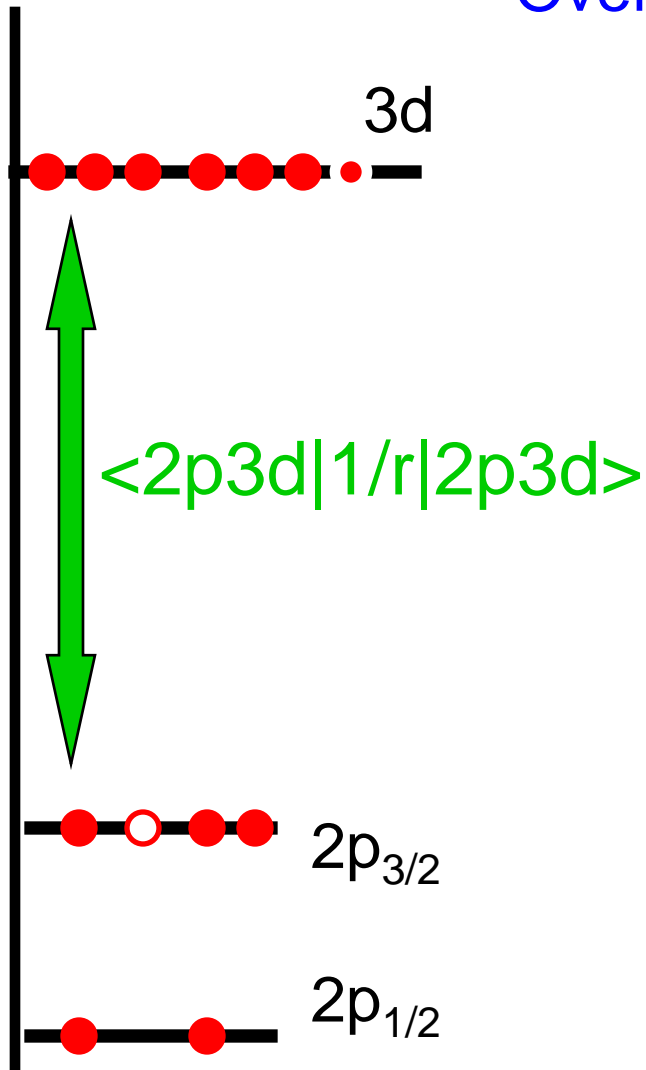
$$\Phi_{\text{empty}} = 3d$$

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

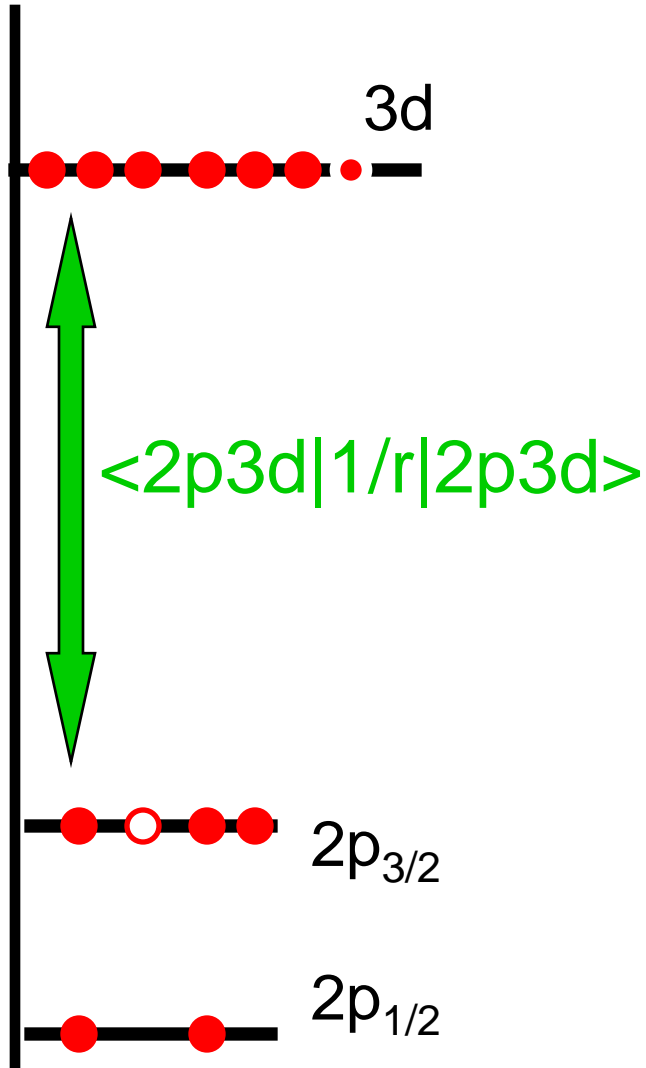


# XAS of an iron atom

Overlap of core and valence wave functions



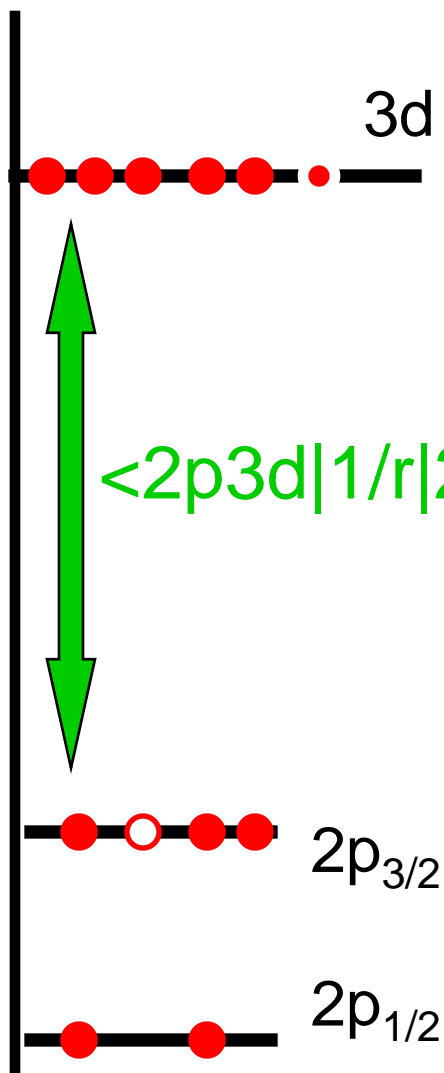
# XAS of atoms and solids



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

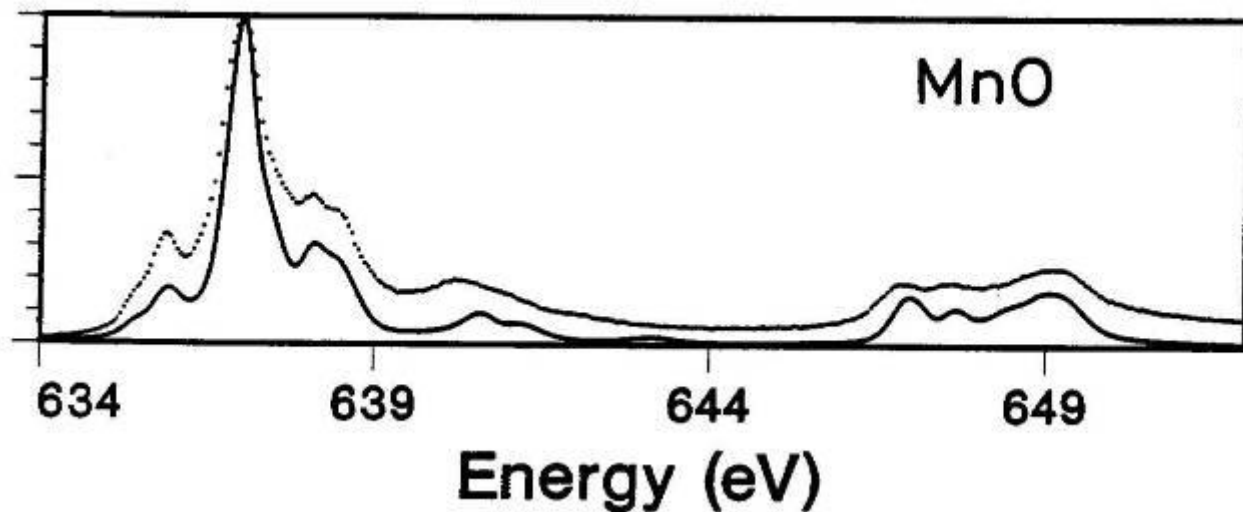
Higher order terms (Coulomb and exchange) are **NOT** screened in molecules and solids

# XAS of atoms and solids

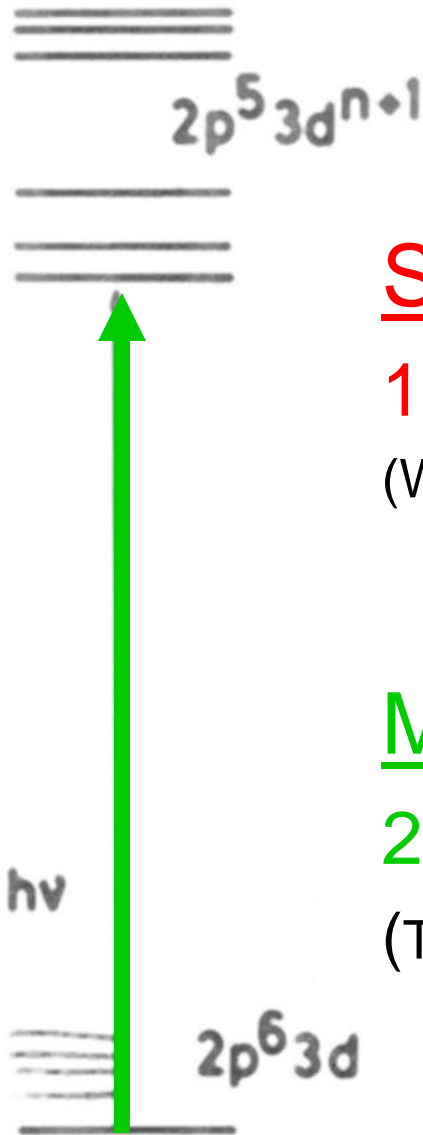
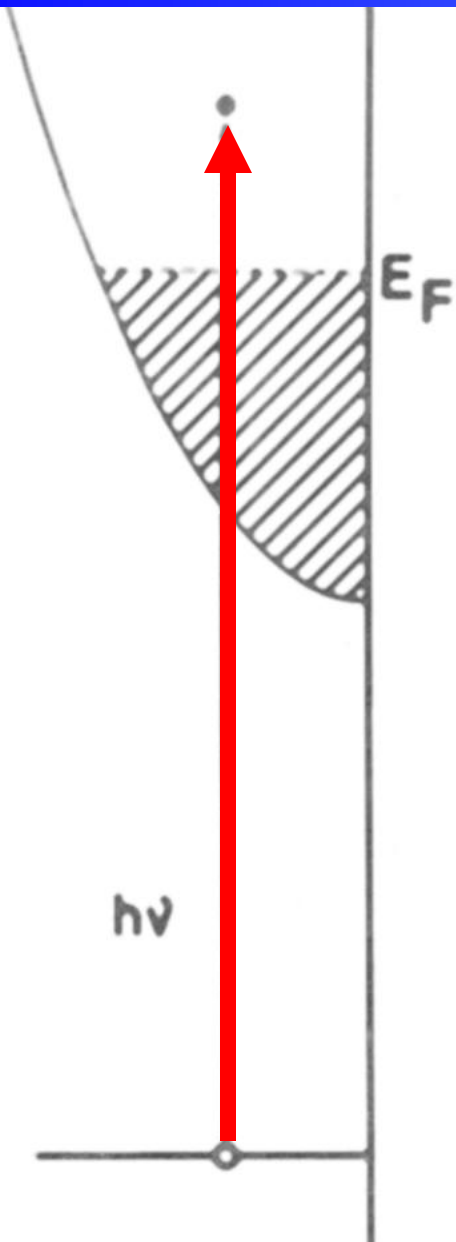


→ Single Particle model breaks down

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



# 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)

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

$2p^6 3d$

# Charge transfer multiplet program

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

ATOMIC PHYSICS

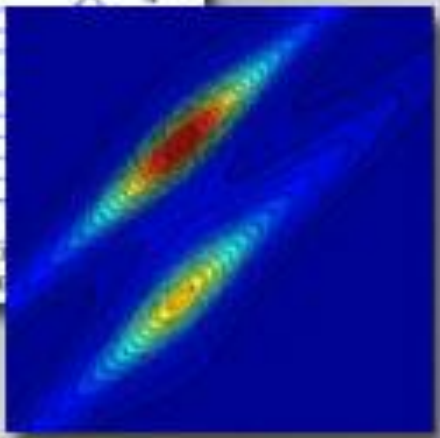
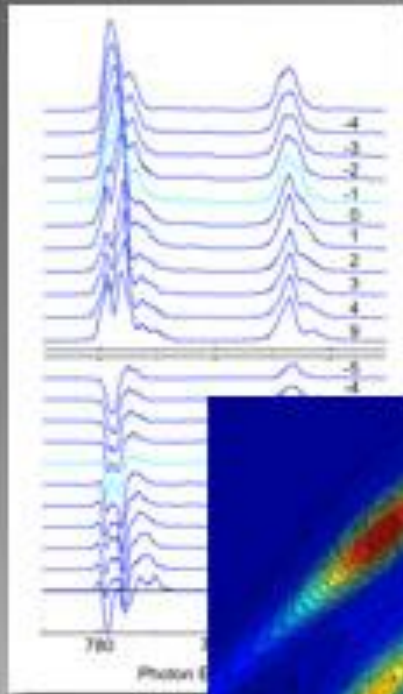


GROUP THEORY



MODEL HAMILTONIANS

# CTM4XAS program



## CTM4XAS 5.1

CHARGE TRANSFER MULTIPLY CALCULATIONS  
FOR X-RAY ABSORPTION SPECTROSCOPY

© Eli Stavitski and Frank de Groot, 2008-2010

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



# CTM4XAS program

CTM4XAS 5.2

Calculate Plot Fit Bundle Report Help

Configuration and spectroscopy

Electronic configuration  ...

Initial state

Final state

Initial state

Final state

XAS	XPS	XES	RIXS
<input checked="" type="radio"/> 2p	<input type="radio"/> 2p	<input type="radio"/> 1s2p	<input type="radio"/> 2p3d
<input type="radio"/> 3p	<input type="radio"/> 3p	<input type="radio"/> 1s3p	<input type="radio"/> 3p3d
<input type="radio"/> 4p	<input type="radio"/> 1s		<input type="radio"/> 1s2p
<input type="radio"/> 3d	<input type="radio"/> 2s		<input type="radio"/> 1s3p
<input type="radio"/> 4d	<input type="radio"/> 3s		
<input type="radio"/> 5d			
<input checked="" type="radio"/> 1s			

Slater integral reduction (%)

Fdd Fpd Gpd

SO coupling reduction (%)

Core Valence

Crystal field parameters (eV)

Symmetry  ...

Initial state Final state

10 Dq	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>
Dt	<input type="text" value="0"/>	<input type="text" value="0"/>
Ds	<input type="text" value="0"/>	<input type="text" value="0"/>
M (meV)	<input type="text" value="0"/>	<input type="text" value="0"/>

Charge transfer parameters (eV)

<input type="checkbox"/> CT	<input type="text" value="2.0"/>	T(eg)
Delta	<input type="text" value="0"/>	<input type="text" value="2.0"/> T(eg)
Udd	<input type="text" value="0"/>	<input type="text" value="1.0"/> T(t2g)
Upd	<input type="text" value="0"/>	<input type="text" value="1.0"/> T(t2g)

Clean up

Autaname

Bundle

Run

Plotting

Spectrum  ... i X

Lorentzian broadening

Split

Gaussian broadening

Temperature, K

Energy range (eV)  -

Suppress sticks

Normalize

Auto Plot

Stack

Plot

Plot  Batch  Fit

Ready

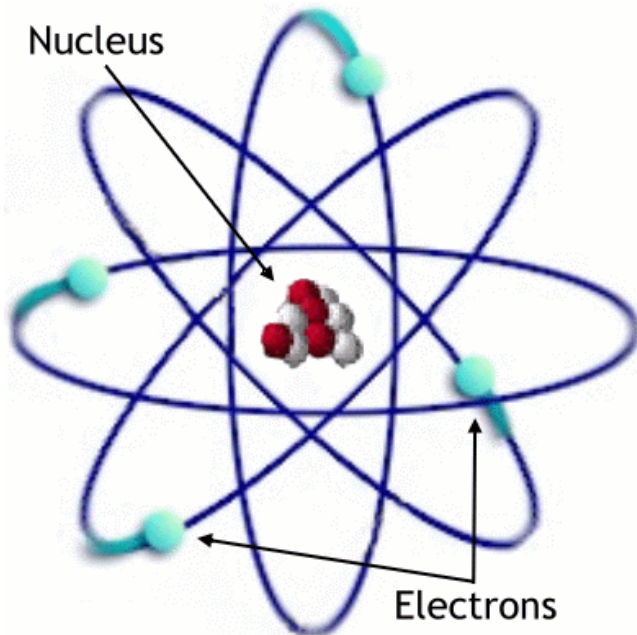


# Atomic Multiplet Theory

$$H\Psi = E\Psi$$

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

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

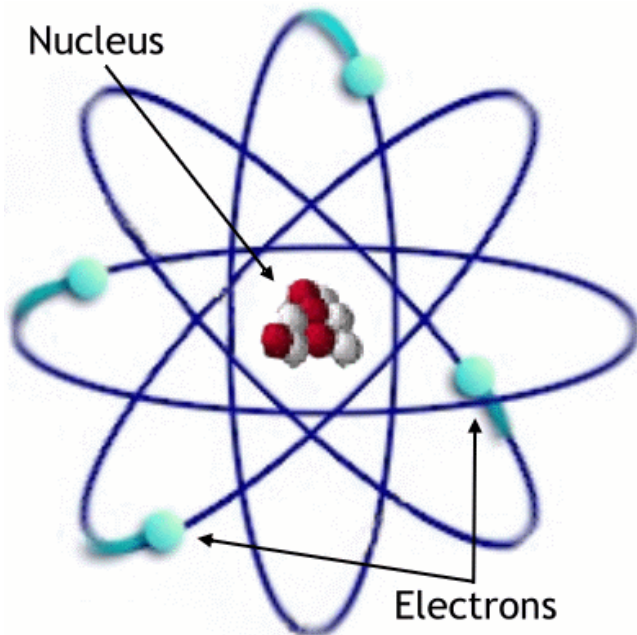


# Atomic Multiplet Theory

$$H\Psi = E\Psi$$

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

- 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:

$$\underline{\Delta S = 1 \text{ and } \Delta L = \pm 1}$$

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

$$\Delta J = \pm 1 \text{ or } 0$$

$$(J \neq 0)$$

# Term symbols

- Term Symbol  $2S+1L_J$
- $L=0,1,2,3,4 \rightarrow S, P, D, F, G$
- 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

- $S=1/2, \quad L=0$

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

## Term symbols of a 3d electron

- $S=1/2, \quad L=2$

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

# Term symbols

2p3d-configuration (6x10 = 60 states)

all combinations are possible:

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

Add J-quantum numbers:

$$\begin{aligned} & {}^1P_1, {}^1D_2, {}^1F_3 \\ & + {}^3P_0, {}^3P_1, {}^3P_2 \\ & + {}^3D_1, {}^3D_2, {}^3D_3, \\ & + {}^3F_2, {}^3F_3, {}^3F_4, \end{aligned}$$



## 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

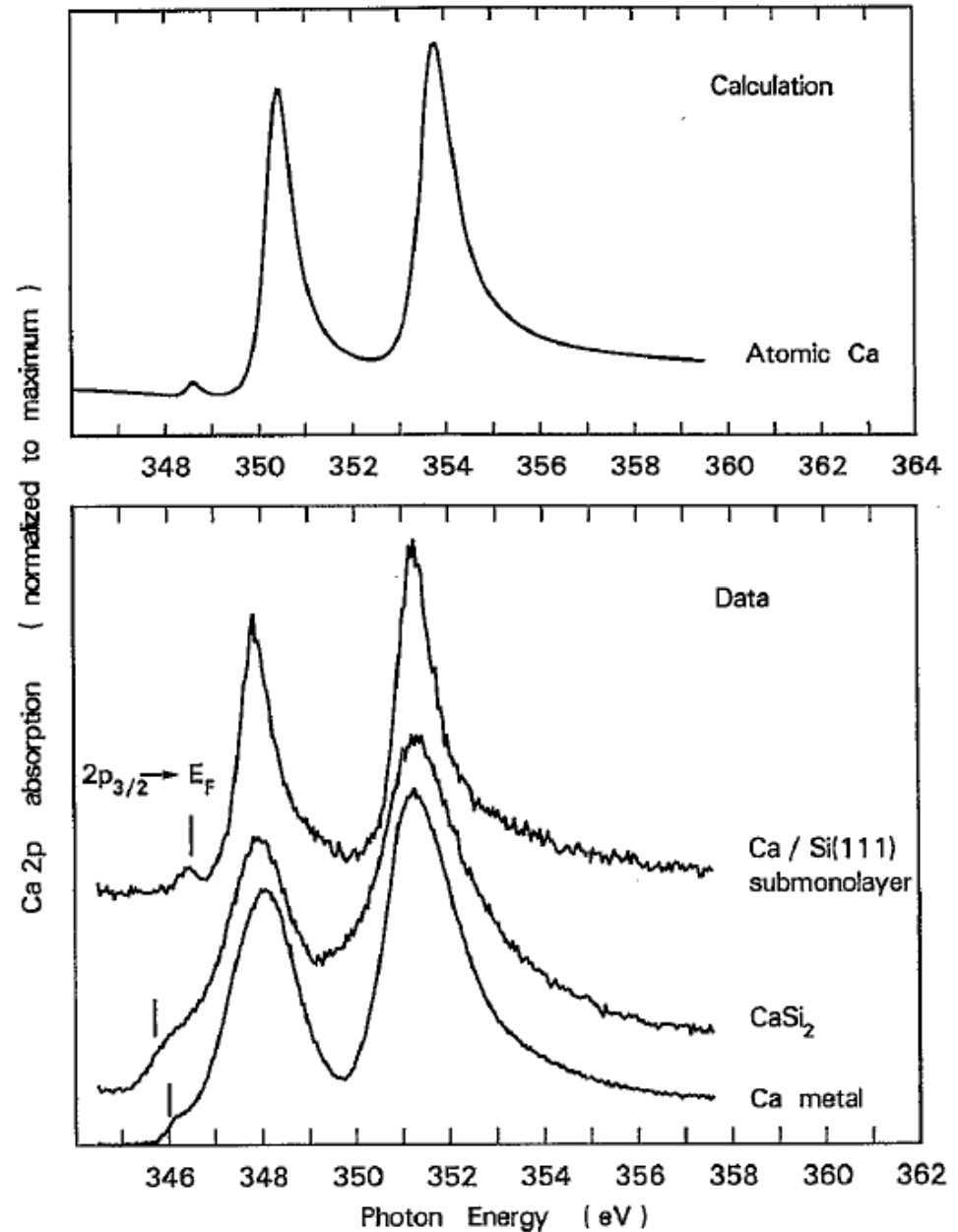
→	$^3P_0$	$^1P_1$ $^3P_1$ $^3D_1$	$^3P_2$			
→			$^1D_2$ $^3D_2$	$^3D_3$		
→			$^3F_2$	$^1F_3$ $^3F_3$	$^3F_4$	
	[	1	3	4	3	1]
		1	3x3	4x5	3x7	1x9

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

Selection rule: Final state must have  $J'=1$

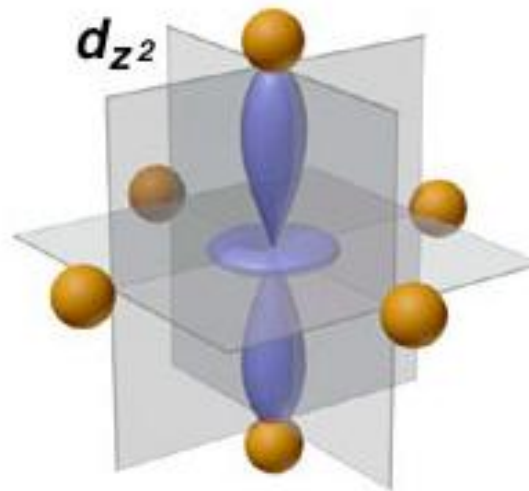
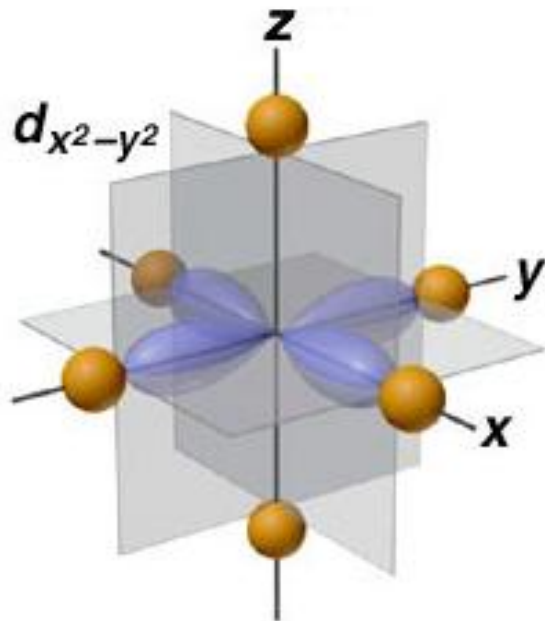
# 2p XAS of a Ca atom

Ground state is  $3d^0$

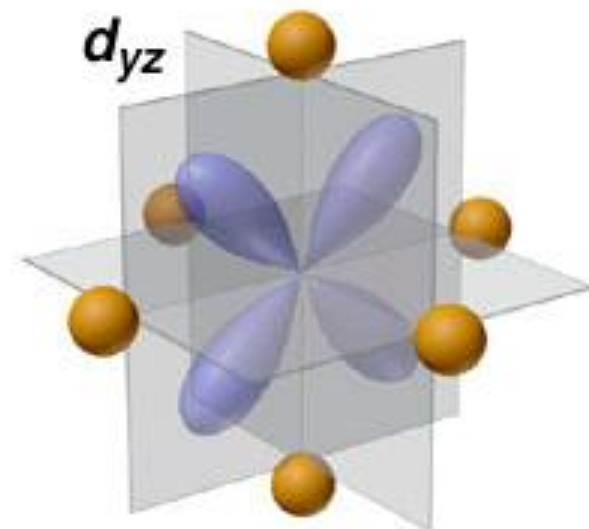
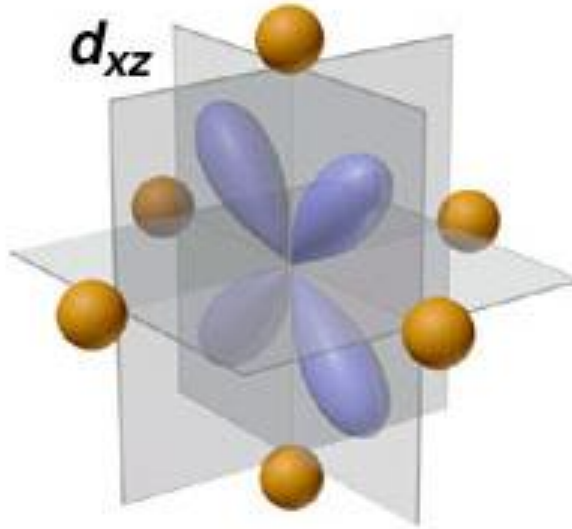
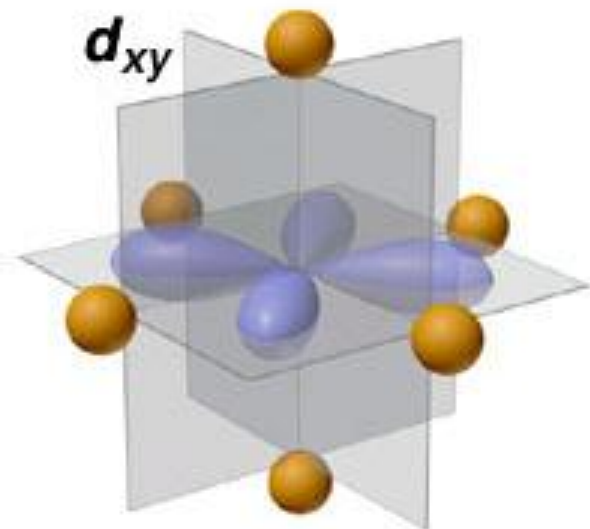


# 2p XAS of $\text{ScF}_3$ : crystal fields

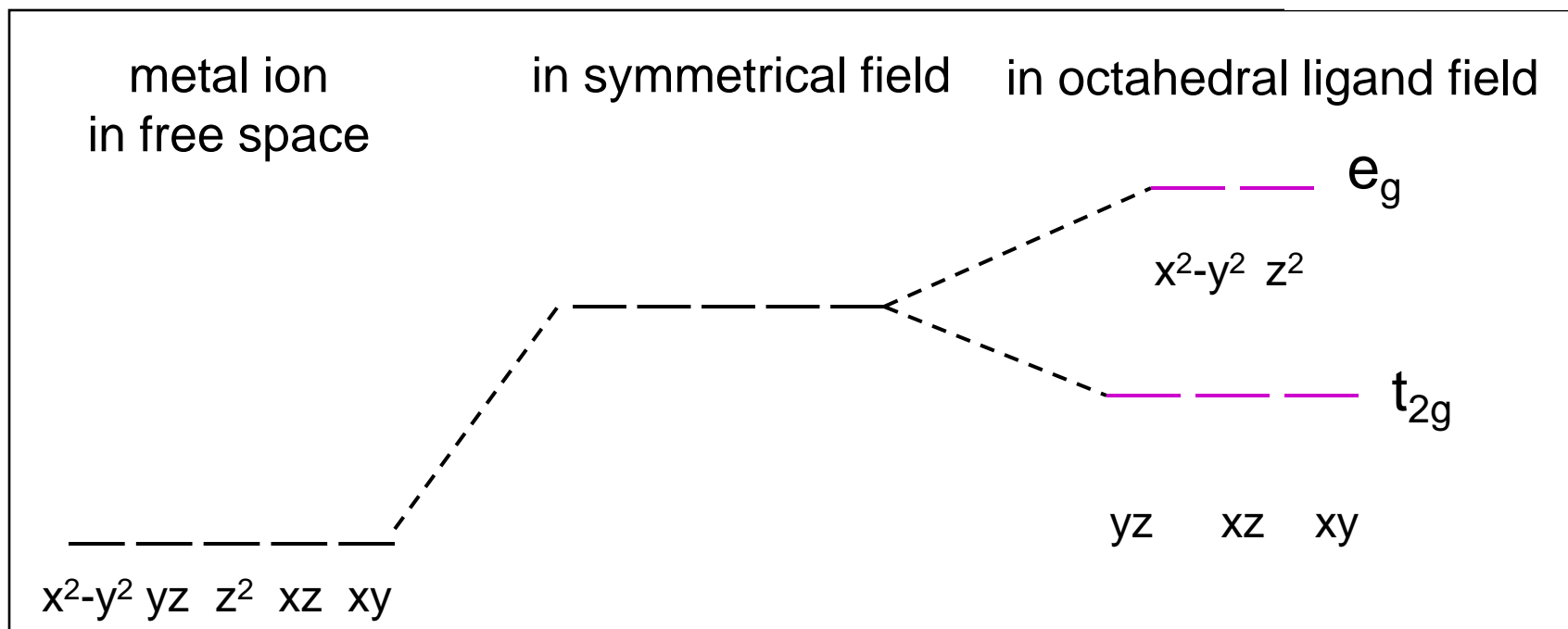
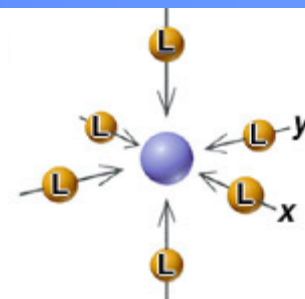
$e_g$  states



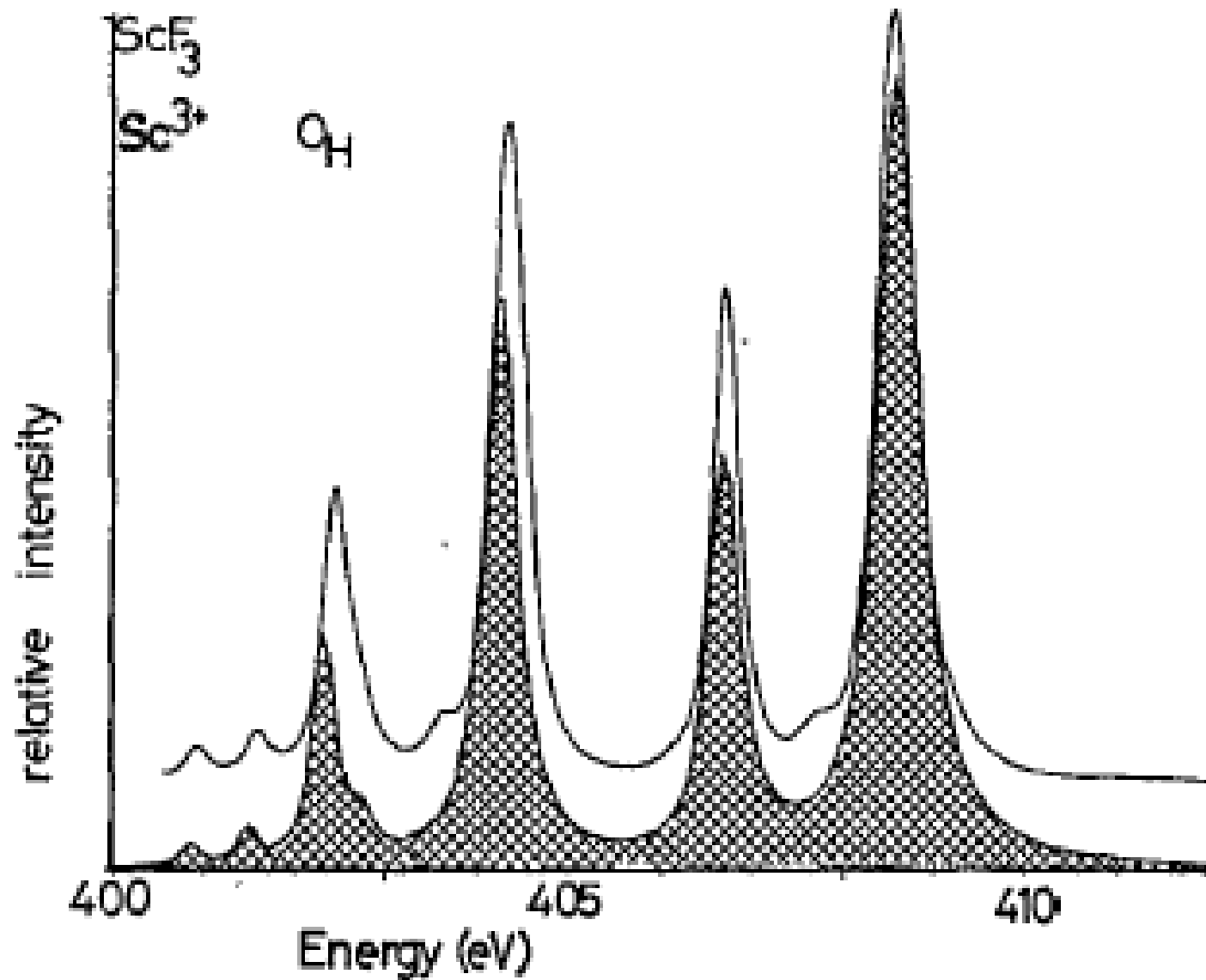
$t_{2g}$  states



# 2p XAS of $\text{ScF}_3$ : crystal fields



# 2p XAS of ScF<sub>3</sub>



# Calculations with CTM4XAS

The screenshot displays the CTM4XAS 5.2 software interface, which is used for calculating and plotting XAS, XPS, XES, and RIXS spectra. The interface is divided into several sections:

- Configuration and spectroscopy:** This section allows users to define the electronic configuration (e.g., Ni<sup>2+</sup>), initial and final states, and Slater integrals for Fdd, Fpd, and Gpd. It also includes options for SO coupling reduction and XAS/XPS/XES/RIXS selection.
- Crystal field parameters (eV):** This section is highlighted with a red box and includes a Symmetry dropdown menu (set to Oh), initial and final state checkboxes, and input fields for 10 Dq, Dt, Ds, and M (meV).
- Charge transfer parameters (eV):** This section includes checkboxes for CT and input fields for Delta, Udd, and Upd, along with their corresponding transition energies (T(eg), T(t2g)).
- Plotting:** This section includes a Spectrum dropdown menu (set to XAS), Lorentzian broadening parameters (0.2 and 0.4), a Split checkbox (800), Gaussian broadening (0.2), Temperature (K), Energy range (eV), and checkboxes for Suppress sticks, Normalize, Stack, and Auto Plot.

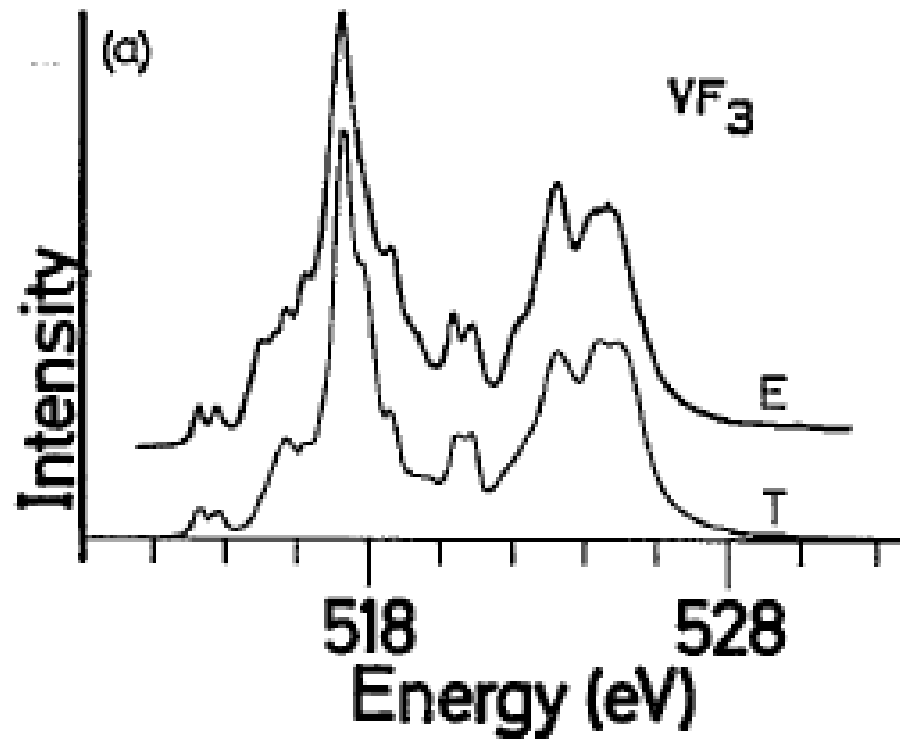
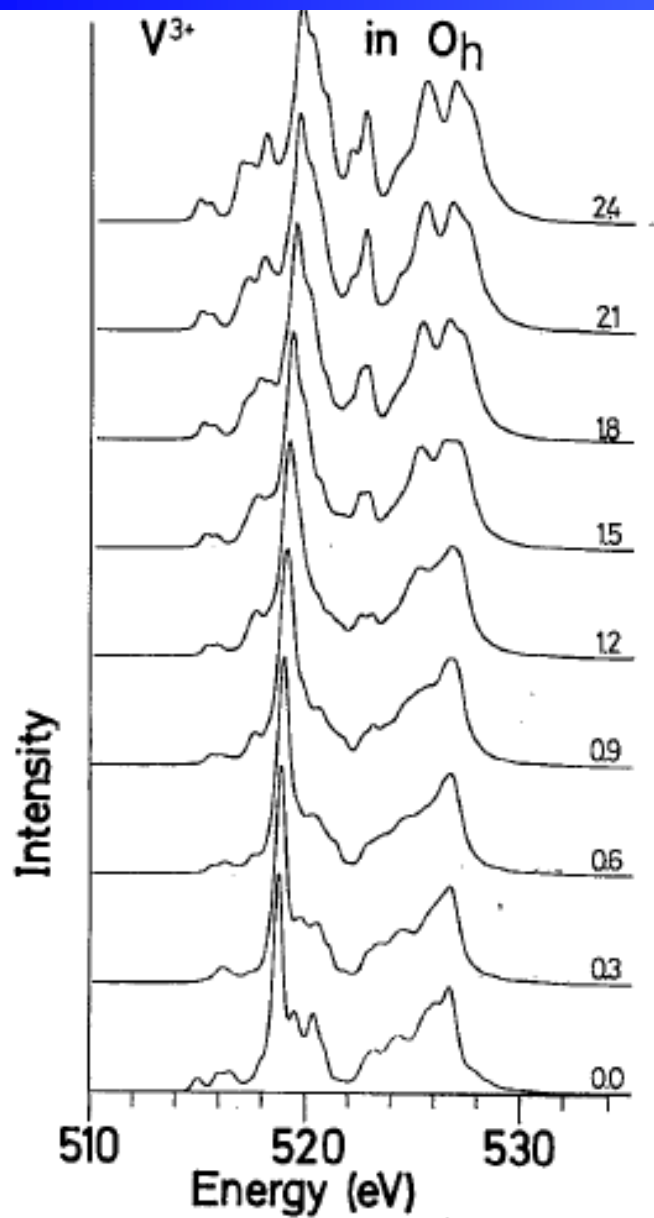
The interface also features a menu bar (Calculate, Plot, Fit, Bundle, Report, Help) and a status bar at the bottom left showing "Ready". A "Run" button is located at the bottom center, and a "Plot" button is at the bottom right.

## 2p XAS of transition metal ions

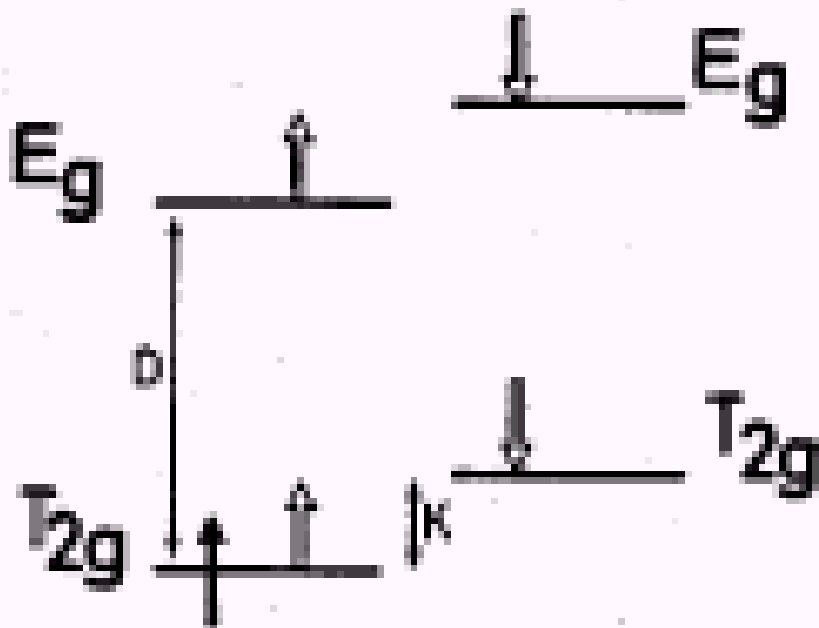
- Ground state is  $3d^N$ : determine symmetry
- Hund's rule: High-spin ground states
- max S, max L, max J
- Effect of crystal field splitting
- High spin or low spin
- Effect of 3d spin-orbit coupling
- Charge transfer effects



# 2p XAS of $\text{VF}_3$



# High-spin or low-spin



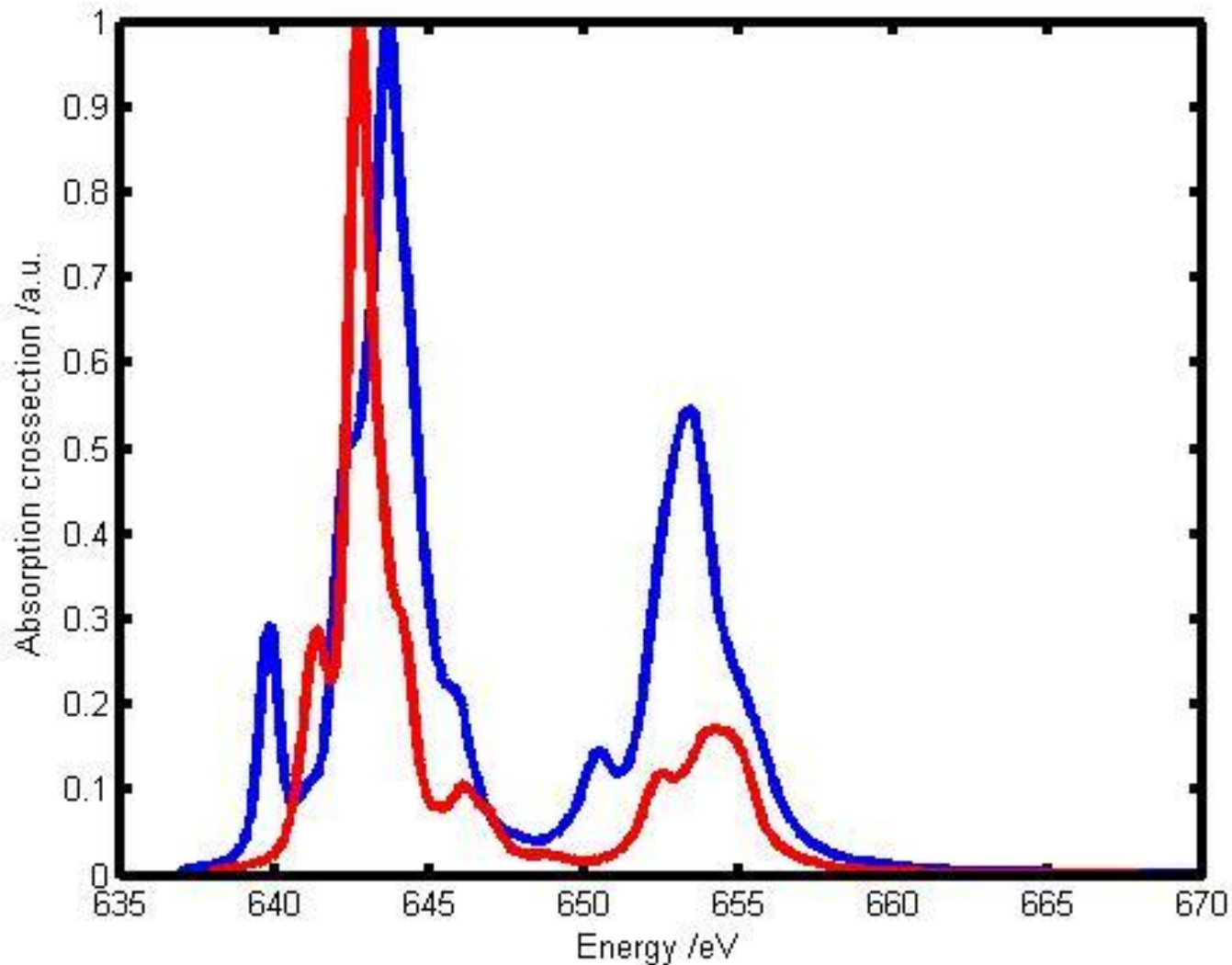
$10Dq > 3J$   
( $d^4$  and  $d^5$ )

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

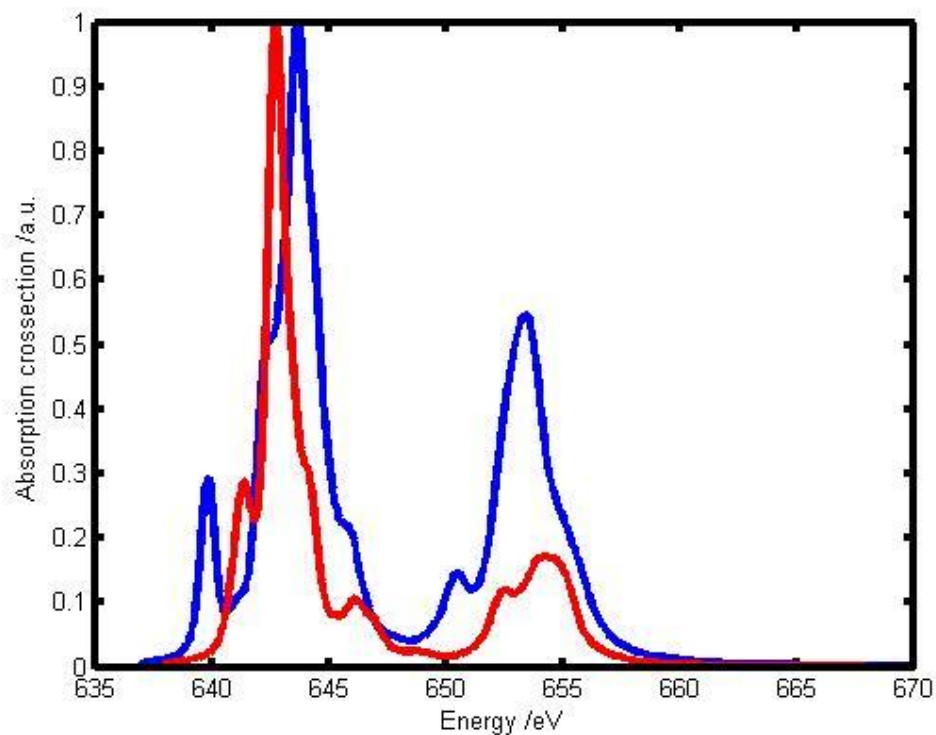
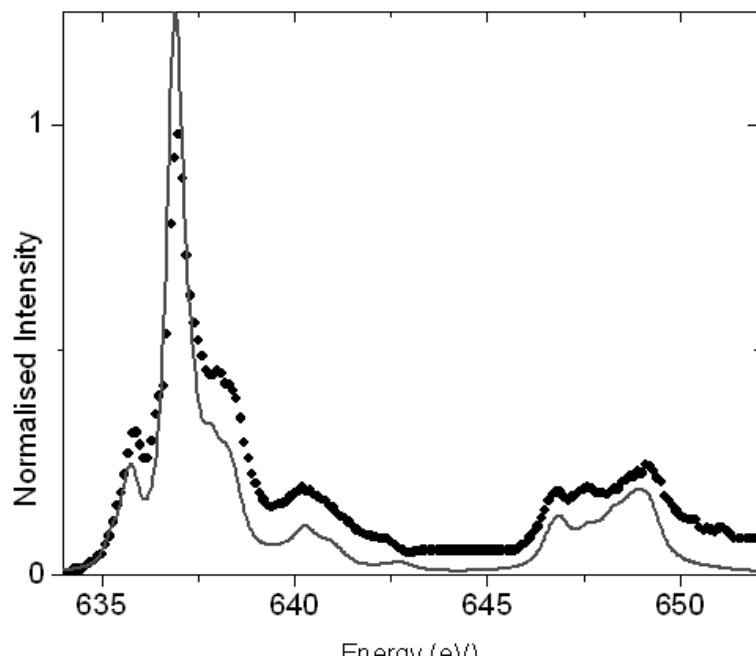
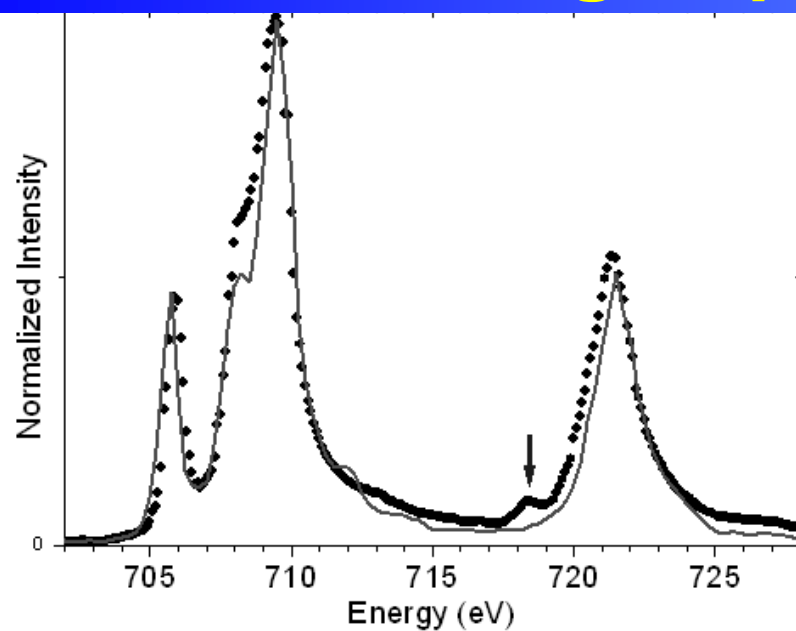
# High-spin or low-spin

High-spin:  $10Dq = 1.2$

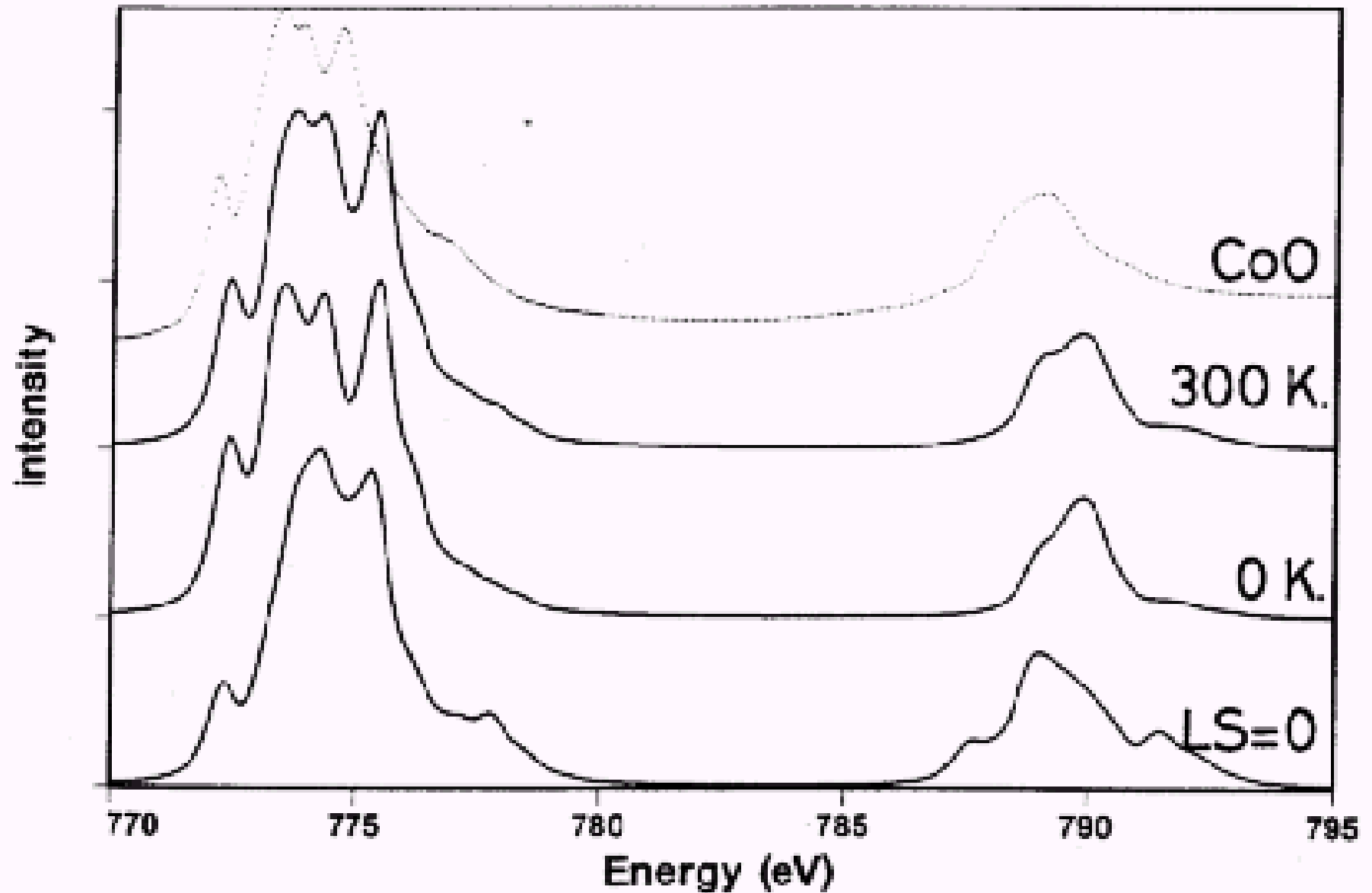
Low-spin:  $10Dq = 3.0$



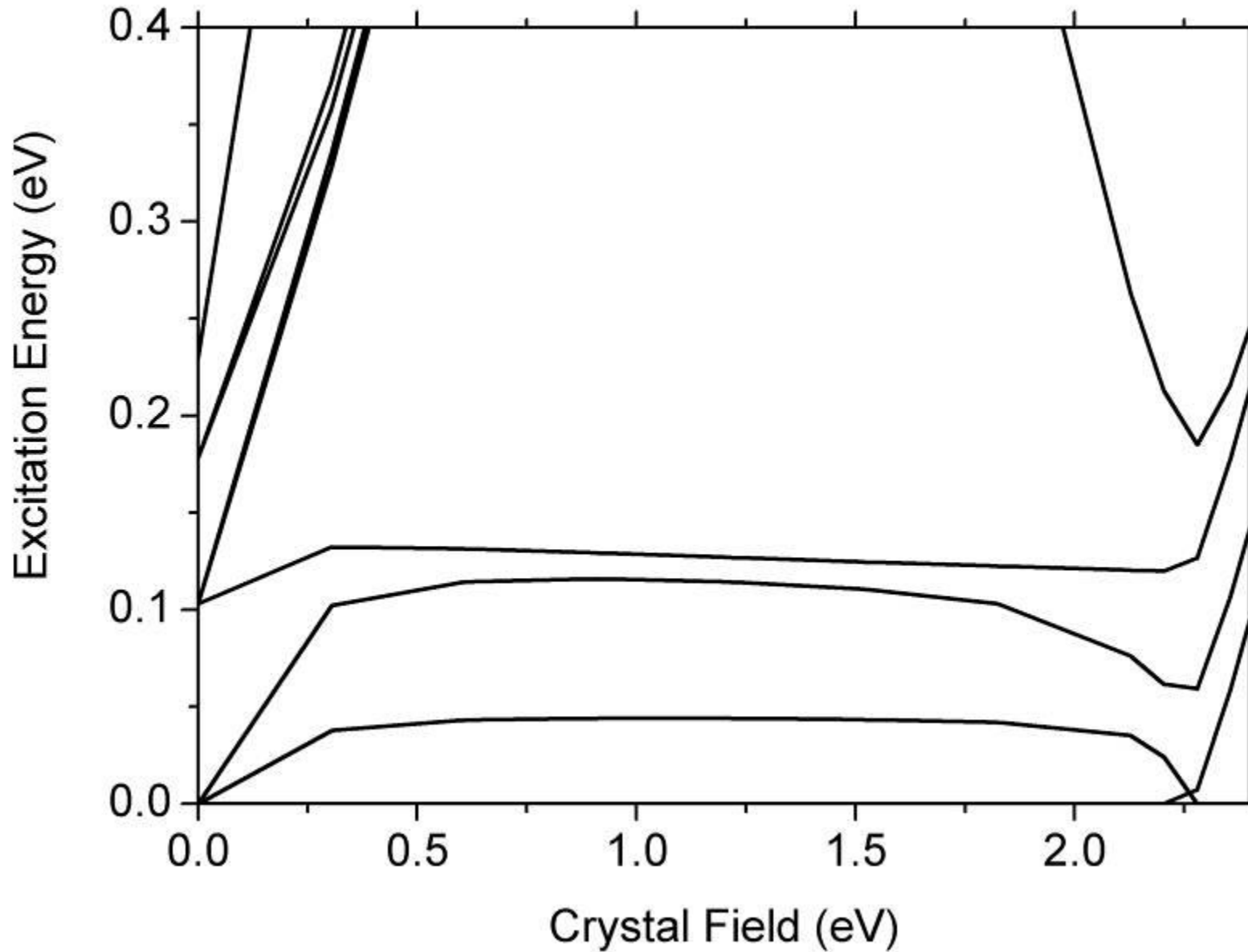
# High-spin or low-spin



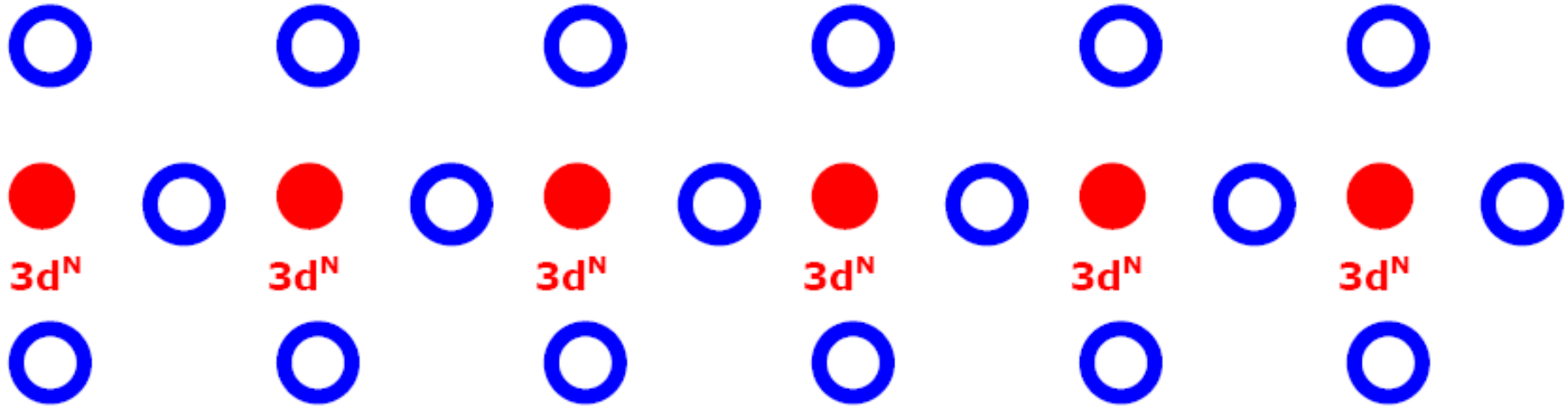
# 3d spin-orbit coupling



# 3d spin-orbit coupling



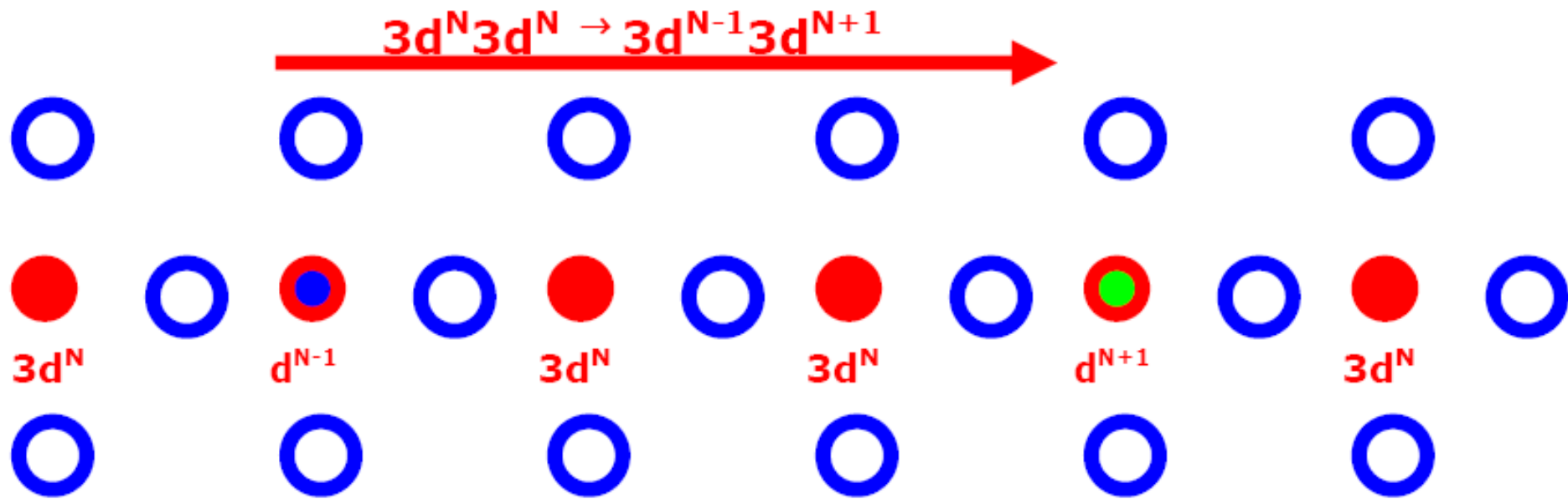
# Charge transfer effects



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

Charge fluctuations

# Charge transfer effects



Hubbard  $U$  for a  $3d^8$  ground state:

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

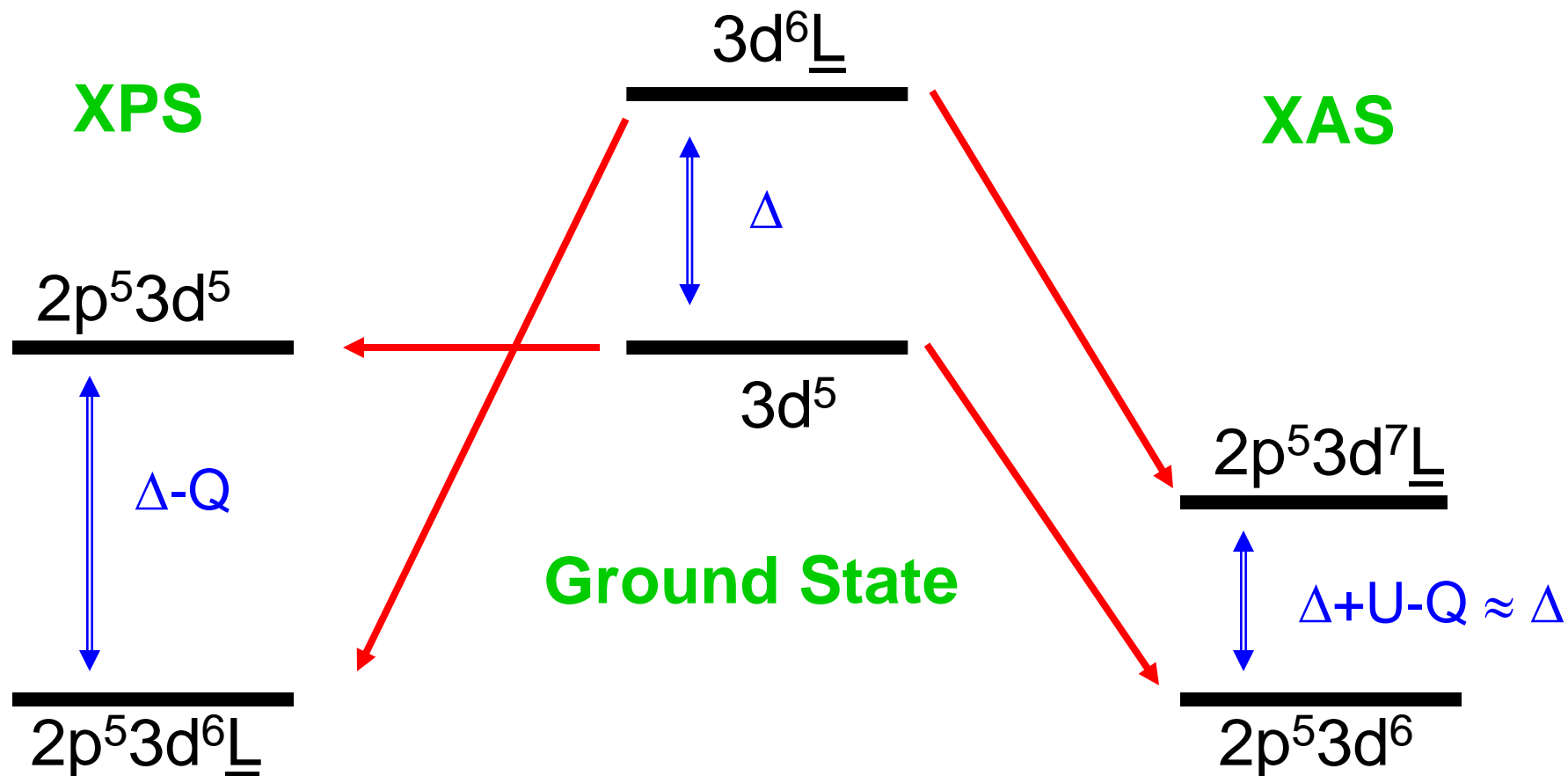
Ligand-to-Metal Charge Transfer (LMCT):

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



# Charge transfer effects

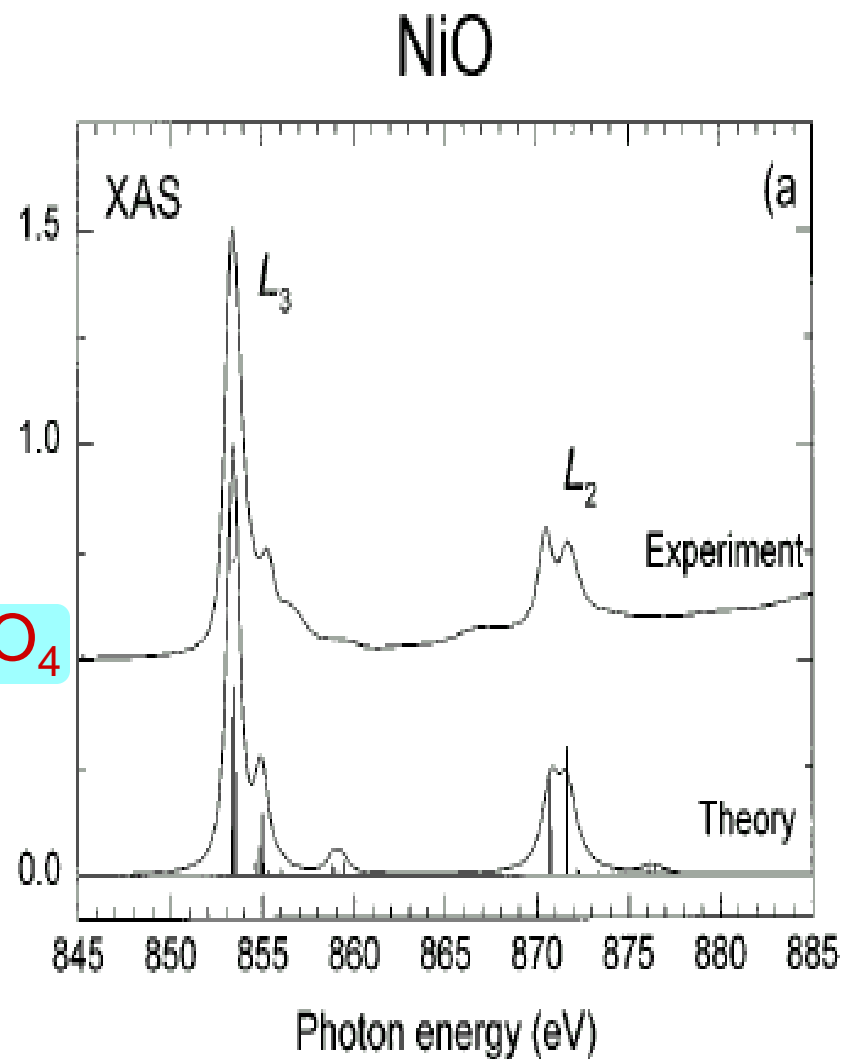
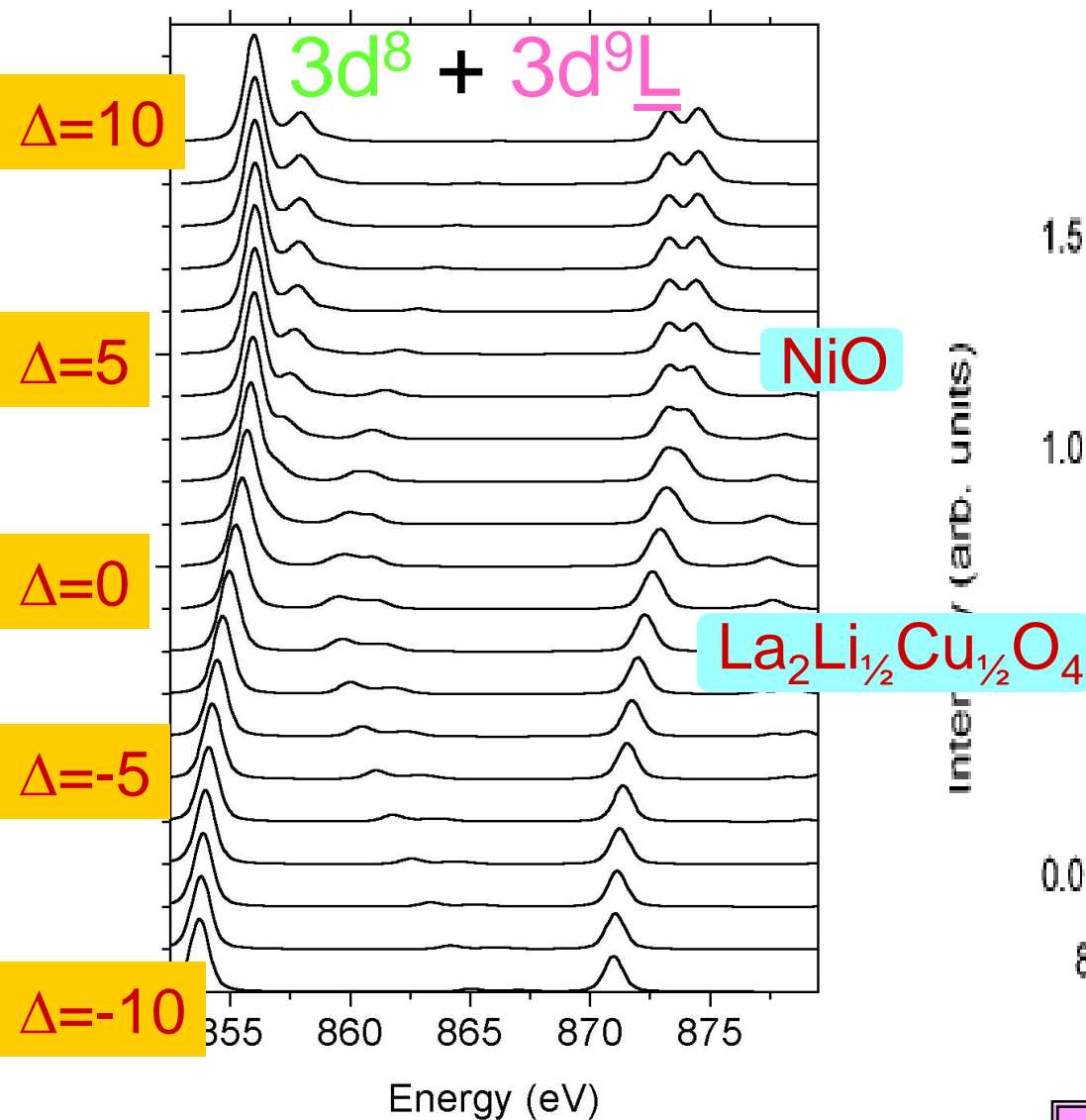
- Transition metal oxide: Ground state:  $3d^5 + 3d^6\bar{\underline{L}}$
- Energy of  $3d^6\bar{\underline{L}}$ : Charge transfer energy  $\Delta$



# Charge Transfer effects

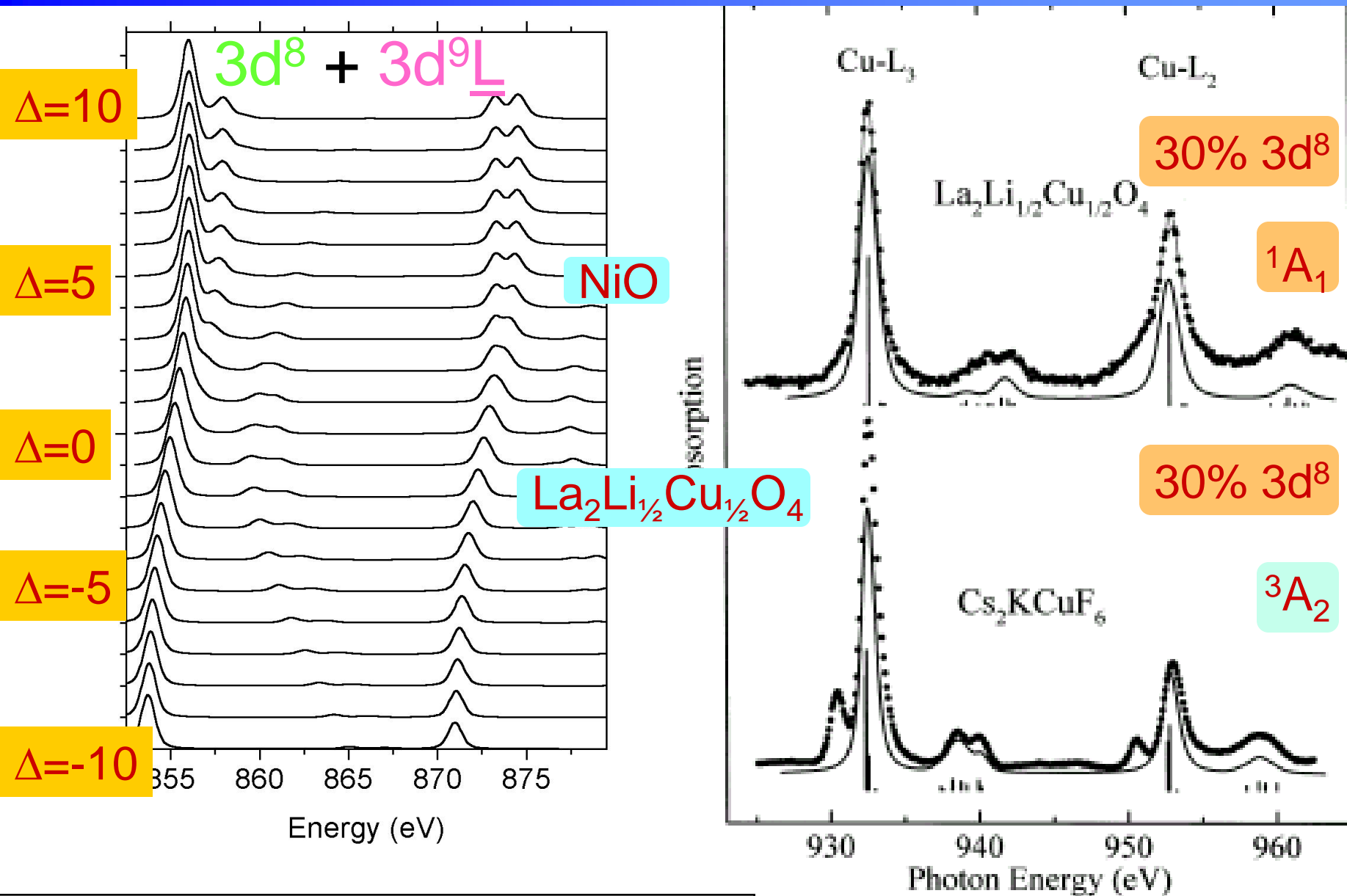
- High valent oxides ( $\text{Cu}^{3+}$ )
- Systems with  $\pi$ -bonds

# Charge Transfer effects in XAS



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

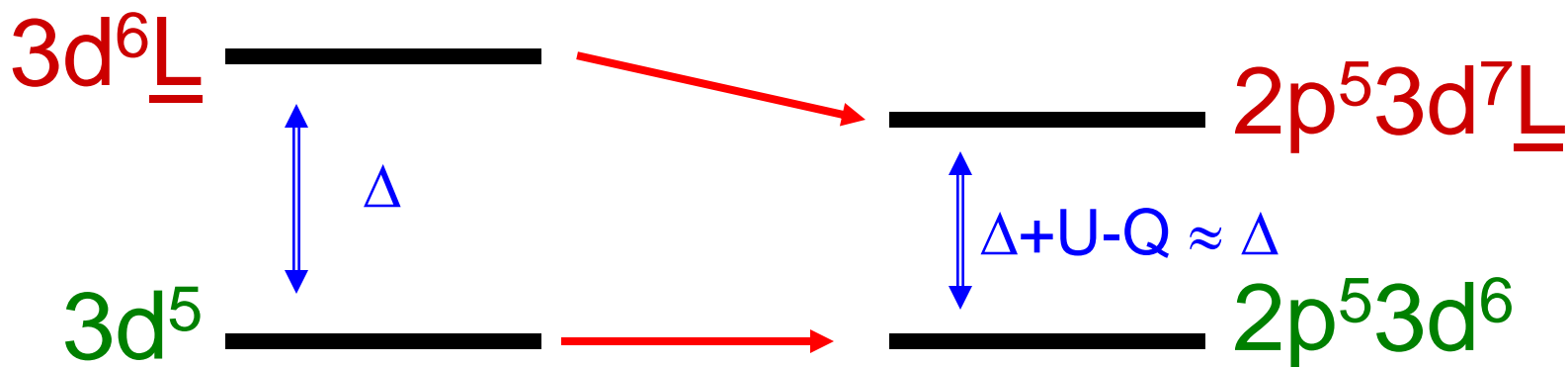
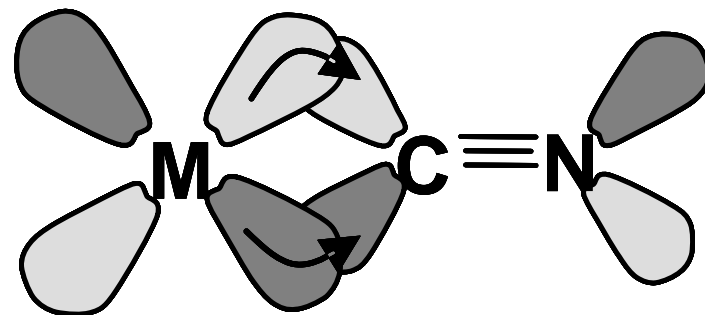
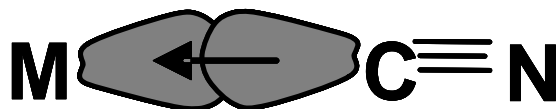
# Charge Transfer effects in XAS



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

# LMCT and MLCT: $\pi$ - bonding

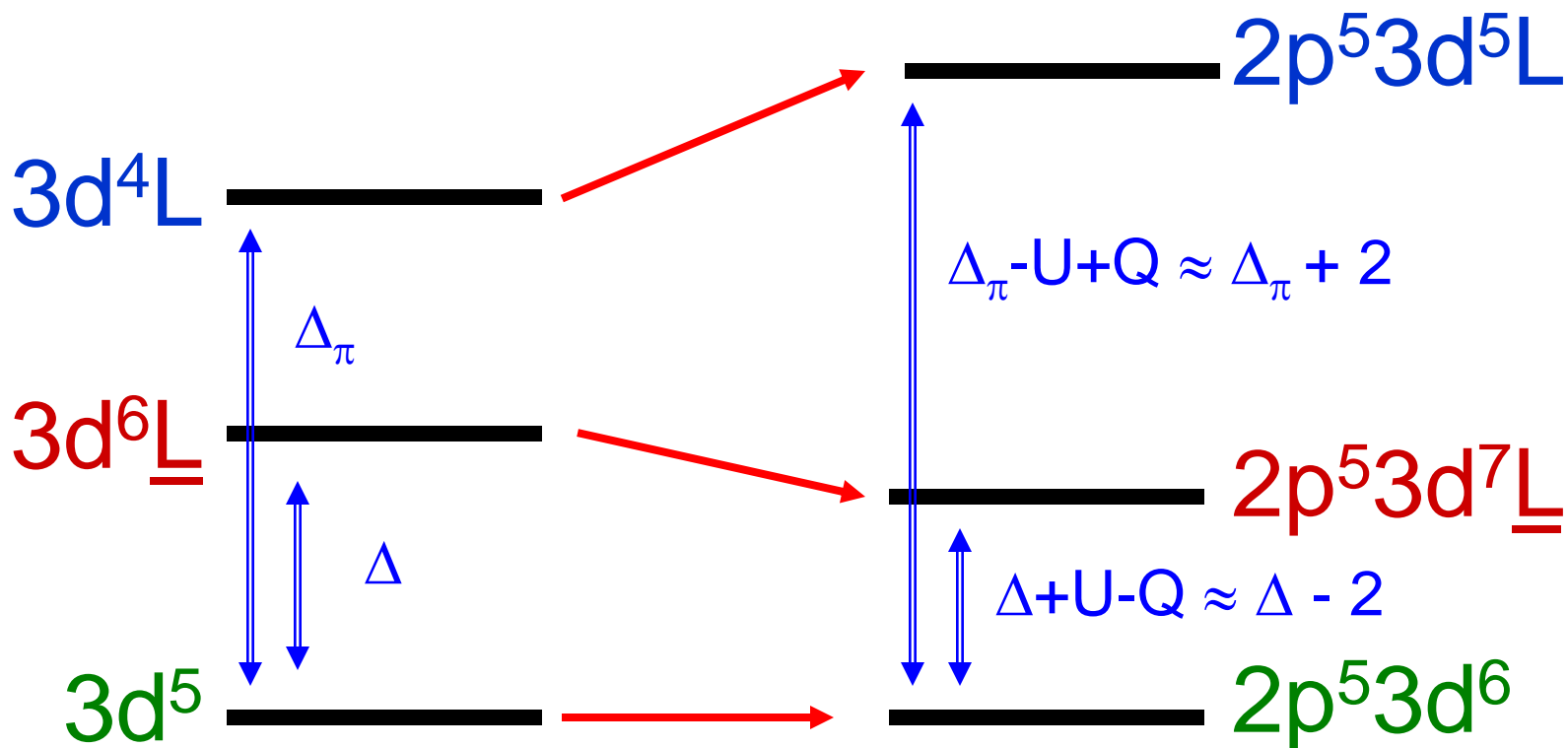
Fe<sup>III</sup>: Ground state:  $3d^5 + 3d^6\underline{\underline{L}}$



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

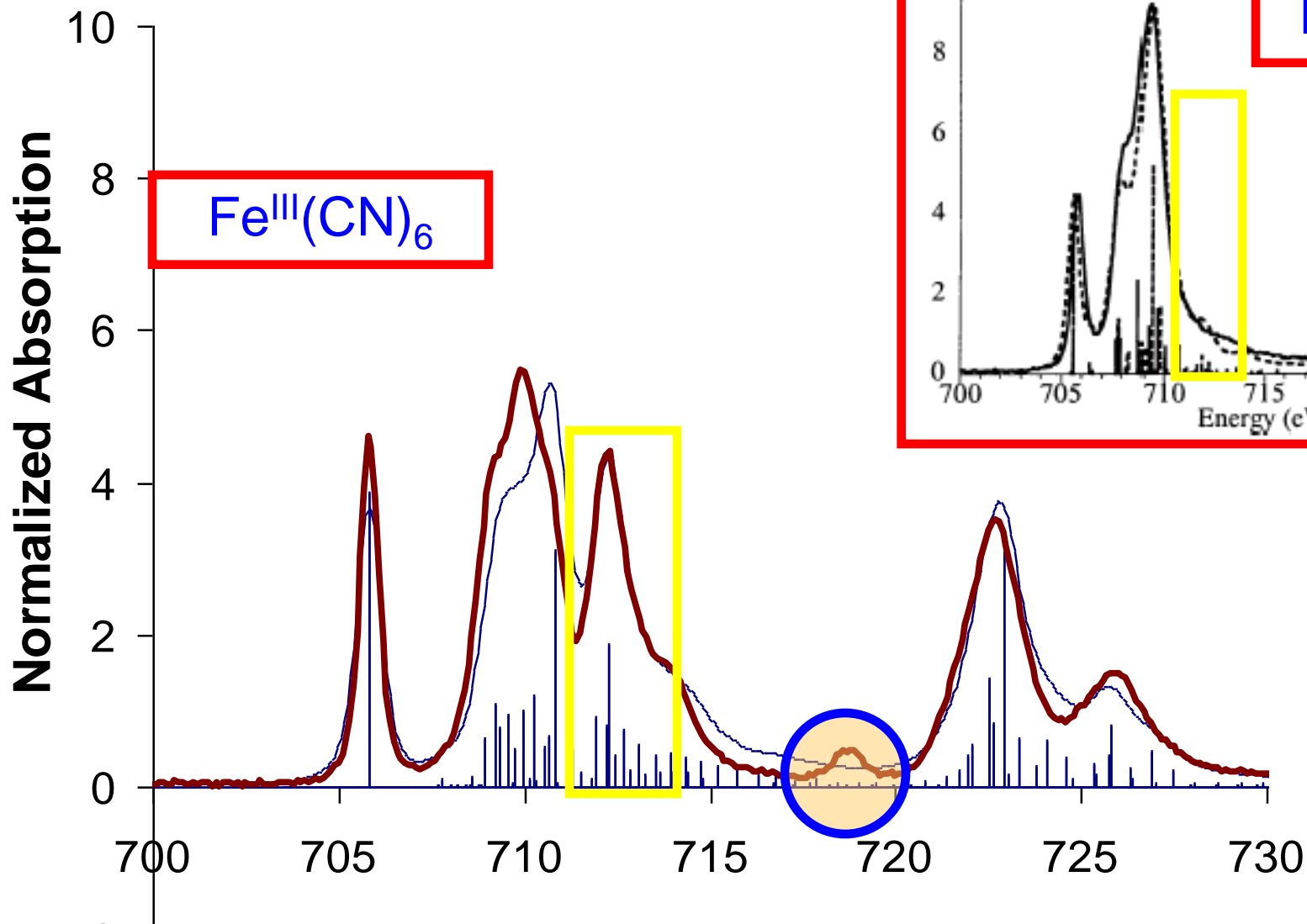
# LMCT and MLCT: $\pi$ - bonding

Fe<sup>III</sup>: Ground state:  $3d^5$  +  $3d^6\bar{\underline{L}}$  +  $3d^4L$



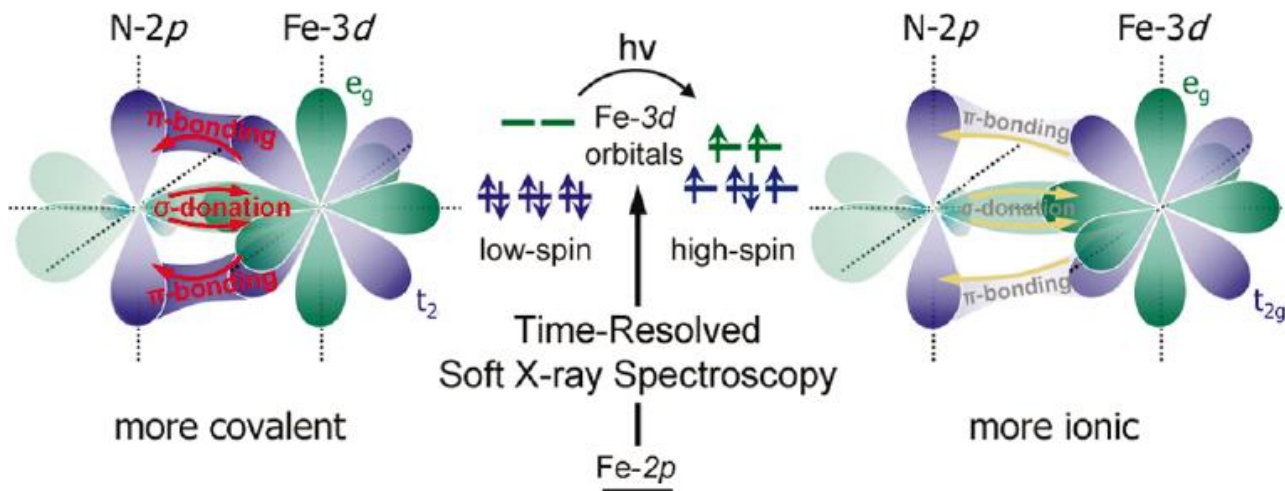
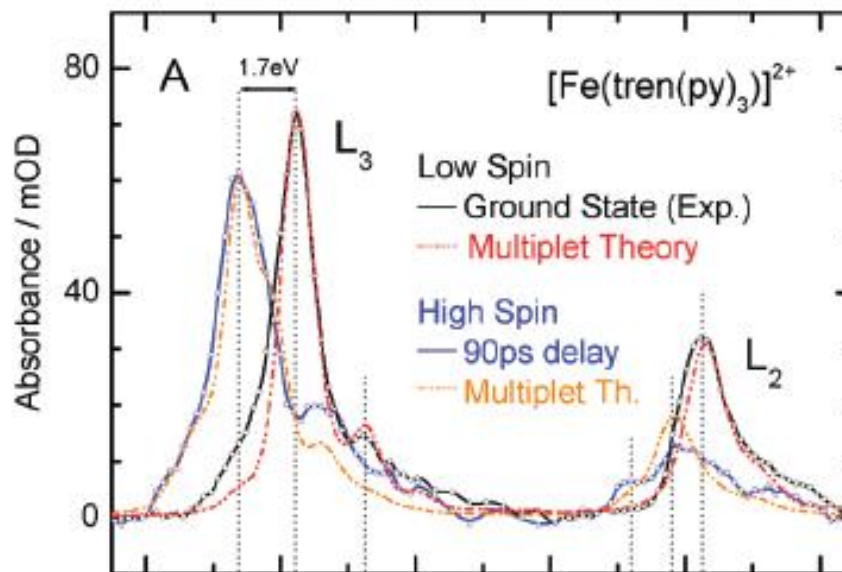
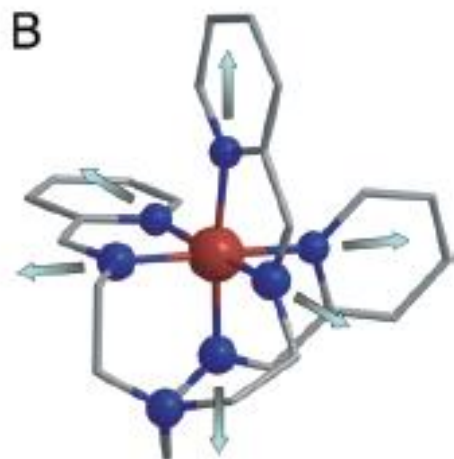
with Ed Solomon (Stanford) JACS 125, 12894 (2003),  
JACS 128, 10442 (2006), JACS 129, 113 (2007)

# LMCT and MLCT: $\pi$ - bonding



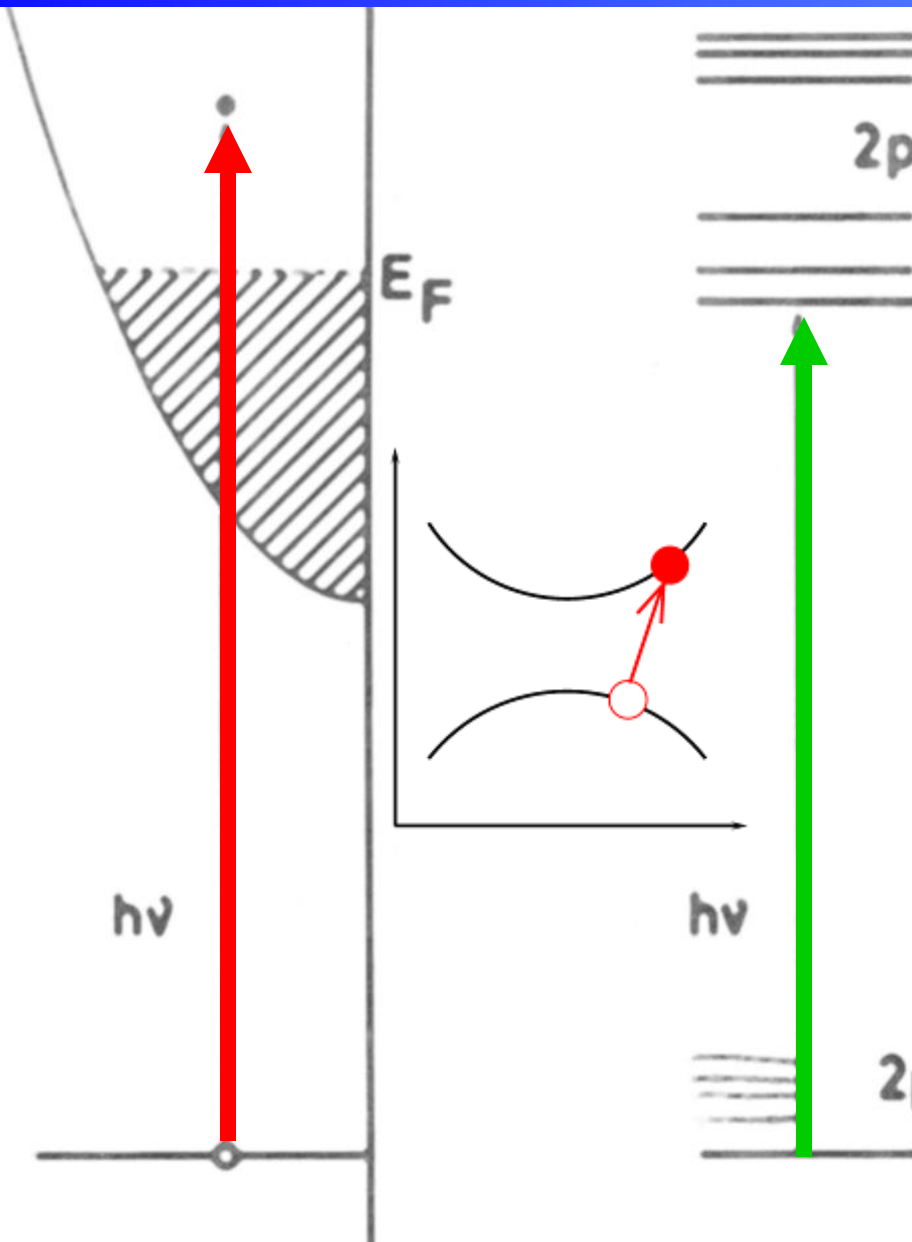
with Ed Solomon (Stanford) JACS 125, 12894 (2003),  
JACS 128, 10442 (2006), JACS 129, 113 (2007)

# Time resolved XAS





# XAS: multiplet effects



Single Particle:  
1s edges  
(DFT + core hole (+U))

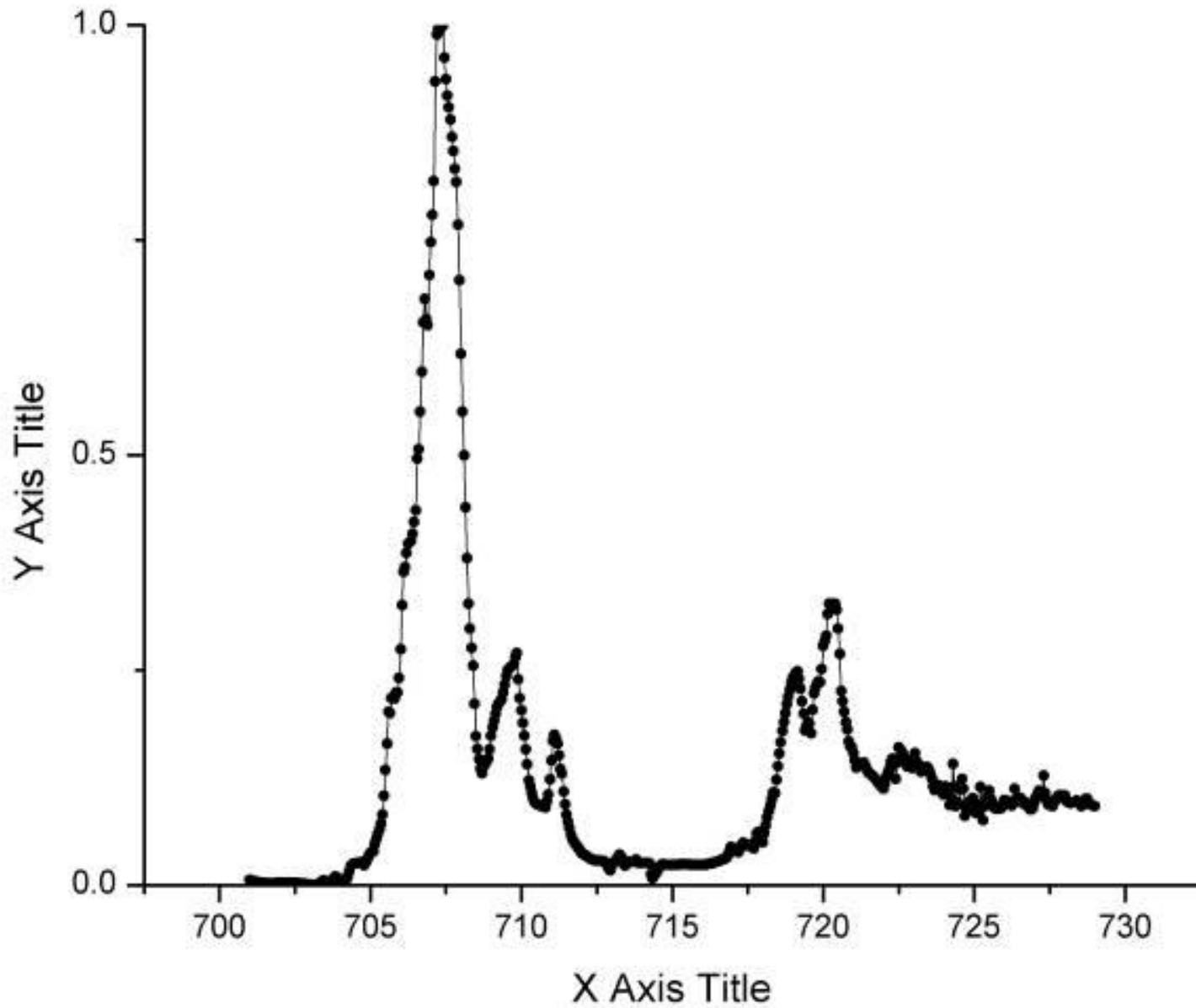
2-particle:  
(TDDFT, BSE)  
+ L edges of  $3d^0$

Multiplets:  
2p, 3s, 3p edges  
(CTM4XAS)

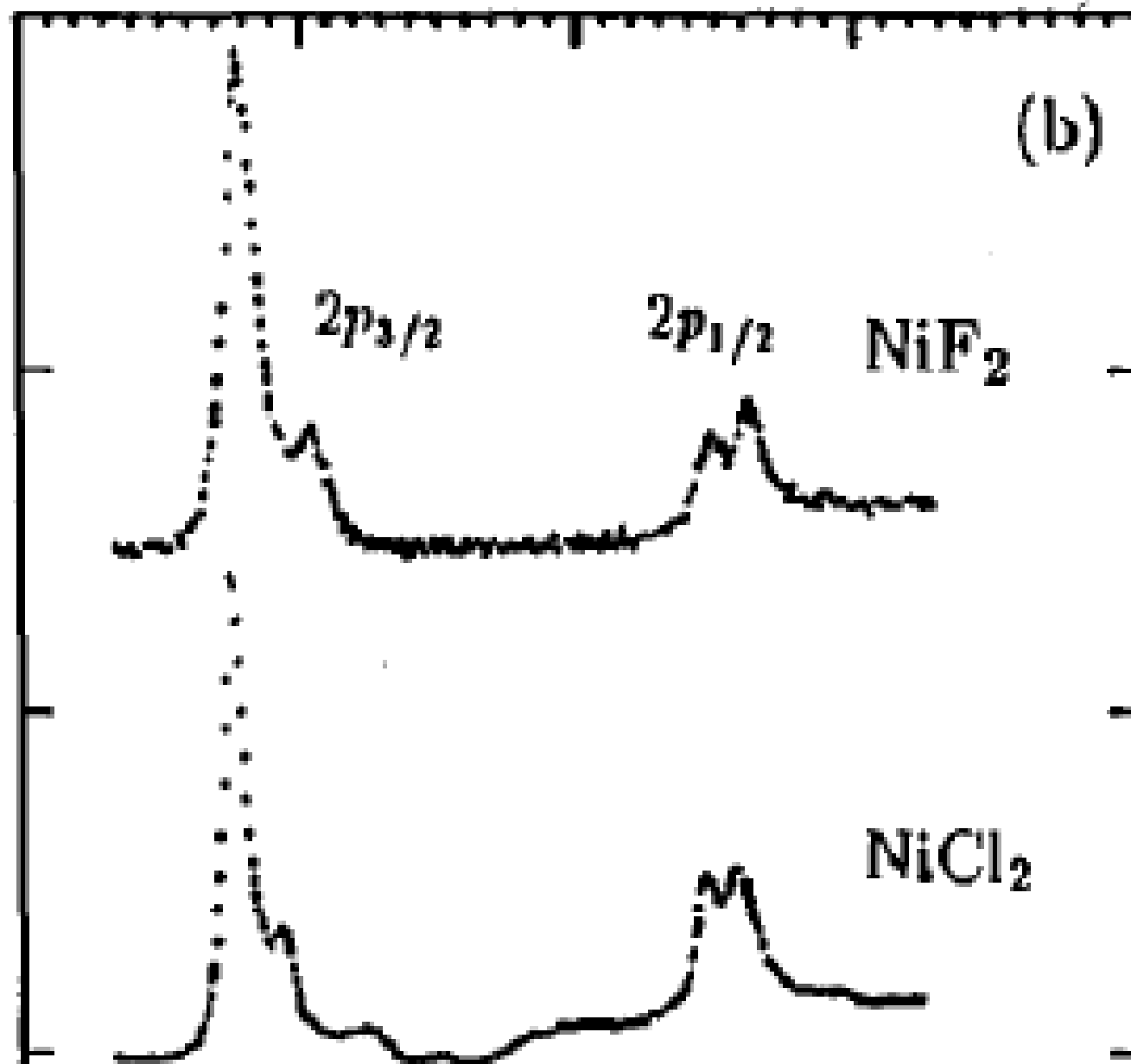
# Why X-ray absorption?

- 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 °C flowing gas
  - **Space:** 0.5 nm (STEM), 20 nm (STXM)

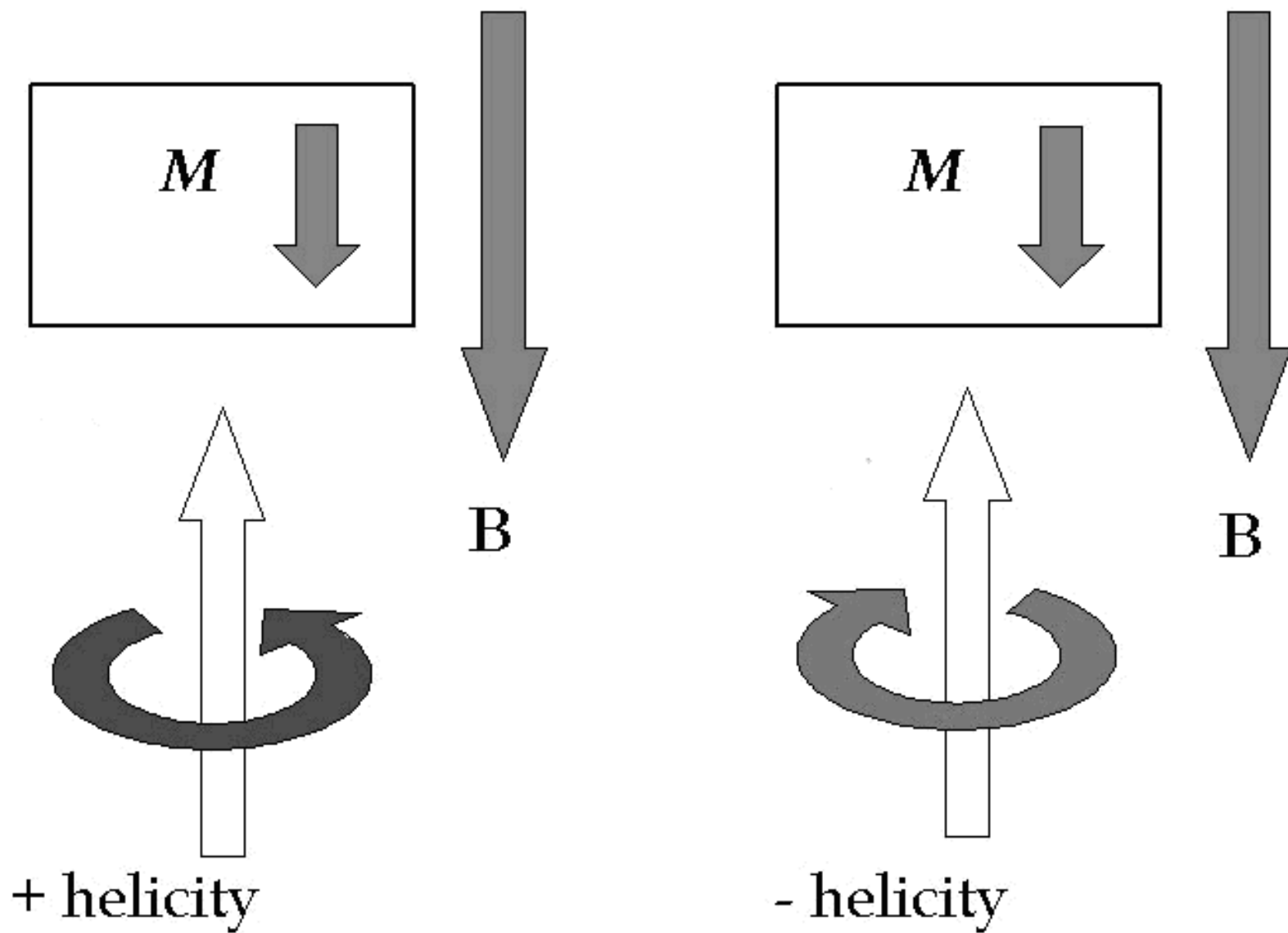
# Quiz: Calculate the 2p XAS spectrum of Fe atom



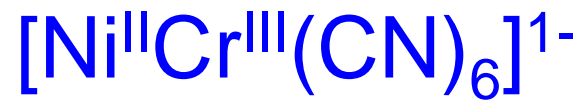
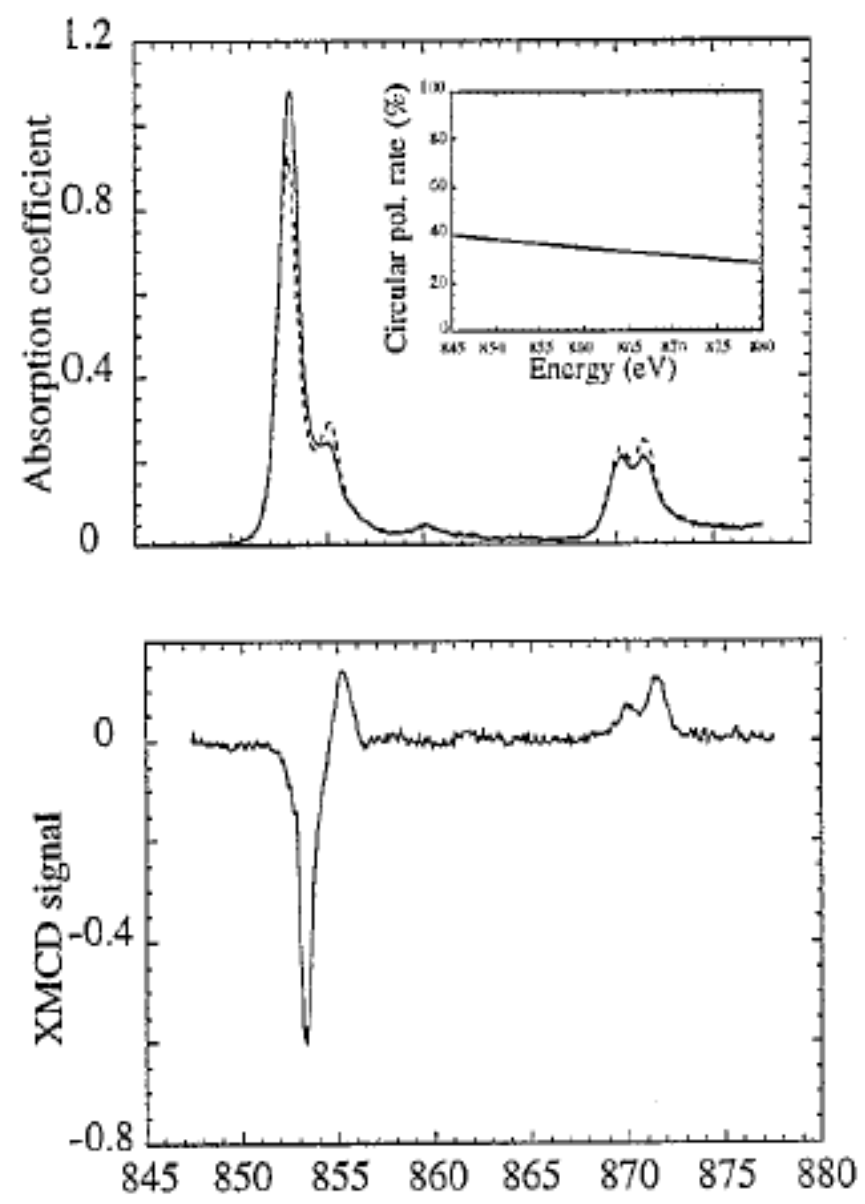
# Quiz: Calculate the 2p XAS of NiF<sub>2</sub> and NiCl<sub>2</sub>



# Magnetic circular dichroism

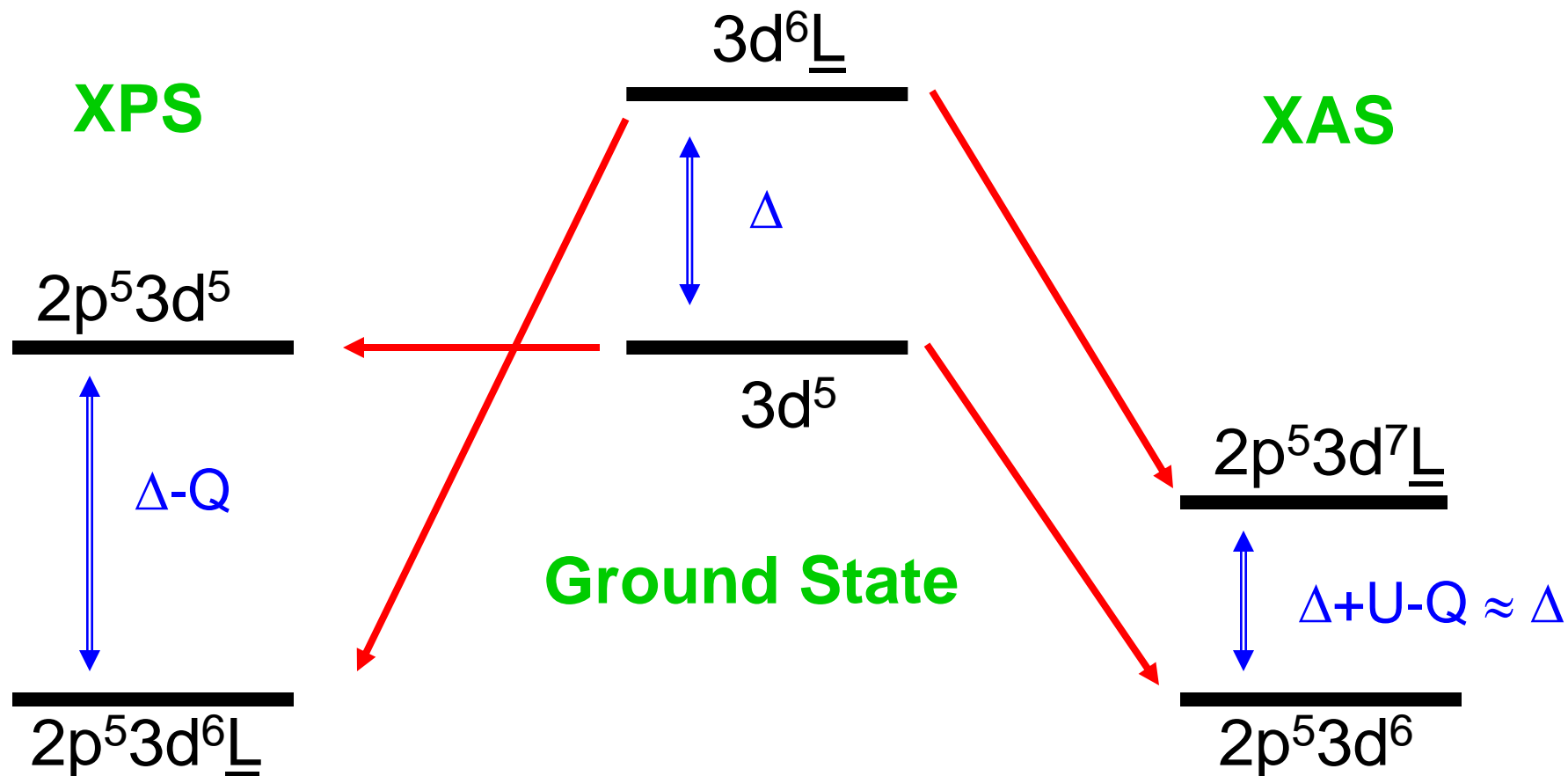


# Quiz: Calculate the X-MCD of ferromagnetic Ni<sup>2+</sup>

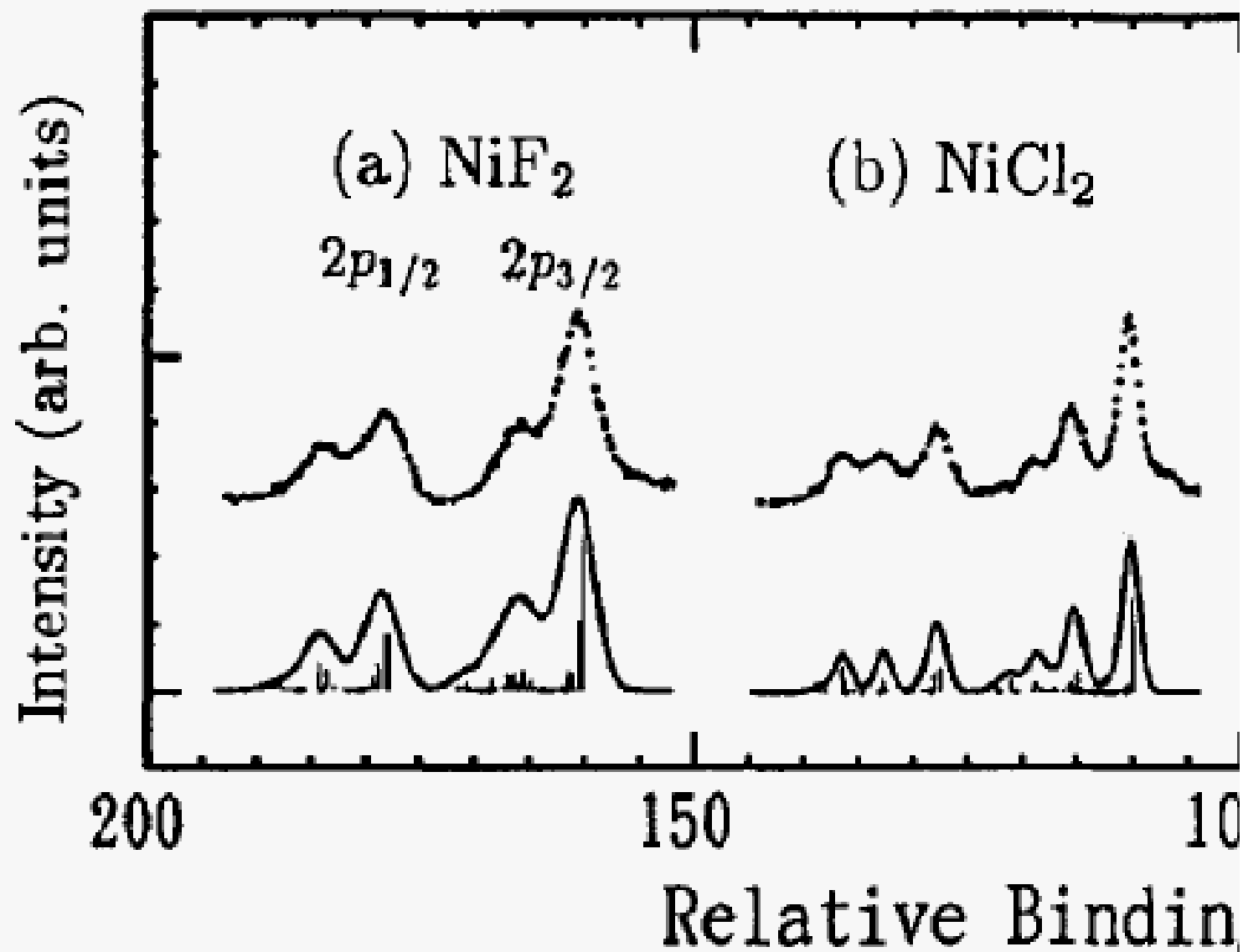


# Charge transfer effects

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



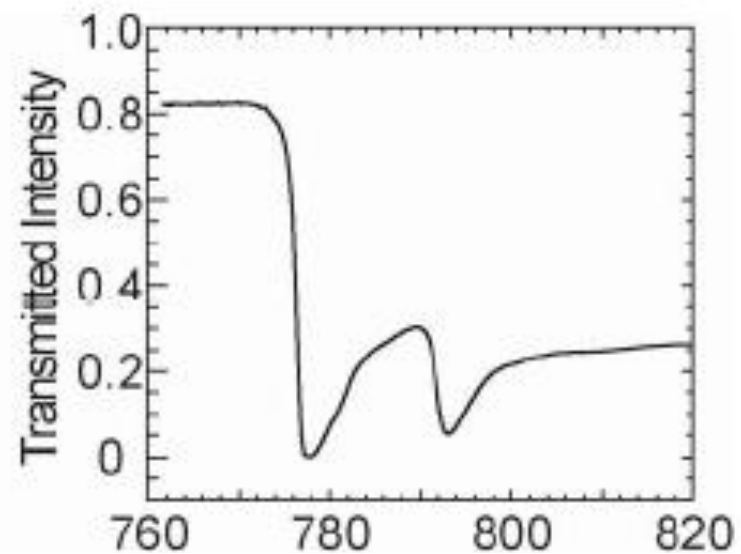
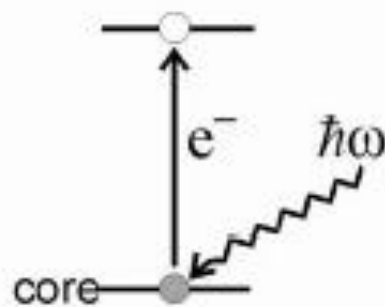
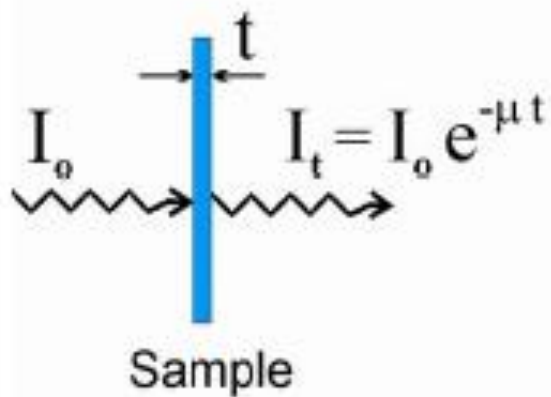
# Quiz: Calculate the 2p XPS of NiF<sub>2</sub> and NiCl<sub>2</sub>





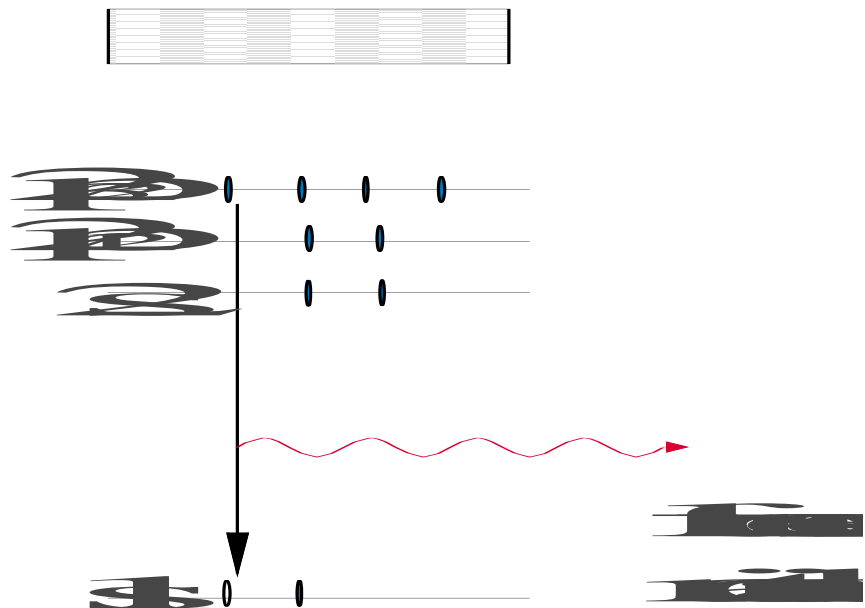
# XAS experiments

## Transmission

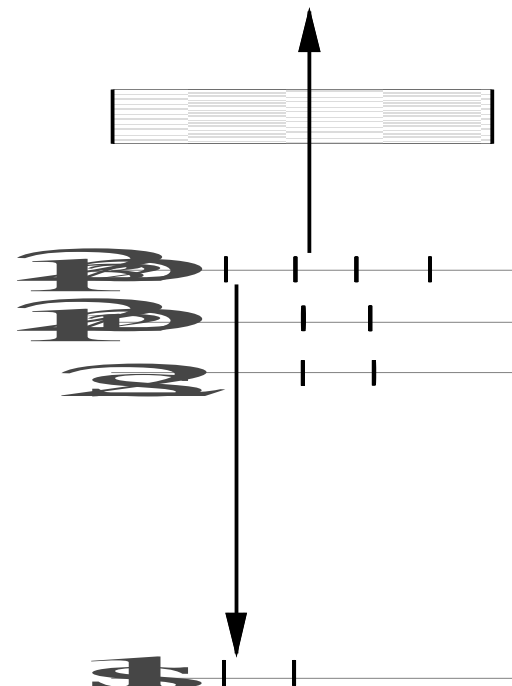


# XAS experiments: using the core hole decay

## Fluorescence

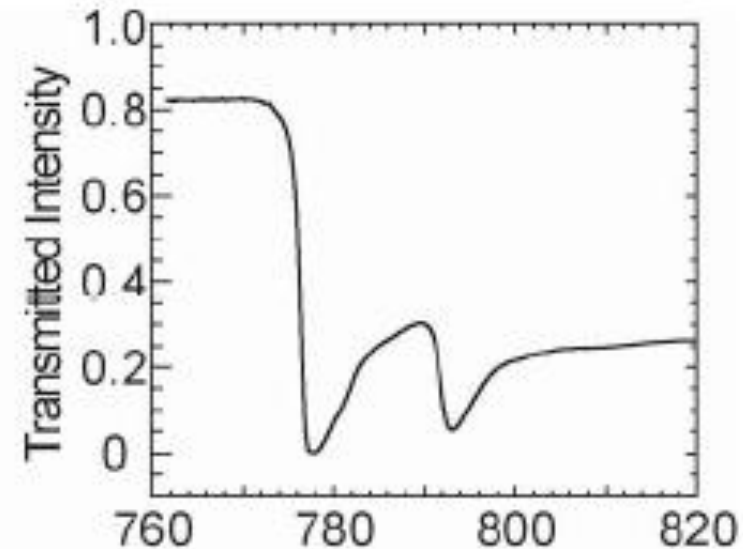
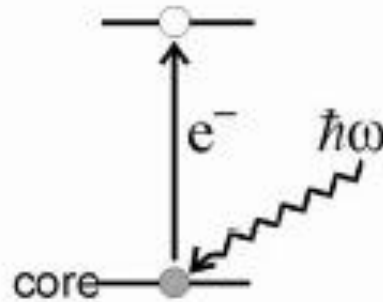
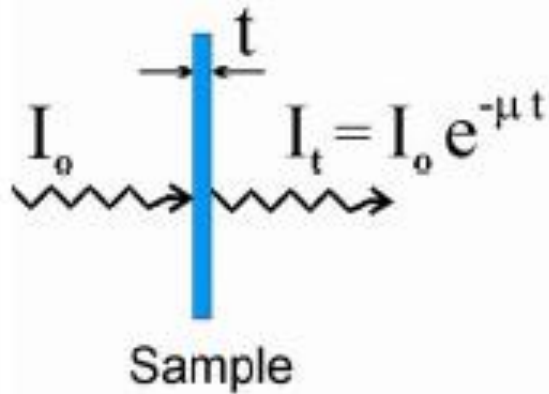


## Auger



# XAS experiments

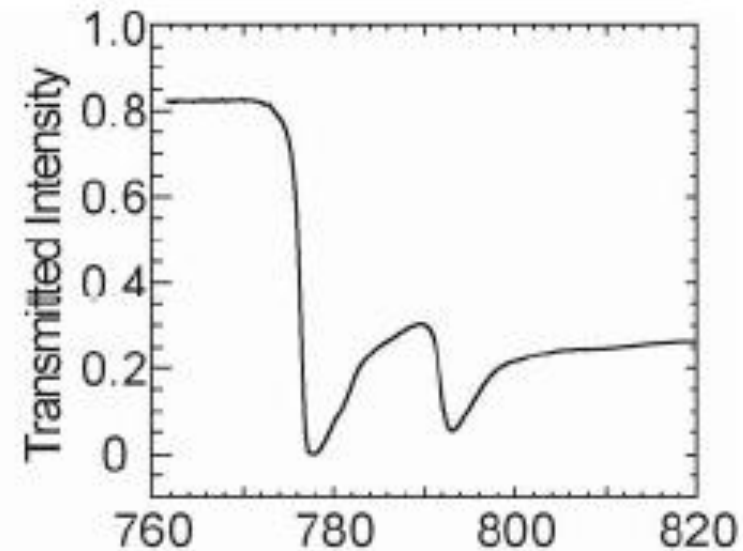
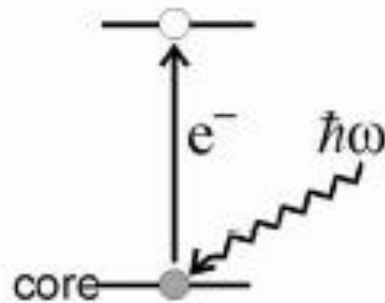
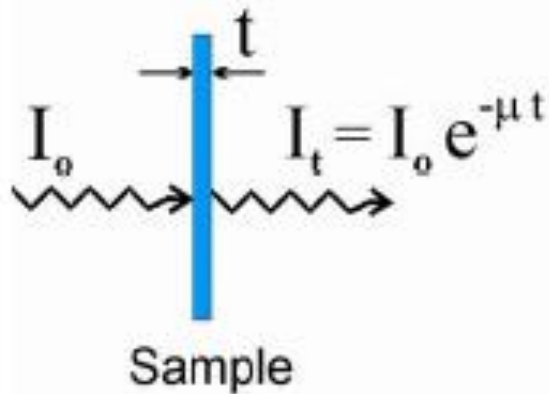
## Transmission



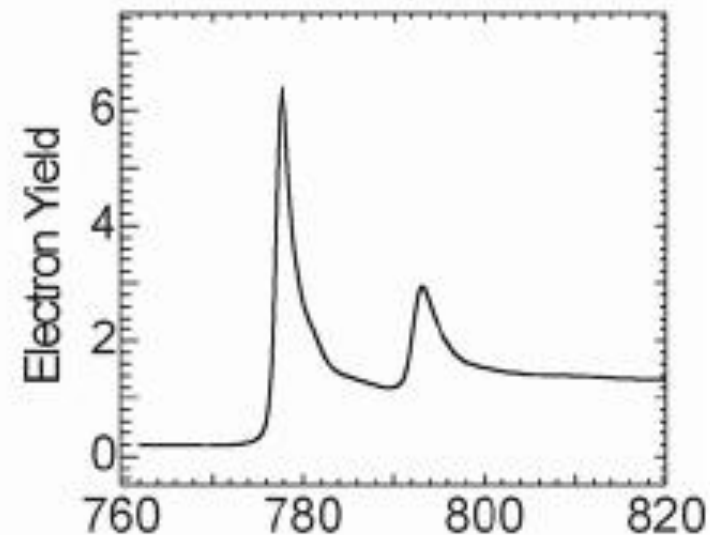
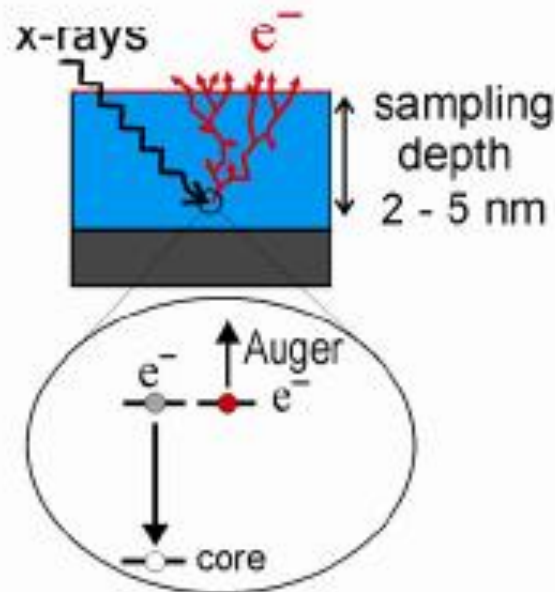
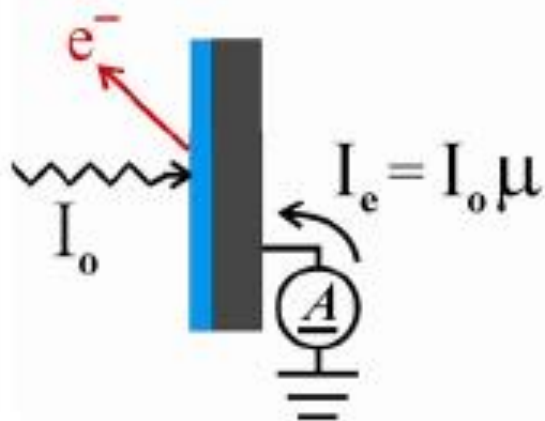
Quiz: How to measure XAS of a solid

# XAS experiments

## Transmission



## Electron Yield



# Core Level Spectroscopy of Solids

Frank de Groot  
Akio Kotani

 CRC Press  
Taylor & Francis Group