MAX-PLANCK-GESELLSCHAFT

AC FHI

LECTURE SERIES
HETEROGENEOUS CATALYSIS

X-Ray Emission Spectroscopy

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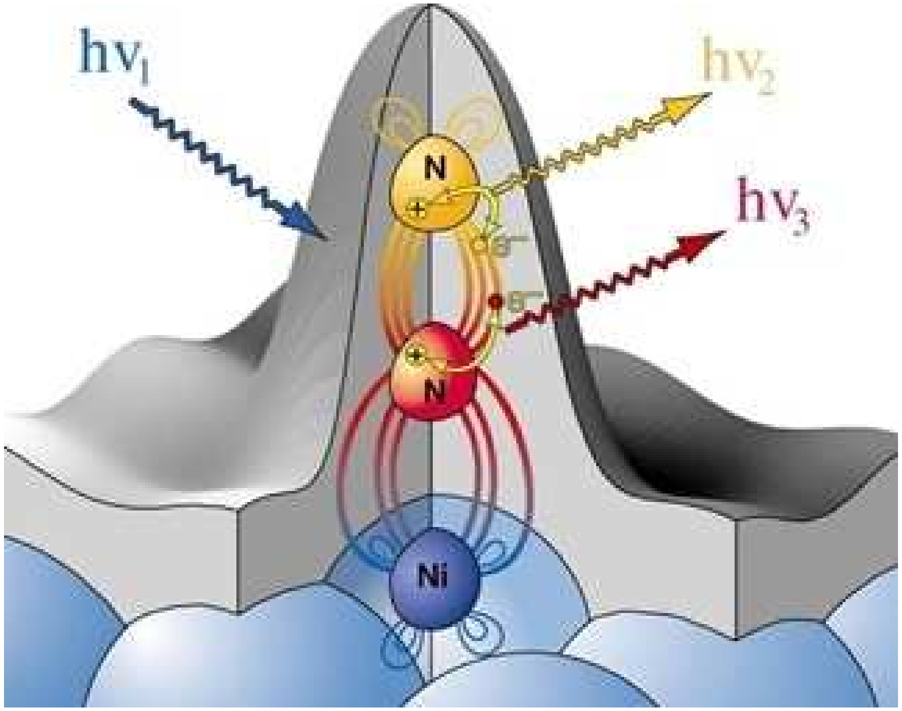
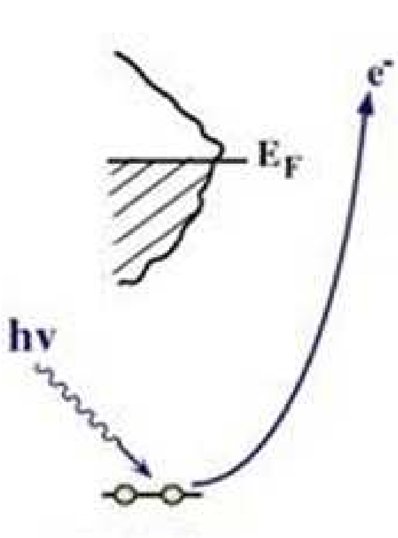
Core Level Spectroscopy



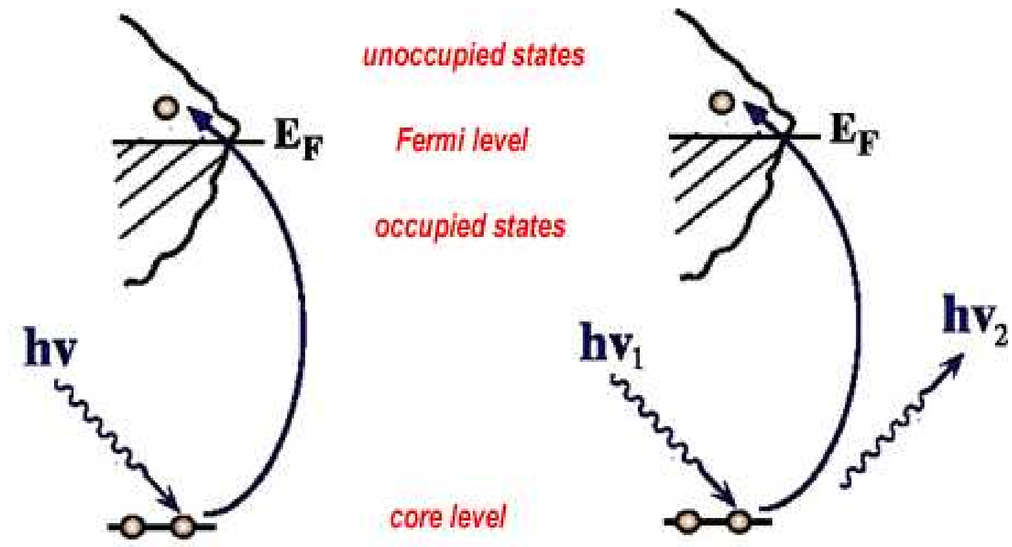
Creation of Core holes

Ionisation



X-ray photoelectron spectroscopy (XPS)

Excitation

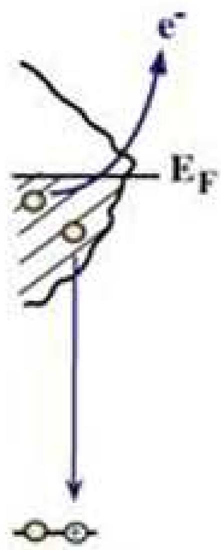


X-ray absorption spectroscopy XAS

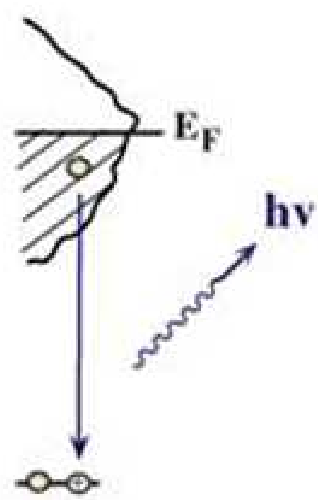
X-ray Inelastic scattering (XIS)

Decay of core holes

Non radiant



radiant

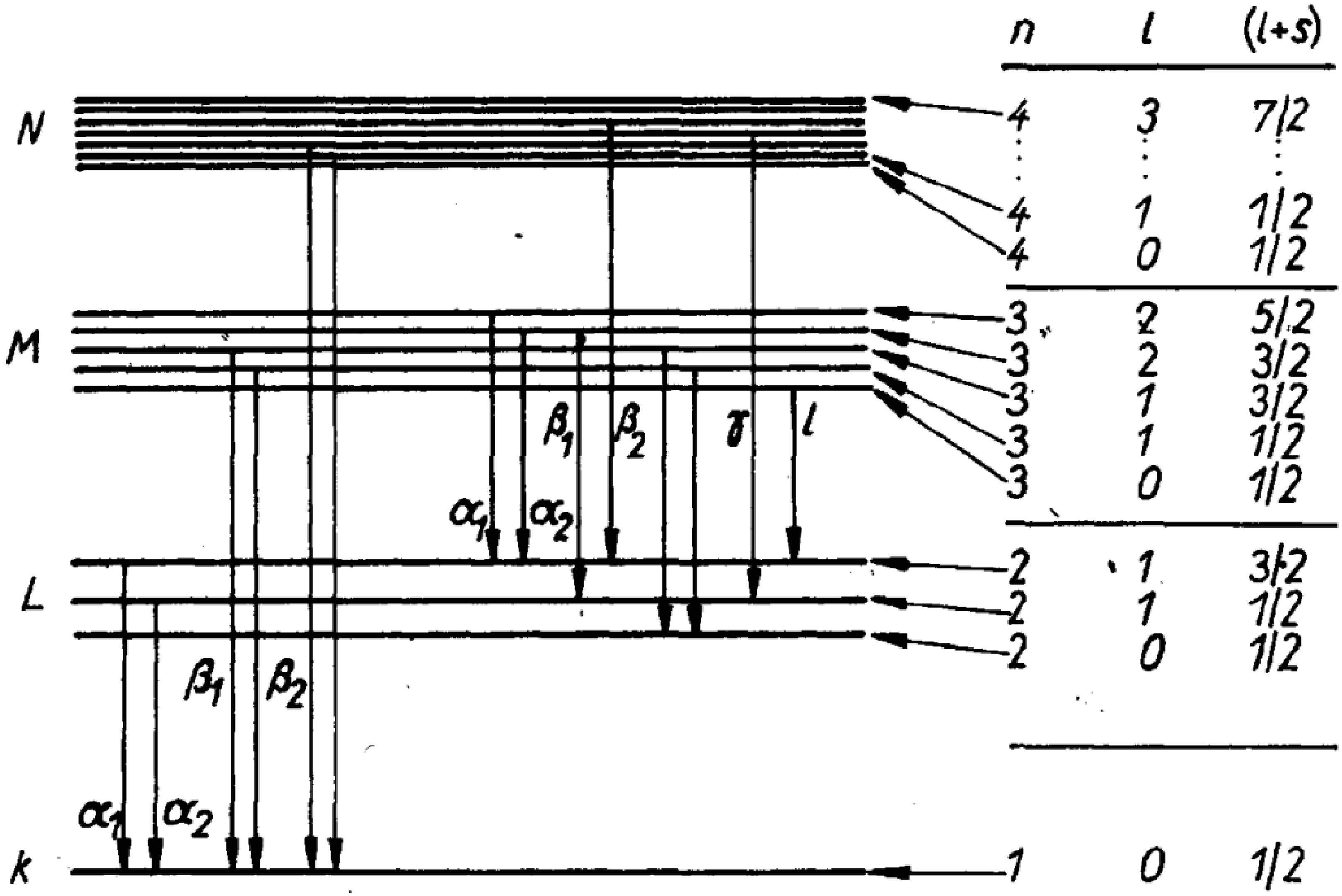


Auger Electron Spectroscopy (AES)

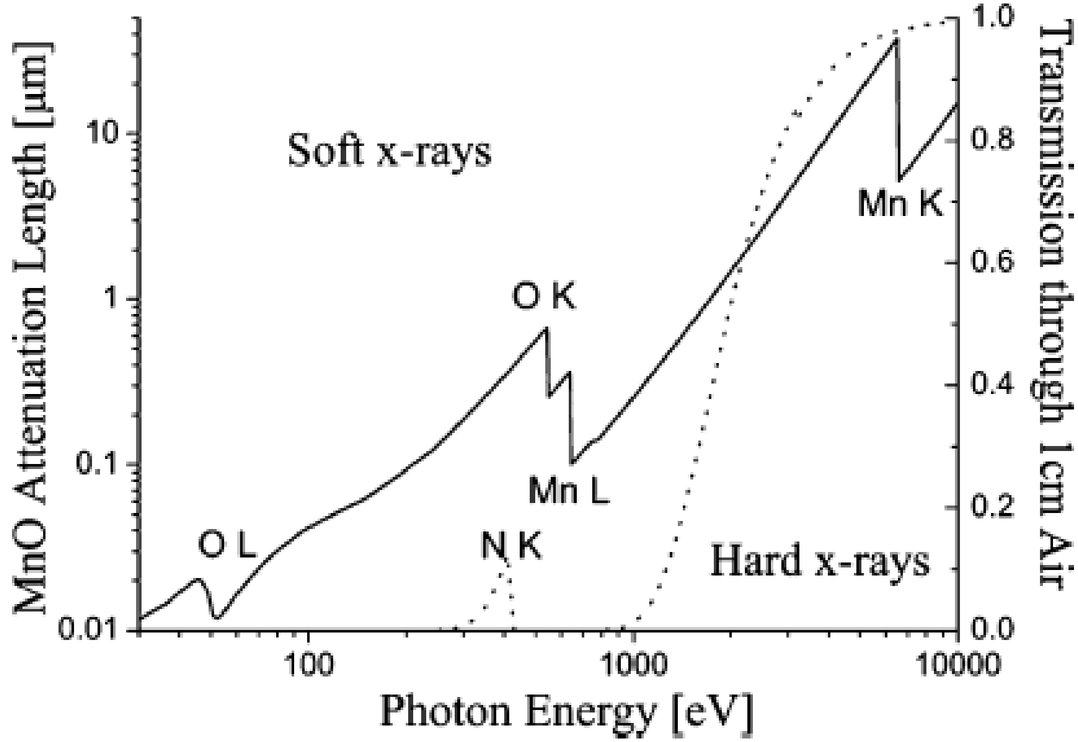
X-ray Emission Spectroscopy (XES)

http://ssrl.slac.stanford.edu/nilssongroup/pages/core_spec_xps.html

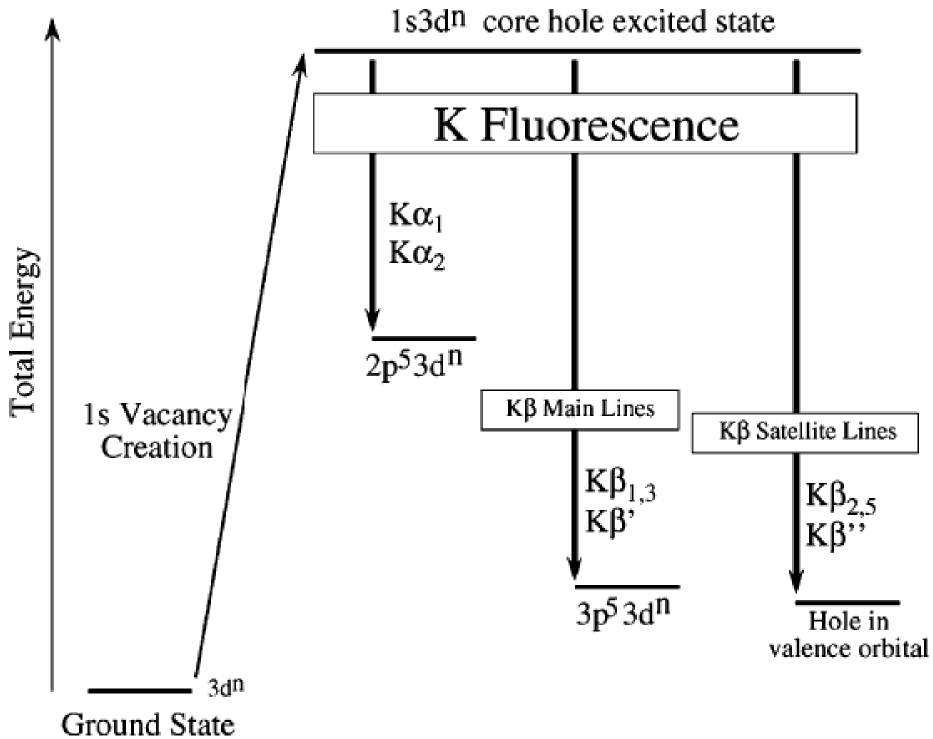
Assignment of X-ray emission lines



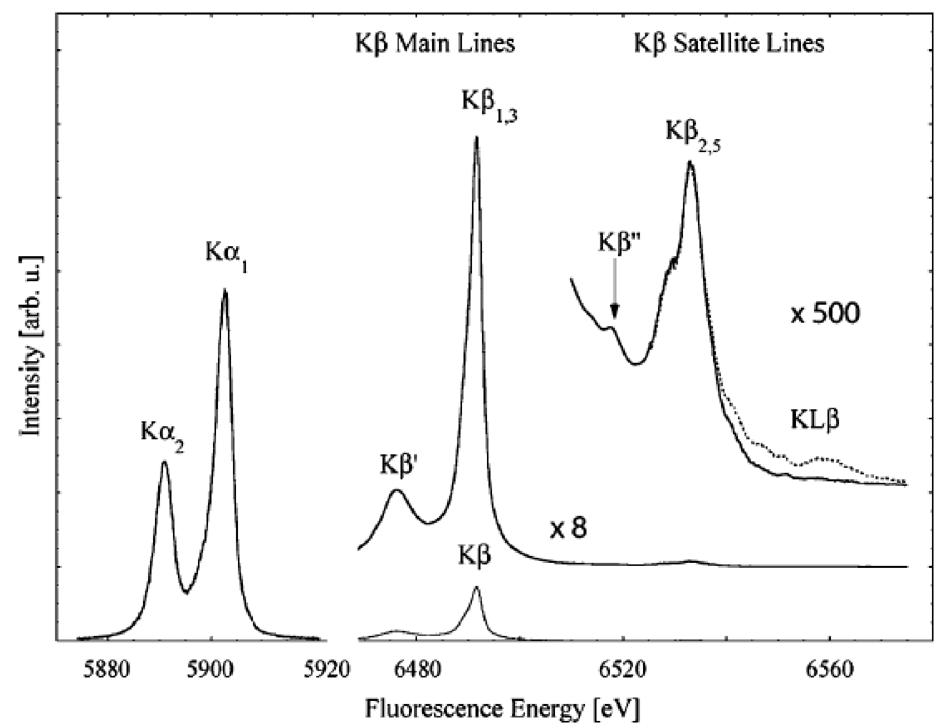
X-ray attenuation length



K fluorescence emission



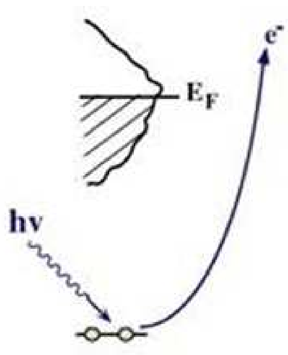
K shell emission lines in MnO

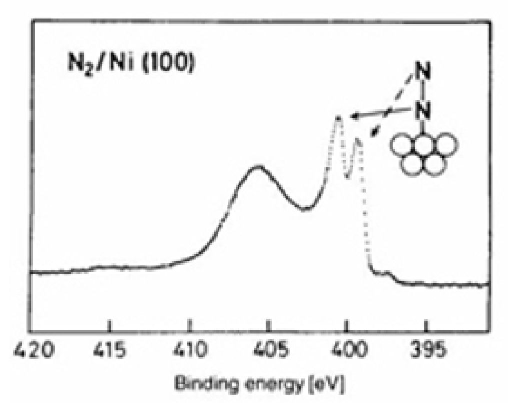


Kβ$_1$: $3p_{3/2}$, Kβ$_3$:$3p_{1/2}$ final states
Kβ$_2$: transition from 4p orbitals, Kβ$_5$: from 3d orbitals

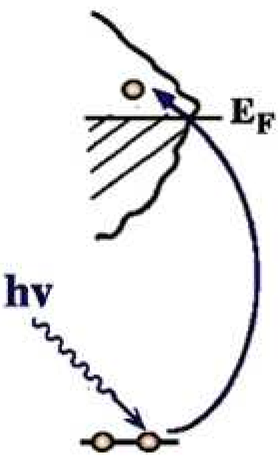
Core Level Spectroscopy

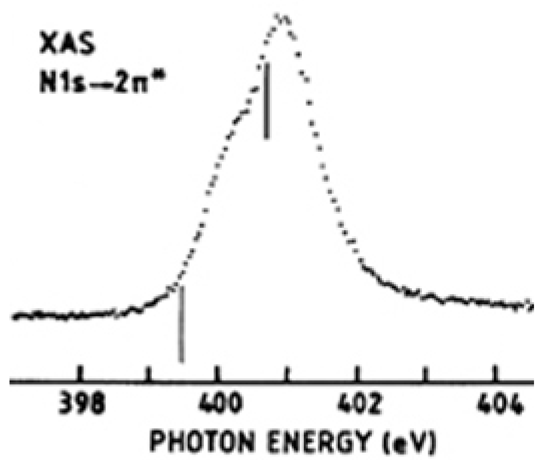
XPS

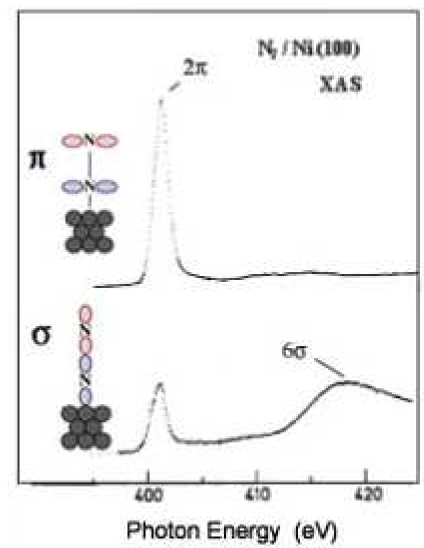




XAS



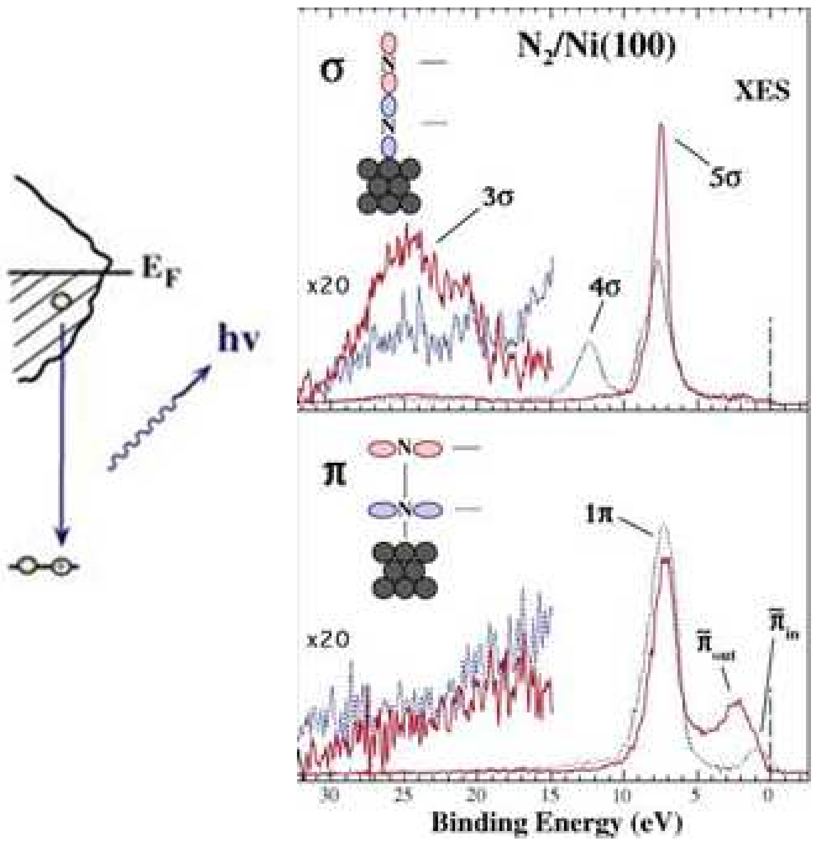


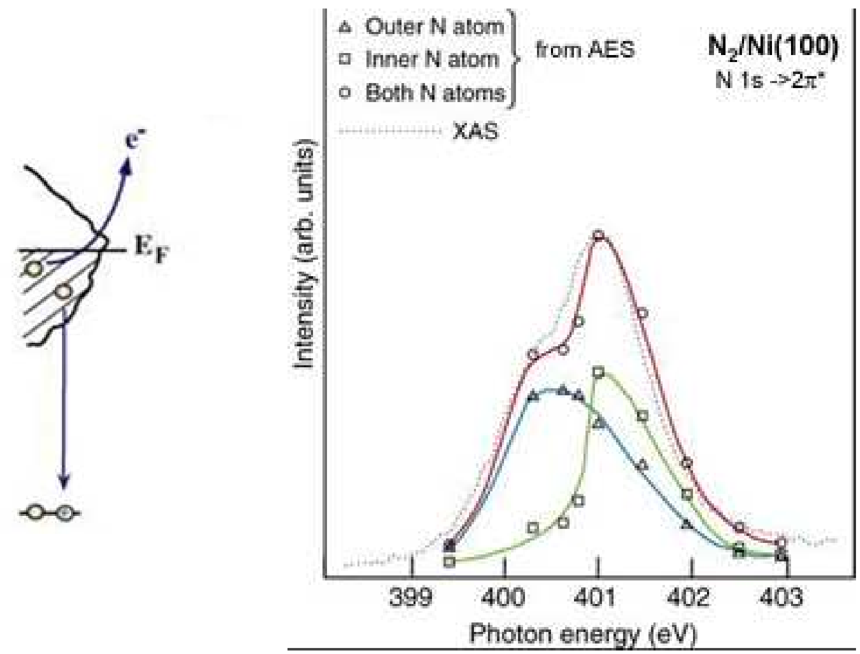


Core Level Spectroscopy

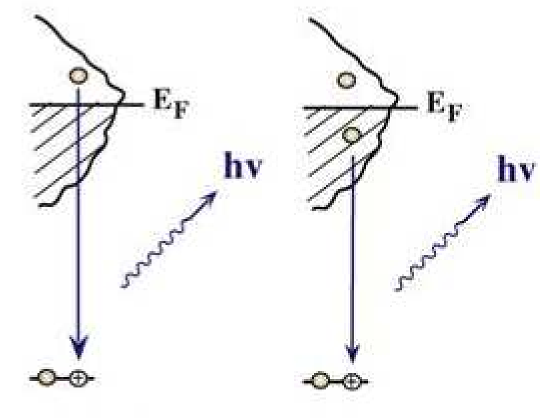
XES

AES





Resonant Processes



Resonant X-ray Emission Spectroscopy (RXES)
Resonant Inelastic X-ray Scattering (RIXS)

X-ray Emission Techniques

High-Energy Resolution Fluorescence Detected (HERFD) XAS

Experiment: The emitted energy ω is tuned to a fluorescence line and the incident energy Ω is scanned through an absorption edge. The intensity variation of the fluorescence line is recorded as a function of the incident energy.

Dispersive solid state detector: energy bandwith of 200-300 eV at Fe Kα line

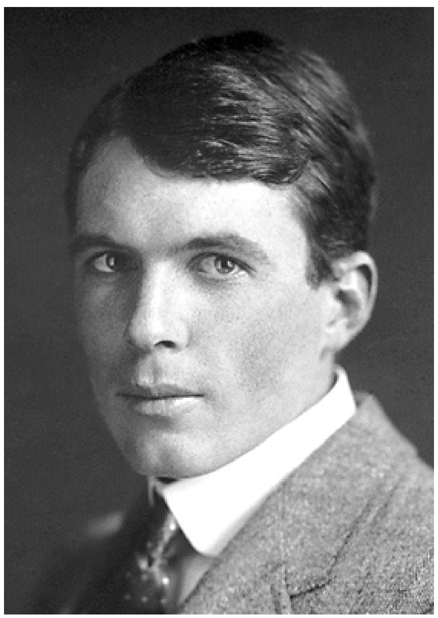
Non linearity at high count rates (pileup effect)

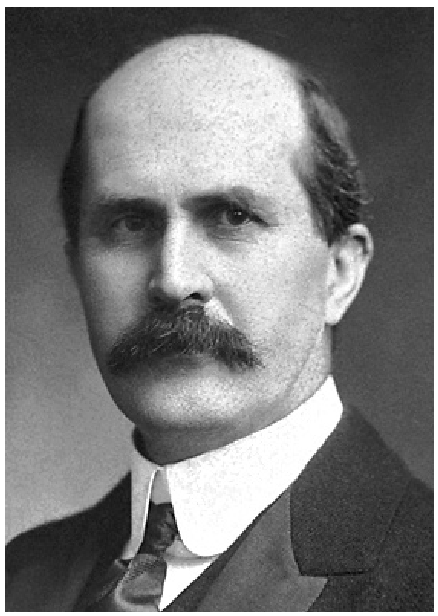
Other option: use an X-ray spectrometer and avalanche photodiode (no background)

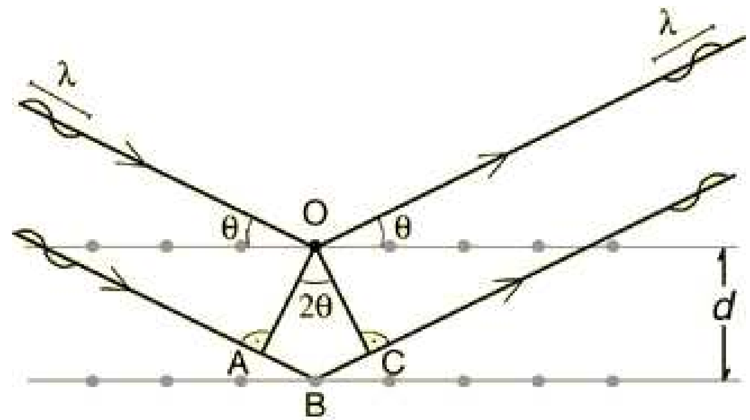
Bragg Equation

William Lawrence Bragg and Henry Bragg

Noble Prize of Physics in 1914





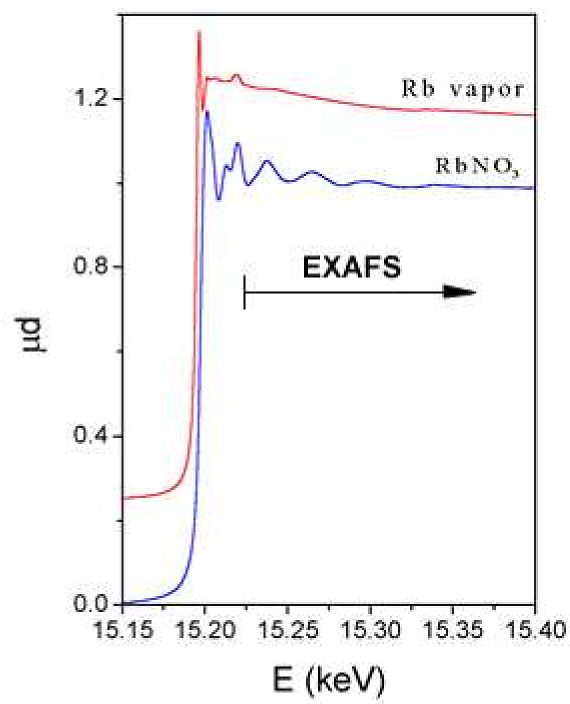


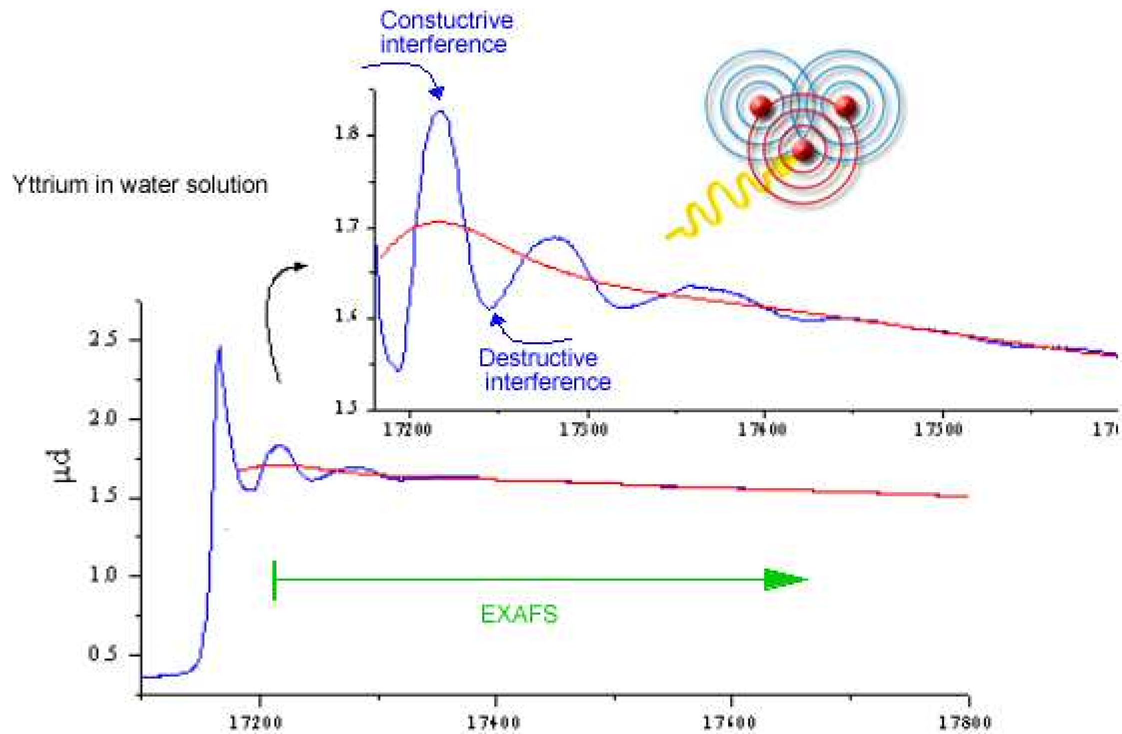
$$n\,\lambda = 2\,d\,\sin\theta$$

λ = Wellenlänge
d = Netzebenenabstand
θ = Glanzwinkel
n = ganze Zahl

Extended X-ray Absorption Fines Structure -EXAFS

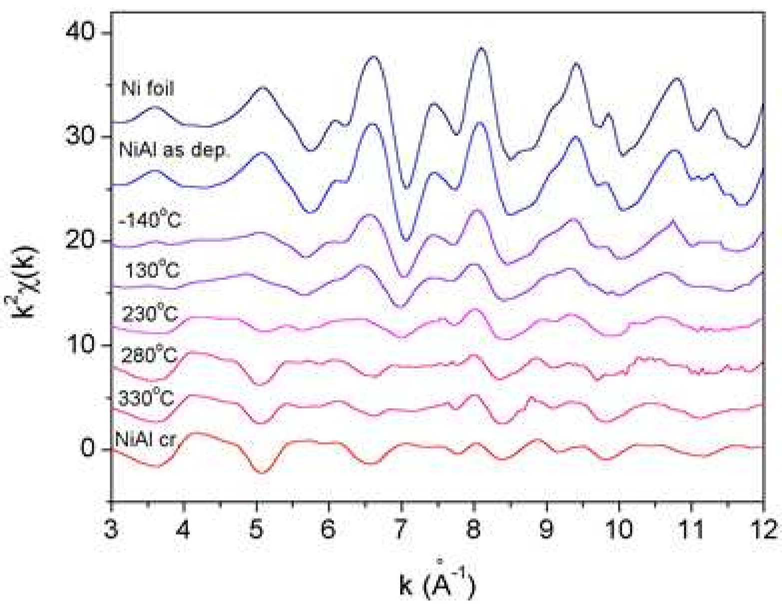
$RbNO_3$ water solution and Rb vapour @ Rb K edge

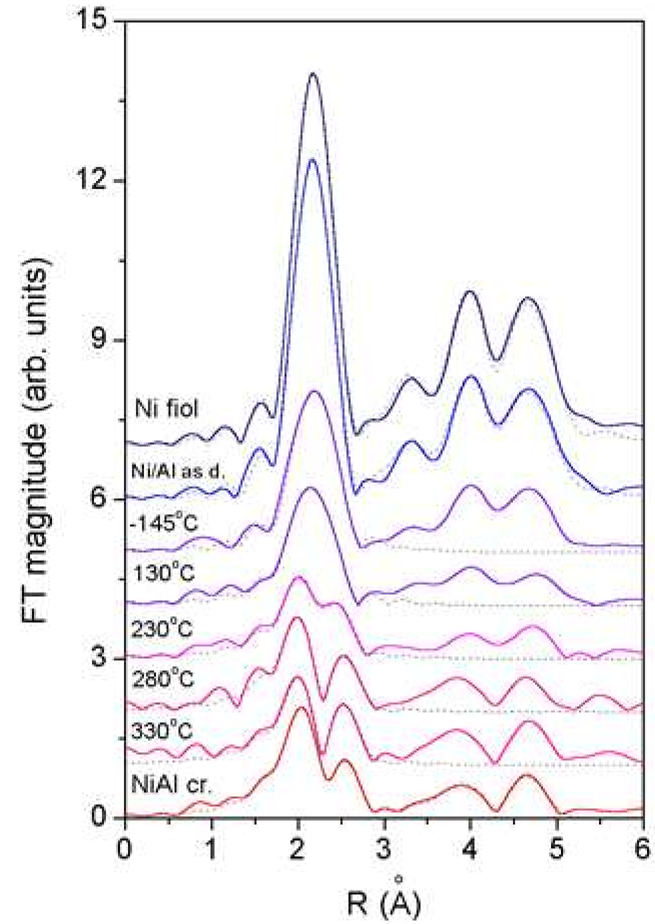




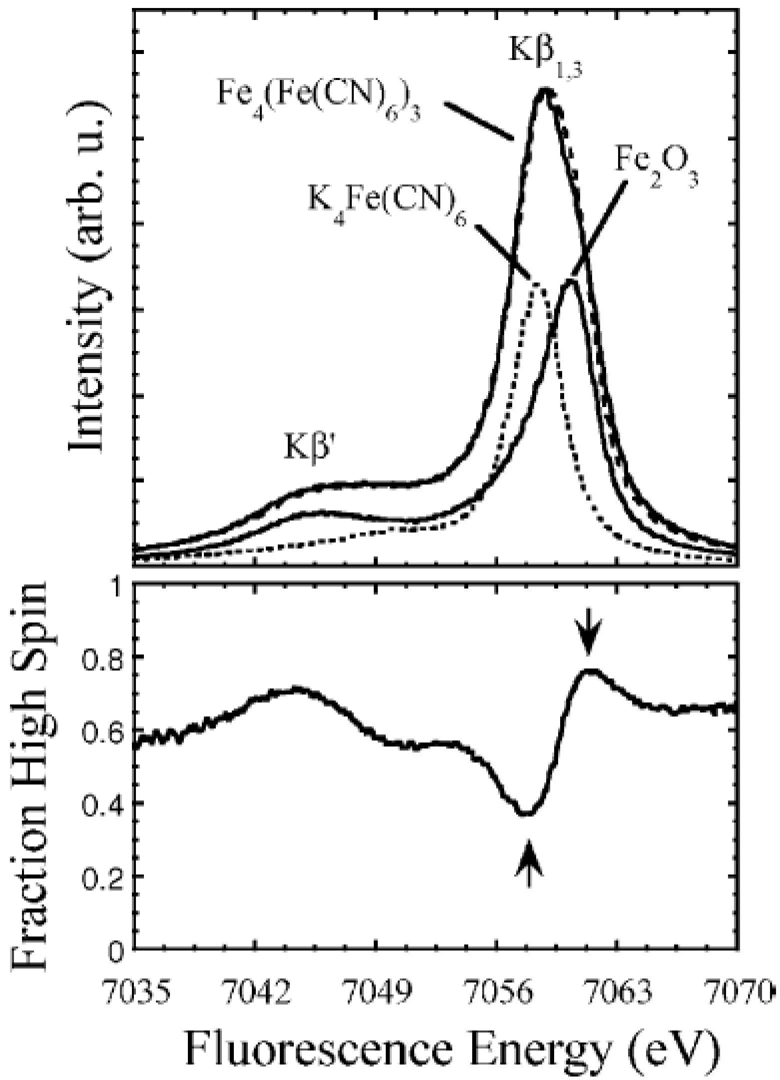
Extended X-ray Absorption Fines Structure -EXAFS

Ni K-edge EXAFS spectra (left) and their Fourier transform magnitudes (right) measured on the as deposited Ni/Al multilayer sample and on samples after ion mixing at substrate temperatures -140°C, 130°C, 230°C, 280°C and 330°C. For comparison the spectra of Ni metal and NiAl monocrystal are added. Solid line - experiment; dashed line - EXAFS model.





Site selective EXAFS

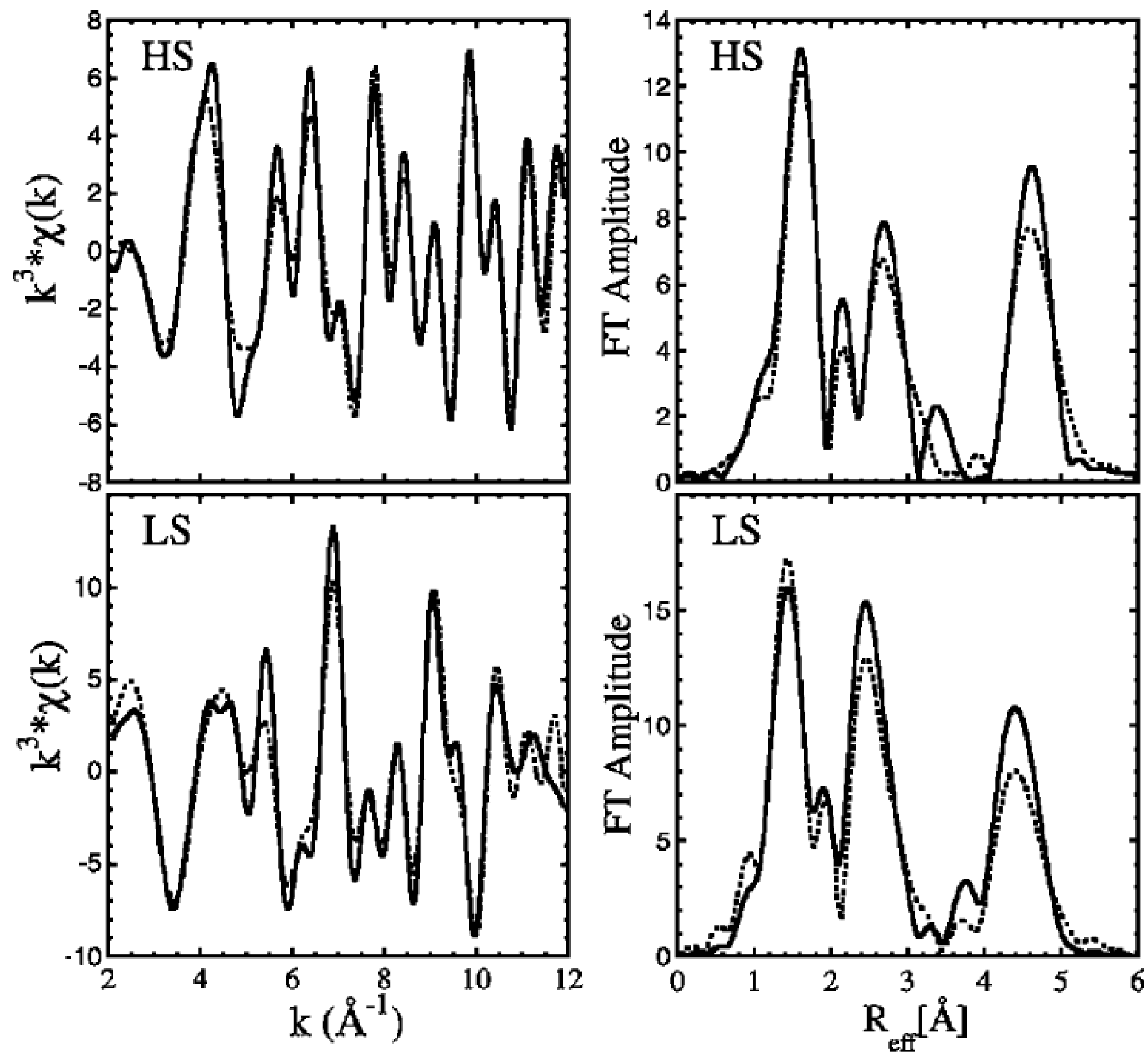


Kβ emission in Prussian Blue ($Fe_4[Fe(CN)_6]_3$)

High spin component : Fe(III) Fe_2O_3

Low spin component : $K_4Fe(CN)_6$

Deduced site selective EXAFS spectra



X-ray Emission Techniques

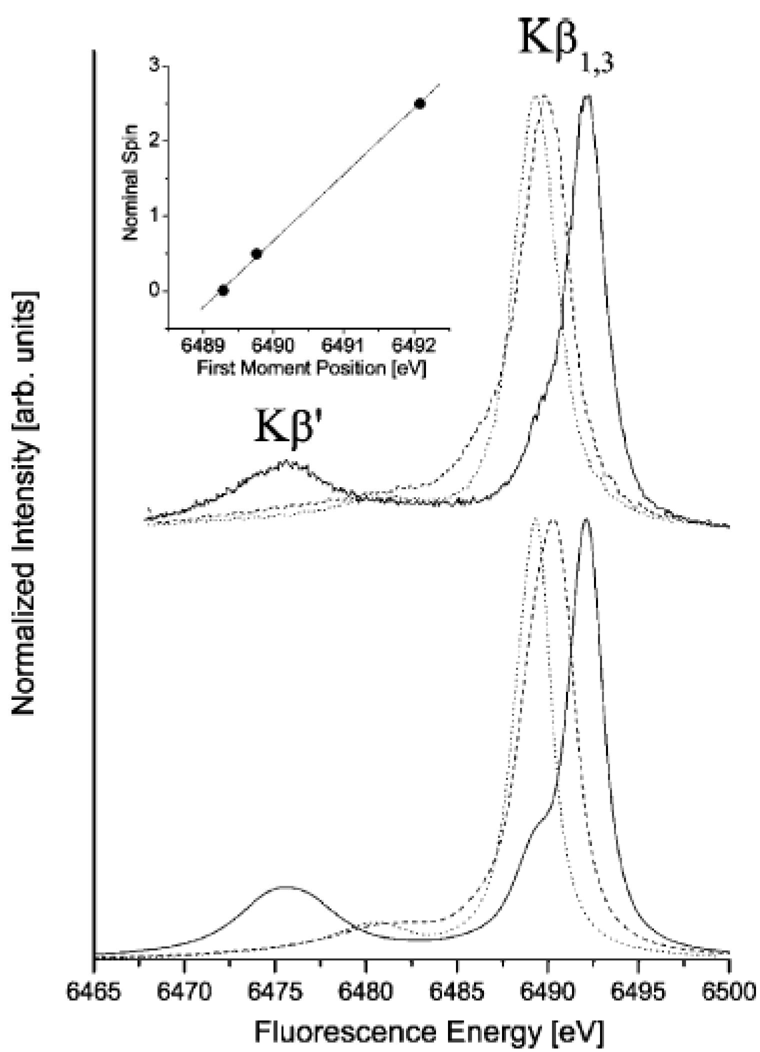
Non-Resonant X-Ray Emission Spectroscopy (XES)

Experiment: The incident energy Ω is tuned well above an absorption and the emitted energy ω is scanned over the energy range of a fluorescence line

XES is a second order process. If the core hole is replaced by another core hole, e.g. 3p to 1s ($K\beta$) transition in a 3d transition metal, the sensitivity to the valence electrons is indirect. The final state core hole interacts with the valence electrons and this interaction shapes the emission line.

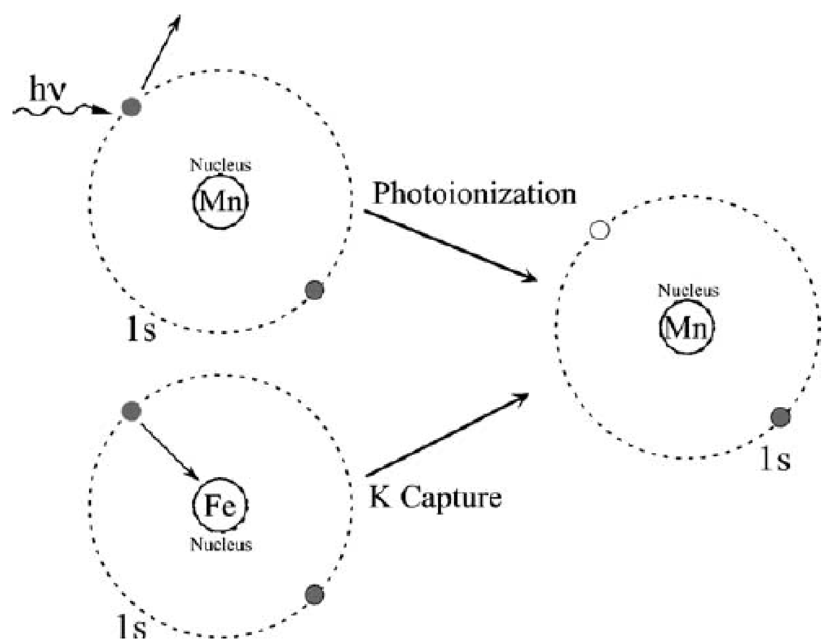
The $K\beta$ main line, for example, are sensitive to the valence shell spin state.

K β lines

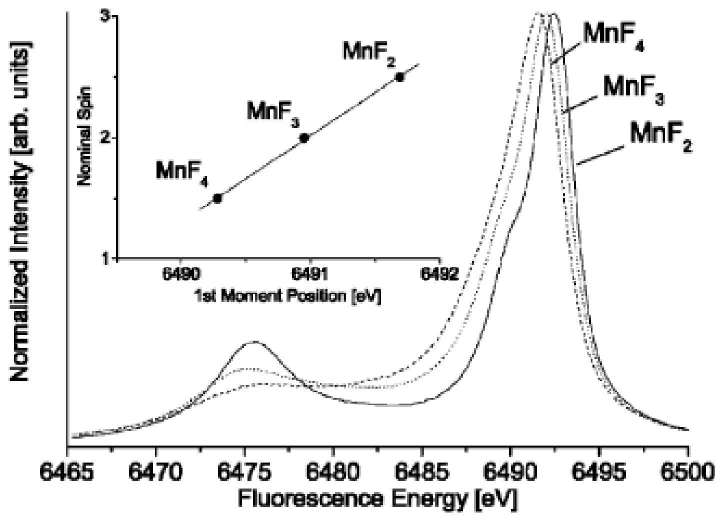


$^{55}Fe_2O_3$ (solid line) S=5/2
$K_3{}^{55}Fe(CN)_6$ (dashed line) S=1/2
$K_4{}^{55}Fe(CN)_6$ (dotted line) S=0

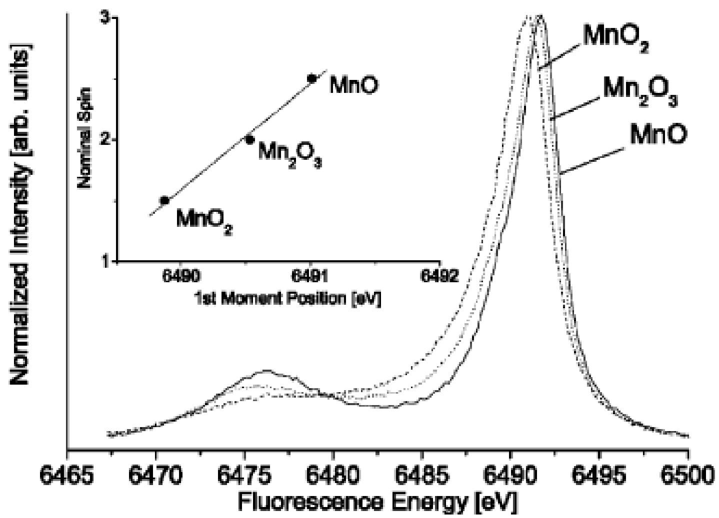
Measured after K capture decay



Kβ lines of Mn fluorides and oxides



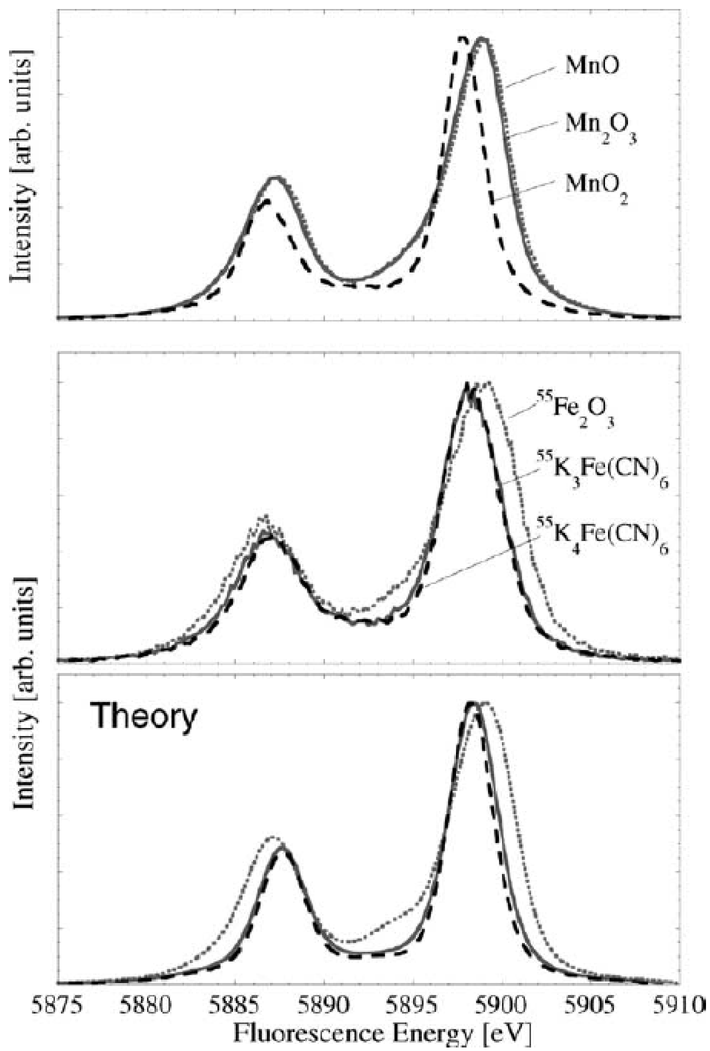
MnF_2 (solid line)
MnF_3 (dashed line)
MnF_4 (dotted line)



MnO (solid line)
Mn_2O_3 (dashed line)
MnO_2 (dotted line)

Different correlation of fluorides and oxides due to different degree of covalent bonding!
Short-range (3p,3d) exchange interaction: Sensitive just to the number of unpaired 3d electrons

Kα lines



Spectral changes for Kα lines are less pronounced

The 2p and 3d orbitals interact less with each other than 3p and 3d because of the smaller overlap of the wave function.

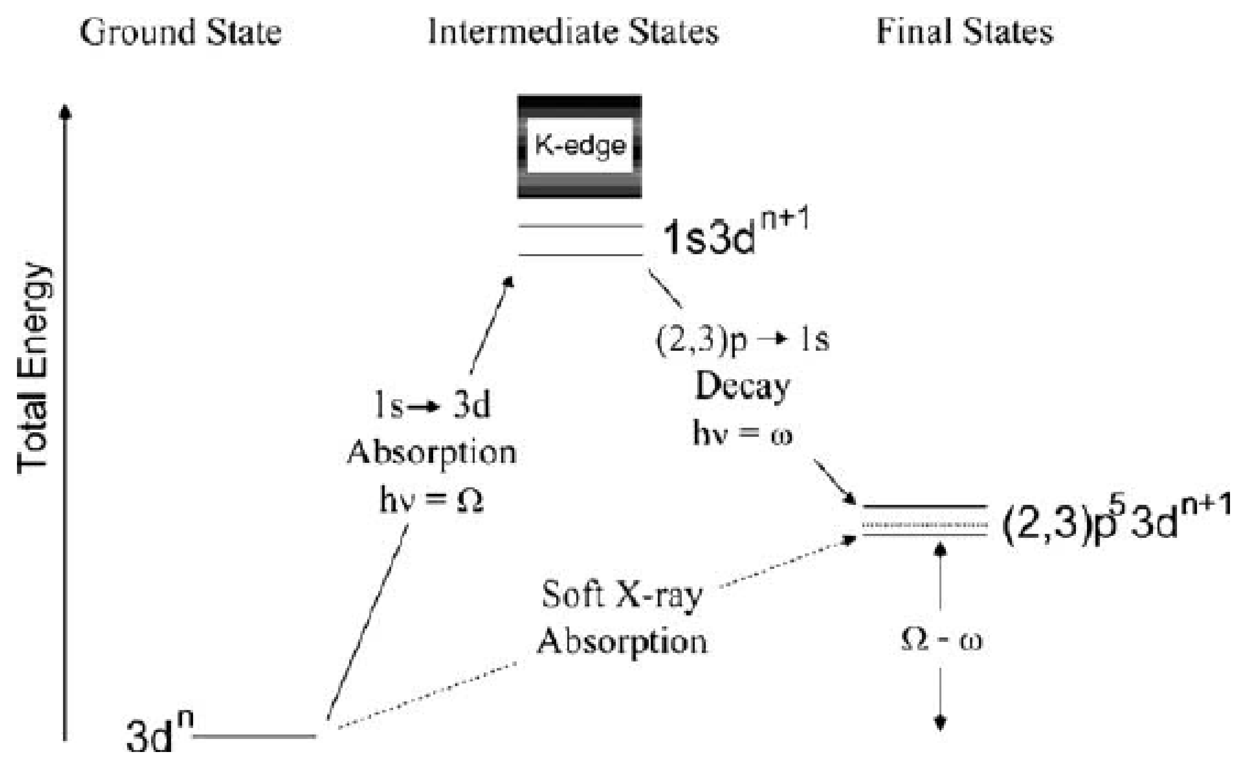
Resonant Inelastic X-Ray Scattering (RIXS)

Experiment: The incident energy Ω is scanned across an absorption edge. The emitted energy ω is also scanned either over the fluorescence lines or over energies just below the elastically scattered peak. In the later case, the energy transfer Ω-ω becomes small (on the order of a few eV) and valence band excitations are observed.

- A fluorescence line can be measured after resonant excitation. This is referred to as resonant X-ray emission

- Spectral features may occur at emission energies different to the energies of the fluorescence lines. These features are frequently observed at an energy transfer of a few eV. The technique is often referred to as resonant inelastic x-ray scattering (RIXS).

RIXS energy scheme for 1s(2,3)p RIXS in a transition metal atom



Resonant inelastic X-ray scattering (RIXS)

Inelastic scattering of the incident photon at a resonance energy of the metal ion and is theoretically described by the Kramers-Heisenberg formular:

$$F(\Omega,\omega)=\sum_f\left|\sum_n\frac{\langle f|T_2|n\rangle\langle n|T_1|g\rangle}{E_g-E_n+\Omega-i\Gamma_n/2}\right|^2\times\frac{\Gamma_f/2\pi}{\left(E_g-E_f+\Omega-\omega\right)^2+\Gamma_f^2/4}$$

$|n\rangle$ = $1s3d^{n+1}$

$|g\rangle$ = $3d^n$

$|f\rangle$ = $(2,3)p^5 3d^{n+1}$

E_g, E_n and E_f : Energies of ground, intermediate and final state

Γ_n, Γ_f: lifetime broadenings of the intermediate and final state

T_1, T_2: transition operators for absorption and emission

Resonant inelastic X-ray scattering

1) The absorbing atom is not ionized in the case of resonant excitation, as the photoexcited electron stays within a bound state.

2) The spectral feature become sharper because it i the lifetime of the final state which determines the broadening

3) The final state electronic configuration may formally be equal to other spectroscopies, e.g. the L-edge in 1s2p RIXS of 3d transition metals or UV-Vis in RIXS that exhibits a hole in the valence band in the final state.

   investigate the dipol allowed 2p-3d transition (below 1.1 KeV in ambient pressure)

4) Less radiation damage

Resonant inelastic X-ray scattering

How to study the 3d shell by K shell spectroscopy?

Dipol selection rules $\Delta l = \pm 1$

Quadrupol transition are by more than two orders of magnitude lower

Two approaches: investigate 2p or 3p - 1s fluorescence lines that emitted after 1s hole creation

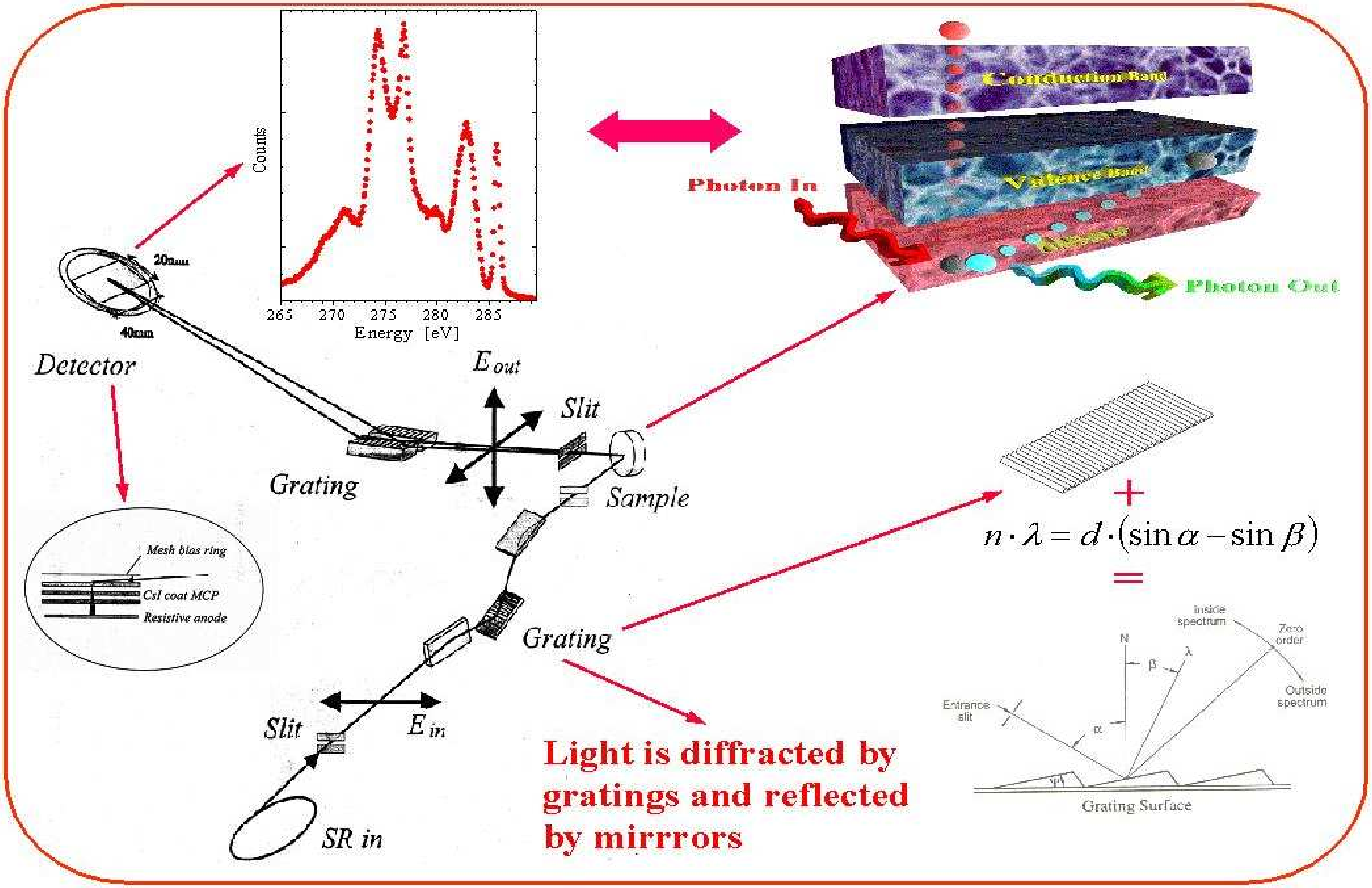
Information on the 3d metal shell will be derived indirectly by analysing the interaction of the 2p or 3p hole with the 3d electrons (large overlap of wave functions) K fluorescence show a pronounced chemical sensitivity

Resonant inelastic X-ray scattering

Second approach:
Study the weak K absorption pre-edge structure by probing directly the transition 1s-3d

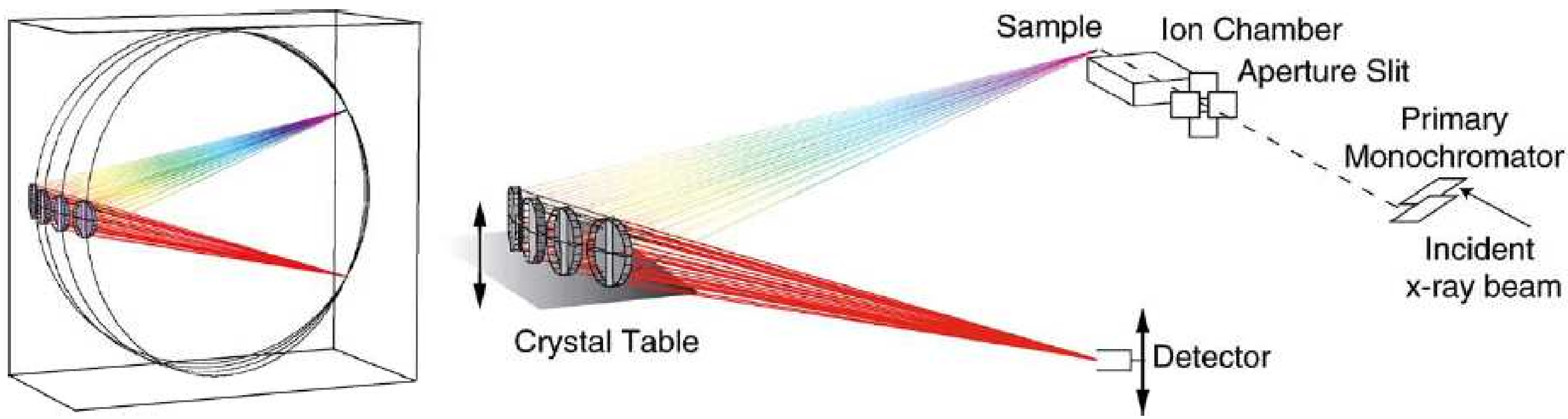
RIXS enables the separation of pre-edge structures from main K absorption edge

RIXS setup



Counts
265 270 275 280 285
Energy [eV]
20mm
40mm
Detector
Mesh bias ring
CsI coat MCP
Resistive anode
Photon In
Photon Out
E_{out}
Slit
Grating
Sample
Grating
Slit
E_{in}
SR in
$n \cdot \lambda = d \cdot (\sin\alpha - \sin\beta)$
Entrance slit
Inside spectrum
Zero order
Outside spectrum
Grating Surface
Light is diffracted by gratings and reflected by mirrors

RIXS setup

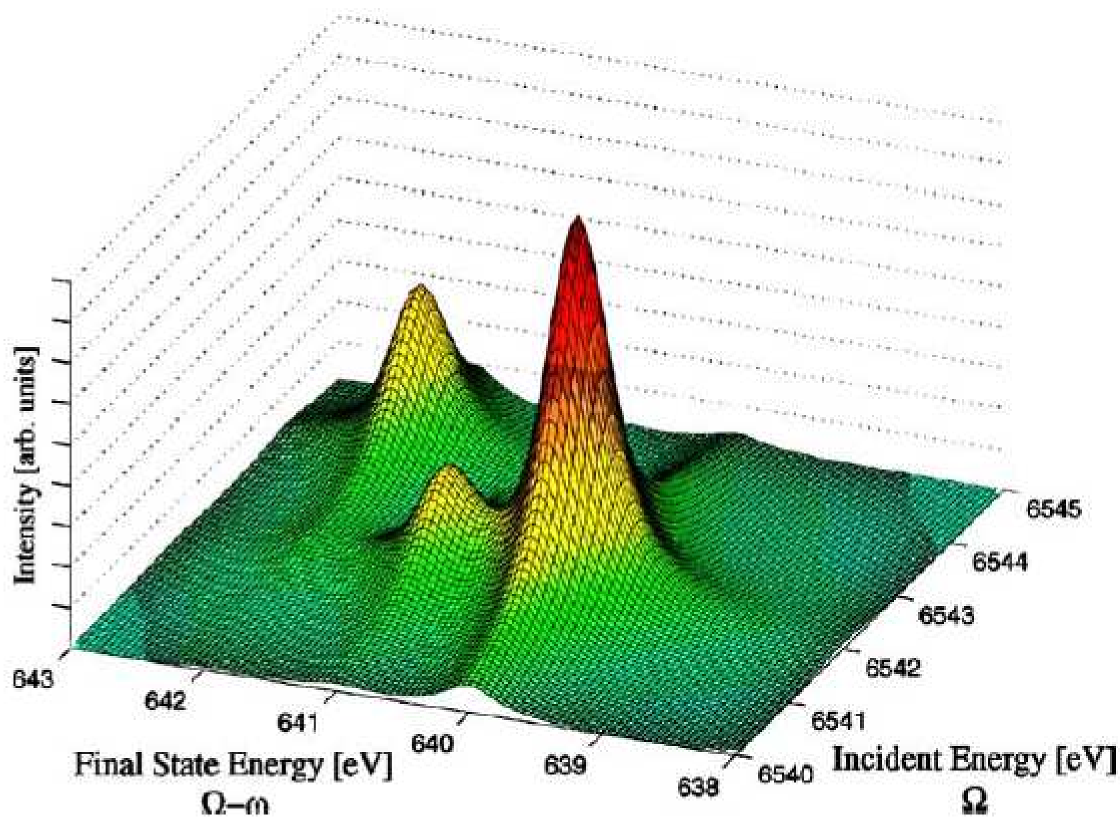


Additional ion chamber to measure absorption in transition mode, calibrtion standard for energy calibration

Photon flux: 10^{11} photons/s (second generation synchrotron radiation facility)
Photon flux: 10^{13} photons/s (third genaration synchrotron radiation facility)

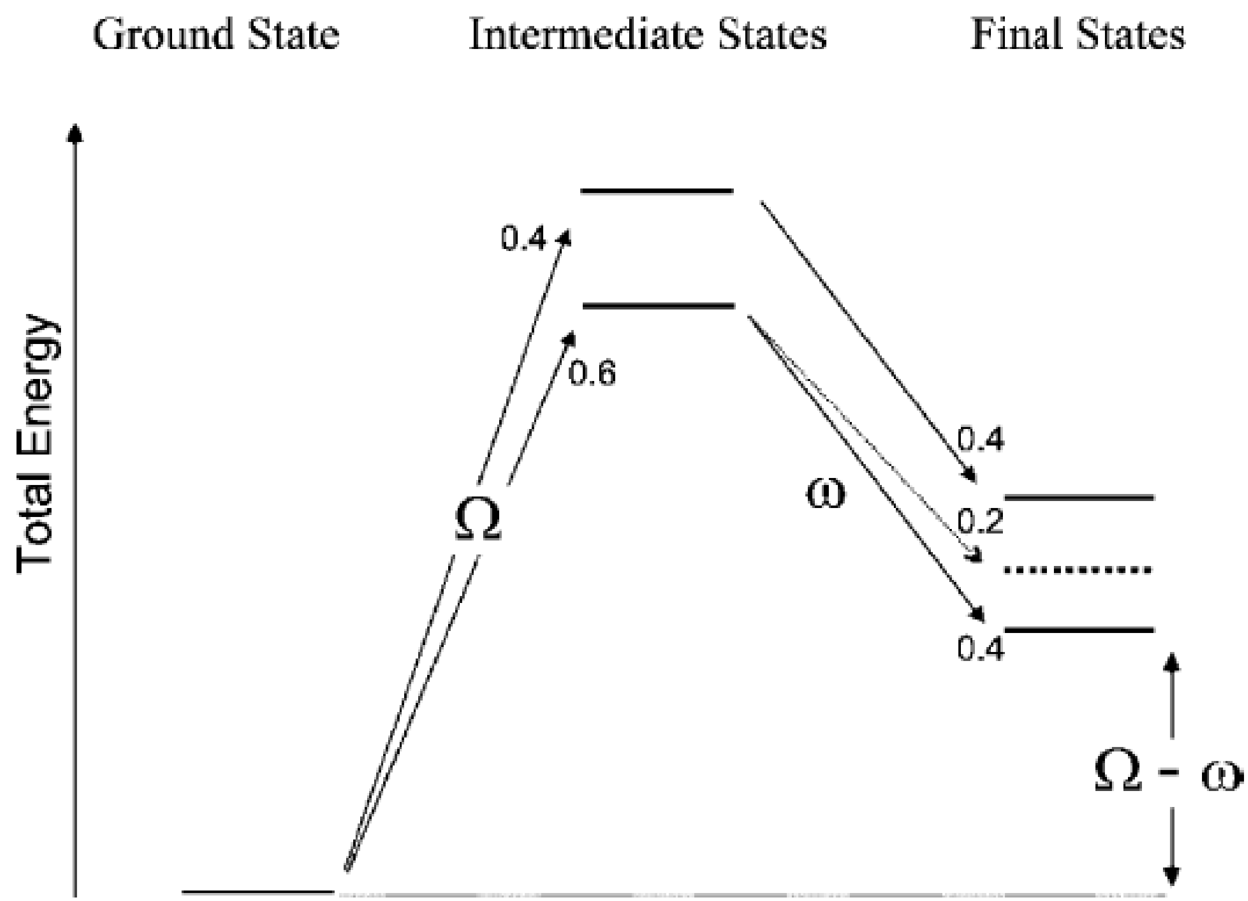
ESRF, APS, Spring8, PetraIII, SOLEIL, DIAMOND

Surface plot of the RIXS plane



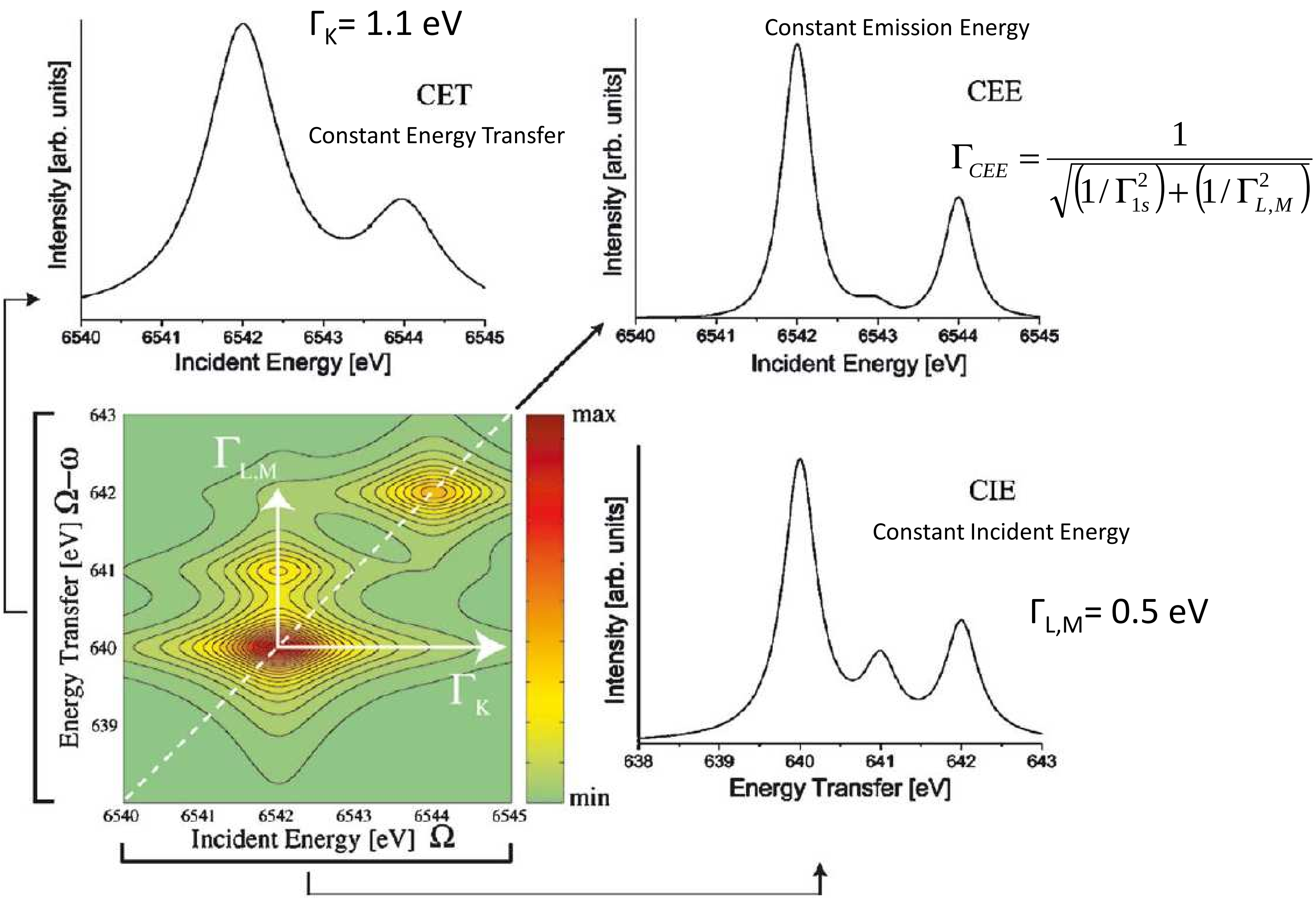
These energies relates to the excitation energy of L-M-edge absorption spectra

Energy scheme for a model system

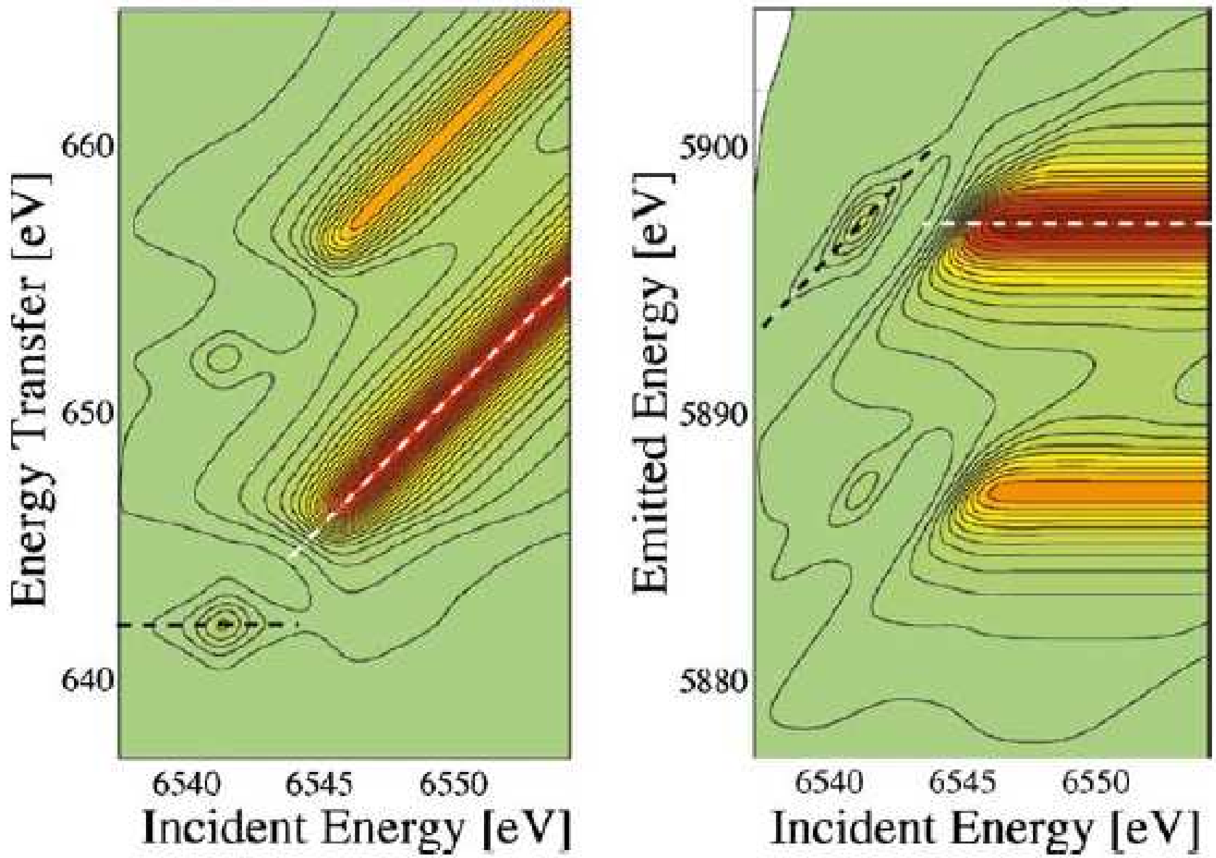


Theoretical RIXS plane with three line plots

Splitting due to ligand field



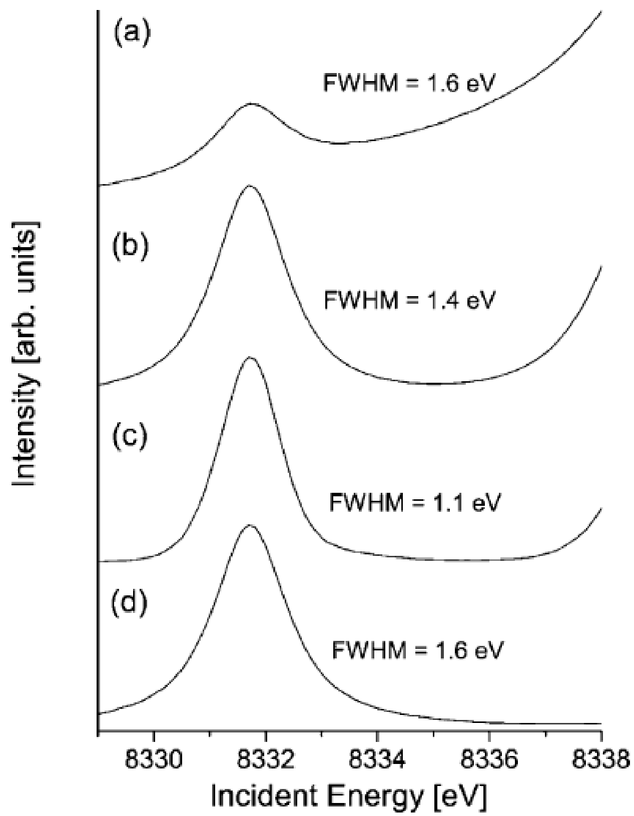
Continuum excitations

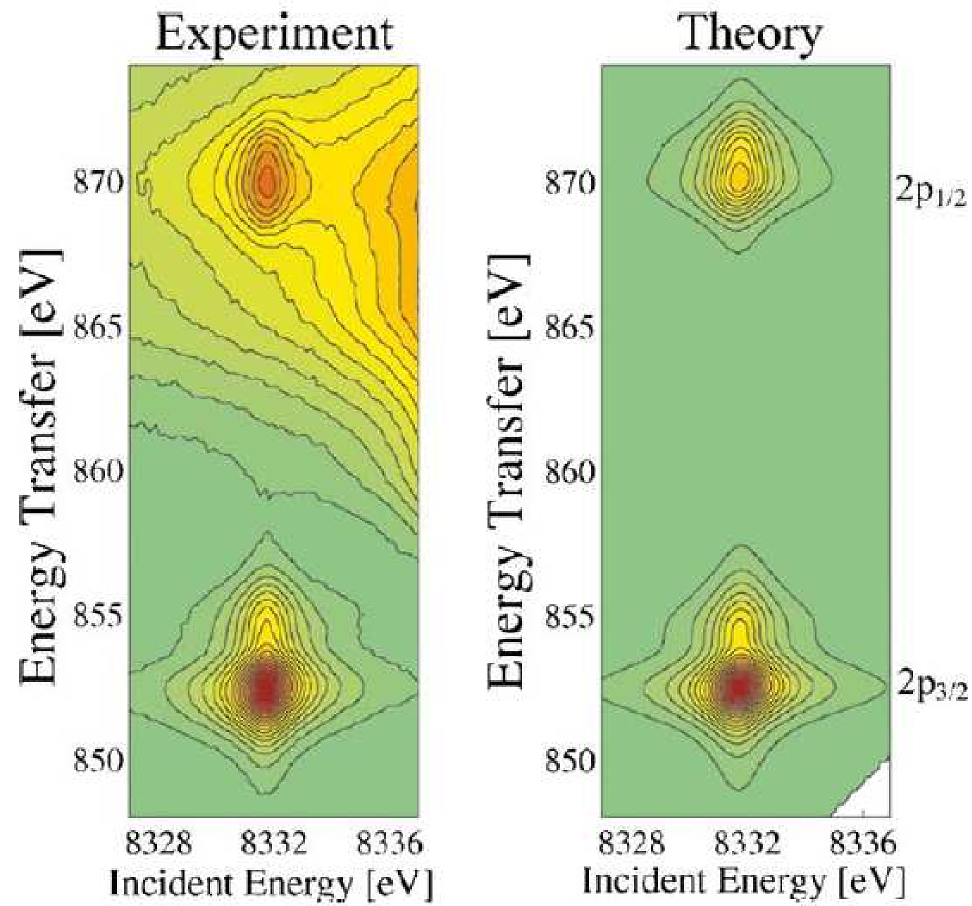


Spin-orbit splitting $2p_{3/2}$ and $2p_{1/2}$

Raman-Stokes line shift

Experimental data of the 1s – 3d resonance in NiF_2



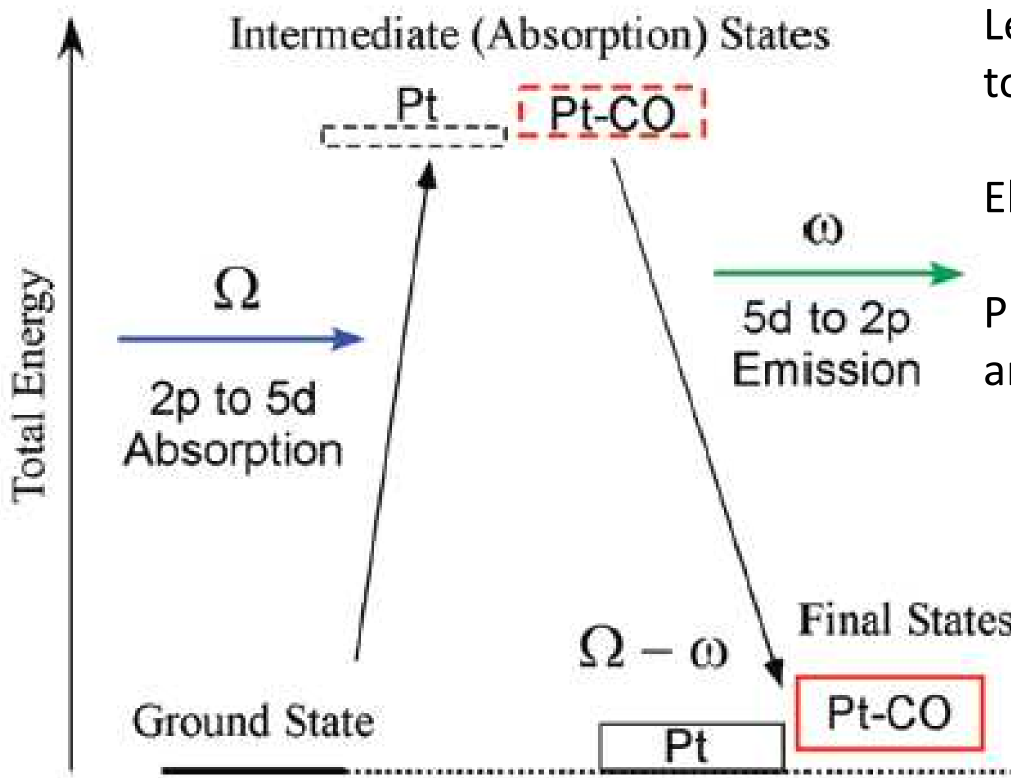


a) K absorption pre-edge
b) CEE line plot with 5 eV emission analyser bandwith
c) CEE line plot with 1 eV emission analyser bandwith
d) CET line plot integrated over 2p3/2 final states

Γ_K= 1.4 eV lifetime broadening

Γ_L= 0.7 eV lifetime broadening

Resonant inelastic X-ray scattering



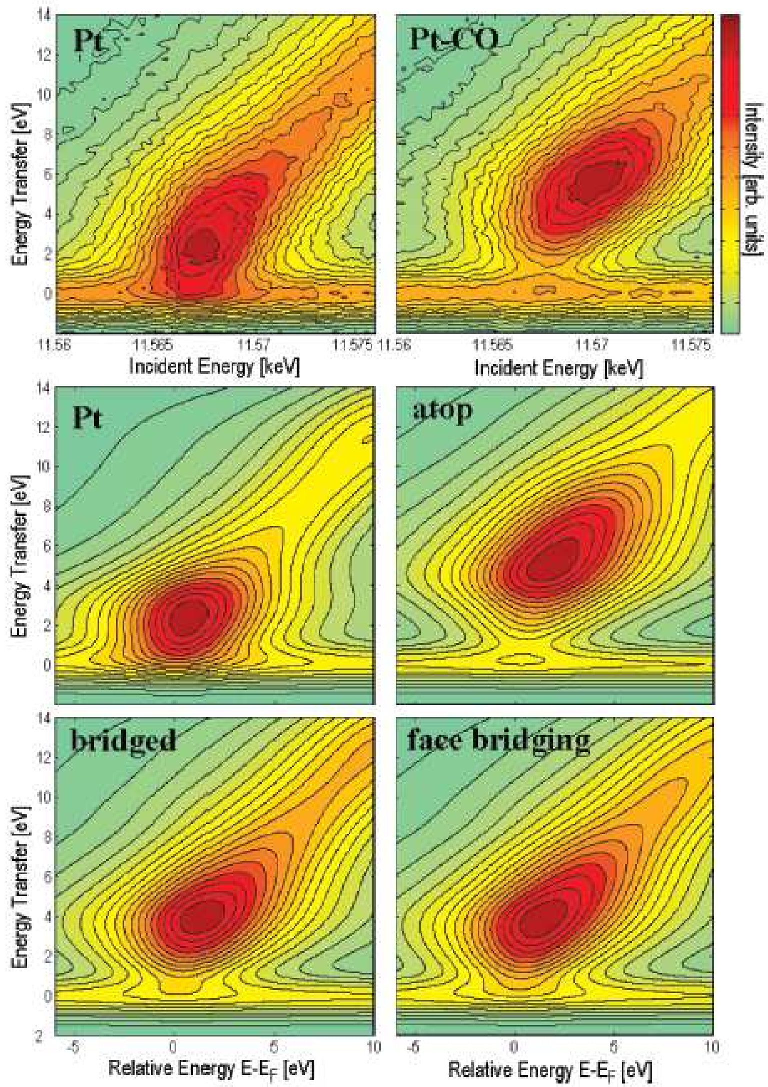
Less resrictive than UPS with respect to the sample environment

Element selective

Probing the electronic structure around the Fermi level

$2p_{3/2}$ RIXS planes of Pt nanoparticles: metallic and with CO adsorbed

Metallic state: elastic peak merge with valance-band excitations
Fermi level lies within a partially filled band



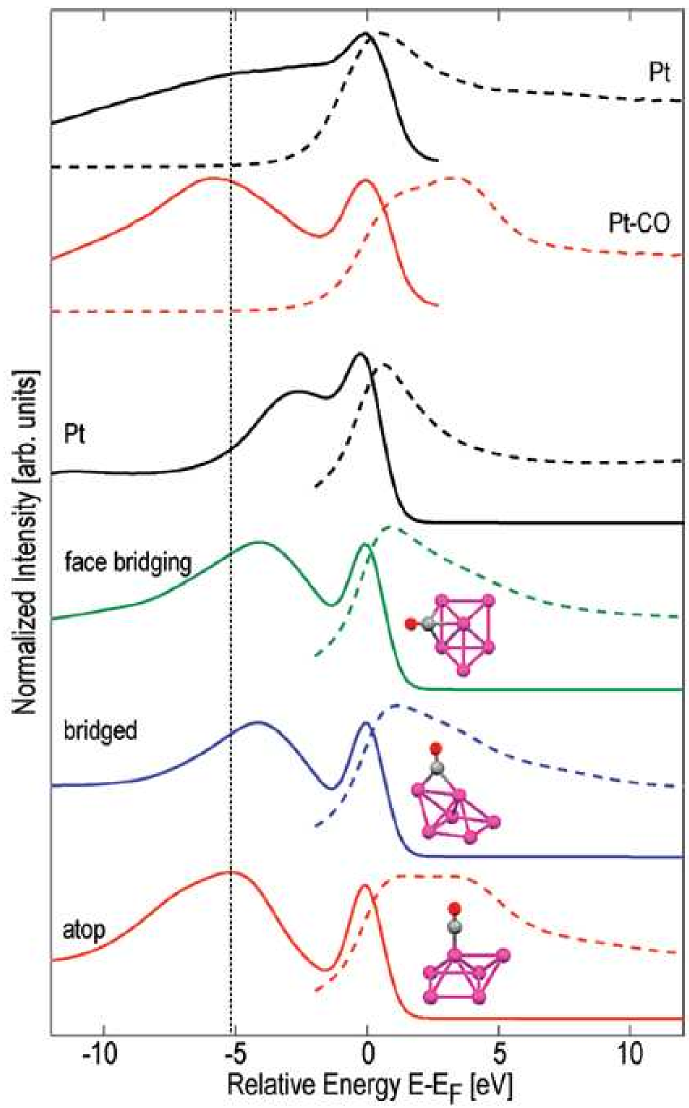
Left: metal
Right: CO adsorbed

Calculated RIXS planes of Pt_6 clusters

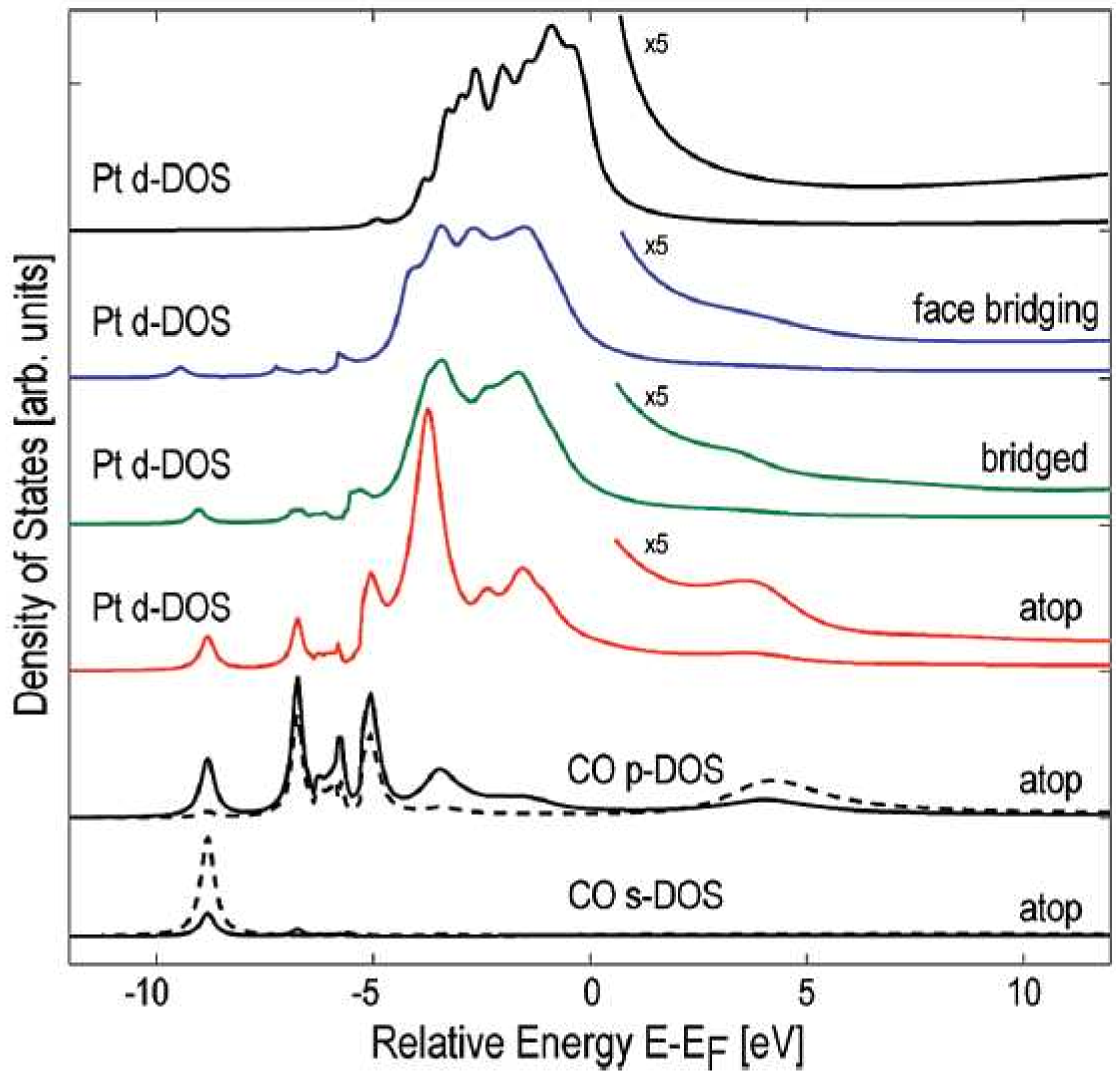
HERFD Pt L_3 XAS ↔ RIXS

Dashed lines: exp.
HERFD XAS
Solid lines: RIXS

Calculated spectra:
HERFD XAS
Solid lines: RIXS



Calculated orbital angular momentum-projected density of states



Dashed: C
Solid: O

Literature

P. Glatzel, U. Bergmann
Coordination Chemistry Reviews 249 (2005) 65-95

Summary

RIXS is valuable to separate out the K-absorption pre-edge features and hence to study the local electronic structure of transition metal compounds

The energy transfer spectra are not broadened by the short 1s care hole lifetime but only by the longer final state lifetime resulting in sharper spectral features

By using an emission analyser with a modest energy bandwidth of a few eV and recording the $2p_{3/2}$ ($K\alpha_1$) CEE intensity the Kedge spectral features can be better resolved than in conventional absorption spectroscopy