X-Ray Emission Spectroscopy

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Core Level Spectroscopy

Creation of core holes

X-Ray Photoelectron Spectroscopy (XPS)

Creation of core holes

X-Ray Absorption Spectroscopy (XAS)

Decay of core holes

X-Ray Emission Spectroscopy (XES)

Decay of core holes

Auger Electron Spectroscopy

Resonant Excitation

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

X-ray attenuation length

B. L. Henke Atom Data Nucl. Data 54, 181 (1993)
K fluorescence

K shell emission lines in MnO

Kβ₁: 3p₃/₂, Kβ₃:3p₁/₂ final states
Kβ₂: transition from 4p orbitals, Kβ₅: from 3d orbitals
High-Energy Resolution Fluorescence Detected (HERFD) XAS

Experiment: The emitted energy $\omega$ is tuned to a fluorescence line and the incident energy $\Omega$ 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 bandwidth of 200-300 eV at Fe K$\alpha$ line

Non linearity at high count rates (pileup effect)

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

Light is diffracted by gratings and reflected by mirrors

\[ n \cdot \lambda = d \cdot (\sin \alpha - \sin \beta) \]
Bragg Equation

William Lawrence Bragg and Henry Bragg

Noble Prize of Physics in 1914

\[ n \lambda = 2d \sin \theta \]

- \( \lambda \) = Wellenlänge
- \( d \) = Netzebenenabstand
- \( \theta \) = Glanzwinkel
- \( n \) = ganze Zahl
TFY-HERFD Detection Mode

Pt L$_3$ edge XANES of a Pt foil

[Graph showing normalized XANES vs energy (eV), with two traces labeled Total fluorescence and HERFD]

M. Tromp,
Non-Resonant X-Ray Emission Spectroscopy (XES)

Experiment: The incident energy $\Omega$ is tuned well above an absorption and the emitted energy $\omega$ 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\textbeta) 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\textbeta main line, for example, are sensitive to the valence shell spin state.
K $\beta$ lines

$^{55}\text{Fe}_2\text{O}_3$ (solid line) $S=5/2$

$K_3^{55}\text{Fe(CN)}_6$ (dashed line) $S=1/2$

$K_4^{55}\text{Fe(CN)}_6$ (dotted line) $S=0$

Prussian Blue ($\text{Fe}_4[\text{Fe(CN)}_6]_3$)

Measured after K capture decay

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Kβ lines of Mn fluorides and oxides

MnF₂ (solid line)  
MnF₃ (dashed line)  
MnF₄ (dotted line)

MnO (solid line)  
Mn₂O₃ (dashed line)  
MnO₂ (dotted line)

Different correlation of fluorides and oxides due to different degree of covalent bonding!

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Extended X-ray Absorption Fines Structure - EXAFS

RbNO$_3$ water solution and Rb vapour @ Rb K edge
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 (Fe₄[Fe(CN)₆]₃)

High spin component: Fe(III) Fe₂O₃
Low spin component: K₄Fe(CN)₆

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Deduced site selective EXAFS spectra

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.

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Valence electron perturbation upon 1s photoionisation

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Resonant X-Ray Emission Spectroscopy (RXES) and Resonant Inelastic X-Ray Scattering (RIXS)

Experiment: The incident energy $\Omega$ is scanned across an absorption edge. The emitted energy $\omega$ is also scanned either over the fluorescence lines or over energies just below the elastically scattered peak. In the later case, the energy transfer $\Omega - \omega$ 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

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

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

- \( |n\rangle = 1s3d^{n+1} \)
- \( |g\rangle = 3d^n \)
- \( |f\rangle = (2,3)p^5 3d^{n+1} \)

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

\( \Gamma_n, \Gamma_f \): 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 becomes sharper because it is 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 1s3d2p 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
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
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
Photon flux: $10^{11}$ photons/s (second generation synchrotron radiation facility)
Photon flux: $10^{13}$ photons/s (third generation synchrotron radiation facility)

ESRF, APS, Spring8, PetraIII, SOLEIL, DIAMOND

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Surface plot of the RIXS plane

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Theoretical RIXS plane with three line plots

\[ \Gamma_K = 1.1 \text{ eV} \]
\[ \Gamma_L = 0.5 \text{ eV} \]

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

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Experimental data of the 1s – 3d resonance in NiF₂

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

P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Resonant inelastic X-ray scattering

Less restrictive than UPS with respect to the sample environment

Element selective

Probing the electronic structure around the Fermi level

van Bokhoven et al. JACS 132, 2555 (2010)
Metallic state: elastic peak merge with valance-band excitations. Fermi level lies within a partially filled band.

\[
F(\Omega, \omega) = \int \rho_d(\varepsilon) \rho_d'(\varepsilon + \Omega - \omega) \frac{1}{(\varepsilon - \omega)^2 + \left(\frac{\Gamma_n}{4}\right)^2}
\]

\(\rho\) : densities of occupied Pt d states
\(\rho'\) : densities of unoccupied Pt states
\(\Gamma_n\) : lifetime broadening of the 2p\(_{3/2}\) core hole (5.4 eV)

2p\(_{3/2}\)RIXS planes of Pt nanoparticles: metallic and with CO adsorbed

van Bokhoven et al. JACS 132, 2555 (2010)
HERFD $L_3$ XAS $\leftrightarrow$ RIXS

Dashed lines: exp.
HERFD XAS
Solid lines: RIXS

Calculated spectra:
HERFD XAS
Solid lines: RIXS

van Bokhoven et al. JACS 132, 2555 (2010)
P. Glatzel, U. Bergmann; Coordination Chemistry Reviews 249 (2005) 65-95
Literature
Creation of Core holes

Ionisation

X-ray photoelectron spectroscopy (XPS)

Excitation

X-ray absorption spectroscopy (XAS)

X-ray Inelastic scattering (XIS)

Core Level Spectroscopy

XPS

XAS
Core Level Spectroscopy

XES

AES

[Images of XES and AES spectroscopy graphs]