

Search MOOC



Video



Contents and objectives of this video



- Relationship between XAS and XES
- X-ray emission lines
- Applications

Hello and welcome to week four of this six-week course on Synchrotron and XFEL Radiation Techniques and Applications. Last week we concentrated on X-ray photoabsorption techniques. This week we will consider techniques that exploit the nature of the products of photo absorption, including fluorescence and photoelectron spectroscopy. In this first section, we discuss techniques based on fluorescence, namely X-ray fluorescence spectroscopy and resonant inelastic X-ray scattering. Fluorescent spectroscopies are photon-in, photon-out techniques and can be carried out on both conducting and insulating samples. As a result, these techniques can often be applied under ambient or indeed in vivo environments, depending on the energy range of interest. X-ray fluorescence generally probes the fluorescence spectrum resulting from absorption at a fixed incident photon energy. Although excitation can also be via impact of energetic electrons. Resonant, inelastic scattering, on the other hand probes the emission spectra as a function of incident photon energy.

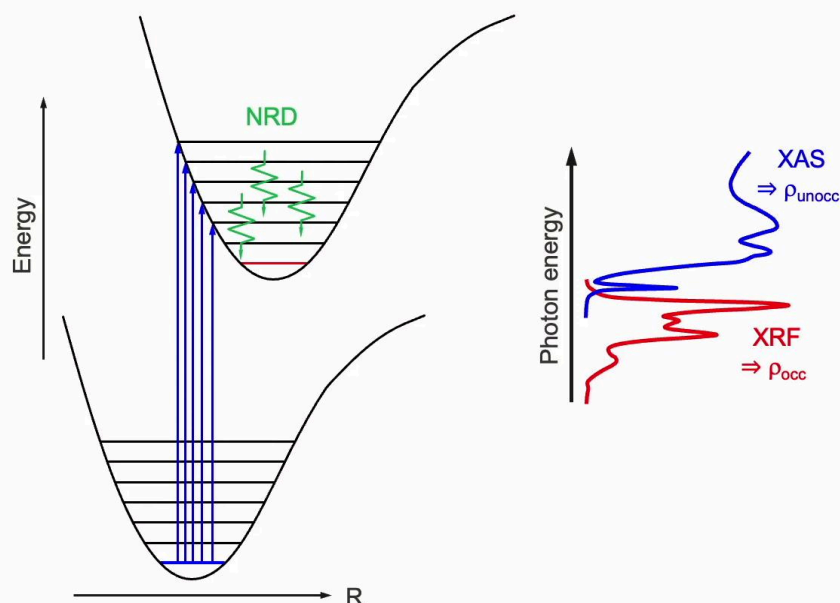
Notes

Summary



0m 05s

Relationship between XAS and XES (XRF)



- NRD = nonradiative decay
 - Might be missing in isolated gas-phase molecules
 - In condensed matter \Rightarrow lowest-energy excited state
- Intensity of a transition depends on Franck-Condon principle
 - "Vertical" transitions
 - Electronic motion much faster than nuclear motion
 - Located at turning point of excited state for absorption, final state for fluorescence
 - Biggest overlap of wavefunctions

$$I \propto |\langle \psi_1 | \psi_2 \rangle|^2$$

X-ray fluorescence probes the photons emitted as a consequence of relaxation of the system after photoabsorption. It is a powerful method for determining the chemical composition of objects that are either too thick for transmission absorption measurements or are insulating, and therefore preclude photoemission techniques. X-ray fluorescence is used widely in geochemistry, archaeology, forensic science, and investigations of rare or ancient artefacts. Among other things, it exploits the fingerprint characteristic radiation of the elements for chemical and elemental analysis. In X-ray fluorescence spectromicroscopy the dispersed XRF signal is mapped out spatially using a focussed beam. This can be performed either using dispersive solid-state detectors in EDX or either a multi-Rowland Circle monochromatic detector or a von Hamos spectrometer. The energy ranges of X-ray fluorescence and X-ray absorption spectra are related insofar that where X-ray fluorescence ends, X-ray absorption spectra begin. The spectra tend to mirror one another. This is because in the excited state, rapid nonradiative decay to the lowest state will occur before the initially excited state has time to fluoresce.

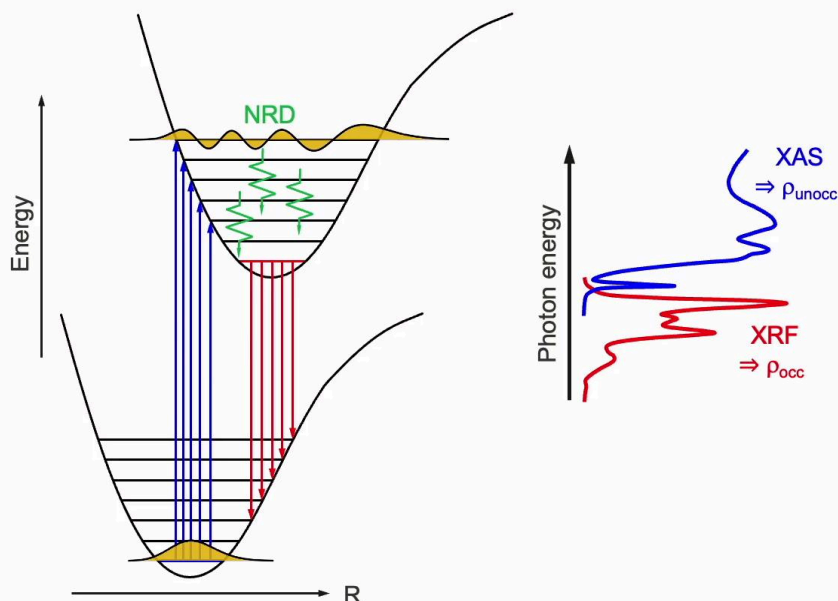
Notes

Summary



1m 30s

Relationship between XAS and XES (XRF)



- NRD = nonradiative decay
 - Might be missing in isolated gas-phase molecules
 - In condensed matter \Rightarrow lowest-energy excited state
- Intensity of a transition depends on Franck-Condon principle
 - "Vertical" transitions
 - Electronic motion much faster than nuclear motion
 - Located at turning point of excited state for absorption, final state for fluorescence
 - Biggest overlap of wavefunctions

$$I \propto |\langle \psi_1 | \psi_2 \rangle|^2$$

The intensity of each transition in both absorption and emission is governed by the Franck-Condon principle. The strength of a transition is proportional to the squared modulus of the two wave functions connected by the absorbing or emitting photon respectively. In practice, this means that overlap between vibrational levels in the two states is largest at the turning point of the wavefunctions where their amplitudes are greatest. The transitions are vertical due to the fact that the change in atomic positions, denoted here by the abscissa R , is negligible on the time scale of absorption or emission. The system has no time to readjust to the new electronic distribution.

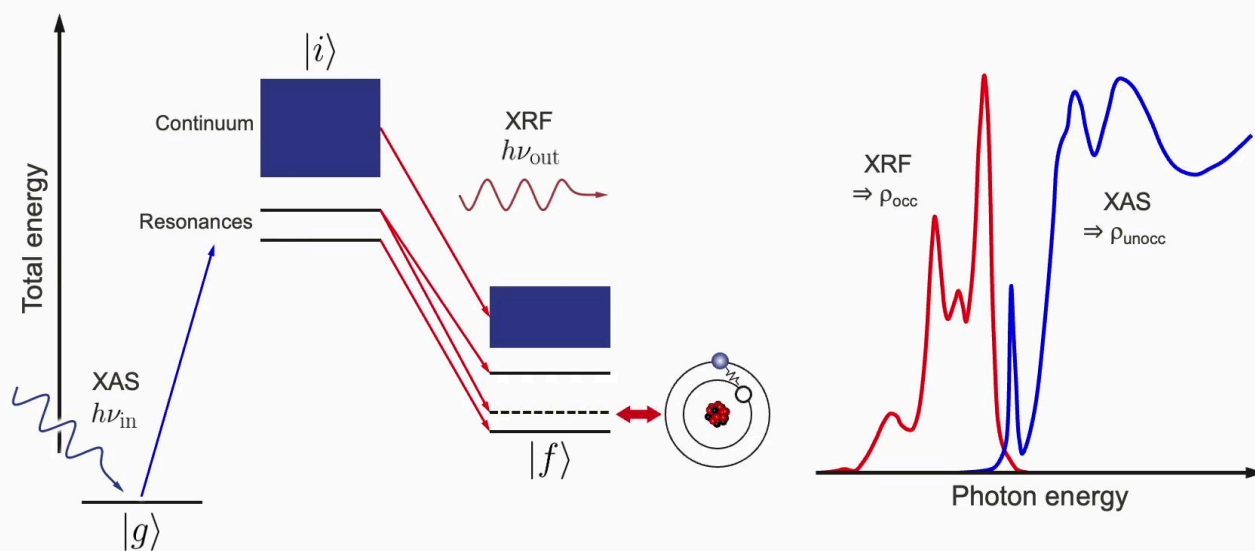
Notes

Summary



3m 11s

Energy balance in XAS and XES (XRF)



Note also that in the excited state a rearrangement can occur of the atoms on the timescale of picoseconds that can shift the energy level as shown here.

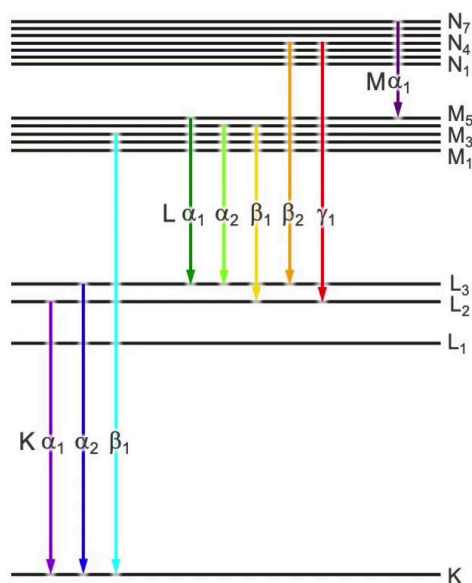
Notes

Summary



4m 05s

X-ray emission-line energies



Edge	n	l	j	Configuration
K	1	0	$1/2$	$1s$
L ₁	2	0	$1/2$	$2s$
L ₂	2	1	$1/2$	$2p_{1/2}$
L ₃	2	1	$3/2$	$2p_{3/2}$
M ₁	3	0	$1/2$	$3s$
M ₂	3	1	$1/2$	$3p_{1/2}$
M ₃	3	1	$3/2$	$3p_{3/2}$
M ₄	3	2	$3/2$	$3d_{3/2}$
M ₅	3	2	$5/2$	$3d_{5/2}$
N ₁	4	0	$1/2$	$4s$
N ₂	4	1	$1/2$	$4p_{1/2}$
N ₃	4	1	$3/2$	$4p_{3/2}$
N ₄	4	2	$3/2$	$4d_{3/2}$
N ₅	4	2	$5/2$	$4d_{5/2}$
N ₆	4	3	$5/2$	$4f_{5/2}$
N ₇	4	3	$7/2$	$4f_{7/2}$
O ₁	5	0	$1/2$	$5s$
O ₂	5	1	$1/2$	$5p_{1/2}$

See also: https://xdb.lbl.gov/Section1/Table_1-2.pdf and https://xdb.lbl.gov/Section1/Table_1-3.pdf and <https://www.synchrotronmovies.com/download/xremissiondata.dat>

An energy level diagram and fluorescence transitions, including their labels, is shown on the left, while their associated quantum numbers and configurations are shown on the right. Note that some transitions are forbidden. For example L1 to K, as this is from an s orbital to another s orbital which we have already argued is not allowed on account of the dipole matrix element being antisymmetric.

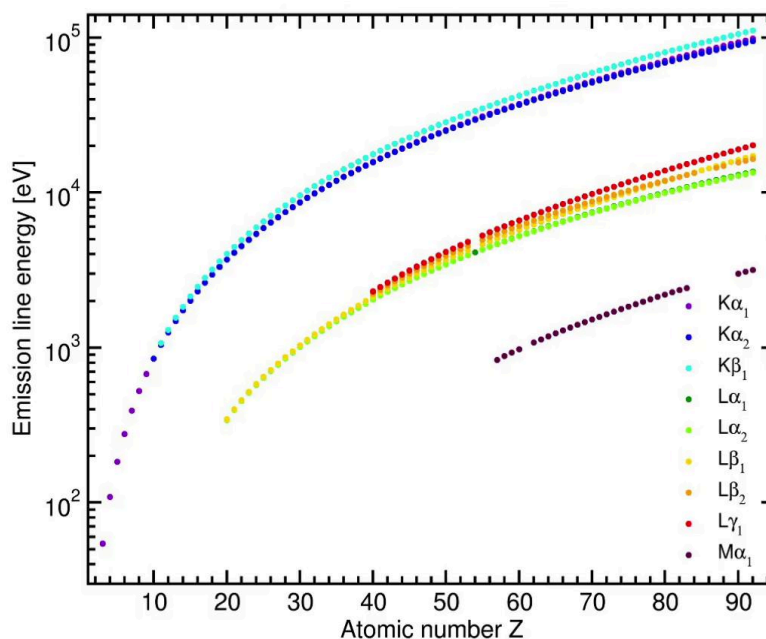
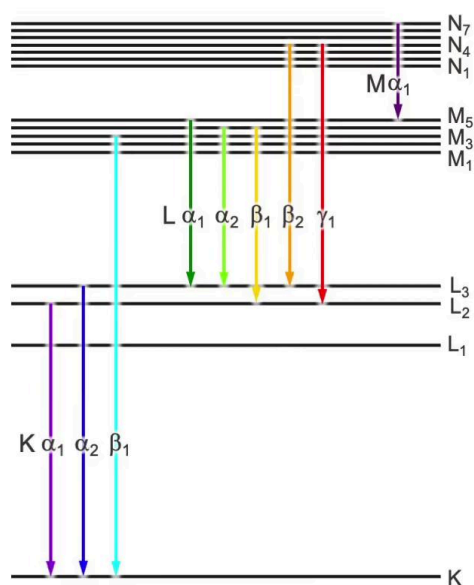
Notes

Summary



4m 17s

X-ray emission-line energies



See also: https://xdb.lbl.gov/Section1/Table_1-2.pdf and https://xdb.lbl.gov/Section1/Table_1-3.pdf and <https://www.synchrotronmovies.com/download/xremissiondata.dat>

The energies of the fluorescent lines for the elements are also provided here. Note that most of the lines are above one kiloelectronvolt, with the exception of K lines below sodium in atomic number, and the first 10 L transitions to the n equals 2 energy levels between chromium and arsenic.

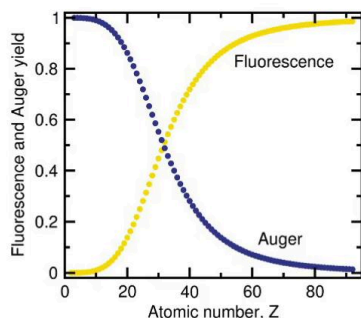
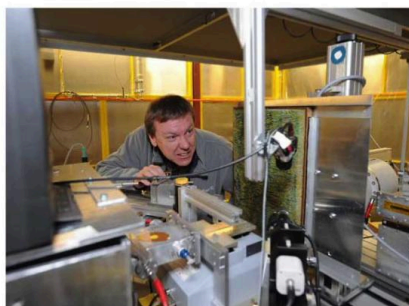
Notes

Summary



4m 47s

Applications of XRF



$$p_{fl} \propto (h\nu)^3$$

$$Y_K = \frac{Z^4}{10^6 + Z^4}$$

- XRF = nonresonant XES
- Does not require SR
 - Can use electron-beam excitation
 - Danger of artefacts!
 - Lab-based sources also possible
- Mainly hard x-rays (c.f. RXES)
 - Easier sample handling
 - Lower dose rates
 - Higher fluorescence yield c.f. Auger etc.
- Detailed shifts in photon energies
 - Local chemistry (similar to XPS, XANES)
 - Requires high-resolution detector
- Fingerprints for presence of elements
 - Trace concentrations possible
 - Low-resolution (but fast!) detectors

X-ray fluorescence or non-resonant X-ray emission spectroscopy does not in principle require synchrotron radiation, or indeed X-rays at all. Electron bombardment can also induce fluorescence, though with the possibility of some artefacts or damage. Most X-ray fluorescence experiments are carried out using hard X-rays as this simplifies the experimental setup and sample handling and is associated with lower dose rates on the samples. Moreover, for relaxation transitions in the hard X-ray regime, fluorescence dominates over Auger emission, according to the two equations shown here. X-ray fluorescence signal is strongly absorbed by air for emission below approximately 3,500 electron volts, which corresponds to calcium or thereabouts, which has its K emission line at 3,692 electron volts. For emission signal below approximately three-and-a-half keV, the path to the detector should be evacuated in order to avoid absorption by the residual gas such that the product of sample detector distance and pressure is lower than approximately one Pascal metre.

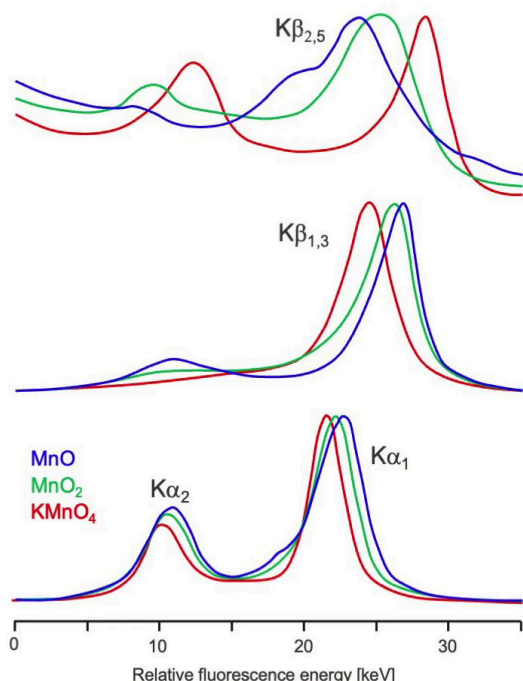
Notes

Summary



5m 12s

Applications of XRF



- XRF = nonresonant XES
- Does not require SR
 - Can use electron-beam excitation
 - Danger of artefacts!
 - Lab-based sources also possible
- Mainly hard x-rays (c.f. RXES)
 - Easier sample handling
 - Lower dose rates
 - Higher fluorescence yield c.f. Auger etc.
- Detailed shifts in photon energies
 - Local chemistry (similar to XPS, XANES)
 - Requires high-resolution detector ~ eV
- Fingerprints for presence of elements
 - Trace concentrations possible
 - Low-resolution (but fast!) detectors

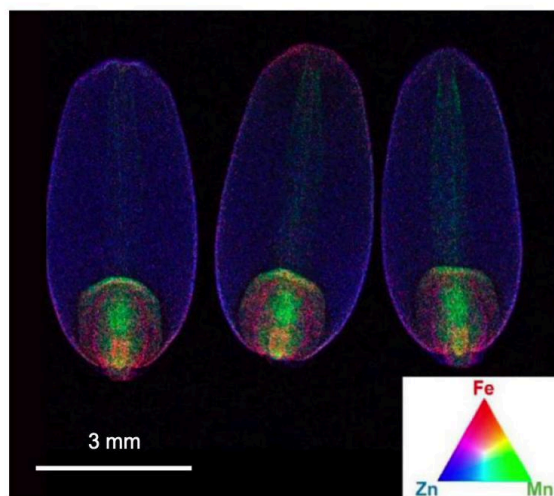
Just as in X-ray absorption and X-ray photo-electron spectroscopy, chemical shifts in the fluorescence peak positions reveal valuable information in their local chemistry, such as the valence state, as can be seen here for the manganese fluorescence for different chemical species. In order to resolve this, the fluorescence detectors need to have a resolution of the order of one electronvolt or better.

Notes

Summary



Applications of XRF



Tricolour image of wheat seeds, courtesy E. Lombi, University of South Australia
P.M. Kopittke *et al.*, <https://doi.org/10.1104/pp.18.00759>

- XRF = nonresonant XES
- Does not require SR
 - Can use electron-beam excitation
 - Danger of artefacts!
 - Lab-based sources also possible
- Mainly hard x-rays (c.f. RXES)
 - Easier sample handling
 - Lower dose rates
 - Higher fluorescence yield c.f. Auger etc.
- Detailed shifts in photon energies
 - Local chemistry (similar to XPS, XANES)
 - Requires high-resolution detector
- Fingerprints for presence of elements
 - Trace concentrations possible
 - Low-resolution (but fast!) detectors

On a more practical level, and using detectors with poorer resolving powers, fluorescent signal can act as a fingerprint for the presence of elements down to trace concentrations as low as a few parts per million, such as shown here in this arresting image of scanning fluorescence of wheat seeds with cell nuclei containing significant concentrations of iron and manganese.

Notes

Summary



7m 02s

In the next video...



In the second video on X-ray fluorescence, we will consider further experimental and practical aspects and finish with an example of scanning X-ray fluorescence that was used to reveal exciting insights into the early oeuvre of one of the foremost post-impressionist painters, Vincent van Gogh.

Notes

Summary



7m 32s