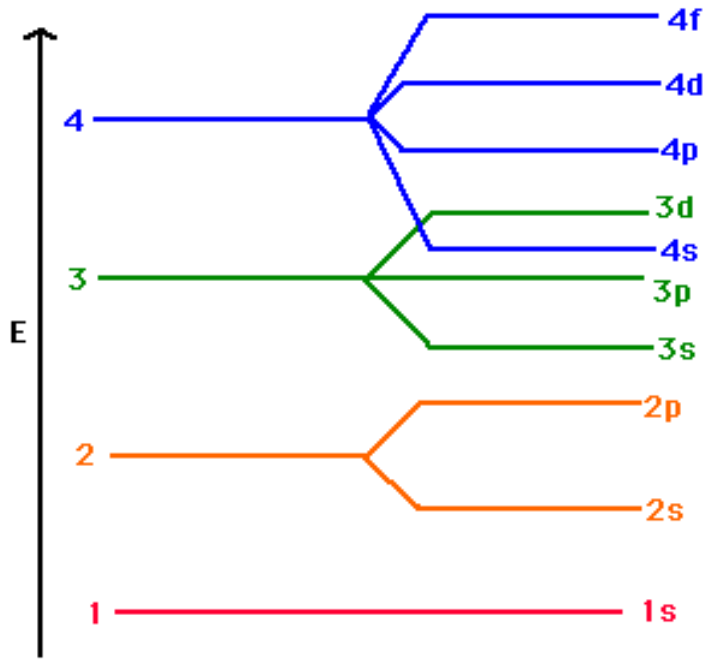
Outline of the day

- Introduction
- Basic X-ray diffraction
  - Powders, thin films, single crystals
- Small-angle X-ray scattering
- X-ray absorption spectroscopy
  - Atomic structure
  - Electronic structure (Ben Ruck)
- Advanced X-ray diffraction
  - Anomalous diffraction
  - Total X-ray scattering
- Designing experiments
  - In situ measurements

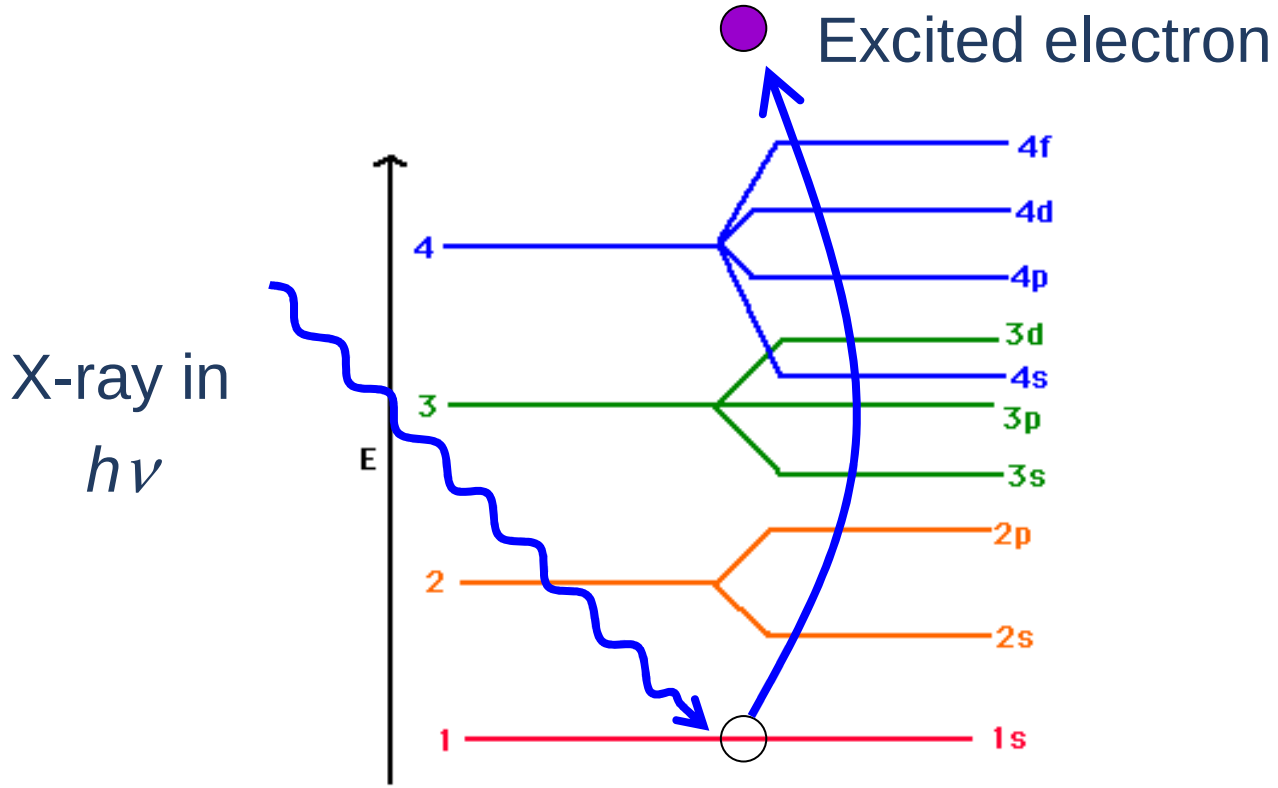
X-ray Absorption Spectroscopy for atomic structure

- What is XAS?
- Using the same data for different things: XANES and EXAFS
- What information can I get using XANES?
- What information can I get using EXAFS?
- How are data collected?
- Examples

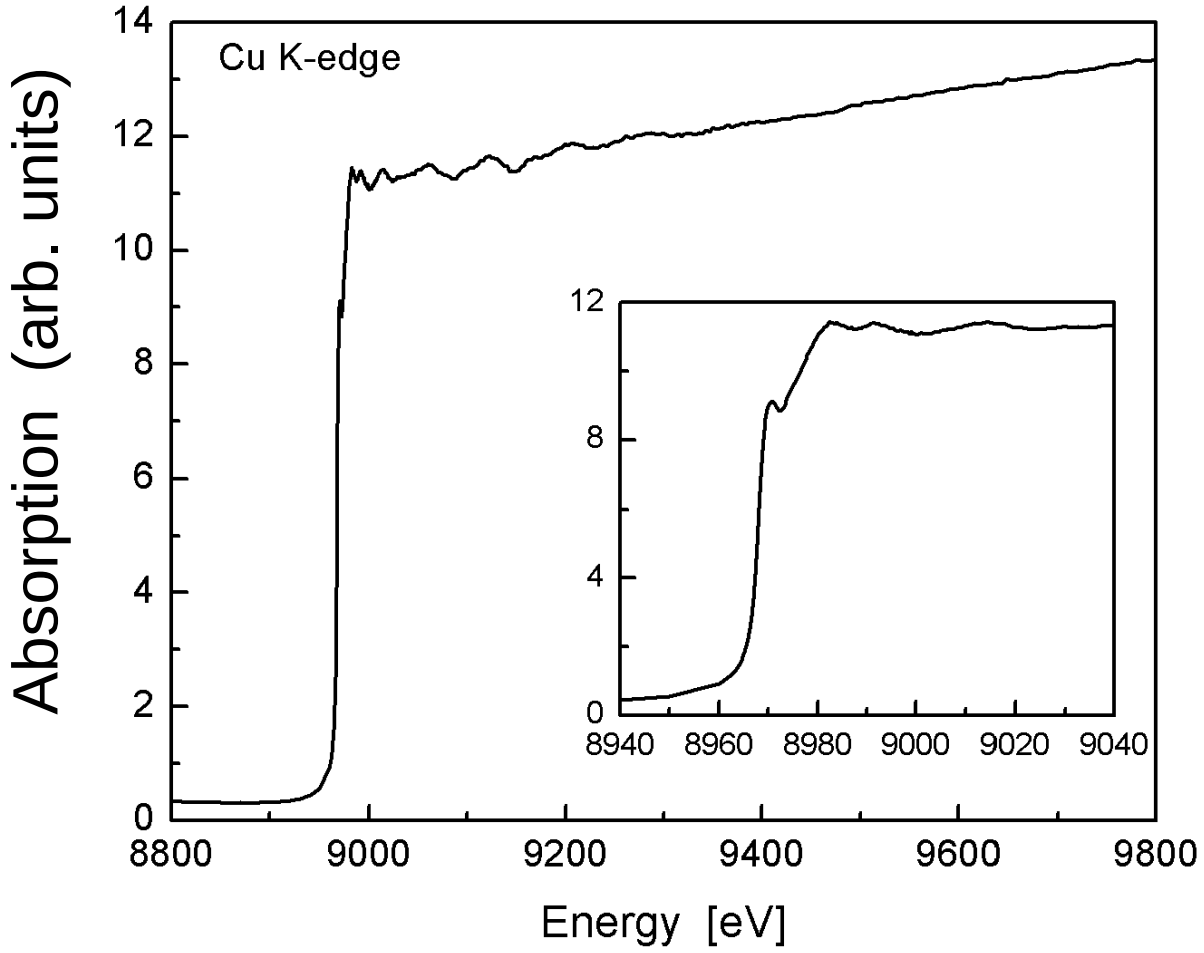
What is XAS?



What is XAS?



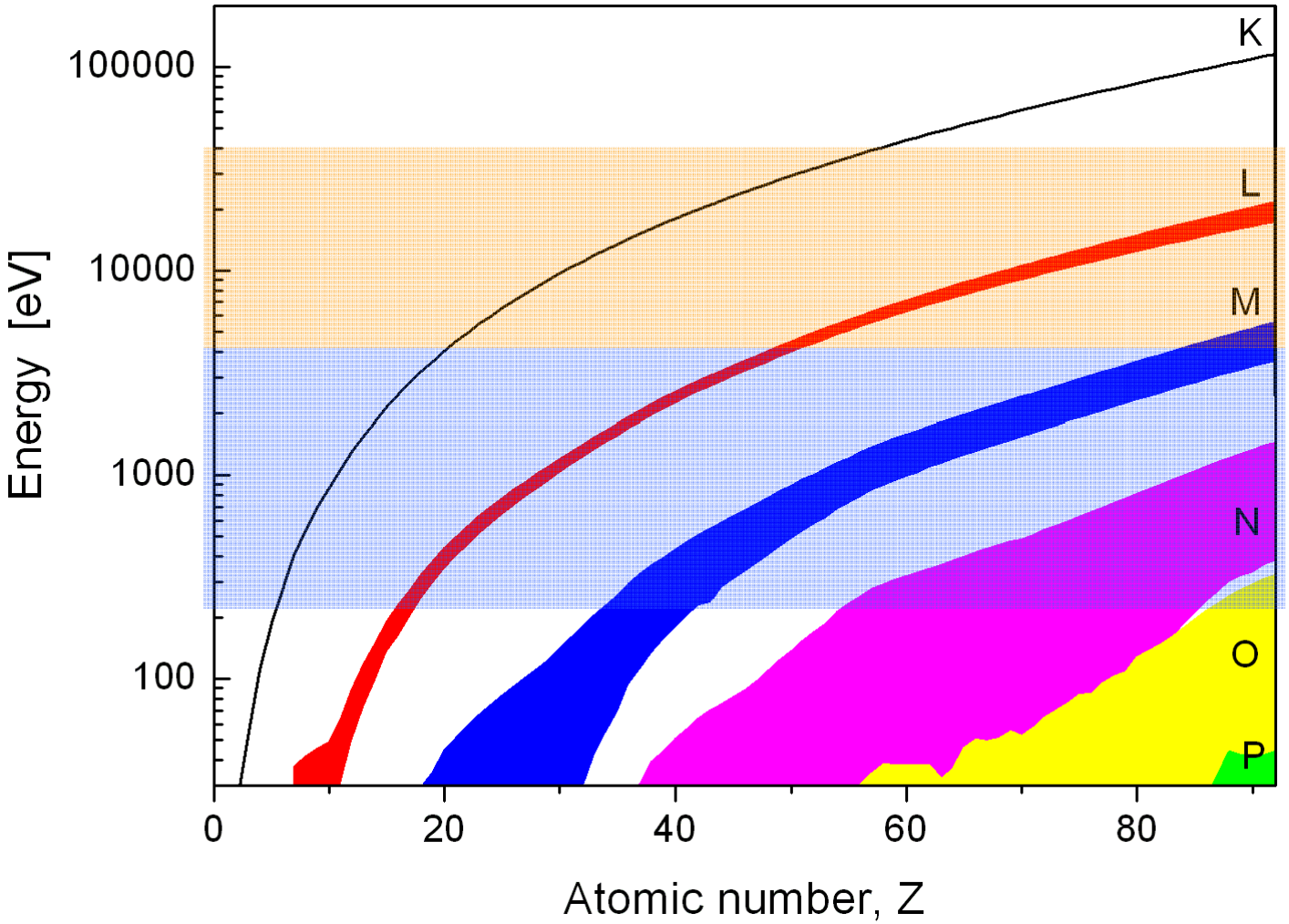
What does an XAS spectrum look like?



Measure absorption as a function of energy → need a tuneable source!

Question: Would a bend magnet, wiggler, or undulator be suitable for XAS?

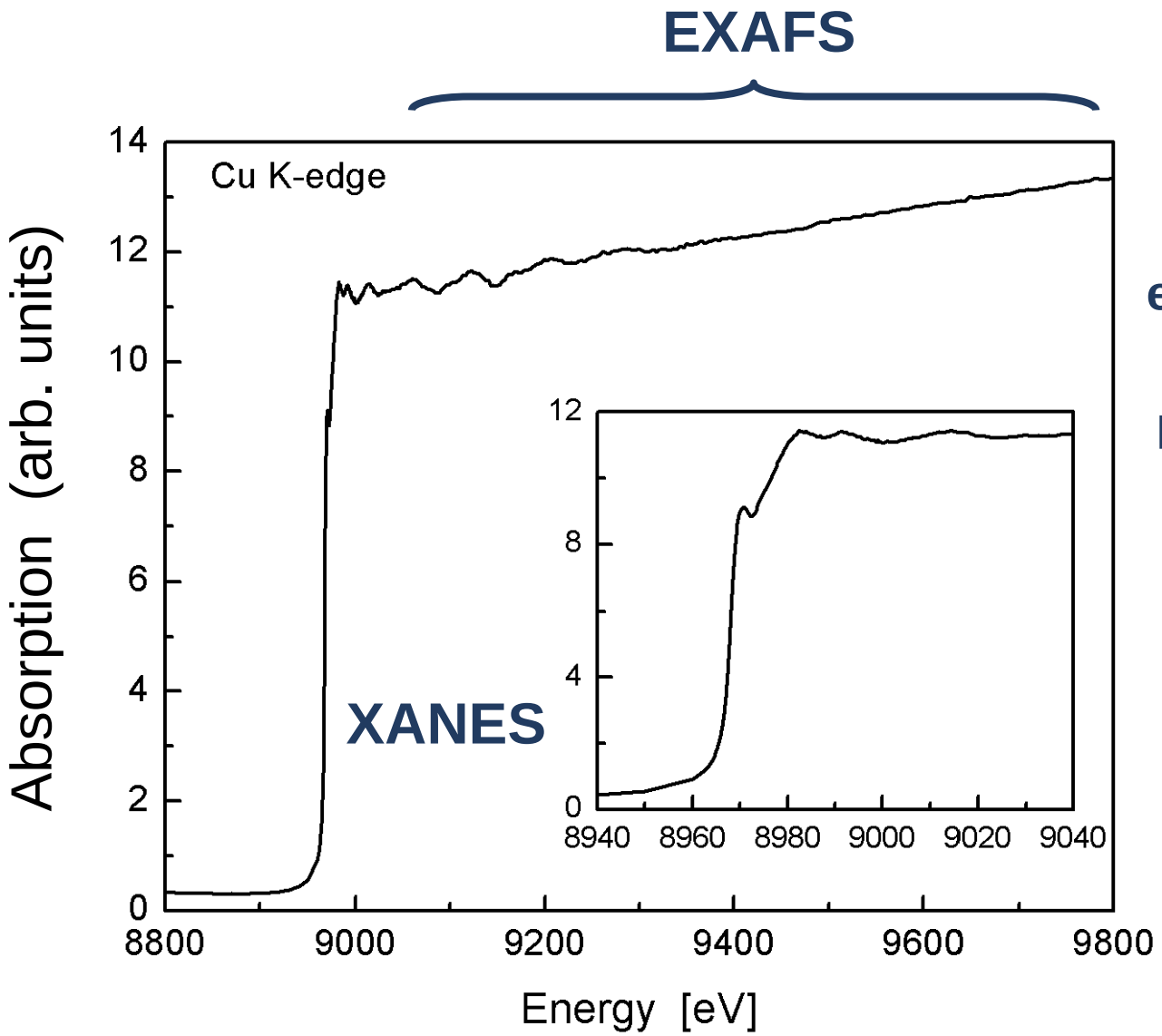
Where are the absorption edges?



Hard X-ray region:
4-40 keV

Soft X-ray region:
0.2-4 keV

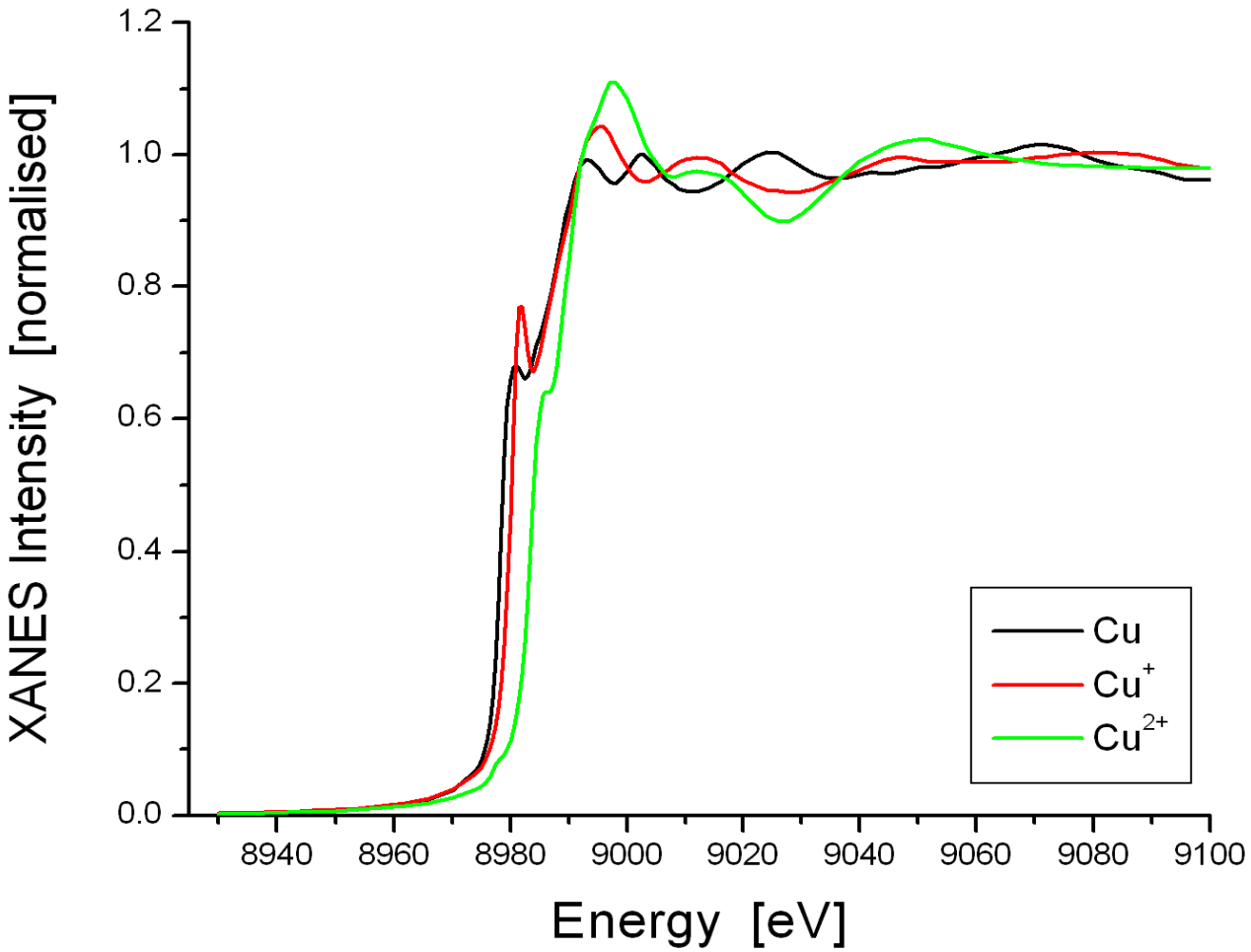
Using the data



XANES: **X**-ray **a**bsorption **n**ear **e**dge **s**pectroscopy

EXAFS: **E**xtended **X**-ray **a**bsorption **f**ine **s**tructure

XANES: key features

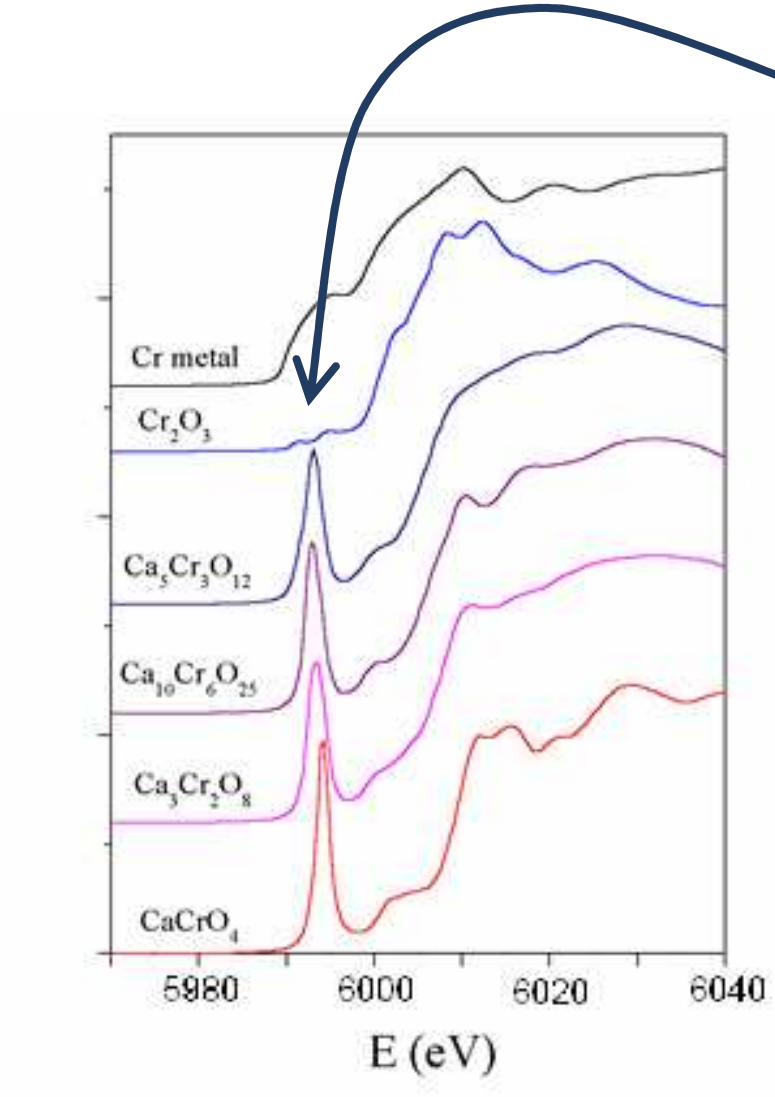


Edge position

Usually defined as $d^2y/dx^2 = 0$

Depends on valence

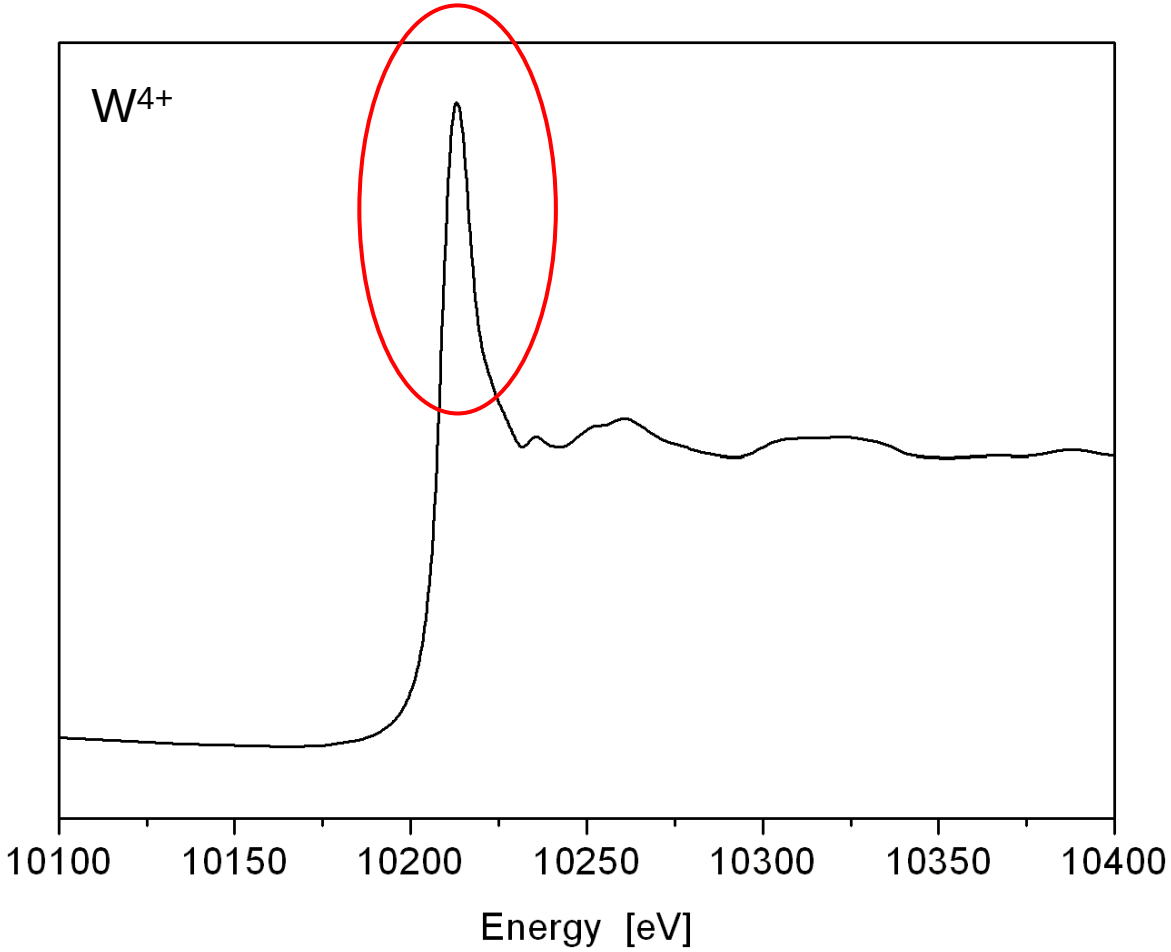
XANES: key features



Pre-edge peak

Common in TMs, electron transitions to an empty bound state

XANES: key features



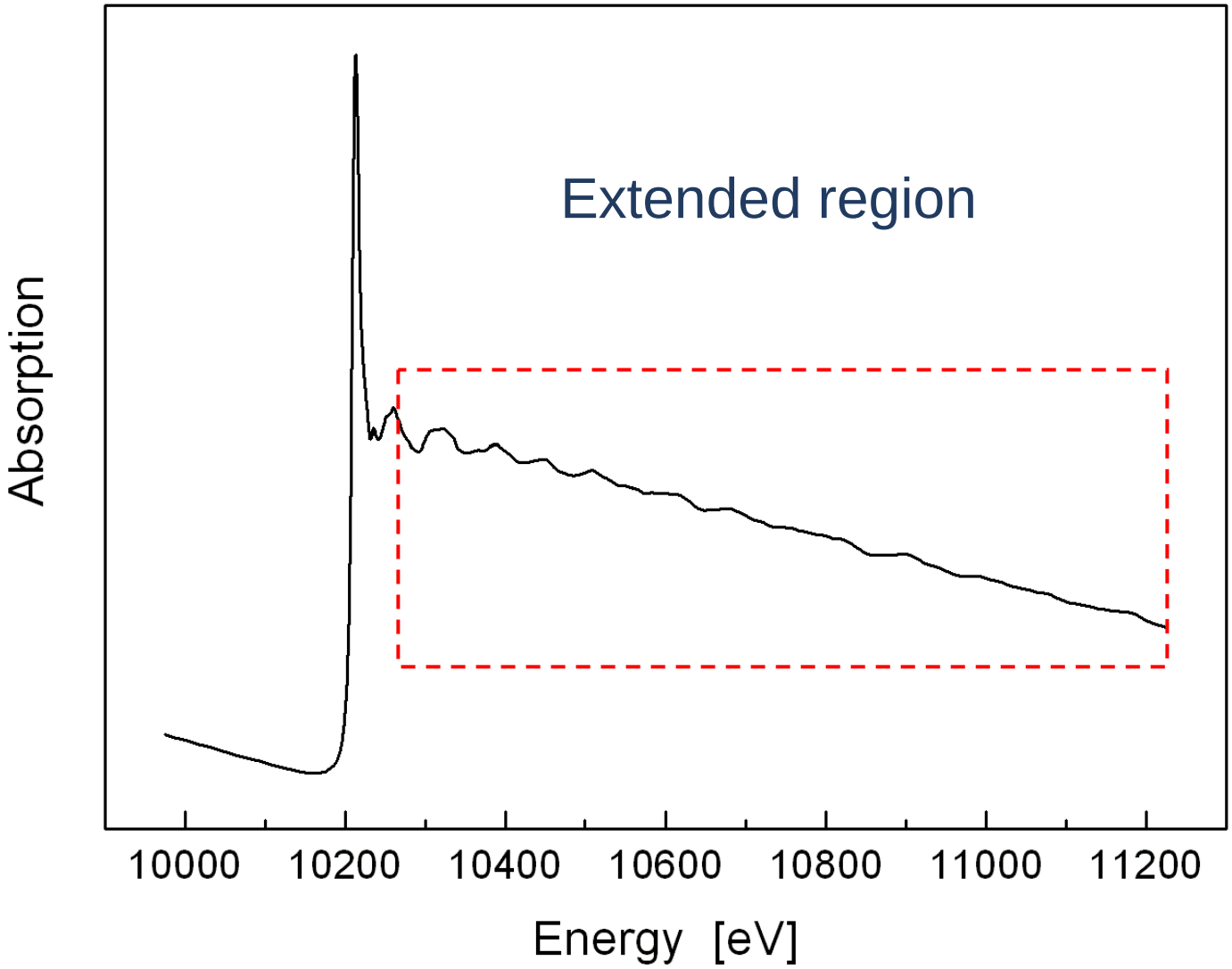
‘White line’

Common for L-edges of
TMs in high oxidation states

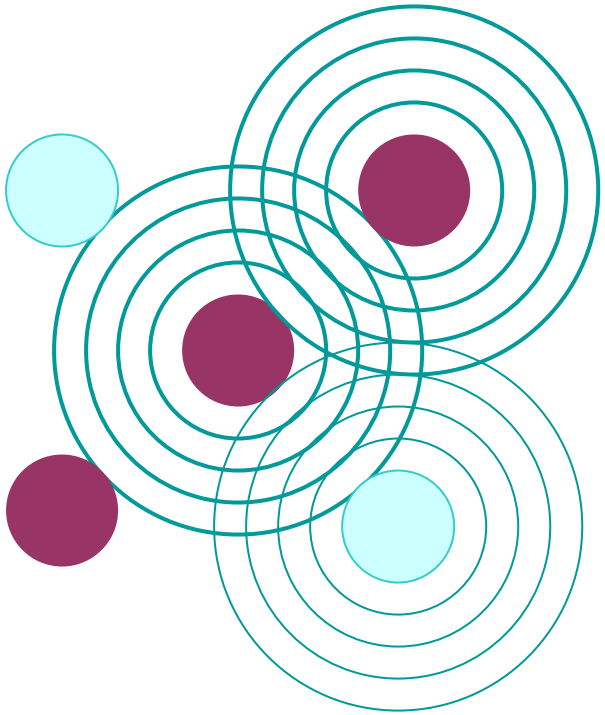
What information can we get from XANES?

- Element
- Valence
- Local co-ordination
- More qualitative than quantitative
- Compare with standards (known compounds)

EXAFS


Extended region
Absorption
10000
10200
10400
10600
10800
11000
11200
Energy [eV]

EXAFS



The electron has sufficient kinetic energy to escape the atom and interact with the nearest neighbours, next-nearest neighbours, etc.

These interactions show up as an ‘interference pattern’ in energy space (the EXAFS spectrum).

Obtain information about:

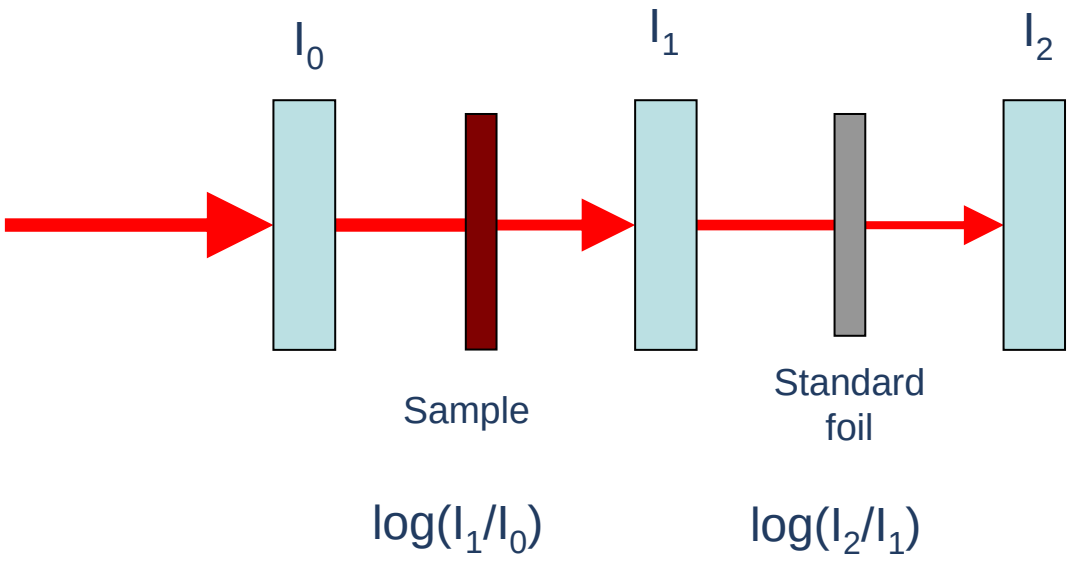
- Local atomic environment
- Number of each type of neighbour
- Distance to neighbours

EXAFS is not dependent on long-range structure

How are XAS data collected?

1. Transmission mode

Suitable for powders and liquids



Advantage:

- Better quality data out to high energy (high k)

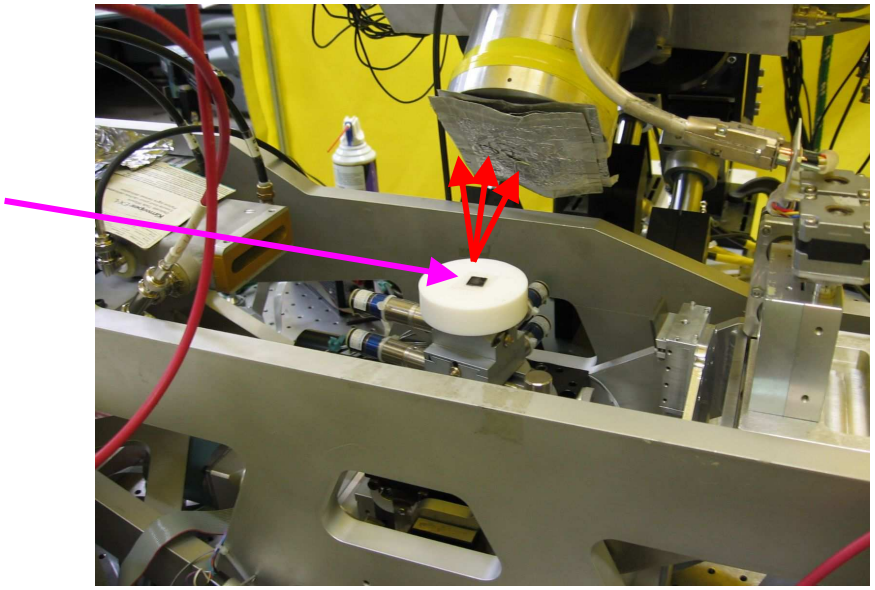
Disadvantage:

- Types of samples this mode is suitable for is limited

How are XAS data collected?

2. Fluorescence mode

Measure fluorescence (emitted by secondary electron falling to core level)



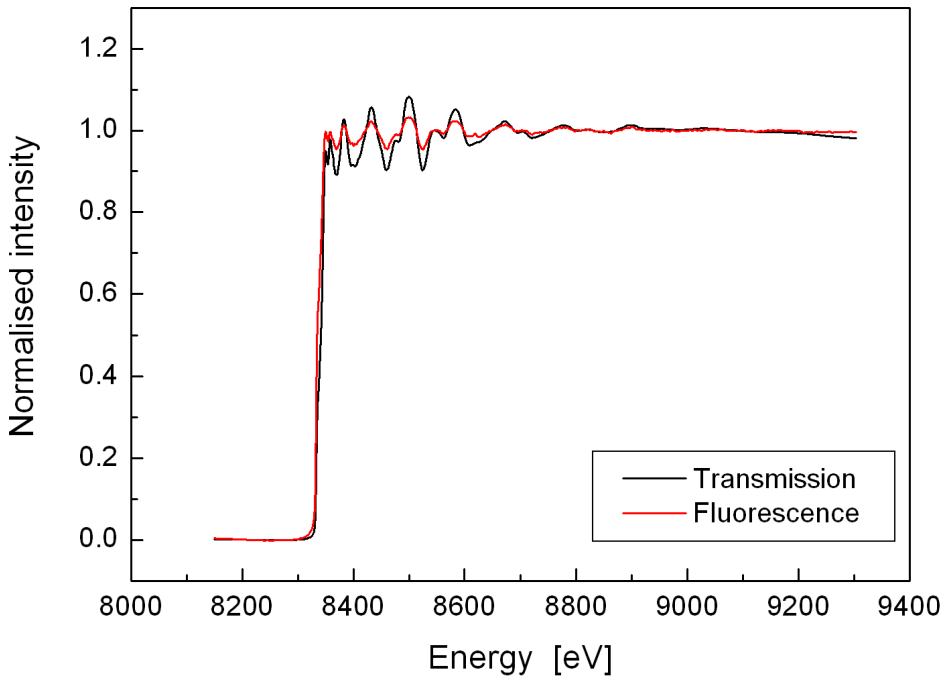
Advantage:

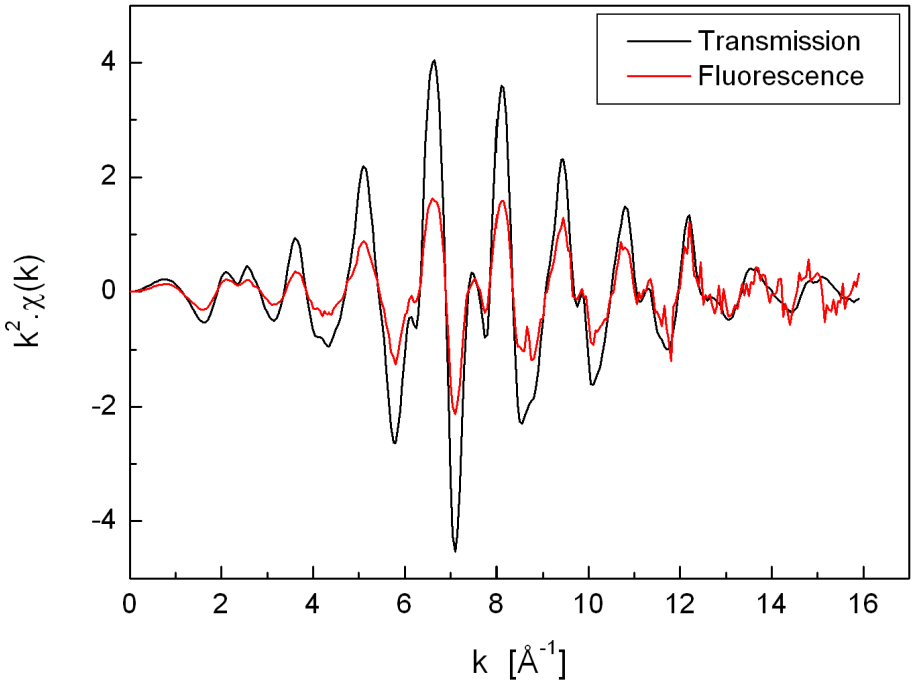
- Suits most types of samples

Disadvantage:

- Data quality inferior to transmission, especially at high energy (high k)

Transmission vs. fluorescence

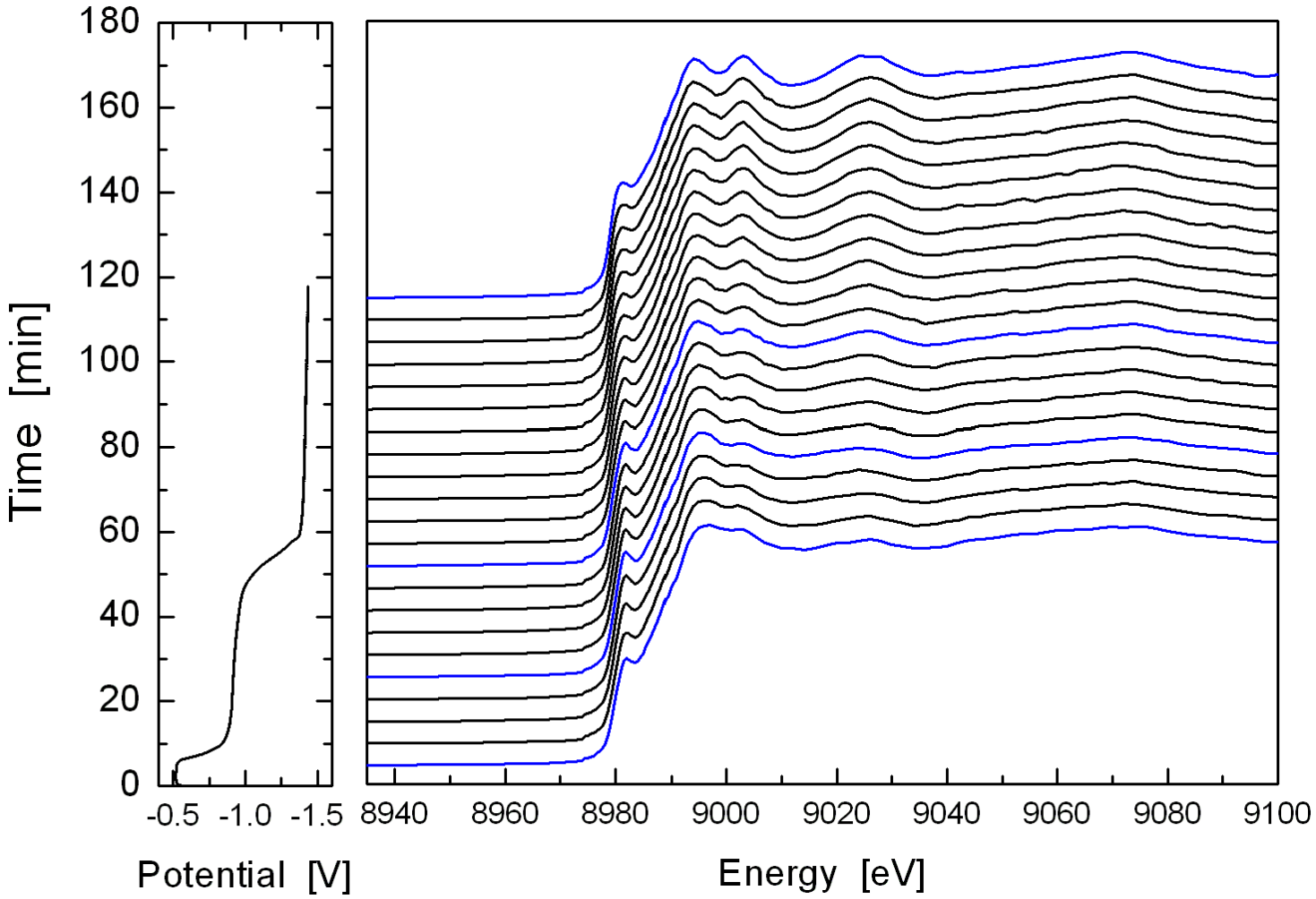




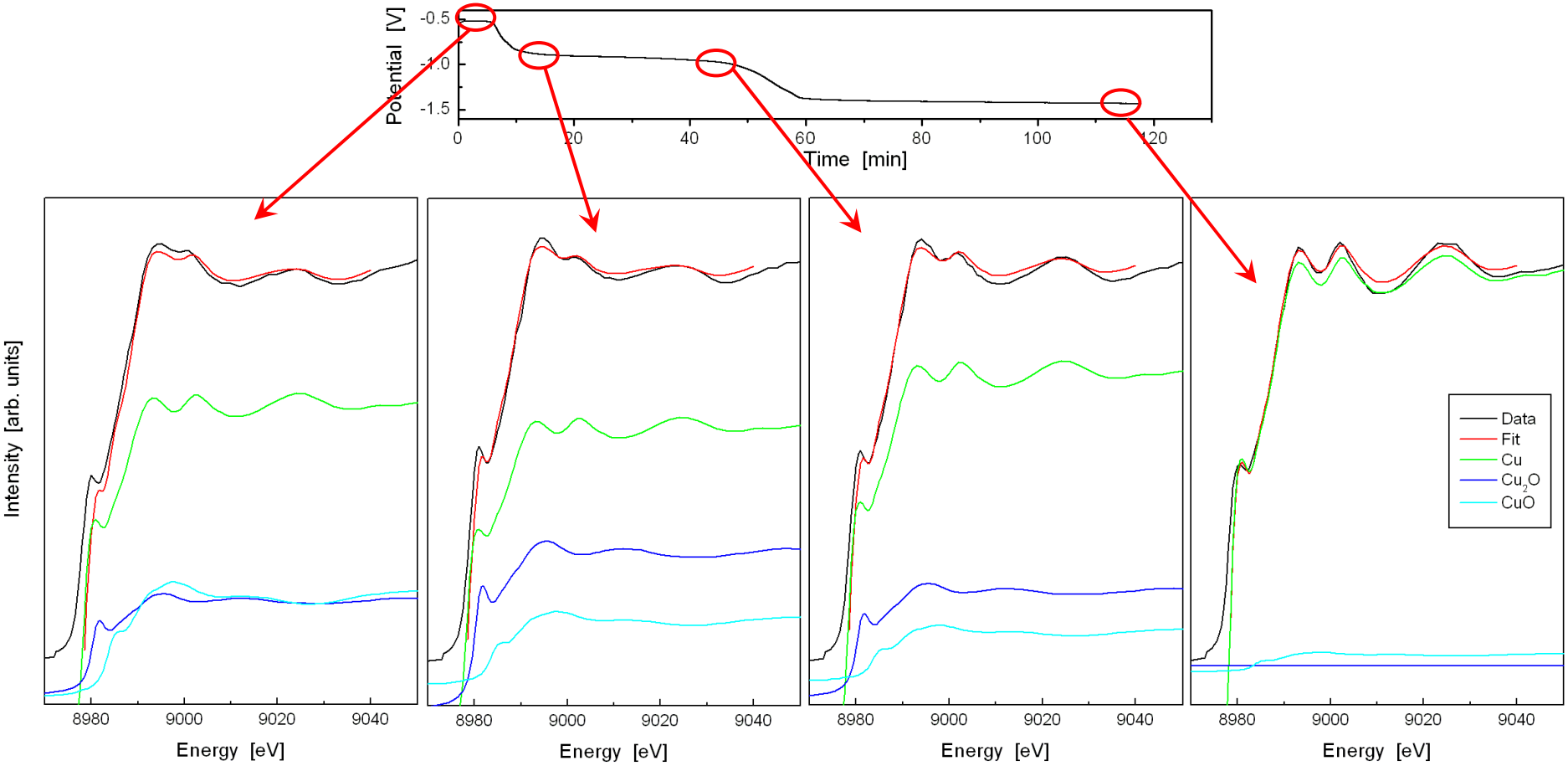
Ni foil

XANES example

Electrochemically removing the air-formed oxide on a Cu film

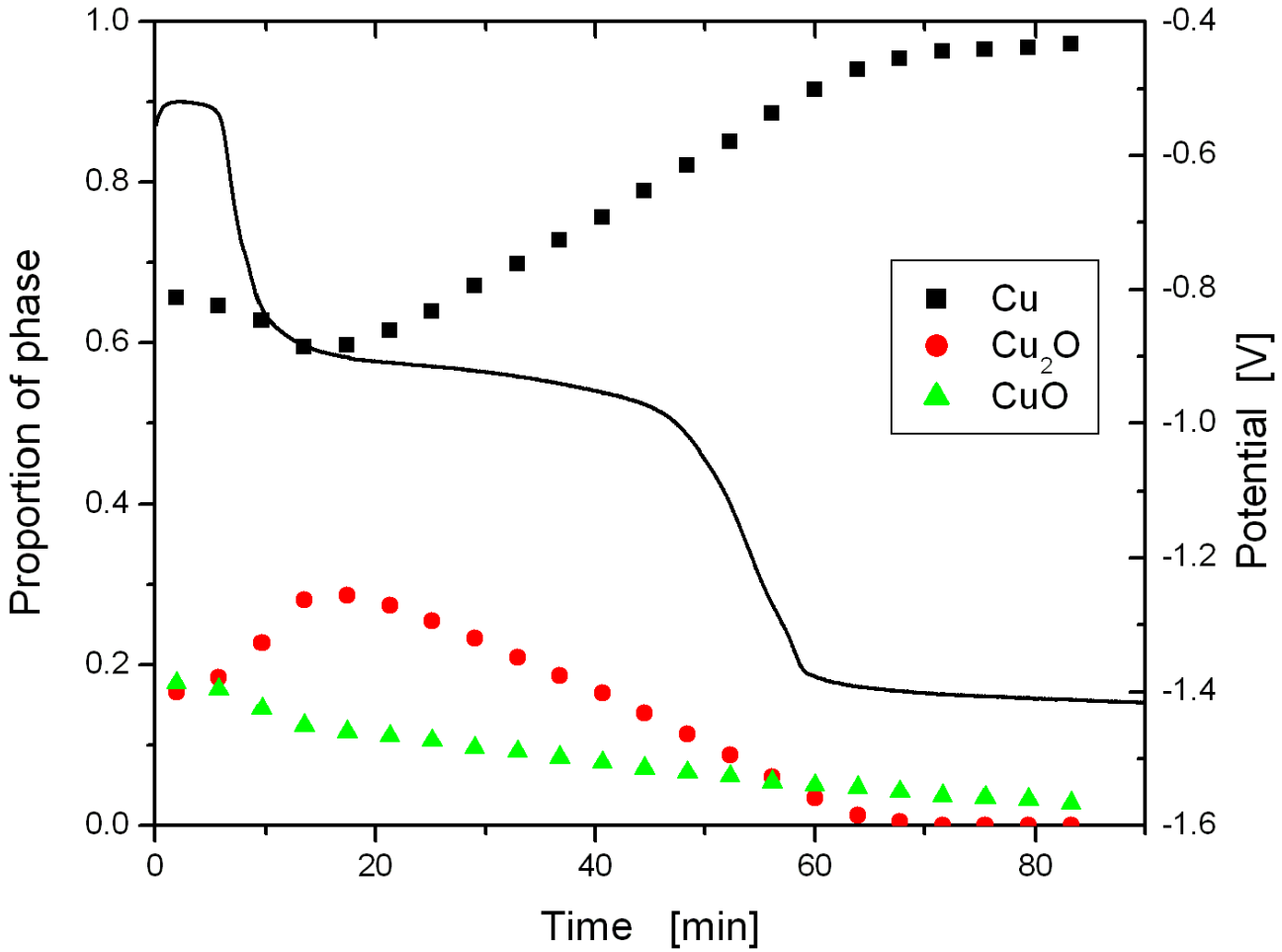


Deconvolution using XANES standards



Cu: 65.6%	Cu: 59.7%	Cu: 72.8%	Cu: 97.2%
Cu_2O: 16.7%	Cu_2O: 28.7%	Cu_2O: 18.7%	Cu_2O: 0%
CuO: 17.7%	CuO: 11.6%	CuO: 8.5%	CuO: 2.8%

Deconvolution results



- Some CuO converts to Cu_2O
- Then Cu_2O converts to Cu
- Some CuO remaining at the end of the experiment

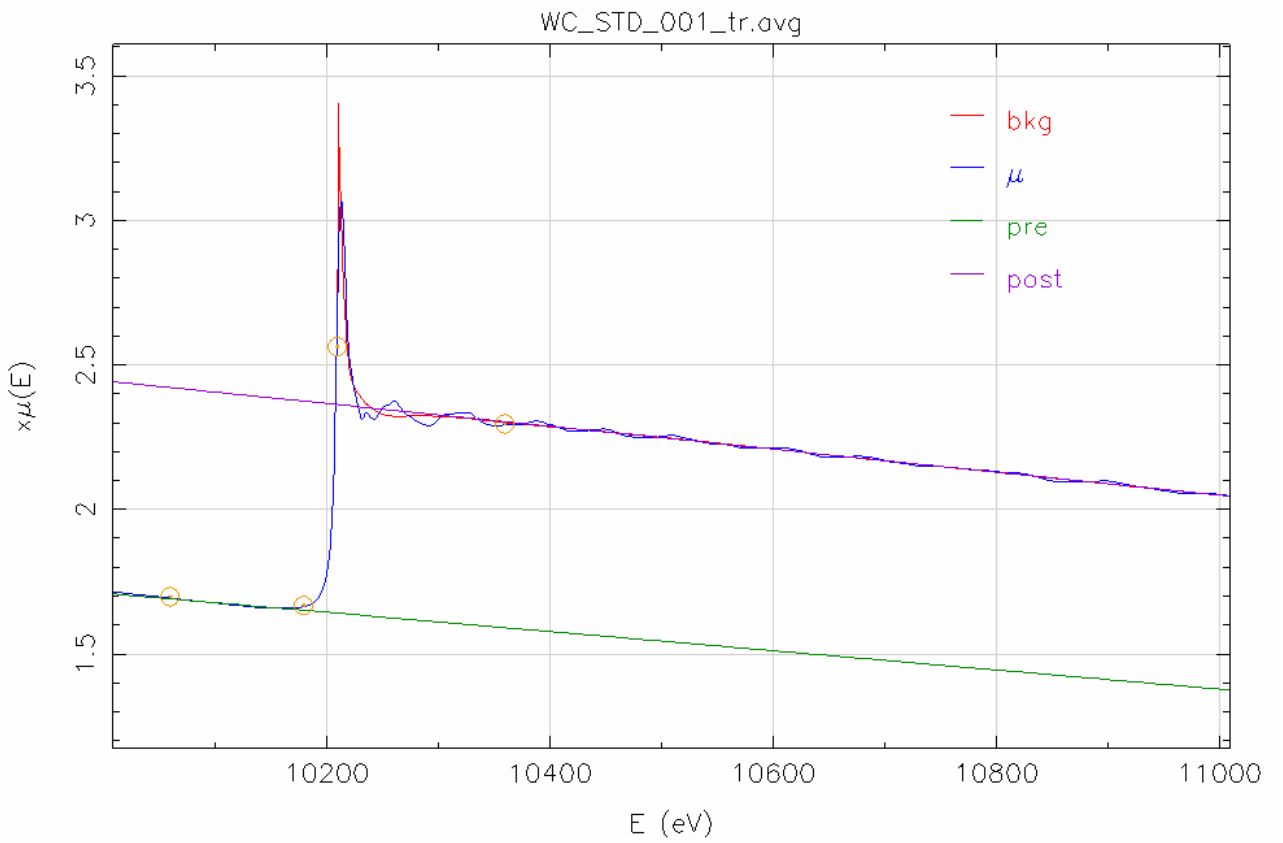
EXAFS example

WC electrodes for fuel cell catalysts need to have good electrocatalytic activity, while being resistant against corrosion. WC has similar electronic structure to Pt near the Fermi level. Therefore its electrocatalytic behaviour might be expected to be similar, but perhaps the problems associated with Pt (namely CO poisoning) might be alleviated.

Measure:

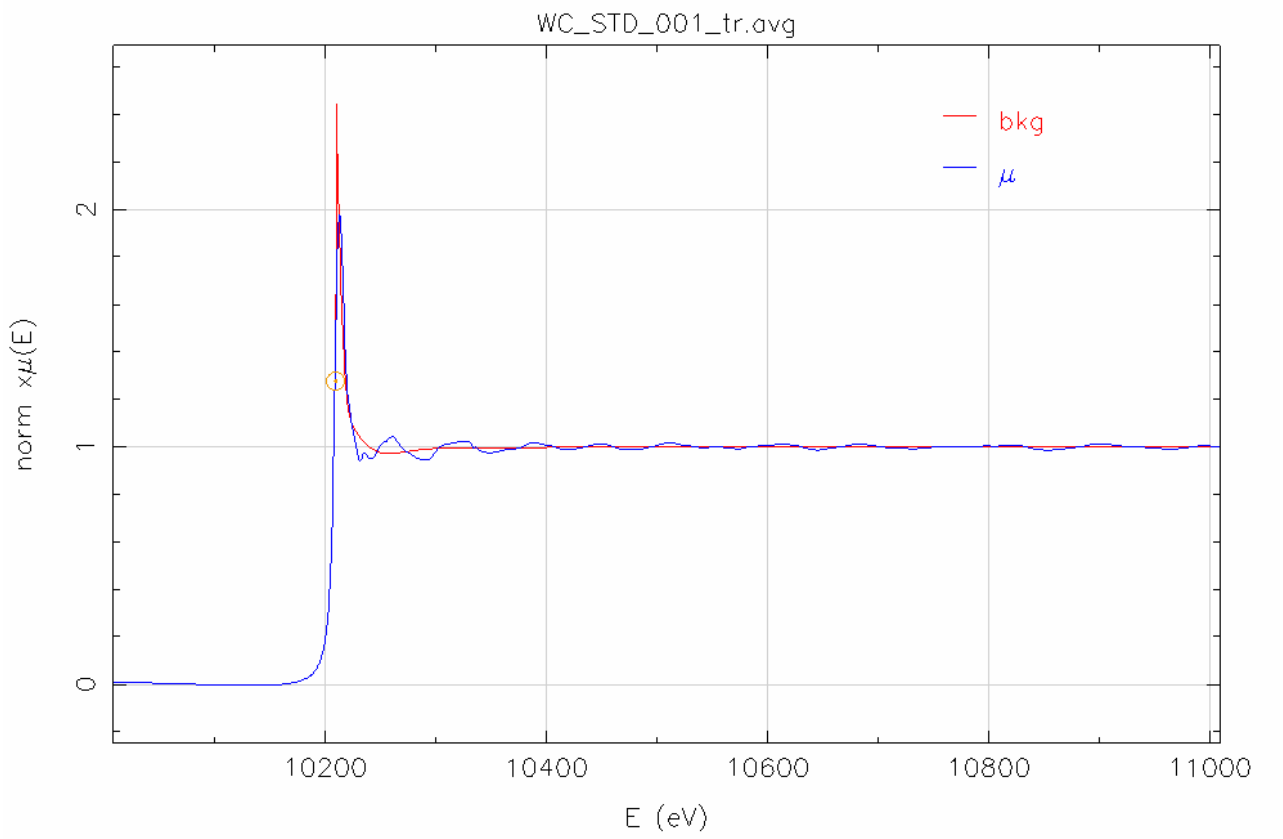
- W, WC and WO_2 standards
- WC as-prepared (‘untreated’)
- WC subjected to passivation treatment

EXAFS analysis



Subtract background

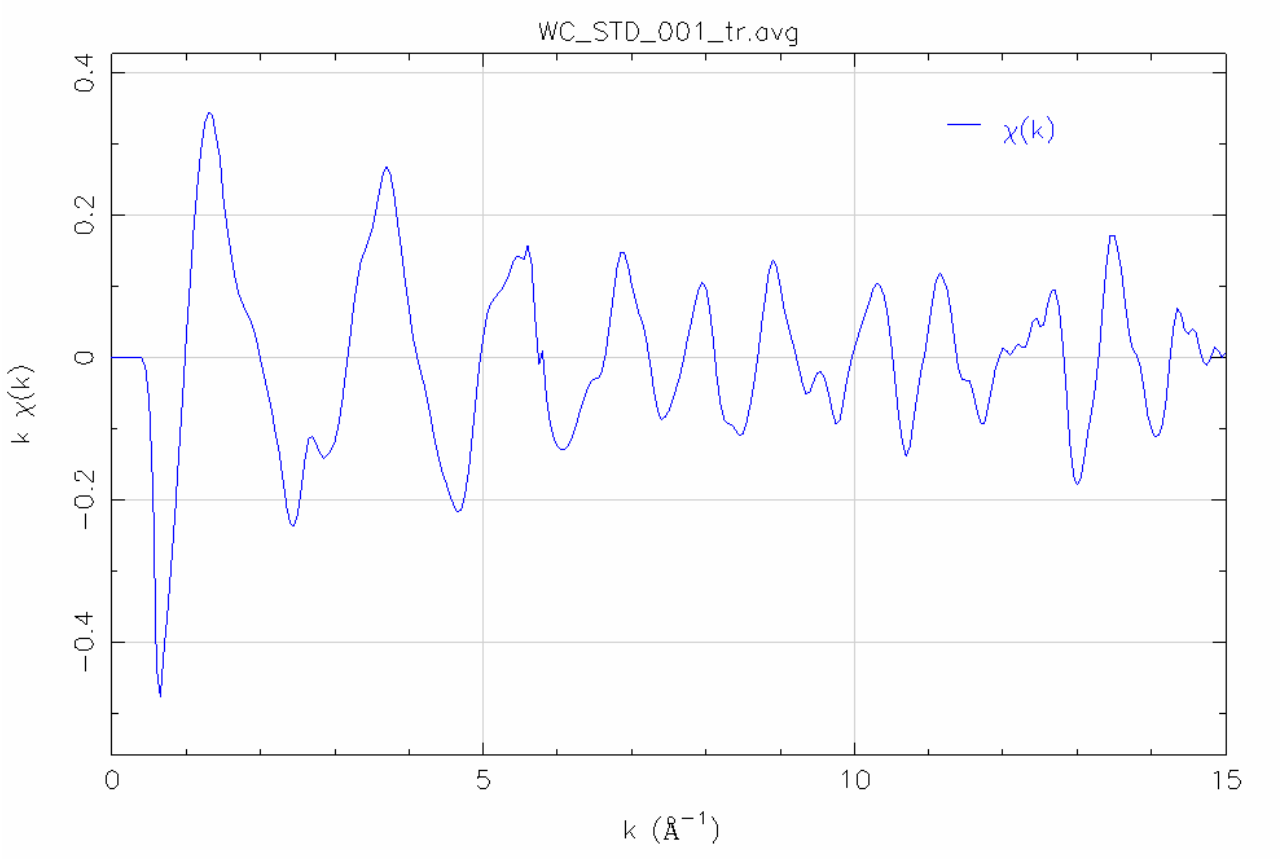
EXAFS analysis



Subtract background

Normalise

EXAFS analysis

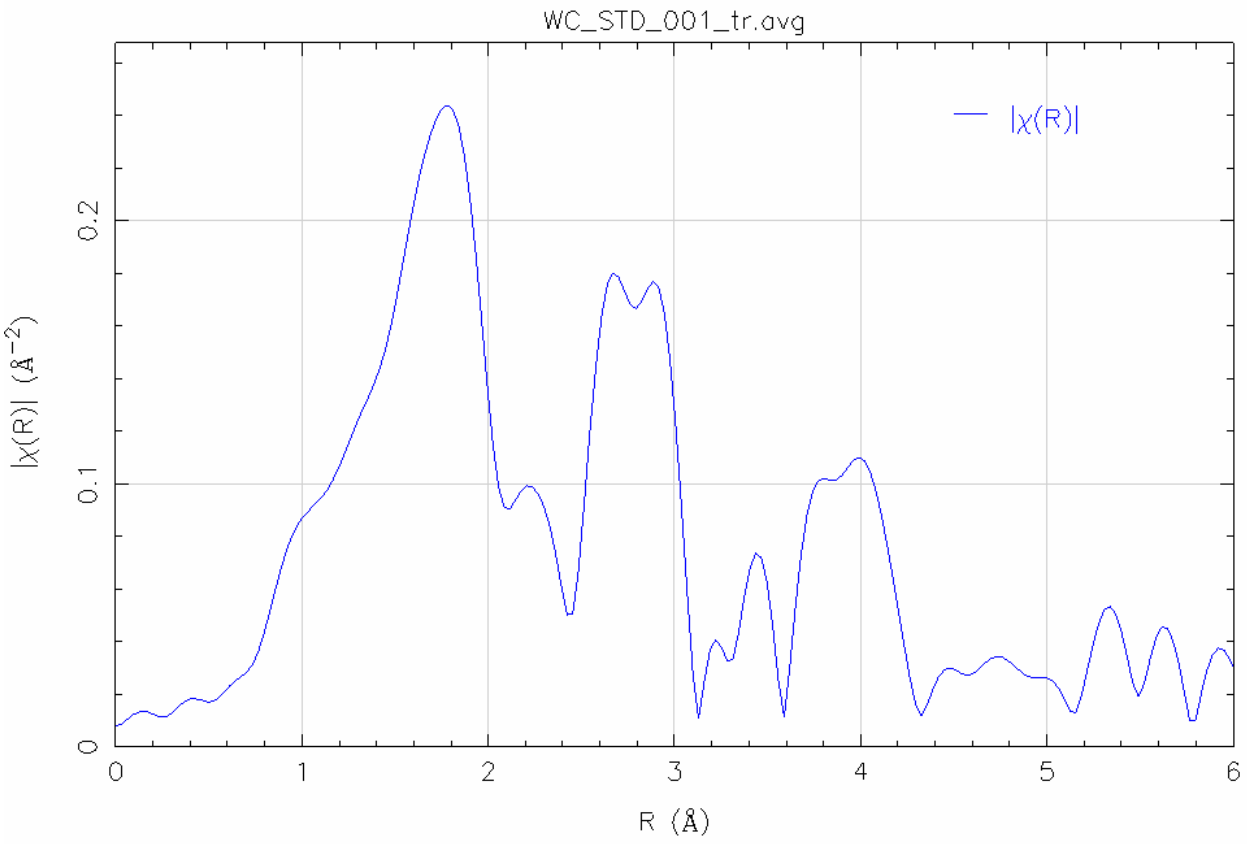


Subtract background

Normalise

Convert from energy to k

EXAFS analysis



Subtract background

Normalise

Convert from energy to k

Fourier transform

Fit...

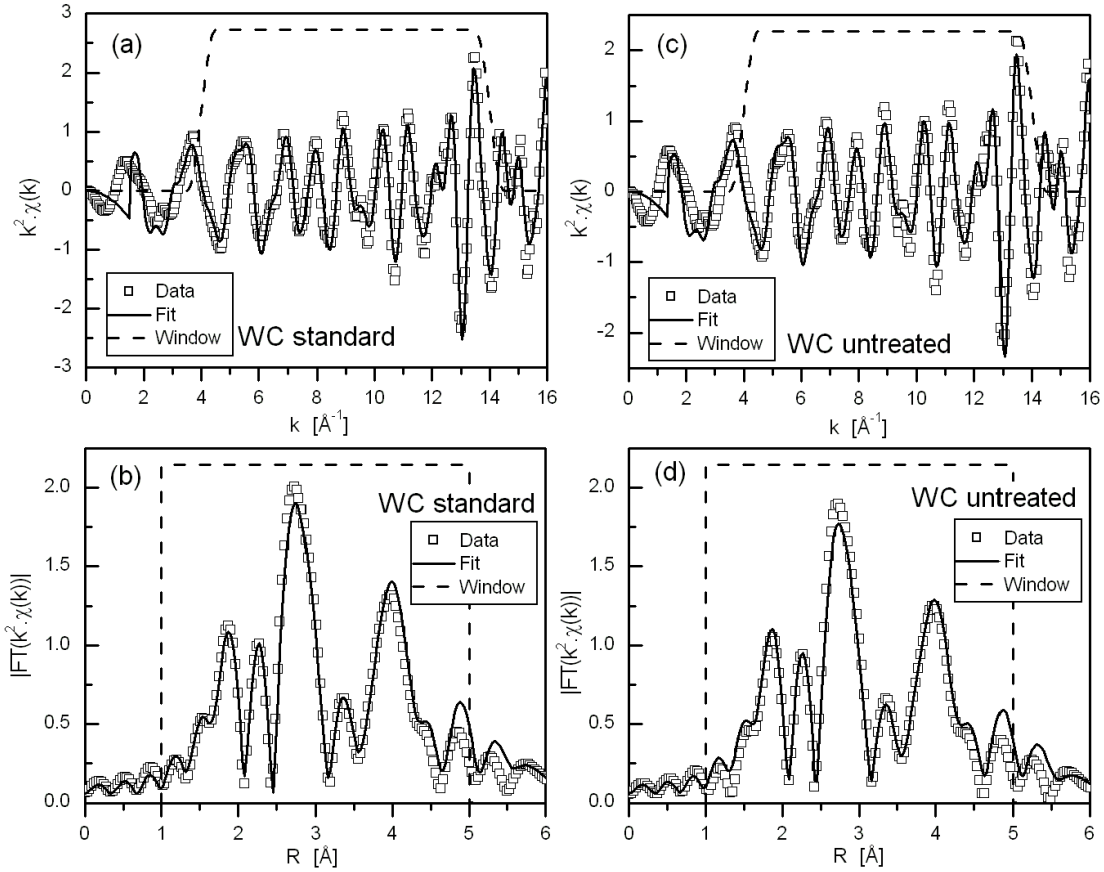
WC standard and untreated sample

Use crystal structure of WC to generate ‘paths’ taken by the emitted electron → nearest-neighbours, next-nearest-neighbours, etc.

Use this as a model to fit co-ordination numbers, bond distances.

Fitting in k-space and R-space helps confirm the appropriateness of the model being used.

Use different k-weightings to accentuate heavy and light atoms.



WC standard:

$CN_1 = 6$ (known)

WC untreated sample:

$CN_1 = 5.7 \pm 0.4$ (expect 6)

Ingham et al., *J. Phys. Chem. C* 113 (2009) 17407

WC passivated sample

A model using only the WC crystal structure does not adequately fit the data.

Including the first shell calculated from the WO_2 crystal structure (WO_6 octahedron) produces a good fit.

WC passivated sample

CN_1 (W-C) = 3.2 ± 0.3

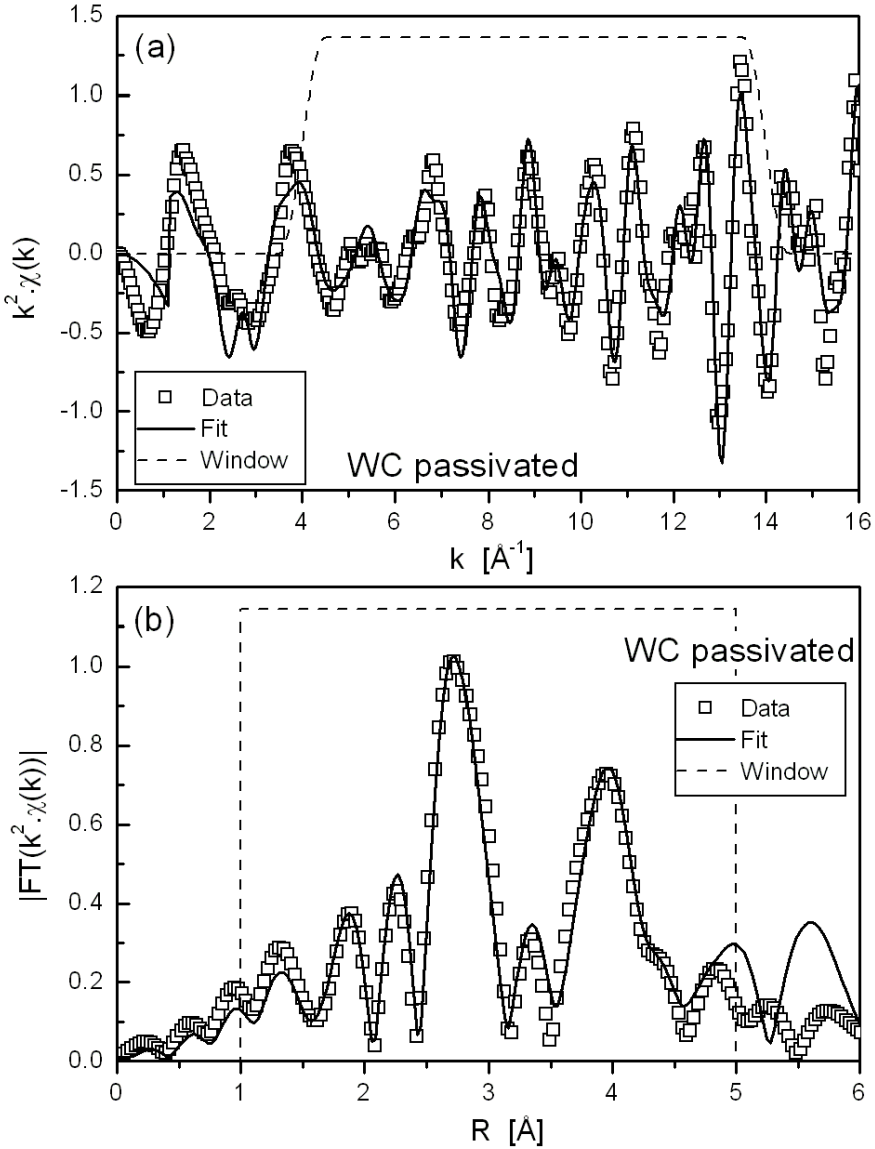
CN_1 (W-O) = 3.4 ± 0.9

r_1 (W-C) = 2.192 ± 0.002 Å

(bulk WC: 2.1971 Å)

r_1 (W-O) = 1.84 ± 0.01 Å

(bulk WO_2: 2.020 Å)



Ingham et al., *J. Phys. Chem. C* 113 (2009) 17407

Summary

- XANES:
  - Element
  - Valence
  - Local co-ordination
  - More qualitative than quantitative
  - Compare with standards (known compounds)
- EXAFS:
  - Co-ordination numbers
  - Bond distances
  - Based on a model (full or partial crystal structure)

- Electronic structure – Ben’s talk next

Outline of the day

- Introduction
- Basic X-ray diffraction
  - Powders, thin films, single crystals
- Small-angle X-ray scattering
- X-ray absorption spectroscopy
  - Atomic structure
  - Electronic structure (Ben Ruck)
- Advanced X-ray diffraction
  - Anomalous diffraction
  - Total X-ray scattering
- Designing experiments
  - In situ measurements