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ENERGY

Introduction to X-ray Absorption Spectroscopy

Eli Stavitski, Lead Beamline Scientist, Inner Shell Spectroscopy beamline

XAS 2025: Fundamentals of XAS Data Analysis: A Hands-on Tutorial, March 11th 2025

Overview

1. A little physics behind XAS
2. How to obtain XAS data (beamlines and detectors)
3. What can we learn from XANES?
4. What can we learn from EXAFS?

1. Basic physics behind XAS

X-A-S

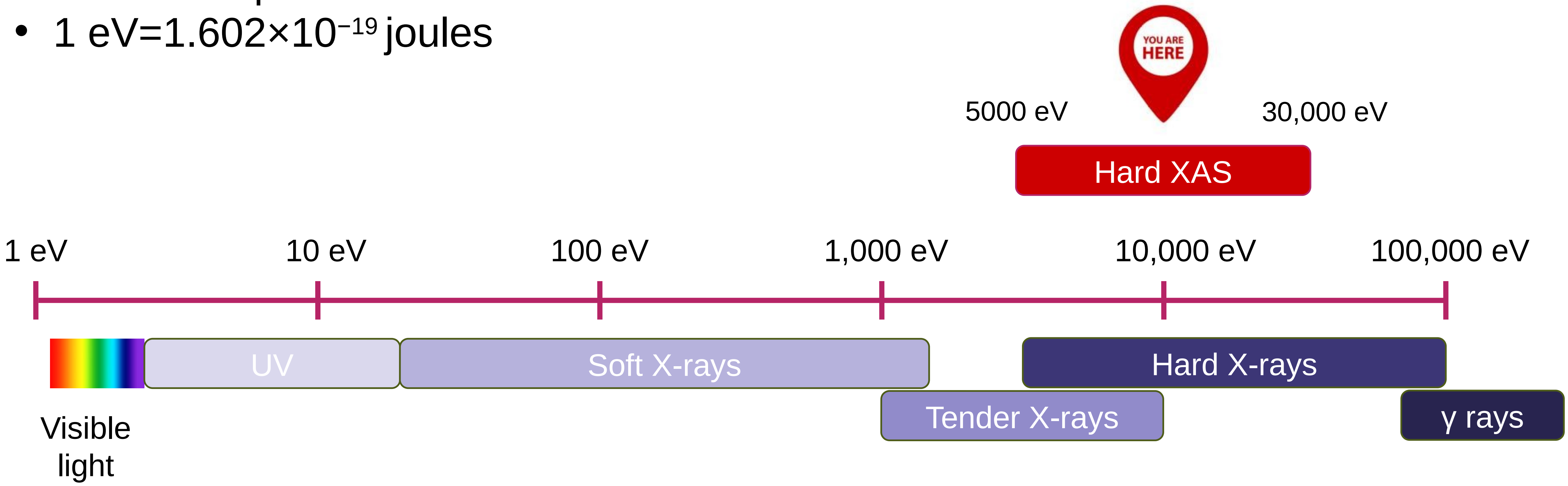
X-ray – we use X-ray photons as a probe, (just like visible light in optical spectroscopy)

Absorption – we learn from the X-ray photons are absorbed in your sample

Spectroscopy – we need use different energies of X-ray photons to interrogate the sample

X-ray spectrum units

- Common unit in XAS is an electron-volt (eV)
- 1 eV is amount of energy gained or lost by an electron when it moves through an electric potential difference of **one volt**.
- 1 eV=1.602×10^{-19} joules



YOU ARE HERE

5000 eV

30,000 eV

Hard XAS

1 eV

10 eV

100 eV

1,000 eV

10,000 eV

100,000 eV

UV

Soft X-rays

Hard X-rays

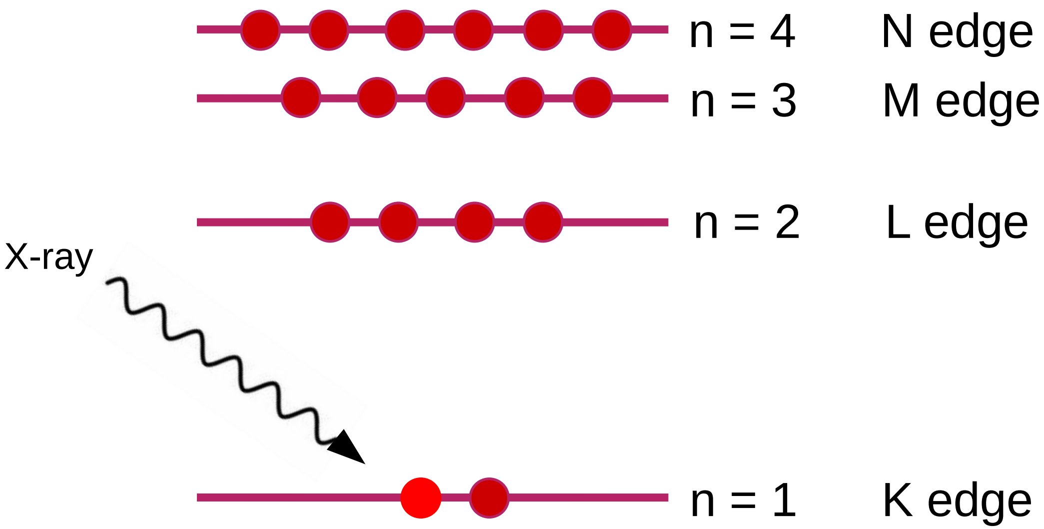
Tender X-rays

γ rays

Visible light

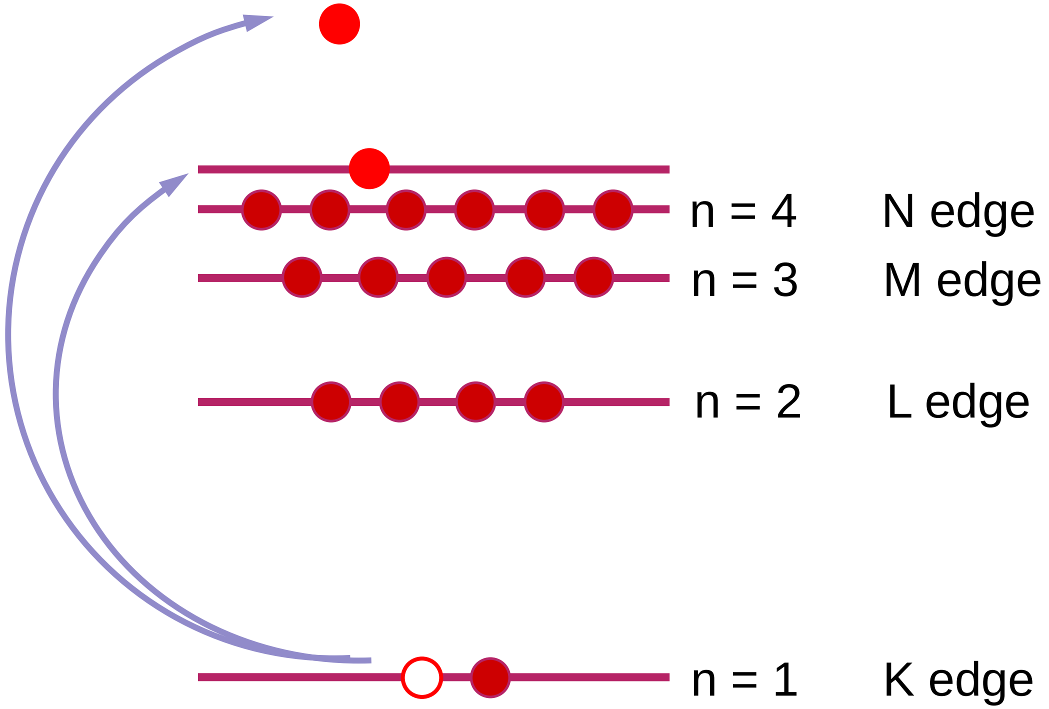
Basic physics of XAS

XAS is often called an inner-shell spectroscopy, because core electrons (1s, 2s, 2p) interact with X-rays



X-ray photon interacts with the electron.

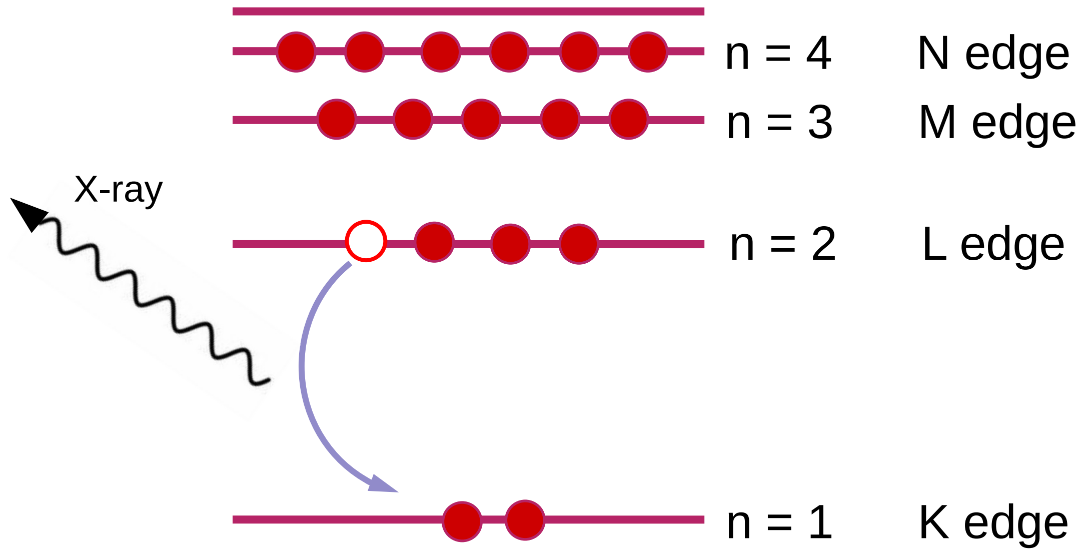
Basic physics of XAS



X-ray photon interacts with the electron.

The core electron is excited to an unoccupied state or gets ejected from the atom

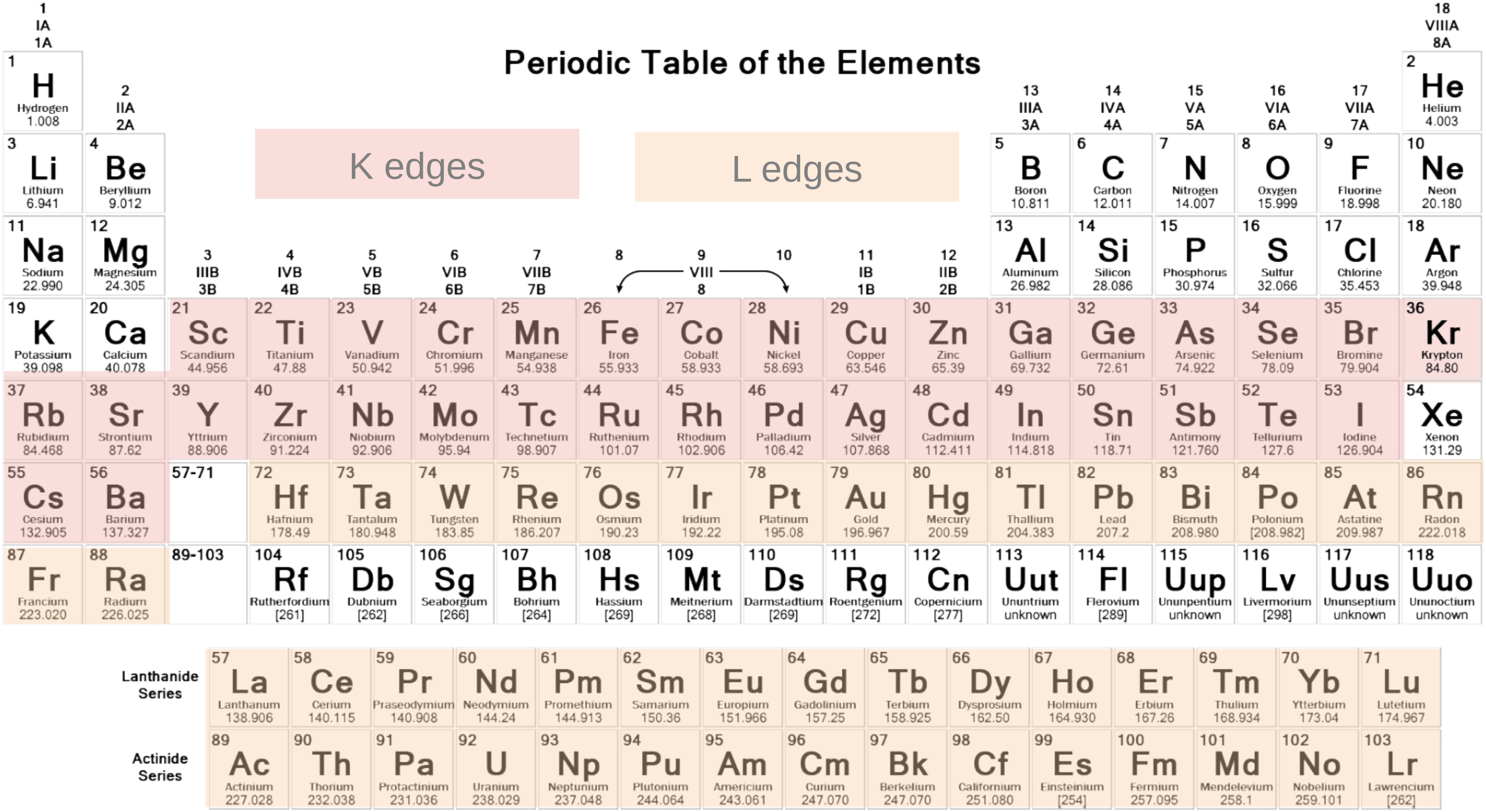
Basic physics of XAS



⚠ * The core lifetime is very short, introducing uncertainty in energy
** Emitted X-ray photon is lower in energy than the incoming one

X-ray photon interacts with the electron.
The core electron is excited to an unoccupied state or get ejected from the atom
Within femtoseconds* the electron from a higher level fills the core hole, emitting an X-ray photon**

What elements can we probe with hard X-rays



1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.933	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.732	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.922	34 **Se** Selenium 78.09	35 **Br** Bromine 79.904	36 **Kr** Krypton 84.80
37 **Rb** Rubidium 84.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.327	57-71	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.967	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]	113 **Uut** Ununtrium unknown	114 **Fl** Flerovium [289]	115 **Uup** Ununpentium unknown	116 **Lv** Livermorium [298]	117 **Uus** Ununseptium unknown	118 **Uuo** Ununoctium unknown

Lanthanide Series	57 **La** Lanthanum 138.906	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.24	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.966	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
Actinide Series	89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]

21
Sc
Scandium
44.95591

K 1s	4492 eV
L_1 2s	498 eV
L_2 $2p_{1/2}$	403 eV
L_3 $2p_{3/2}$	398 eV

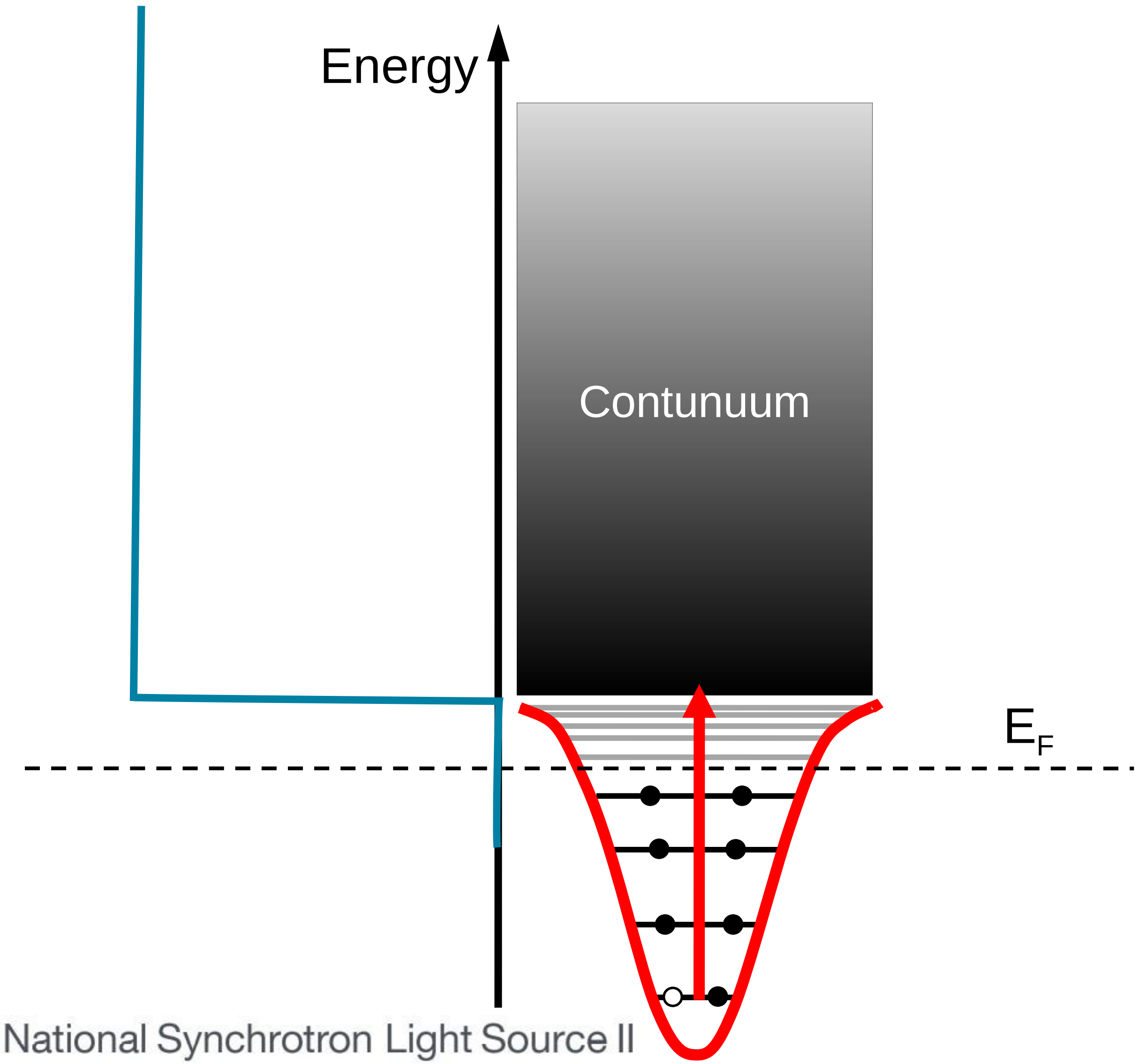
K 1s	115606 eV
L_1 2s	21757 eV
L_2 $2p_{1/2}$	20948 eV
L_3 $2p_{3/2}$	17166 eV

92
U
Uranium
238.03

XAS is element-specific technique – each element has a set of unique energies* at which X-ray absorption occurs

⚠ * Until it isn't

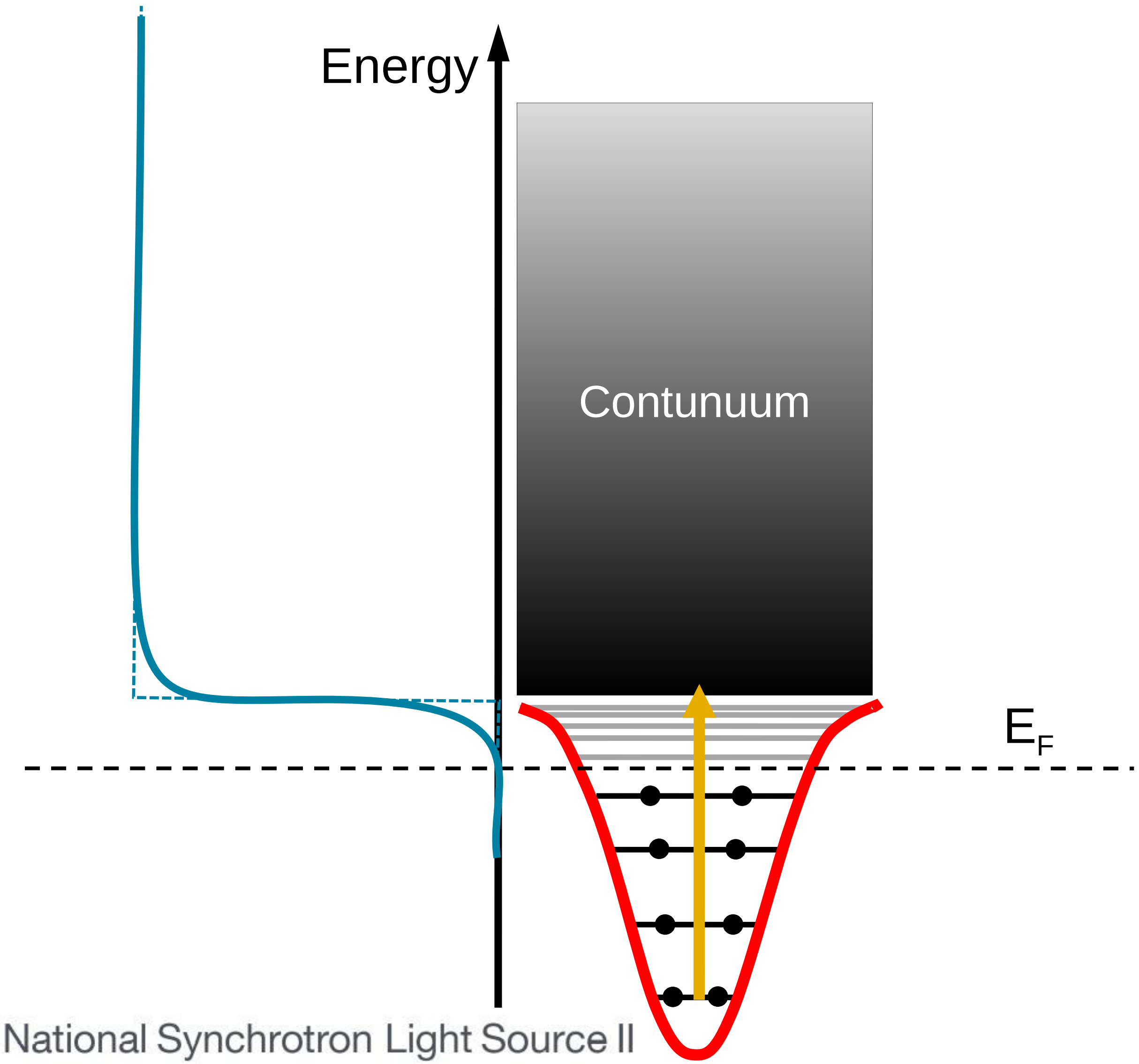
Processes behind X-ray absorption (1)



We will consider 3d element, K-edge

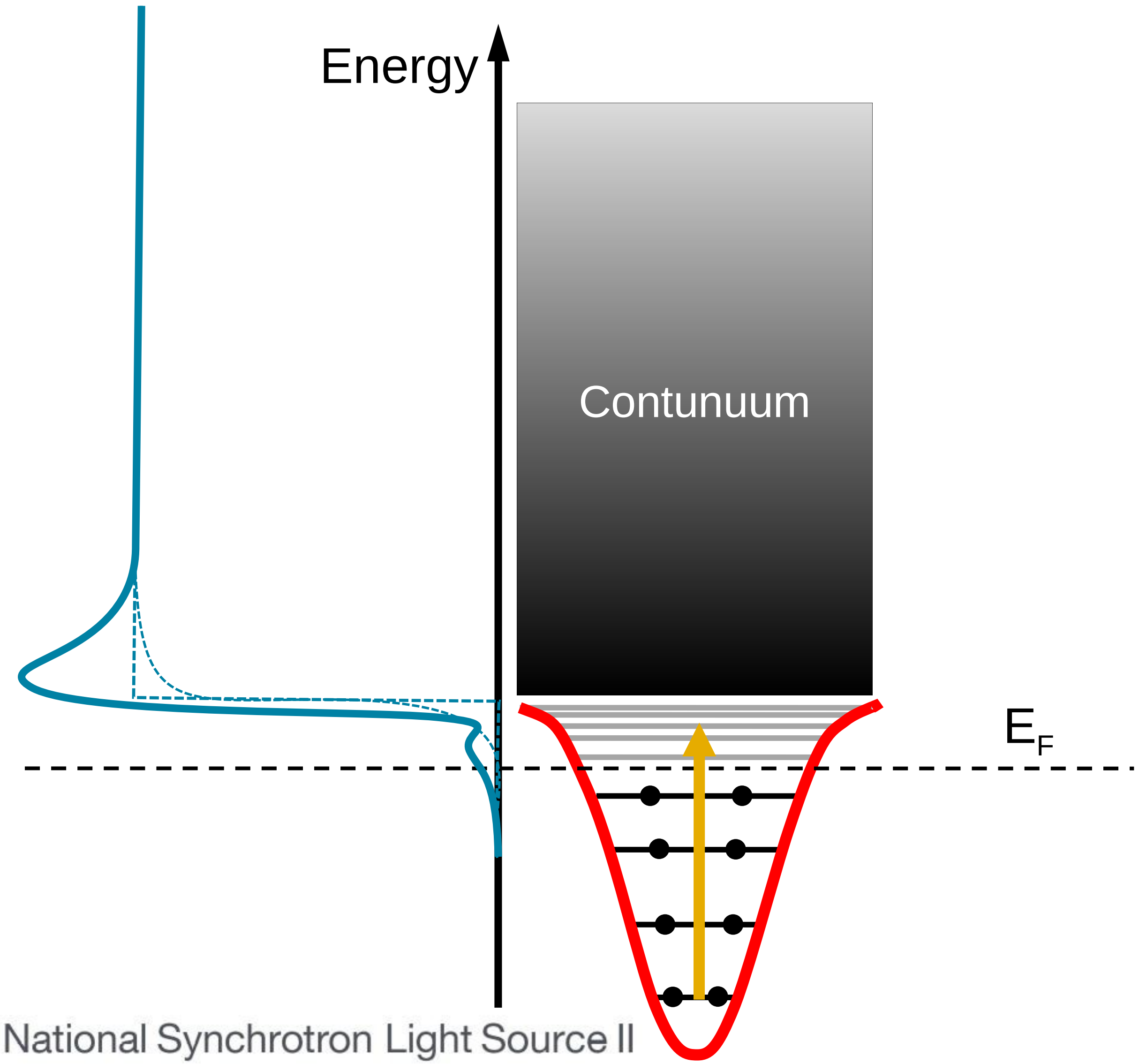
- Once the energy of the X-ray photons is high enough, they will start kicking core electrons out of the atoms as photoelectrons
- The spectrum will have a sharp onset and constant absorption after that

Processes behind X-ray absorption (2)



- Once the electron is kicked out of the 1s-orbital, another low-lying electron takes its place, within femtoseconds
- Heisenberg uncertainty principle dictates how well the energy of a state can be established
- This “core-level lifetime broadening” adds uncertainty in energy, between 1 and several eVs

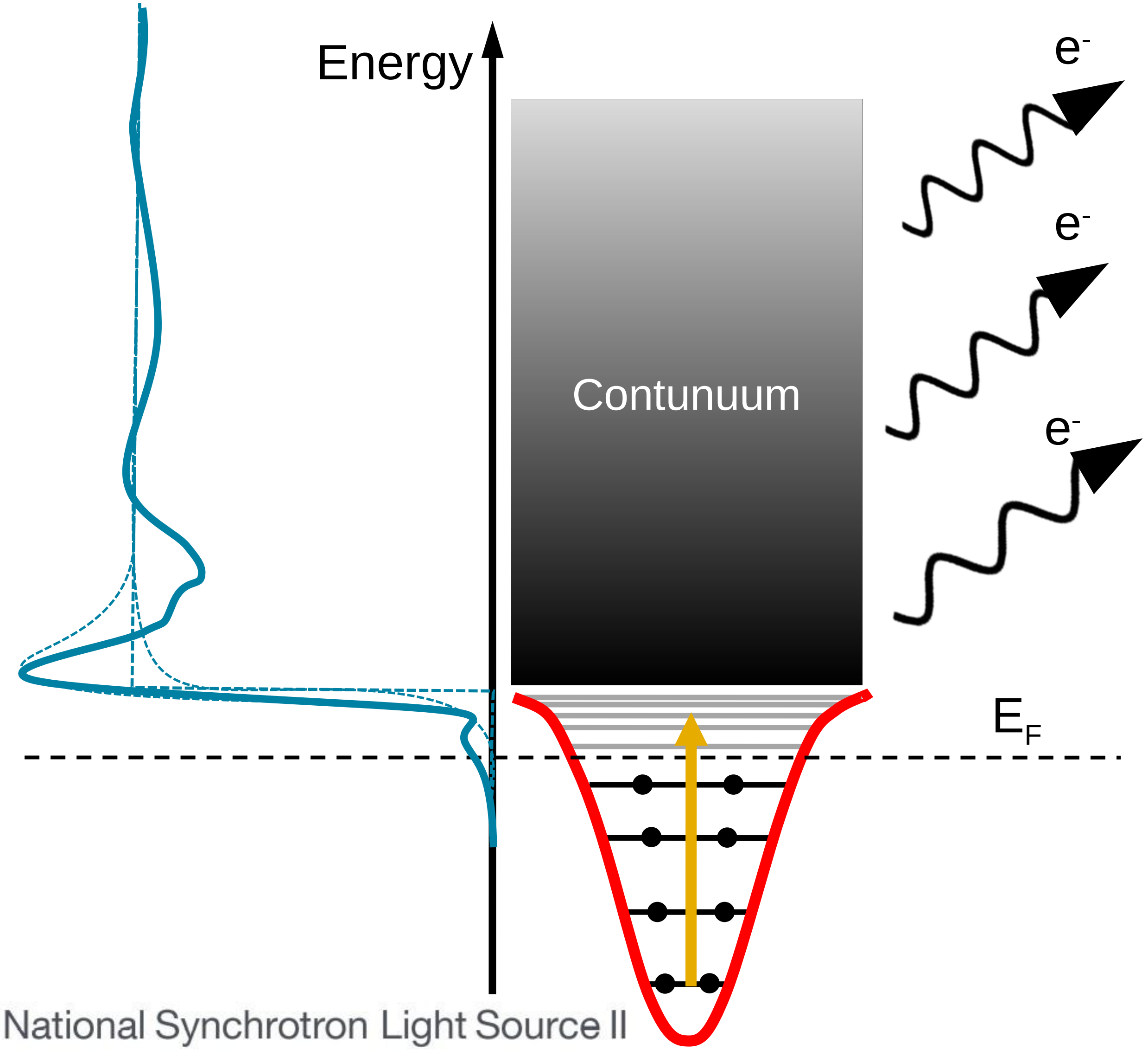
Processes behind X-ray absorption (3)



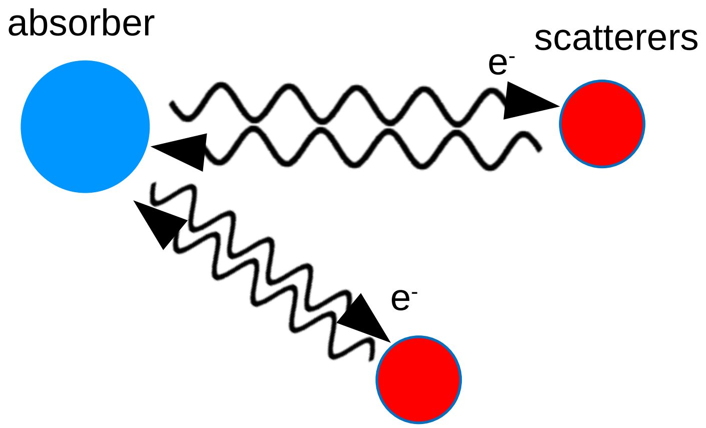
- Let’s now look into the unoccupied orbitals just above Fermi level

- Per Dipole Selection Rule, the 1s→4p is allowed (), leading to strong absorption.
- 1s→3d transitions are dipole forbidden, but quadrupole transitions sometimes are allowed due to symmetry reasons

Processes behind X-ray absorption (4)



- In real materials, the photoelectron is scattered by the neighboring atoms, some back to the absorbing atoms
- Electromagnetic wave due to photoelectron interferes with back-scattered wave
- Depending on the distance, the photoelectron energy the interference modulates the electronic density on the absorbing atom – and, in turn its absorption coefficient



Acronym soup

https://u.osu.edu/brokenshire

XAS: X-ray absorption spectroscopy

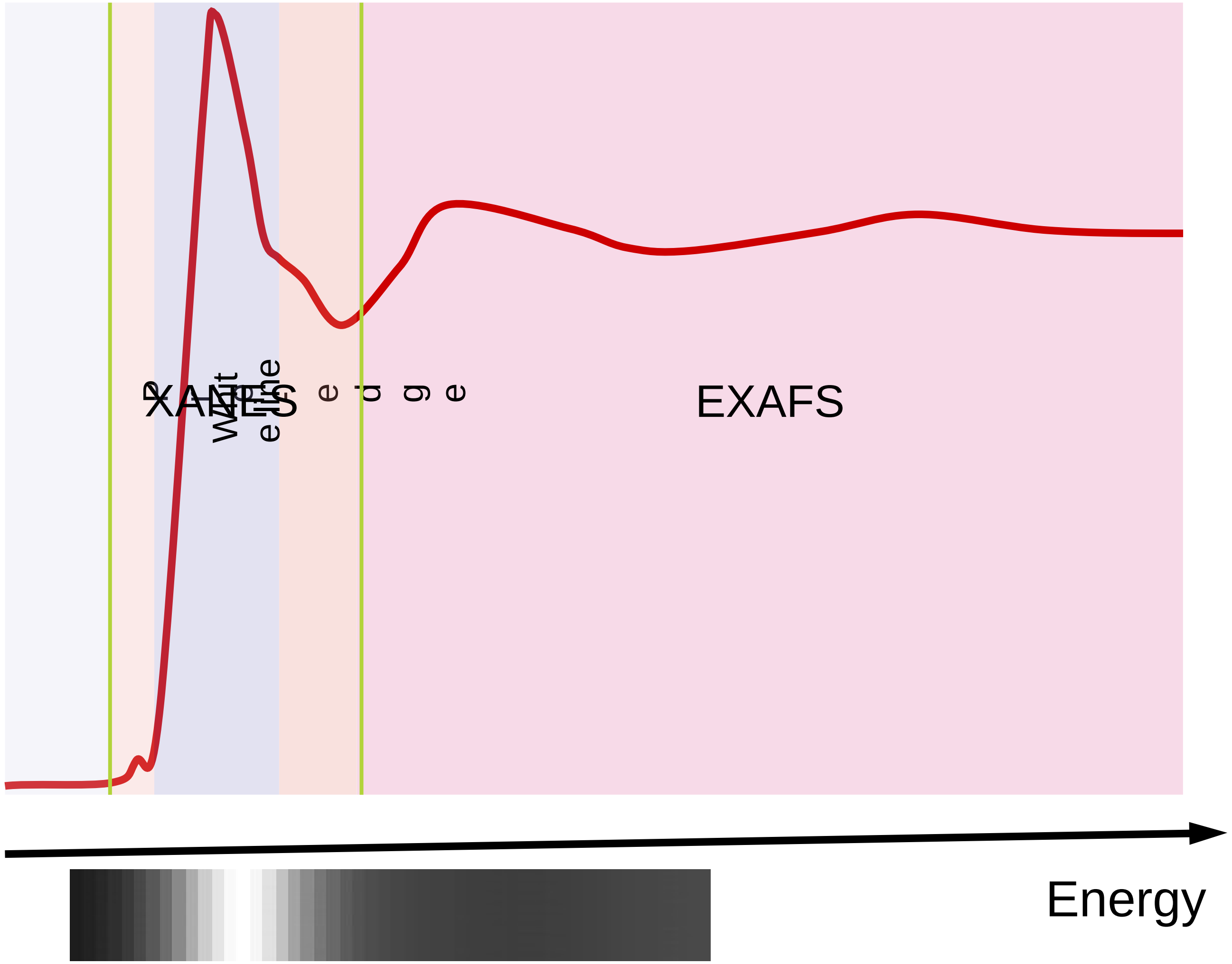
XANES: X-ray Absorption Near Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure

XAFS: X-ray Absorption Fine Structure

NEXAFS: Near Edge X-ray Absorption Fine Structure

Components of the XAS spectrum



No absorption – X-ray photon energy is too low

XANES

Pre-edge region – transitions within the atom (e.g., 1s→3d)

White line – transition to just above Fermi levels (e.g., 1s→4p)

This region often contains signatures spectral features

EXAFS – where oscillations occur

How versatile is XAS

- Different elements in heterogeneous samples can be probed individually (NMC cathodes in Li ion batteries – Nickel-Manganese-Cobalt are good example).
- XAS can probe any phase of matter (gas, liquid, or solid) and is applicable to all materials, regardless of their crystallinity.
- Due to penetrative power of X-rays, various sample environments may be used (catalysis reactors, electrochemical cells, growth chambers etc). More on that at 4:15 PM

2. Tools you need

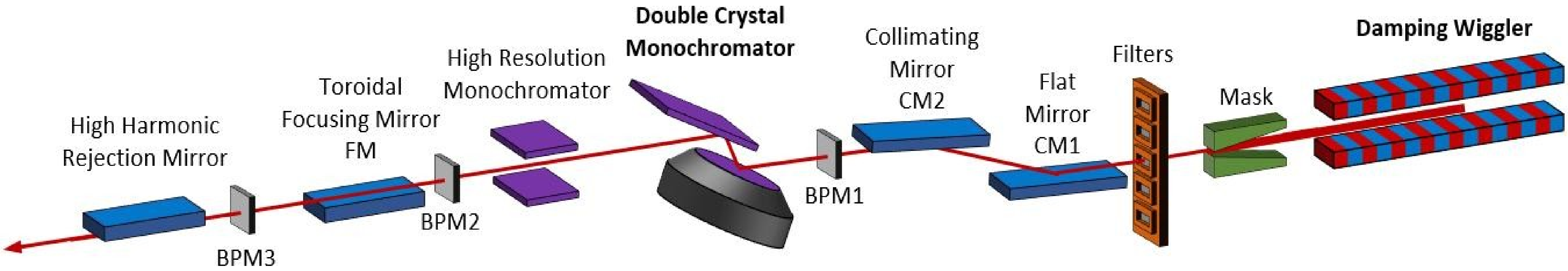
DISCLOSURE

These days you do not need synchrotrons to obtain XAS spectra. The bench-top instruments are becoming increasingly more common*

⚠ Synchrotron vs bench top XAS discussion is outside of this workshop's scope

Having said that – now that you are here at NSLS-II – bear with me

Typical layout of an XAS beamline



Critical components:

XAS beamline 1.0

Monochromator!!!

Yes, one can record an XAS spectrum with one beamline components

XAS beamline 2.0

Harmonic Rejection Mirror

Focusing Mirror

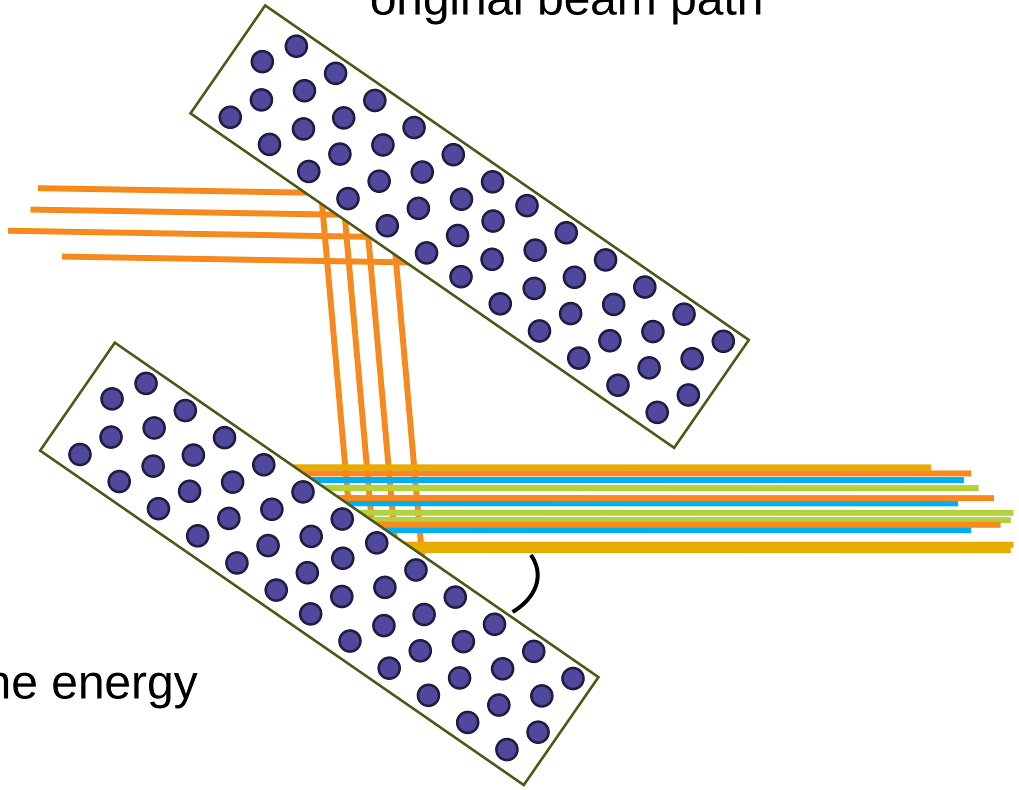
Monochromator

Collimating Mirror

National Synchrotron Light Source II

Monochromators

- Monochromator uses (typically two) Si crystals to select a narrow energy range
- Crystal acts as a diffraction grid for X-rays*



2nd crystal sends beam along original beam path

1st crystal
Selects the energy

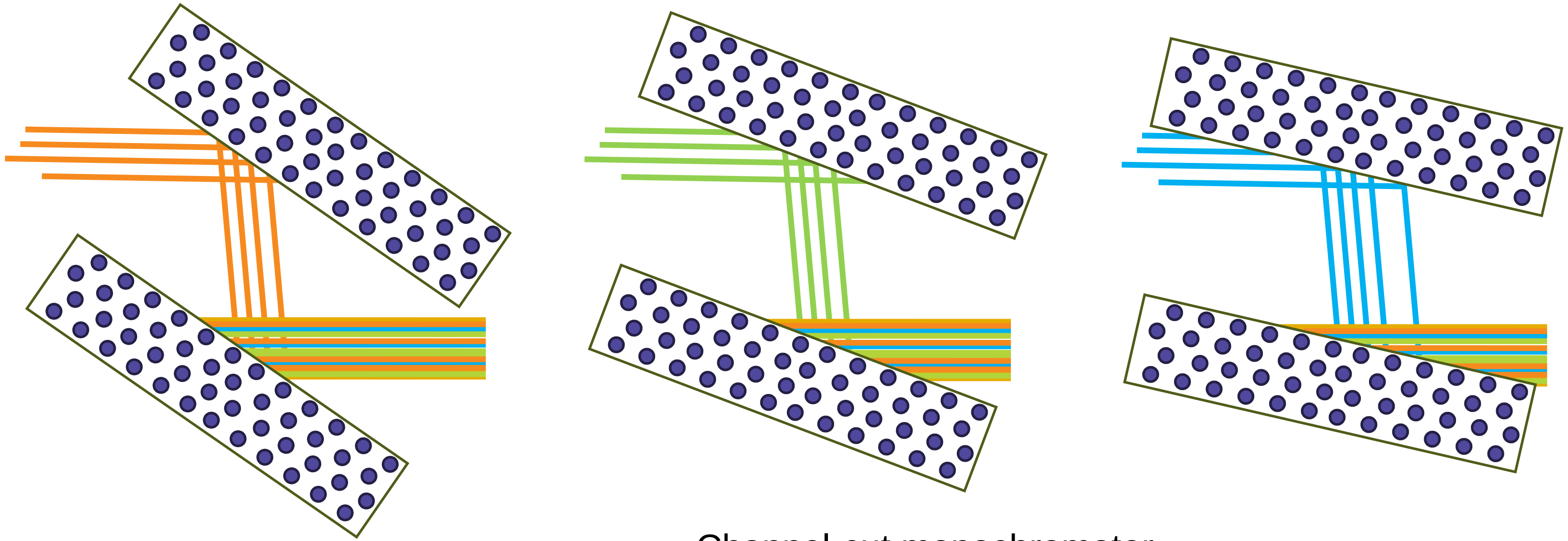
* Range is narrow but finite, ~1/10^4 of the energy

Bragg angle for specific energy

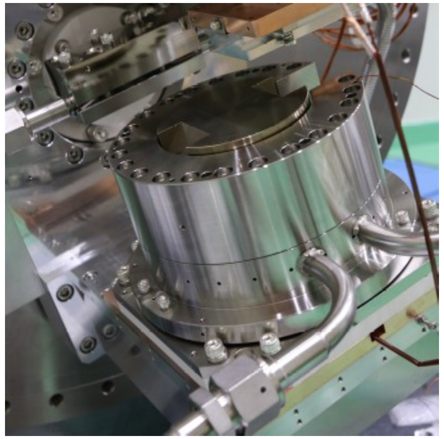
$$2d \sin \theta = n \lambda$$

Monochromators

- Energy is changed by changing the incident angle* (the steeper the angle the lower the energy)

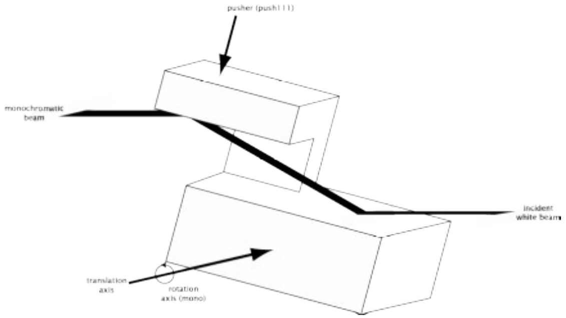


High heat load monochromator

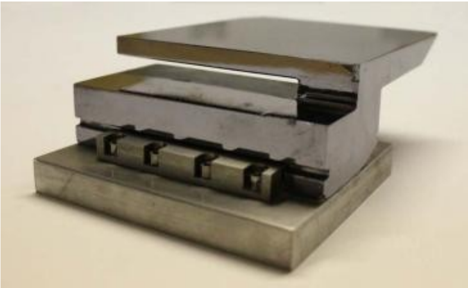


- Monochromators have to dissipate a high headload from low energy photons
- Cooling (liquid nitrogen or water) is often required

Channel-cut monochromator



https://www.esrf.fr/UsersAndScience/Experiments/MX/

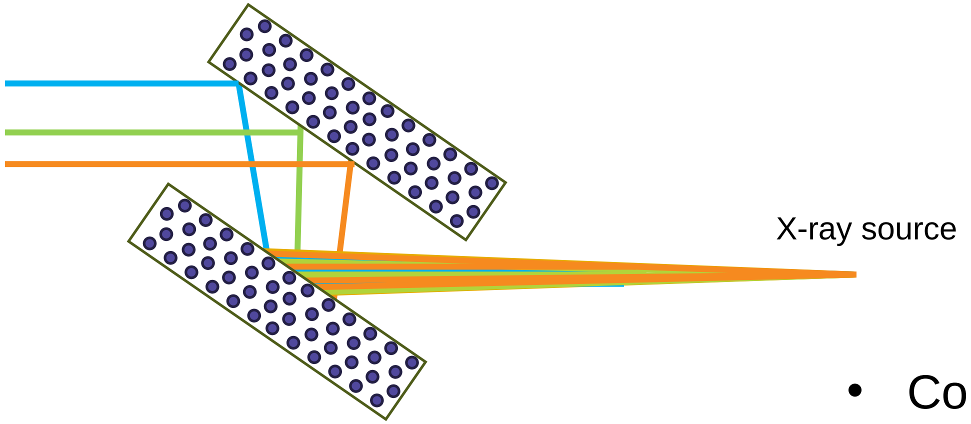


https://crystal-scientific.com/crystal_channel_cut.html

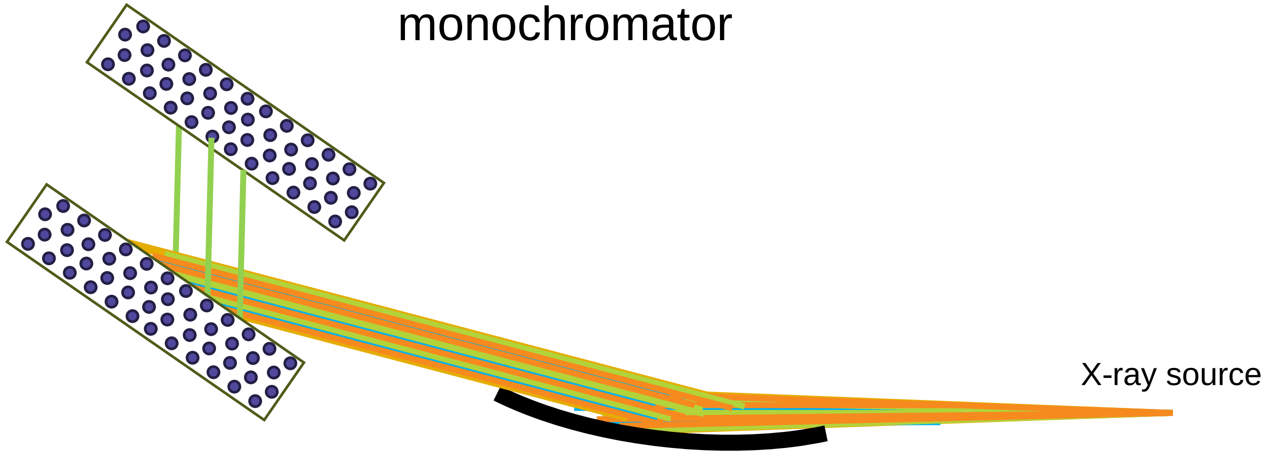
* Same change in angle means different change in energy (see Bragg's law)

Collimating mirror

- X-ray beam coming from the synchrotron is divergent
- We want to keep all X-ray photons to hit the monochromator crystal at the same angle



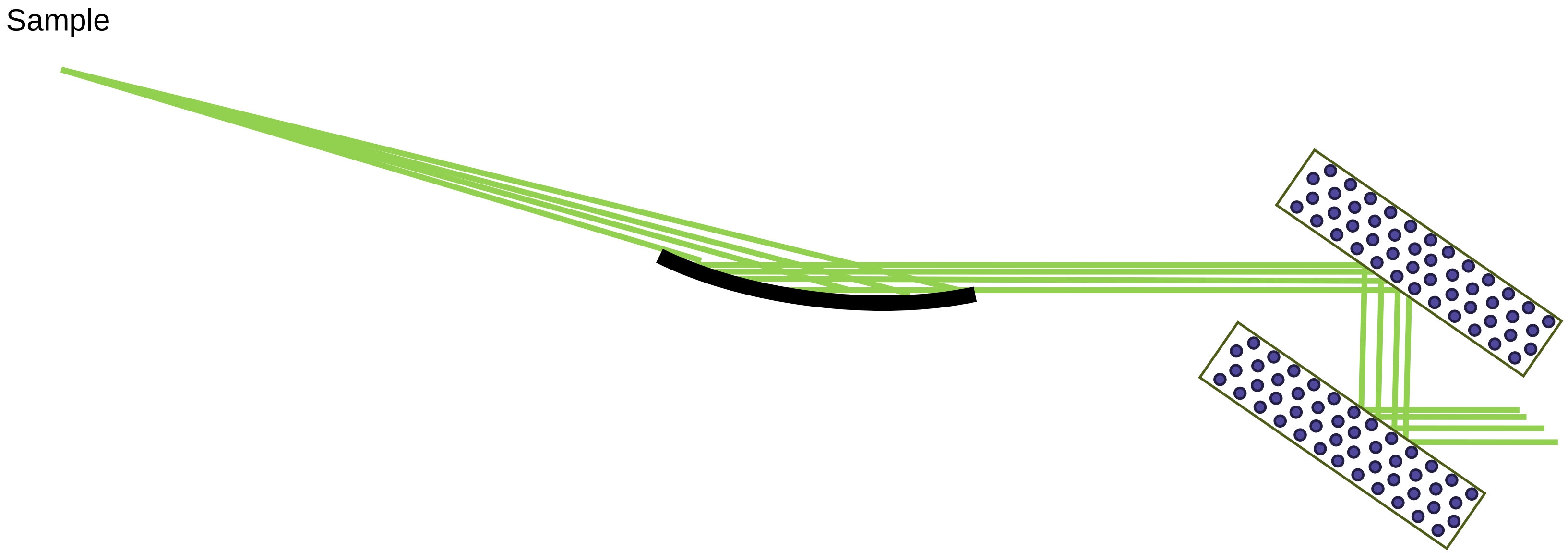
- Collimating mirror is placed upstream of the monochromator

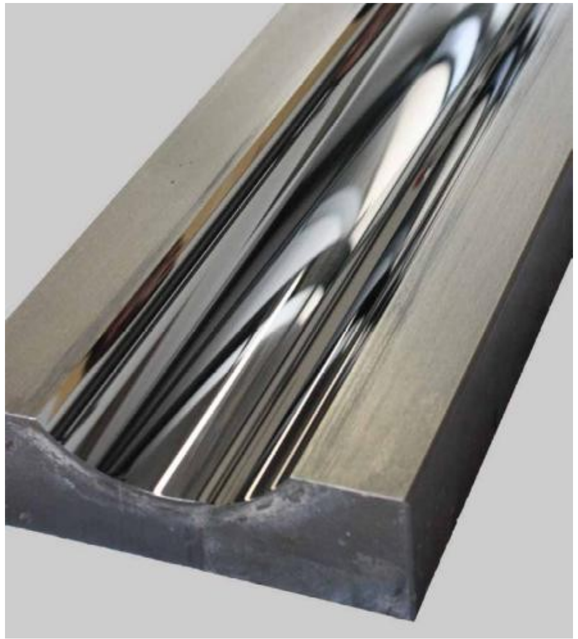


https://crystal-scientific.com/mirror_plano.html

Focusing mirror

- Collimation only happens vertically, beam continues to expand horizontally
- X-ray beam spot on the sample is application dependent (from µm to cm)
- We need a focusing mirror downstream of the mono to control the spot size

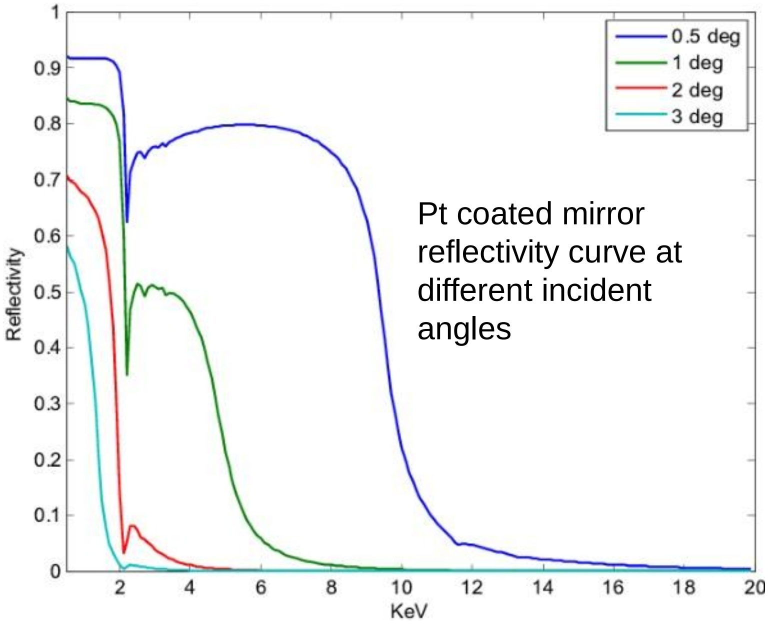




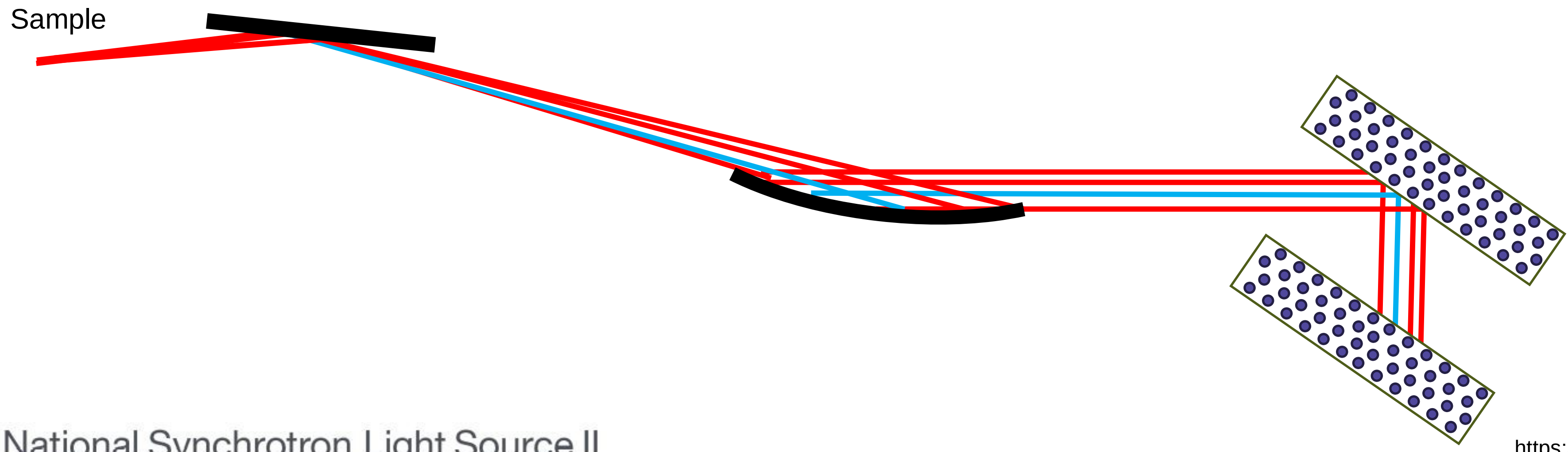
https://crystal-scientific.com/mirror_cylindrical.html

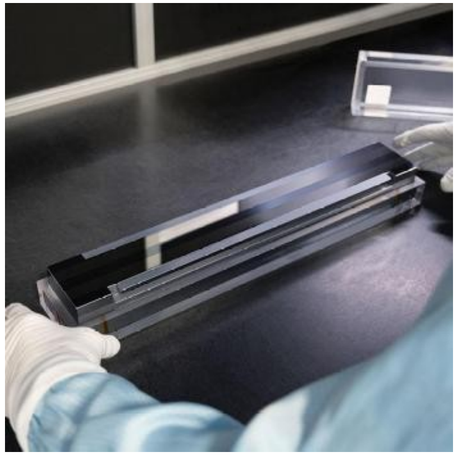
Harmonic Rejection mirror

- X-ray gratings or crystals generate not only the primary (fundamental) wavelength but also its integer multiples, known as harmonics which interfere with the experiment by contributing unwanted photon energies.
  - Beamline is set to 5,000 eV. Third harmonics is 15,000 eV
- When X-rays or other high-energy photons hit a mirror at very shallow (grazing) angles, they can be totally externally reflected.
- These mirrors often have multiple coatings and adjustable angles to tune to the correct energy range



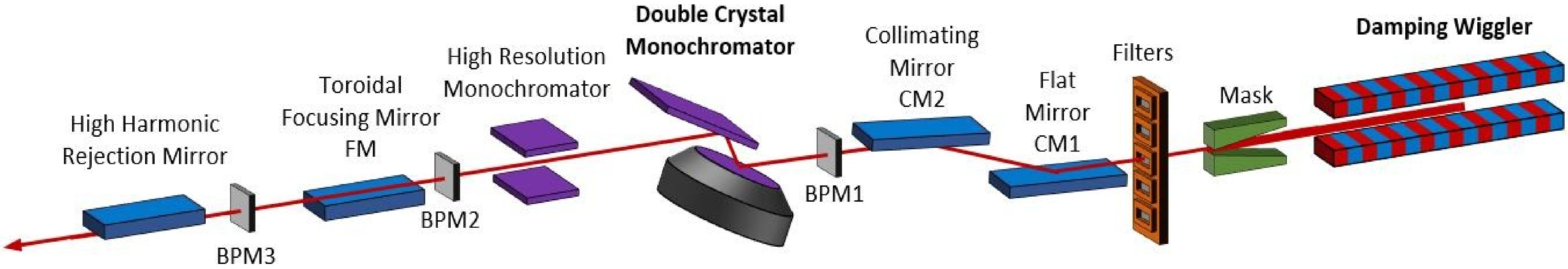
Pt coated mirror reflectivity curve at different incident angles





https://www.zeiss.com/semiconductor-manufacturing-technology

Typical layout of an XAS beamline



Critical components:

XAS beamline 1.0

1. Monochromator

Yes, one can record an XAS spectrum with one beamline components

XAS beamline 2.0

Harmonic Rejection Mirror

Focusing Mirror

Monochromator

Collimating Mirror

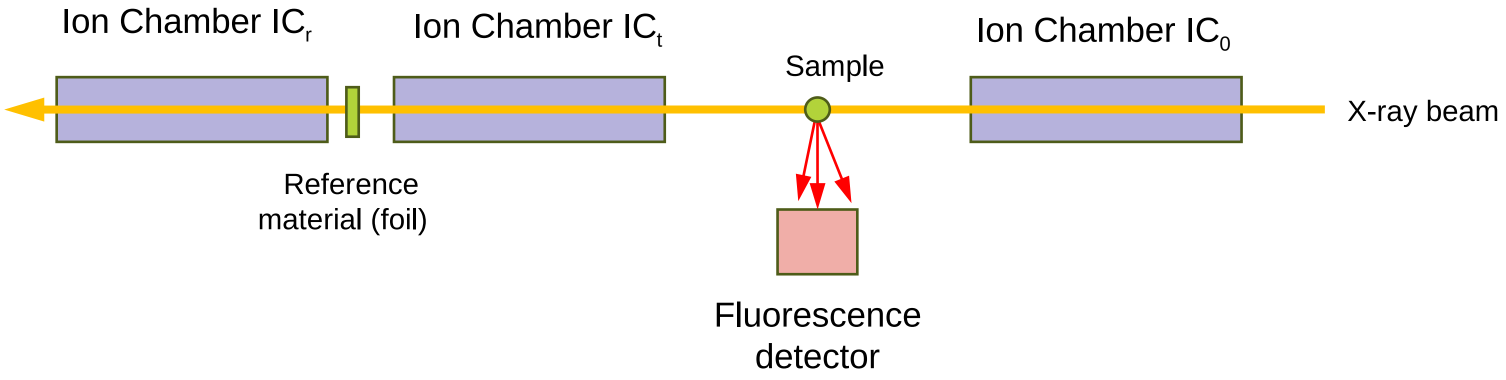
Detectors for XAS

- Ion chambers
- Integrating fluorescence detectors
- Energy discriminating fluorescence detectors

https://xds-oxford.com/products/

https://www.mirion.com/products/technologies/

Typical layout of XAS experimental station



Ion Chamber IC_r

Ion Chamber IC_t

Ion Chamber IC_0

Sample

X-ray beam

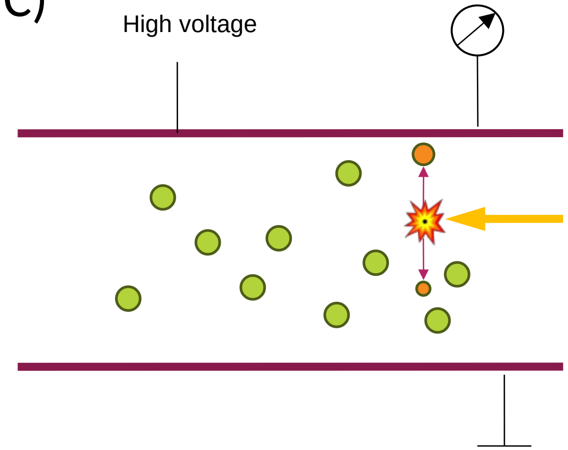
Reference material (foil)

Fluorescence detector

https://www.hitachi-hightech.com/us/en/products

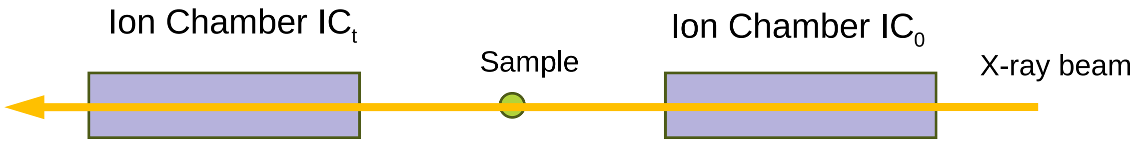
Detectors - ion chambers

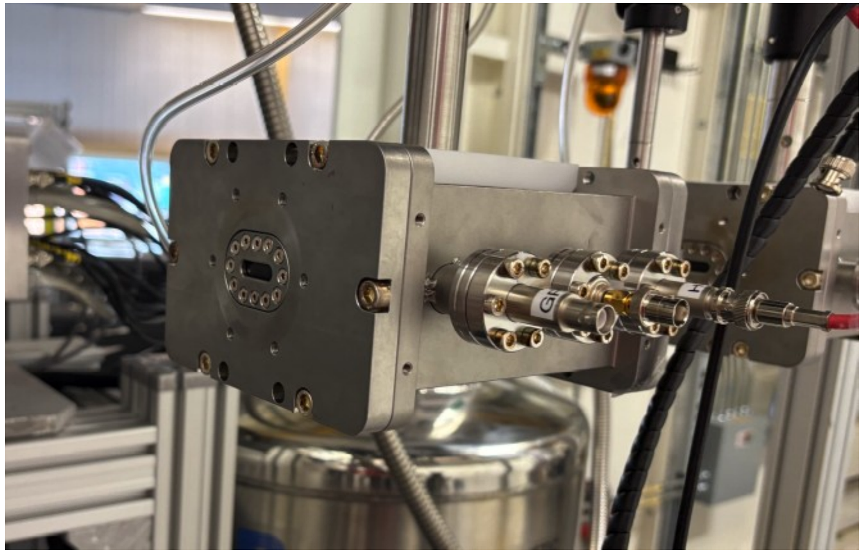
- Gas mixture confined between two flat electrodes, with high voltage potential applied (typically 500-2000 V)
- X-ray photons ionize the gas molecules/atoms. Ions are pulled to electrodes by applied electric field and produce electrical current (in the order of nanoamps to microamps).
- ~~If beamline scientist has done a really good job~~, the current is proportional to the flux (number of photons passing through the IC)



- XAS absorption is defined by the Beer–Bouguer–Lambert law as a log of ratio of incident and transmitted beam intensities

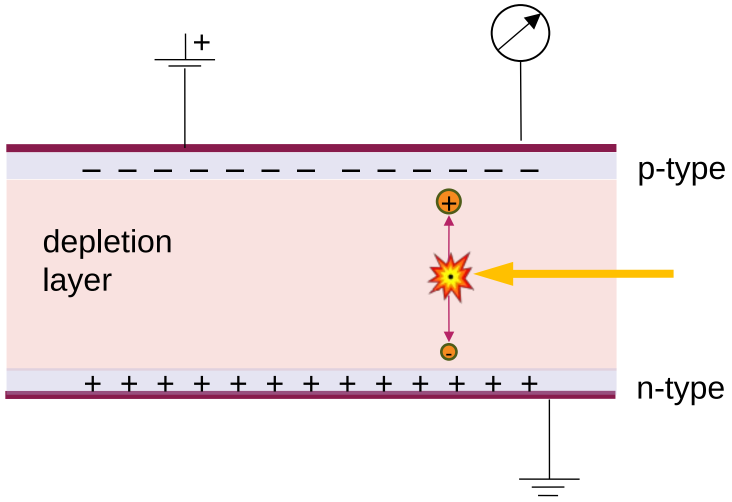
$$\mu(E) = ln\,(I_0/I_t)$$





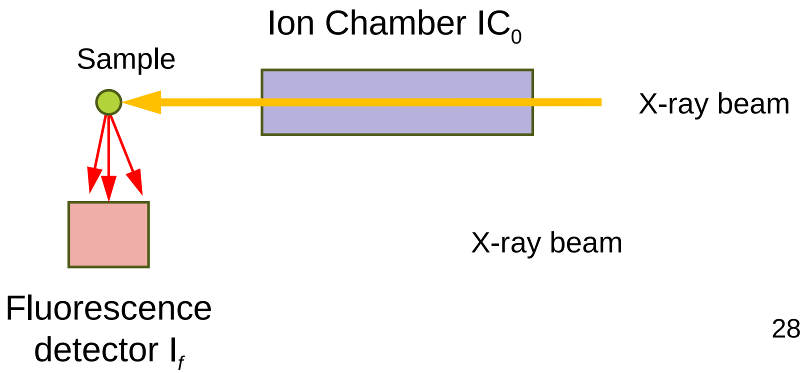
Solid state detectors

- Semiconductor diode, typically made of silicon (Si) or high-Z materials like germanium (Ge) or cadmium telluride (CdTe) for hard X-rays. It has a p-n junction that creates an electric field in the depletion region
- X-ray photons ionizes atoms in the semiconductor, generating electron-hole pairs. The charge signal is collected by the electrodes and amplified using preamplifiers.



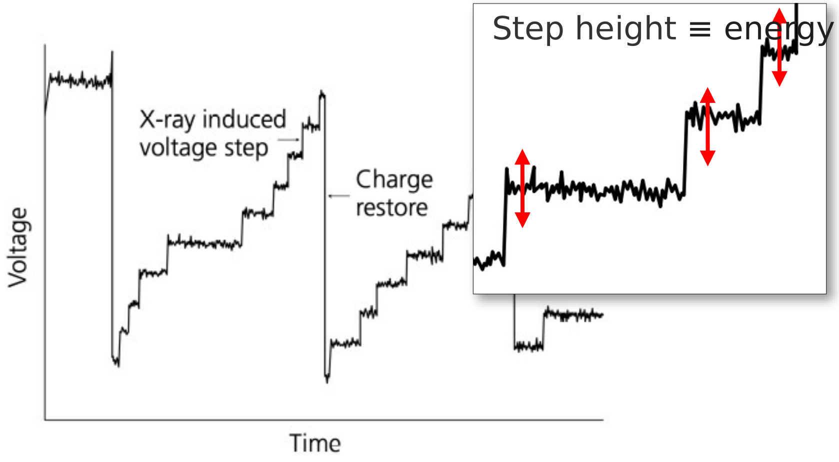
- XAS absorption proportional to the ratio of fluorescence photon count and incident beam intensity

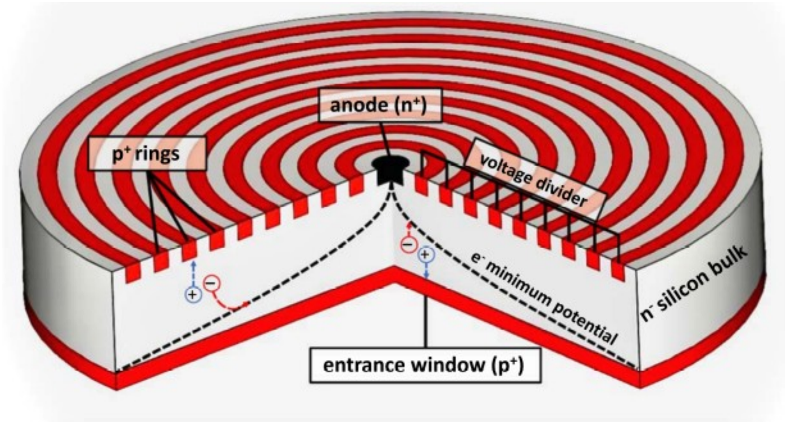
$$\mu(E) \propto I_f/I_0$$



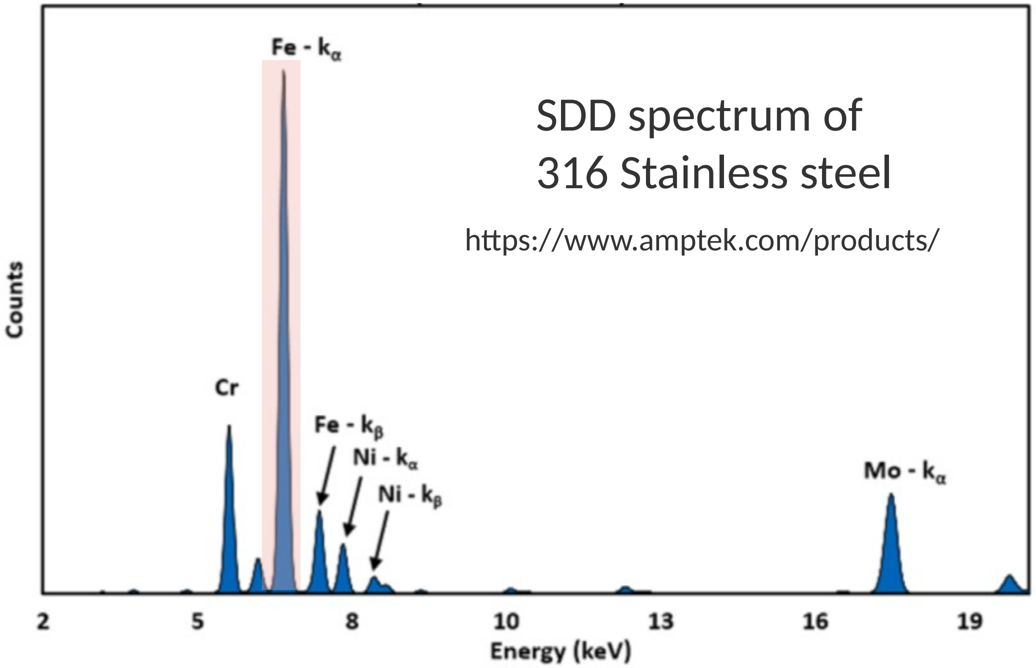
Silicon drift detectors

- Si or Ge semiconductor diode with a large depletion region with an array of concentric electrodes that create a radial electric field.
- Incoming X-ray photons generating electron-hole pairs through the photoelectric effect.
- Readout electronics quantifies the number of charge carriers which is proportional to the X-ray energy.





Sgaramella *et al* 2022 *Phys. Scr.* **97** 114002



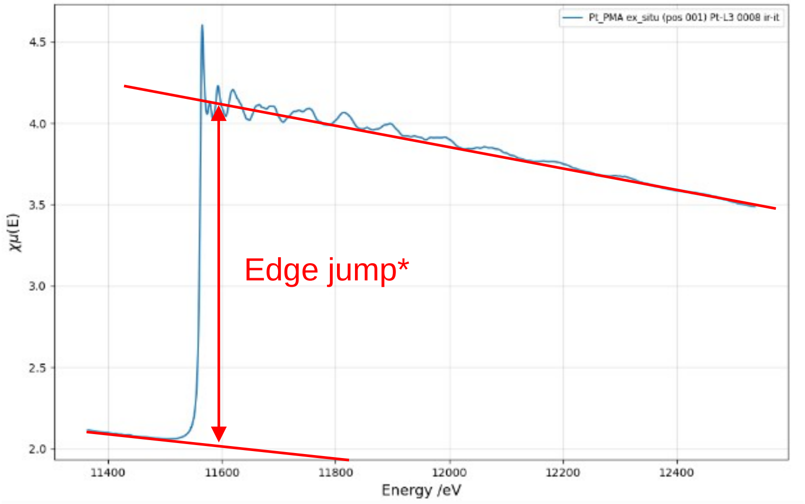
SDD spectrum of
316 Stainless steel

https://www.amptek.com/products/

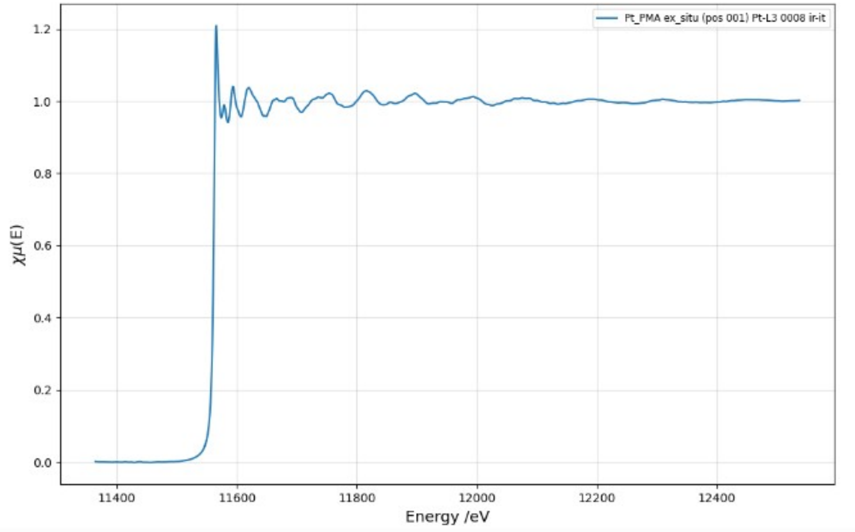
To obtain XAS spectrum, the spectra are integrated over the region-of-interest corresponding to a probed atom fluorescence line

Basics of data reduction

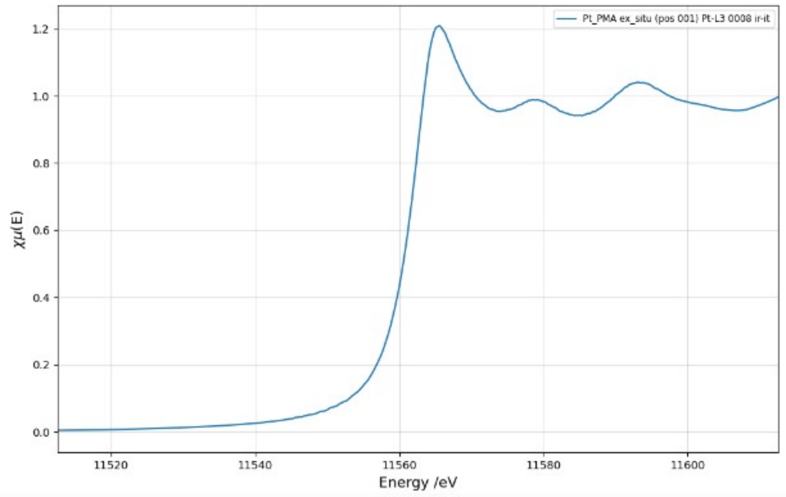
This is the spectrum as it comes from the beamline.
It sits on top of the background



Pre-edge and post-edge subtraction and normalization
(more on that at 11:10am)



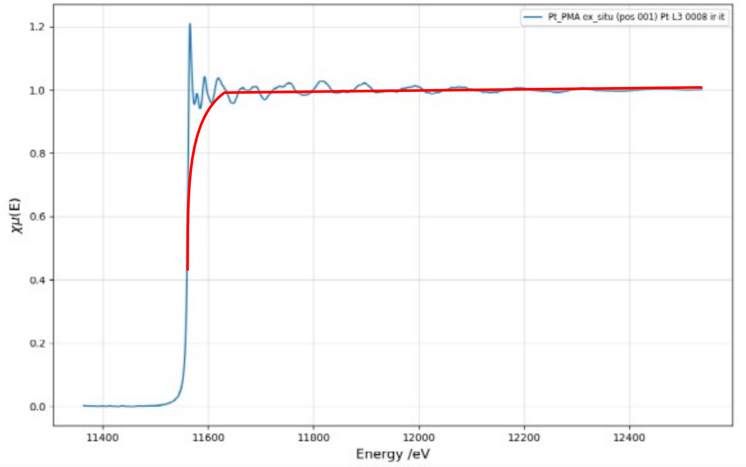
Zoom on XANES
(more on that on Tue, 9:00am)



* Edge jump is proportional to the amount of probed element in the beam

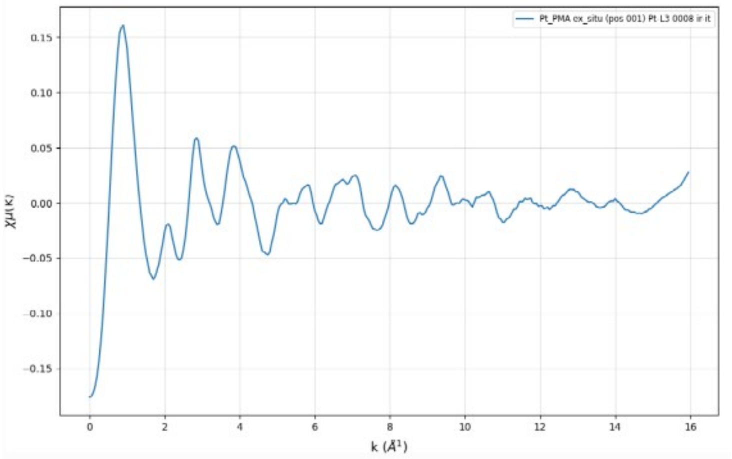
Basics of data reduction

One can now extract EXAFS wiggles from the spectrum



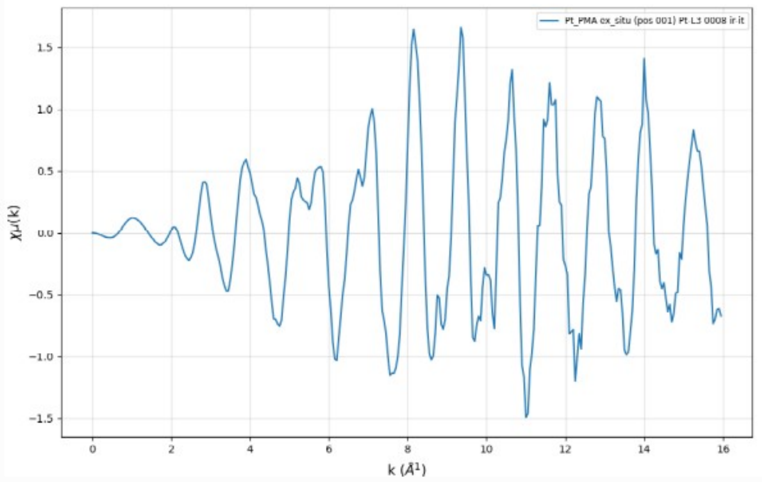
Background subtraction
(more on that at 11:10am)

EXAFS in k-space (momentum space) - removing energy dependence



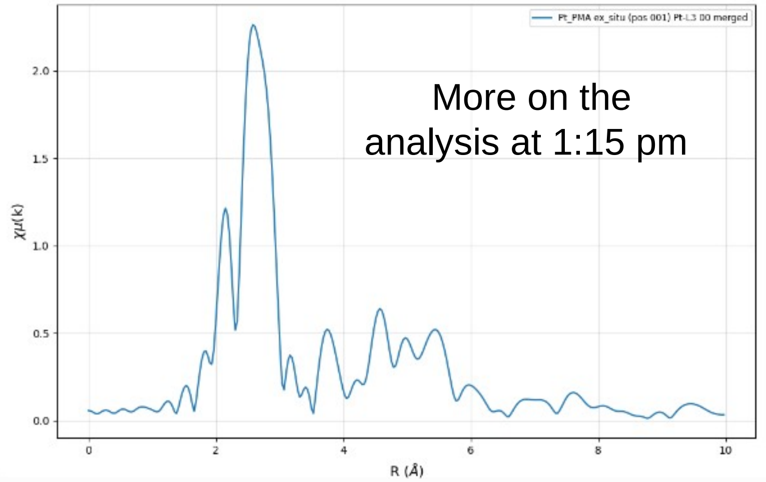
$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

Applying weighting factor k^n to emphasize high-k oscillations



Fourier Transform
to R-space

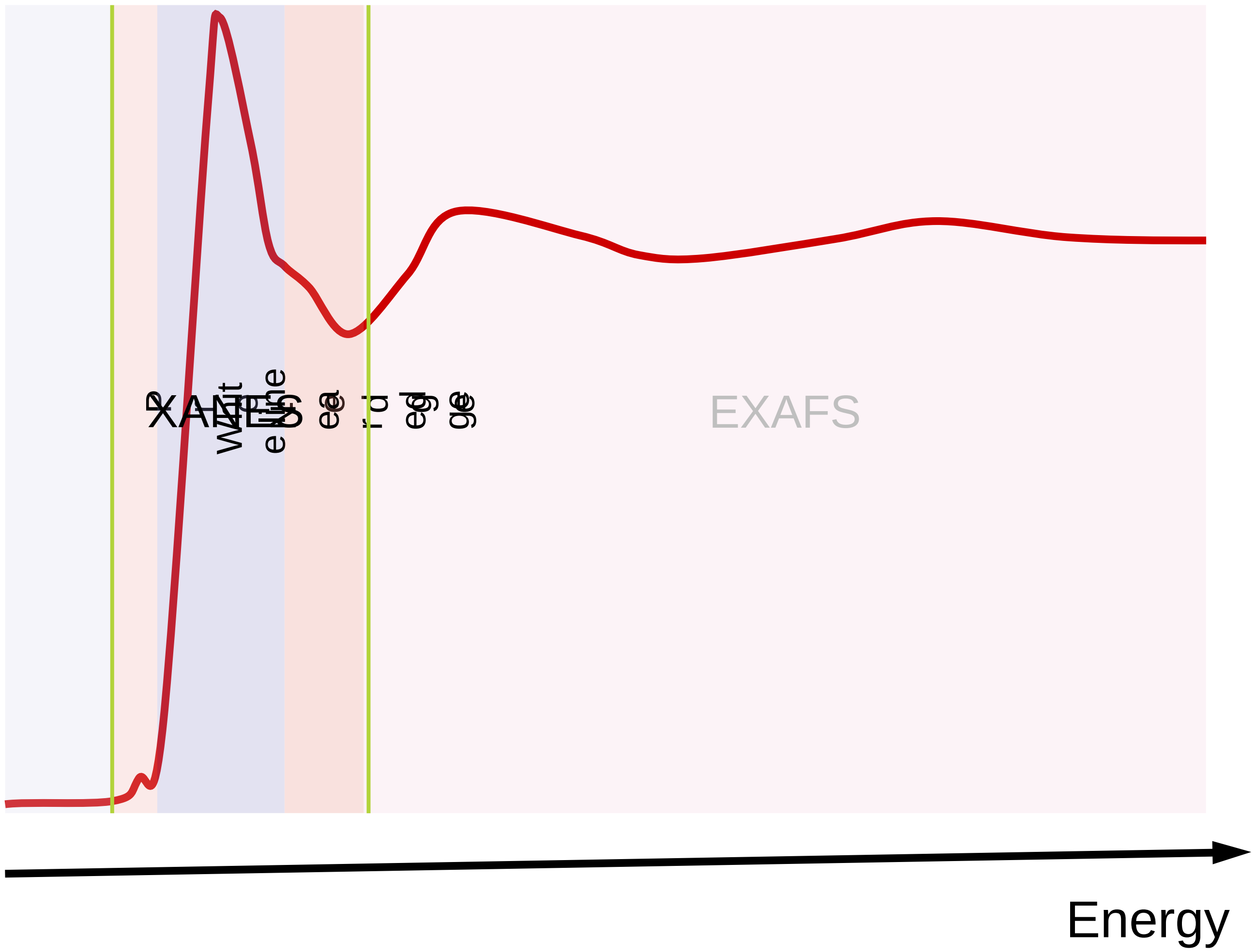
FT-EXAFS in R-space

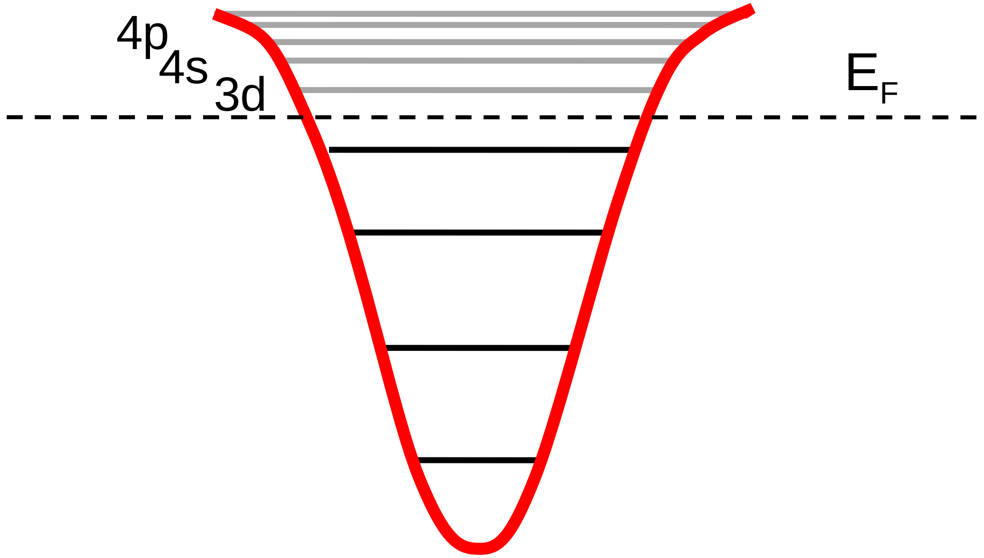


More on the
analysis at 1:15 pm

3. What can we learn from XANES

Components of the XAS spectrum



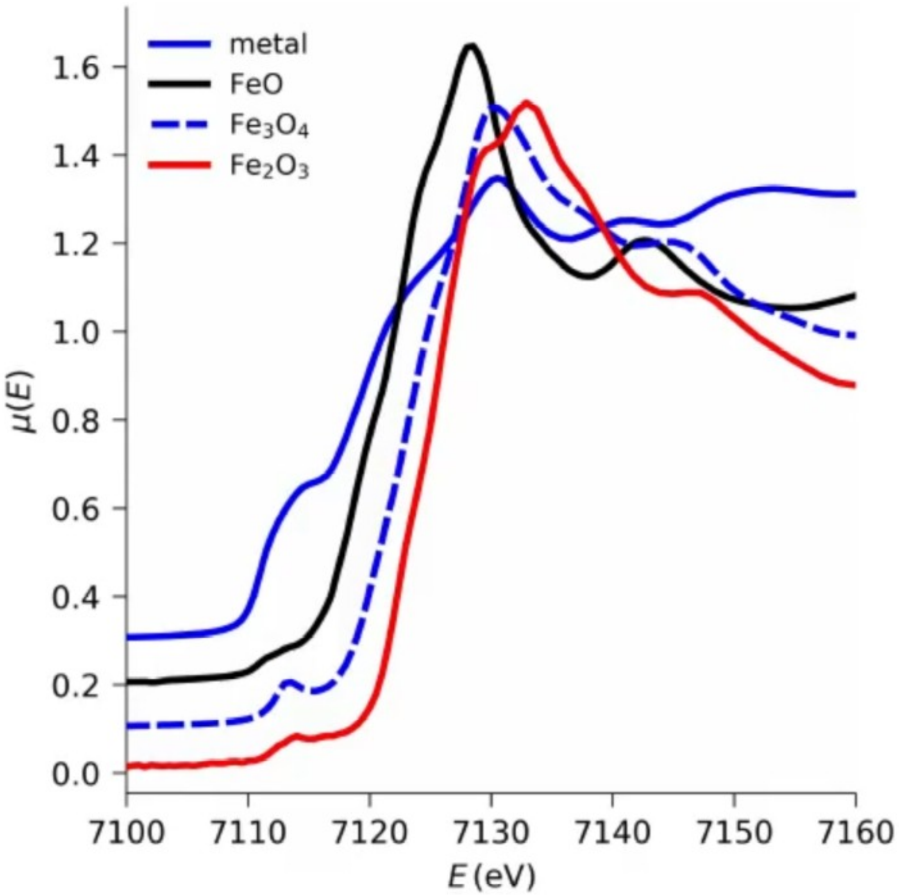


XANES	Pre-edge region – transitions within the atom occur here (e.g., 1s→3d)
	White line – transition to just above Fermi levels (e.g., 1s→4p)
	Near edge – often contains signature spectral features

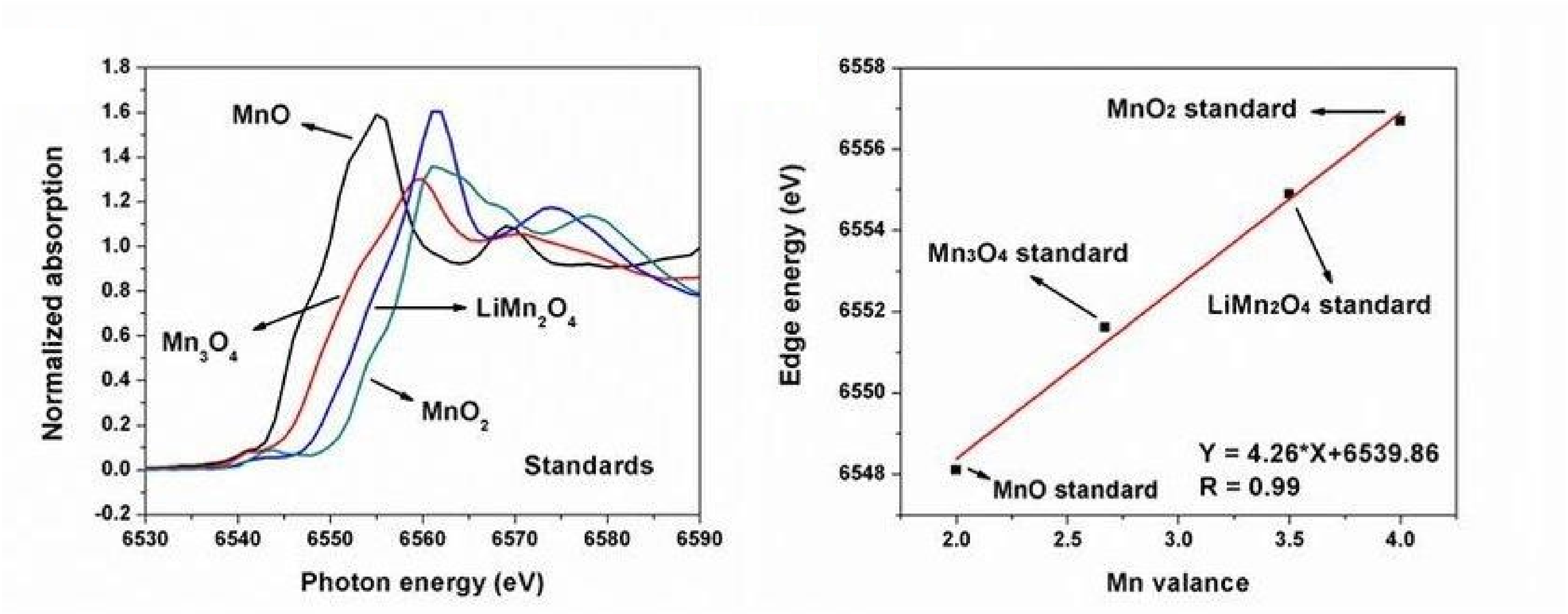
National Synchrotron Light Source II

Edge position and oxidation state

- Edge onset shifts to the higher energy with oxidation state increase (Mn^{2+}, $Mn^{2.67+}$, $Mn^{3.5+}$, Mn^{4+}) due to weaker shielding effect of valence electrons and increase in Coulomb attraction



More on oxidation state



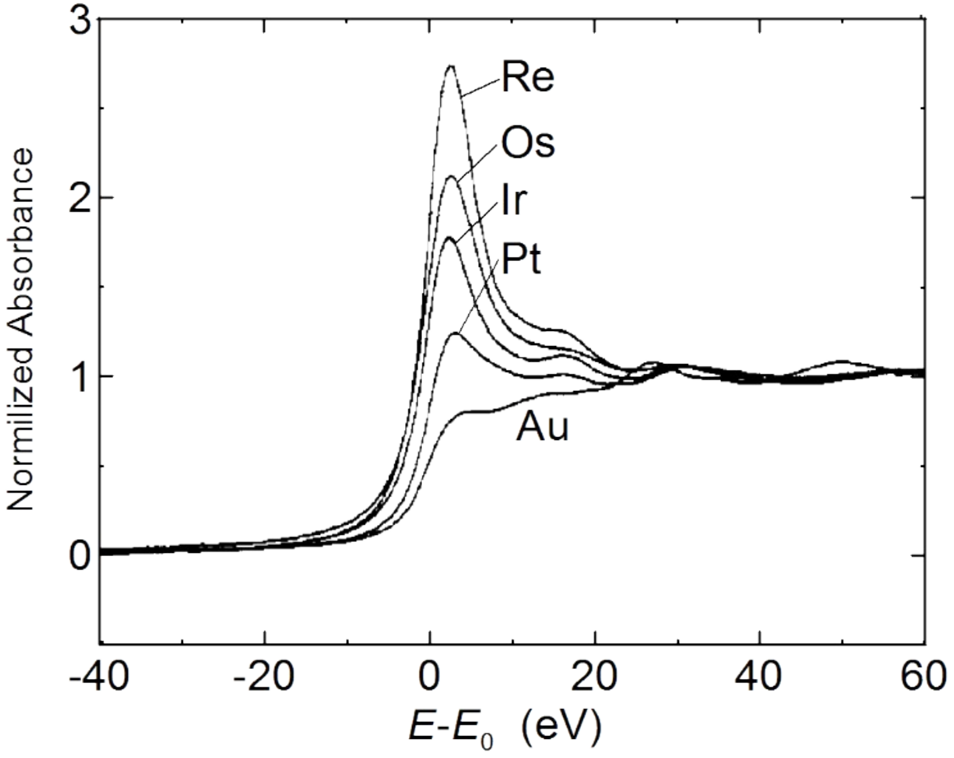
- This example shows a linear relationship between edge position and effective oxidation state (it’s not always linear)*

* Edges are useful for determining oxidation states – but there are many additional factors contributing to the edge position (more at 9am Wed)

White line intensity

75	76	77	78	79
Re	**Os**	**Ir**	**Pt**	**Au**
Rhenium	Osmium	Iridium	Platinum	Gold
186.207	190.23	192.22	195.08	196.967

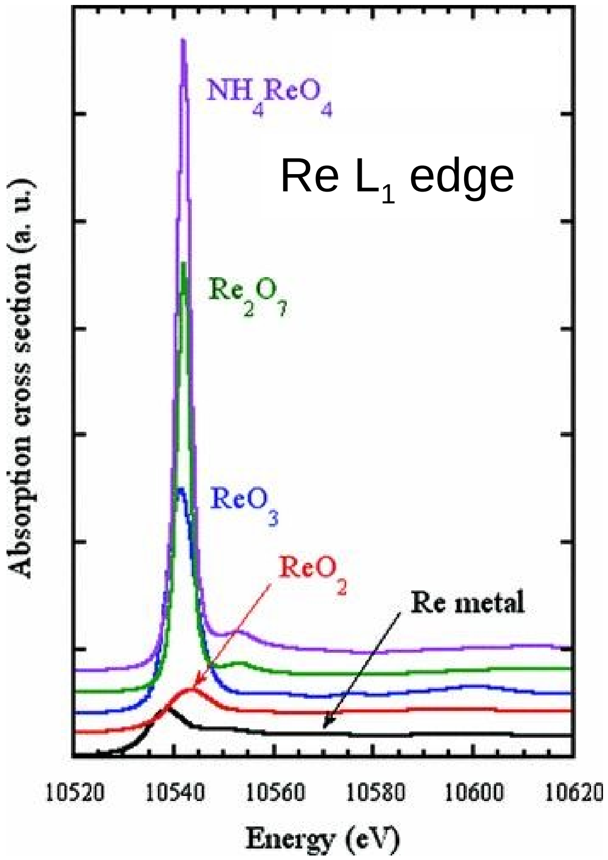
$5d^5$ $5d^6$ $5d^7$ $5d^9$ $5d^{10}$



J. Phys. Chem. **96** (1992) 4960

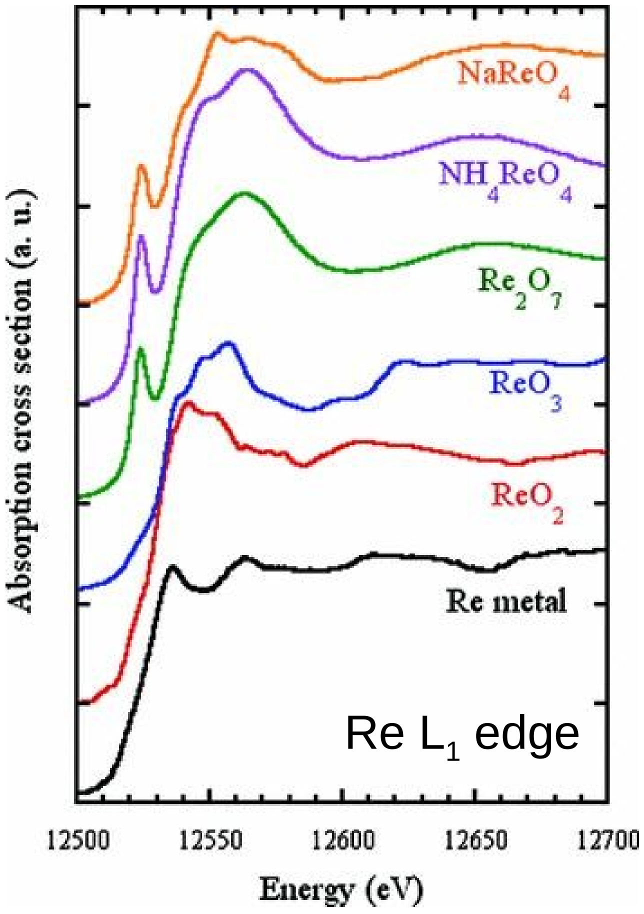
- L_{III} XANES of 5d elements
- White line is due to transitions of $2p_{3/2}$ electrons to unoccupied 5d states
- White line intensity/area increases with the number of 5d holes
- Gold edge does not exhibit white line (electrons are directly excited into continuum)

White line intensity and oxidation state



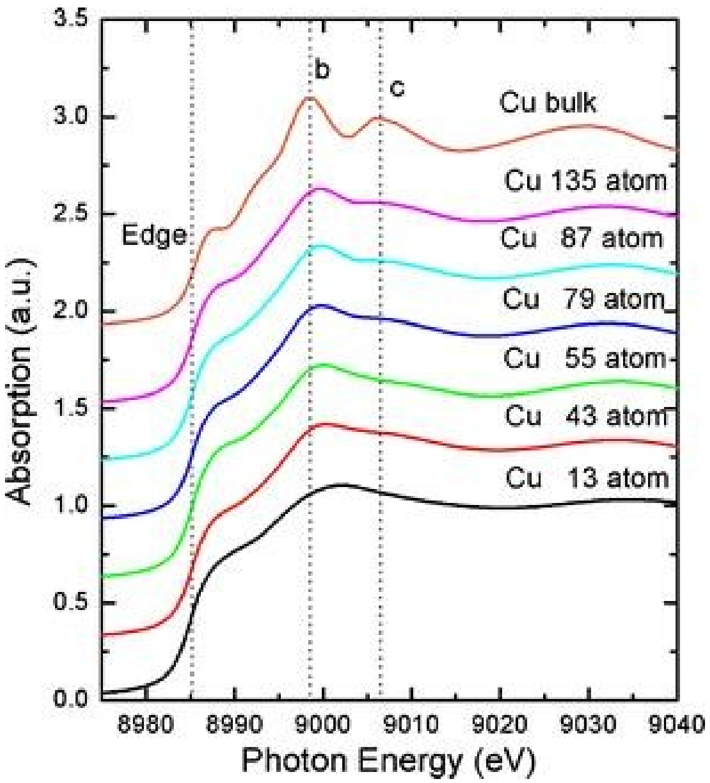
Phys. Rev. B **85**, 125136 (2021)

- Absorption at the L$_3$ edge due to transition from the core level 2$p_{3/2}$ to unoccupied 5*d*
- White line intensity/area increases with the number 5d holes, which is the measure for oxidations state
- In contrast, at the Re L$_1$ edge, the transition is from 2*s* to 6*p* state, which is highly and strongly highly hybridized with the ligands' orbitals, which makes it a very sensitive probe for local geometry

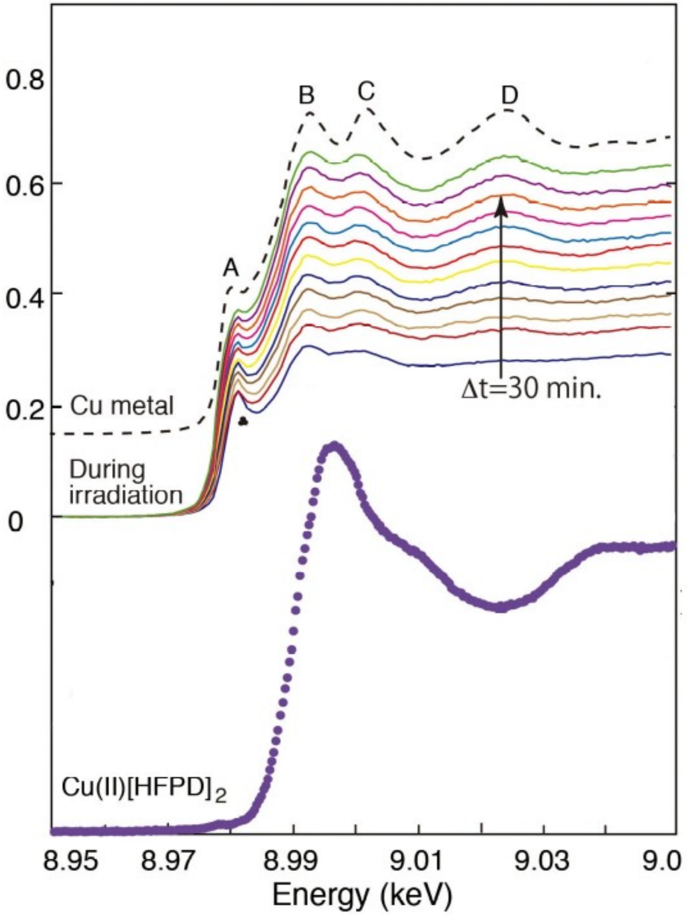


Nanoparticles vs bulk

Pronounced features in XANES spectra of bulk metals are often smeared when the material becomes nanoparticulate



Analytical and Bioanalytical Chemistry
399, 3033–3040 (2011)

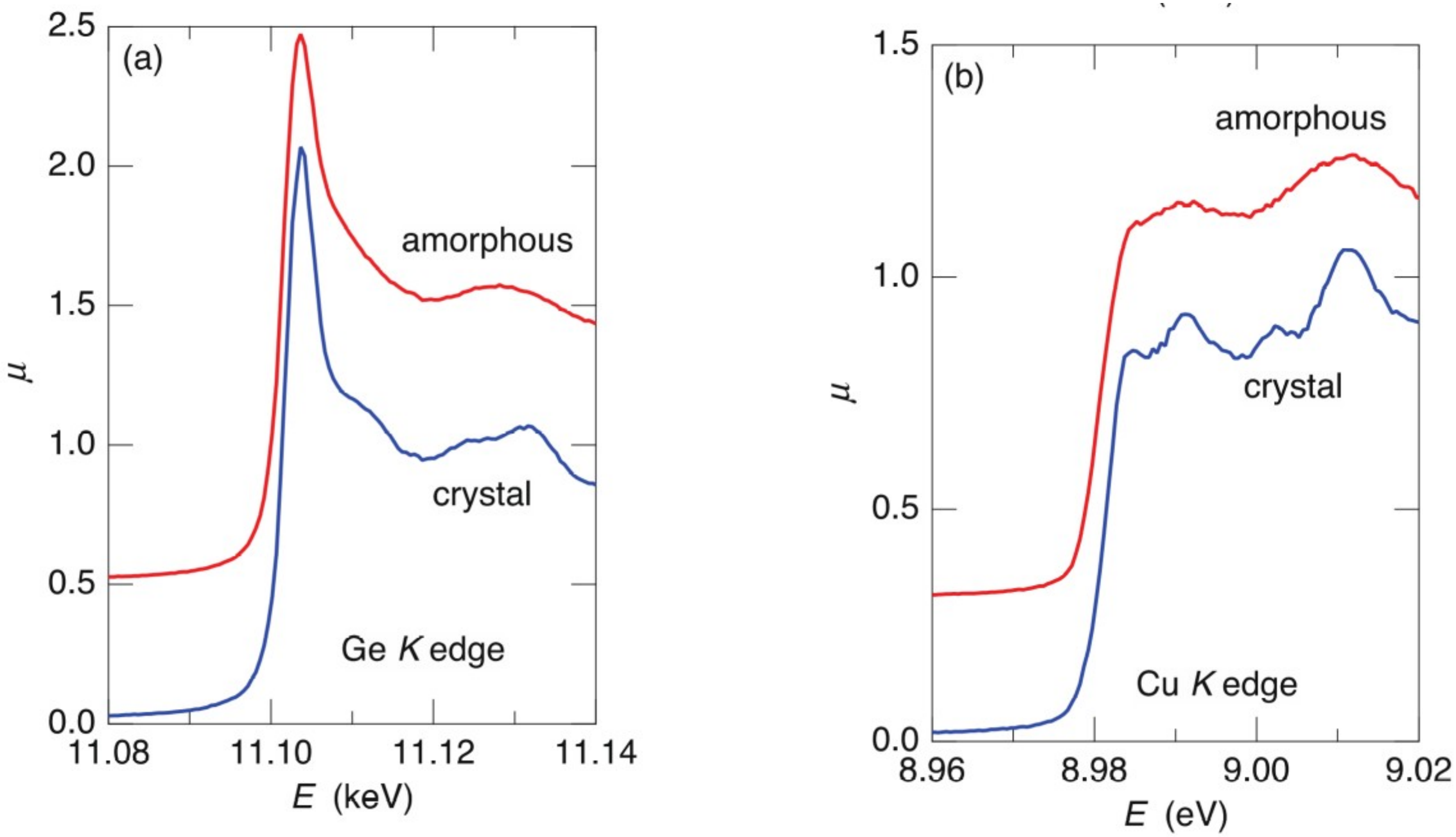


Scientific Reports 4, 7199 (2014)

- Here the Cu particles grow from solution under radiolysis. As the size increases, the features in XANES sharperen

Amorphous vs. crystalline materials

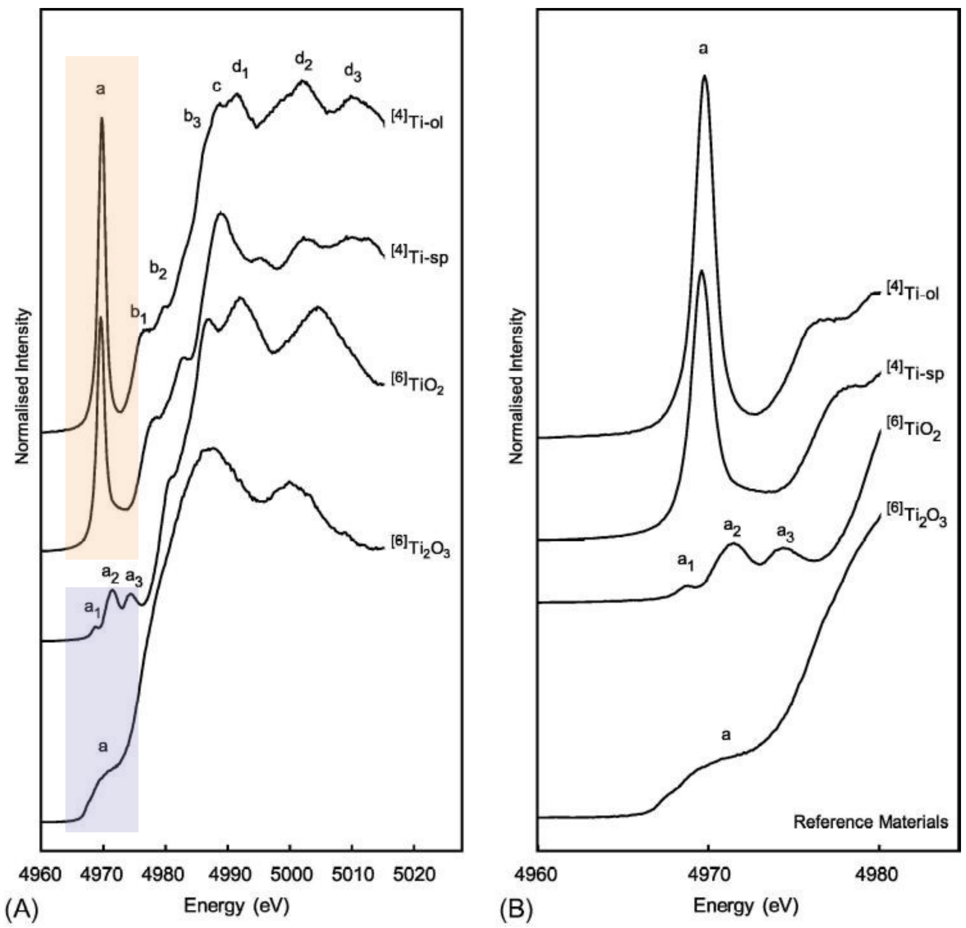
Similar to nanoparticles vs bulk, the spectra features in crystalline materials are sharper than their amorphous counterparts



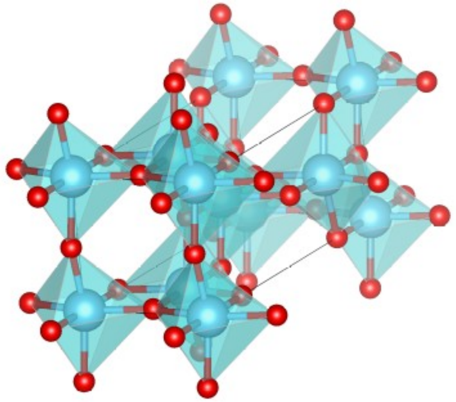
- Phase-changing $GeCu_2Te_3$ material before and after annealing

Journal of Optoelectronics and Advanced Materials 18, 248-253 (2016)

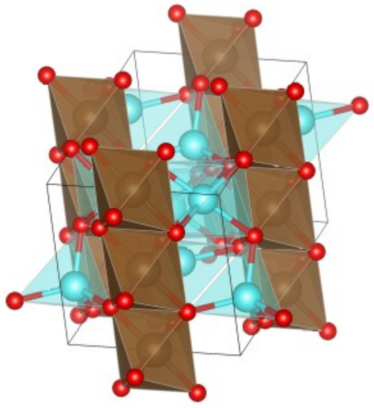
Pre-edge - coordination



Tetrahedral vs octahedral Ti



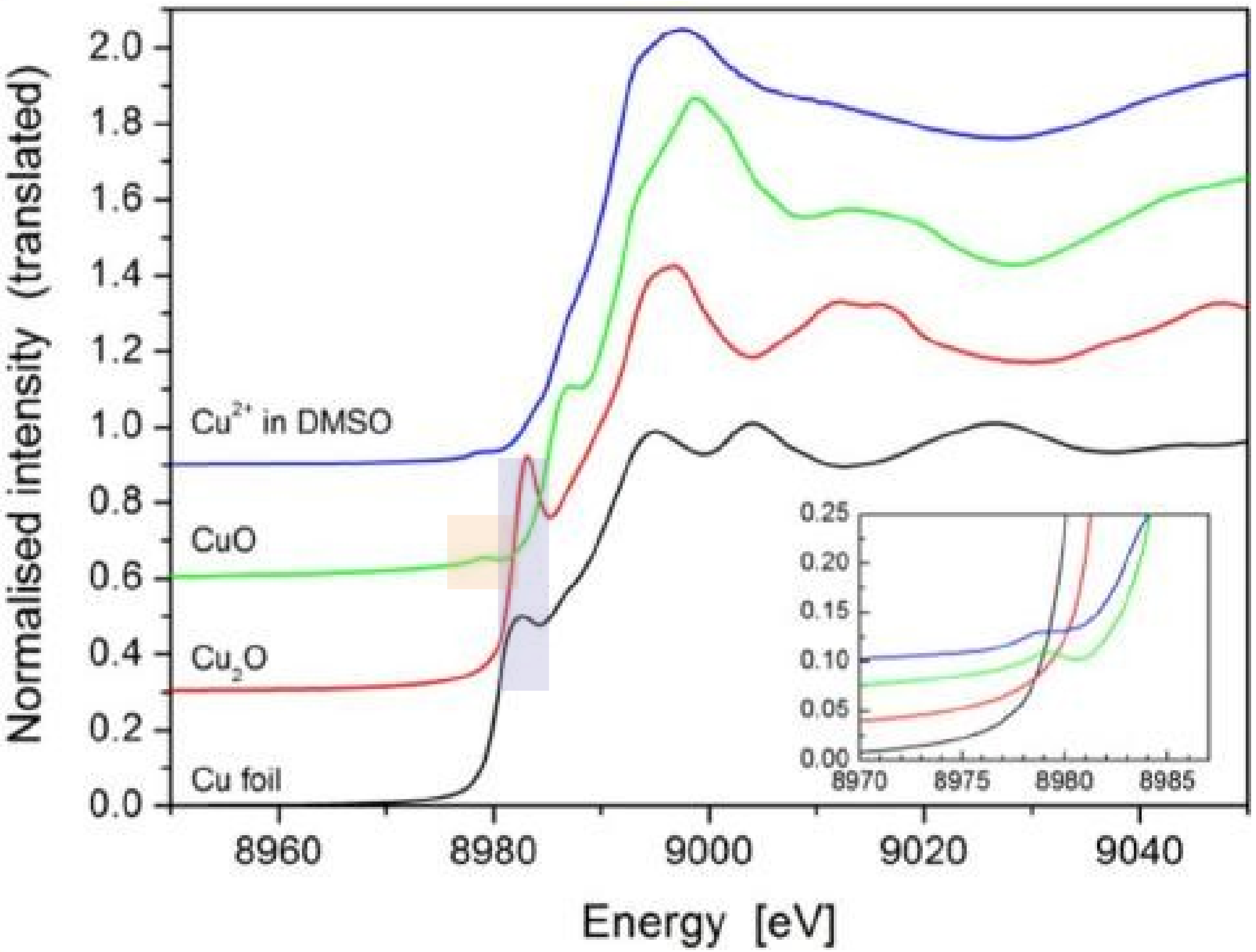
TiO_2



Fe_2TiO_4

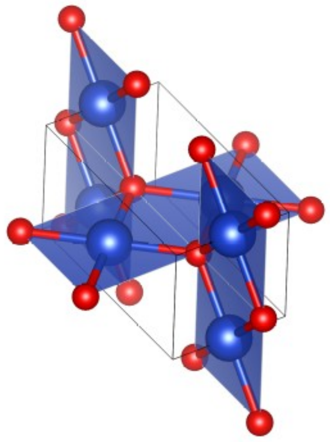
- In tetrahedral coordination, Ti lacks an inversion center, which allows $1s \rightarrow 3d$ transitions to gain dipole-allowed character due to *p*-*d* orbital mixing.
- The distortion and lack of centrosymmetry in tetrahedral Ti lead to stronger hybridization between Ti 3*d* and ligand orbitals,

Pre-edge - coordination

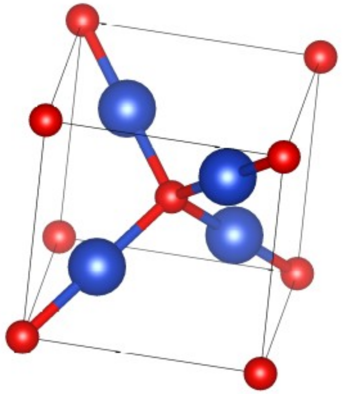


Journal of Physics 190 (2009) 012084

Square planar vs linear Cu



CuO



Cu$_2$O

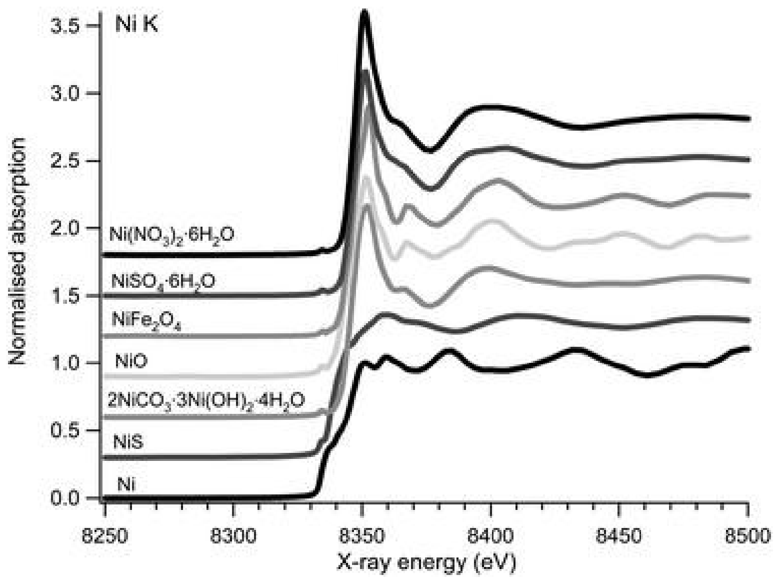
- When Cu is in linear coordination, dipole-allowed transition $1s \rightarrow 4p_{xy}$ appears as a sharp pre-edge peak

Linear combination analysis

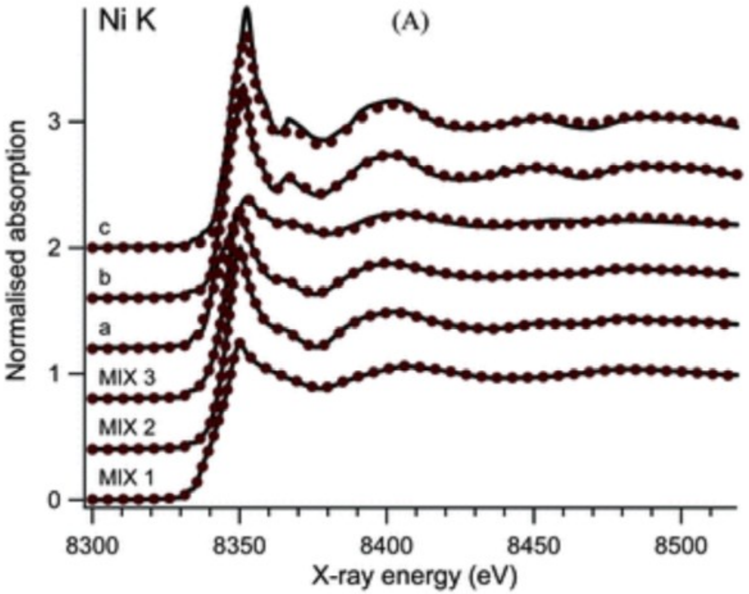
Imagine we have a mixture of different compounds of the same elements

If we have an idea of what could be in the samples… we can determine the composition by linear combination fitting

First you need to collect reference compound spectra…



Now we can find what combination best describes the real samples

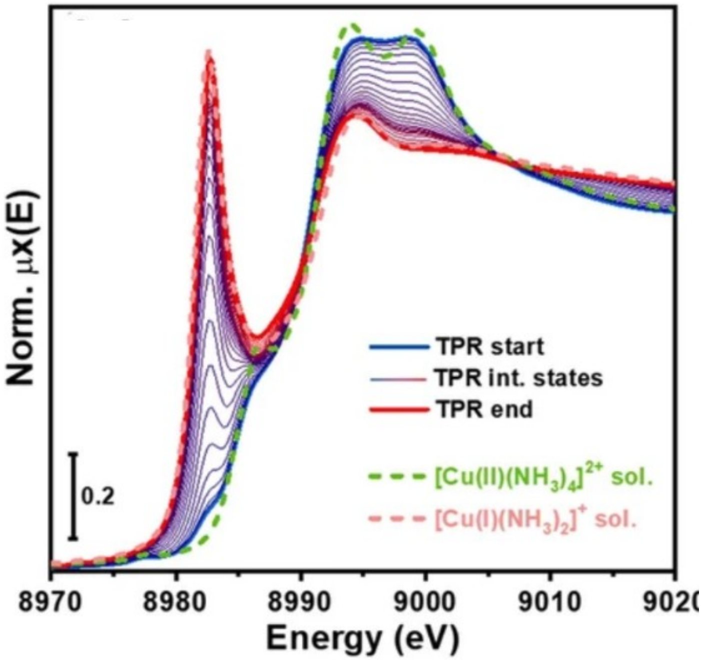


	$NiSO_4$	$Ni(NO_3)_2$	$2NiCO_3{\cdot}3Ni(OH)_2$	NiS	Ni	NiO
Sample 1	36%			64%		
Sample 2	49%	18%		16%		18%
Sample 3	9%	21%	33%	19%	3%	15%

J. Anal. At. Spectrom., 2011,26, 51

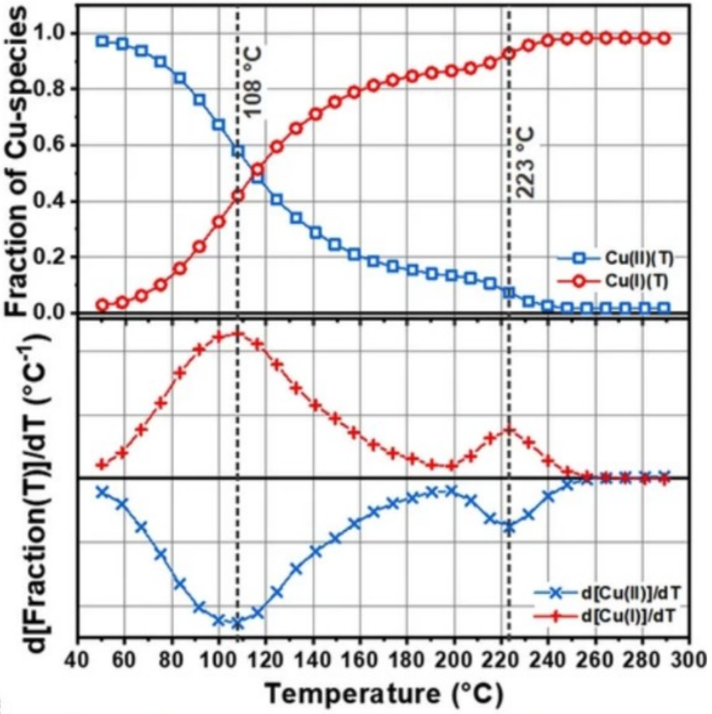
Monitoring oxidation states in *in-situ* experiments

When XANES is used for following time-resolved processes, such as catalyst pretreatment and reactions, the dynamics of oxidation states can be extracted from data series



Evolution of Cu species under temperature programmed reduction

Principal Component Analysis, Multivariate Curve Resolution



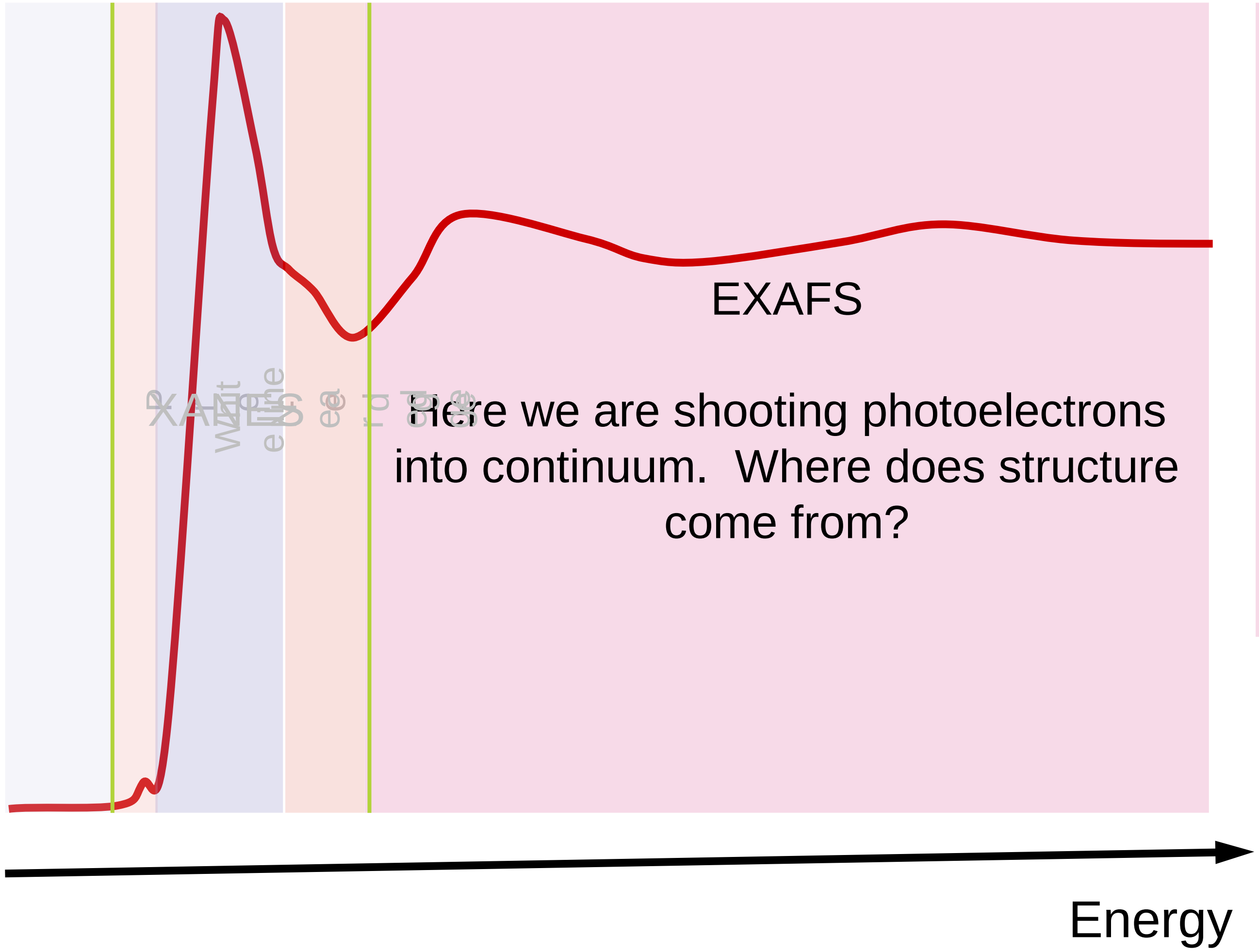
Research on Chemical Intermediates (2021) 47:357–375

XANES - summary

1. Oxidation state
    - The energy position of the absorption edge shifts depending on the oxidation state of the absorbing atom.
    - Higher oxidation states generally result in a higher energy shift due to increased nuclear attraction on core electrons.
2. Electronic structure and coordination environment
    - Pre-edge features give information about electronic transitions and local symmetry.
    - The shape and intensity of the near-edge structure provide insights into the coordination geometry (tetrahedral, octahedral, etc.).
3. Bonding characteristics
    - The fine structure in XANES can reveal hybridization effects and covalency in metal-ligand bonds.
    - The presence of multiple scattering features informs about the local atomic arrangement.
4. Local structural distortions
    - XANES is sensitive to local distortions that may not be apparent in long-range structural techniques like X-ray diffraction.
    - Subtle changes in peak shape and intensity can indicate Jahn-Teller distortions or ligand disorder.
5. Phase identification and chemical speciation
    - Comparing experimental XANES spectra with reference compounds helps in identifying unknown phases.

4. What can we learn from EXAFS

EXAFS region of XAS spectrum



Here we are shooting photoelectrons into continuum. Where does structure come from?

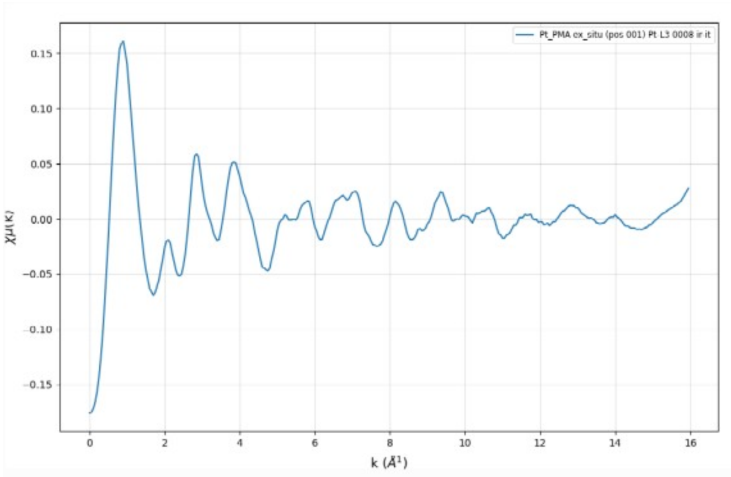
EXAFS – where oscillations occur
What can we learn from it?

- Distance to the neighboring scattering atoms*
- Number of the scattering atoms*
- Identity of the scattering atoms**

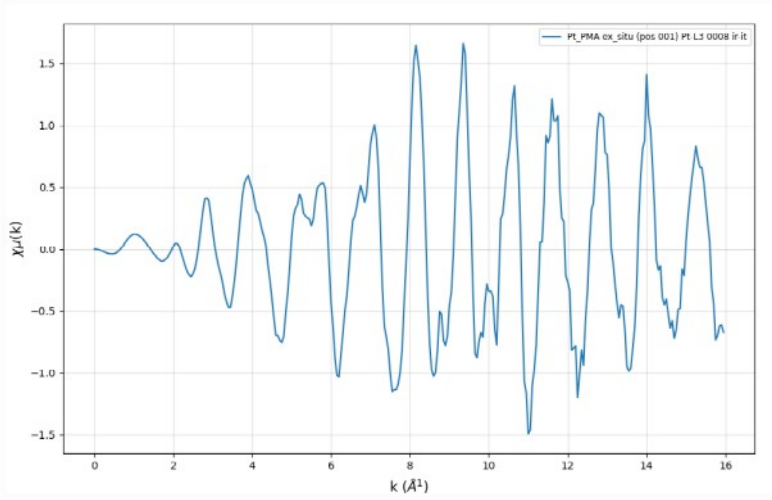
* EXAFS provides an average of the scattering parameters
** Hydrogen atoms are invisible

Data reduction - reminder

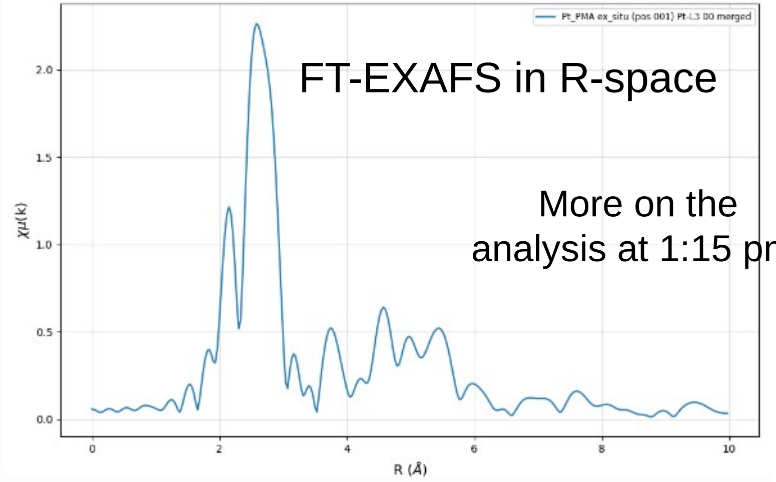
EXAFS in k-space



Applying weighting factor k^n to emphasize high-k oscillations



Fourier Transform
to R-space

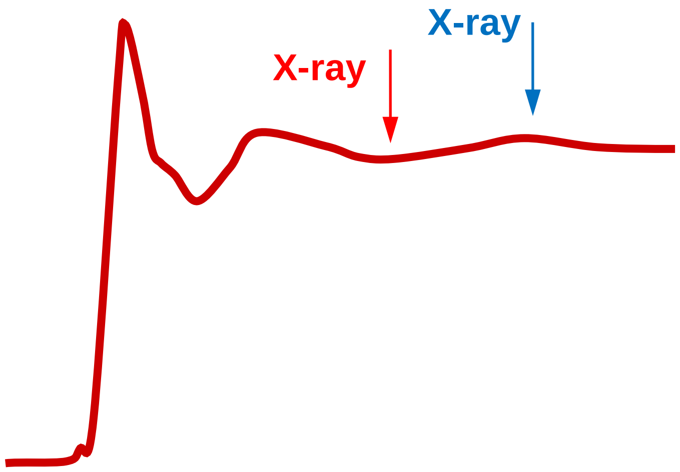


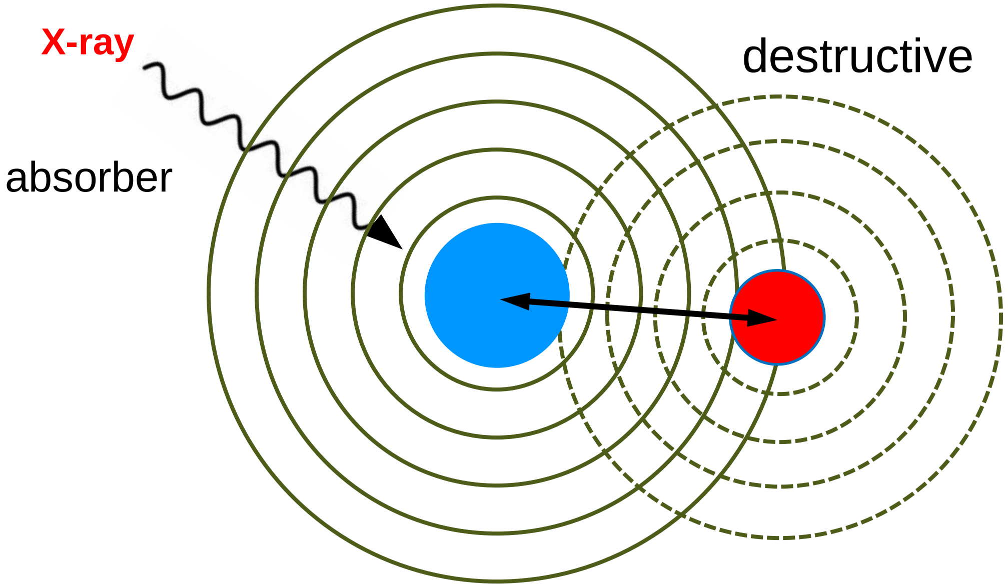
FT-EXAFS in R-space

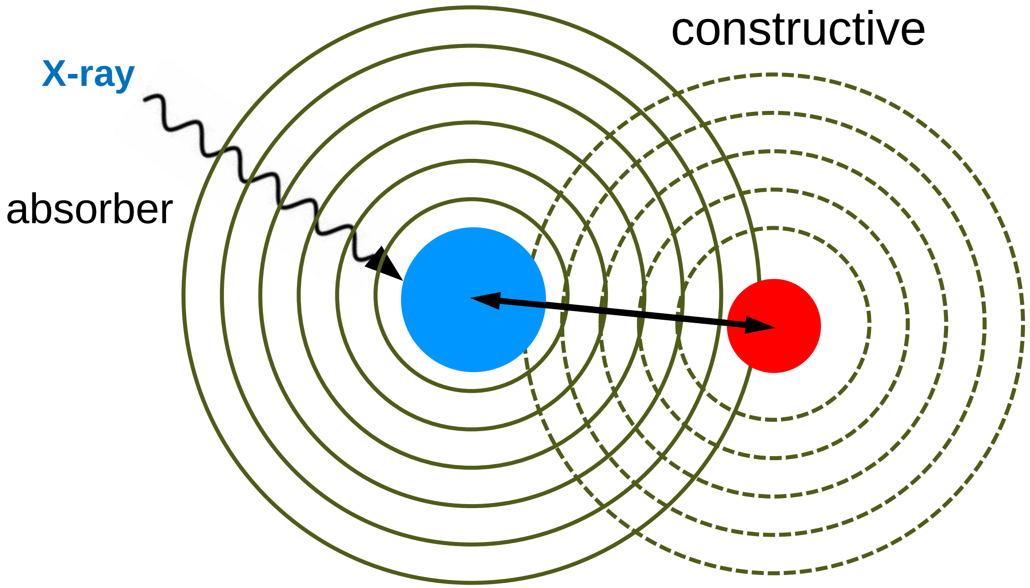
More on the
analysis at 1:15 pm

Making waves…

As we scan the energy in EXAFS range, we change the energy of the photoelectron – and its wavelength. With constant distance between absorber and scattering atoms the interference between the outgoing and backscattering waves will alternate between constructive and destructive

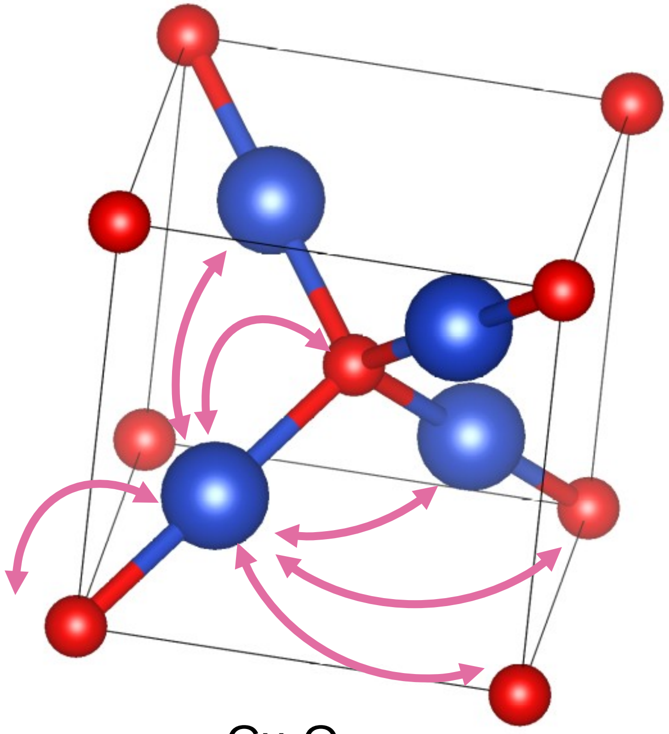






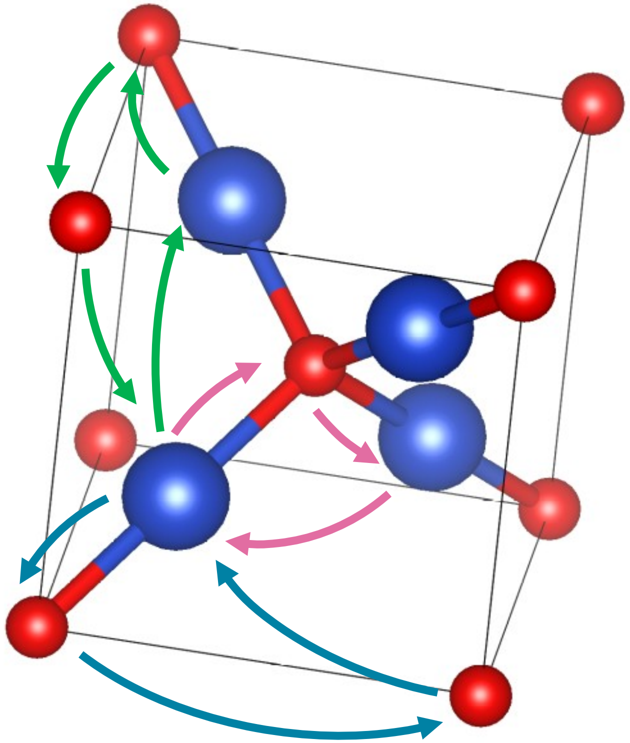
More than one scattering path

All “single” scattering paths are active at the same time



Cu_2O

Scattering between more than two atoms - multiple scattering - plays a significant role



A little EXAFS math

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]\, S_0{}^2$$

N_j	number of scattering atoms of type j
k	photoelectron wavenumber,
$f_j(k)$	scattering amplitude
R_j	distance to scattering atoms
σ_j^2	Debye-Waller factor
$\delta_j(k)$	phase shift introduced by atom j
S_0^2	amplitude reduction factor

…and we sum all the scattering paths together!

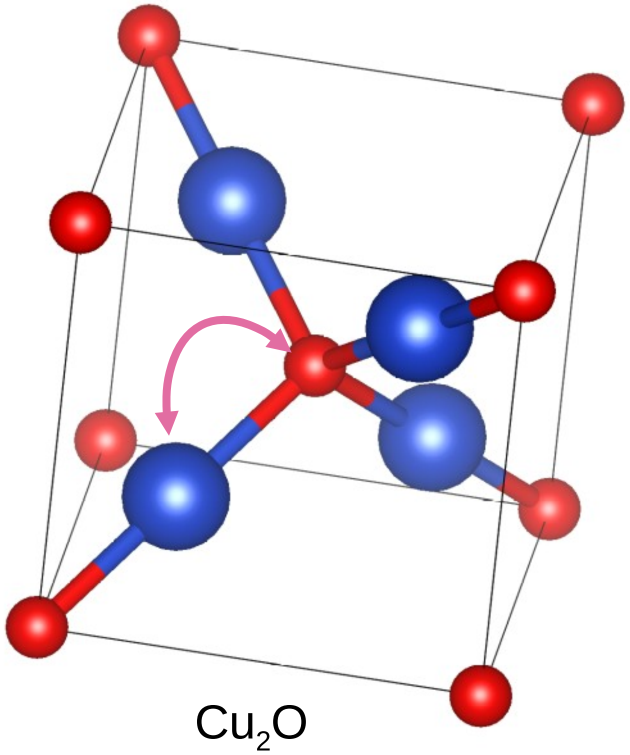
$f_j(k)$ and $\delta_j(k)$ are calculated (in this tutorial, using a code called FEFF*

* To attempt an EXAFS fit you NEED to know something about the structure

We determine N, R and σ_j^2 from the fit**

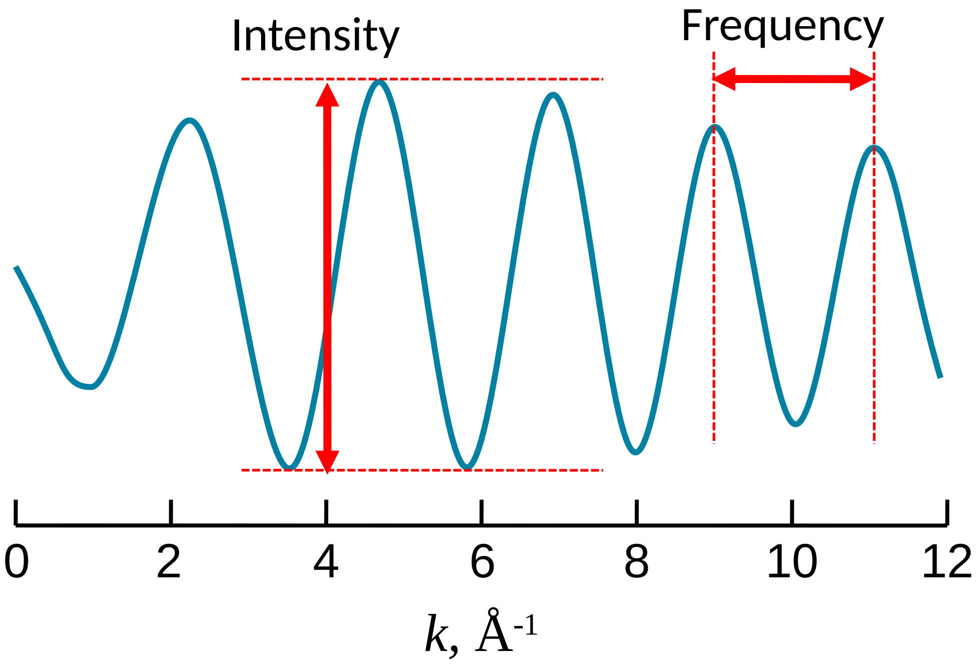
* S_0^2, N and σ_j^2 are correlated

How does a single path look like



To generate a scattering path, we use quantum physics codes (FEFF in our case)

FEFF calculates $f_j(k)$ and $\delta_j(k)$



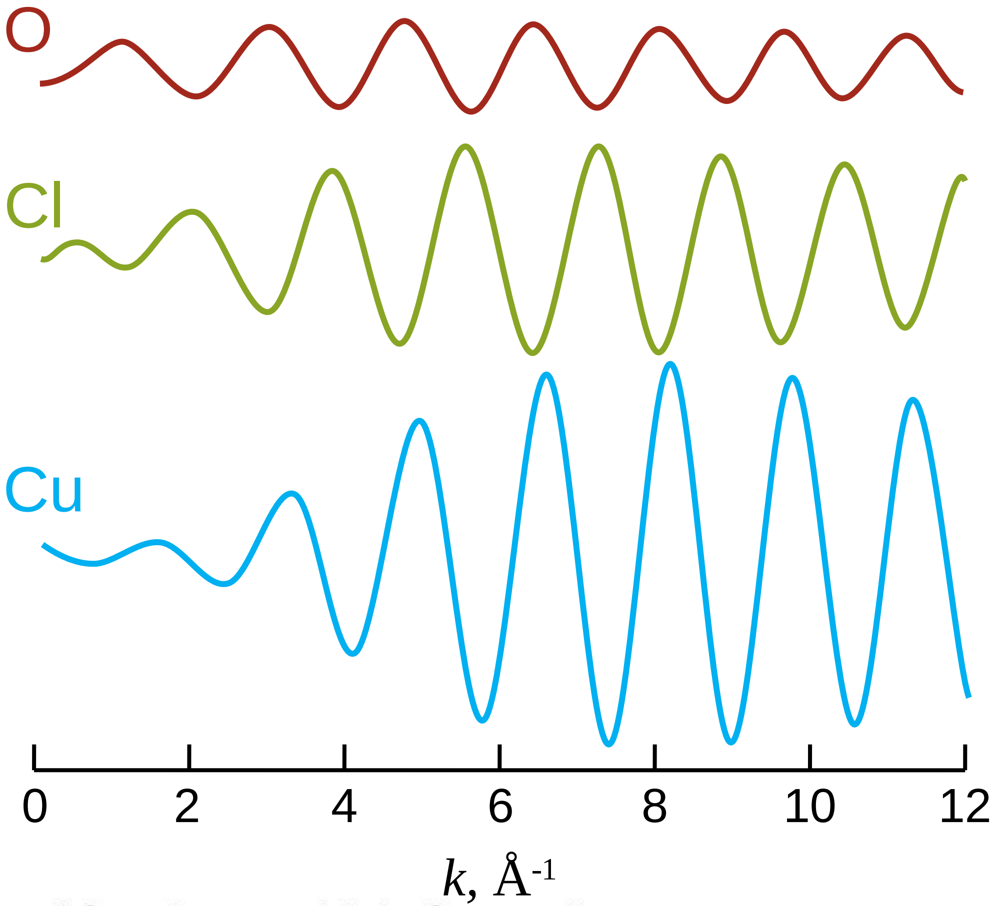
Intensity is defined by
$S_0^2, N_j, f_j(k), \sigma_j^2, R_j$

Frequency is defined by
$R_j, \delta_j(k)$

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

Scattering intensity

$f_j(k)$ which contributes to the intensity is dependent on the identity of the scattering atom. The heavier the atom the more intense the scattering

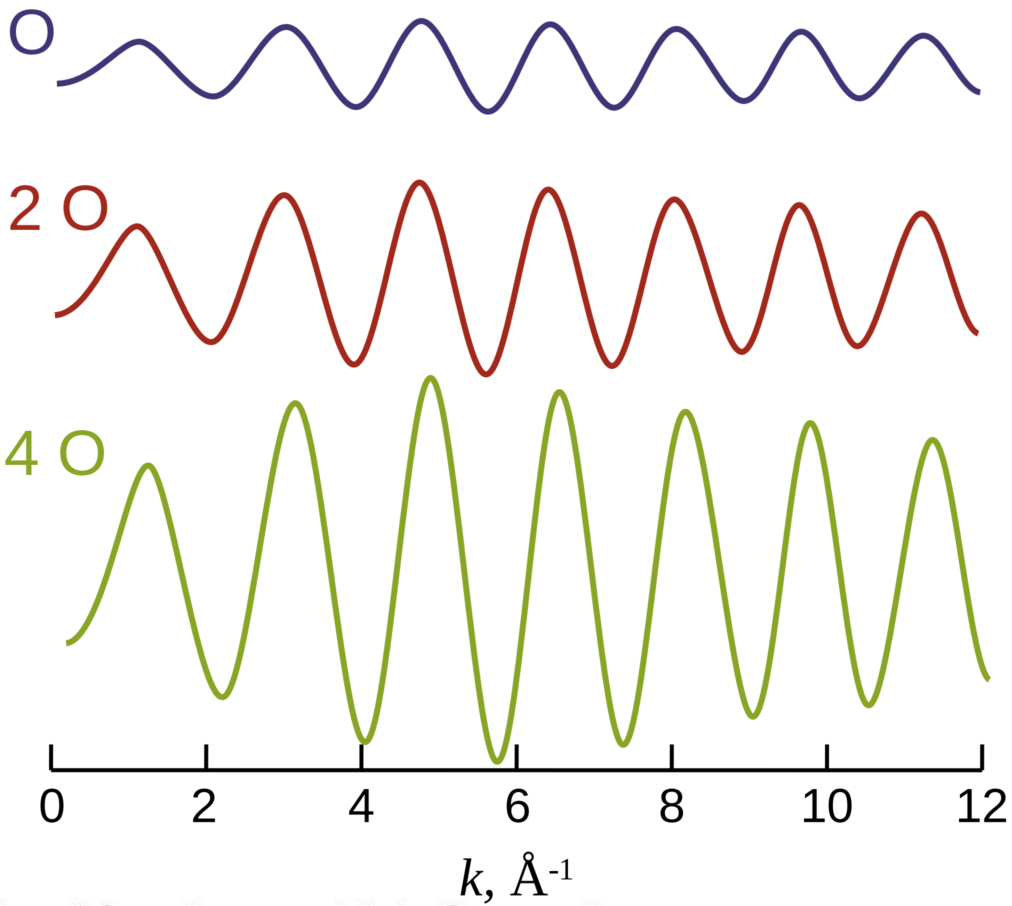


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{k R_j{}^2} \sin[2kR_j + \delta_j(k)]\, S_0{}^2$$

⚠ In this graph, I assumed that the O, Cl and Cu are at the same distance from the absorber which is a gross violation of physics

Number of scatterers

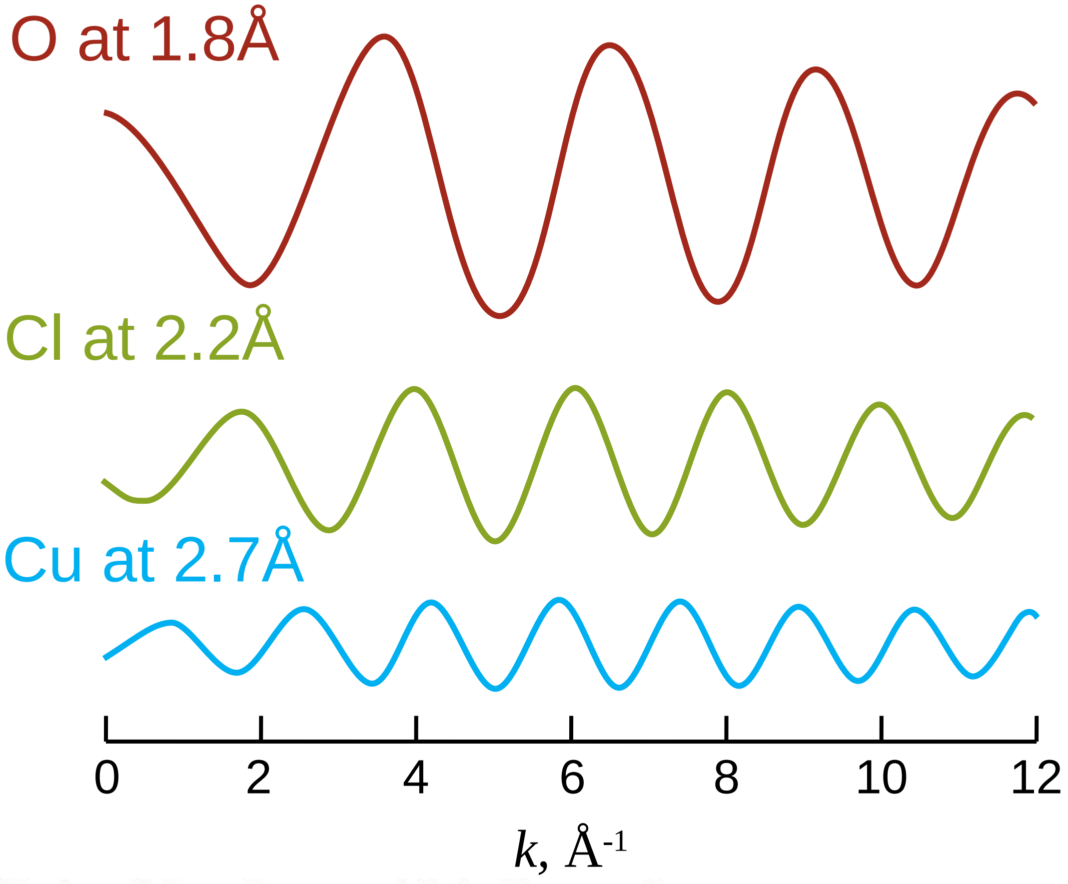
Scattering intensity scales with the number of scattering atoms

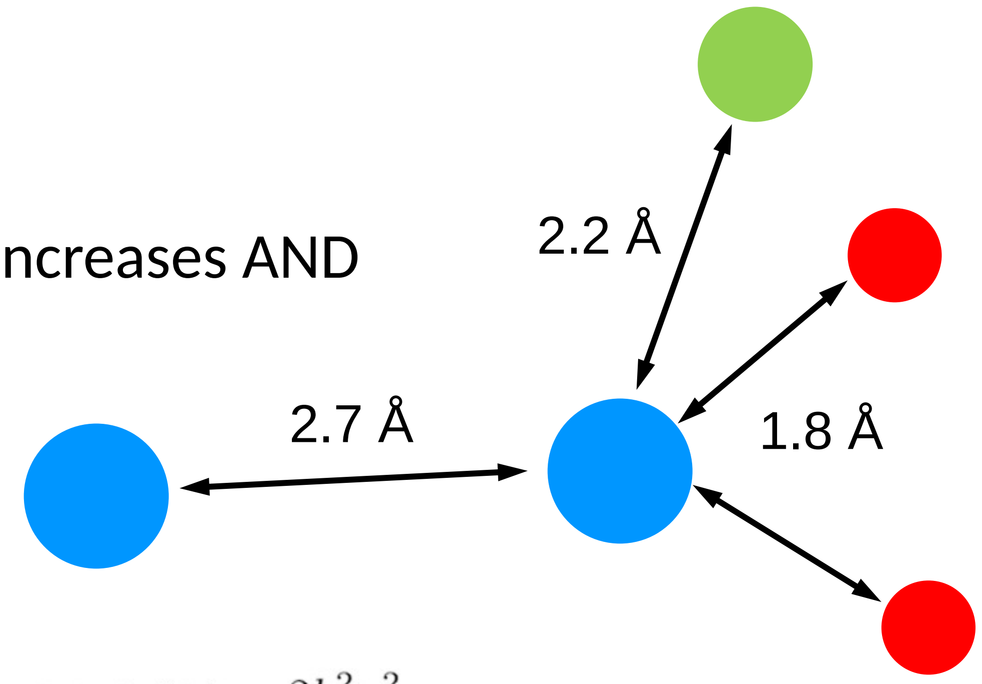


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^{\,2}} \sin[2kR_j + \delta_j(k)]\, S_0^{\,2}$$

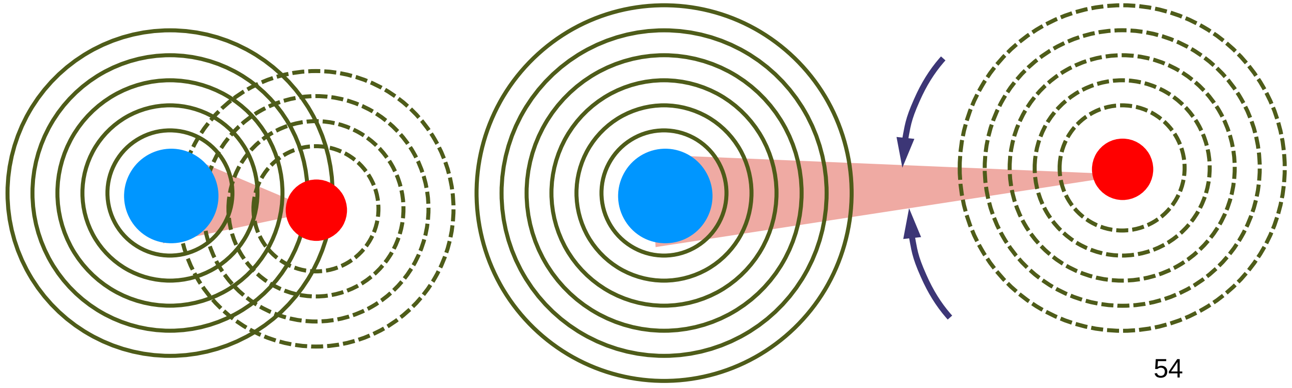
Distance to scatterers

With scatterer farther away, the oscillation frequency increases AND intensity decreases



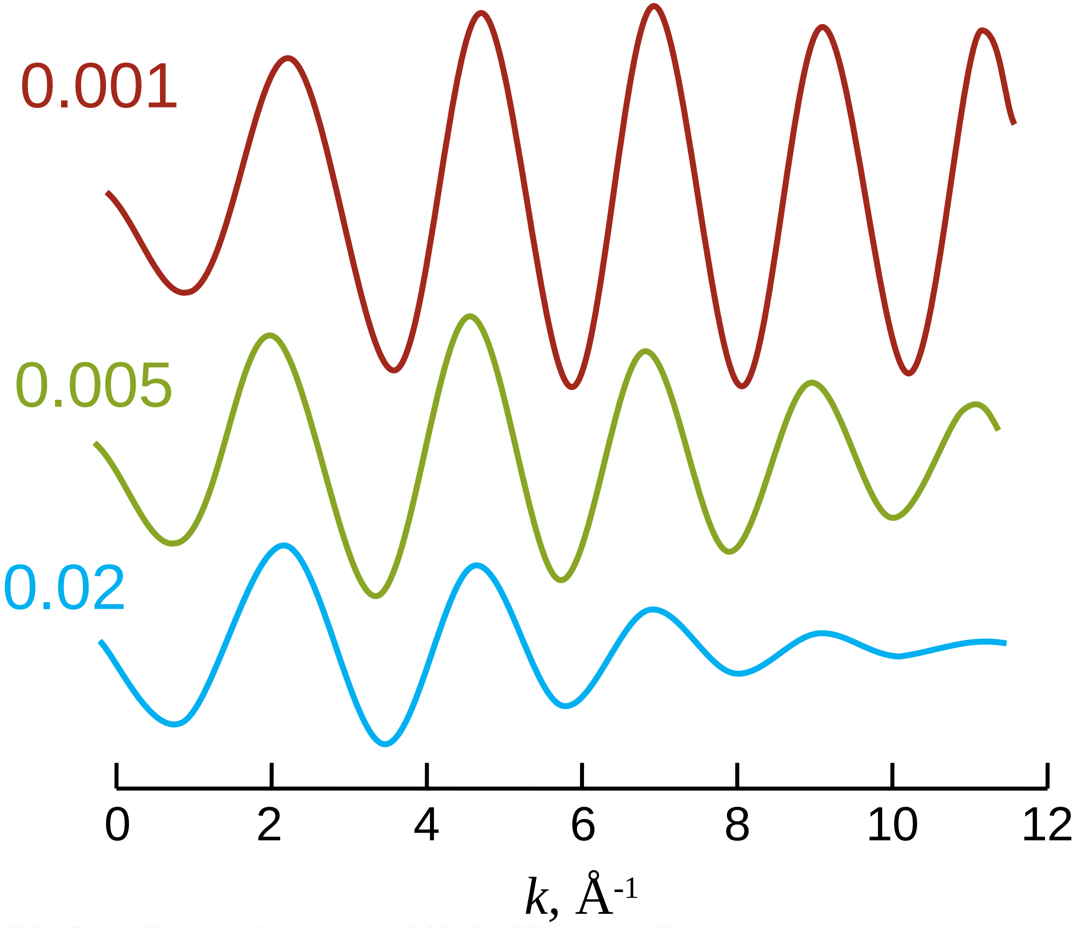


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{k R_j{}^2} \sin[2kR_j + \delta_j(k)]\, S_0{}^2$$



Debye-Waller factor

The Debye Waller factor is the measure of disorder. The disorder can have many origins - thermal, structural etc*

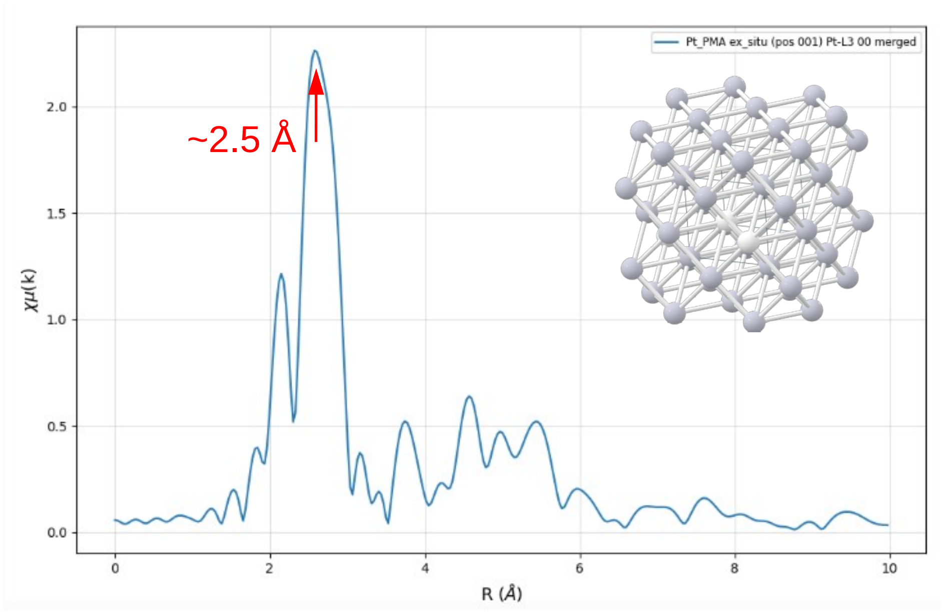


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2 \sigma_j^2}}{k {R_j}^2} \sin[2kR_j + \delta_j(k)]\, {S_0}^2$$

⚠ By reducing disorder, you can obtain better information about the shells further away from the atom. One approach is to cool the sample down.

Phase shift

You might notice that the peaks in FT-EXAFS are not exactly at the real interatomic distances



This is FT-EXAFS of metallic platinum,
the real Pt distance is 2.79 Å

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]\, S_0{}^2$$

$\delta_j(k)$ is an element specific phase shift that causes the distance in FT-EXAFS to underestimate the real one by up to 0.5 Å.

And finally … S_0^2

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{k{R_j}^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

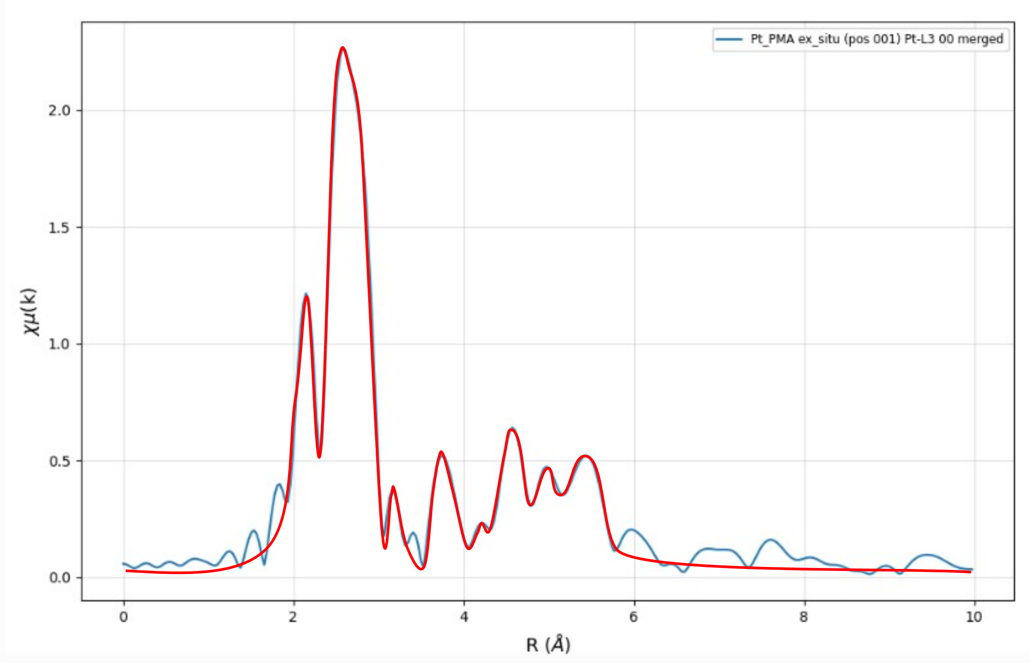
This is a factor that helps us reconcile between the experimental data and theory
We need to find it using the spectrum of a very well-defined structure, such as metal foil

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{k{R_j}^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

N_j and S_0^2 are correlated. If your S_0^2 is off, one of the most important parameters – coordination numbers – will be skewed

EXAFS fitting philosophy

EXAFS fitting is not a power trip. Listen what it tells you and improve



1. Obtain an experimental spectrum
2. Based on the knowledge of the samples, explore structural models with similar atomic arrangements*
3. Calculate scattering paths for the model
4. Select relevant single and multiple paths
5. Fit the free parameters (*R*, *N* etc)
6. Refine model
7. Repeat from step 3

* To attempt an EXAFS fit you NEED to know something about the sample

Oftentimes, the simplest model is the right one

When trying to understand your material consider XANES and EXAFS together

Science

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HOME > SCIENCE > VOL. 385, NO. 6706 > DEFECTIVE TIO$_X$ OVERLAYERS CATALYZE PROPANE DEHYDROGENATION PROMOTED BY BASE METALS

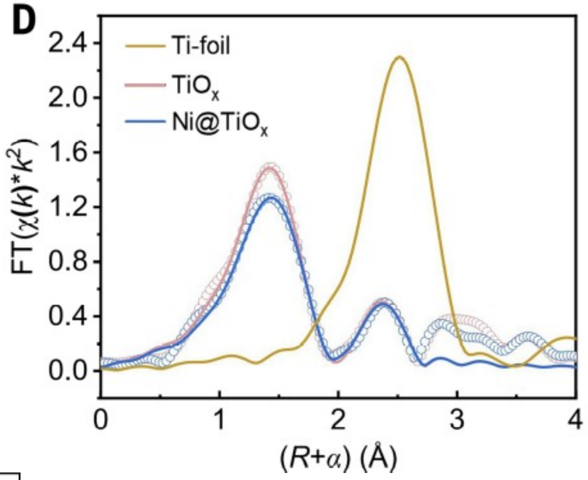
RESEARCH ARTICLE | CATALYSIS

Defective TiO$_x$ overlayers catalyze propane dehydrogenation promoted by base metals

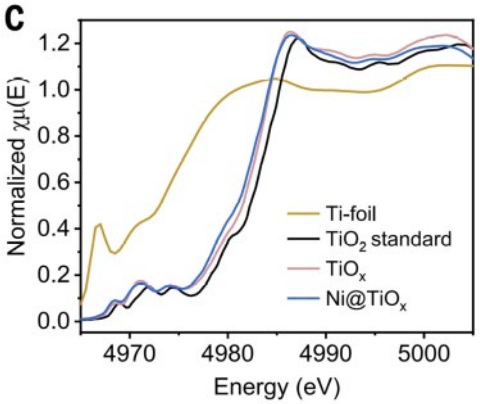
SAI CHEN, YIYI XU, XIN CHANG, YUE PAN, [...], AND JINLONG GONG +6 authors Authors Info & Affiliations

SCIENCE • 18 Jul 2024 • Vol 385, Issue 6706 • pp. 295-300 • DOI: 10.1126/science.adp7379

13,370 32 CHECK ACCESS

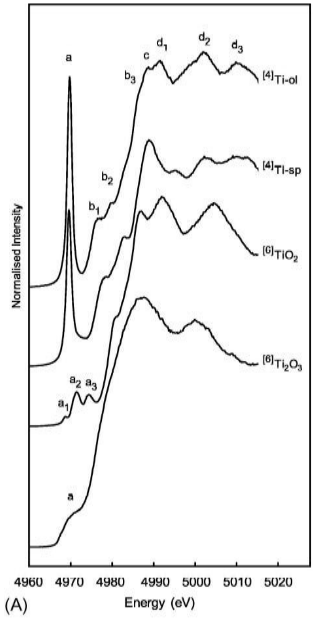


From the EXAFS fitting the authors claim that 4-coordinated Ti sites are critical for the catalyst activity

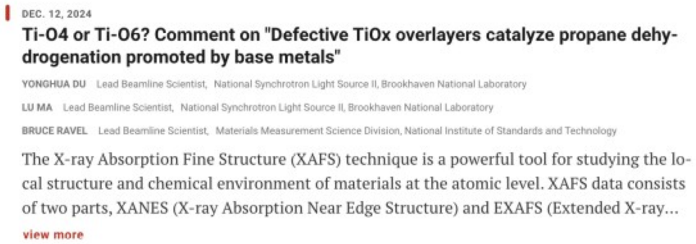


However, the XANES doesn't show the characteristic pre-edge feature of tetragonal Ti

- see my cartoon from the few slides ago



Authors of this paper had clearly mistaken disorder for a NEW and EXCITING species. Don't make this mistake - we will be writing letters to the editor



DEC. 12, 2024

Ti-O4 or Ti-O6? Comment on "Defective TiOx overlayers catalyze propane dehydrogenation promoted by base metals"

YONGHUA DU Lead Beamline Scientist, National Synchrotron Light Source II, Brookhaven National Laboratory

LU MA Lead Beamline Scientist, National Synchrotron Light Source II, Brookhaven National Laboratory

BRUCE RAVEL Lead Beamline Scientist, Materials Measurement Science Division, National Institute of Standards and Technology

The X-ray Absorption Fine Structure (XAFS) technique is a powerful tool for studying the local structure and chemical environment of materials at the atomic level. XAFS data consists of two parts, XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray...

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