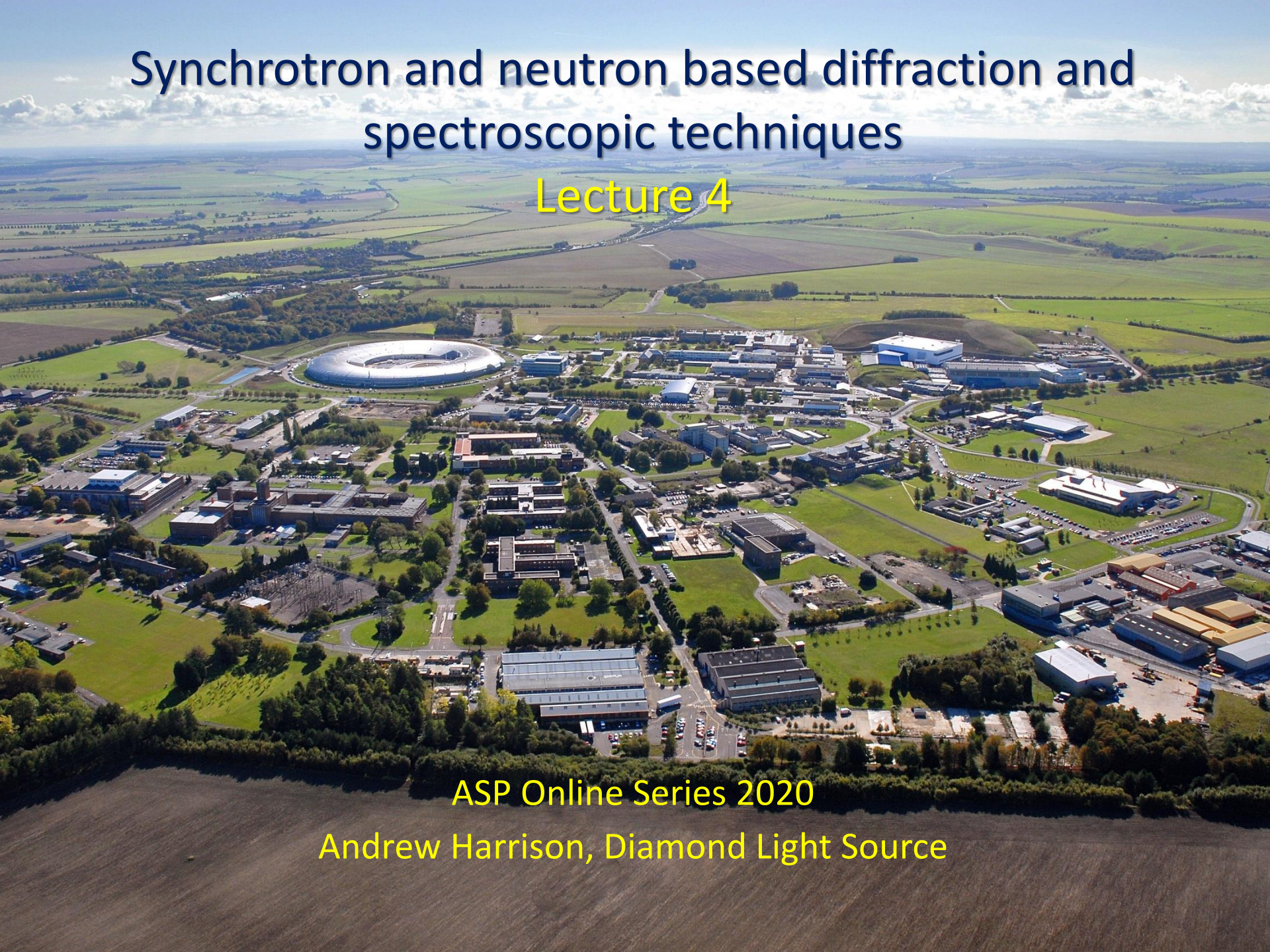
Synchrotron and neutron based diffraction and spectroscopic techniques

Lecture 4



ASP Online Series 2020

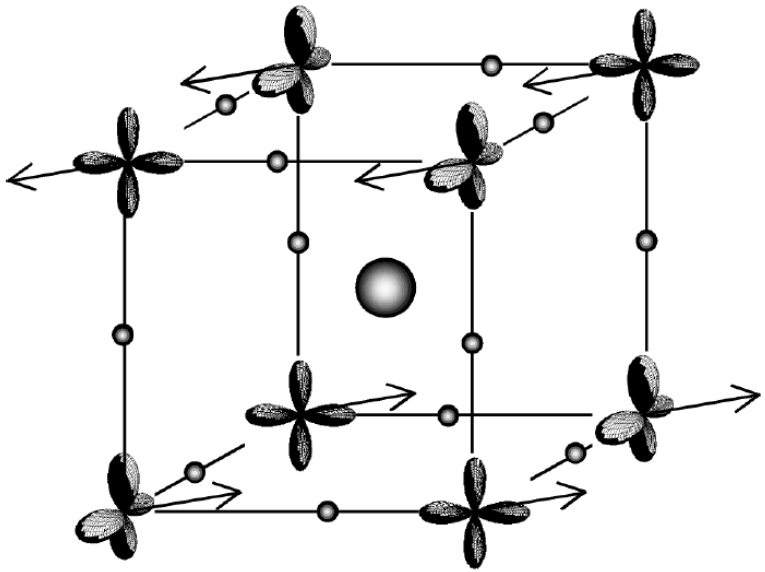
Andrew Harrison, Diamond Light Source

Revealing orbital and magnetic ordering by RXS

- Certain TM ions are Jahn-Teller active and display distinct anisotropy of local bonding in complexes and extended crystalline solids
- These distortions can have a profound effect on the electronic and magnetic character often interlinked e.g. in magnetoresistant materials whose conductivity can be controlled by the application of a magnetic field, and very likely involved in high-T_c superconductivity
- E.g. (though not conducting) Cu^{2+} in $KCuF_3$ has a $3d^9$ configuration in which the hole is in the d_{x2-y2} orbital so there is elongation along the z-axis (ABO doubly occupied). The ion also has an unpaired electron spin which gives rise to a spin-only moment.

Revealing orbital and magnetic ordering by RXS

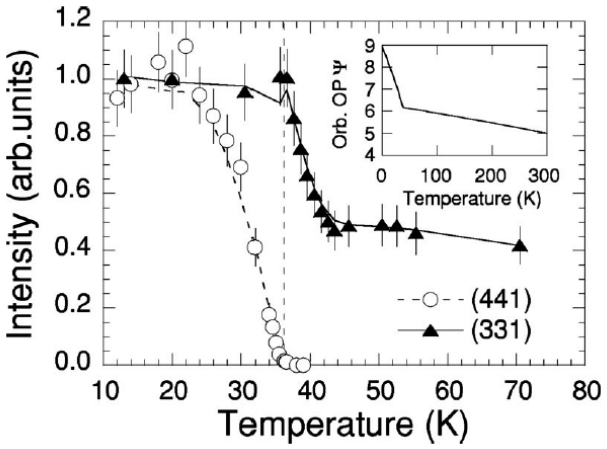
- The structure of $KCuF_3$ is based on cubic perovskite but closer inspection at low temperature reveals more detail.
  - JT-distorted Cu^{2+} centres are ordered in the crystal < 800K such that the local axis of elongation alternates along any cubic edge
  - The magnetic moments interact weakly with their neighbours, freezing into an ordered array on cooling to 38 K



Revealing orbital and magnetic ordering by RXS

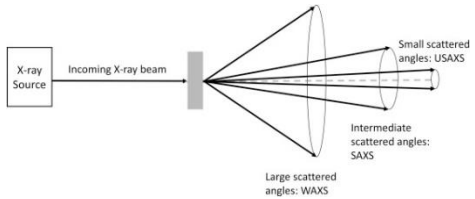
- As the energy is tuned below the Cu K edge two types of resonant transition might be brought into play.
  - 1s$\rightarrow$ 3d is dipole forbidden but probes the spin states and orbital occupancy directly
  - 1s $\rightarrow$ 4p is dipole allowed but only probes the spin states and orbital occupancy indirectly through (weak) 3d-4p mixing
- Both factors contribute and reveal the orbital and magnetic order through new diffraction peaks that are forbidden in the simple cubic structure

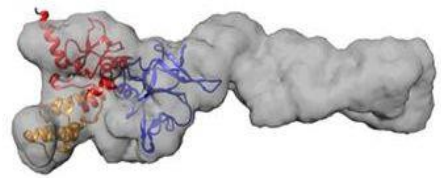
Measurement of intensity of reflections characteristic of orbital order (331) and magnetic order (441) at 8.922 keV, 1s $\rightarrow$ 4p
Caciuffo et al, Phys. Rev. B65 (2002) 174425



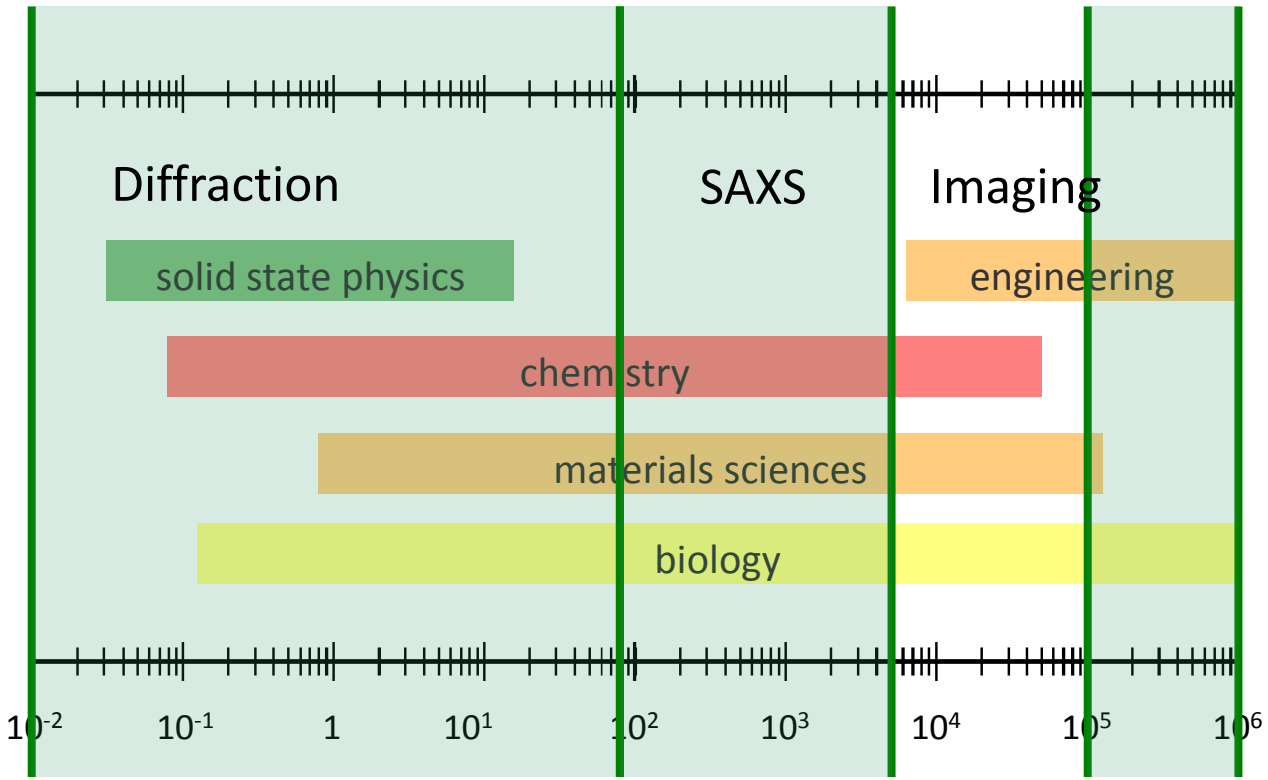
Other forms of diffraction

- Small-angle scattering (SAXS) to probe the size and shape of large objects (e.g. macromolecules in solution), material pores e.g. (bone) and defects (e.g. inhomogeneities in engineering materials)



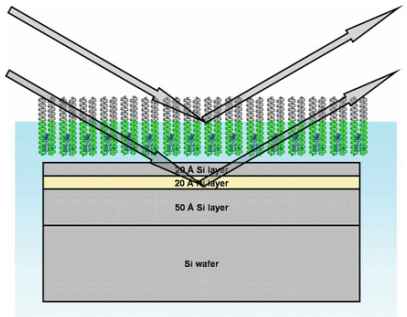


$$n\lambda = 2d \sin\theta$$

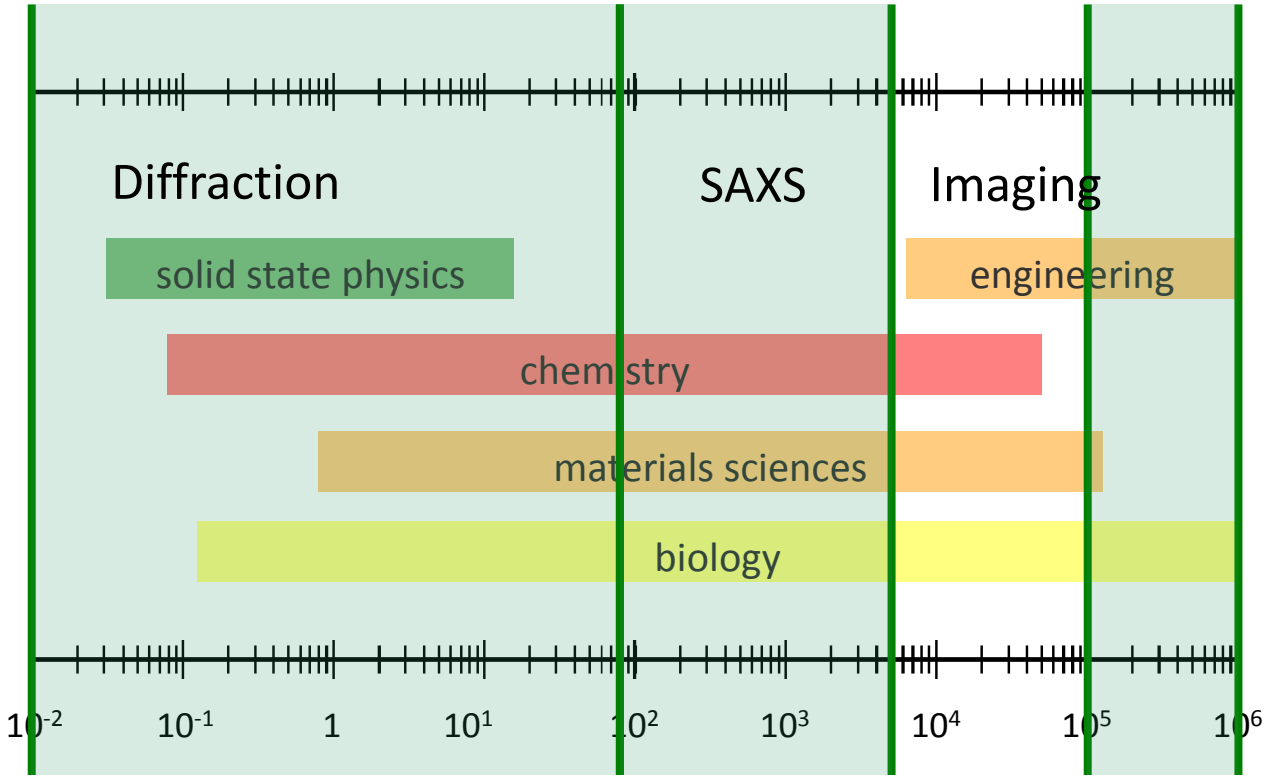


Other forms of diffraction

- Reflectometry to study surfaces, interfaces and depth profiles



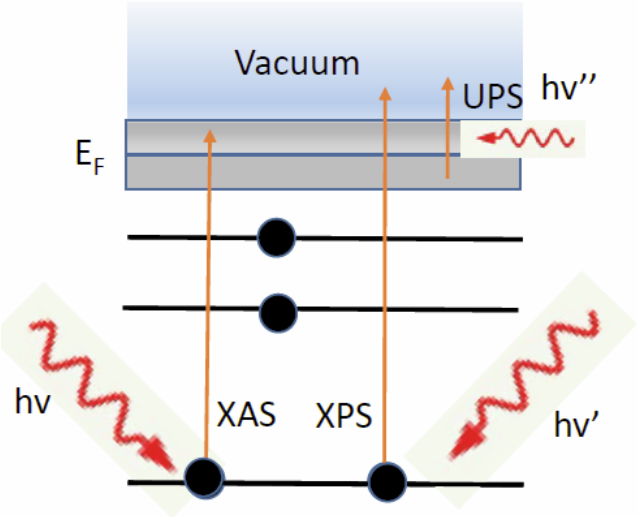
$$n\lambda = 2d \sin\theta$$

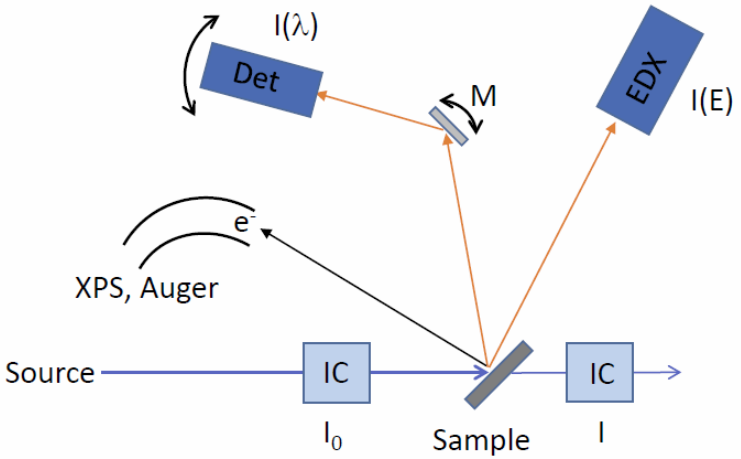


Spectroscopy

Spectroscopy

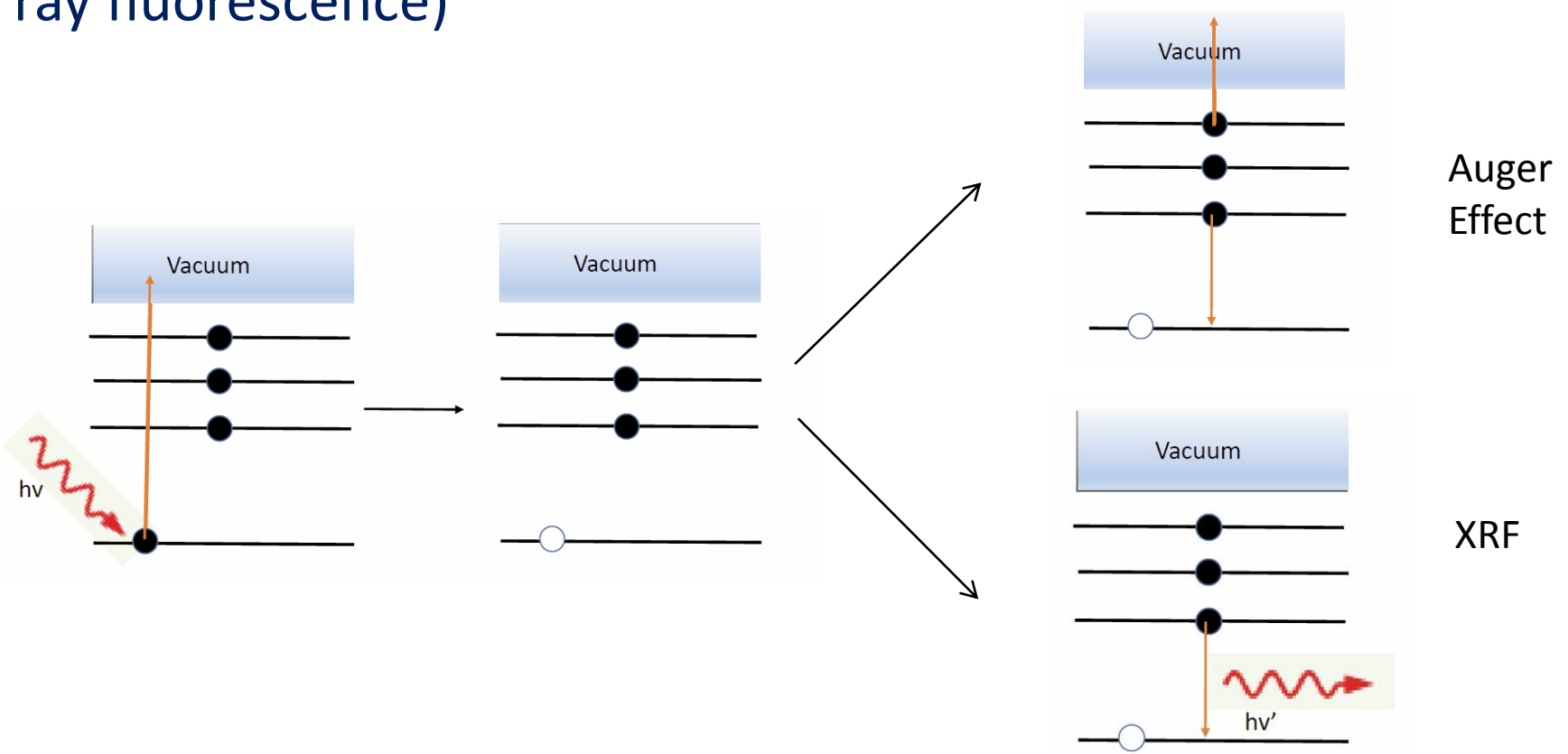
- Both X-ray Absorption and Fluorescence spectroscopies - XAS and XRF - are used as very sensitive probes of chemical character, with spatial resolutions of the order 1 μm or less
- Energy of photoelectrons may also be analysed as chemical probe – of valence (UPS) and more tightly bound (XPS) electrons
- General experimental set-up





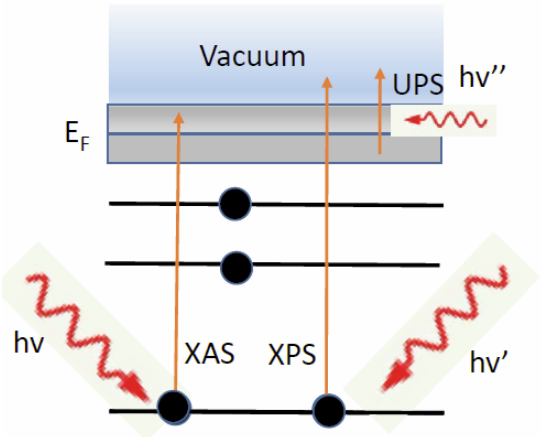
Relaxation after photoionisation ?

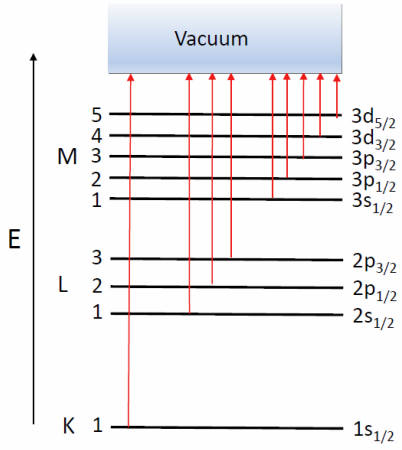
- Photoionisation leaves a hole behind which is electronically unstable and is rapidly filled by relaxation of higher-energy electrons and the additional energy is carried away either by a secondary photoionisation event (Auger effect) or photons (X-ray fluorescence)

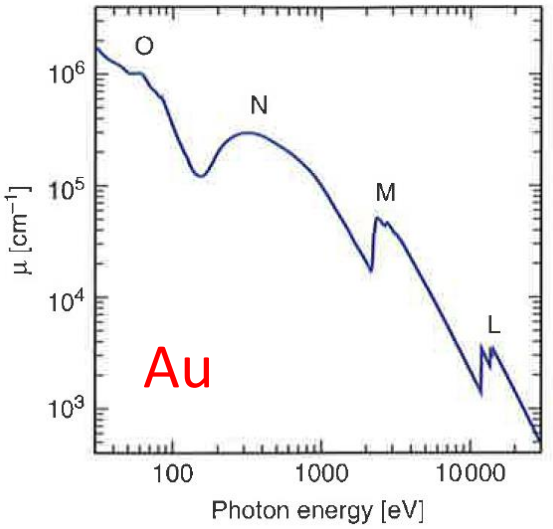


XAS

- Recall that X-ray absorption edges are observed for photoionisation from bound states with successively higher values of n, l and j. Edges get broader with n (more states with higher l, e.g. below Au)
- For atoms bound in a molecule or extended solid the transitions from core levels are similar to those in atoms, while transitions from valence orbitals can change markedly – particularly for metals and semiconductors where there is generally a continuum of states (band) with empty levels below the photoionisation threshold

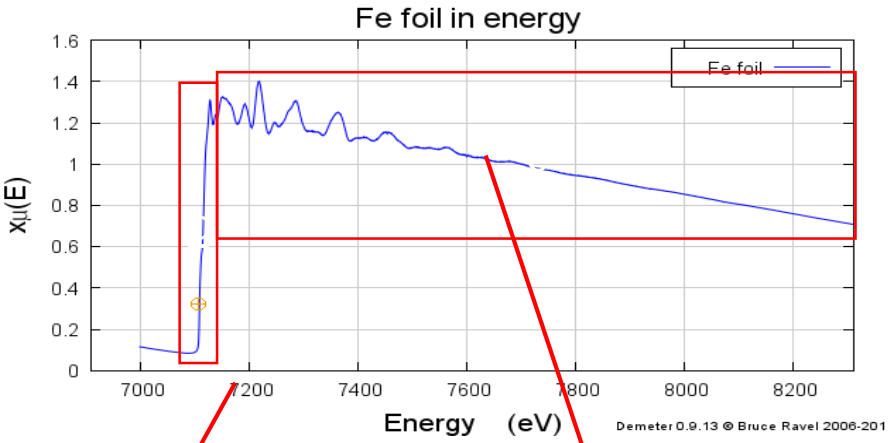


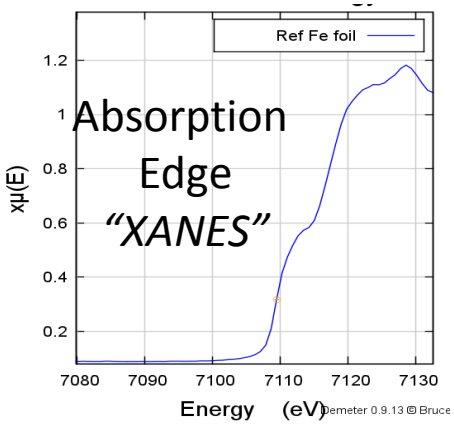


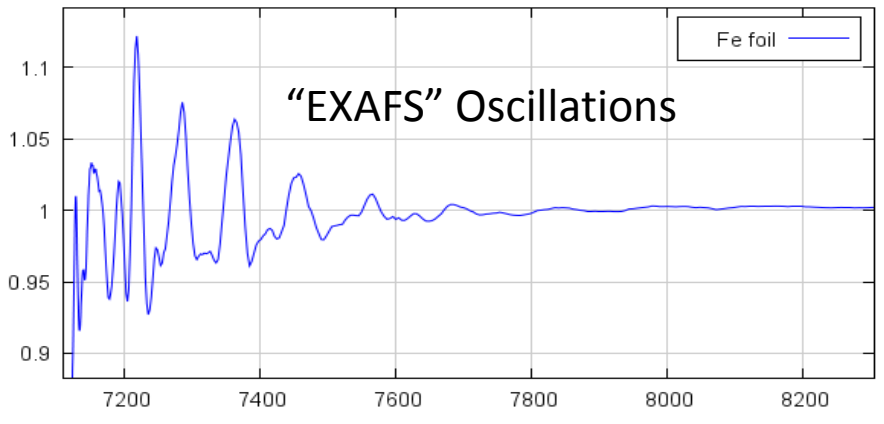


XAS and fine structure

- Closer study of an absorption edge reveals fine structure
  - XANES – X-Ray Absorption Near Edge Spectroscopy
  - EXAFS – Extended X-Ray fine structure – 50-100's eV above edge







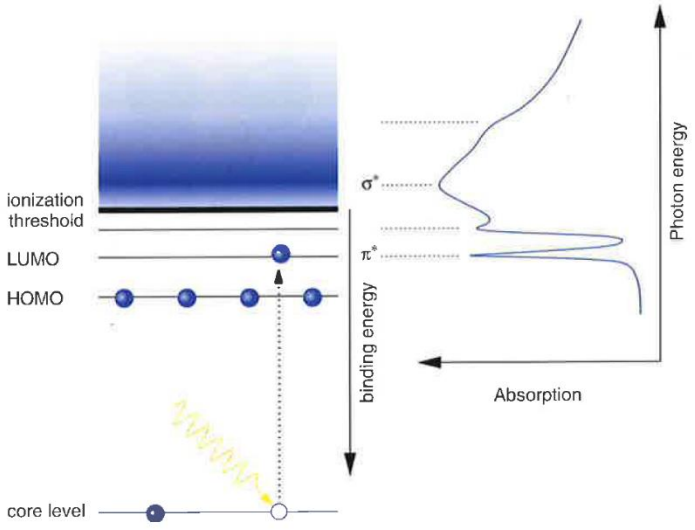
XANES– X-Ray Absorption Near Edge Spectroscopy

- Closer study of an absorption edge reveals fine structure corresponding to excitation of electrons to empty bound states and to low-lying states in the unbound continuum
- Intensity of transition i $\rightarrow$ f given by Fermi's Golden Rule:

$$P_{if} \sim |\langle f|H'|i\rangle|^2 \rho$$

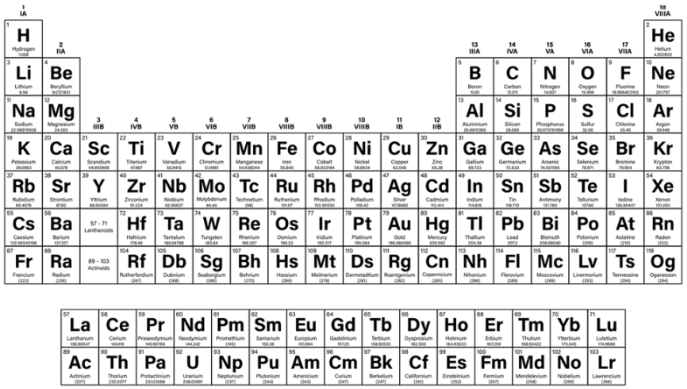
ρ is density of states for f, and H' is the operator representing the effect of the light – dipole nature – so $\Delta l = \pm 1$ when f is a bound state

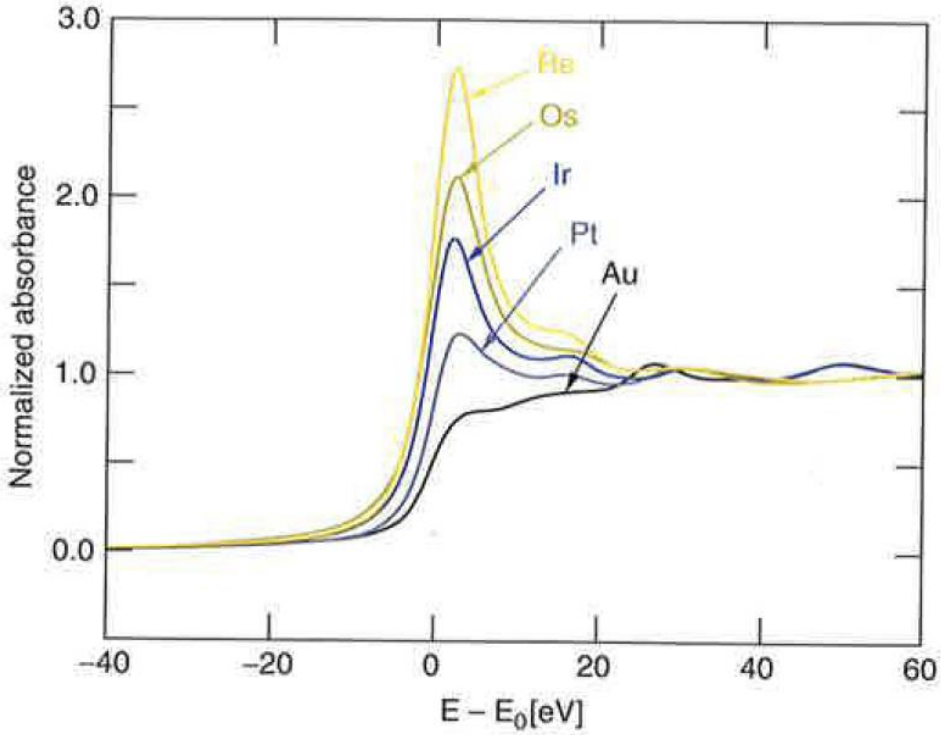
In practice this often breaks down because s-p, p-d mixing is allowed, particularly when the atom at the centre of the study is non-centro-symmetric so can occur for isolated atoms and also molecules



XANES– X-Ray Absorption Near Edge Spectroscopy

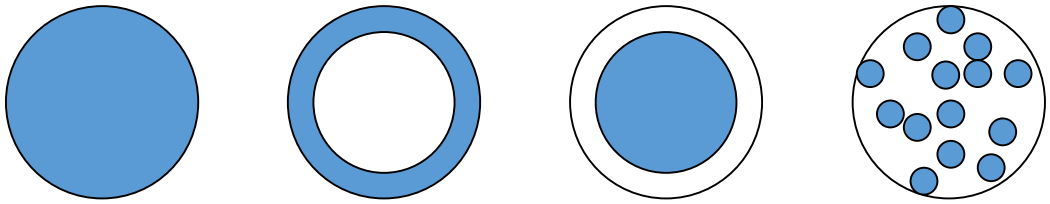
- Dependence of P_{if} illustrated by XAS for series of elements from Re to Au - [Xe] $4f^{14}5d^{5}6s^{2}$ to [Xe]$4f^{14}5d^{10}$ $6s^{1}$ - changes as 5d fills up
- All of these features may be modelled and then the model refined to optimise the goodness of fit to the data to determine the local binding and thus the local structure around the absorbing centre





Mapping chemistry with μ-XANES

- Effectiveness of heterogenous catalysts depends *inter alia* on physical state/distribution and nature of active centres
- E.g. commercial BASF catalyst for hydrogenation of nitrobenzene to aniline using colloidal Pt-containing catalyst (0.8wt %) supported on carbon particles with Mo-containing promoter (0.3wt %)



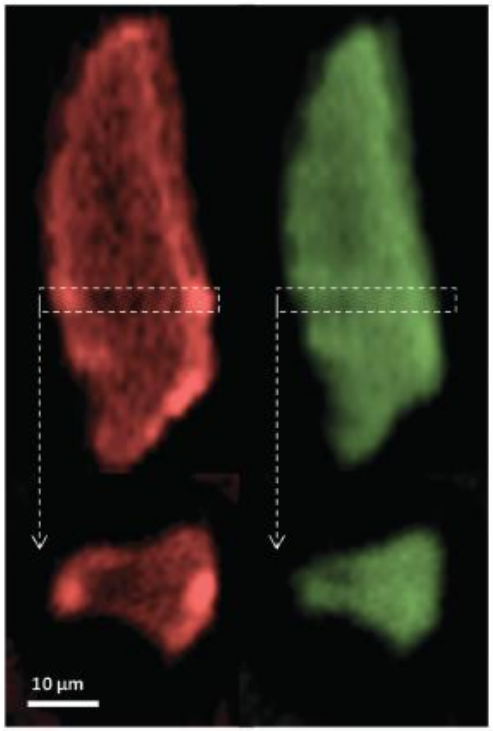
Even distribution

Egg-shell distribution

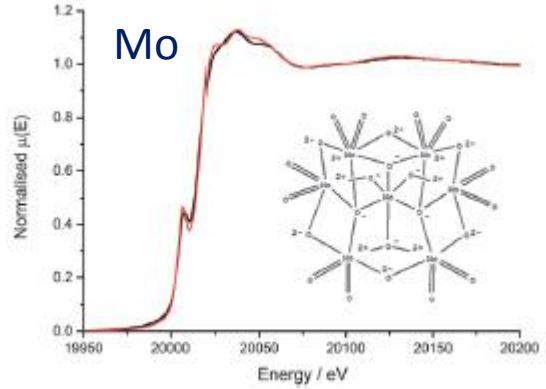
Egg-yolk distribution

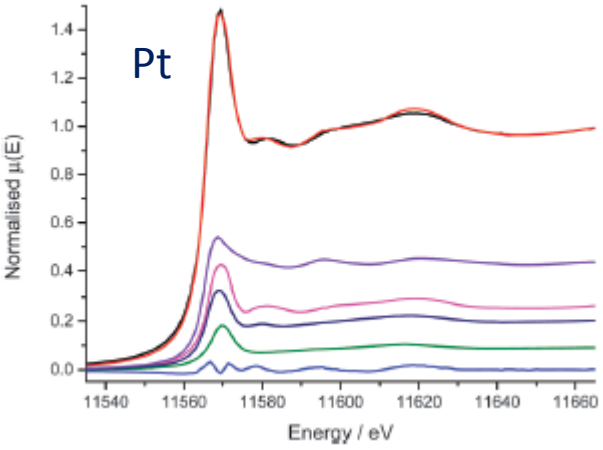
Uneven distribution

Crafting catalysts

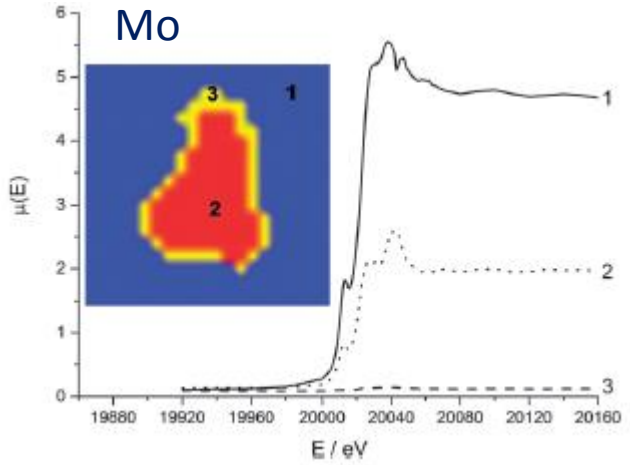


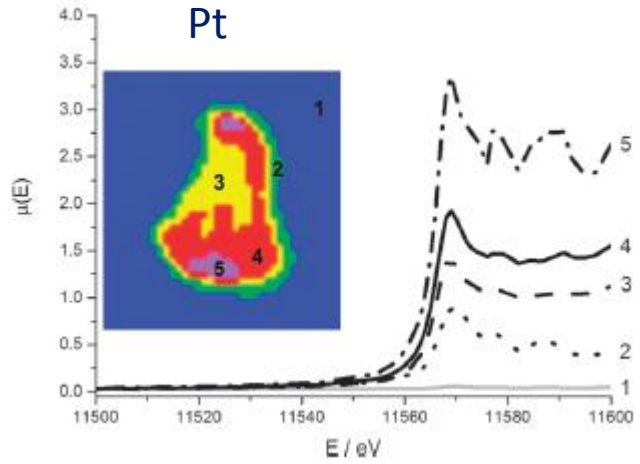
XRF tomography –
Mo (green) and Pt (red)





Species identification



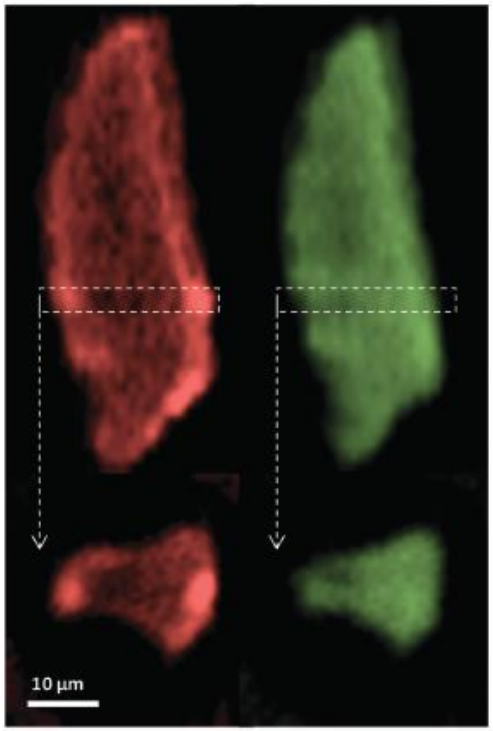


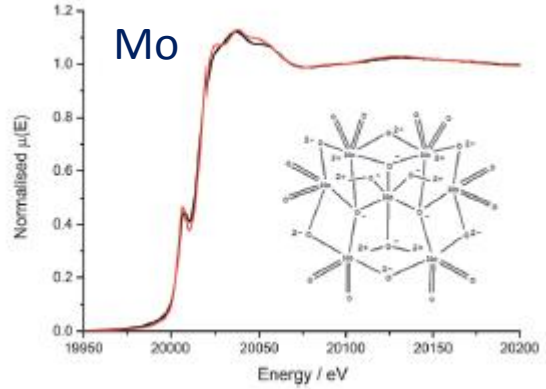
Species mapping

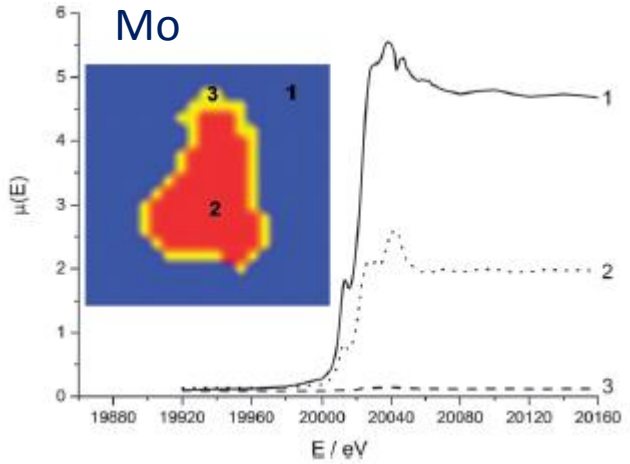
Price et al, PCCP, Phys. Chem. Chem. Phys., 17 (2015) 521

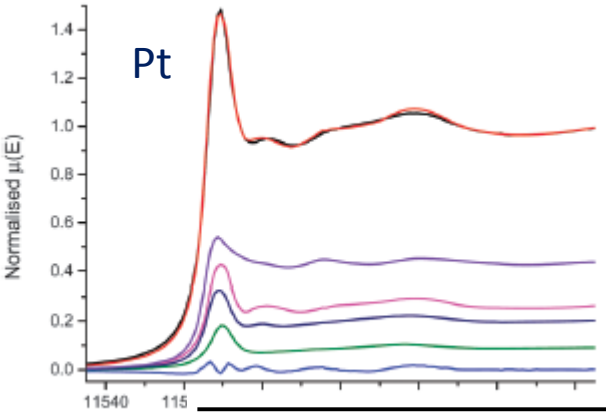
Now *in operando* (XRF, XRD) Price, et al., *Angewandte Chemie International Edition* **2015**, *54*, 9886-9889

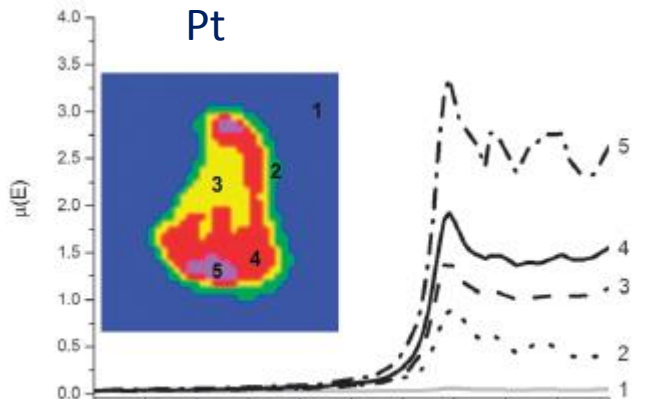
Crafting catalysts











XRF tomography –
Mo (green) and Pt (red)

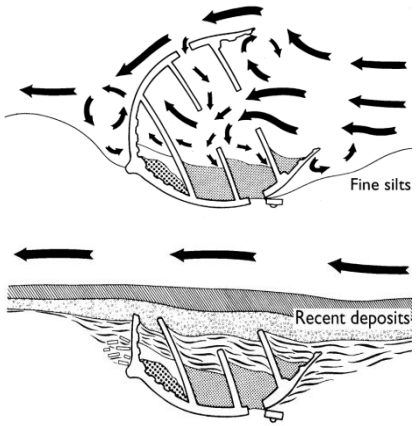
Spec

Component	Weight/%	R_f	Reduced χ^2
Pt/C nano	44 (2)	0.0007	0.0001
PtO_2	9 (5)		
$PtCl_2$	21 (3)		
K_2PtCl_6	26 (3)		

Price et al, PCCP, Phys. Chem. Che

Now *in operando* (XRF, XRD) Price, et

Preserving the past with X-ray spectroscopy



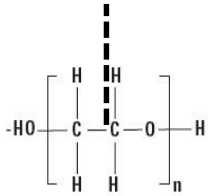
Sank 1545

Hull conservation

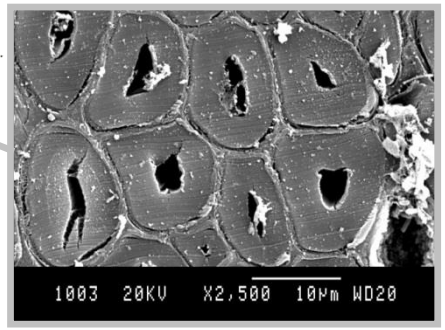
Raised 1982

1982 – 1994: Cold water

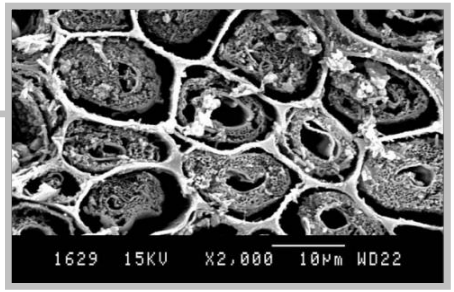
1994 – 2013: PEG



1994 – 2006

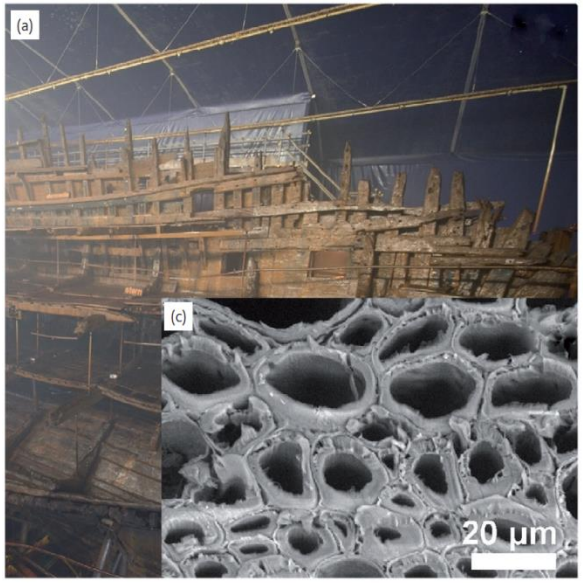


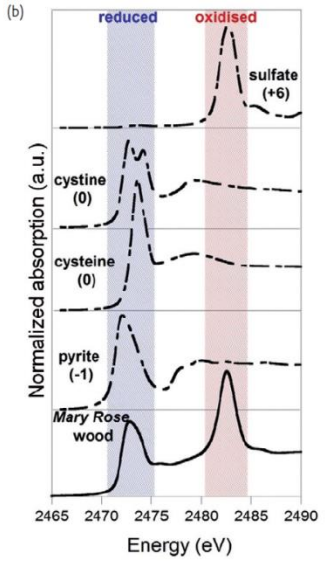
2006-2013

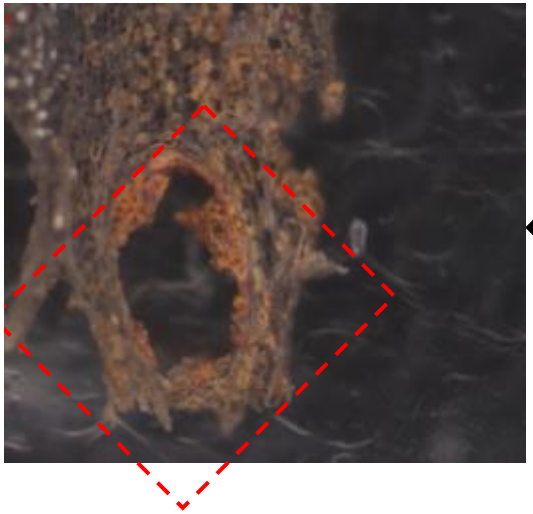


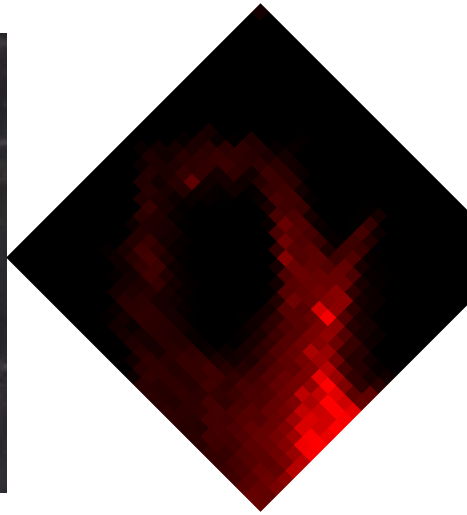
The sulfur problem

Sulfate salts



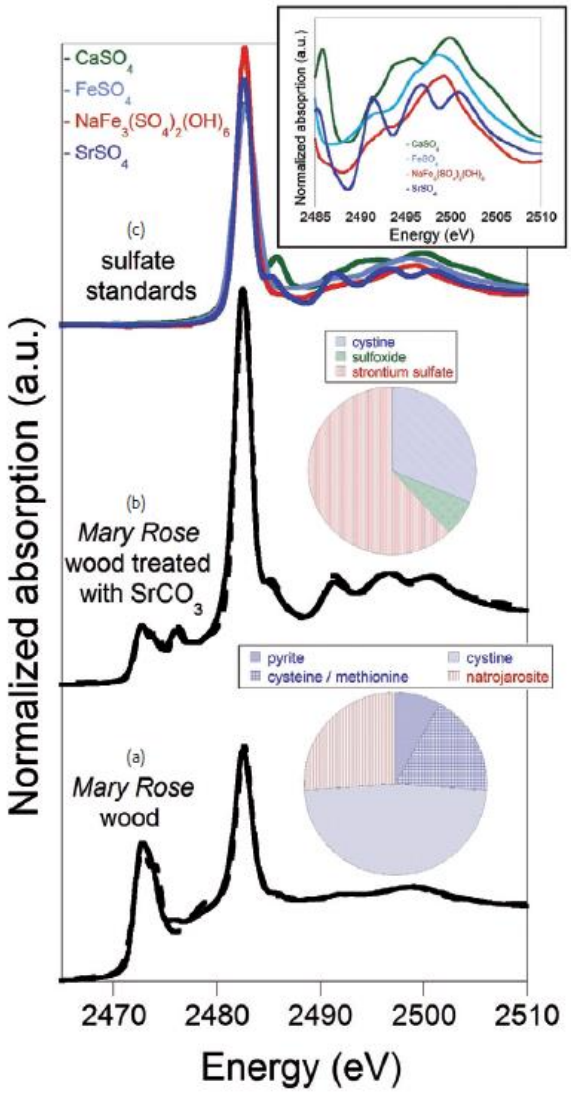






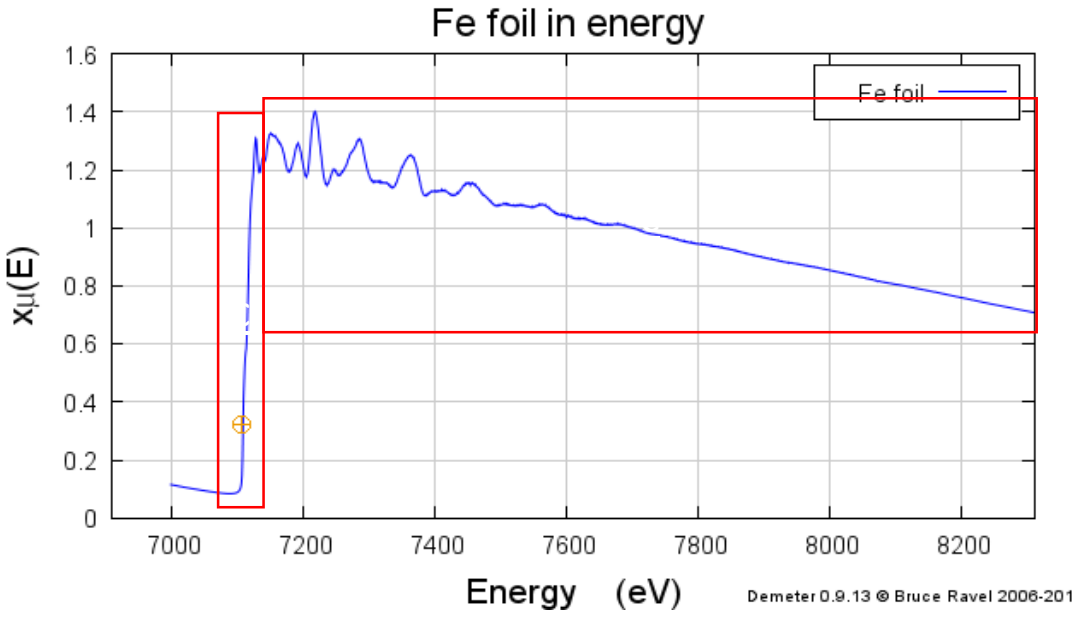
e.g. Eleanor J. Schofield, Ritimukta Sarangi, Apurva Mehtab. Mark Jones, Fred J. W. Mosselmans, and Alan V. Chadwick,* Materials Today, 14 (2011) 354

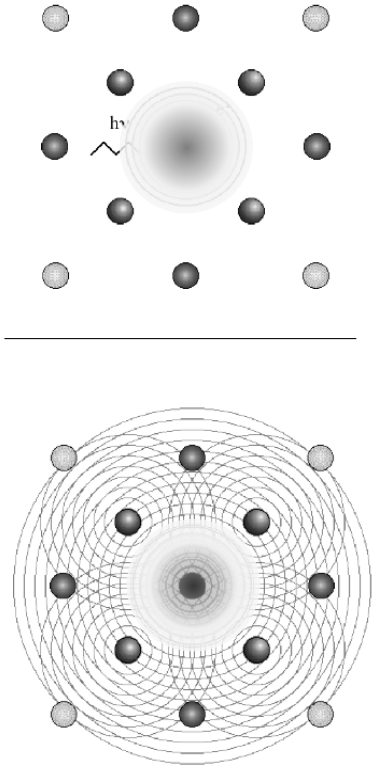
The sulfur problem - solved



EXAFS

- Extended X-Ray Absorption Fine Structure – arises from the interference between the wave of a photoelectron and the waves backscattered from neighbouring atoms, giving constructive and destructive interference – so we need to know the wavelength λ_e of these waves (destructive interference when d is odd multiple $\lambda_e/2$)





EXAFS

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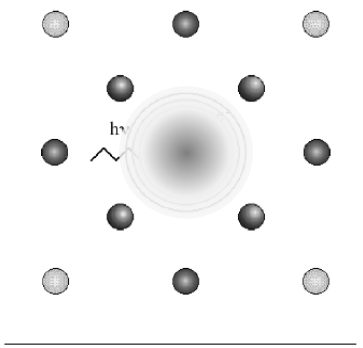
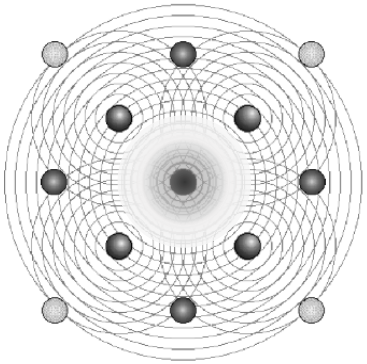
By de Broglie: $p = h/\lambda_e$ and $E_e = \frac{p^2}{2m_e} = \frac{h^2}{2\lambda_e^2 m_e}$



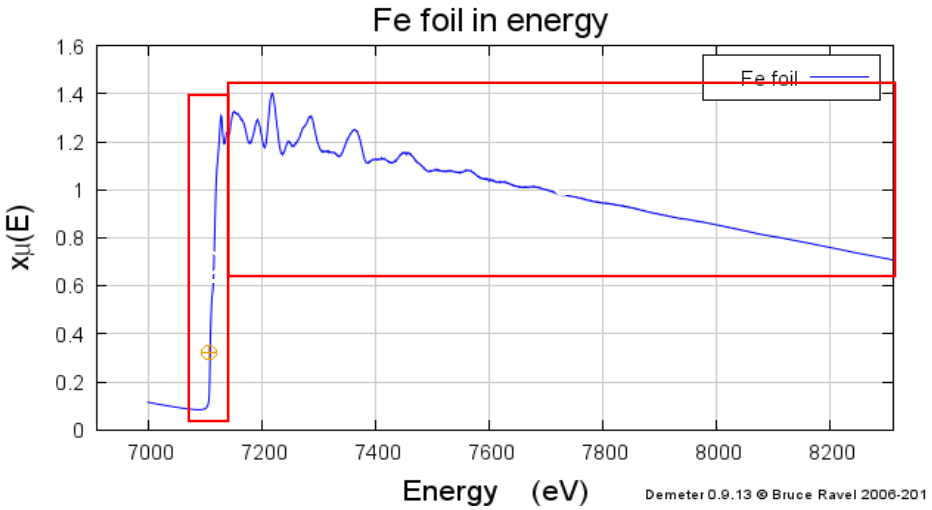
Also $E_e = h\nu - E_B$ where E_B is electron binding energy and $h\nu$ is incident photon energy

Therefore $\lambda_e = h[2m_e(h\nu - E_B)]^{\frac{-1}{2}}$

So the condition for minima in the EXAFS spectra arises when $2d = nh[2m_e(h\nu - E_B)]^{\frac{-1}{2}}$ with n = 1,3,5



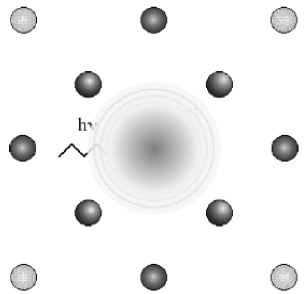
So $h\nu = \frac{1}{2m_e}\left(\frac{nh}{2d}\right)^2 + E_B$ with n = 1,3,5



By de Broglie: $p = h/\lambda_e$ and $E_e = \frac{p^2}{2m_e} = \frac{h^2}{2\lambda_e^2 m_e}$

Also $E_e = h\nu - E_B$ where E_B is electron binding energy

Therefore $\lambda_e = h[2m_e(h\nu - E_B)]^{\frac{-1}{2}}$



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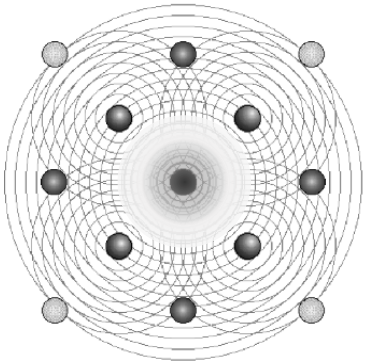

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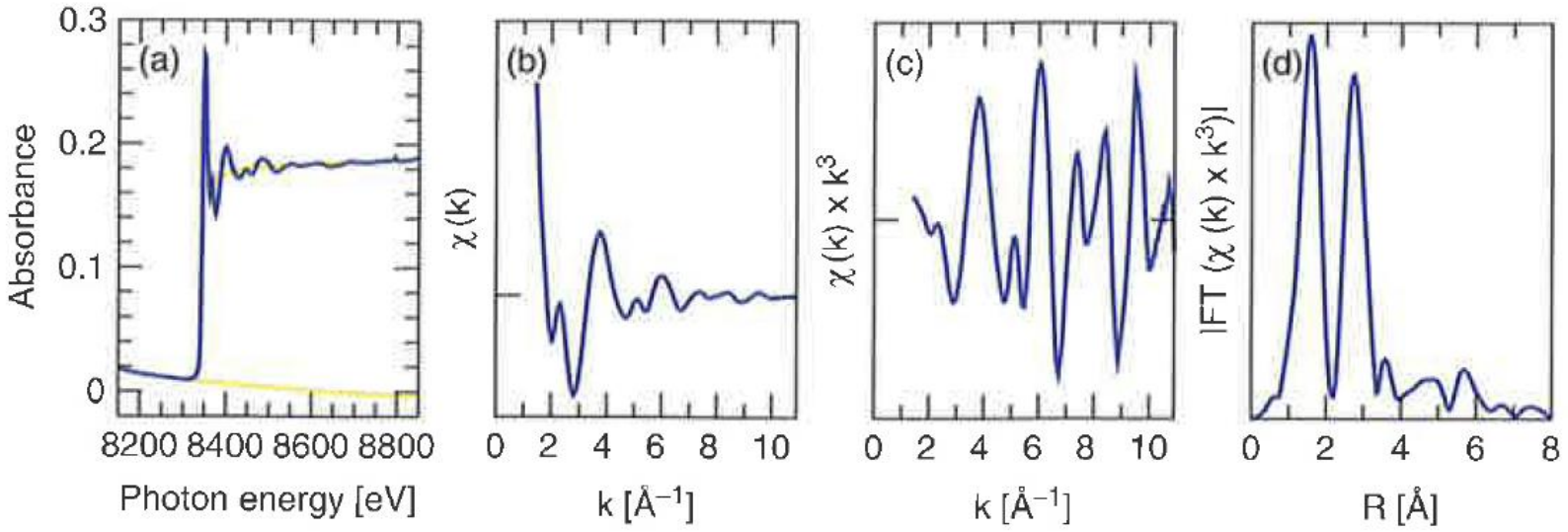
EXAFS

- In practice we convert the EXASF spectrum (i.e. absorbance μ vs E) into units proportional to the momentum of the photoelectron, i.e. as function of wavevector $k = 2\pi/\lambda_e$ ($=2\pi p/h$) once it has been corrected for the absorption of the free atom, $\mu_0(k)$. Note $E = h^2k^2/(8\pi^2 m_e)$ from $E=p^2/2m_e$

This is called the EXAFS function, $\chi(k) = \frac{\mu(k)-\mu_0(k)}{\mu_0(k)}$

The oscillations fall off rapidly with k so they are often multiplied by k^2 or k^3 to enhance them then Fourier transformed to real space to reveal the atom-atom distribution *e.g.* below Ni K-edge for Ni adsorbates in the mineral montmorillonite



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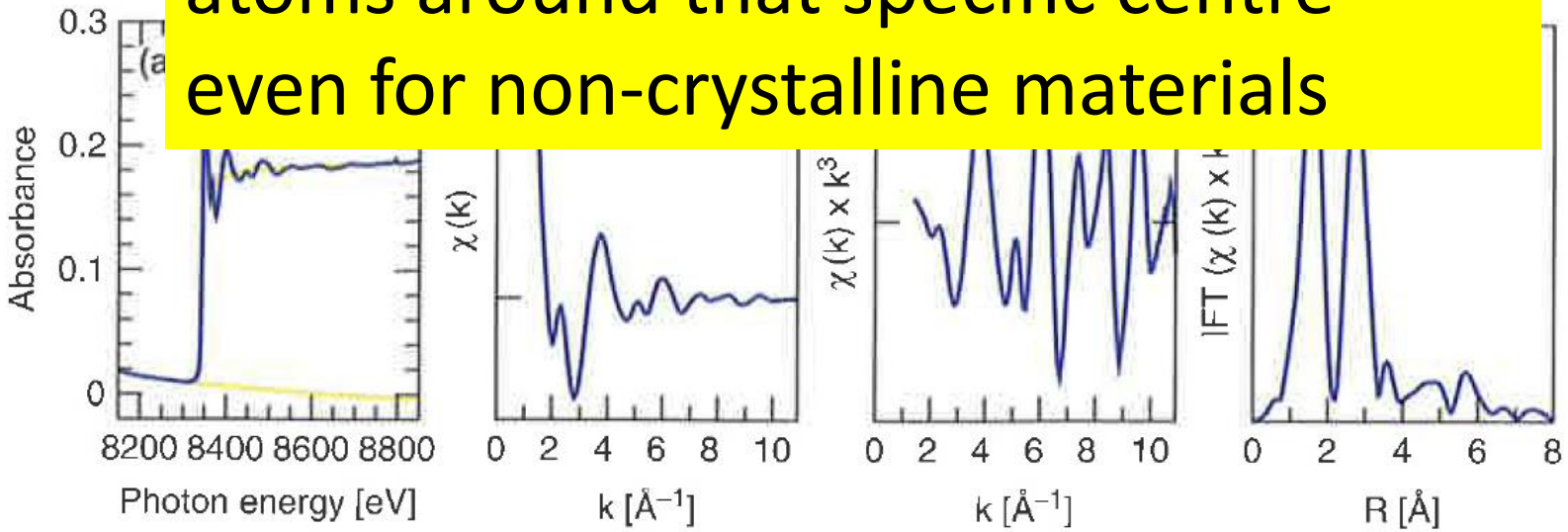
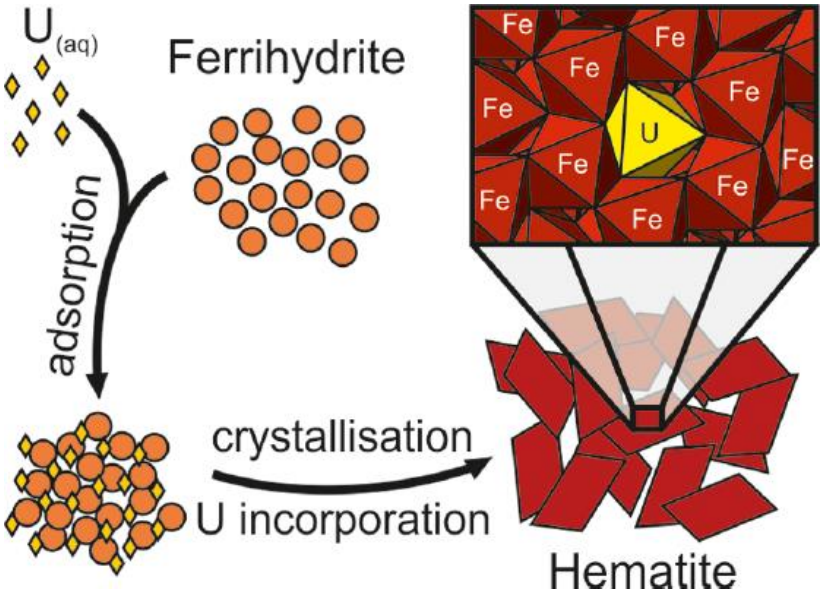
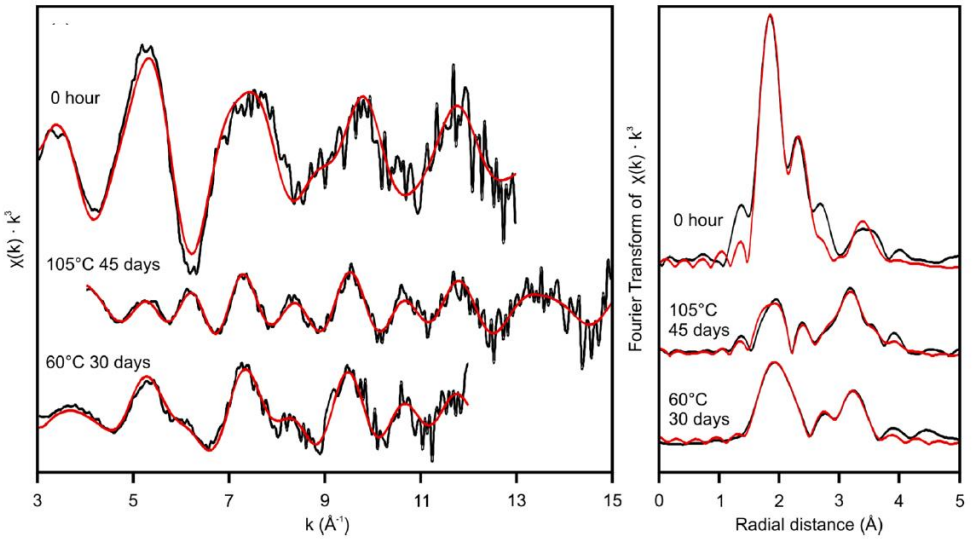
EXAFS provides an element specific probe of the distribution of other atoms around that specific centre – even for non-crystalline materials

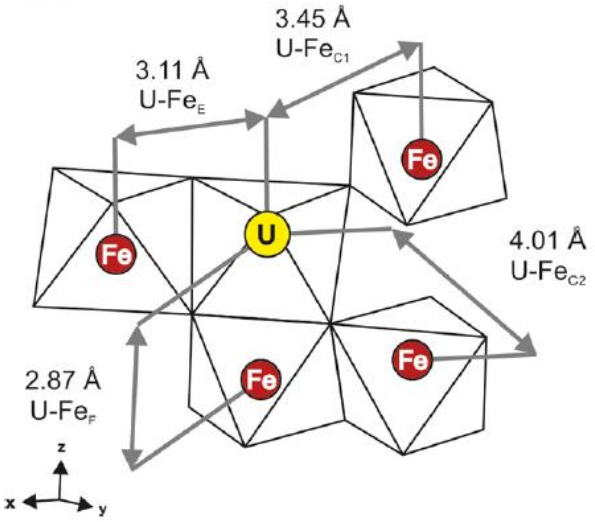


Looking for U



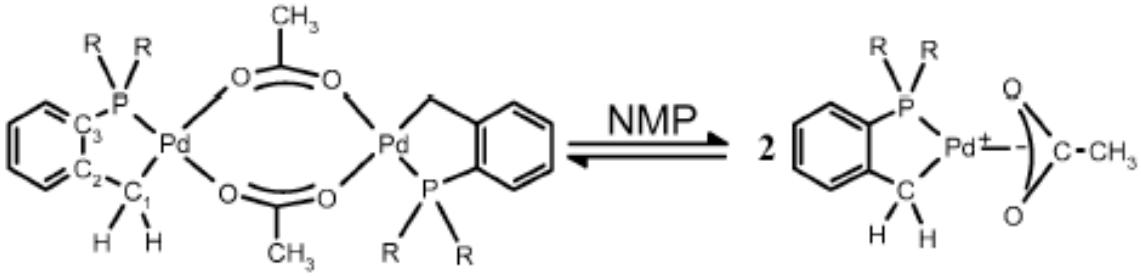


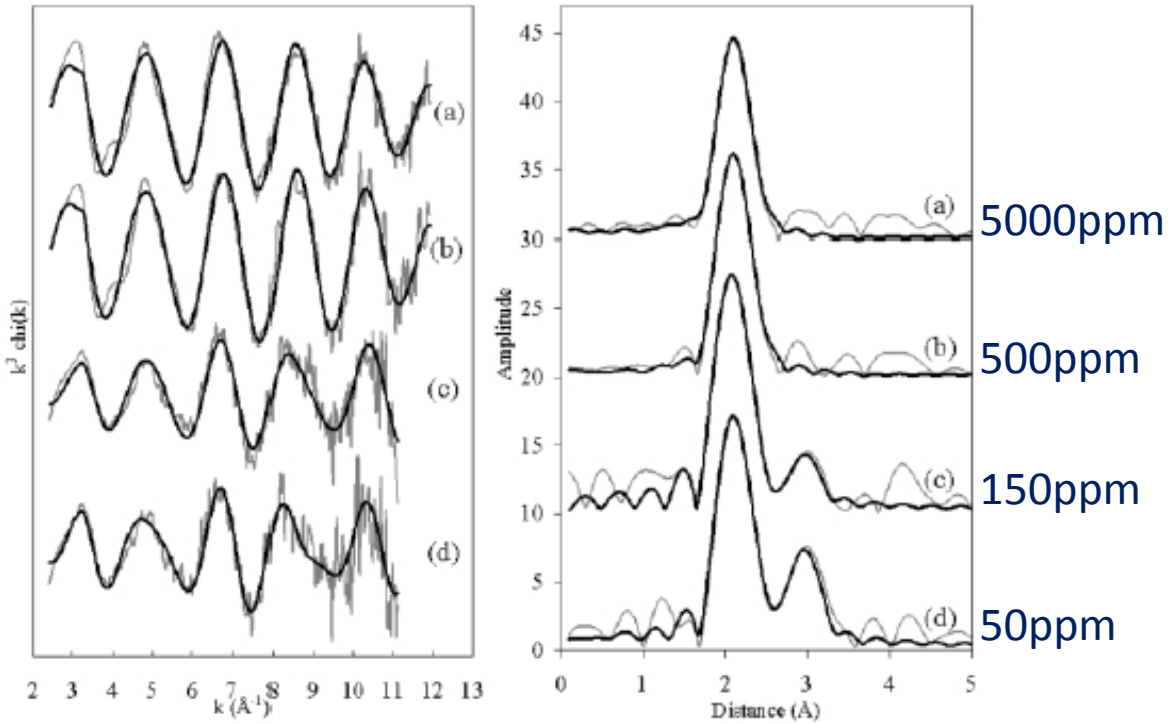
Follow incorporation of U compounds into iron oxides by EXAFS – confirms not only presence of element in particular oxidation state at 1000's of ppm but nature of binding



Marshall *et al*, Env. Sci. Tech. 48 (2014) 3724

What the Heck ?





Future limits ?
I20 at Diamond will give ppb of chemical species - *much* more sensitive chemical analysis especially for env/earth sciences

S. G. Fiddy et al, Chem. Commun. , 2682 (2003)