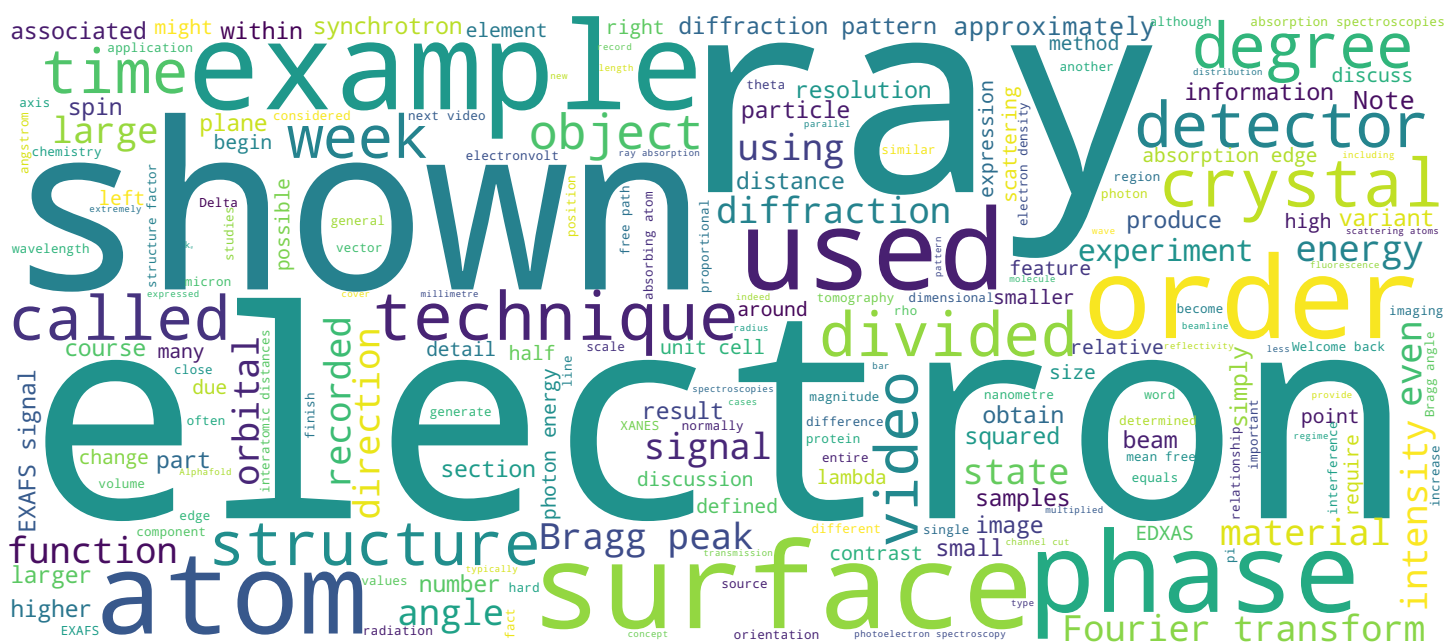


# Synchrotrons and x-ray free-electron lasers

## Techniques and applications

Prof. Philip Willmott



## Search MOOC



## Video



# Contents and objectives of this video



- The shell model
- Quantitative expression
- Extracting interatomic distances
- Variants of EXAFS

Welcome back to the last video of this week, in which we investigate in detail the EXAFS signal and expression before finishing with a brief discussion of variants of EXAFS. We use the so-called shell model in which we sum sets of atom types that are defined by their absolute distance from the absorbing atom. This allows us to generate a quantitative expression for the EXAFS signal, which in turn allows us to extract interatomic distances via Fourier transforms.

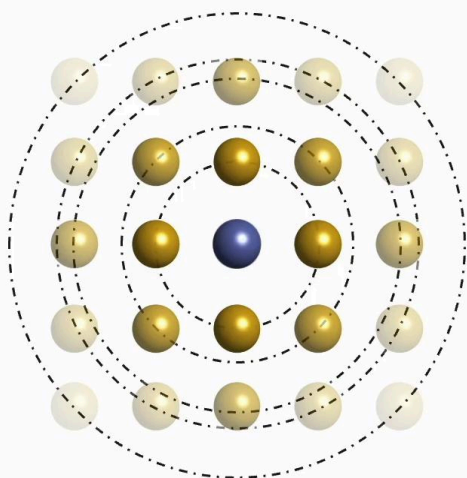
Notes

Summary



0m 04s

# The EXAFS signal quantitatively



- Based on “shell model”
  - $j$  concentric shells centered on absorbing atom
  - Each shell has
    - Radius  $R_j$
    - $N_j$  scattering atoms
    - Each atom has scattering amplitude  $t_j(k_e)$
  - But scattering strength dependent on 3D-angle between electric-field vector of incident radiation and the vector connecting the absorbing and backscattering atoms
  - In most cases, no long-range order and sample is amorphous or polycrystalline  
 $\Rightarrow$  anisotropy can be ignored
  - EXAFS signal summed over all  $j$  shells is thus

$$\chi(k_e) = \sum_j \chi_j^{\text{iso}}(k_e)$$

In the shell model, we consider all-atom distances,  $R_j$  of  $j$  shells, out to a distance from the absorbing atom of a few angstroms, typically no larger than the inelastic mean-free path. Each shell has a radius  $R_j$  containing  $N_j$  scattering atoms, each with a scattering amplitude  $t_j$ , which is a function of  $k_e$ . A potential complication is that the scattering strength depends on the angle between the electric field vector of the incident radiation and the vector connecting the absorbing and back-scattering atoms. However, in most cases, there is no long-range order in the sample under study, and this anisotropy averages out. The EXAFS signal  $\chi(k_e)$  is thus simply the sum of the isotropically average signal from each shell.


Notes

Summary



0m 37s

# The EXAFS signal quantitatively

$$\chi^{\text{iso}}(k_e) = \sum_j N_j \frac{t_j(k_e) \sin [2k_e R_j + \delta_j(k_e)]}{R_j^2} \times \exp(-2k_e^2 \sigma_j^2) \exp(-2R_j/\Lambda_e)$$


We now present the standard expression used for  $\chi^{\text{iso}}$  of  $k_e$ , and then justify its contents. The EXAFS equation is shown here. Now, although this might seem at first intimidatingly complex, we can break it down into individual components as follows. As we've just intimated, we can consider each shell individually and sum these to generate the total EXAFS signal. This is where the sum sign comes from. Each shell contains  $N_j$  back-scattering atoms. While the scattering amplitude of these atoms is expressed through the term  $t_j$  of  $k_e$ . Now, the beating heart of the EXAFS equation is given by the sinusoidal term expressing the interference between the outgoing and back-scattered electron waves. It's this part, which through Fourier analysis, yields the interatomic distances. The one upon  $R_j^2$  term is simply the inverse square law of a spherically expanding wave and should be self-explanatory. The further out the scattered atom at a distance  $R_j$ , the weaker is the back-scattered wave at the initially absorbing atom. The Gaussian term here accounts for the fact that the neighbouring atoms are not stationary but vibrating with an amplitude  $\sigma_j$ , parallel to  $k$ .

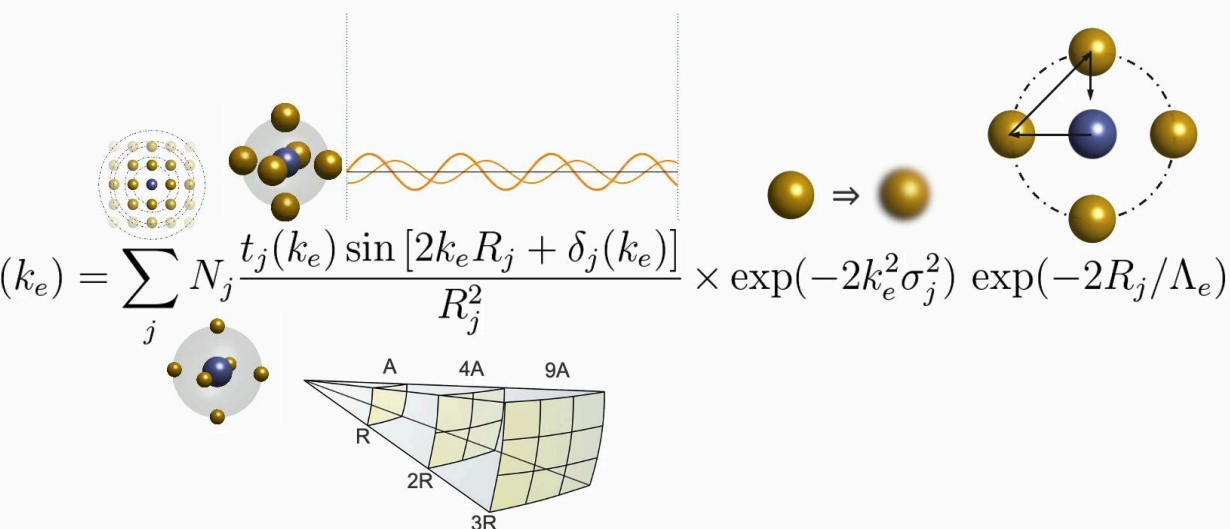
Notes

Summary



1m 34s

# The EXAFS signal quantitatively



$$\chi^{\text{iso}}(k_e) = \sum_j N_j \frac{t_j(k_e) \sin [2k_e R_j + \delta_j(k_e)]}{R_j^2} \times \exp(-2k_e^2 \sigma_j^2) \exp(-2R_j/\Lambda_e)$$

This is the well-known Debye-Waller factor, and is normally only marginally below unity for samples at room temperature. Lastly, the exponential term accounts for inelastic and multiple scattering of the electron wave, mainly by plasmons and phonons on its round trip of  $2R_j$ , where  $\Lambda_e$  is the electron's mean-free path length. The entire equation is shown again here with the visual prompts for completeness.

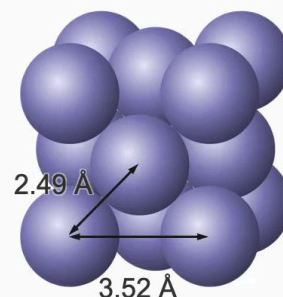
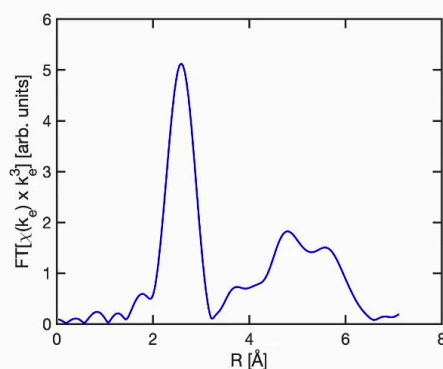
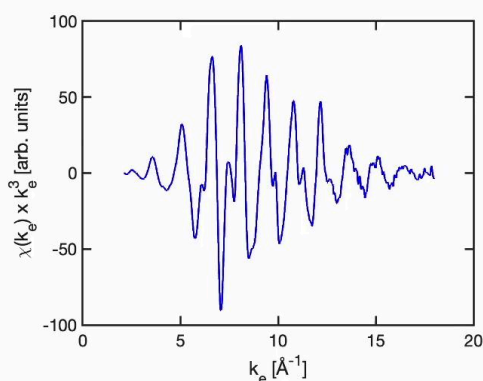
Notes

Summary



3m 07s

# From the EXAFS signal to interatomic distances



The interatomic distances associated with these oscillations can be determined by taking the Fourier transform of the EXAFS signal. We see here in the case of nickel metal, a face centre cubic structure, the dominant maximum in the Fourier transform at 2.5 Å. This corresponds to the 12 nearest neighbours at a distance equal to the lattice constant, 3.52 Å, divided by the square root of two, which is equal to 2.49 Å in excellent agreement with the results.

Notes

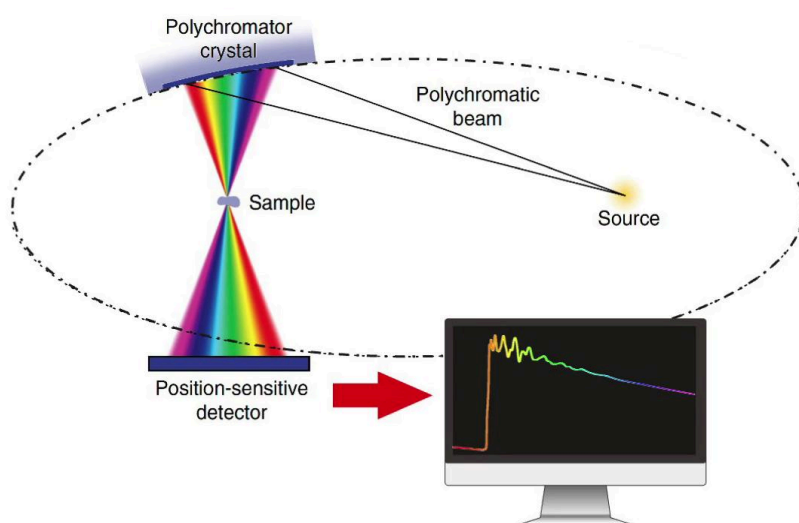
Summary



3m 43s



# Variants of EXAFS – EDXAS



## EDXAS

### Pros

- Sub  $\mu\text{m}$  spatial resolution
  - Scanning/mapping
- Sub ms temporal resolution
  - Kinetics

### Cons

- Extremely sensitive to mechanical and thermal drifts
- No possibility of fluorescence, Auger, etc
- Sample must be thin enough

## Interesting for XFEL measurements

S. Pascarelli and O. Mathon, Phys. Chem. Chem. Phys. **12** 5535 (2010)

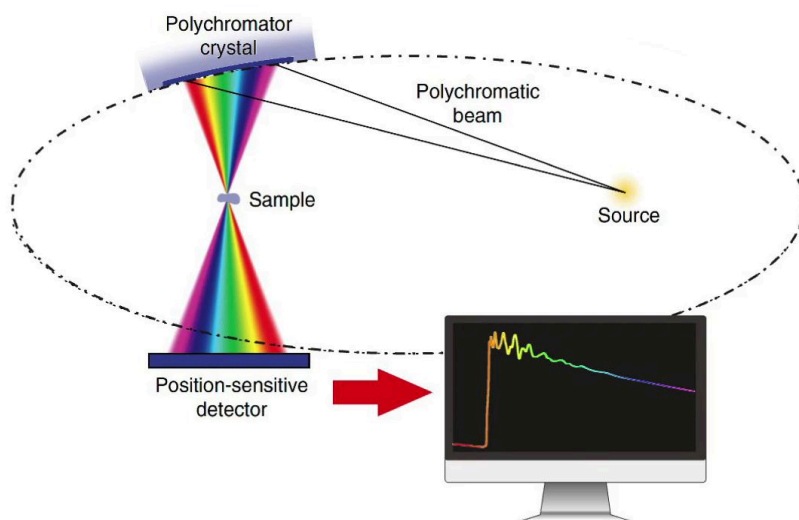
A variant of XAS covering both XANES and EXAFS is energy-dispersive XAS or EDXAS. One angularly disperses a polychromatic beam using a curved crystal on an ellipsoidal surface whereby the source lies at one of the ellipses' foci and the sample at the other. The polychromatic radiation converges on the sample and the transmitted signal can be recorded on a position-sensitive detector. This allows parallel data acquisition. The advantages of EDXAS include sub-micron spatial resolution and sub-millisecond temporal resolution. There are no moving parts in EDXAS, hence very rapid changes can be monitored. The disadvantages of EDXAS are that even very small distortions of the polychromator signal due to thermal drifts or other effects will cause the dispersed signal to drift spatially. This sets exceedingly stringent specifications in EDXAS for mechanical and thermal stability. EDXAS is also often used for studies at extreme conditions of pressure using diamond anvil cells, which have small volumes and limited acceptance angles. Another limitation of EDXAS is that it assumes that the sample is homogeneous across the focus spot. If this is not the case, artefacts will arise in the recorded spectra.

Notes

Summary



# Variants of EXAFS – EDXAS



## EDXAS

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- Sub  $\mu\text{m}$  spatial resolution
  - Scanning/mapping
- Sub ms temporal resolution
  - Kinetics

### Cons

- Extremely sensitive to mechanical and thermal drifts
- No possibility of fluorescence, Auger, etc
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## Interesting for XFEL measurements

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EDXAS also forbids the use in parallel of fluorescence or Auger spectroscopies and is limited to samples with the appropriate thickness. It is, however, definitely interesting for one-shot XFEL measurements.

Notes

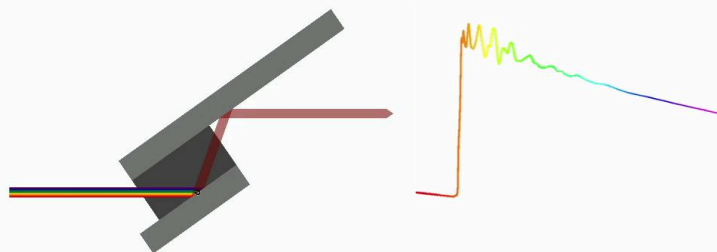
Summary



5m 49s



# Variants of EXAFS – QEXAFS



Up to 100 Hz (200 spectra)

## Quick-EXAFS

- Smooth rotation of CCM crystal
- Continuous monitoring of
  - CCM Bragg angle
  - Detector signal
- Typical DAQ rates > 100 kHz
  - ca. 1000x faster than shown here!
- $\Delta E$  range of energy > 1 keV even at 100 Hz
  - Enough for full XANES/EXAFS scan

$$\Delta\theta \approx \frac{hc}{2d} \frac{\Delta E}{E^2} = \frac{355.188}{d[\text{\AA}] E^2[\text{keV}^2]} \Delta E[\text{keV}]$$

O. Müller *et al.*, J. Synch. Rad. **23** 260 (2016)

Quick-EXAFS or QEXAFS was first presented by Ronald Frahm in 1988. Essentially, the idea is to minimise the number of motor movements and make these as smooth as possible. In modern QEXAFS stations, a single motor continuously rotates a channel-cut monochromator crystal with lattice spacing  $D$ , often using piezo drives, which are notably free of vibrations, while modern encoded systems are able to monitor the crystal's Bragg angle with sufficient resolution and on the fly, in other words, without stopping the motor. Consider, for example, a silicon (111) crystal scanning the energy across the iron K edge from 7,000 to 8,000 electronvolts. This requires the Bragg angle to change by marginally more than two degrees. The encoder must therefore be able to rapidly read out the angular position with an accuracy measured in thousandths of a degree and gate the detector within the time needed to rotate the crystal through an angle corresponding to the required energy resolution. For shallow Bragg angles, the relationship between the angular step size,  $\Delta\theta$ , and energy step,  $\Delta E$ , is almost perfectly linear and approximately given by  $\Delta\theta$  is equal to  $hc$  upon  $2d$ ,  $\Delta E$  upon  $E^2$  which is equal to 355.188 divided by  $d$  in  $\text{\AA}$  and  $E^2$  in  $\text{keV}^2$ , multiplied by  $\Delta E$  in  $\text{keV}$ .

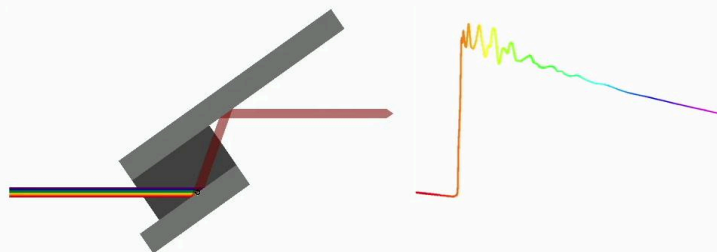
Notes

Summary



6m 04s

# Variants of EXAFS – QEXAFS



Up to 100 Hz (200 spectra)

- Quick-EXAFS
  - Smooth rotation of CCM crystal
  - Continuous monitoring of
    - CCM Bragg angle
    - Detector signal
  - Typical DAQ rates > 100 kHz
    - ca. 1000x faster than shown here!
  - $\Delta E$  range of energy > 1 keV even at 100 Hz
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O. Müller *et al.*, J. Synch. Rad. **23** 260 (2016)

$\Delta\theta$  is expressed in degrees in this case. Modern QEXAFS set-ups are capable of measuring complete EXAFS spectra within a few tens of milliseconds, meaning that individual data points on any given spectrum must be recorded with up to megahertz frequencies, depending on the signal-to-noise ratio. Because in QEXAFS, one limits the monochromator movements to a single motor rotation of a channel-cut crystal, the beam will drift vertically during the scan by an amount proportional to the channel height. Hence, the channel cut crystals using QEXAFS are normally made to be as compact as possible.

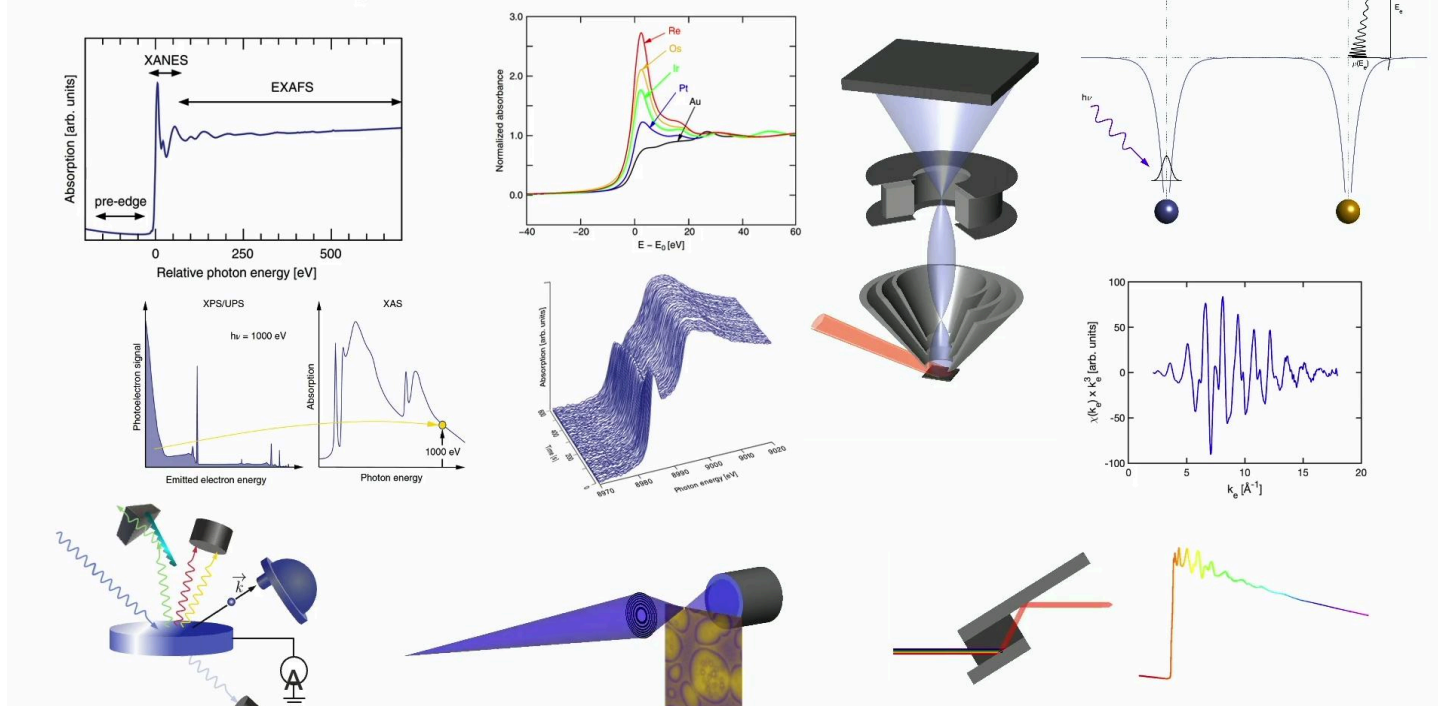
Notes

Summary



7m 44s

# Summary of this section



This completes our discussion of absorption spectroscopies. To summarise this week, we began by looking at the different energy regions around absorption edges typically investigated in absorption spectroscopies and considered the relationship between, on the one hand, photoelectron and fluorescent techniques, and on the other, absorption spectroscopies, and also the probes used to extract spectroscopic information. We then began to consider near-edge absorption spectroscopies and how they can probe different low-energy excited states and their application in many different fields of chemistry and biology. We then took a closer look at variants of the XANES, namely scanning transmission X-ray microscopy and photoelectron emission microscopy. We completed this week with a discussion of extended X-ray absorption fine structure spectroscopy, and how local structural information can be extracted from its features. Moreover, we looked at QEXAFS, which allows time-resolved chemical studies on the millisecond timescale.

Notes

Summary



8m 27s

## Next week...



Now, in next week's videos, we consider spectroscopies that probe products of absorption, namely fluorescent photons and photoelectrons.

Notes

Summary



9m 45s