

# **The CAMD XAS Tutorial**

the very very short tutorial for the chemist, geologist and other non-physicists to basically run a XAS experiment and understand in general how to analyze the data at CAMD.

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## Chapter 1: Introduction

Synchrotron techniques such as XAS, SAXS, and XRD are getting more and more popular for the characterization of all kinds of materials (nanoparticles, catalysts, new materials), all from all kinds of backgrounds: geology (e.g. analysis of sulfur in volcanos, arsenic in wells and rivers), environmental (e.g. heavy metal contamination, oil spill), biology (e.g. understanding the role and effect of metals in biological systems), archeology (e.g. ancient glasses), and of course chemistry, chemical engineering, and physics.

Although the demand for XAS experiments is increasing in general, the student/scientist researcher who is new to this field may not be attempting it, because mastering the method is quite challenging. The beamline scientists will certainly help as much as possible with explanations on how to successfully collect and analyze the data, but the amount of work needed for the researcher to really understand what to get out from the analysis is quite high.

There are a few books on XAS now: Grant Bunker and Scott Calvin wrote the most recent ones compared to the old Koningsberger and Prins (1986) book. The book "Soil Science Society of America" contains a chapter (much shorter than a whole book) on XAS, by S Kelly, D. Hesterberg, and B. Ravel, which is very good to delve deeper into the subject. And there are a number of other tutorials on the web that are of various quality. But who wants to read all of that just to get a little taste of the method? This little tutorial covers the basics to explain some vocabulary, shows how to collect data while avoiding some pitfalls, explains the basics how to analyze the data, and what it can mean – only to get you, the user, through your first days at the beamline.

We begin:

**XAS = X-ray Absorption Spectroscopy** asks: What is the **chemical environment** of atoms?

The advantages of XAS are:

- the method is element specific
- amorphous materials are possible
- no high vacuum necessary
- liquids or gases are possible
- spectra are additive (analysis)

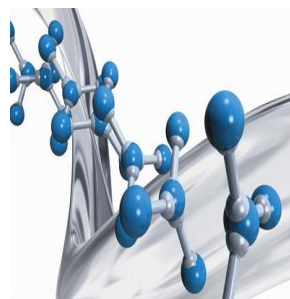


Figure 1.1: XAS looks at the chemical environment

There is a lot that can be investigated and analyzed using XAS – all kinds of materials. But XAS is not a black box! Unlike other methods (mostly used in chemistry) that are used to get information about materials the data collection and analysis in XAS is not done solely by a computer program by pushing a button and out comes the answer. It all has to be done by a person! That may be you, the user, or the beamline scientist that introduces you to the experiment. In case you choose to ask for the help of the beamline scientist in your analysis understand that each problem is special and the beamline scientist might not have the insights that you have into your project. The beamline scientist is also not a machine but a person, usually a PhD physicist. And she/he would appreciate that their assistance is a real collaboration (including having her/him on your paper)!

## Chapter 2: The Basic Words in XAS

### 2.1 Absorption and Attenuation – where XAS comes from

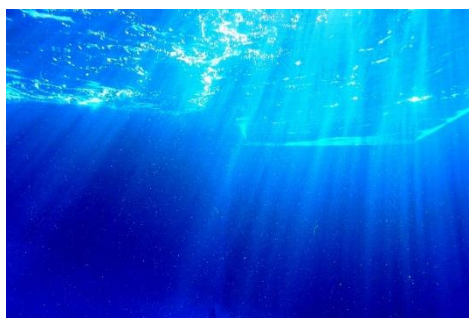


Figure 2.1: Light is attenuated in water

Like light in water (Fig. 2.1) the thickness of the material (water column) determines how much light is still coming through. The light is attenuated by the material. The law of **attenuation** by Lambert-Beer is this:

$$I_t = I_o e^{-\rho\mu_m x}$$

Eq. 1

The parameters in this formula are:

$\mu_m$	linear mass absorption coefficient
$\mu$	absorption
$\rho$	density of the material
$x$	thickness of the material/sample
$I_o$	incident x-ray intensity
$I_t$	transmitted x-ray intensity

The reason why the light/ x-rays in our case is attenuated is **absorption**. The light is absorbed by the material and only a fraction is passing through. Also, the energy of the light has an effect of how much is passing through (Fig 2.2).

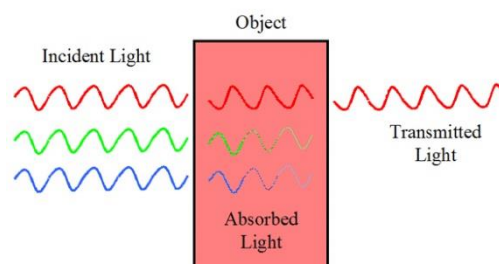


Figure 2.2: Absorption depends on the energy of the light

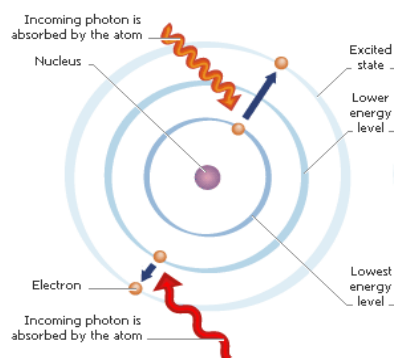



Figure 2.3: This is what absorption "really" looks like - one atom can absorb one photon

To be a little more precise about what absorption really means: Since all matter consists of atoms the light has to react with the atoms somehow – and the photons actually interact with the electrons, not the core. This is depicted in figure 2.3: Light as photons hits an atom and knocks out an electron from one of the shells. Depending on the energy of the photon the kicked (excited) electron can go to a higher shell or completely leave the atom (called going into a continuum state or the free state). Since the photon makes an electron move this electron is called a **photo electron**. This terminology comes from the famous scientist Albert Einstein who coined the name for this interaction between atoms and electromagnetic radiation: the **photoelectric effect**.

## 2.2 Electron binding energies and Absorption edges – how we see XAS

An electron that is excited into a free state is called ionized. The energy necessary to ionize an (the first) electron from the core level 1s (most inner shell) is different for each element of the periodic table (Fig. 2.4).

Why are we interested in this? If every element in the periodic table shows this absorption feature (and more we will see below) then this is worth investigating: We call the study of these absorption features **X-ray Absorption Spectroscopy** (in short: XAS). When the energy of the photon is high enough it is absorbed and the photo electron emitted. A beam of light at CAMD (e.g. LEXAS beamline) contains about  $10^9$ - $10^{10}$  X-ray photons. When this beam is absorbed by a material (say a metal) the absorption is seen to increase sharply in a plot depending on energy. This sharp rise in the energy plot is called the **absorption edge**  $E_0$ . The energies for the absorption edges for each element are listed in the **Hephaestus**  program.

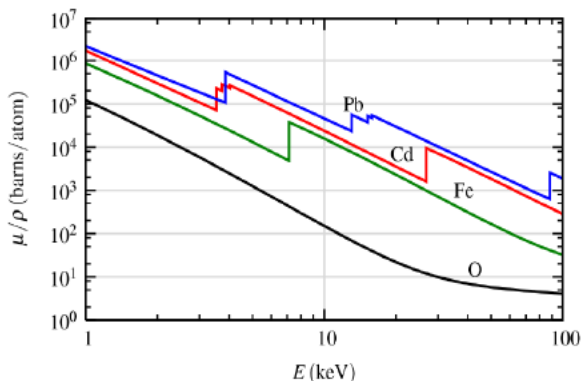


Figure 2.4: Absorption edges for different elements are at different energies

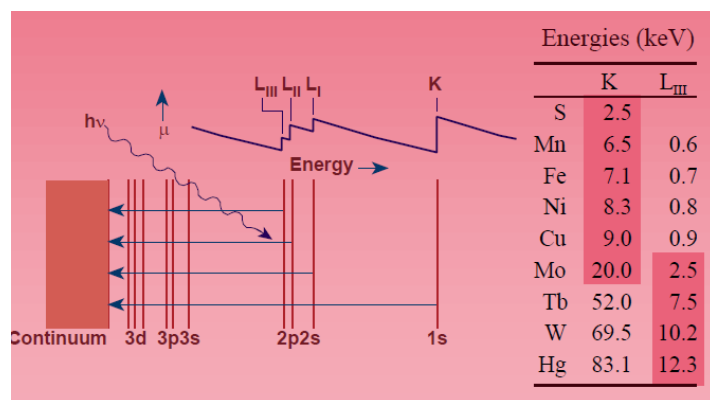


Figure 2.5: Core level transitions and the naming of edges with some examples for edge energies e.g. Cu K-edge at about 9 keV

Edges are named by the element that is used for the investigation and by the core level the electron was excited from (transition, cf. Fig. 2.5): 1s is called **K-edge**, 2s is called **L<sub>1</sub>-edge**. For the two spin depending shells 2p<sub>1/2</sub> and 2p<sub>3/2</sub> the edge names are **L<sub>2</sub>** and **L<sub>3</sub>-edge**, respectively. The usual range for XAS experiments is 1 keV to 30 keV. For some elements only K-edges are in this range (e.g. Fe, Cu) for other elements only L edges are in this range (e.g. Sb, Te, Xe), and for some element both L and M-edges (shell 3) are in this range.

If more than one element in the sample has edges in the range 1 keV to 30 keV then XAS measurements at all these edges are possible and can give better insight into the chemistry of the sample.

## 2.3 The XAS spectrum – EXAFS and XANES – what it can mean

When the photoelectron leaves the absorbing atom (center) it scatters with the surrounding atoms and creates a backscattering wave that affects the absorption of the center atom and results in oscillations in the spectrum.

The XAS spectrum is a plot of the absorption,  $\mu(E)$ , as it changes with varying energy (Fig. 2.6). The region around the sharp rise (absorption edge) is called XANES (X-ray Absorption Near Edge Structure) and everything beyond about 50 eV above the edge until about 1000 eV +  $E_0$  is called EXAFS (Extended X-ray Absorption Fine Structure).

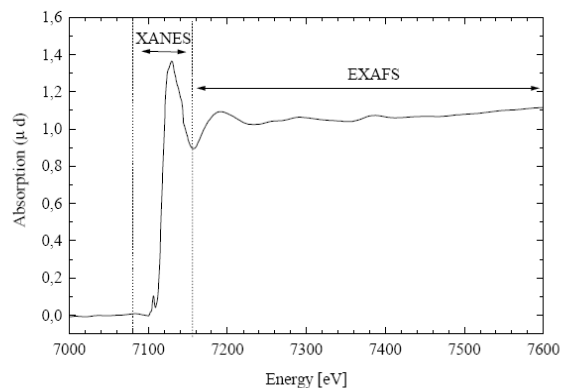



Figure 2.6: The XAS spectrum - showing XANES and EXAFS regions – example:  $Fe_2O_3$  at Fe K-edge - with White Line

The XAS spectrum is the fingerprint of the specific chemical environment for each element/absorbing atom. This idea is used in the linear combination fitting (LCF) analysis of XANES spectra: in addition to the unknown sample a set of reference spectra is also measured and later

compared (with the **Athena**  program) to the spectra of the unknown sample to determine the proportions of the reference materials (or more accurately proportions of bonding characteristics) in the unknown sample. In order to succeed using this analysis method you need to have the correct references (e.g. as powders of inorganic compounds). Another method uses theoretical calculations (e.g. with FEFF). However, this method is extremely complicated and takes a good while to learn. Simulations with FEFF will not be discussed in this tutorial. Some more info is given on this type of analysis in section 5. The XANES spectrum also contains the **White Line**. This is the main feature in the main rise of the absorption and mostly the highest peak. The White Line is related to transitions of the photo electron into bond states such as molecular orbitals.

With **EXAFS** on the other hand in some specific cases very good information about the distance and coordination numbers of neighboring atoms around the element under observation can be determined.


This method uses also theoretical calculations but these are all implemented in the **Artemis**  program together with the analysis. Some more info on this type of analysis is given in section 4.6. The spectra collected with XAS are in any case **additive**. If the sample is not 100% one type of material its observed spectrum will be a combination of the spectra of its components. If there is too much peak overlap this can make analysis of the spectrum with EXAFS difficult or impossible.

Table 2.1: What can we learn from XAS

Method	XANES	EXAFS
distance to neighbors	-	yes
number of neighbors	indirect	yes
chemical environment	yes	indirect
geometry/angles	yes somewhat	-
combination of materials	yes	not good
oxidation state	yes	-

## 2.4 Scanning the energy – what is spectroscopy?

Using the **Bragg Law of diffraction** a specific energy can be selected.

$$n\lambda = n\frac{hc}{E} = 2d \sin \theta \quad \text{Eq. 2}$$

(n: integer;  $\lambda$ : wavelength of the light; hc: constants of particle physics; E: energy; d: crystal spacing;  $\theta$ : angle between beam and crystal).

**Spectroscopy** is everything that deals with the “different colors” of the light used. In XAS we deal with X-rays. By rotating the crystal (in the monochromator) with respect to the beam (which is always stable) the angle is changed continuously (actually in small steps) giving a beam for the experiment with different energies and enabling an energy range (or area) to be scanned. This area is set in the XAS program at the beamline (see section 3.3).

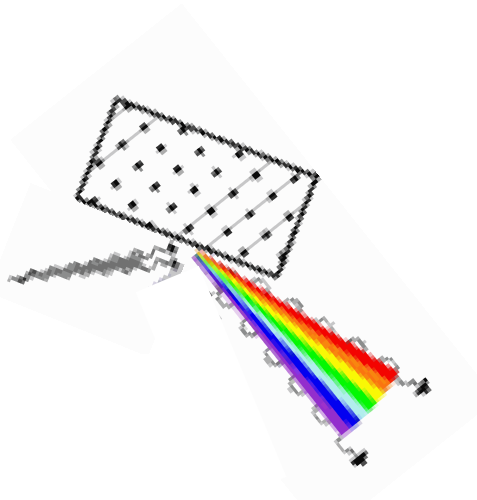


Figure 2.7: Visualization of Bragg diffraction. Depending on the angle of the incoming beam of light different energies (colors) are emitted

Other spectroscopic techniques are: FTIR – Fourier Transformed Infrared Spectroscopy

UV-vis – spectroscopy using UV and Visible light

Raman – spectroscopy based on inelastic scattering of monochromatic light

etc.

To make something clear where is often much confusion (for XAS):

A **Standard** in XAS is the sample that is measured each time (or day) to check the calibration or use as alignment for data processing.

A **Reference** (compound) is every compound that is measured and used for LCF to identify the chemical environment of the unknown sample mainly for XANES.

## Chapter 3: The Experiment and how to do it right

### 3.1 What does the experiment look like?

In this section we learn a couple more terms and get an idea of the experimental setup. Using the law of attenuation by Lambert-Beer from above and shuffling the formula some we get:

$$\mu(E) \propto \ln\left(\frac{I_0}{I_t}\right) \quad \text{Eq. 3}$$

This is an excellent example of how to translate a physics law into an experimental setup. The devices that can measure the intensities  $I_0$  and  $I_t$  are called ionization chambers. The sample is positioned between the ionization chambers.

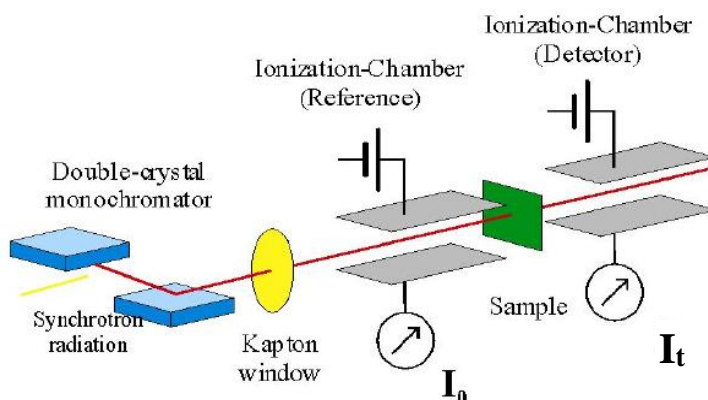


Figure 3.1 Experimental XAS setup transmission mode

If the concentration of the absorbing element is very low (1% and less), or if the sample is very thick there is another way to detect the absorption: from the fluorescence signal. This signal is detected with a device called a fluorescence (solid state) detector. This detector is positioned in  $90^\circ$  with regards to the beam and in this case the sample has to be positioned in  $45^\circ$  with regards to the beam. The formula for the fluorescence mode is:

$$\mu(E) \propto \ln\left(\frac{I_f}{I_0}\right) \quad \text{Eq. 4}$$

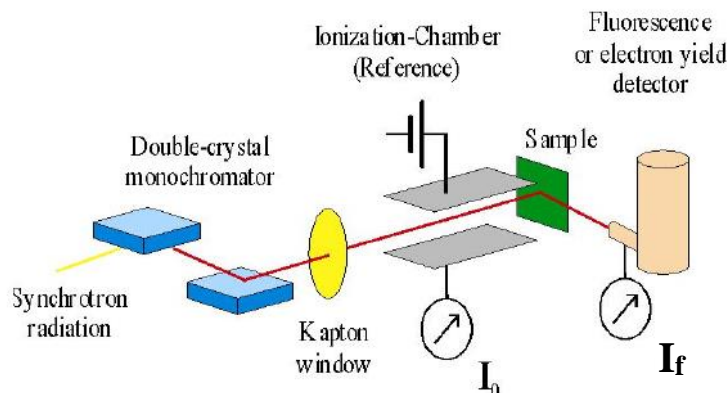


Figure 3.2 Experimental XAS setup fluorescence mode

The difference between the formulas for transmission and fluorescence mode is: no logarithm for fluorescence and  $I_0$  is in the denominator! The derivation for the formula for fluorescence is quite lengthy and will not be repeated here.

This is how the experiment looks for real:

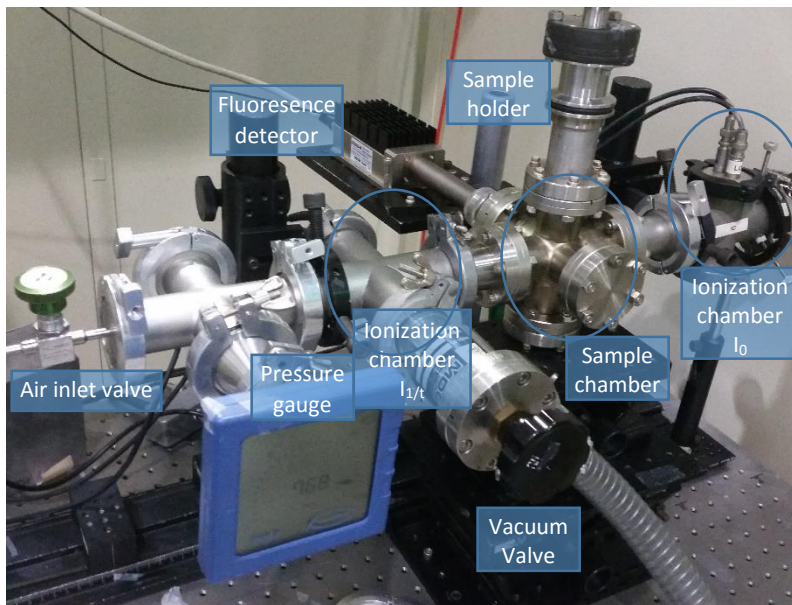


Figure 3.3 The setup of an XAS experiment – in this case at LEXAS beamline

Compare the components of the diagrams above with this picture to get used to what you have to deal with.

### 3.2 How to prepare samples

What other preparations are needed before the user can get to do the experiment? The samples need to be prepared. The sample preparation for XAS is really not much (and in some cases really nothing has to be done but those are special circumstances). However, prepare your samples carefully to get good data!

For XAS experiments nearly all samples are “hand-made”. The size and shape of the x-ray beam at the position of the sample determines the size of the sample. At CAMD the cross-section of this beam is generally a rectangle of about 2 x 10 mm. In order to get good data (without weird holes in the spectrum) the sample has to be prepared as homogeneously and evenly as possible with a size of about 5-10 mm x 15 mm. This takes practice!

“For transmission measurements, we need a sample that is of uniform and appropriate sample thickness of  $\sim 2$  absorption lengths. It should be free from pinholes. If a powder, the grains should be very fine grained (absorption length) and uniform.” Matt Newville

So, for XAS experiments we need to use a mortar and pestle to grind the material into a fine powder. The size of the grains can have an effect on the spectrum that we want to avoid: so, grind it! There are in principle two different kinds of experiments in XAS: low energy and high energy. In this tutorial we will



not talk about special experiments with cooling, heating, or special cells. In this case the people involved have to learn their special technique.

### 3.2.1 The “normal samples” 4.5 keV and up (high energies)

In this present section measurements for materials at 4.5 keV and above are discussed. At higher energies the beam can penetrate low Z materials really well, as if there is nothing there. So we can use low-Z materials for dilution (e.g. boronitrite, cellulose). The elements investigated in this energy range will be most likely metals, e.g. Fe, Cu, Pb. For these “high energy” measurements some simple techniques can be used to prepare samples. The first technique is shown in figures 3.4.1-3.4.6: The samples are prepared on Kapton® tape with the help of some Scotch tape.



*Figures 3.4.1 – 3.4.3: Stepwise preparation of samples for high energy measurements*

Place a long piece of Kapton tape with the sticky side up on the table and tape it down with Scotch tape. The top, bottom, and sides of the sticky side of the Kapton tape need to be covered with Scotch tape as well, leaving a rectangle uncovered in the center (Fig. 3.4.1). Spread the powder on the sticky Kapton as a thin film. The fine grains will stick to the glue and the excess can be removed (Figs. 3.4.2 and 3.4.3).



*Figures 3.4.4 – 3.4.6: Stepwise preparation of samples for high energy measurements*

Remove the Scotch tape (Fig. 3.4.4). Fold the Kapton over from the middle and press down (Fig. 3.4.5). Fold a couple of times (depending on the experiment/ absorption edge) (Fig. 3.4.6). Alternatively to folding, you can cut the long tape with powder (Fig. 3.4.4) into small pieces of the same size and stack together.

Another technique of sample preparation involves mixing the sample compound with a low Z material to fill a space, and press a pellet. These techniques are less used at CAMD.

### 3.2.2 Samples at the low energies below 4 keV (low energies)

At low energies below 4 keV the beam is absorbed by nearly anything – even air. In these cases the experimental setup has to be operated at reduced pressure (e.g. down to 5 Torr). The elements investigated

in this energy range will be Si, P, S, K, and Ca. Also, M edges of heavy elements like Pb or Au are in this region. The strategy of sample preparation here is similar to the above technique. Just use a smaller piece of Kapton tape. These samples will not be folded: Place a piece of Kapton tape with the sticky side up on the table (better on a piece of weighing paper to reduce contamination by other compounds) and tape it down with Scotch tape. The top, bottom, and sides of the sticky side of the Kapton tape need to be covered with Scotch tape as well (Fig. 3.5.1). Use only a tiny amount (like 1 mg if you measure it) and pick it up with your clean (!! ) glove (Fig. 3.5.2).



Figures 3.5.1 – 3.5.3: Stepwise preparation of samples for low energy measurements

Spread the powder on the sticky Kapton as a thin film. For the low energies in general the samples have to be very thin. Using a (clean!) glove to spread out a very small amount evenly on the Kapton is a good method (Fig. 3.5.3). It is also possible to use a “q-tip” kind of applicator or a small spatula. The fine grains will stick to the glue (Fig. 3.5.4). Then remove the tape covering the edges of the Kapton.



Figures 3.5.4 – 3.5.6: Stepwise preparation of samples for low energy measurements

Now we use Mylar®. This is a transparent and thinner low Z-material similar to Kapton but without glue (Fig. 3.5.5). Cover the sample with Mylar®. The parts that were covered with the Scotch tape before are now used to hold the Mylar®. This side will be heading towards the beam; this is very important for fluorescence measurements: Mylar® does not absorb too many of the fluorescence photons that are leaving the sample to be detected in the fluorescence detector (Fig. 3.5.6).

### 3.2.3 The effect of uneven samples on the transmission data

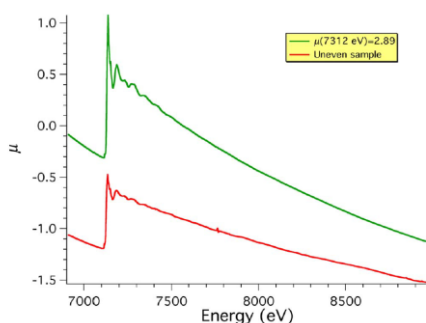


Figure 3.6: Spectra of uneven vs. good sample

This little section explains how important it is to learn how to prepare samples and be ready to make a new one if the spectrum is not very good. Fig. 3.6 shows how compressed (and therefore bad) the spectrum (red) can get if the sample has holes or is uneven in any kind of way. The green spectrum represents a good sample with a strong White Line and smooth curve up to 1000 eV above ca. 7500 eV. The White Line in the red spectrum on the other hand is rather compressed. In an magnified view we could see that all the little features that are

visible in the green spectrum are not visible in the red spectrum. Also, at about 7700 eV there is a little peak and the curve is not smooth in one direction. These are all signs that the sample “has problems” and a new sample has to be prepared.

### 3.3 How to take the data

#### 3.3.1 The beamline – what to do to start the experiment?

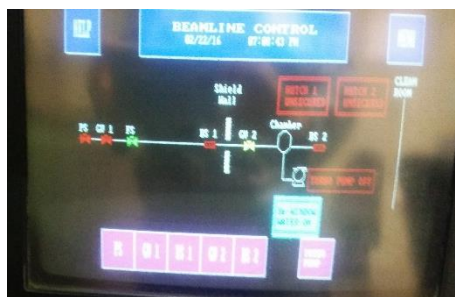


Figure 3.7: Overview of beamline shutters

All X-ray beamlines have hutches to protect the user against the radiation. This screen shot of the Allen-Bradley (Fig. 3.7) shows the list of **shutters** for the beamstop and valves in the beamline. During normal beamtime the user only has to deal with the button BS2 on the right of the left row of pink buttons. This is a touch screen, so, you put your finger on the **BS2** square.

Hutch securing: before you can open the shutter BS2 the hutch has to be “secured”. This means the person who is running the experiment/measurements has to make sure that no one is inside the hutch before locking it. For that reason, she/he presses the

**green (search and secure) button** (location different for each beamline) and tells everybody in the hutch to leave. (NOTE: THIS IS **NOT THE RED BUTTON!** That is the **emergency** stop for the entire ring – think of the big red button in an action movie.) Once everybody is outside she/he can lock the hutch: taking out the key on the bottom and locking the lock on the top – now a green light should glow here. After waiting 5 secs you can open BS2 and start your experiment.

For the various beamlines different steps have to be taken to put the sample in the beam position.

As the picture (Fig. 3.3, from LEXAS) shows: in some cases, the user has to reduce the pressure of air in the setup. This will be explained by the beamline scientist.

#### 3.3.2 Taking data

An XAS spectrum is collected by measuring  $I_0$  and  $I_t$  while changing the energy in steps. This is what the software is doing for you when the scan parameters are set up:

- The tabs on the top: As a first time user you do not have to worry about those (Ion chambers: check the signal, Fluorescence: check the signal from SDD detector (sample must be set in 45° angle to the beam!!)).
- Writing the folder – Where to put the data.  
Name of the scan: Every scan **is saved** at the end (even if aborted).
- The **scan parameters** include: Edge position  $E_0$ /element, energy positions for the different areas (these can be absolute (e.g. 2470) or relative to  $E_0$  (e.g. -20)), step size for each area, and integration time (time how long each point is measured). The scan parameters will be saved with the other meta data in the scan. Press Start to start the scan and abort if something is wrong.
- Estimated duration: how much time is estimated by the program that the scan should take.
- Room for your notes about the scan. This information can be input even while the scan is running and will be saved with the data at the end of the scan.

This is the beamline software (Fig. 3.8):

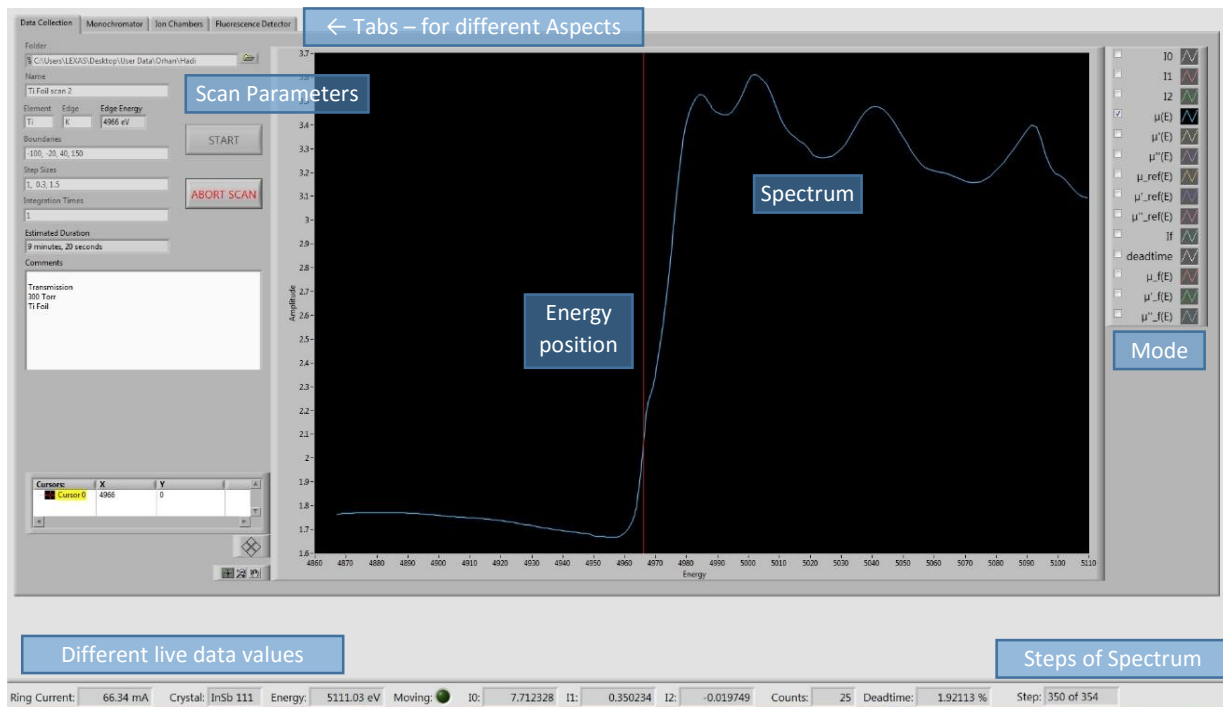


Figure 3.8: The beamline software for XAS measurements

- f) **Live data** values: On the bottom is a band with data readouts: What the current storage ring current is, what crystals are installed, at what energy the scan is, what  $I_0$ ,  $I_{t/1}$  are measured (you can ignore  $I_2$  at LEXAS). If fluorescence is chosen counts are the real time counts, and dead time is what the detector reports as dead time (if above 12% talk to beamline scientist).
- g) **Mode**: Whichever of the boxes on the band on the right is checked will be displayed (**transmission, or fluorescence, or  $I_0$ , or any combination**) However, the data displayed in this way (checked box) will not be saved with a channel dedicated to the checked box. The data is stored in columns dedicated to Energy,  $I_0$ ,  $I_1$ ,  $I_2$ ,  $I_f$  (ROI sum), dead time (in %). Thus, when opening the data in the Athena program you have to apply equations 3 and 4 (This will be explained below).

### 3.3.3 Finishing up

After one scan (or more for each sample) has been taken and you need to change the sample: close BS2, take the key from the top lock and open the bottom lock. Now you can open the door and get inside. Change the sample and redo what is written in 3.3.1.

After all data is collected the beamline (this means each of the shutters) has to be closed. For this, contact the beamline scientist.

Copy the data onto your flash drive...

## 4. How to analyze the data

Right now there are 2 major software packages that can be used to analyze the data, Athena (Demeter) and WinXAS. In this tutorial we will focus on Athena because we think that the support and user friendliness is better. To get the first idea how to use the software there are already a couple of tutorial videos made by Bruce Ravel at the DIAMOND lightsource freely available (<http://www.diamond.ac.uk/Beamlines/Spectroscopy/Techniques/XAS.html> ).

To understand what will be discussed here and how to handle the software better we recommend that the user first watches the video and familiarizes themselves with the program. There is no use to continue unless you know what you are doing. However, here is a short overview of the features that we are talking about.

### 4.1 Data import

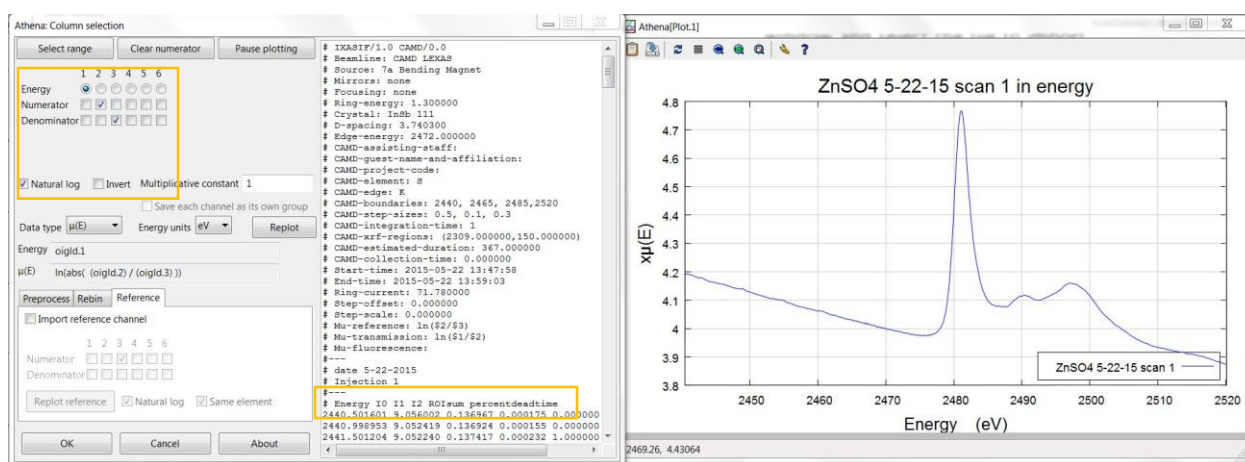


Figure 4.1: Data import into Athena dialog (left) and spectrum of selected channels (right)

To import the data into the Athena program, open the data import window and select the file to import. The dialog that opens looks like Fig. 4.1. The columns that are stored in the data file are shown in the window on the bottom right: Energy,  $I_0$ ,  $I_1$ ,  $I_2$ ,  $I_r$  (ROI sum), dead time (in %). Select the correct columns according to Eq. 3 for transmission mode or Eq. 4 for fluorescence mode. The selection for transmission mode is shown in Fig. 4.1 (top window). To confirm that your selection is correct check the gnu plot window that displays the data as a XAS spectrum (Fig. 4.1 (right)).

The raw XAS spectrum  $\mu(E)$  is divided into 3 sections (cf. Fig. 4.2): 1: the **pre-edge** region below the edge  $E_0$  mainly shows a linear downward-sloping background, 2: the **edge region** where  $E_0$  is defined; 3: the **post-edge** region above the edge  $E_0$  with the typical wiggles/oscillations that contain the information about the neighbors and chemistry (including White Line and Shape Resonances).

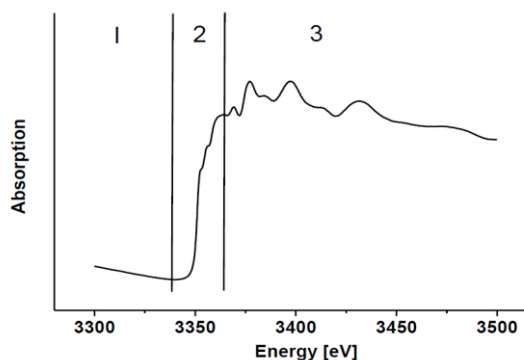


Figure 4.2: The 3 sections of the XAS

## 4.2 Normalization of the data – post-processing

One of the features of any XAS data analysis software is normalization of the data (according to Eq. 5) to prepare them for comparison. The first step in this approach is **background subtraction**. The background  $\mu_0(E)$  is in principle a linear function and can be approximated using two points in region 1. In a good number of cases the user has to change these points in the Athena program from the automatically determined points to fit that linear function better to the background.

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)} \quad \text{Eq. 5}$$

As a rule  $E_0$  for XAS is determined as the **maximum of the first derivative**. The Athena program does that quite nicely but not without errors. Use the derivative button to determine if the point automatically selected by the program is on the peak of the first maximum (yellow circle in Fig 4.3).

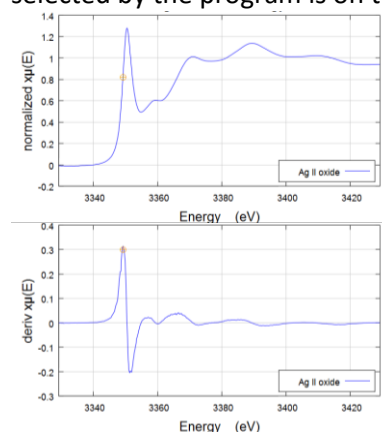


Figure 4.3: XANES spectrum and the first derivative

At  $E_0$  the post-edge part of the spectrum  $\mu(E)$  is approximated either by a line (XANES) or a spline (EXAFS). The intensity difference between the background  $\mu_0(E)$  and this post-edge function at  $E_0$  is  $\Delta\mu_0$ . Dividing the background removed spectrum by this number sets the offset of background and post-edge features to 1. Here as well the points selected by the program have to be reevaluated. And now the spectrum is normalized (compare the y-axis in Fig 4.4. for the raw and normalized spectra).

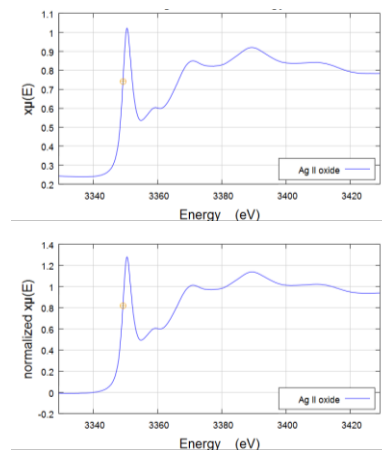


Figure 4.4: Raw and normalized XANES spectra

## 4.2 Oxidation States

One technique of analysis of XANES data is the determination of the shift of  $E_0$  as a function of oxidation state. This is depicted in Fig. 4.6 for Chromium oxides. The edge position  $E_0$  is determined as the max. of the first derivative (on the edge – in this case it is the second peak of the derivative, Fig. 4.5).

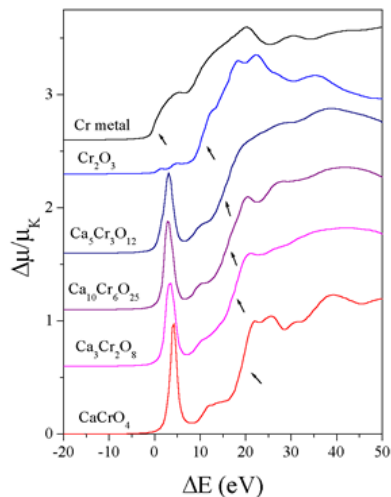


Figure 4.5: Cr K-edge XANES spectra of Chromium oxides

If determined correctly as in Fig 4.5. the energy shifts of  $E_0$  (absolute or on a relative scale) can display a relation to the chemical shift or oxidation state of the absorbing atom in the compound. This has been proven true for sulfur, chromium, mostly K-edges, but not for all elements and all edges (e.g. Pb at the  $L_3$ -edge).

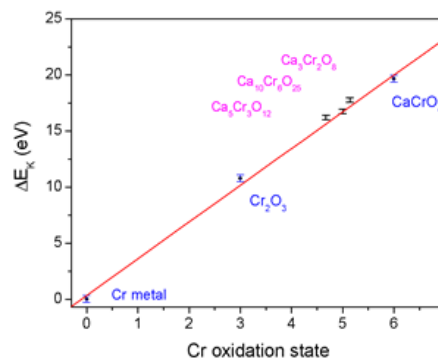


Figure 4.6: Energy shift vs. oxidation state for chromium oxide compounds

The determination of a change in oxidation state is mainly useful for bimodal experiments where one compound changes into another and the XAS investigation should show the phase transition. Since this relationship between energy shift and oxidation state is not proven for all elements the user should not assume and use this information until a refereed paper is found that shows this.

## 4.5 LCF

The most used technique of XANES analysis is linear combination fitting (LCF). XAS spectra are additive. That means that each photon reacting with a chemical environment makes an impact on the spectrum recorded. Assuming more than one compound (A and B) are in your unknown sample the fractions of the mixture can be determined, if the pure compounds (A and B) are measured under the same conditions (i.e. same beamline). See the example in Fig. 4.7. These two compounds have quite different XANES spectra mainly seen at the pre-edge peak (around 0 eV). The chemical environment of the Cr atom in both compounds is quite different – one being tetrahedral and the other octahedral (coordinated with O). An unknown sample (e.g. water sample from a plant) containing both compounds can be analyzed with the LCF technique. Using the Athena program the user can easily play with this idea using only 2 spectra of pure compounds and mixing them in different proportions. This is shown in Fig. 4.8.

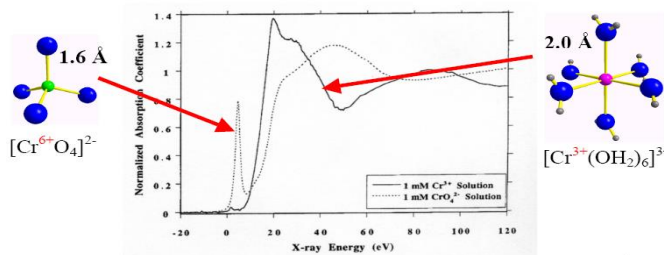
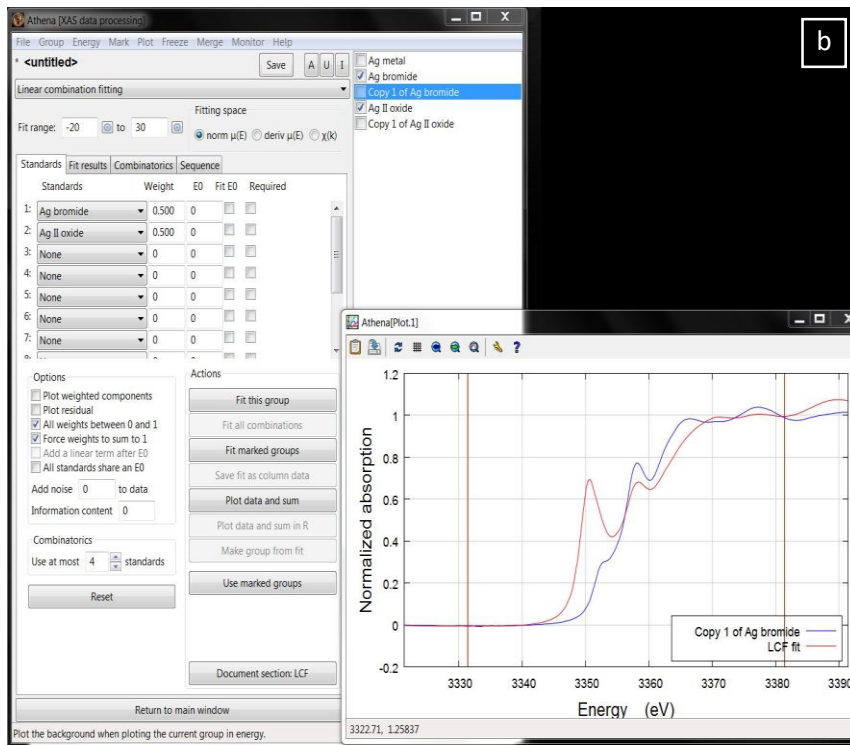
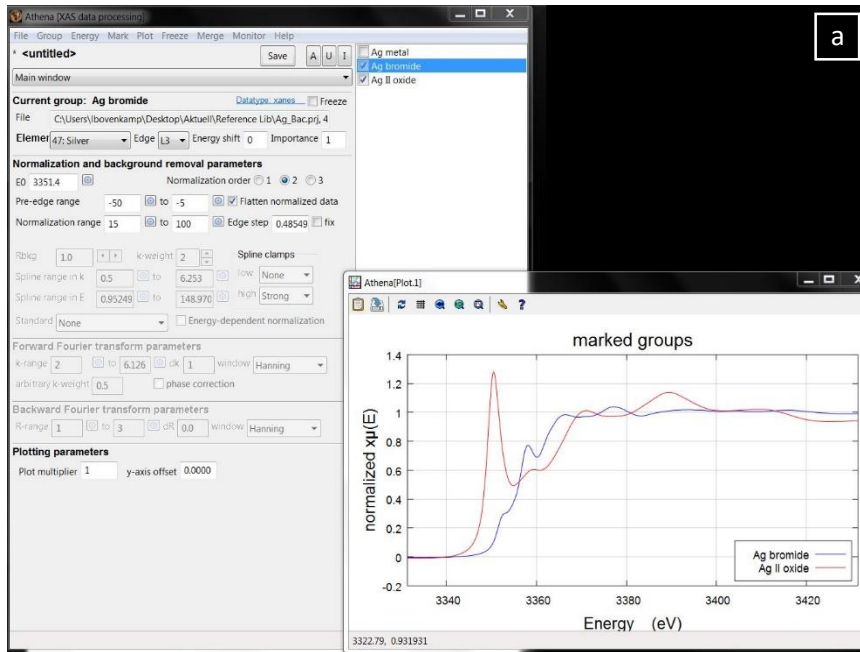


Figure 4.7: Cr K-edge spectra of two very different Cr compounds

Example for AgBr and AgO:





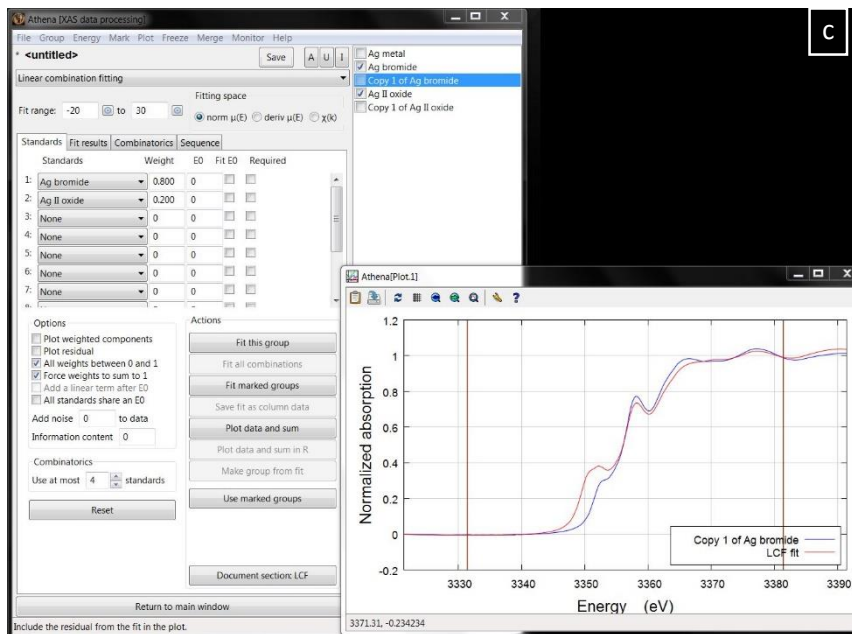


Figure 4.8: Using Linear Combination Fitting dialog to create new spectra

The two XANES spectra of AgBr and AgO (at Ag  $L_3$ -edge) are quite different (sharp peak or not), which is shown in Fig. 4.8a. With the LCF tool (drop down list) check the spectra to use for LCF and push “use marked groups”. They will be displayed in the list of spectra (Fig. 4.8b). If you push “Plot data and sum” you can see a linear combination (50/50) of the two spectra and the comparison to the unknown sample (here a copy of AgBr). The fractions can be changed manually to see how the two spectra contribute to the LC/sum (Fig. 4.8c). Usually the spectra that should comprise the unknown data are selected and “Fit this group” is pushed to get the LCF. For more specific understanding of the tool read the Athena manual or ask your beamline scientist.

#### 4.6 EXAFS

The analysis using EXAFS data is much more complicated to cover in a short form like this. For EXAFS measurements and analysis watch the Bruce Ravel videos at:

<http://www.diamond.ac.uk/Beamlines/Spectroscopy/Techniques/XAS.html>

## 5. The Theory and Simulations of XAS spectra

Not for all possible chemical environments there are real chemical compounds to be measured at an XAS beamline. In such cases theoretical XAS spectra using the FEFF code can be simulated. The code is licensed, so, not everybody can just use it. Also, understand this: The code will also produce an XAS spectrum (unless there is an error). This does not mean that this represents the “real” spectrum. There can be multiple problems with the crystal structure (being actually wrong or somewhat wrong), the theory not covering the structures you are looking at (the theory is not complicated enough for certain structures) or other issues.

Every theoretical calculation starts with a crystal structure. These can be found at crystal structure databases and mainly have a .cif ending. They can be loaded with atoms.exe and create a feff.inp file to be loaded into FEFF.

The center or core is the absorbing atom you choose. This is usually a metal (e.g. Ag for AgO). This is depicted in Fig. 5.1. Take AgO for example (even though this structure does not look like Fig. 5.1). The center or absorbing atom here is Ag. The atoms in the first shell (blue ring) are all O. The atoms in the next second shell (pink ring) are Ag again and in the third shell O (green ring) again.

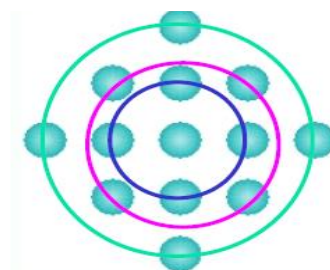


Figure 5.1: Coordination shells around the absorbing atom

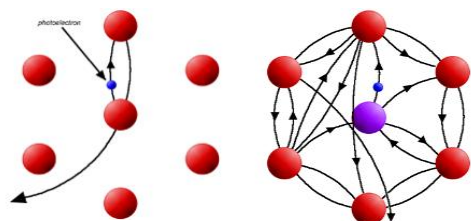


Figure 5.2: Scattering of the photoelectron in the environment of the absorbing atom

The theory involves further the basic idea of how is the photoelectron that leaves the absorbing atom “quasi free” affecting the neighboring atoms. In one picture the photoelectron is a ball scattering with the neighboring atoms: possible is single scattering (left) or multiple scattering (right) as depicted in Fig. 5.2. Single scattering is the main process for EXAFS while multiple scattering mainly contributes to XANES.

As an example see Fig. 6.1 below: AgO actually contains some silver atoms in oxidation state +1 (Ag1) and some in oxidation state +3 (Ag2). In order to correctly display and calculate a spectrum Ag1 and Ag2 need to be used a core in 2 separate calculations. A LCF for this case can show that about 1/3 of Ag atoms are in oxidation state +1 and the other 2/3 have 2+.

## 6. How to Publish the Data

Using the Athena or Artemis program you can produce nice pictures that can be included in Word documents quite easily (press the left most button on the picture screen called “copy to clipboard” and press “paste” in the word processor). However, this format is not accepted in publications. The user should be able to produce figures with other programs (Igor Pro, Origin, etc.).

Example:

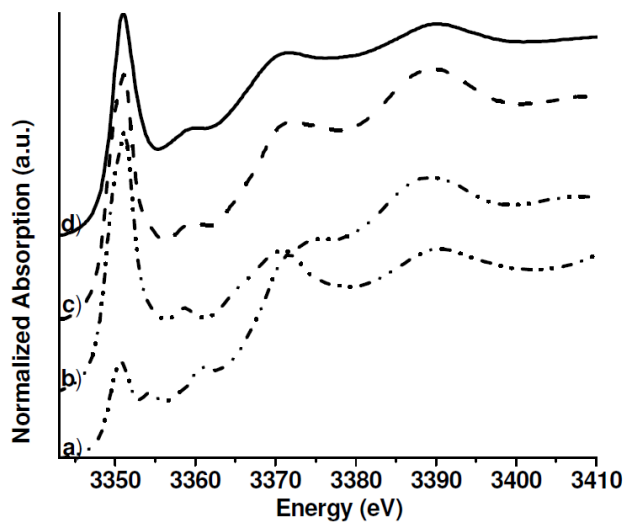


Figure 6.1: Ag L3-edge XANES spectra of AgO (d) and FEFF simulated spectra of the two core Ag1 (a) and Ag2 (b) and the LCF of Ag1/Ag2 to produce a fit to compare with the experimental data (c)

Aspects of Fig. 6.1:

- Experimental data is plotted in as a solid line.
- Simulated data or LCF are plotted in dotted/ dashed or other lines.
- In some cases (not here) the LCF and experimental data can overlap to show the good agreement with the fit.
- Spectra should be displayed stacked for better viewing.

For a good publication it is necessary to have good data and clear figures. The next requirement is to clearly describe the important features of the spectra, for example, where the white line has a maximum for each unknown sample and for the reference compounds.