Lecture 4

Fine Structure Spectroscopy

4.1. Absorption and Transmission of X-Ray through Matter

When an X-ray beam passes through an absorbing medium several important processes take place, namely scattering, ionization, excitation, heating and breaking of molecular bonds. The four major processes are photo absorption, coherent scattering (Rayleigh scattering), incoherent scattering (Compton scattering), and pair production. Consequently, the initial beam is absorbed, reflected or transmitted through the matter. The absorption of energy, on the other hand, is directly related to excitation of atoms or molecules of the matter and emission of characteristic x-rays from the irradiated material.

The attenuation of the x-ray depends on various absorption processes, and is well described by a general exponential behavior in nature. Lambert's law states that equal paths in the same absorbing medium attenuate equal fractions of the radiation. Suppose that for the path length dx, the intensity I is reduced by an amount dI. Then, the intensity can be described by equations of the following form:

$$\frac{dI}{I} = -\mu_1 \cdot dx, \quad I = I_0 \cdot e^{-\mu_1 x}, \qquad (4.1)$$

where μ_l is the linear attenuation coefficient which depends on the state (gas, liquid or solid) of the material. Therefore, it is useful to define the mass attenuation coefficient μ_m, that is independent of the particular phase of the material. Consider an x-ray beam of intensity I with a unit cross-section crossing along a path length of dx in a material with the density ρ. In this layer,

$$\frac{dI}{I} = -\mu_m \cdot dm = -\mu_m \cdot \rho \cdot dx, \qquad (4.2)$$

Where $m = \rho x$ is the mass per unit area, or area density, in $g \cdot cm^{-2}$. Equation (4.2) represents the so called *Bouguer-Lambert-Beer exponential attenuation law*. The mass attenuation coefficient $\mu_m = \mu_l / \rho$ [cm^2/g] is a characteristic value of the substance.

4.2. X-ray Absorption Fine Structure

When an x-ray beam passes through a medium, fractions of the x-rays are absorbed in it so that the intensity of incident x-ray beam is attenuated. The relationship between the incident beam intensity I_0 and the transmitted intensity I through an absorbing medium with thickness t is described by the Lambert's law,

$$I = I_0 \, exp \, (-\mu t) \qquad (4.3)$$

where μ is the absorption coefficient. The absorption coefficient for pure element matter generally shows a monotonic decrease with x-ray energy, but with a sharp discontinuities characterized by sudden increases at certain energies, corresponding to inner-shell ionization.

When observed with good energy resolution (eV range), these so-called absorption edges exhibit fine structures. In the early days around the 1920's the structures within 20 eV of the edges were known as a Kossel structure and were attributed to bound excited states. The features observed above the edge beyond about 20 eV were known as the Kronig structure. This division between structures below and above 20 eV from the edge was maintained for a long time. For complex matter, the structure was used to separate the low-energy range strongly affected by the electronic structure of individual atoms from the high-energy range affected by the local spatial structure of neighboring atoms. The Kossel structure of the x-ray absorption fine structure is now called XANES (x-ray absorption near-edge structure), which provides information on the valence state of the elemental atom [1, 2].

XANES and EXAFS (extended X-ray absorption fine structure) have now been widely applied to the fields of biology, material science, fundamental physics, and are known generically as XAFS (X-ray absorption fine structure) spectroscopy, carried out by measuring the x-ray absorption of a substance as a function of energy [3].

4.3. EXAFS and XANES

The electromagnetic wave loses its energy because of the interactions with various motions of an atomic nucleus or electrons within a material. X-ray is also absorbed in materials as a result of the interaction with them. If the x-ray beam is irradiated to a certain material, many phenomena can be observed, for example the Compton, elastic and Raman scattering, the generation of fluorescence x-ray, photoelectrons and Auger electrons. According to materials and energy of the incident x-ray, the generation probabilities of them have their own values. The x-ray absorption

spectra are obtained by measuring the intensities of the incident and transmission x-rays according to the continuous change of the incident x-ray energy. The proportional values of the mass attenuation coefficient, which is *ln (I_0/I)*, are plotted at each energy of the incident x-ray.

Each element has its own ionization energy. The inner electron jumps out as a photoelectron after the absorption of higher energy x-ray than its ionization energy. Therefore, the absorption of the incident x-ray rapidly increases at the ionization energy. By making the detailed investigation into the absorption spectrum, the fine structure is observed in the energy range from the absorption edge to about 1000 eV. This fine structure is called XAFS (x-ray absorption fine structure). The fine structure near the immediate vicinity of the x-ray absorption edge is called x-ray absorption near-edge structure (XANES). Beyond the XANES region, starting about 30-40 eV above the edge absorption maximum, are the fine structure oscillations now generally termed extended x-ray absorption fine structure (EXAFS) [4].

The reason why the fine structure appears in the absorption spectrum is explained by the interference of photoelectrons in the EXAFS region. When an atom absorbs the x-ray energy, the inner shell electrons separate from the binding of the atomic nucleus and jump out as photoelectrons. If the atom is isolated, the photoelectrons are described as the dispersing spherical wave and able to occupy any energy states. Therefore, in this case, the fine structure does not appear in the absorption spectrum. However, in the case of the atom surrounded by other atoms, the probability of the backscattering of photoelectrons is generated and the transition probability is modulated by the interference with it. As a result of it, the fine structure appears in the absorption spectrum. The cyclical structure is not required in the measured sample because EXAFS is the local physics phenomenon around the center atom absorbing x-ray. Therefore, EXAFS analysis can determine the number, kind and distance of the surrounding atoms for the materials that do not display the distinct diffraction patterns, such as amorphous, liquid, molecules and fine grains. The features of EXAFS analysis are described as follows,

a. It can measure the samples with any phases.
b. It can to determine the kind and number of surrounding atoms.
c. It can determine the distance between the center and surrounding atoms.

On the other hand, EXAFS analysis has some defects as follows.

    a.   The information obtained by this analysis is limited in the area, which is extremely near the center atom (maximum to 5 or 6 angstroms).

    b.   The procedures of this analysis include voluntariness.

    c.   It is difficult to measure the light elements.

The origin of XANES is different from that of EXAFS. Because of the electron multiple-scattering process occurring in the XANES range, the spectra do not depend only on atomic distances and coordination numbers but also to some extend on higher-order correlation functions like bond angles or the ratio of distances of the x-ray absorbing atom to its first and second shell neighbor atoms [5]. In the molecular-orbital concept, XANES spectral features are sensitive to the electron structure. On the other hand, in a multiple-scattering one, XANES spectral features are due to the interference effects in the final state by multiple scattering of photoelectrons with neighboring atoms mainly depending on the local geometry. However, the two concepts could not be eventually differentiated because the electronic configuration and the local geometry are closely correlated with each other [6]. The interpretation of XANES is complicated by multiple-scattering effects as well as by the nonvalidity of the plane-wave-scattering approximation applicable in the EXAFS range.

4.4. Measurement Procedure

In transmission mode, the incident and transmitted x-ray are detected by ionization chambers. They make use of the ionization of the gas within them induced by the incident x-ray beam radiation between the flat plates with several hundreds of voltages. However, the ionization chamber can not distinguish the energy. Therefore, it is necessary to eliminate the higher harmonics. Beam line 39XU in SPring-8 is equipped with an in-vacuum type undulator and a rotated-inclined double-crystal monochromator. A combination of the fundamental and third harmonics of the undulator with an Si (111) reflection of the monochromator covers the energy range from 5.7 to 37 keV. A platinum-coated plane mirror is used to reduce the amount of higher harmonics to less than 10^{-4}. The glancing angle can be changed from 2 to 9 μrad with a cut-off energy as low as 8 keV. The signals detected by the ionization chamber are amplified and converted to electric pulses by V-F converter. They are counted and displayed on the screen.

In fluorescence mode, the fluorescence x-ray is detected by SSD. In order to correspond to the absorption coefficient, the intensity of it is divided by that of the incident x-ray beam.

4.5. Experimental Layout for XAFS Analysis

The experimental layout of XAFS analysis is shown in figure 4.1. The sample to be analyzed is irradiated with the monochromatic X-ray beam, and the beam energy varied in appropriate small increments to enable observation of the structure. The incident and transmitted beam intensities are monitored by ionization chambers. In the case of low absorption, for example when thin samples are analyzed, $\mu t \cong 0$, the Lambert's equation can be approximated as follows:

$$I_0 - I = I_0 \left(1 - \exp(-\mu\ t)\right) \cong I_0 \mu\ t \qquad (4.6)$$
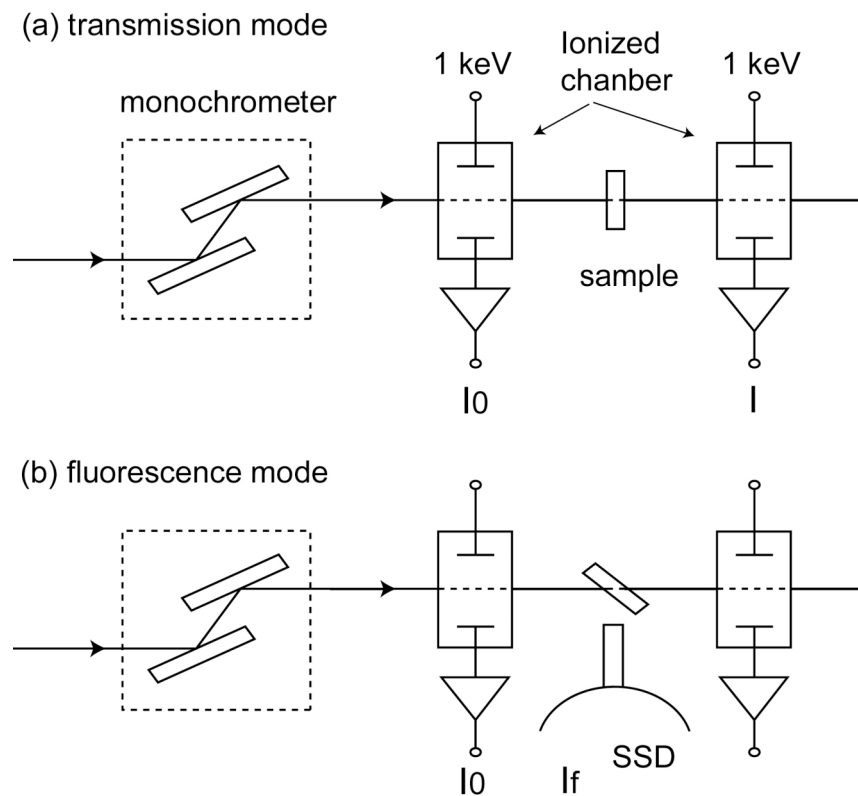
Figure 4.1. The experimental setup for XAFS. (a) Transmission mode. (b) Fluorescence mode.

4.6. Chemical Shift

X-ray absorption near edge structure (XANES) is sensitive to the valence state and neighboring atoms of the absorbing elements, especially the relative position of absorption edge known as chemical shift. K-edge x-ray absorption reflects the transition probability from a $1s$ orbital to the unfilled conduction band.

The effect of oxidation state on chemical shift is significant for biological applications. The chemical state of iron in a biological specimen is complex because the chemical state of iron is a mixture of some kinds of states. However, the chemical shift of x-ray absorption edge structure of iron provides information from which the oxidation state of iron can be obtained. An example of Fe K-edge XANES spectra obtained from a biological specimen is shown in figure 4.2. The XANES spectra of reference samples show that the absorption edge of iron with high valence state is shifted to higher energy. In figure 4.2, the shift of sample (b) is larger than that of sample (a), therefore it can be concluded that iron contained in the sample (b) has higher oxidative state that in sample (a).
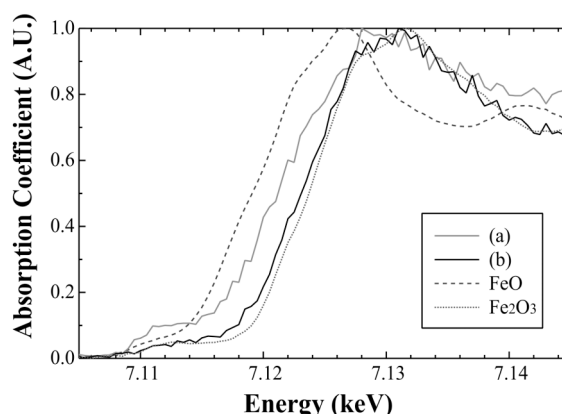
Figure 4.2. Fe K-edge micro-XANES spectra measured in neuromelanin granules within a surviving neuron (a) and in neuromelanin aggregates from a dead neuron (b) with Parkinson's disease. This figure is referenced from Yoshida, et al 2001.

4.7. Chemical State Imaging and Selectively Induced X-ray Emission Spectroscopy

X-ray absorption near edge structure is sensitive to the valence state and neighboring atoms of the absorbing elements. The chemical shift of absorption edge can be used for chemical state analysis. If the incident energy near the absorption edge is chosen properly, selective excitation of specific chemical species will occur. Since fluorescent x-rays are emitted accompanied with the excitation of the absorbing elements, the differences of fluorescent yield can be observed in between different

chemical species. Here, XANES spectra of FeO (Fe^{2+}) and Fe_2O_3 (Fe^{3+}) are shown in figure 4.2. At energies above the absorption edge, such as 7.160 keV, both Fe^{2+} and Fe^{3+} are excited. On the other hand, at energies near absorption edge, such as 7.120 keV, Fe^{2+} is selectively excited and the excitation of Fe^{3+} is suppressed. Using this phenomenon, the yields of Fe^{2+} and Fe^{3+} can be separated [10]. Using the technique, XRF imaging that distinguishes chemical state can be obtained.

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