XAS is a general name for all X-ray absorption spectroscopy. Common used techniques are XANES (X-ray absorption near edge structure) and EXAFS (Extended X-ray absorption fine structure), which are distinguished by their different energy region. XANES can be applied on determine the oxidation state and coordination, so widely used in transition metal complex study. EXAFS is more sensitive to the local structure of atoms enable it used to determine crystal structure without perfect long-range order. The application of XAS will be related to several fields, especially biochemical, environmental, and catalysis chemistry.

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1. Principle of XAS

X-ray absorption spectroscopy has some similarity with the UV-Vis absorption spectroscopy by the principle of investigating the difference between the intensity of incidence light and transmitted light. As showing below, when the x-ray interact with a sample, several interaction occurred, including scattering, fluorescence light emission, Auger emission, and transmission. So XAS will have different detection mode by different purposees. In transmission mode, XAS detect the transmitted x-ray, which then can tell the types of atoms due to different absorption edge energies for different atoms.
If the incident intensity of X-rays is $I_0$, and the transmitted intensity is $I$, with a fixed thickness of sample $x$, XAS will obey an equation:

$$\ln \left( \frac{I_0}{I} \right) = \mu x$$

Different types of atoms will give different value of $\mu$.

When the x-ray is "absorbed", what really happened is the radiation knocked the inner electrons out of the atom, which is continuum state, and then gives out as photoelectron. The energies used to overcome different layers of binding energy are absorption edge. The absorption edge is named by the orbital shell the electron coming from. So K edge is the transition that electron was excited from 1s orbital, and L edge if electron was excited from 2s, 2p, M edge if electrons excited from 3s, 3p, 3d as shown in figure 2.

For light elements, the energy of K edge is not high so usually it is available. But for heavy element, such as many transition metals, especially late transition metals, the energy of K edges are too high to find proper X-ray source. In that case, L or M edges will be used to investigate samples.
The X-ray absorption spectrum consists of two different regions, the XANES and the EXAFS regions. The XANES region includes the region before the absorption edge to the beginning of the EXAFS region (about 50eV above the absorption edge).

The EXAFS region usually starts from the point where the wavelength of photoelectron equals the distance between the absorbing atom and the closest neighboring atom to the point about 1000 eV past the inflection point of the absorption edge[1-2].

Figure 2 Transitions resulting from absorption of X-ray

Figure 3 Different region in XAS spectra
2. XAS Instrumentation

The source of X-rays for XAS experiments could be a X-ray tube or synchrotron. Once the X-rays are created, they are passed through a monochromator to separate into single energies. Then they are passed through a slit. The slit is used to reduce the scatter that may produce from components of the beam line. Detection modes for an XAS analysis depend upon the sample types and concentration. Usually in transmission mode, ionization chambers based on ionization of noble gases by photons can be used to detect transmission X-rays, followed by signal processing[3-4].

![Figure 4 Schematic Diagram of transmission XAS Instrument](image)

3. Basic Observable Characteristics

3.1. XANES and Oxidation state

An important information included in the XANES spectrum is the oxidation state of elements. The oxidation state of an element can influence the position of the XAS absorption edge. The most important features existing in XANES spectroscopy are the pre-edges and the white-lines. Pre-edge features are due to the electron transitions from the core level (1s) to the higher unfilled or half-filled orbitals. For same metal atoms in different oxidation states, the pre-edge features could be much different. At the L\text{III} edges in heavier elements, electronic transitions of p electrons into the d and f orbitals are known as white lines, which are only observed in elements with partially filled d and f orbitals. The intensity of a white line is proportional to the number of unfilled d or f states and also depends on the oxidation state of metal ions[1-2]. Besides of oxidation state, the geometry and coordination also are important factors to influence the chemical shift of absorption edges on XAS.

3.2. EXAFS and Geometry/Bond length

In the EXAFS region, the most important feature is oscillations. When a photoelectron interacts with its neighboring atoms, it will be scattered. In the XANES, multiple scattering patterns will be dominant. In contrast, in the EXAFS region single scattering pattern would be the mainly pattern. The interactions among the scattering and backscattering photoelectron waves produce the EXAFS oscillations (Figure 5).
This oscillation is a radial distribution that decay quickly with the distance from the absorbing atom which limits EXAFS to investigate local structures. Information of atomic distances and nearest neighboring atoms can be extracted from the EXAFS. For metal-ligand bonds between same elements, the first EXAFS peak would show at the similar positions, but small oscillations following the first peak will be different to indicate different geometry or coordination environment\[1-2\]. Similar information can also be extracted from XANES based on its multiple scattering, but would be more complicated than EXAFS.

4. Application

4.1. Biochemical Application

4.1.1. Protein XAS

Many techniques have been applied to study the structure and components of protein, such as XRD and solid NMR. But there is one major problem for these methods that surfactants or salts would be used to grow crystals or precipitate the protein to prepare samples. This causes some concerns about the validity of the data. One major advantage of using XAS to study proteins is that this technique can be applied to the sample of crystal, solution or amorphous form, so the raw sample can be studied without further treatment and the interactions of metals in protein could represent a more real state of the interactions between proteins and metal ions. XAS has been used to determine the coordination of metals, metal binding sites in proteins, the local structural environment of metal binding to proteins, and the oxidation states of metals in protein systems\[^{[5]}\].

L-edge of Fe was used to study the active center of catalase which has similar reported haem groups with methaemoglobin but different function towards hydrogen peroxide, the former can decompose it to H\(_2\)O and O\(_2\), but the latter has no such function. Previous research has revealed different conformation of haem groups in catalase and methaemoglobin, and different residues binding with catalase (Tyr) and methaemoglobin (His). The function of catalase was ascribed to the formation of Fe\(^{4+}\). In this research, L\(_{II/III}\)-edge XAS of iron was carried out in physiological conditions. On the XAS, doublet peaks of L\(_{III}\)pre-edge are derived from transitions of p-d\(_{xy}\), d\(_{xz}\), d\(_{yz}\) and p-d\(_{z^2}\), d\(_{x^2-y^2}\) and indicate...
Fe$^{3+}$ ($d^7$) was in high spin states. And the intensity ratio between the two components of the doublet peaks varies from methaemoglobin to catalase. This result can be explained by different occupancy of $d_{xy}$, $d_{xz}$, $d_{yz}$ and $d_{z^2}$, $d_{x^2-y^2}$, which was caused by ligand donation and metal back-bonding. Combined with charge-transfer calculation, the author thought the activity of catalase was from strong metal back-bonding which are much weaker in methaemoglobin. Metal back-bonding increased the delocalization of electrons which can facilitate electron exchange in the catalytical circle[6].

4.1.2. Metal Interactions with Living Systems

XAS is also used to study transition metal in living plant or trace metal left in vegetables. In some cases, oxidation states change can be observed in specific part of plants. The recent development of X-ray focusing optics has extended XAS application to single cell analysis and enabled the characterization of the local structure (oxidation state, site ligation, and coordination) of the elements within subcellular structures[7-8].

4.2. Environmental Application

4.2.1. Metal Phytofiltration and Phytoextraction Systems

In environmental field, most samples show amorphous state in nature, which limit the application of XRD. From the advantage shown above, XAS has been widely used in this field. The use of biomaterials to remove toxic heavy metal ions from contaminated waters has been a research hot-point recently. Investigators have found that XAS is an powerful tool to study the interactions of metals with dead (or inactivated) plant material. One XAS research showed inactivated alfalfa biomass can reduce gold (III) to gold (0) and chromium (VI) to chromium (III) in waste water[9-10]. Much research has proven biomass can be used to remEDIATE metal contamination water. But identifying the absorption sites in biomass would be another problem. In another research, XAS was used to study lead binding mechanism using alfalfa biomass. The experiment was carried out at Pb LIII edge and there are three kinds of samples investigated, including sample without chemical modification, esterification sample and hydrolysis sample. The results showed esterification of available carboxyl groups on biomass can dramatically weaken its efficiency to remove lead from waste water. And hydrolysis sample showed even much higher efficiency than the sample without chemical treatment. So the research indicated the carboxyl groups contained in biomass play the key role in its absorption activity towards lead[11].

4.2.2. Soil

Soil metal-contamination has been a serious environmental problem. Metal toxicity greatly depends on the oxidation state, which is one of the most useful information given by XAS. The intensity of pre-edge absorption for chromium (VI) has been used to calibrate the concentration of chromium (VI) in simulated soil samples[12].

In another research of soil, copper was selected to study its uptake absorption behavior in five vineyard soils and under variant pH and metal concentration conditions. The experiment was carried out at Cu K-edge and soil structure and components were characterized through XRD and XPS. The research showed five samples has similar trend of kinetic behavior when conditions were changed. On the XANES spectral, weak pre-edge feature (1s-3d) can be observed.
The big peak before the edge was ascribed to 1s-4p absorption, which indicated a distorted tetragonal geometry. The absorption energy difference between 1s-4p and 1s-continuum can be used to estimate the bond length of Cu-Ligand. By compared with bond length from other research, it was believed that copper was absorbed by organic matter in soil. Four Cu-O with equal bond length and two axial Cu-O with different bond length can be extracted from EXAFS and suggested a distorted octagonal coordination, which was derived from Jahn-Teller effect for a typical Cu$^{2+}$(d$^9$)[13].

4.2.3. Metal Ion Interactions with Mineral Surfaces

Some researchers proposed that minerals may be a method to remediate or mitigate metal pollution, because mineral surfaces provide a coordination environment for metal ions. XAS was used to study selenate and the result showed selenate can adsorb onto goethite (an iron hydroxide mineral) by forming an inner sphere surface complex. Selenate was bound to the iron centers in the goethite[14].

The local structures of Cr, Cu, Zn, Cd, Hg, Pb on clay mixture system were studied with EXAFS. The experiments were carried out in K-edge of Cr, Cu, Zn, Cd and LIII edge of Hg, Pb. The mixture clay consists of several minerals, such as illite, kaolinite, carbonate fluoroapatite and smectite. The Cr$^{3+}$ EXAFS suggested it forms one dimension chain on the surface of mineral through Cr-O bonds. The data of Cu$^{2+}$ fits well with the situation in phosphate, so that means copper atoms were absorbed on mineral through oxygen atom from phosphate groups. EXAFS indicated a polymeric structure of Zn$^{2+}$ on the surface of mineral by forming Zn-O bonds with mineral and O bridge between Zn atoms. Cr$^{2+}$ could be in its hydrated form when it precipitates on the surface of clay. The local structure of Hg$^{2+}$ depends on pH values. In low pH region, there will be some Hg$^+$ existing. The absorption experiment proved lead strongly absorbed on clay, but its EXAFS was very weak, so the author thought it means it has no well defined structure on surface of clay. This research provided useful reference to choose mineral and remove metal from solution[15].

4.2.4. Ash and Particulate Matter

XAS has been used to study the speciation of metals in ash and particulate matter (PM) which are easily transported throughout the atmosphere and can cause adverse health effects. In the investigation of the speciation of copper in solidified fly ash, researcher found copper coordinates to about three oxygen or nitrogen atoms. XAS research indicated the copper in the fly ash was present in several forms including copper (II) chloride, copper (I) oxide, copper (II) hydroxide, and copper (II) oxide. XAS was also used to determine the relative amounts of Cr (VI) and Cr (III) in coal combustion by-products, fly ash and bottom ash[16-17].

XAS was used to study the mechanism of chlorination in fly ash. Real fly ash was selected to carry out the experiment at K-edge of Cl and its composition was determined which contains carbon, chlorine and several kinds of metal atoms. Several model fly ash sample were also prepared and examined. Dioxin was measured as the major chlorinated compounds in this research. Interaction between chlorine and metal was thought to be the driving force of dioxin formation. By adding different metal chlorides to prepare model samples and comparing the amount of formed dioxin, the research revealed Cu, Fe and Zn has strong effects on formation of dioxin at 300K or higher temperature. In contrast, Na and K has weak effect on formation of dioxin. So removing trace metal from fly ash could be a promising way to reduce dioxin discharge[18].
4.3. Catalysis Application

For its advantage in situ study, XAS has been used in both heterogeneous and homogeneous catalysis research. XAS was used to determine reaction intermediates, catalytic active sites, gas absorption behavior on metal cluster, oxidation state of active species, and geometry of catalyst in active states. Investigations of liquid samples using time-resolved XAS (TR-XAS) at synchrotron radiation sources can be performed in the range from 100 fs to minutes or above. In the picosecond and nanosecond time domains, this technique permits to obtain structural dynamic information of excited states and transient species of photochemical reactions. At time order from milliseconds to seconds (homogeneous or heterogeneous catalyzed reactions), this technique permits to determine structure of intermediate species that are within this time scale. Very dilute samples such as reactions involving enzymes cannot be measured in transmission mode and therefore for such materials it was often done by combining standard fluorescent XAS measurements with stopped-flow freeze-quench methods. The rapid freezing can trap the system at different stages of the reaction[19].

In a CO oxidation study, EXAFS showed that supported Pt particles form a Pt-oxide overlayer above 225°C under oxygen, which is highly active for CO oxidation. Research also found the formation of Pt-oxide overlayer accompanied with the initiation of the oxidation reaction, which indicated that the oxide overlayer was crucial for catalytic activity[20].

Changes in the reactivity of supported oxides in catalytic reactions induced by the doping agents can be ascribed to changes in the structure of the supported phase or changes in the electronic state of the active sites. The effect of Sm-doping in the XAS spectra of well-dispersed V_2O_5/A_12O_3 samples was studied using XAS. Both V K-edge EXAFS data and XANES spectra indicated that tetrahedral coordination of V atoms exist in all the samples under study. The normalized intensity as well as and the position of V^{5+} pre-edge peak (ls-*3d transition) are dependent on the V loading and the amount of the Sm dopant. The intensity of this peak increasing after Sm doping suggested that the electronic density in V(3d) levels increases[21].

The Michael addition of β-dicarbonyl compounds is one of the most important C–C bond forming reactions in organic chemistry. The most efficient system is based on the iron (III) salts FeCl_3.6H_2O and Fe(ClO_4)_3.9H_2O as catalysts. Under reaction conditions, XAS was used to study a model homogeneous iron-catalyzed Michael addition reaction. EXAFS analysis and XANES measurements were used to determined the real catalytically active compound in solution. The results also proved that chloride ion can coordinate to available iron catalyst centers and act as catalyst poison[22].

On the benefit of indifference to samples and the techniques developed to measure active species in situ or quench intermediates, XAS has found its wide application in several research fields. In future, development of instrumentation will permit XAS to monitor/measure more accurate and extend its application to more fields.

5. References

4. J. G. Parsons, M. V. Aldrich, Environmental and Biological Applications of Extended X-RAY Absorption Fine Structure (EXAFS) and X-RAY Absorption Near Edge Structure (XANES) Spectroscopy, Applied Spectroscopy


6. External links

- X-ray absorption spectroscopy
- XANES measurements and interpretation
- The fundamentals of XAFS
7. Contributors

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