PART 2

In-situ X-ray Absorption Spectroscopy
CHAPTER 5

X-ray Absorption Near Edge Spectroscopy

F. M. F. de Groot¹, A. Knop-Gericke², T. Ressler²,
J. A. van Bokhoven³

¹Department of Inorganic Chemistry and Catalysis, Utrecht University,
Sorbonnelaan 16, 3508 TB Utrecht, The Netherlands

²Fritz-Haber-Institut der MPG, Department of Inorganic Chemistry,
Faradayweg 4-6, 14195 Berlin, Germany

³Laboratory for Technical Chemistry, ETH Hönggerberg, CH-8093
Zurich, Switzerland

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Email: f.m.f.degroot@chem.uu.nl

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**PREFACE**

X-ray Absorption Spectroscopy (XAS) using synchrotron radiation is a well-established technique, providing information on the electronic, structural and magnetic properties of matter. In X-ray absorption, a photon is absorbed by the atom, giving rise to the transition of an electron from a core state to an empty state above the Fermi level. The absorption cross-section depends on the energy. To excite an electron in a given core-level, the photon energy has to be equal or higher than the energy of this core-level. This gives rise to the opening of a new absorption channel when the photon energy is scanned from below to above this core-level energy. The energy of an absorption edge, therefore, corresponds to the core-level energy which is characteristic for each element, making X-ray absorption an element-selective technique.

In general, two regions can be discerned in X-ray absorption spectra: the X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) regions. The spectral shape in the near-edge region is determined by electron correlation and density of states (multiple scattering) effects, and gives mainly information about the electronic properties and the local geometry of the absorbing atom. The EXAFS region is dominated by single-scattering events of the outgoing electron on the neighboring atoms, giving information about the local atomic structure around the absorbing site. In this chapter we will treat the theoretical basis of XANES, while EXAFS spectroscopy will be described in the next chapter.

A number of reviews and special issues of journals have been dedicated to XANES and EXAFS analysis of catalysts in the last few years. In particular, we would like to mention the review of Fernandez-Garcia [1] and the volumes 10 nos. 3–4 and 18 nos. 1–2 of Topics in Catalysis. In addition, the proceedings of the XAFS conferences contain a section dedicated to XAS of catalysts. The last two proceedings have been published in the Journal of Synchrotron Radiation Volume 6 part 3 (1999) and Volume 8 part 2 (2001).

**1. INTRODUCTION**

XANES is an important tool for the characterization of materials as well as for fundamental studies of adsorbates, surfaces and solids. The particular assets of XANES spectroscopy are its element specificity and the possibility to obtain detailed information in the absence of long-range order. Below, it will be shown that the X-ray absorption spectrum, in many cases, is closely related to the density of empty states of a system. As such, XANES is able to provide a detailed picture of the local electronic and geometric structure of the element studied.

1.1. **Interaction of X-rays with Matter**

In XANES, the absorption of X-rays by a sample is measured. Figure 1 shows that the intensity of the transmitted beam ($I(\omega)$) at a certain energy is related to the intensity of the beam before the sample ($I_0(\omega)$) divided by an exponential containing the length of the sample ($x$) multiplied by the absorption cross section $\mu(\omega)$:

$$I(\omega) = I_0(\omega)e^{-\mu(\omega)x}$$  \hspace{1cm} (1)

This equation can be rewritten as the energy dependence of the absorption cross section $\mu(\omega)$:

$$\mu(\omega) = \frac{1}{x} \ln \frac{I_0}{I}$$  \hspace{1cm} (2)

The XANES spectrum is given by the absorption cross section $\mu$. An X-ray photon acts on charged particles such as electrons. As an X-ray passes an electron, its electric field pushes the electron first in one direction, then in the opposite direction. In other words, the field oscillates in both directions and strength. In most descriptions of X-ray absorption, one uses the vector field $A$ to describe the electromagnetic wave. The vector field $A$ is given in the form of a plane wave of electromagnetic radiation:

$$A = \hat{e}qA_0 \cos(kx - \omega t) = \frac{1}{2} \hat{e}qA_0 e^{i(kx - \omega t)}$$  \hspace{1cm} (3)

The cosine plane wave function contains the wave vector $k$ multiplied by the displacement $x$ and the frequency $\omega$ multiplied by the time $t$. The cosine function is rewritten as an exponential function, for which only the absorbing $e^{-ix}$ term has been retained. $\hat{e}$ is a unit vector for a polarization $q$.

The transition operator $T$, describing the interaction of X-rays with electrons, can be approximated in perturbation theory and its first term can be written as:

$$T = \frac{\hbar}{mc} \hat{p} \cdot A = \frac{\hbar}{mc} \hat{p} \cdot \frac{1}{2} \hat{e}qA_0 e^{ix}$$  \hspace{1cm} (4)

The electric field $E$ is collinear to the vector field, in other words, this term can also be understood as the electric field $E$ acting on the electron moments. The proportionality factor contains the electron charge $e$, its mass $m$ and the speed of light $c$. The Golden Rule states that the transition probability

![Figure 1. Transmission through a uniform sample.](image-url)
In-situ X-ray Absorption Spectroscopy in Catalysis: 1: In-situ XANES

In-situ X-ray Absorption Spectroscopy in Catalysis: 1: In-situ XANES

W between a system in its initial state $\Phi_i$ and final state $\Phi_f$ is given by:

$$W_{fi} = \frac{2\pi}{\hbar} |\langle \Phi_f | \Gamma | \Phi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega} \quad (5)$$

The delta function takes care of the energy conservation and a transition takes place if the energy of the final state is equal to the energy of the initial state plus the X-ray energy. The squared matrix element gives the transition rate.

The transition operator contains the $e^{ikr}$ exponential, which can be rewritten as $1 + ikr + \ldots$ using a Taylor expansion. The first term gives the electric dipole transition ($\hat{e}_q \cdot p$) and the second term gives the electric quadrupole transition. The quadrupole transition is smaller by the factor $k/r$, which can be approximated from the edge energy in eV and the atomic number Z, using:

$$k \cdot r = \sqrt{\hbar \omega_{\text{edge}} (eV) / 80Z} \quad (6)$$

In cases when K edges from carbon ($Z = 6, \hbar \omega_{\text{edge}} = 284$ eV) to zinc ($Z = 30, \hbar \omega_{\text{edge}} = 9659$ eV), the value of $k \cdot r$ lies between 0.03 and 0.04. The transition probability is equal to the matrix element squared, hence the quadrupole transition is smaller by approximately $5 \times 10^{-3}$ than the dipole transition and often can be neglected, which defines the well-known dipole approximation. However, in the case of pre-edge structures of the metal K edges, the quadrupole transition is nevertheless important because the 3d-density of states is much larger than the 4p-density of states. Including the dipole operator into the Fermi Golden Rule gives:

$$W_{fi} \propto \sum_q |\langle \Phi_f | \hat{e}_q \cdot r | \Phi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega} \quad (7)$$

1.2. Basics of XANES Spectroscopy

If an assembly of atoms is exposed to X-rays, it will absorb part of the incoming photons. At a certain energy, a sharp rise in the absorption will be observed (cf. Figure 2). This sharp rise in absorption is called the absorption edge.

The energy of the absorption edge is determined by the binding energy of a core level. Exactly at the edge, the photon energy is equal to the binding energy, or more precisely the edge identifies transitions from the ground state to the lowest empty state. Figure 3 shows the X-ray absorption spectra of manganese and nickel. The L$_{2,3}$ edges relate to a 2p core level and the K edge relates to a 1s core level binding energy.

In the case of solids, a typical XAFS spectrum is shown in Figure 4. Instead of a smooth background, we observe many peaks. The peaks can be explained if we assume the excited electron scatter at neighboring atoms. This results in a series of peaks and valleys due to energy-dependent interference effects. This will be explained in detail in the chapter on EXAFS. In order to arrive at such description, we must assume that the electron excitation process is a one-electron process. This makes it possible to rewrite the initial state wave function as a core wave function and the final state wave function as a free electron wave function ($\epsilon$). This implicitly assumes that all other electrons do not participate in the X-ray induced transition. In this approximation, the (squared) matrix element $M^2$ can be written as:

$$M^2 \equiv |\langle \Phi_f | \hat{e}_q \cdot r | \Phi_i \rangle|^2 = |\langle \Phi_f | \epsilon | \hat{e}_q \cdot r | \Phi_i \rangle|^2 = |\langle \epsilon | \hat{e}_q \cdot r | \epsilon \rangle|^2 \quad (8)$$

The squared matrix element $M^2$ can often be assumed to be constant or only slightly varying with energy. The delta func-

- Figure 2. The X-ray absorption cross sections of manganese and nickel. Visible are the L$_{2,3}$ edges at 680 and 830 eV, respectively, and the K edges at 6500 eV and 8500 eV, respectively.
- Figure 3. The L$_1$ XAFS spectrum of platinum metal. The edge jump is seen at 11564 eV, and above, one observes a decaying background modulated by oscillations.
Figure 4. The schematic density of states of an oxide. The 1s core electron at 530 eV binding energy is excited to an empty state: the oxygen p-projected density of states.

The X-ray absorption selection rules determine that the dipole matrix element $M$ is non-zero if the orbital quantum number of the final state differs by 1 from the initial state ($\Delta L = \pm 1$, i.e., $s \rightarrow p$, $p \rightarrow s$ or $d$, etc.) and the spin is conserved ($\Delta S = 0$). The quadrupole transitions imply final states that differ by 2 from the initial state ($\Delta L = \pm 2$, i.e., $s \rightarrow d$, $p \rightarrow f$). In the dipole approximation, the shape of the absorption spectrum should look like the partial density of the ($\Delta L = \pm 1$) empty states projected on the absorbing site, convoluted with a Lorentzian. This Lorentzian broadening is due to the finite lifetime of the core-hole, leading to an uncertainty in its energy according to Heisenberg’s principle. A more accurate approximation can be obtained if the unperturbed density of states is replaced by the density of states in presence of the core-hole. The single electron approximation as stated in equation 10 gives an adequate simulation of the XANES spectral shape if the interactions between the electrons in the final state are relatively weak. This is the case for all K edges, and to a very good degree, also for all other edges with binding energies above 3 keV, with an exception of the pre-edge structures of the 3d metal K edges.

1.3. XANES Calculations

Equation 11 states that the XANES spectral shape is reflecting the density of states. The density of states of complex systems is usually calculated using Density Functional Theory (DFT) within its local spin density approximation (LSD) [2]. Both band structure methods and multiple scattering calculations can be used. Programs to calculate the X-ray absorption spectral shape include FEFF (http://leonardo.phys.washington.edu/feff/), GNXAS (http://www.aquila.infn.it/gnxas/) and Wien2k (http://www.wien2k.at/). These and other software packages can be found at http://ixs.iit.edu/catalog/ XAFS_Programs.

In these programs, a number of approximations and assumptions are made. Below, we will, in short, sketch some of the important conceptual issues. We will respectively discuss: (1.3.1) many body effects in the ground state, (1.3.2) core hole effects, (1.3.3) multiplet effects, (1.3.4) the influence of the matrix element, (1.3.5) calculations over a large energy range, (1.3.6) approximations in the potential, and (1.3.7) real space versus reciprocal space calculations.

1.3.1. Many Body Effects in the Ground State

The use of the Local Spin Density to calculate the density of states is a poorly justified approximation, and a large number of improvements upon LSD exist. In particular, we would like to mention the generalized gradient approximation (GGA), the GW approach, the inclusion of the Coulomb interaction $U$ into LSD, the inclusion of self-interaction corrections and the inclusion of orbital polarization effects. The recent review of Rehr and Albers [2] discusses these issues in some detail. Within the context of this review, we will not go into detail on many body effects. We would like to indicate though that most XANES programs use LSD, or LSD+GGA, as starting models. This implies that many body effects in the ground state are not treated properly. In the case of correlated electron states, such as the 3d-band in transition metal catalysts, this can introduce serious errors in the (pre-)edge region. A special type of final-state many body effect is the multiplet effect (Section 1.3.3).

1.3.2. Core Hole Effects

Following the final state rule [3], one has to calculate the distribution of empty states in the final state of the absorption process. The final state includes a core hole on the absorbing site. The inclusion of the core hole introduces a significantly larger unit cell in case of reciprocal space calculations. In the case of real-space calculations, the inclusion of a core hole is straightforward and only the potential of the central atom is modified. It has been shown for many examples that the inclusion of the core hole improves the agreement with experiment [4, 5].

1.3.3. Multiplet Effects

The core hole that is part of the XANES final state does not only have an influence on the potential, but the core state also has a wave function. In the case of a 1s core state, this wave function is spherically symmetric (carries no orbital momentum) and sits close to the nucleus, hence far from the valence electrons. This implies that for 1s core holes, one can neglect the effects of the core wave function overlap. In case of 2s and 3s wave functions, the overlap is larger, but the only effect that plays a role is the spin-up or spin-down character of the core hole. The spin-moment of the core hole interacts with the valence electrons (or holes), giving rise to an exchange splitting in 2s and 3s XANES. The same exchange interaction plays a role in 2s and 3s XPS spectra, which are more often studied than their XANES counterparts [6].

Things become dramatically more complex in those cases where a core hole carries an orbital momentum. Very well
known is the core hole spin-orbit coupling that separates the 2p XANES spectra into their 2p(3/2) (L3) and 2p(1/2) (L2) parts. But this is not all: the 2p wave function can have significant overlap with the valence electrons. In case of 5d-systems, the 2p5d overlap is small and can, in first approximation, be neglected. However, in the case of 3d-systems, the 2p3d overlap is significant and, in fact, completely modifies the spectral shape. The term ‘Multiplet effect’ is used to indicate this overlap. The largest effect of core-valence overlap occurs for relatively shallow core states. Multiplet effects play a much larger role for soft X-ray absorption than for hard X-ray absorption. A detailed discussion of their inclusion into XANES simulations is given in the chapter of soft X-rays.

1.3.4. The Influence of the Matrix Element

Equation 11 clearly states that XANES is given by the squared matrix element ($M^2$) multiplied by the density of states. In many cases, the matrix element is (assumed to be) relatively constant over the XANES energy range. For simplicity, this is assumed, and the density of states is directly compared with the XANES spectrum. If one uses the element and orbital momentum projected DOS, the agreement between DOS and XANES is often very good [7], but this is not a general result. It is, therefore, preferable to include the matrix elements into the explicit calculation of the XANES spectral shapes. At this moment, most XANES codes include the matrix elements explicitly [4].

1.3.5. Calculations Over a Large Energy Range

Multiple scattering is particularly appropriate for the calculation of the empty states because they can be easily calculated for arbitrarily large energies. Multiple scattering calculations are usually performed with the Green function approach, where the Green function describes the propagation of the electron in the solid, which is scattered by the atoms surrounding the absorbing atom [8–11]. Band structure codes are used to calculate the optimized structure and, as such, need only to calculate the occupied electron states, i.e., the electron distribution and the accompanying potential. Most of these band structure codes are not easily applicable to the calculation of large energy ranges of unoccupied states. In particular, codes that make use of limited basis sets can be accurate for the occupied states, but inaccurate for unoccupied states in particular at energies more than 10–20 eV above the Fermi level. Recently, some elegant codes have been written that circumvent this problem, and are able to combine accurate band structure codes to optimize the structure with special projection operators to calculate the empty states at all energies [4, 12].

1.3.6. Approximations in the Potential

The approximations made to the electronic potential that is used in the calculations play an important role in their development and improvements. Some fifteen years ago, most DFT codes used various approximations to the potential, such as the atomic-sphere-approximation in LMTO and the muffin-tin approximation in many other codes. Most ab-initio DFT codes use a full-potential description, where these approximations are not made any more. However, the FEFF code still operates under the muffin-tin approximation. The muffin-tin approximation is known to lead to errors in some XANES calculations.

1.3.7. Real Space Versus Reciprocal Space

Because codes such as FEFF perform multiple scattering calculations in real space, the calculations can be relatively easily carried out for disordered systems. The core hole potential on the absorbing atom can be added directly, and one can carry out the multiple scattering in steps of growing cluster size. These advantages probably make FEFF the most popular code for XANES calculations, despite the limitations in the accuracy of the potential. For comparison, both band structure calculations and multiple scattering results will be treated on the same footing, using the ‘density of states’ picture as a guide.

2. EXPERIMENTAL ASPECTS OF XANES

2.1. Transmission Detection of XANES

An X-ray absorption spectrum originates from the fact that the probability of an electron to be ejected from a core level is dependent on the energy of the incoming beam. For this reason, the energy of the X-rays is varied during an experiment. After the beam has passed the monochromator, its intensity ($I_0$) is measured in an ionization chamber using a thin metallic foil, a grid absorbing part of the photons or a photo diode. The X-ray interacts with the sample of interest and the intensity after the sample is measured with a second ionization chamber or a photodiode. This is the transmission mode of X-ray absorption. Transmission experiments are standard for hard X-rays. Figure 5 gives the attenuation lengths of X-rays from 300 eV to 10 keV through C, Fe and Pb. It can be observed that X-rays with energies of less than 1 keV have an attenuation length of less than 1 μm.

![Figure 5. The attenuation length of X-rays through carbon (solid), iron (dotted) and lead (dash-dotted).](https://example.com/figure5.png)
Figure 6 shows the transmission through 1 μm and 10 μm iron and it can be seen that X-rays with energies less than 1 keV have little transmission through 1 μm iron. In addition, X-rays with energies below approximately 3 keV have a large absorption cross section with air, hence the experiments have to be performed in vacuum. We will use 2.5 keV as the boundary between soft and hard X-rays. An important limitation of transmission detection is the requirement for a homogeneous sample. Variations in the thickness or pinholes are reasons for the so-called thickness effect that can significantly affect the spectral shape by introducing a non-linear response [13]. The combination of the extremely short attenuation length with the thickness effect makes transmission experiments not suitable for soft X-ray absorption.

2.2. Yield Detection of XANES

The decay of the core hole gives rise to an avalanche of electrons, photons and ions escaping from the surface of the substrate. By measuring any of these decay products, it is possible to measure samples of arbitrary thickness. An important prerequisite for the use of decay channels is that the channels that are measured are linearly proportional to the absorption cross section. In general, this linear proportionality holds, but there are cases where, for example, the ratio between radiative and non-radiative decay varies significantly over a relatively short energy range [14].

2.2.1. Fluorescence Yield

The fluorescence decay of the core hole can be used as the basis for the absorption measurement. The amount of fluorescent decay increases with energy and a comparison with the amount of Auger decay shows that Auger decay dominates for hard X-ray experiments. The photon created in the fluorescent decay has a mean free path of the same order of magnitude as the incoming X-ray, which implies that there will be saturation effects if the sample is not dilute. Under certain approximations [13], the relation between the intensity of the fluorescence yield $I_f$ and the absorption cross section ($\mu$) can be written as:

$$I_f(\omega) \propto \frac{\mu(\omega)}{[\mu(\omega) + \mu_B(\omega)] \sin \theta + [\mu(\omega_F) + \mu_B(\omega_F)] \sin \gamma}$$

(10)

The absorption cross section $\mu(\omega)$ is divided by the summation of itself, the background absorption below the edge $\mu_B(\omega)$, the absorption at the fluorescent energy $\mu(\omega_F)$ and the background absorption at the fluorescent energy $\mu_B(\omega_F)$. The angular dependence of $\mu(\omega_F)$ and $\gamma \mu_B(\omega_F)$ is given by $\sin \gamma$, where $\gamma$ is the angle between the surface normal and the X-ray beam. In the limit of grazing incidence, $\sin \gamma$ is equal to zero and, essentially, there is no sample penetration, hence any fluorescence. The angular dependence $\mu(\omega)$ and $\mu_B(\omega)$ is given by $\sin \theta$, where $\theta$ is the angle between the surface normal and the X-rays toward the detector. The absorption at the energy of the fluorescent X-rays is usually negligible, which turns $\mu(\omega_F)$ to zero. The background absorption is usually only slowly varying and assuming a constant background implies that we can approximate $\mu_B(\omega)$ and $\mu_B(\omega_F)$ as a constant $\mu_B$. The angle between the penetration and escape directions is usually set to 90 degrees and to simplify the formula, we further assume that the direction of incidence is set at 45 degrees. Including these approximations in equation 13 yields:

$$I_f(\omega) \propto \frac{\mu(\omega)}{\mu(\omega) + \mu_B \sqrt{2} + \mu_B \sqrt{2}} = \frac{\mu(\omega)}{\mu(\omega) + 2 \mu_B}$$

(11)

For dilute materials, the background absorption $\mu_B$ dominates the absorption of the specific edge and the measured intensity is proportional to the absorption coefficient. For less dilute materials, the spectral shape is modified and the highest peaks will appear compressed with respect to the lower peaks, an effect known as self-absorption or saturation.

Figure 7 shows the main effect of self-absorption: a reduction of the peak heights and depths and, as such, a blurring of

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Transmission through air and bulk iron. Given are 10 cm air (solid), 10 m air (dashed), 1 μm iron (dash-dotted) and 10 μm iron (dotted), respectively.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** The effect of self-absorption on the platinum L₂ spectrum measured in fluorescence yield assuming a relative background absorption of $2\mu_B = 1.5$. The transmission spectrum is given with the solid line, and the saturated (and re-normalized) fluorescence spectrum with the dashed line.
the spectral information. Using the inverse of formula 13, one can, in principle, reconstruct the original absorption spectrum from the saturated one. An uncertainty in this procedure is the exact value of $\mu_0$ and, in addition, such data treatment increases the noise.

2.2.2. Partial Fluorescence Yield and X-ray Raman

Recently, it became possible to use fluorescence detectors with approximately 1 eV resolution to tune to a particular fluorescence channel. This can be denoted as partial fluorescence yield. The technique is also known as selective X-ray absorption because one can select, for example, a particular valence and measure the X-ray absorption spectrum of that valence only [15–17]. Partial fluorescence yield can be considered as a coherent X-ray scattering effect and, as such, it effectively removes the lifetime broadening of the intermediate state. This effect can be used to measure X-ray absorption spectra with unprecedented spectral resolution.

Instead of measuring X-ray absorption directly, one can detect the same spectra by measuring the energy loss of hard X-rays. This technique is known as X-ray Raman scattering and allows for the measurement of soft X-ray edges with hard X-rays. The count rate related to X-ray Raman processes are extremely weak and, because of this, the practical application of X-ray Raman seems to be limited to the elements with $Z$ less than 10, including the important edges of carbon, nitrogen and oxygen. With hard X-rays, these edges become accessible at ambient pressures and even at high pressure [18].

2.2.3. Electron Yield

With the total electron yield method, one detects all electrons that emerge from the sample surface, independent of their energy. One can use a number of detection devices: (i) one can detect the current that flows to the sample with a pico-ampere meter, and (ii) one can use a channeltron to amplify the electrons to a detectable signal. The interaction of electrons with solids is much larger than the interaction of X-rays, which implies that the electrons that escape from the surface must originate close to the surface. The chapter on soft X-rays discusses measurements in a gaseous atmosphere. In that case, the detected ionized gas molecules can also yield a signal that is proportional to the absorption cross section [13, 19]. The probing depth of total electron yield lies in the range between approximately 1 to 10 nm, depending on the edge strength and the material studied. A quantitative study on the oxygen K edge of Ta$_2$O$_5$ determined an electron escape depth of 4 nm [20]. Studies of rare earth overlayers on nickel revealed very short escape depths of the order of 1 nm [21].

3. XANES SPECTRAL SHAPE ANALYSIS

An important set of (in-situ) XANES studies of catalysts involve the 1s X-ray absorption spectra, K edges of the 3d-metals. We will discuss, respectively, the shape, energy position and white line intensity of the 1s XANES spectra. The 1s edges of the 3d transition metals have energies ranging from about 4 to 9 keV. Self-consistent full potential multiple scattering calculations have recently been carried out for TiO$_2$ by Cabaret and co-workers [22]. They show that with polarization dependent calculations, the complete spectral shape of TiO$_2$ is nicely reproduced and it can be concluded that the 1s XANES of 3d transition metals does indeed correspond to the metal p-projected density of state. In addition, the pre-edge region is found to be an addition of dipole and quadrupole transitions.

In many applications in catalysis research, the systems studied are not well characterized. The metal 1s edges show fine structure and edge shifts that can be used without the explicit calculation of the density of states. For example, the Fe$^{III}$ edges are shifted to higher energy with respect to the Fe$^{II}$ edges. The shift to higher energies with higher valence is a general phenomenon that can be used to determine the valence of 3d transition metals in unknown systems.

3.1. The Energy Position of X-ray Absorption Edges

It is not a trivial task to determine the energy position of a XANES edge. There are, at least, three different methods to define the energy of the edge:

a. The inflection point
b. The energy where the intensity is 50% of the edge maximum
c. The average of the energies at 20% and 80% of the edge maximum

The inflection point is well defined and can be accurately determined from the maximum of the first derivative. In the case of a single, non-structured edge, the methods (a) to (c) all find exactly the same energy. The situation becomes more complicated with a spectrum for which a clear shoulder is visible on the leading edge. For example, iron metal has an edge on which a clear shoulder is visible. The inflection point might lose its value in such a case and, in fact, there can be two inflection points. In any case, the inflection point can be rather different from the 50% point, and from the average of the 20% and 80% points. In our opinion, there is no clear criterion to decide which procedure should be followed. Much depends on the spectral details of the observed spectra. The best procedure, perhaps, would be the use of two or three methods for edge determination. Differences in the values from the three methods would immediately indicate the presence of additional structure. The edge position does not relate to a physical parameter. Instead, the Fermi level $E_F$ corresponds to the lowest unoccupied state and, formally, $E_0$ is related to the vacuum level, i.e., the energy at which the electron would have zero kinetic energy. The energy difference between $E_F$ and $E_0$ is the work function. The next problem is the determination and use of $E_0$ in an experimental spectrum. Formally, $E_0$ can be determined from a comparison to a theoretical density of states and correcting for the work function. Theoretical simulations, however, are not always available, and one has to resort to a determination of $E_0$ from the experimental spectrum itself. This can lead to the following possible determinations of $E_0$:

a’. The energy of the Fermi level, corrected for the work function (from an alignment with theory)
b’. The onset or energy position of the lowest (pre-)peak visible in the spectrum
c’. The onset of the edge
d’. The edge itself
e’. The energy that is found from an EXAFS fitting procedure

In many papers, the value of $E_0$ is determined from an EXAFS fitting procedure (e’), in which case, it is more often treated as a free fitting parameter, than as an energy that indicates the energy of zero kinetic energy. The use of pre-edges for the determination of $E_0$ is complicated by the fact that they caused by ‘excitonic effects’. At least they are assigned to excitonic effects. The calculations of the K edges of the 3d transition metals clearly show that most of the pre-edge intensity comes from dipole transitions to the 3d-band, i.e., these pre-edges are no excitons and the Fermi level is positioned below these pre-edges. The large variety in $E_0$ determinations makes it impossible to compare values blindly from one paper to another.

Despite the variety of procedures to determine the edge energy and $E_0$, the use of consistent procedures to determine energy positions can lead to clear trends of these energies with the formal valence of the system. The best known example is the determination of the pre-edge energies and the edge energies of a series of vanadium oxides by Wong et al. [23]. They find a linear relation between the edge position and the formal oxidation state. In addition, a linear relation was found between the pre-edge energy and the formal oxidation state. The slope of the pre-edge and edge energies is, however, very different, about 2 eV/valence for the edge energy and 0.6 eV/valence for the pre-edge energy, respectively. This also implies that the energy difference between the pre-edge position and the edge position is linear with the formal oxidation state. An interesting question relates to the relative energy position of the edge and peak position of octahedral and tetrahedral sites. In the case of iron, equivalent energy positions are found [24], whereas for example in the case of titanium, copper and aluminum, a systematic shift is observed with the tetrahedral peak shifted by approximately 1 eV in the case of copper [25].

3.2. The Intensity of the White Line

In Section 1, we have discussed that the XANES spectral shape reflects the density of empty states. An important question about the electronic state of an active catalyst is its number of d-electrons. It would be very important if one could derive the number of occupied d-electrons from XANES. Using the dipole selection rule, this implies that one would need to use 2p (or 3p) core states to probe the d-band. In the case of 3d-systems, this poses a problem because the 2p core states occur at the soft X-ray range between 400 and 900 eV. It will be shown in the chapter of soft X-ray absorption that their spectral shape is completely dominated by multiplet effects, but that careful analysis still allows the determination of the occupation of the 3d-band. The 1s core states are excited into 4p and higher p-orbitals. As such, the K edges do not probe the occupation of the 3d-states. It will be shown below that the pre-edge intensity probes the 3d4p mixing, but not the 3d occupation.

In the case of 4d and 5d, the L1 and L2 edges are separated by a relatively large energy that allows for the separate determination of the L1 and L2 white line intensity. One subtracts the edge jump, for example, from a reference material with full d-band and, as such, one determines values for the L1 and L2 white line area that is related to the empty 3d-states. This allows one to determine a (relative) scale for the number of empty d-states. This technique has often been used, for example, for the determination of the d-occupancy in binary alloys and to compare metals with compounds [26]. In the case of catalysis research, it can be very useful to measure the white line intensity under reaction conditions or, for example, to study the effects of oxidation and reduction. It is one of the few probes to study the effect of hydrogen bonding, as will be discussed in Section 4.4.

The fact that one can measure both the L1 and the L2 edge yields additional information. In principle, the L3 edge and the L2 edge probe the same 5d (or 4d) density of states. One observes, however, that the L1 edge usually has larger white line intensity than the L2 edge. The reason can be found in relativistic effects. The 5d spin-orbit coupling splits the 5d-valence band into two sub-bands. Most papers that analyze the 2p edges of the 5d-elements assume that the $2p_{1/2}5d_{3/2}$ and $2p_{3/2}5d_{5/2}$ transitions are possible. Following band structure results on Pt, a fixed ratio is assumed for these three transitions. The ratio between the $2p_{3/2}5d_{5/2}$ and $2p_{1/2}5d_{5/2}$ transitions is assumed to be 6:1. Detailed analysis shows that the $2p_{1/2}5d_{5/2}$ transition is not completely forbidden [27]. This implies that even in the case of a completely filled 5d$^2$ band (for example, Pt metal), there will be a non-zero white line intensity related to the $2p_{1/2}5d_{5/2}$ transition at the L3 edge. In Section 4.4, we describe the application of the white line intensity determination for the study of hydrogen bonding on alumina supported Pt particles.

3.2.1. Peaks at Higher Energies in the XANES Region

In most studies, only the pre-edge and edge region of the XANES spectrum are used. Some studies use in addition spectral features at higher energies. A well-known example is the use of the $1/R^2$ rule, which relates the energy of a peak in the XANES with the distance R between the absorbing atom and its neighbors. In a sense, this is a scattering (EXAFS) feature in the XANES region. The scattering vector k is proportional to $\sqrt{E_0}$. In the chapter on EXAFS, it is shown that within the single scattering approximation, the distance R is inversely proportional to the scattering vector k, yielding the $1/R^2$ rule. In fact, some additional approximations must be valid such as small variations in the phase shifts (cf. the chapter on EXAFS). The $1/R^2$ rule has been applied successfully for the determination of bond lengths in (adsorbed) small molecules [28]. Kizler analyzed the $1/R^2$ rule for a number of cases and found that, in general, the rule is not very accurate [29, 30].

A rather special rule for peaks at higher energy has been determined empirically for a series of metalproteins [31]. They correlate the intensity ratio of two peaks at 40 to 60 eV above the edge to the out-of-plane position of iron from its porphyrine plane. FEFF8 calculations confirmed that the density of states indeed varies as a function of the out-of-plane distance as found experimentally.
3.3. The Pre-Edge Region

The pre-edge region of the transition metal 1s edges has led to a number of debates regarding the quadrupole and/or dipole nature and possible excitonic effects. The pre-edge region is related to transitions to the 3d-bands. Both direct 1s3d-quadrupole transitions and dipole transitions to 4p-character hybridized with the 3d-band are possible. For the quadrupole transitions, the matrix elements are less than 1% of the dipole transition, but on the other hand, the amount of 3d-character is by far larger than the p-character. Depending on the particular system, this can make the contributions of quadrupole and dipole transitions equivalent in intensity. A direct manner to check the nature of the transitions is to measure the polarization dependence that is different for quadrupole and dipole transitions, respectively. The multiple scattering results of TiO$_2$ reproduce the three pre-peaks that are caused by two effects: (1) the crystal field splitting between the $T_{2g}$ and $E_g$ orbitals, and (2) the core hole effect on the quadrupole peaks shifting them by 2.5 eV with respect to the dipole peaks [32][22]. This assignment is in contrast to the usual assumption that the dipole and quadrupole peaks are positioned at the same energy.

The pre-edge region of iron compounds has systematically been investigated by Westre and co-workers [24]. The pre-edges are analyzed in terms of quadrupole transitions, and analysis showed that the spectra should be interpreted in terms of multiplet theory, including the crystal field and the atomic interactions. The Fe$^{II}$ spectra are calculated from the quadrupole transitions of 3d$^6$ to 1s3d$^6$. The Fe$^{III}$ spectra use 3d$^5$ as the ground state. The fact that the pre-edge region in the case of Fe$_2$O$_3$ is almost completely of quadrupole nature can be shown from 1s2p resonant X-ray emission experiments [33].

The intensity of the pre-edge region is much larger for compounds in which the metal site has tetrahedral symmetry than for octahedral systems. In tetrahedral systems, the local mixing of p and d nature is symmetrically allowed, while for a system with inversion symmetry such as octahedral symmetry it is ‘forbidden’. This rule is relaxed in the solid, and if the density of states is calculated, one finds small admixtures of p-states into the 3d-band even for perfect octahedral systems like SrTiO$_3$ [34]. This admixture is less than admixtures for tetrahedral systems, which explains the small pre-edge. P-character will be mixed into the 3d-band if an octahedral metal site is distorted, the amount depending on the particular distortion. The result is an increased intensity of the pre-edge peak(s). In a recent paper of Arrio and co-workers [35], the pre-edges are calculated with multiplet theory in low symmetry, allowing for the explicit inclusion of the coupling of the dipole and quadrupole transitions. A number of iron mineral pre-edge spectra are divided into their dipole and quadrupole nature, respectively.

The assignment of the pre-edge structures in terms of both quadrupole and dipole transitions, for example, as applied by Westre and co-workers [24], seems to yield a uniform and consistent description of all iron K pre-edge structures. In this analysis, the energy positioned of dipole and quadrupole peaks are assumed to be equal, where this assumption is in agreement with the observation that the peak positions of the octahedral complexes (dominated by quadrupole transitions) are essentially equal to the peak positions of the tetrahedral complexes (dominated by dipole transitions). In contrast, the analysis of the titanium K pre-edge structures of TiO$_2$ clearly shows an energy shift of 2.5 eV between the dipole and quadrupole peaks. In the case of iron pre-edges of low-spin Fe$^{II}$, there is an unaccounted peak at 3.0 eV above the single peaked pre-edge. This feature has been assumed not to be related to a 1s3d feature and has been assigned as an edge transition [24]. An alternative explanation could be to assign it to the dipole transition to the 3d-band shifted by 3.0 eV with respect to the quadrupole peak. At this moment, there is no clear answer to this matter. It can be expected that resonant inelastic X-ray scattering (RIXS) measurements will shed more light on this matter, as will be discussed in Section 4.

Waychunas and co-workers did show for a series of minerals that a distortion of the octahedron will show up as an increased intensity of the pre-edge peak(s) [36]. They show a roughly linear relationship between the bond angle variance (a measure of the distortion) and the pre-edge intensity relative to the step. A detailed analysis of the pre-edge intensity and relative energy position has been developed by Farges and co-workers [37].

From the analysis of a large number of titanium and iron compounds, the intensity and position of the pre-edge has been determined, where the center-of-gravity is chosen for the determination of the position. Figure 8 shows the case of the titanium K edges, where Ti$^{IV}$ is found to have its peak at 4969.5 eV with a relative height between 0.7 and 1.0. The relative height of the pre-peak is defined with respect to an edge jump of 1.0. The precise value found depends partly on the experimental resolution, and one should take care to compare data taken with different monochromators. Going from Ti$^{IV}$...
to TiV, an energy shift of 1.0 eV can be observed and a relative intensity that is much lower, while TiVI is again shifted and moved to lower intensity. A similar analysis has been made on FeII and FeIII compounds, where in addition, a clear difference has been determined between tetrahedral and octahedral compounds. The energy position of FeIII is 7113.5 eV both for tetrahedral and octahedral symmetry, while their relative intensities are 0.35 for tetrahedral and 0.06 for octahedral symmetry, respectively. The main difference is the much larger dipole contribution to the tetrahedral site. A similar phenomenon can be observed for FeII, which leads to a tool to analyze both the valence and symmetry of iron sites from the pre-edge analysis. Applications in the field of catalysis will be discussed below.

As discussed above, the dipole and quadrupole transitions are commonly assumed to overlap in energy, or actually they are assumed to be transitions to the same states that therefore must be degenerate. In contrast, for TiO2, it has been assumed that there is a 2.5 eV energy shift between the dipole and quadrupole transitions, as discussed above. In this section, we will use charge transfer multiplet (CTM) theory in an attempt to unify both models. CTM theory will be outlined in detail in the chapter on soft X-ray absorption. In CTM theory, the ground state of a 3d-metal is described as 3dN4p0, where N indicates the number of 3d electrons. This configuration is mixed with 3dN+1L4p0, where a virtual excitation from the ligand band (L) to the 3d-band is included. If the relative energy of 3dN+1L4p0 is set to zero, the energy of the 3dN+1L4p0 configuration is defined as the charge transfer energy Δ. The number of 4p electrons has been set to zero, but this could be changed to any finite number α. There are two extreme cases for the pre-edge calculations:

1. A system with inversion symmetry, for example octahedral, where dipole and quadrupole transitions reach final states belonging to different parity and, hence, do not mix.
2. A system without inversion symmetry, for example tetrahedral, where dipole and quadrupole transitions can reach the same final states.

Starting with situation (1), the transitions are:

- 3dN4p0 + 3dN+1L4p0 ➞ (dipole) ➞ 1s3dN4p1 + 1s3dN+1L4p1
- 3dN4p0 + 3dN+1L4p0 ➞ (quad.) ➞ 1s3dN+14p0 + 1s3dN+2L4p0

The crucial interaction in the final state is the core hole potential on the 3d-electrons. This interaction pulls down the states with additional 3d electrons with a value that is defined as the core hole potential Q. Looking at the dipole and quadrupole transitions, respectively, a completely different screening behavior is seen. The quadrupole transition is self-screening, as the 1s core electron directly fills a localized 3d state. This situation is much like the situation of the soft X-ray L edges, and the energy ordering of the final states is essentially the same as the ground state, i.e., 1s3dN+2L4p0 has an energy of Δ with respect to 1s3dN+14p0. In practice, this implies that transitions to 1s3dN+2L4p0 will not be visible in the spectral shape. The situation is completely different for dipole transitions that behave much like 2p-XPS, and the two final state configurations reverse their energy position. The complete energy situation is sketched in Figure 9.

In a system without inversion symmetry, the dipole final states (dark) and the quadrupole final states (light) do not mix and will be visible independently. This is the case for TiO2, where a shift is seen between the dipole and quadrupole peaks. The final states at higher energy will, in general, be (much) weaker than the states at lower energy, and they will not be visible because of the presence of additional edge transitions. In systems without inversion symmetry, the 4p and 3d states mix and form bonding and anti-bonding combinations, both in the initial state and in the final state. This will further complicate the picture, but it will result in the same energy position of the final state configurations with the same number of 3d electrons. This explains why, in most cases, the energy position of the dipole and quadrupole final states can be assumed to be equal. It is extremely difficult to shed light on this complex situation from an experiment due to the large lifetime broadening. However, one can expect new insights from selective XANES and RIXS experiments that will be discussed in Section 5.

4. EXAMPLES OF IN-SITU XANES ON CATALYTIC SYSTEMS

An enormous range of in-situ XANES experiments has been published, often in connection with the in-situ EXAFS analysis. In addition, because XANES measurements are faster and need shorter energy ranges, XANES spectra are more applicable for time-resolved experiments, discussed in the chapter on time-resolved XANES. Also, spectro-microscopy studies often use XANES signal as contrast. Below, a few examples will be chosen to highlight the use of XANES for in-situ studies of catalysts.

4.1. The Ti Active Sites in Epoxidation Catalysts

The catalytic conversion of propylene to propylene oxide over Ti-SiO2 in the presence of hydro-peroxides as oxidants is an industrially important epoxidation that accounts for an annual production of more than one million tons of propylene oxide. Both the nature of the Ti active site and the reaction mechanism have been studied often. The group of Thomas...
and coworkers studied the titanium active sites in various selective oxidations [38–40].

The Ti active site in Ti/SiO₂ catalysts had been proposed to contain 3-fold, 4-fold, 5-fold and 6-fold coordinated sites, oxygen-linked dimers and sites containing titanyl (Ti=O) groups. The nature of the active site has been studied using in-situ XANES and EXAFS on Ti active sites on MCM-41. It was found that the Ti active sites were 4-fold coordinated before the reaction starts. During catalysis, the 4-fold surroundings were found to extend to 6-fold surroundings. In-situ XANES and EXAFS showed that in addition to the four original neighbors, two oxygen neighbors were present at a longer distance. The XANES spectra were analyzed using the pre-edge intensity and energy position according to the ideas outlined in Figure 8. From the XANES analysis and the comparison between XANES and DFT calculations, the 3-fold and 5-fold sites could be ruled out, and the ‘resting’ 4-fold and ‘active’ 6-fold sites were confirmed [40].

4.2. Binuclear Fe-Complexes in Over-Exchanged Fe/ZSM5

Iron-exchanged ZSM5 has recently attracted considerable attention due to its ability to catalyze a range of selective oxidation reactions. Its activity has been demonstrated for the selective oxidation of benzene to phenol using N₂O and the catalytic decomposition of N₂O, and for the hydrocarbon-assisted reduction of nitrogen oxides [41][42, 43]. Despite a great deal of attention, the nature and the reactivity of the Fe-active phase are still not completely understood. The situation is complex because of the large diversity in Fe/ZSM5 synthesis methods and materials used, for example, the loading of iron into ZSM5, the Si/Al ratio, the amount of iron loaded and the activation treatment.

Battiston and coworkers analyzed the behavior of the in-situ XANES and EXAFS spectra of mildly calcined over-exchanged Fe/ZSM5, prepared by CVD of FeCl₃ during heating treatments in He, O₂ and H₂ [43]. The pre-edges were analyzed according to the procedure outlined above. They were isolated from the main edge and the energy position of the center of gravity, plus the integrated intensity of the pre-edge normalized to the edge jump was determined. These pre-edge characteristics are plotted in Fig. 10 with small black dots. This figure also gives the pre-edge features of well-defined Fe-crystalline materials, with known Fe oxidation state and coordination geometry, as measured by Wilke and coworkers [44]. As a comparison, the results obtained for hematite measured in He at 30°C under identical experimental conditions is also shown. It can be concluded from Figure 10 that iron in Fe/ZSM5 measured in He at 30°C is present as slightly distorted octahedral Fe³⁺. Its oxidation state and coordination geometry appear to be very similar to that of hematite. By heating Fe/ZSM5 in He to 130°C, an increase is visible in the pre-edge integrated intensity, while only a slight shift (−0.2 eV) of the centroid position is observed. The main effect of moderate heating in He is a decrease in symmetry or in the number of neighbors coordinated to iron, without a significant reduction in the average Fe oxidation state. A plausible interpretation for these results appears to be the removal of water molecules from the coordination of iron. An additional increase of the temperature to 260°C caused a clear shift of the pre-edge (−0.7eV), together with only a slight decrease of its integrated intensity. As can be seen in Fig. 10, the features of the pre-edge at 260°C in He appear to be similar to that of a 50:50 (6)Fe³⁺/(4)Fe⁴⁺ mixture. In other words, the results show reduction involving a considerable fraction of iron. The reduction is accompanied by an additional decrease in the average Fe coordination-number. This can be ascribed to a further desorption of water and, in addition, with the removal of oxygen. Additional analysis of the active site has been made using the EXAFS spectra under the same experimental conditions [43].

This example shows the richness of pre-edge analysis for the in-situ determination of the local electronic and geometric structure of metal sites in a complex catalyst. Detailed and quantitative XANES analysis reveals much information of the catalyst under reaction conditions. An important advantage of pre-edge analysis is that only an energy range of 10 eV is needed. This makes it easier to make measurements in shorter time intervals.

4.3. The Use of Cu K XANES for Site Determination

The group of Kyoto University studied 0.5 to 5.0 wt% Cu/Al₂O₃ at BL01B1 of SPring8. The Cu/Al₂O₃ catalyst is used in the deNOx reaction using both CO and O₂ [45]. Using a range of reference compounds, the Cu K edge was used to determine the trends in the edge positions (maximum of first derivative) and peak positions (maximum of XANES). A series of Cu/Al₂O₃ samples with loading of 0.5, 1, 3, 5 and 10 wt% and calcined at 773K and 1073 K, respectively, have been analyzed. Samples with up to 5 wt% Cu (at 773 K) and samples with up to 3 wt% Cu (at 1073 K) all show equivalent XANES spectra related to a distorted octahedron. The 5 and 10 wt% samples calcined at 1073 K showed an increased pre-edge peak related to tetrahedral sites, and the spectral shape
4.4. Effect of the Metal-Support Interaction on the Pt L2,3 XANES

Köningsberger, Ramaker and co-workers studied the effects of the metal-support interaction on the Pt L2,3 XANES spectral shapes. In particular, they devised a method to derive electronic structure information from a comparison of the L2 and L3 edge XANES spectra of a system in two states, in particular, in a state with and without hydrogen [46–48]. As discussed in Section 3.2, the L3 and the L2 edges reflect the empty 3d-states. Because of spin-orbit coupling, the L2 edge reflects only the d5/2 level. For small platinum clusters, the 5d5/2 band is filled due to band narrowing relative to platinum bulk. Therefore, it is assumed that there is little or no 5d contribution to the L3 white line, and the L2 spectrum of the Pt clusters can be used as the reference (called REF). The L3 edge shows states of both the 5d5/2 and 5d3/2 bands, weighted as d5/2/d3/2 = 6. In other words, the L3 spectrum of the Pt cluster is equal to the L2 edge (REF) plus the empty 5d states (ΔVB). Subtracting the L2 edge from the L3 edge yields ΔVB. Detailed analysis of Pt metal shows that this is not entirely correct because there is some minor 5d3/2 contribution to the L2 edge [27]. A small correction factor for ΔVB must be taken into account.

Chemisorption of hydrogen induces a Pt-H anti-bonding state just above the Fermi level at the Pt-L3 edge. The L3 spectrum for the H-Pt sample is different from the Pt-L3 spectrum because of changes in the geometry of the cluster induced by chemisorption of hydrogen. These changes in geometry include H-induced changes in the Pt-Pt coordination as well as the presence of Pt-H EXAFS. The overall changes are indicated as (ΔXAFS). The L3 spectrum for the H-Pt sample also contains the anti-bonding state. The antibonding state is assumed to be below the Fermi level for the 5d3/2 states. Combining these assignments one can show that L3 Hydrogen is given as an addition of REF + ΔXAFS + AS, where AS is the anti-bonding state. Subtracting the different edges from each other isolates the different contributions: ΔVB, ΔXAFS and AS, where a crucial step in the analysis is the proper alignment of the edges [46, 48].

Analysis of the Pt L3 and L2 edges of supported Pt/LTL catalysts showed that the difference in energy of this anti-bonding state (AS) with respect to the Fermi level decreases with increasing support acidity [49]. This increasing support acidity can be correlated with the decrease of the neopentane hydrogenolysis turnover frequency of Pt/LTL. The acidity (the charge on the support oxygens) is a function of the Si/Al ratio of the support and the polarization field of the charge compensating cations (H+, Na+, La3+ and extra-framework Al3+). FEFF8 calculations of acidic and basic oxide supports to Pt nanoparticles confirm these trends. These results clarify that the analysis of the L3 and L2 white lines as a function of a catalytically relevant parameters, for example the support acidity, is an important tool to obtain information about the influence of the support on the electronic structure of supported metal particles.

5. RELATED TECHNIQUES

In this Section, we introduce a number of related experiments to X-ray absorption. This includes X-ray emission and a number of combinations between X-ray absorption and X-ray emission, known as resonant inelastic X-ray scattering (RIXS), resonant X-ray Raman scattering (RXRS) and selective X-ray absorption.

5.1. X-ray Emission

Instead of X-ray absorption spectra, one can also measure the inverse process of X-ray emission or fluorescence. The X-ray emission spectral shape can be obtained with a crystal monochromator, for example, using spherically bent analyzer crystals in a backscattering, Rowland circle, geometry [50]. In the case of a 1s core hole, the X-ray emission spectra are the 1s2p (Kα), 1s3p (Kβ) and 1s to valence band decay (Kβ2,3). The X-ray energies involved are hard X-rays, for example, in the case of iron between 7110 eV and 6300 eV, i.e., between the energy of the K edge absorption and this energy minus the 2p binding energy. Thus, the X-ray emission experiments involve only hard X-rays, an X-ray from a synchrotron or other source with an energy that allows for the creation of a 1s core hole (7110 eV or higher) and the X-ray emission energy, respectively.

5.2. Selective X-ray Absorption

Selective X-ray absorption is an experiment that makes use of a particularly chosen X-ray emission decay channel [51]. Hämmäläinen and co-workers showed that selective X-ray absorption effectively removes the lifetime broadening [52]. One can make use of one of these possibilities to improve the normal 2p X-ray absorption experiments on platinum. One can remove the 2p lifetime broadening of about 4 eV, and replace it by the 3d or 4d lifetime broadening of less than 0.5 eV. This results in sharper L2,3 edges. Figure 11 shows the platinum L3 edge of Pt/alumina particles with fluorescence yield X-ray absorption (solid line) and with 2p3/2-3d-detected X-ray absorption (dashed), both measured simultaneously at beamline ID26 at ESRF. Details on the experiment and the analysis will be published elsewhere. As expected, the L3 is sharper if the 2p lifetime broadening is removed. This sharpening makes it possible to measure the L3 edge with very high resolution, provided the monochromator resolution is very good. The high-resolution XANES spectra can be used to study small variations in the lowest empty states.

The central point of selective X-ray absorption is to make use of a particular fluorescence channel to measure the X-ray absorption spectrum. The 1s3p fluorescence spectral shapes shift to higher energy with increasing valence. One can tune the energy of the fluorescence detector to the peak position of one valence and vary the energy of the incoming X-ray, thereby measuring the X-ray absorption spectrum of that particular valence. This can be repeated for the other valence. Consequently, one obtains separate X-ray absorption spectra for the various valences, or in other words, valence-selective
X-ray absorption. Recently, valence-selective X-ray absorption has been applied to \( \text{Fe}^{III}_2(\text{Fe}^{II}(\text{CN})_6)_3 \) (Prussian Blue). Prussian Blue can be considered a prototype of a mixed-valence compound. It contains two kinds of iron in different oxidation and spin states. The ferrous ion presents a coordination shell constituted by six carbons at 1.92 Å, and is surrounded by six nitrogens at 3.04 Å and six ferric ions at 5.08 Å. The formal oxidation state number is II and the strong crystal field exhibited by the carbon atoms yields a low-spin ground state configuration. The ferric ion \( \text{Fe}^{III} \) has a high-spin configuration. The bulk ratio \( \text{Fe}^{III} \) to \( \text{Fe}^{II} \) is 4:3. Glatzel and co-workers showed that the 1s3p X-ray emission spectrum of Prussian Blue can be simulated by a 4:3 ratio of the spectra of \( \text{Fe}_2\text{O}_3 \) and \( \text{K}_6\text{Fe}^{(CN)}_6 \). Using these two systems as reference for the \( \text{Fe}^{III} \) and \( \text{Fe}^{II} \) spectra, valence-selective X-ray absorption spectra were measured by tuning the crystal analyzer to fluorescence energies that mainly detect contributions from the element in one specific site, while the energy of the incident X-ray beam is scanned through the iron K edge region, including the EXAFS. EXAFS analysis shows good agreement of the \( \text{Fe}^{III} \) and \( \text{Fe}^{II} \) sites with X-ray diffraction data.

A final possibility is site-selective X-ray absorption. This possibility arises from the oxygen to metal cross-over decay channel. Because the oxygen 2s peak is present only for the metal atoms that are neighbors to the oxygen, one can measure the X-ray absorption spectra of only those metal atoms. It is important to note that the X-ray absorption (including EXAFS) analysis is essentially the same as for normal X-ray absorption, and all atoms surrounding the excited atom do contribute to the electron scattering. Only the X-ray excitation and decay process are specific for one type of neighbor, while the electron scattering determining the X-ray absorption spectral shape is not. Site-selective X-ray absorption opens a large range of new experiments, but the intrinsic low-intensity will make it very hard to experiment.

It can be concluded that selective X-ray absorption provides a new useful tool for the study of systems that contain an element in two distinct situations. This adds an extra advantage to the element selectivity of normal X-ray absorption. Because only hard X-rays are involved, in-situ studies are possible.

### 5.3. RIXS

As discussed above, the combination of X-ray absorption and X-ray emission gives rise to valence-selective X-ray absorption, the removal of lifetime broadening and (resonant) valence band X-ray emission. All of these techniques are, in fact, part of the complete resonant inelastic X-ray scattering (RIXS) experiment. In RIXS, one measures the complete two-dimensional spectrum of the excitation (\( \omega \)) and the emission (\( \omega' \)) X-ray energies. The spectrum \( I(\omega, \omega') \) can be used to make a specific cross section, for example valence-selective X-ray absorption, etc. The complete RIXS spectral shapes for 1s3p RIXS at the pre-edge of \( \text{Fe}^{III} \) is described with the Kramers-Heisenberg formula:

\[
I(\omega, \omega') \sim \sum_{i, j} \frac{<3p^5 3d^6 | \hat{e}^r | 1s^3 3d^6 <1s^3 3d^6 | rr | 3d^5 >^2}{E_{1s^3 3d^6} - E_{3d^5} - \hbar \omega - i\Gamma_{1s}}
\]

This formula forms the basis of all resonant X-ray processes. The initial state \( 3d^6 \) is excited to an intermediate state \( 1s^3 3d^6 \) with the quadrupole operator \( rr \), and the dipole operator \( \hat{e}^r \) describes the decay to the final state \( 3p^5 3d^6 \). The denominator contains the binding energy of the 1s core state and its lifetime broadening. A resonance occurs if the excitation energy is equal to the binding energy of the 1s state. Note that we have approximated the pre-edge of \( \text{Fe}^{III} \) with only the quadrupole excitation and without charge transfer (cf. Section 3.2.3).

The complete RIXS spectra offer additional advantages over the various cross sections as the complete resonant (and non-resonant) behavior becomes visible. The use of RIXS for catalytic samples is very recent and, in Figure 12, we show some preliminary results on overexchanged \( \text{Fe}^{III} / \text{ZSM5} \) in its oxidized form. The 1s3p RIXS of \( \text{Fe}^{III} / \text{ZSM5} \) is compared with that of \( \text{Fe}_2\text{O}_3 \) for reference. It can be seen that for \( \text{Fe}_2\text{O}_3 \), two maxima are visible related to the \( t_{2g} \) and \( e_g \) states in the pre-edge [53], respectively. \( \text{Fe}^{III} / \text{ZSM5} \) only shows a single maximum, which indicates the presence of distorted octahedral sites. In-situ RIXS experiments are in progress and will be published elsewhere.

### 5.4. X-ray Raman

X-ray Raman spectroscopy (or scattering) is the X-ray analog of optical and UV Raman. A hard X-ray, typically with an energy of about 10,000 eV, impinges on the sample and the scattered radiation is measured at an energy lower than 10,000 eV. Similar to normal Raman, one can study vibrations (meV range) and electronic excitations (eV range). In addition, one can study core electron excitations that relate to...
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energy losses of several hundred eV. Vibrational X-ray Raman will not be further discussed; some preliminary results can be found in a recent paper of Bergmann and coworkers [54]. Note that such core level X-ray Raman could be named X-ray energy loss spectroscopy (XELS) and, as such, is the direct analog of electron energy loss spectroscopy (EELS). Exactly as is the case for EELS, the core excitation spectra from XRS can be described in complete analogy with X-ray absorption, at least if one remains within the dipole approximation and uses small scattering moments. In fact, X-ray Raman provides additional possibilities by changing the scattering moments, but such experiments will not be treated within this review.

It is obvious that X-ray Raman has great potential for in-situ measurements. The complete experiment involves hard X-rays (10 keV), hence there is considerable penetrating power and cell design should not be an issue. X-ray Raman spectroscopy represents a hard X-ray alternative to conventional XAS techniques in the study of systems with light elements, including C, N and O. As such, it complements the in-situ soft X-ray absorption developments using either electron-yield detection [55] or fluorescence yield detection [56]. These soft X-ray techniques will be discussed in detail in the chapter on soft X-ray XANES. In addition, the same spectral shape can be obtained, ex-situ, using EELS in electron microscopes [57].

X-ray Raman is particularly useful for carbon, nitrogen and oxygen edges. Figure 13 shows the X-ray Raman spectra of benzene and n-octacosane (C_{28}H_{58}). The total resolution of the experiment is approximately 0.5 eV. The spectra are equivalent to the spectra measured by soft X-ray absorption, showing that it is feasible to carry out X-ray Raman experi-

Figure 12. 1s3p RIXS spectra of (a) Fe/ZSM5 and (b) Fe2O3. The intensity contour-plot is shown with the maximum in red.

Figure 13. X-ray Raman K-edge spectra showing extreme cases of aromatic (solid) and aliphatic hydrocarbons (dashed). The benzene spectrum was taken at a sample temperature of 10 K, the n-octacosane (C_{28}H_{58}) spectrum was taken at room temperature.
ments \textit{in-situ}. An important application would be the \textit{in-situ} measurement of carbon deposition on catalysts. In such experiment, one would be able to quantitatively follow the amount of carbon and, in addition, the chemical nature of the carbon species.

6. OUTLOOK

We have discussed the application of XANES spectroscopy to catalysis. It is our perception that much improvement can still be obtained in the use of XANES for \textit{in-situ} determinations. Improvements can be made in three aspects: better quantitative analysis, new techniques and better \textit{in-situ} cells.

Quantitative Analysis

We have shown that a number of methods exist to quantify XANES information. For example, the edge position correlates with the valence, and the white line intensity with the number of empty d-states. In addition, the pre-edge energy position correlates with valence and its normalized intensity with the geometry. The complete XANES spectral shape corresponds to the density of empty states and the programs to calculate this density of states are accurate (at least for the energy resolution visible with XANES). Therefore, if one derives a certain geometric structure from XANES (and/or EXAFS) analysis, it would be a good approach to calculate the XANES spectrum corresponding to this structure as an additional consistency check.

New Techniques

As discussed in Section 5, a range of new X-ray techniques has recently been developed. At the center of these techniques is the development of high-resolution X-ray emission detectors with a reasonable solid angle. These detectors allow high-resolution detection of X-ray emission spectra. Together, with a high-resolution monochromator, this opens detectors with a reasonable solid angle. These detectors can be used will depend on the specific conditions of the experiment and the kind of information that is targeted.

In conclusion, we can state that from a combination of quantitative interpretation, new techniques and improved re-

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