X-RAY ABSORPTION SPECTROSCOPY FOR THE CHEMICAL AND MATERIALS SCIENCES

JOHN EVANS

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About the Author

John Evans hails from Newcastle upon Tyne. He studied Chemistry at Imperial College, London, and carried out his PhD at the University of Cambridge supervised by Lord (Jack) Lewis and Brian Johnson. His postdoctoral research was at Princeton University, with Jack Norton, and then with ICI and Royal Society Pickering Research Fellowships back at Cambridge. He moved with the Pickering Fellowship to Southampton in 1976, became a lecturer in 1978, and a professor in 1990. He is now an emeritus professor there. He was science program advisor at the Diamond Light Source Ltd from 2002 to 2007. His experience in applying XAFS spectroscopy to chemical problems extends over 35 years; his research group has carried out experiments at the SRS, ESRF, SLS, Hasylab, Diamond, and APS.

Preface

This is a textbook aimed at master's-level students, including fourth-year UK MSci degrees, of the chemical and related sciences suitable as an introductory text for PhD students embarking on x-ray absorption fine structure (XAFS) spectroscopy. The background should also appeal to established scientists from other fields (environmental, life, and engineering sciences), wishing to assess the potential of x-ray spectroscopy for their science. The chapters progress initially through the history and principles of XAFS. The next two chapters deal with experimental design: first, light sources and beamlines and then at the experimental station itself. Chapter 5 provides the background to the methods of extracting and using the results in materials and chemical analyses. The final chapter provides a series of case studies to illustrate a variety of applications. Each chapter concludes with a set of problems. There is a strong emphasis on the need to make the right choices for experimental design, and guidance provided to do so.

John Evans
Southampton UK
April 2017

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Glossary and Abbreviations

Absorption edge	Rapid increase in absorption with increasing energy
AEY	Auger electron yield
APD	Avalanche photodiode
Auger process	Relaxation of a core-hole via electron emission
CCD	Charge-coupled device
CEE	Constant emission energy
CIE	Constant incident energy
Compton scattering	Inelastic scattering
Debye-Waller	Factor describing disorder in interatomic distances
DFT	Density functional theory
EDE	Energy dispersive EXAFS
EDX	Energy dispersive x-ray spectroscopy
EXAFS	Extended x-ray absorption fine structure
FEL	Free electron laser
FT	Fourier transform
FY	Fluorescence yield
FZL	Fresnel zone plate
HARPES	Hard x-ray photoelectron spectroscopy
HERFD	High-energy resolution fluorescence detection
IV	In vacuum
KB	Kirkpatrick-Baez (mirrors)
MLL	Multilayer Laue lens
NEXAFS	Near-edge x-ray fine structure
NIXS	Nonresonant Inelastic x-ray Scattering
OD	Optically detected
PCA	Principal component analysis
QEXAFS	Quick extended x-ray absorption fine structure
Rayleigh scattering	Elastic scattering
REXS	Resonant x-ray Emission Spectroscopy
RIXS	Resonant Inelastic x-ray scattering or spectroscopy

SR	Synchrotron radiation
STXM	Scanning transmission x-ray microscopy
TEY	Total electron yield
TXM	Transmission x-ray microscopy
VtC	Valence to core
X-PEEM	X-ray photoelectron emission microscopy
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XEOL	X-ray excited optical luminescence
XES	X-ray emission spectroscopy
XFEL	X-ray free electron laser
XMCD	X-ray magnetic circular dichroism
XMLD	X-ray magnetic linear dichroism
XRS	(Inelastic) X-ray Raman Scattering

1

Introduction to X-Ray Absorption Fine Structure (XAFS)

1.1 Materials: Texture and Order

Today, research laboratories have powerful techniques for establishing the chemical nature and structure of pure materials. Our view of chemical structure is formed around the results of x-ray diffraction, recorded from single crystals or from polycrystalline powders. Structures in the liquid phase can be inferred from expectations for bond lengths and angles derived from crystallography; to do so, information is gathered about the local symmetry, atomic connectivity, and proximity in the material derived from structurally sensitive spectroscopies, particularly nuclear magnetic resonance (NMR) and infrared (IR) and Raman vibrational spectroscopies.

But many materials with a function are textured, such as pigments in paintings in the Louvre, a stained glass window in Westminster Abbey, an automotive exhaust catalyst, a dental filling, and others in nature, such as mineral inclusions or the shells of mollusks. They possess identifiable local structures on the Å scale that form the basis of their capabilities. However, these may be randomly spread through their three-dimensional shape or, alternatively, be located in a particular region, such as at a surface. Correlating the structure and the function of materials is a key to the design of further development, as well as providing its own intrinsic scientific elegance.

X-ray absorption fine structure (XAFS) spectroscopy has developed to the point when it can be applied to probe complex and faceted materials, for example, to reveal chromophores in glass and to probe the organic-inorganic composites in shells. In this book, the aim is to guide the readers to identify whether and how the technique might be used to advantage to study the materials that interests them within this wide spectrum of samples.

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1.2 Absorption and Emission of X-Rays

About 100 years ago, with the discovery of x-ray absorption (XAS) and emission (XES) spectroscopies, observation of the absorption and emission of x-rays were at the forefront of atomic physics, rather than the basis of materials characterization. The observations of the x-ray absorption edge of elements were first made by Maurice de Broglie in 1913 and published in 1916;[1] the elements were the silver and bromine in a photographic plate. Moseley[2] measured the energies of the emissions of over 40 elements and showed that there was a square root relationship with the atomic number of the element; tragically, his further contributions were cut short by a sniper at the Battle of Gallipoli in 1915. W.H. and W.L. Bragg had also noted that x-ray emission lines were also characteristic of an element.[3] Hence, both the absorption edge and the emission lines had been shown to provide a means of elemental speciation of sites.

Shortly thereafter the group of Manne Siegbahn at Lund improved the resolution of the crystal spectrometers to 1/10,000 allowing them to establish that the absorption edge position was chemically as well as elementally dependent; this was initially observed for allotropes of phosphorus, reported by Bergengren in 1920. In the next year, Lindh reported a chemical shift of 5.4 eV between Cl_2 and HCl. The use of edge positions for chemical speciation was thus established and by the mid-1920s the energies of emission lines were also shown to display a chemical shift.

1.3 XANES and EXAFS

In 1920, Fricke published photographic measurements of *K* absorption edges of elements between magnesium and chromium,[4] and Lindh reported structures around the Cl *K* edges. These reports showed fine structure both before and after the absorption edge energy, and XAFS (x-ray absorption fine structure) had been identified. Most photographic plates with the x-ray spectrum dispersed across them showed a bright line, marking the maximum in the x-ray absorption and thus little darkening of the photographic plate. For some samples, for example, the Ca *K* edge in calcite and gypsum, this feature was especially intense and by 1926, it was known as the white line.[5] Lindsay and van Dyke also reported features up to nearly 50 volts above the first main feature of the edge. Two years later, Nuttall[6] reported that the potassium *K* edges post-edge features could be used to distinguish between different minerals, and that the "fine structure… extended over a range of about 67 volts." And in 1930 Kievert and Lindsay[7] observed fine structures in metals extending to about 400 eV to higher energy of the absorption edge. Hence, by 1930 most of the core characteristics of XAFS spectroscopy had been identified, apart from polarization effects.

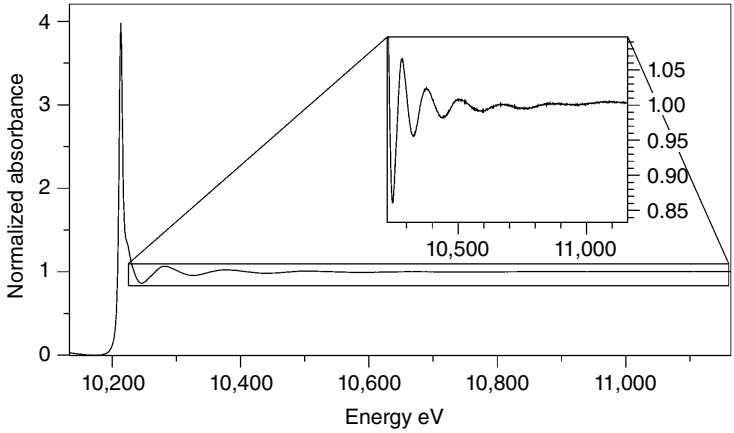

Figure 1.1 The normalized W L_3 edge x-ray absorption spectrum of a solution of $(NBu_4)_2[WO_4]$ (10 mM) in acetonitrile (*Source:* Diamond Light Source, B18; data from Richard Ilsley).

An example of an XAFS spectrum is shown in Figure 1.1 for the tungsten L_3 edge of an acetonitrile solution of $(NBu_4)_2[WO_4]$; the L_3 edge is a transition of a *2p* electron of the absorbing atom, tungsten in this example. The technique pinpoints the anion containing the absorbing atom and the solvent and counter ion do not interfere. This spectrum shows some of the characteristic components that might be observed associated with an absorption edge. The x-ray absorption near-edge structure (XANES) is dominated in this case by an example of a white line, due to an intense (Laporte-allowed) transition to vacant *5d* states. The extended x-ray absorption fine structure (EXAFS) has been expanded vertically to become visible at higher energies. Each of these types of features contributes to the information than can be derived from the entire spectrum.

1.4 Information Content

It was quickly recognized that x-ray spectra provided information about atomic energy levels, as commented by W.H. Bragg.[3] It was also noted that the position and shape of the XANES features at the absorption edge were dependent upon the local environment and on the effective charge on the absorbing atom. More problematical was a working explanation of the extended structure, EXAFS. There were three possibilities proposed:

1) The peaks above the edge were due to additional atomic transitions. However, Coster and van der Tuuk[8] showed that this was a minor contribution in their study on argon gas.

2) The oscillations were due to long-range periodicity through the sample, as described by Kronig in 1931.[9]
3) Instead the oscillations were due to short-range electron scattering, as Hartree, Kronig, and Petersen reported in 1934, thus accounting for EXAFS features up to 200 eV above the Ge *K* edge in molecular $GeCl_4$.[10]

The dichotomy between local- and long-range order explanations for solid-state arrays and molecular materials remained for about 40 years. The basis of the current understanding emanates from analyses by Stern and his co-workers, Sayers and Lytle, in 1970 and published in 1974–1975.[11–13] The key aspects of this development were the demonstration of the short-range order theory for all materials and the efficacy of Fourier transform methods for displaying the differing oscillations in an EXAFS patterns as distinguishable interatomic distances. In Figure 1.1, the EXAFS features are dominated by a single damped oscillation, which is due to the scattering between the tungsten and oxygen atoms in the anion. Hence the method provides measurement of that bond-length in solution and other disordered media.

1.5 Using X-Ray Sources as They Were

Viewing that oscillation in Figure 1.1, it is evident that EXAFS features are weak and thus a high signal/noise ratio is required to reliably extract the potential information in a XAS spectrum. Until 1970, all XAS measurements utilized laboratory x-ray tubes. For x-ray spectroscopy it is the brehmsstrahlung background that provides the necessary range of x-ray energies, rather than the more intense emission lines used for x-ray diffraction. The combined characteristics of weak sources and weak signals severely limited the application of XAFS. But the breakthrough in understanding provided by Stern added to the impetus for finding an experimental solution.

Much higher intensity sources were in prospect from synchrotron accelerators, an effect first demonstrated in 1947.[14] This report, from the General Electric Company, described a brilliant white spot emanating from the tangent point of the orbit in a 70 MeV device of radius 29.2 cm. When synchrotrons first became available as x-ray sources in the 1970s, the effect was dramatic. For example, the experimental backdrop to the theoretical developments was a suite of three x-ray spectrometers at the Boeing Scientific Research Laboratories. Lytle later offered the following observation[15] about an experimental trip to the then new x-ray spectrometer at Stanford Synchrotron Radiation Laboratory (SSRL) in the early 1970s: “In one trip to the synchrotron we collected more and better data in three days than in the previous ten years. I shut down all three X-ray spectrometers in the Boeing laboratory. A new era had arrived!”

1.6 Using Light Sources Now and To Be

That new era transformed x-ray spectroscopy from being a poorly understood technique of considerable experimental challenge, to one of wide applicability. Stern, Sayers, and Lytle concluded in 1975:[13] "Its greatest usefulness should be in unraveling complicated structures with no long-range order such as biological molecules and commercially practical catalysts."

Since that statement was made, x-ray sources display brilliances that have increased faster than computing power over the same time period. The advantages envisaged then for studies of macroscopic samples can now be applied with great spatial and temporal resolution. Functional materials may be investigated in their textured nature and their structures tracked during processing. Current storage ring light sources have the stability and reliability to make these experiments viable.

A new class of x-ray sources is within the horizon now. Lasing by free electron lasers in the x-ray region was demonstrated in the United States in 2010 and in Japan in 2011, and both are available as user facilities now. This type of source will be able to interrogate structure with a time resolution that is faster than vibrations and thus they offer structural snapshots of molecular dynamics. The last century has been a good one for x-ray science, and the future is extraordinarily bright!

For now though, this is what we hope to probe by XAFS experiments:

- The absorption edge jump and fluorescence yield can be used to quantify elemental compositions.
- The XANES features and observed edge position interrogate the effective nuclear charge of the absorbing atom and the local geometry.
- The oscillations in the EXAFS region provide information about the types of neighboring atom, the number of them, and the interatomic distances.
- Spatial resolutions of μm down to 10s of nm provide scope for using the spectral features for mapping chemical states though textured materials.
- Sub-second time resolutions allow tracking of structural changes in response to a stimulus, thus giving real-time structure-function studies.
- With specialized laser-based x-ray sources, structures can be monitored with sub picosecond time resolution.

The events involved can be envisaged with a physical model. In Figure 1.2, an energy source (a stone) is exciting a calm lake, creating a core hole and also a wave from the impact site.

In XAFS, there are generally neighboring atoms as well as the excitation site, so perhaps a better model is provided by a coot (*fulica atra*). Coots dive like a stone to feed and this "excited state" has a central void with an outgoing wave. The wave can interact with a nearby coot and the "excited" coot relaxes (Figure 1.3). A portion of the outgoing wave can be scattered back from the hungry coot back to the one that has just fed.