

Development and applications of accurate measurement of X-ray absorption

The X-ray extended range technique for high accuracy absolute XAFS by transmission and fluorescence

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Abstract. Over recent synchrotron experiments and publications we have developed methods for measuring the absorption coefficient in the XAFS (X-ray Absorption Fine Structure) region and far from an edge in neutral atoms, simple compounds and organometallics which can reach accuracies of below 0.02%. This is 50–500 times more accurate than earlier methods, and 50–250 times more accurate than claimed uncertainties in theoretical computations for these systems. The data and methodology is useful for a wide range of applications, including dominant synchrotron and laboratory techniques relating to fine structure, near-edge analysis and standard crystallography. The experiments are sensitive to many theoretical and computational issues, including correlation and convergence of individual electronic and atomic orbitals and wavefunctions.

1 Development and history of XERT and applications

Traditionally, measurements of absorption of X-rays by ideal condensed matter systems have provided critical data for experimental tabulations [1,2], tests of theoretical computations and databases [3–10], and material for experimental-theoretical empirical syntheses [11,12]. These are then used in plasma diagnosis, X-ray and radiographic filters, anode tube design, medical imaging, weapons research and fundamental investigations to name a few.

Computational issues suggested that relativistic theory from the 1970's was limited and needed to be addressed with more developed computational schemes [13,14]. The new results of the 1990's and 2000's are certainly superior. However, different formulations still remain discrepant from one another by several or even 10–20% especially in near-edge or soft X-ray energy regimes for many elements. This is one key issue which has sparked not only our series of experimental investigations, but also those of many other research groups.

Careful studies from 1987 and 1990 began to define some issues and problems in the careful measurement of attenuation coefficients in general and in the accurate determination of photoabsorption coefficients in particular [15,16]. Development of modelling and computation has enabled the resolution of several earlier discrepancies between experiment and theory [17,18], yielding the FFAST database (<http://physics.nist.gov/ffast>). However, in many cases the experimental data has been inconsistent between or within datasets, with apparent precisions of order 1%–20%, which therefore has prevented detailed investigation of the experimental or theoretical discrepancies. It was claimed that accuracies below 1%, even for metals or single crystalline elements, were not possible (due to the difficulties of addressing experimental systematics). We developed some of the principles earlier established by the International

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Union of Crystallography [19,20] and implemented them and others at a synchrotron to achieve accuracies of 0.2% [21,22] and later 0.02% [23,24].

The accuracy enabled new processes to be observed and new approaches to old problems. We were able to directly observe the contribution of scattering processes in X-ray attenuation measurements, and show evidence for Rayleigh scattering from copper samples [25]. We developed techniques for diagnosing more detailed systematics [26] including the quantitative determination of harmonic content in synchrotron beams [27] and the measurement of X-ray bandwidth from the effect on on-edge absorption coefficients [28].

In the series of experiments at the Australian National Beam-line Facility in Tsukuba, Japan, energy calibration is carried out using a powder diffractometer BigDiff using National Institute for Standards and Technology standard reference powders of silicon and lanthanum hexaboride. The accuracy of our energy determinations over a large range of X-ray energies revealed a discrepancy between the reported lattice spacings of the standards, and implied that such standards could be calibrated at a synchrotron [29]. Sequel experiments have so far supported these conclusions, but more work is required [30,31], especially with respect to the high accuracies of recent powder standards. Our analogue of this energy calibration technique at the Advanced Photon Source, Chicago, uses a large-circle goniometer with perfect silicon (or germanium) crystal wafers to determine energies by single crystal diffraction. This technique is currently being developed and implemented at the Australian Synchrotron in Melbourne. A typical example of this XERT layout is given from the tin experiment (Fig. 2).

The precision of our first experiments was below 0.1%; but the absolute accuracy of the early experiments was limited to around 0.2% by systematics. One of the key problems with attenuation and absorption coefficients is the overall normalisation and calibration of the absolute coefficient, or equivalently of the sample thickness or sample column density in the X-ray beam. Our efforts developed tools for the accurate determination of the thickness of thin foils and single-crystal wafers [32] and the full-foil mapping of integrated column density [33].

The investigation of secondary coefficients which are more difficult to observe and model, including fluorescence and inelastic scattering, could then be pursued, [34] since these effects were typically 0.1% in magnitude compared to the photoelectric absorption over the central energy range for most experiments. These experiments are difficult, and we look towards the possibility of an absolute calibration of a scattering coefficient.

One of the areas which is little appreciated is that the range of systematics varies significantly with atomic number, absorption and the range of energies. Whereas the early experiments were with light elements (silicon and copper), later experiments investigated the rise of the significance of scattering at higher energies such as for tin and silver [35]. In principle, our accuracies may allow direct measurement of coherences between amplitudes.

However, it is becoming clear that much discussion and interest focusses on the near-edge region of the absorption spectrum. At synchrotrons, X-ray Absorption Fine Structure (XAFS) and X-ray Absorption Near-Edge Structure (XANES) have been major techniques for local structural investigation for decades. For crystalline structure, powder diffraction or single-crystal crystallography is the primary vehicle for determining structure, but for non-crystalline systems the bond lengths and orientations around an active site can be determined most effectively by investigating the interference of the outgoing photoelectron wave with that reflected (scattered) back from any electron (charge) density. Many synchrotron beam-lines specialize in XAFS or XANES techniques, and many hundreds of papers investigate coordination and bonding effects using XAFS or XANES per annum.

One difficulty is that XAFS is not calibrated, and accuracies and error propagation are often not treated carefully. We have begun investigations into the robust determination of structure from XAFS [36,37] and investigations of the underlying condensed matter theory with promising results so far [38]. In principle these techniques can be applied generally to elemental and complex organometallic systems, and we look forward to opportunities for future developments. Developments have been pursued with Rehr, Joly and others.

Kodre [39] and other groups have been pursuing high-accuracy XAFS of monatomic and other atomic vapours and solids. In a careful experiment from 300°C–1000°C, the dissociation of the molecular binding was shown to progressively shift the photoexcitation spectrum in the

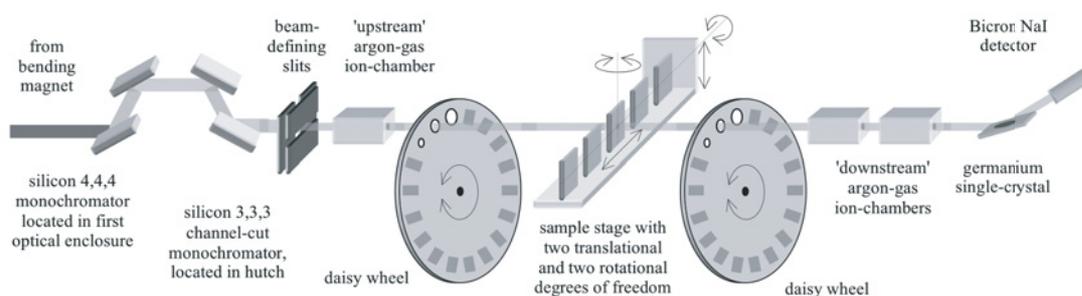


Fig. 1. Typical layout of an XERT experiment at the APS.

X-ray Absorption Near-Edge Structure (XANES). The limit of fully dissociated iodine can then be an indication of the atomic, isolated atom spectrum.

Such work highlights interrelation between atomic physics, cluster theory, band theory and condensed matter computations. High temperature XAFS and disordered system XAFS of any type have softening of structure due to thermal broadening of the photoelectron interference wave; and gases have the problem of density calibration. We have begun some experiments to investigate disordered solutions and the quality and accuracy of XANES and XAFS which can lead to investigations of theory or of materials, and hence perhaps to an accurate elucidation of purely atomic structure. Separately, this may quantify the true baseline for condensed interference effects from XAFS as opposed to Fermi level shifts, shake processes and related XANES or discrete processes. Another burgeoning area is the possible investigation of complex systems (dilute or organometallic) and the theoretical and computational information which may be extracted [40]. Work is in progress on these fronts.

2 Basic methodology of XERT

Fig.1 illustrates a typical XERT set-up. Measurement will make an absolute calibration of the energy axis at many points along the extended XAFS region, from below the edge to perhaps 10 keV above the edge. This is not done at each data point (that is too expensive in time) but for example may be made at 10–30 energies so that the scale, offset and curvature errors of the monochromator hysteresis or the previous foil or other calibration are all quantified. For some experiments powder diffraction standards are used to calibrate the energy, with image plates; at others an analyzer 6-circle goniometer is used with either single crystal standards or powder standards with a scanning arm. The choice is usually dictated by the beam-line availability. However, in most cases this guarantees a reproducible and beam-line independent calibration to a few eV, dependent upon the energy range of interest.

We have an independent check on electronic noise and higher harmonic contamination of the beam-line monochromation, as this is a large potential error source. Harmonic suppression may be achieved by detuning, and work well over higher energies; or may be by mirrors and work very well up to some cutoff; however, by testing these assumptions we generate an explicit confirmation at all energies and reveal unexpected problems, particularly at low energies.

We make explicit measurements at each energy of the blank (sample removed) signals and of the dark (no-beam) signals to normalise the detector response from any air-path absorption, scattering and electronic noise. These effects can be energy-dependent and several percent.

For each data point in energy, we make multiple samplings so that the precision is rigorously defined. This then is a limit to any accuracy which may be obtained, but also gives an indication of which systematic effects we may be sensitive to.

We bring in specialised equipment (daisy wheels) to explicitly measure aperture dependence, which often reveals the magnitude of the scattering signature. This then allows us to observe and measure the correct total attenuation coefficient and to have some handle upon

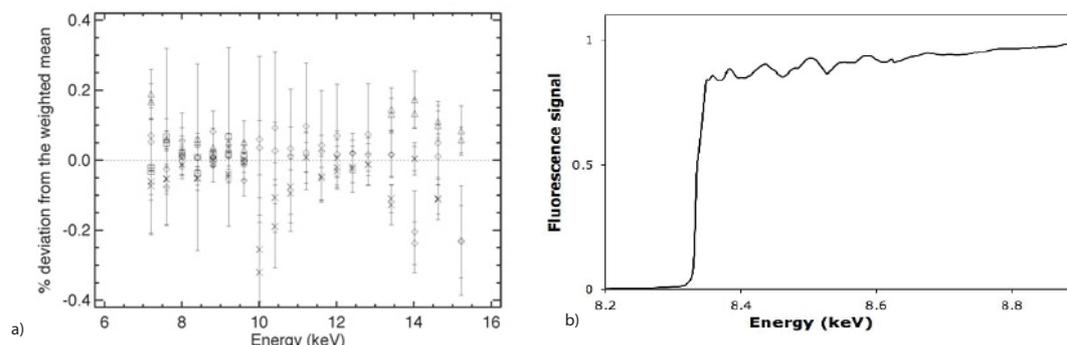


Fig. 2. a) New raw data quality for zinc metal. Note that these error bars contain a signature for scattering at the several standard deviation level because of the discrepancy between different sample thicknesses [10, 25, 50 and 100 μm , respectively]. b) Fluorescence data (XAFS of 3% w/w NiO in borate glass) exhibiting the typical slope and curvature from self-absorption and other systematic effects. Statistical quality is high but how well are the amplitudes preserved?

absolute scattering coefficients (and to thereby extract an actual photo-absorption coefficient with restricted error bars).

In some recent experiments we have been able to measure the experimental band-pass of the monochromated beam independently of any beam-line operator estimates. This is very useful for the local synchrotron staff and, if implemented routinely, can be an extremely accurate diagnostic for any users.

By measuring the same energy data point but with multiple thickness samples, we separate key systematics and can probe the attenuation coefficient to much higher levels. In principle this can demonstrate the linearity (or non-linearities) of the detector chain and analysis procedures, or can investigate roughness in material samples.

Also in recent experiments, we are investigating whether the techniques of XERT can be used to diagnose and correct large non-linearities in the response function of fluorescence experiments. Often XAFS and XANES experiments on dilute samples require fluorescence techniques, but it is well known that the precision and accuracy of these drop dramatically away from the edge. This then questions the accuracy and utility of the k -transforms and hence the uncertainties in determined structures. Early data is promising in this regard.

In analysis of XERT data, we conventionally produce a calibrated absorption spectrum which can then be used to fit XAFS/XANES data with suitable modelling. Our theory group has concentrated upon FEFF because of its widespread use, and upon Finite Difference Methods (because of their historical effectiveness with XANES). The data and analysis have so far led to some strong conclusions and insights about the current assumptions behind theoretical modelling. In particular, it suggests the value of FDM in several applications, and suggests that further theoretical development is needed in others. It also suggests that the analysis can be applied to isolated atoms, pure metals and complex dilute organometallics if suitable care is taken on the data collection.

We present three particular applications of XERT to recent data, as illustrations of the technique.

3 Application of XERT to new ideal systems such as Zn

In a recent experiment, our group has measured the attenuation coefficient and photoabsorption coefficient for pure zinc metal. This is not an XAFS measurement but will serve as a baseline for standards and absorption measurements, and helps to test the theory of the atomic and condensed matter quantum mechanical wavefunctions and multipole matrix elements. Fig. 2a illustrates the quality of the raw data, which appears to represent a new record in the field.

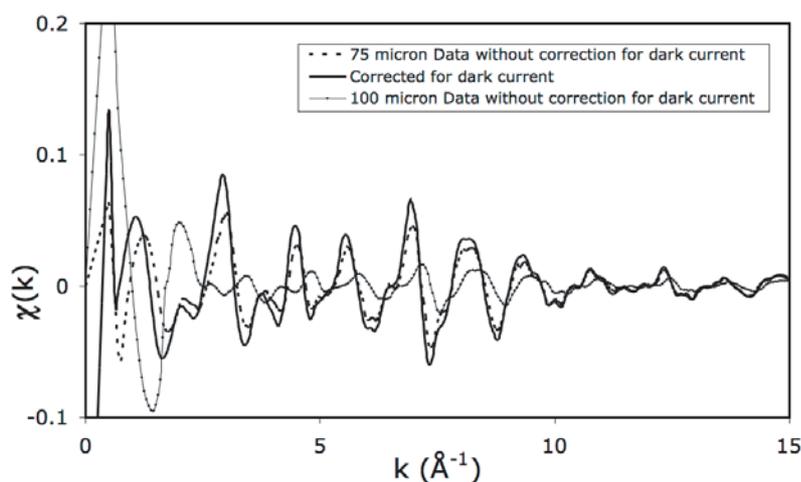


Fig. 3. Detailed accurate structure serves as both an opportunity and a challenge for theory.

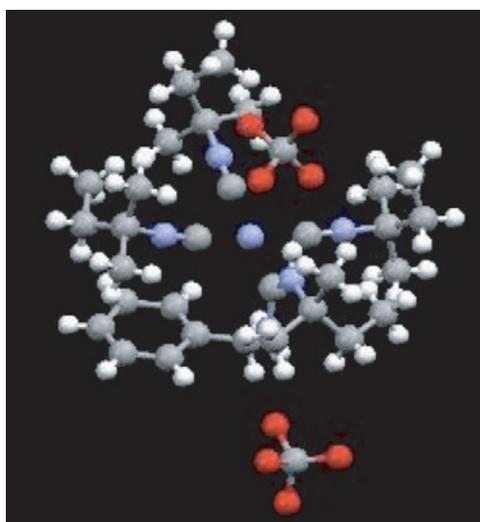


Fig. 4. Structures such as this organometallic can now be addressed with Finite Difference Method theory.

4 Application of XERT to fluorescence and dilute systems

As mentioned above, many systems require fluorescence methods to collect the XAFS or XANES data, but are affected by self-absorption and other systematics which change the slope and amplitude of XAFS structure, as illustrated in Fig. 2b. Commonly, the baseline is fitted with a spline as for absorption XAFS, which corrects for part of the slope effect near the edge. However, the trend and significance of the above edge structure are compromised, so the information content of the resulting data is limited. A question which XERT is beginning to answer is ‘How much information can be recovered from this system for XAFS analysis?’ and ‘Can we improve our approaches to fluorescence XAFS data collection to achieve better results?’

5 Testing and development of XAFS theory

Our Mo data [23] has shown that standard theoretical predictions lead to reduced χ^2 values of several hundreds [36], even if restricted over the XAFS rather than the XANES region (Fig. 3).

As such, this helps to identify limitations in the modelling and how to improve the theoretical assumptions to make a more useful system for many users [37]. This is currently a work in progress with Rehr et al. [41].

We have shown independently that some FDM approaches can be developed from the earlier FDMNES to be applied to XAFS and XANES regions simultaneously with good results [38]. This can then be applied to compare and contrast different approaches for copper XERT data. We have also demonstrated that this allows quite novel interpretations of the comparison between crystallographic unit cell dimensions and the bonding distances reported by standard XAFS approaches.

Separately, we have shown that FDM has some value in describing asymmetric or complex organometallics with active centres (Fig. 4) [40] and that therefore there is real information content in this data which can be explained or used to determine local structure. We are often asked ‘What is the limit of the information content of XAFS data?’ and our answer is ‘We do not know yet what that limit is, but it will be exciting to get greater information content from any given system.’

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