ＥＸＡＦＳの標準化に関する国際ワークショップについて

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今年の２月に筆者はSayers 氏からEXAFS の標準化に関するワークショップに参加するよう依頼を受けた。会議の期間はちょうどフォトンファクトリーでの実験に重なっていたが，予定を変更して出席することにした。ワークショップはEXAFS の創始者であるStern，Lytle およびSayersの諸氏の提唱によるもので米国ブルックヘブン国立研究所（NSLS）において３月７－９日に開かれた。ワークショップの表題にあるXAFS（X－Ray Absorption Fine Structure の略）はEXAFSとXANESを含めたＸ線吸収スペクトルを意味する。その趣旨は最近急速に発展しつつあるEXAFS・XANESの構造研究手法としての標準化を計り信頼性をより高めようとするもので，７カ国の研究者（28名）が骨子となるべき提案をとりまとめ，８月にシアトルで開催予定のEXAFS国際会議で承認を得ることになっている。

ワークショップは１）実験，２）データ処理，３）理論，４）データベースの４つのサブグループに分れて行われたが筆者は実験サブグループに参加した。他のグループの作業を直接知ることはできなかったが，各サブグループは途中経過を頻繁に報告しあっていたので，全体の流れを比較的容易に把握できた。実験サブグループでは各種実験モード（エネルギー走査／分散，透過／蛍光／電子収量）について問題点を整理した上で，実験の信頼性を向上させるためのチェックリストを作成した。XAFSの各種実験モードの特徴と測定対象によってそれぞれ異なる選択基準が簡潔にまとめられている。チェックリストの各項目にはポイントとなる実験条件を整理してある。これらは実験を再現するためのいわば必要条件であり，実験において注意するとともに論文を書く際にこれらを記述しておくことが望ましい。

２）のデータ処理についてはこれまでのＥＸＡＦＳ による研究論文には構造解析結果の誤差について記述が欠けていることが指摘された。正しく結果を評価し信頼性を高めるために，ワークショップでは誤差評価についての基準を提案する他，論文に記載すべきデータ解析条件をまとめた。3）の理論に関しては１），２）ほど具体的ではないがEXAFS 理論の問題点と位相シフトや散乱振幅の計算精度を上げるための計算手法に関する提案がなされている。４）のデータベースについてはデータベースの内容と利用形態についての議論が活発に行われた。データの所有権の問題，設置場所，経費については今後の検討課題であるが，近い将来，各国の主要ＳＲ施設が分散してデータベースを維持することになるものと思われる。この点については国内の研究者の意見を早期にまとめておく必要があるだろう。

今回のワークショップは短い期間ではあったが，提案をまとめるに際して共通の問題意識があるせいか，意見の不一致はほとんどなく実に要領良く作業が進んだ。なおNSLS のＸ－リングは会議の期間中は長期シャットダウン中であったがKnotek 氏によればRF，真空，フィードバック系を大幅に増強したため〝全く別のリング〟となったという。ＳＲ実験の途中で日本を離れたので時差ぼけはほとんどなかった。３日間の会議の後はさすがに疲れたが，貴重な体験であった。ワークショップの報告が遅くなってしまったが，報告書の最終稿は日本語に訳して日本結晶学会誌に掲載する予定である。

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INTERNATIONAL WORKSHOP ON STANDARDS AND CRITERIA IN X-RAY ABSORPTION SPECTROSCOPY

MARCH 7-9, 1988
BROOKHAVEN NATIONAL LABORATORY

CO-CHAIRMEN

F.W. LYTLE
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I. INTRODUCTION

On March 7-9, 1988 a workshop was held at Brookhaven National Laboratory to discuss the need for developing standards and criteria for the field of x-ray absorption spectroscopy(XAS) and to recommend methods to implement any suggestions. The workshop was attended by 28 participants from 7 countries who represented both a broad geographical distribution and also a range of interests and points of view regarding both experimental and theoretical aspects of XAS.

The participants were divided into four working groups: experiment, data analysis, theory, and XAS standards database. The workshop was organized into plenary sessions each morning to discuss the charge of the workshop and the progress of the working groups and into individual sessions of the working groups each afternoon. This format was chosen to optimize the development of specific suggestions and their evaluation by the broader group, especially since most participants had interests which overlapped with several groups. It was generally felt that this format was very successful in meeting these goals.

The range of suggestions and recommendations from all of the groups clearly demonstrates the need for the implementation of uniform standards and criteria in the field. The focussing and convergence on specific recommendations by each of the groups, particular those which contained representatives of different approaches in the areas of data analysis and theory, clearly demonstrates the maturity of the field at this time. A considerable amount of time was spent discussing the methods of implementing the recommendations of the groups. It was generally agreed that specific recommendations will be brought to the International Conference on X-ray Absorption Fine Structure V to be held in Seattle, Washington in August, 1988 at a plenary session for the approval of the community. In addition, each group will work on a number of specific activities between now and the International Conference.

The remainder of this report contains the detailed suggestions of each group. Contained within the separate reports are the recommendations for implementation from each group. The participants of the workshop are included as an appendix.

II. WORKING GROUP REPORTS

A. EXPERIMENT GROUP

Group Leaders: José Goulon, Steve Heald
Group Members: Chuck Bouldin, Alain Fontaine, Britt Hedman, Keith Hodgson, Kunquan Lu, Farrel Lytle, Hiroyuki Oyanagi

Experimental techniques involve a wide variety of issues. We have separated them into three main areas: user controlled issues, data collection modes, and facility hardware. User controlled issues include sample preparation techniques, harmonic monitoring and control, detector checkout at the start of a measurement, energy calibration and characterization of the energy resolution. The choice of data collection made requires a detailed understanding of their strengths and weaknesses. It appears that electron yield detection schemes may offer some important advantages and these are discussed along with some disadvantages. Another recent development is the use of dispersive EXAFS techniques. Facility hardware questions are often not under user control, and improvements can only come through the EXAFS community clearly making its wants and needs known to machine and beam line operators. Finally, we have summarized our discussions in the form of a checklist to be followed by users when planning and carrying out an experiment. These also form a recommendation for the types of information to be reported when presenting experimental results.

i. User Controlled Parameters

Noise levels in EXAFS measurements are usually not limited by photon statistics. Instead, the overall noise level is usually dominated by a number of systematic measurements errors, many of which can be minimized by individual experimenters. The purpose of this section is to identify the most obvious of these and suggest some possible solutions.

First, sample preparation is a critical issue that can only be controlled by the user. Transmission samples should be uniform, with $\Delta\mu x \leq 1.0$. Sample thickness should be optimized to minimize systematic errors, not to maximize photon statistics [Rose and Shapiro, Phys. Rev. (1948)]. When powder samples are measured, particle size should be as small as possible, preferably smaller than an x-ray absorption length [Lu and Stern, Nucl. Instrum. Methods 212, 475 (1983)]. If possible, samples should be measured at two different thicknesses.

For fluorescence, samples must be measured in the "thin-concentrated" or "thick-dilute" limits. Errors caused by departure from these limits should be estimated. Comparisons between samples measured in transmission and those measured by fluorescence or other indirect techniques require correction of EXAFS amplitudes to account for the energy dependence of detector response.

Harmonics from the x-ray monochromator should be evaluated quantitatively and methodology used to eliminate them should be reported. If possible a harmonic detector should be operated throughout the data collection. Harmonics may be eliminated by detuning the monochromator, or using a total external reflection mirror. The effect of residual harmonics can be minimized by use of samples and x-ray detectors which are not strongly absorbing of the harmonic. Monochromator crystals may also be chosen to minimize harmonic content of the beam, specifically by using reflections for which the second harmonic is forbidden.

Detectors must be characterized as completely as possible. Running I-V characteristics can verify that ion chambers are operating in the linear range by determining the saturation region where I is independent of V. Overall linearity of I/I_0 can be checked by placing attenuators in front of I_0. The x-ray beam must be defined by slits in front of the I_0 detectors, and, except for attenuation by the sample, the same beam must be measured in both detectors. To insure accurate digitization, voltage-to-frequency converters should be operated near the center of their range.

Energy calibration can be checked by measuring standard absorption edges or from monochromator glitches. Energy resolution can also be checked by measuring known absorption features. Since there are no universal standards for energy resolution or calibration, it is crucial to state how calibration and resolution were determined. It is recommended that a catalog of standard edges be developed with well characterized absorption features which can be used to check both energy resolution and calibration.

ii. Data Collection Modes

Depending on the nature of the samples to be measured there are several methods for collecting data:

(1)Direct transmission measurements can be carried out using two schemes. The original one is the scanning mode where the monochromator crystals rotate to increase step-by-step the energy of the selected photons. The other method uses a combination of a bent crystal and a position sensitive detector, which, under high flux conditions allows the recording of the entire XAFS spectrum in a single time interval. This is the energy dispersive mode since the diffracting angle of the impinging photons along the crystal varies continuously from one side of the footprint of the beam to the other side. One should emphasize that for constant collected solid angle, the two types of monochromators should yield essentially the same flux of reflected photons.

(2)The absorption process results in the creation of a hole in a core shell. The excited atom and the system will relax either in radiative or nonradiative ways. For x-ray fluorescence emission which leaves the excited atom in a lower energy excited state, the quantum yield is assumed to be energy-independent, making the intensity of the fluorescent signal proportional to the primary absorption process. This may also be true for optical emission, especially away from the near edge region.

(3)Nonradiative decay is a two-electron process, one of which, the Auger electron, is ejected from the excited atom. In the Auger process, the electron detector is tuned to the energy of the Auger electron which is specific to the probe atom. Thus, there is no basic difference, in principle, in detecting this process or the fluorescence yield. The choice of one scheme with respect to the other has to take into account: (1) the atomic number (Z). Low Z atoms decay preferentially through the Auger electron process; (2) the ability to collect electrons emitted in a large solid angle; (3) the difficulty in collecting electrons with good energy selectivity without a vacuum; (4) the large probability that the Auger electron will undergo inelastic collisions. Because of the relatively short inelastic mean free path of the ejected electron, Auger detection provides a signal specific to the near surface region. For most cases Auger yield is restricted to surface investigations. If the energy band pass of the detector is opened partially (partial yield) or opened totally (total yield) the signal comes in part from Auger electrons which have undergone inelastic collisions. In any case, the electron yield is energy independent and the mean free path is short so that the signal arises from a layer which is not larger than 1000 Å. As soon as this depth is much smaller than the absorption length of the exciting x-ray, the total yield intensity is proportional to the primary core-hole creation. All the methods using decay channels require a step-by-step collection.

While the assumption of an energy independent yield for both electron and fluorescent detection methods seems to work well for many cases, a systematic study is required to verify this observation. We recommend that further work be conducted to understand this situation. In particular, identifying those situations for which the proportionality may break down would be especially helpful to experimenters.

(4) Other modes such as ion yield and related areas such as various forms of electron energy loss are less common or more specialized and were not discussed further at this workshop.

We now consider the special characteristics of the common detection methods: absorption, fluorescence and electron yield.

a) absorption

Issues pertaining to absorption measurements in the standard step-by-step mode were considered in the section on user controlled issues. Most of the same considerations apply to dispersive mode transmission measurements. There are, however, some special characteristics of the dispersive mode.

1. All data are collected at once, hence it opens the possibility of time-resolved experiments. The present time resolution which is available is between 0.003 s and 120 s, according to the dilution and the required signal to noise ratio. Currently published results for real investigations deal with a time resolution larger than 0.2 s.

2. The quality of the data comes from the insensitivity to temporal fluctuation of the source and the lack of mechanical movement during data collection, which yields in addition a high stability of the energy scale.

3. The bent Bragg crystal gives an image which is 500 μ-wide when the 23-cm long crystal is specially designed to get an ellipsoidal shape. Then it is possible to work with small samples (i.e., high pressure experiments). But the homogeneity of the energy distribution within the focus spot is not perfect. This gives a very high sensitivity to sample thickness inhomogeneity. Powdered samples require great care in preparation.

b) fluorescence

4. It is now well appreciated that measuring fluorescence excitation spectra is more efficient than conventional transmission experiments:

a. for dilute systems,

b. when the sample is too absorbing, a situation which often prevails for soft x-ray measurements (e.g., below 5 KeV), and,

c. when it is not possible to prepare samples with enough homogeneity for carrying out transmission experiments.

5. However, one should keep in mind that even though x-ray fluorescence excitation spectra have basically the same structural content as transmission spectra the relative amplitude of the observed structures might be different. There are at least two physical reasons for that:

a. The formulation of the intensity of the fluorescence signal is a more or less complicated function of the absorption coefficient at both the energy (E) of the incident photons and the energy (E_F) of the emitted fluorescence photons. Corrections are thus absolutely necessary in the case of concentrated or highly absorbing samples.

b. As mentioned above the quantum yield of the fluorescence process is usually regarded as being constant over the whole energy range of the XAFS spectra, but there are no reasons to believe that this is correct in the preedge region, especially in the case of XANES spectra recorded in the soft x-ray energy range. One has therefore to be extremely careful when comparing XANES spectra recorded in different modes at low energy.

6. From the experimental point of view there are a number of difficulties which have to be overcome:

a. Detectors should cover as large a solid angle as is possible.

b. Elastic and inelastic scattering contaminating the fluorescence signal should be reduced as much as possible. At present, discrimination between fluorescence and scattered/diffracted photons can be obtained by using Z-1, Z-2 filters, in limited ranges, or by using a large array of energy dispersive solid state detectors.

c) electron yield

7. In the past electron yield techniques were mainly used in SEXAFS experiments where the high surface sensitivity is a distinct advantage. Recently, however, it has been realized that electron yield methods may offer some distinct advantages for bulk samples. Electron yield XAFS consists of biasing the sample (typically 20-100 eV) so that the electrons emitted from the x-ray absorption event can be collected at a convenient grid or wire(s) near the sample. The electrons consist of photoelectrons, Auger electrons and primarily the inelastically scattered electrons. The depth sampled vs energy may be estimated from the universal curve of electron energy vs depth. Sample energy selection may be achieved by a double grid detector and a negative bias on the grid nearest the sample. Since one x-ray photon creates many electrons on the sample and the electrons with energy greater than the first ionization potential of the ambient gas create more ionization, the signal level is much higher than a typical fluorescence measurement. A low Z fill gas (He or H_2) creates a constant environment and also minimizes the absorption of fluorescent x-rays in the e-detector. This minimizes the effect of x-ray diffraction from the sample, a problem with single crystal samples. Some advantages and disadvantages are listed:

a. Advantages

Minimum sample preparation for samples which are constant composition all the way to surface, thickness effect problems have minimum effect on spectra - can measure edge resonances accurately, signal levels are very high, $\sim 10^2$-10^3 more than other detectors, the technique samples the top ~1000 Å of surface but with energy selection (i.e., biasing a two grid detector) selectivity may be the top ~50 Å. Instrumentation is very simple and inexpensive and may be adapted to variety of sample configurations including the reflection technique or in the gas phase. There is reasonable sensitivity to 10^{14}-10^{15} atoms on a surface. At the minimum it has a solid angle of 2π or 4π for gas phase samples. No diffraction glitches from single crystal samples (i.e., He or H_2 used as fill gas).

b. Disadvantages

Detailed physics is not yet well understood, it is sensitive preferentially to surface, e.g., Cu_2O may easily be identified on surface Cu; nonconductive samples must be made conducting by smearing on Al foil or placed on a conducting grid. The sampling depth is the electron escape depth, therefore, it may be of limited use for dilute samples or wet samples unless the wet layers are very thin.

C. Facility Hardware

Hardware related questions are less under the control of users, but can be addressed by the operators of EXAFS beam lines. The most common problem is that of monochromator glitches. These can be minimized by linearizing the detection system, and by careful control of crystal alignment, but are likely to always be a problem for dilute samples. For the users it is important to catalog the glitches from a particular crystal set so that the appropriate set can be chosen for an experiment.

Many of the issues raised in the section on user controlled issues require equipment in addition to the two ion chamber absorption setup. Instead of each group supplying such equipment it makes more sense for the facility to provide it. This would include the detectors and electronics for a third energy calibration and harmonic detection channel. Bragg reflecting energy calibration and polarization detectors, as they are developed, would also fall into this category.

In the future hardware improvements may still be important in improving the quality of data. We believe beam noise is still contributing to the overall signal to noise of the spectra. On-line position monitoring is extremely important in assessing and controlling this problem. Possible improvement in optics include harmonic rejection mirrors and active beam stabilization by moving an optical component such as a mirror or monochromator crystal. Care has to be taken in such a scheme that some other parameter such as harmonic content is not varied in the attempt to stabilize the beam.

Many of these ideas have been suggested to the facilities by local user groups over the years, and progress has been made in many cases. It is safe to conclude, however, that improvements are still possible at all facilities. In order to enhance the process, standardize beam line equipment and to communicate advances at one facility to the others, we believe that the international community needs a voice in addressing such problems. (Note: the workshop later formed a committee chaired by D. Koningsberger to address such issues.)

D. Checklist for Experimental Procedures

The following list of experimental conditions/parameters is recommended:

1. when measuring at the beam line
2. when writing a paper
3. to serve as a checklist for referees

    a. Source/Beam Line

        (1) Facility and beam line used.

        (2) Synchrotron energy (and if applicable, current).
        (3) Monochromator type (double crystal, channel cut, reflection, etc.).

(4) Use of focusing mirror, and if so mrad used and mirror angle.

(5) Estimate of beam polarization (when applicable).

b. Energy

(1) Energy calibration (how determined, which *feature* used, and what *energy assigned* to this feature if reference compound is used).

(2) Energy resolution (when important, particularly for XANES measurements; if a value is quoted it *should* be stated whether it is only spectrometer resolution, or if core-hole effects are taken into account; whether FWHM vs HWHM; it is recommended to run a common standard and compare the achieved spectrum with previously estimated values for a "standard spectrum" of this sample).

(3) Harmonic rejection (method to establish that higher harmonics were eliminated.)

c. Detectors

(1) Determination of energy dependence of the response function for the I_0 ion chamber; if done, whether and how a correction was applied.

(2) Calculation of the number of photons/sec on the sample.

(3) For fluorescence detectors, give count rate, linearity check, if hardware and/or software correction for nonlinearity was applied.

(4) Type and thickness of filters used with fluorescence detectors.

d. Sample

(1) Details of sample preparation (whether diluted and pressed, mounted on tape, number of layers of tape, window and sample cell material for solution and proteins,etc.)

(2) Values of μx and $\Delta\mu x$ for sample.

(3) Suggestion: At the time of the experiment run a "blank" sample, i.e. the same optical density but without the element whose edge is being studied.

B. DATA ANALYSIS

Group Leaders: Grant Bunker, Daryl Crozier
Group Members: Steve Cramer, Diek Koningsberger, Pierre Lagarde, Yanjun Ma, Tim Morrison, Grayson Via

It was agreed that the basic procedures of data analysis are understood. Review papers in the literature and recent books on x-ray absorption spectroscopy provide the beginner with a convenient introduction to data analysis methods. (eg., T.M. Hayes and J.B. Boyce, Solid State Physics, vol. 37 (1982) 173; D. E. Syaers and B.A. Bunker, Chemical Analysis, vol. 92 (1988) 211, Chapter 6 in X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, eds. D.C. Koningsberger and R. Prins, J. Wiley and Sons, (1988); B.K. Teo, EXAFS: Basic Principles and Data Analysis, Springer-Verlag (1986), Inorganic Chemistry Concepts, vol. 9.)

It was agreed that a weakness in EXAFS publications is the assessment of errors associated with deduced structural parameters. An initial suggestion is given below for the estimation of errors, but it requires further refinement by the EXAFS community.

Other topics summarized in this report include a commitment to compare data analysis software, a need to conduct further transferability tests, some technical details on background removal and normalization, a list of details to include in published work, and a summary of some data analysis methods.

i. Estimation of Errors

The errors in an EXAFS experiment are both random and systematic. Random errors result from photon counting statistics, fluctuation in position and intensity of the x-ray beam, and electronic noise. Systematic errors occur both in data acquisition and data analysis. The former includes effects such as: degradation of samples or standards which are hygroscopic, reactive or susceptible to radiation damage; thickness and particle size effects resulting from harmonics, sample inhomogeneity, and large particles ($\mu d \geq 1$); leakage of x-rays around the sample and scattering; monochromator crystal "glitches"; Bragg diffraction from ice crystallites in biochemical samples; and nonlinearities in detectors. The data analysis itself will introduce errors due to effects such as: errors in spectra of reference compounds which occur when the standard and unknown are taken under different experimental conditions, e.g. fluorescence/transmission/conversion electron/energy resolution; incorrect crystallographic form for reference compound; non-transferability of reference amplitude and phase; and technical errors such as background removal, normalization, filter windows and transform artifacts, and omission of monochromator resolution function when comparing theoretical amplitudes with experimental data.

Errors should be evaluated from a functional of the generic form

$$\chi_\nu^2 = \sum_i^{\mathrm{Npts}} (\mathrm{Data}_i - \mathrm{Model}_i)^2/\sigma_i^2 \qquad (1)$$

This is analogous to the reduced chi-squared used in the conventional analysis of errors where the errors follow a normal distribution (e.g. P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, 1969, Chapter 5). In (1), ν= Npts - p, where p is the number of fit parameters, and $\sigma_i^2 = \sigma^2_{\text{statistical}} + \sigma^2_{\text{non-statistical}}$. N is the number of independent data points calculated from $\text{Npts} \approx 2\Delta k \Delta R/\pi$ where $\Delta k = k_{max} - k_{min}$ is the k-space range over which $\chi(k)$ is being fit and $\Delta r = R_{max} - R_{min}$ is the filter window. The expression for Npts can be derived from considerations of the Nyquist sampling rate.

$\sigma^2_{\text{statistical}}$ represents the standard deviation in each data point due to random errors. It could be estimated by taking 3 or more scans for a given edge and then calculating the standard deviation.

$\sigma^2_{\text{non-statistical}}$ represents the systematic errors in data acquisition and data analysis. The errors in data acquisition can be minimized by good experimental procedures. The errors introduced by the data analysis itself are more difficult to estimate. It may be possible to do this by analyzing simulated data with added random noise. (Question: how much random noise?) Errors associated with non-transferability can be estimated by using multiple reference compounds.

The factor 1/v permits one to place on a quantitative basis the error associated with a model in which p parameters are varied. The best fit model is the one for which σ_v^2 is approximately unity or less. This will be the case providing we have the correct fitting function and the correct estimates for $\sigma^2_{\text{non-statistical}}$. The value of σ_v^2 less than 1 does not indicate an improvement of the fit. However, these statements are complicated because getting the correct value of $\sigma^2_{\text{non-statistical}}$ may pose a problem. Until this issue is resolved, we recommend that the error bar to be associated with each parameter should be obtained by changing that particular parameter while least squares refining the others until the χv^2 contribution for that parameter is increased by one. At the same time, if this assignment is to convey useful information, it is essential to quote also the best-fit value of χ_v^2.

To adapt equation (1) to non-linear least squares fitting algorithms, it is convenient to sum over all data points, N, rather than just the number of independent points and then weight the sum by Npts/N. This is equivalent to replacing the contribution to the summand of the data points between the independent points by the average value. In this case (1) is replaced by

$$X_v^2 = (\text{Npts}/v)(1/N)\sum_i^{\text{Npts}}(\text{Data}_i - \text{Model}_i)^2/\sigma_i^2 \qquad (2)$$

ii. <u>Comparison of Data Analysis Software</u>

The following people have agreed to analyze a common set of data: Zhang(ISFS), Crozier (Simon Fraser University), Koningsberger (Eindhoven

University), Lagarde (LURE), Lytle (Boeing), Ma (University of Washington), Morrison (Illinois Institute of Technology), Via (Exxon Research and Engineering Co.), Sayers (North Carolina State University), Scott (University of Georgia), Hasnain (Daresbury)

The data will be selected and and distributed by Grant Bunker. It will include reference systems and an unknown. It is intended that the analysis will be completed by July 1, 1988 in time to permit comparison of the structural results at XAFS V.

iii. Transferability Tests

The question of transferability of amplitude and phase should be re-examined. While separate groups may wish to conduct in-depth studies, in order to expand the range of systems investigated, all experimentalists are encouraged to use multiple reference standards and to perform internal cross-checks to assess errors due to non-transferability. They should comment explicitly upon their results as a routine matter in a subsection of their published papers. So that their transferability conclusions are not "lost" in the literature they could submit a note to the EXAFS database which is being established.

iv. Technical Details

While the committee discussed many aspects of data analysis, it was felt that background removal and normalization required specific comment.

1. Background Removal

Care must be taken to ensure that the background does not alter the first shell data. This can be checked by comparing derivatives of the background with the data to be sure that the background does not contain first shell frequency components. Alteration of the data can be checked by looking at the Fourier transform of the data. Background removal is problematic when the bond lengths are very short and for data at low k because of uncertainties in the detailed behavior of $\mu_0(E)$.

It is advantageous, particularly when studying dilute samples, to run a blank sample, which contains all but the element of interest, to obtain background for the post-edge region.

2. Normalization

A suitable normalization function is

$$\chi(k) = (\mu(E) - \mu(E)_{\mathrm{background}}) \bullet (\Delta\mu/\mu(E))_{\mathrm{McMaster}}/\Delta\mu_{\mathrm{expt}}$$

where $\Delta\mu_{\mathrm{expt}}$ is the jump in the absorption at the edge and $(\Delta\mu/\mu(E)_{\mathrm{McMaster}}$ is the ratio of the absorption coefficient normalized to the value at the edge evaluated using the McMaster coefficients. The latter aproximates the energy dependence of $\mu_0(E)$. However, small errors may occur when comparing to theory, especially near the edge, since the McMaster term is based on an extrapolation from higher energies down to the edge.

v. Summarizing and Presenting Results

The information content of published papers would be improved if the following were done:

1. Display raw data as $\chi(k)$ or $k\chi(k)$.

2. State clearly the numerical procedures used to remove background and to normalize the data.

3. Identify the location $k = 0$ relative to readily distinguishable features in $\mu(E)$ (or its derivative).

4. State window functions used in k-space and in R-space.

5. State window ranges (k_{min}, k_{max}; R_{min}, R_{max}) and type of window used.

6. Scale the ordinate axis on the modulus of the FFT (these are not arbitary units). The numerical magnitude of the Fourier transform provides useful comparative information for the reader. A scaling convention will be suggested before XAFS V.

7. Include the correlation matrix as a table to provide an indication of the correlation between fit parameters. In publications in which more than one system is examined, space restrictions of the journal will probably dictate that the correlation matrix be restricted to the single most significant structure.

vi. Survey of Data Analysis Methods

A brief overview of the most common data analysis strategies follows:

1. Direct Fitting of Multishell Data in E-Space or k-Space

This method, which has been extensively used by groups in the U.K., avoids the complexities and pitfalls of Fourier filtering. The data analysis is usually done shell-by-shell, each previously-fitted shell being included in later firs. It is profitably done in conjunction with Fourier transformation. Empirical or empirically-modified theoretical phase shifts (the $\Delta_L$of scattering theory) and amplitudes must be used in fitting.(Perutz et. al. Nature, 295,535(1982), Hasnain, Life Chem Reports 4,273(1987), Strange et. al. JACS 109,7157(1987)) A full statistical check, on the lines suggested above, is included. Fourier filtering may be used as an aid to construct a starting model for the unknown structure.

2. Analysis of Fourier Filtered Data

The principal disadvantage of Fourier filtered data is that it is necessary to deal with the ensuing truncation effects. It is possible to cause such distortions to cancel out to a good approximation by matching the window functions for the standard and the unknown. If theoretical data are used, it is desirable to filter the theoretical data the same way as the unknown to cancel truncation effects.

a. Ratio Method/Cumulant Expansion

The ratio method (Stern, Sayers, and Lytle, 1975) is beneficial for slightly disordered coordination shells that comprise only a single type of atom. A strong benefit of this method is that, unlike nonlinear least squares fitting, there is a single unique minimum, because the fitting function is linear in the parameters. For systems with moderate disorder, the cumulant expansion (G. Bunker, 1983: Rehr (1983)) provides corrections to the Gaussian approximation.

The higher order cumulants, however, difficult to determine uniquely due to parameter correlation.

b. Parametrization and Splice Methods

For shells containing only one type of atom, but which are strongly disordered ($k\sigma \geq 1$), parametrization of the radial distribution function and nonlinear least squares fitting may be useful. Alternatively the splice method may be used. The splice method replaces the low k data, which often is unavailable for analysis because of multiple scattering and other effects, with an extrapolation using the cumulant expansion. All distributions have a Gaussian Debye Waller factor at sufficiently low k. Higher order cumulants become important at high k, and this cumulant expansion has a known k-dependence that is matched to the filtered data. The whole function then can be inverted using the sine Fourier transform to give an estimate of the radial distribution function.

c. Nonlinear Least Squares Fitting

When more than one type of atom is contained in a coordination shell it is most appropriate to perform nonlinear least squares fitting to the filtered data. This is the most general and commonly used approach for filtered k-space data. When fitting, care must be taken to locate the global minimum because of the presence of multiple local minima. It is also appropriate to fit the R-space data. Transform artifacts can be minimized by creating the model function in k-space and then Fourier transforming it under the identical conditions to the data. In fitting one can minimize the residual sum of squares of the difference between the real and imaginary parts of the transforms of the model and data.

In general it would be advantageous to use both k-space and R-space fitting procedures. They sample the parameter space in different ways and thus can be used to avoid false local minima. In the ideal case, the two fits should converge to the same set of parameters, but usually will not. They can be used to assess the error bounds to be associated with the parameters.

d. Other Methods

(1) Estimation of distances from inspection of Fourier transformed spectra in r-space is problematic and is discouraged. Peak positions may be influenced by the weighting of nonlinear phases and possible asymmetric distributions, and therefore the peak position does not reflect only the average distance. The detection of asymmetric effects is often best done in k-space. Similarly, coordination numbers generally cannot be reliably obtained from Fourier transform peak heights.

(2) Extrapolation/Linear Prediction Methods - Although maximum entropy power spectra do not suffer from truncation ripple, the spectra do suffer from the same spurious peak shifts that ordinary Fourier transforms do. The elimination of truncation effects is accomplished essentially by a "best guess" extrapolation of the data, which, in principle, is done without altering the information content of the data and thus avoids errors due to incorrect assumptions regarding the high k behavior of c(k). Ad hoc extrapolation methods which do not include physical information are of questionable value for data analysis.

(3) Regularization methods - Because low k data are not generally available in EXAFS, the direct inversion of k-space data into a radial distribution function is not possible without the input of additional information. Regularization methods (Babanov et al) do this in a consistent way, and may be useful in some cases. In present form such methods appear unsuitable for general purpose data analysis. The issue of error estimates has also not been addressed. Further development of the methods to overcome present real or perceived limitations is encouraged.

C. THEORY

Group Leaders: John Rehr, Steve Gurman
Group Members: Samar Hasnain, Ed Stern, Antonio Bianconi

i. Theory of EXAFS

The theory of EXAFS has been extensively developed over the past ten years and we now have enough experience to be able to define the minimum level of theoretical analysis. We feel that it is useful to define two levels of theoretical analysis: a simple level based on tabulated standard scattering data and a more detailed level based on any one of the several advanced data analysis programs now available. Both levels have their place in the EXAFS community. For both levels of theory we separate the theoretical description of EXAFS into two parts: one describes the propagation of the photoelectron and the basic process of scattering; the other is concerned with the details of the calculation of the scattering potential.

1. Scattering Theory

The problem of the propagation of the photoelectron is, we feel, essentially solved in the form of the exact spherical wave (Rehr, Albers, Natoli, Stern, Phys Rev B, 1986) or curved wave (Gurman, Binsted, Ross, J. Phys, 1984, 1986) theories which now describe both single and multiple scattering contributions. Single scattering contributions may be calculated very rapidly using either of the exact theories and these should always be used. Multiple scattering contributions take longer to calculate, but may be included using either the fair approximation of the small atom approximation (Gurman) or the more accurate spherical wave expansion (Rehr). If more exact results are required the somewhat slow curved wave theory may be used (Strange et al JACS 109 7157 (1987); these are especially important to test convergence of the spherical wave theory. We feel that the plane wave approximation is now outdated and should not be used.

For the simpler level of theory we propose the publication of a set of tables of $f(\pi,k,R)$, for single scattering contributions, based on curved wave calculations. These represent an improvement in accuracy over the Teo and Lee tables which were based on the plane wave approximation and would be used in the same way. We propose publishing these for perhaps three interatomic distances (including $R=\infty$, corresponding to Teo and Lee) and for two different environments, one close-packed and one open, to show the level of chemical effects (non-transferability) in scattering factors. Such tables already exist (McKale/Knapp) but we feel that a set agreed upon by all major laboratories, based on the best scattering potentials available and extensively tested against standard compounds would be more generally accepted. They would include such non-structure parameters as mean free path and shake-up, shake-off constants.

2. Potentials

We feel that the calculation of good scattering parameters requires the use of the Mattheiss prescription of overlapping charge densities rather than free atom charges, with energy-dependent exchange potentials of the Hedin-Lundquist type (Lee and Beni) or alternatively with an energy-dependent Haru-Dirac (real) potential and a constant imaginary part given by experience. Core hole lifetimes and possible instrumental effects should be included by means of an additional constant imaginary energy part of the photoelectron energy (or equivalently, of the potential). In the future we hope that full self-consistent potentials will become the standard. In order to fix the "zero" potential, i.e., the E_0 parameter which refers the edge to the muffin-tin zero, we may either treat it as a fitting parameter in the major codes or determine it by aligning the phase of the theoretical $f(\pi,k,R)$ plus the emitting atom phase to that of an experimental spectrum from a standard. In order to allow for small differences in distance we suggest comparing $2kR+\phi$ for the two and varying E_0 (and hence k) until the difference is zero when extrapolated to $k=0$.

To describe the emitting atom potential (which will also be tabulated) we recommend the use of fully relaxed Z+1 wave functions with a core hole present, the total occupancy being that of a neutral atom. Again, we hope that self-consistent relativistic atomic codes will be available in the future. Dynamic and many-body effects (shake-up, shake-off, or S_0^2) (Chou, Rehr, Stern, Davidson, 1987) will be tabulated in the form of empirical values which are slowly varying with Z. In the future these effects may be calculable (Lu and Rehr, 1988).

3. Debye-Waller Factors

The Debye-Waller factor $\sigma_j^2(T)$ which is under the assumption of Gaussian peak shapes in the RDF should be fitted for each shell. In multiple scattering paths the plane wave form $\sigma^2(1-\cos q)$ where q is the scattering angle is sufficiently accurate to be of practical use. The asymmetric corrections or higher moments σ_3 and σ_4 (especially σ_3 which describes the thermal expansion) should also be included in the fits if they prove to be necessary.

In order to provide a generally acceptable set of $f(\pi,k,R)$ we propose that each of the three or four major data analysis codes should be run for a set of good experimental spectra from samples which give a good spread across the periodic table so that consistent values be obtained and checked. We propose using:

K edges	Al	Si	Cl_2	NiO	CuO	Nb_2O_3	Cu	Rh	Rh_2O_3
L edges	Pd	Pt	Pb						

ii. Theory of XANES

The general state of the theory of XANES is one of much less development than is the case with EXAFS. The level of agreement between theory and experiment is uncertain and much more work needs to be done: this is particularly the case for energies within about 20 eV of the edge.

The energy origin E_0 is generally given correctly only with the use of energy-dependent potentials (Hedin-Lundquist exchange or something similar). With the use of these the relative separation of peaks in the XANES is given reasonably accurately but the prediction of amplitudes and lineshapes is poor. Structural information on unknown materials can at present only be obtained after accurate comparisons between theory and experiment on standards. The sensitivity of XANES to structure is such that different symmetries may be simply distinguished and distortions on 1st shell distances of about 0.2 Å can, at present, be identified. XANES spectra also contain useful information on more distant shells, to a greater distance than EXAFS due to the longer electron mean free path at low energies although this may be limited by the finite core-hole lifetime. Theoretical developments at present in testing (Rehr, Bianconi) promise major improvements in accuracy.

There are at present several approaches to XANES theory. The most comprehensive, and the most complex, are the many-electron quantum chemistry codes based on cluster calculations. The one-electron approaches are all equivalent, if carried to full convergence, and the choice between them is a matter of convenience and speed. The main one-electron theories, all of which are capable of giving structural information, are the multiple scattering EXAFS codes involving a sum over scattering paths (Rehr) and the cluster multiple-scattering program (Pendy/Durham). These theories all have structural sensitivities at the levels noted above.

We are fairly clear as to the directions in which XANES theory should develop in order to satisfy the needs of the community. Most of these relate to the calculation of the potential: all of the points mentioned in this context in the EXAFS section apply to XANES and are generally even more important - this is particularly true of the energy dependence of the potential and of dynamic effects. There is also much work to be done in determining the structural sensitivity and the range of interatomic distances of importance in XANES.

D. EXAFS STANDARDS DATABASE

Group Leaders: Tony Cox and Bruce Bunker
Group Members:Tim Elam, Samar Hasnain, Dale Sayers, Geoff Woolery

i. Overview

The purpose of the database is to facilitate exchange of:

1. Reference spectra
2. Published spectra
3. Theoretical phases, amplitudes and potentials

4. Software for theoretical calculations, analysis, data acquisition and documentation

The advantages of this database are to allow the access and monitoring of the quality of EXAFS data and software, to facilitate cross-checks between groups, provide corroboration of reference data, and to minimize the duplication of effort.

ii. Contents of Database (Specifics)

Ensuring that the database only contains work of the highest quality would, in our opinion, involve a considerable amount of work in both verification of results, and testing of programs and theoretical expressions. Therefore, we propose that the practicable implementation would be reliant upon the 'bona fide' contributions of the EXAFS community, with minimal 'policing' of the information contents. It would be the responsibility of the end-users of the database information to ensure that they were using data from reliable sources. However, for items to be included in the database, we should insist upon a minimum standard of documentation as detailed below.

Each item entered into the database would have a 'comments' entry, which would permit the end-users to report observations on the quality and applicability of the data and software to their individual needs. Items that subsequently turned out to be inaccurate or misleading could then be deleted, using essentially a 'peer review'.

It is suggested that apart from the formal peer review process, that entry and access of information to the database should essentially mirror the procedures for scientific journal publication. For instance, if data from the database is used in a publication, permission should be sought from the original contributor. We propose no limitations on access to the database, although a small 'subscription charge' might be necessary to provide funding for the maintenance of the database.

1. Reference Compounds

Reference compounds are compounds of known structure, that can be used as an aid to EXAFS analysis, and to provide corroboration of other experimental results.

The database entries will consist of the following information:

a. EXAFS raw (unprocessed) data, ideally with additional data channels that record absorption from a reference channel for calibration, and an indication of harmonic contamination.

b. The authorship and contact addresses of the experimenters.

c. Information concerning the structure and supplier of the sample, which should include whether the structure of the sample was confirmed by x-ray powder diffractometry.

d. The synchrotron source, beamline, and machine operating parameters.

e. Sample preparation techniques, including an estimate of thickness, and the particle size.

f. Temperature.

g. k space range or energy range relative to the edge

h. An estimate of energy resolution, including monochromator information and source size estimates.

i. An estimate of harmonic contamination, and the steps that were taken to reduce the effect of harmonics.

j. Information on the configuration and operating parameters of the detectors.

k. Sample concentrationsize of powder, no. of layers, total $\Delta\mu x$.

l. Comments by the experimenter, and additional comments made by users of the particular database entry (such as reporting any anomalies that could be attributable to problems in the reference sample run).

m. Various 'key words' to facilitate the cross indexing, and retrieval of information.

2. Published Spectra

It is envisioned that experimenters publishing results in the literature would contribute copies of their raw experimental data. The contents of this would generally include as much information as possible from the list above (for reference spectra), and in addition, references to the journal item in which the data was published.

3. Theoretical Amplitudes, Phase Shifts and Potentials

This item would include 'state of the art' calculations of scattering amplitudes and phases, emitting atom phase shifts, and crystal potentials that were used to obtain them. This would typically be modelled upon existing tables (such as Teo and Lee), but would be expanded to include 'r' dependence which is a consequence of curved wave EXAFS theory.

4. Software

This item would include software for data analysis, data collection and theoretical calculations and would also include documentation for the programs, and where applicable, test data that could be used to verify that the programs were operating correctly. Depending upon the software, the code would be available in either executable, object (compiled but not linked), and/or in source code form.

There was considerable discussion at the working group about the form that software would be made available to the community. There are advantages and disadvantages to including source code for programs, which we categorized as follows:

a. Advantages

  (1) User confidence/verification.

  (2) Greater hardware independence, and possibilities of transferring to other computer systems.

b. Disadvantages

  (1) Tendency for proliferation of multiple versions of the programs.

  (2) Possible legal implications of making source code 'public domain'.

An obvious compromise is for the contributor to decide the form that the code would be made available through the database. The database could also act as a bulletin board for the exchange of programming ideas and program implementations.

iii. Implementation

It is envisioned that the database would be truely international, providing a repository for information and ideas from the entire EXAFS community. As a consequence, we see a need for a central facility to manage and coordinate the database.

Because of current limitations in the worldwide computer networks, there is also a need for the database to be made available in the various national and regional centers. A natural location for the regional databases would be the existing synchrotron radiation centers; this would have the advantage of permitting the various user groups to obtain information quickly and reliably from the centers, since it would use much of the currently existing computer and data communicatiosn facilities. To our knowledge, all existing synchrotron facilities (with the possible exception of Novosobirsk) have available VAX/VMS computer systems, which would greatly simplify program development and the exchange of information.

Our estimates of the amount of data and programs that would initially be incorporated into the database, and the likely increase of this data over time, suggests that the volume of information that would need to be exchanged could easily be handled by the existing worldwide computer networks. Since most accesses will be ready 'read only' (users extracting information from the database), the data will be provided by the regional centers and will therefore not generate any excessive traffic on the global computer networks. Updates to the database would be distributed by the central repository to the regional centers, at appropriate time intervals. Additional information to be included in the database would be sent directly from EXAFS contributors to the regional centers for forwarding to the central repository. The regional centers would not add these contributions directly to their own database, thus ensuring that the various database copies around the world reflect the same information.

Experience with existing databases suggests that the likely manpower requirements to service such a faciity would be approximately the equivalent of one full time database administrator/programmer. There would be a considerable initial manpower investment, required to set up communications software to implement both local (regional) access, and the transfer of data between the central repository and the local centers. We estimate this initial time investment could approach 2-5 man-years for the central facility, and probably around 1 man-month at each of the regional centers.

iv. Other Recommendations/Questions for Further Discussion

1. That we establish a standing committee for the implementation of these ideas. A natural starting point for this would be the International Conference on X-ray Absorption Fine Structure (XAFS V).

2. Considerable experience in the maintenance and distribution of other scientific data (such as the crystallographic database) would be useful for the detailed formulation of the scope and structure of the EXAFS database. We recommend that this expertise be 'tapped'.

3. We had discussions about various legal implications of including data into publically accessible databases. While probably not an issue for university users, there may be implications for industrial and governmental users. We have no background to expand upon this question in detail, but feel it should be considered at an early stage.