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Obtaining reliable structural parameters from EXAFS

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Abstract

The accuracy of the structural parameters (i.e. type of neighbour, number of neighbours of a specific type, distance between absorber and neighbour, and disorder) that are obtained from the analysis of EXAFS spectra is in theory only depending on the errors in the data. However, the experimental set-up, the standard used to build the model EXAFS, and data analysis method may introduce systematic errors. This paper discusses several methods to decrease the errors associated with the method of data analysis. With MoS₂ as an example the use of phase corrected Fourier transforms to determine the type of neighbour is demonstrated. The conventionally applied k^3 -weighting of the data was compared to k^1 -weighting and weighting by the inverse of the statistical error in the refinement of the structural parameters of PtO₂. Weighting the data with the inverse of the statistical error gives results in agreement with XRD structure determinations and the best goodness of fit values (ϵ_v^2). © 1998 Elsevier Science B.V.

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1. Introduction

Immediately after Stern and coworkers [1] formulated the current theory of the origin of the extended X-ray absorption fine structure (EXAFS) in the early 1970s, the potential of EXAFS for the study of catalysts was recognized. At first, studies focused on obtaining particle sizes for highly dispersed supported metal catalysts, which yielded data available from neither TEM nor XRD. Developments in the brightness of X-ray sources, sensitivity and linearity of detectors as well as the availability of in situ equipment extended the amount of information that can be obtained with X-ray absorption spectroscopy

(XAS) significantly. The most challenging, but already possible, application of XAS is the determination of the structure of a catalyst during preparation or under reaction conditions.

For particle size determination as aimed for in the first XAS experiments on catalysts, analysis of the first single scattering shell suffices. The structural parameters of a model EXAFS spectrum with one contribution can be refined with non-linear least-squares methods, but phase and log-ratio fits [2] decrease the correlations between the parameters and hence yield more reliable results. In highly dispersed metal catalysts and oxides the first coordination shell contains several different scatterers – often at different distances as well – limiting the applicable analysis methods to non-linear least-squares methods. In order to decrease the correlations between the structural parameters of different contributions with nearly equal

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distances, Koningsberger and coworkers [3,4] developed the “difference file technique”. The difference file technique allows the visualization of the contribution of different scatterers to a single coordination shell, but this ability to look at very small signals does not increase the amount of information that can be obtained from EXAFS.

The momentum to extend the analysis of EXAFS spectra beyond the first coordination shell came from research on enzymes and complexes. However, analysis of higher coordination shells calls for the inclusion of multiple scattering paths in the model EXAFS and it was not until the late 1980s that computer codes [5,6] and hardware became available which made routine analysis using multiple scattering feasible.

The accuracy of the structural parameters derived from the analysis of an EXAFS spectrum is still under debate due to the large number of sources for both systematic and statistical errors. A general approach to the problems and errors that should be dealt with during measurements can be found in the book “X-ray Absorption” edited by Koningsberger and Prins [7], a paper that specifically focuses on XAS experiments with catalysts appeared recently [8]. The errors that arise from errors in the various types of absorber–scatterer potentials or standards were discussed by Vaarkamp et al. [9] and Li et al. [10]. This paper only addresses the errors that are attributable to the analysis of an EXAFS spectrum and the statistical variations (noise, errors) in the data.

It is possible to make a huge systematic error in the analysis of an EXAFS spectrum by choosing the wrong backscatterer for a contribution. Phase corrected Fourier transforms and different k -weightings can be very helpful in this aspect of data analysis.

In 1982, Morrison et al. [11] showed that statistical noise affects the shape of Fourier transforms and generates ghost peaks. In single shell systems that can be analysed with the phase fit and log-ratio method, noise affects the structural parameters for light elements more than the structural parameters for heavy elements due to the shorter data range that can be used to determine the structural parameters of the light elements [12]. However, at high noise levels, distance determinations remained accurate (± 0.02 Å), while the errors in the coordination number and disorder reached 30%. It has also been pointed out that in model spectra with several shells, correlations

between parameters contribute significantly to the errors in the structural parameters [13].

Mathematically, data should be weighted with the inverse of their error to obtain the best parameters from (non-linear) least-squares refinement. The effect of different weighting schemes on the structural parameters derived from the EXAFS of PtO₂ will be demonstrated.

2. Backscatterers

A neighbour of the absorbing atom is characterized by its phase shift $\{\phi(k)\}$ and scattering potential $\{F(k)\}$. Consequently, identification of a scatterer involves the extraction of these two functions from the EXAFS and/or comparison with known values. However, finding the exact atomic number of the neighbouring atom is not as easily accomplished as would be expected due to the similarity of both phase shift and scattering potential of neighbours in the periodic table. Model studies and calculations [14,15] have revealed that it is possible to distinguish between neighbours at the beginning of the periodic table, but that distinguishing between next nearest neighbours becomes very difficult for elements heavier than Ba. Thus, contributions from oxygen or nitrogen to the EXAFS can be identified without any knowledge of the sample composition, but contributions from platinum and osmium are very difficult to distinguish. It is therefore desirable to know the elemental composition of the sample at the time of analysis (it is even better to have this information available at the time of data collection as one can calculate the optimal thickness of the sample from the elemental composition).

Visual inspection of Fourier transforms with different k -weightings and over different intervals often supplies at least as much information on the type of neighbours of the absorber as mathematical comparison of the data with a model. Fig. 1 illustrates this for the Mo K-edge EXAFS of MoS₂. The Mo atoms in MoS₂ has six sulphur neighbours at 2.41 Å and six molybdenum neighbours at 3.16 Å. The difference in imaginary part of the two peaks in the k^1 -weighted Fourier transform (Fig. 1(a)) demonstrates that the peaks at 2.0 and 2.9 Å are due to different scatterers. The relative magnitude of the peaks reverses in the k^3 -

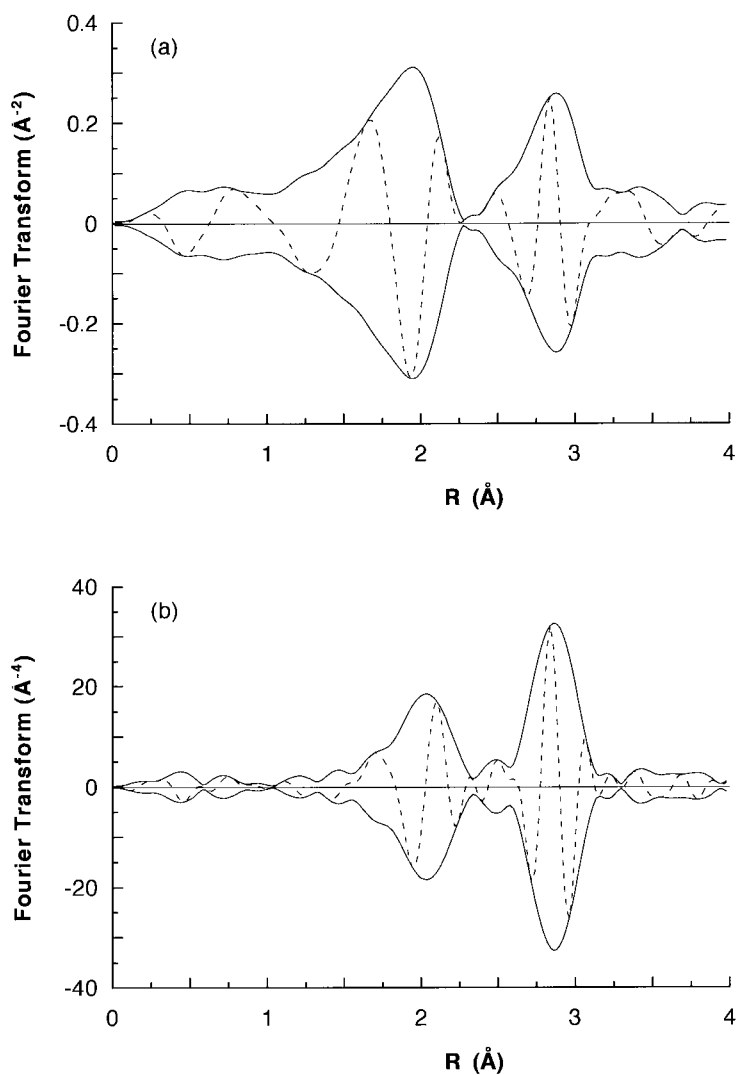


Fig. 1. Uncorrected Fourier transform of the EXAFS of MoS₂, (a) k^1 -weighted, Δk : 3.12–19.9 Å⁻¹, (b) k^3 -weighted, Δk : 3.12–24.4 Å⁻¹. The solid lines are the positive and negative magnitude, and the dotted line is the imaginary part.

weighted Fourier transform (Fig. 1(b)), providing evidence that the scatterer at 2.9 Å (Mo) is heavier than the scatterer at 2.0 Å (S).

The shape of the magnitude and the imaginary part of the Fourier transform (FT) gives a fairly accurate indication of the exact nature of the scatterer. Fig. 2(a) again shows the Fourier transform of the MoS₂ EXAFS, but this time the data were Mo–S phase corrected prior to the calculation of the transform. This results in a large change in the shape and position of the peaks, i.e. the peak at 2.0 Å in the uncorrected

FT shifts to 2.4 Å and becomes symmetric, and the peak at 2.9 Å in the uncorrected FT shifts to 3.2 Å changes shape, but remains asymmetric. Note that the imaginary part of the peak at 2.4 Å has a positive peak at the maximum of the magnitude. All this indicates that the peak at 2.4 Å indeed arises from a Mo–S contribution to the EXAFS. An increase in k -weighting does not affect the peak positions, but affects the peak magnitudes similarly for uncorrected and phase corrected Fourier transforms (Fig. 2(b)). Comparison of the uncorrected FT and the Mo–S phase corrected

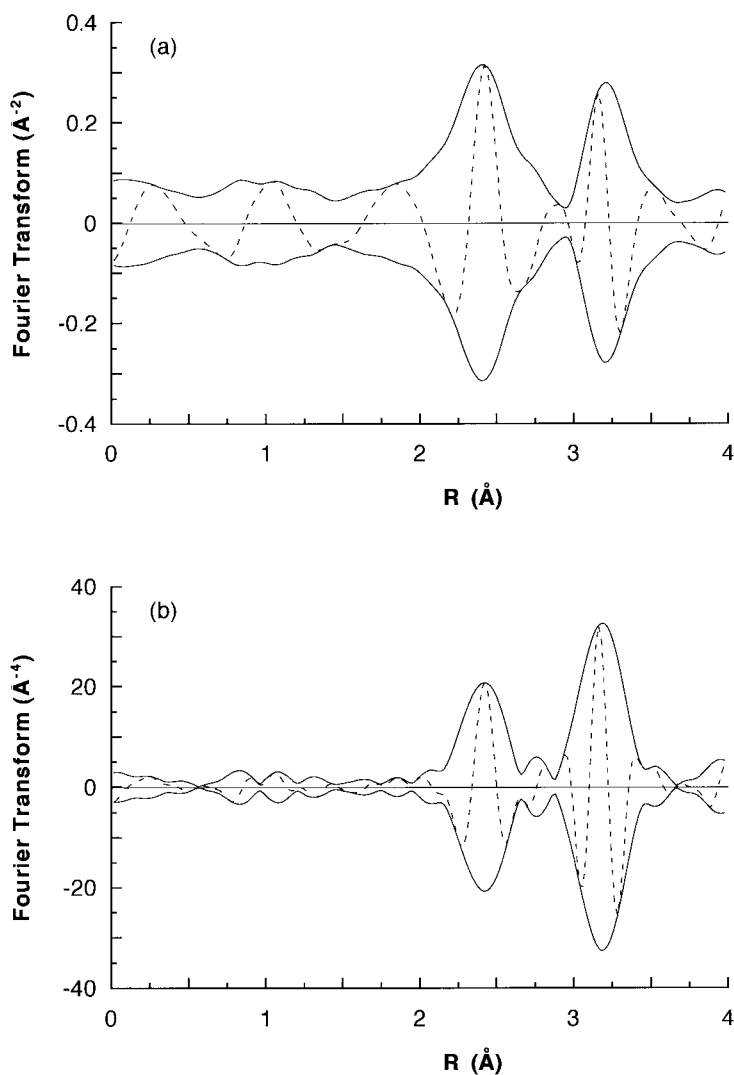


Fig. 2. Mo–S phase corrected Fourier transform of the EXAFS of MoS₂, Δk : 4.0–19.9 Å⁻¹, (a) k^1 -weighted, (b) k^3 -weighted. The solid lines are of positive and negative magnitude, and the dotted line is the imaginary part.

FT reveals that the peak due to the heavy element (Mo) is hardly affected by the phase correction, but that the peak associated with S becomes symmetric. Mo–Mo phase correction (Fig. 3) shifts the peak positions differently from the Mo–S phase correction, i.e. the shifts are smaller. The most striking effect of Mo–Mo phase correction is, however, that in the k^1 weighted FT the peak associated with S smears out over a larger distance interval and loses amplitude, bringing about a reversal in peak amplitudes. In short, one should remember that a change in the weighting of FTs is

useful to identify the presence scatterers of different weight and that phase corrected FTs can be used to identify the scatterer that is present in a peak in the FT.

3. Building a model EXAFS

After identification of the absorber–scatterer pairs that possibly contribute to the EXAFS of the sample, a detailed analysis of these contributions can be undertaken, i.e. the coordination number (N), the distance

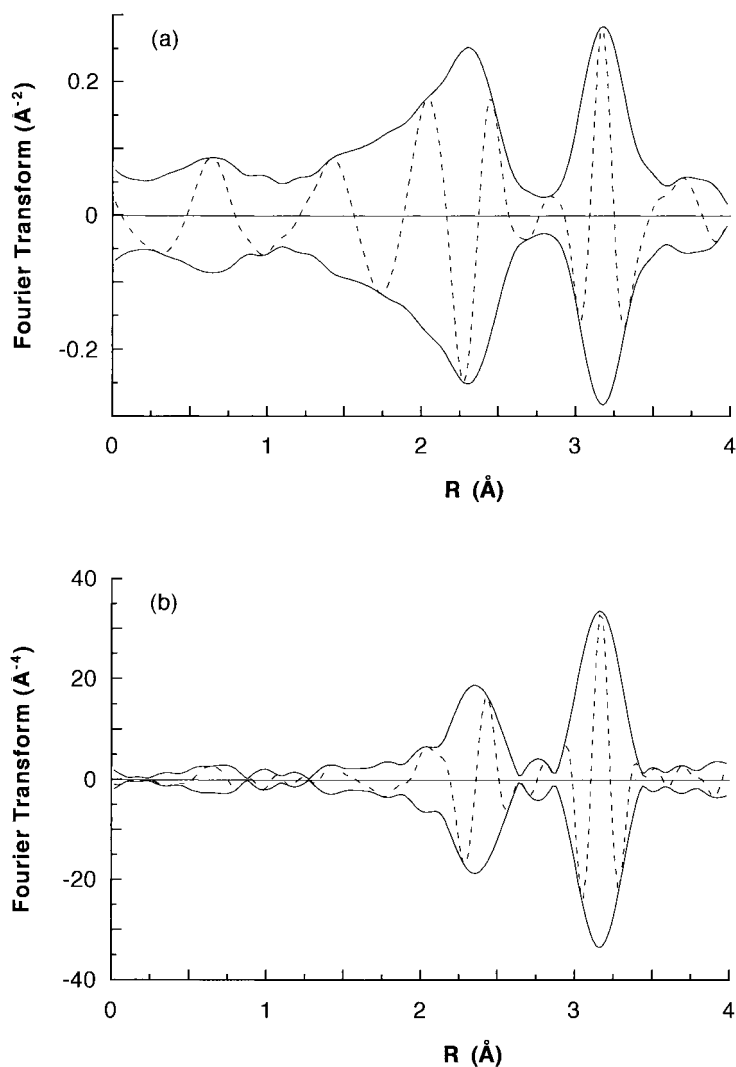


Fig. 3. Mo–Mo phase corrected Fourier transform of the EXAFS of MoS₂, Δk : 4.0–19.9 Å⁻¹, (a) k^1 -weighted, (b) k^3 -weighted. The solid lines are of positive and negative magnitude, and the dotted line is the imaginary part.

(R), and the disorder (σ^2 , DW factor) can be obtained from curve fitting. Besides the above-mentioned structural parameters, each contribution also contains the edge energy shift (ΔE_0) to account for differences in the edge energy of the experimental data and the used prescription of $\phi(k)$ and $F(k)$. Thus, adding one contribution to the model EXAFS involves the optimization of four parameters.

The evaluation of the results of parameter optimization with the presently available computing power is more time consuming than the actual calculations. It is

therefore important to be able to judge the quality of a model in a routinely and versatile manner. An overlay plot of the (Fourier transform of the) experimental data and the model EXAFS is in general suited for this. A well-known quantitative criteria is the percentage difference between the k^n -weighted experimental data and the model EXAFS, this number has also been called k^n -variance [9] or R factor [13]. Low values of these numbers indicate a good agreement between data and model. However, the percentage difference suffers from two weaknesses that make it unsuitable to

judge the quality of models: (1) it does not take into account the accuracy in the data and (2) it has no relation to the amount of information that is present in the data.

The information content (ν) in an EXAFS spectrum is defined by the so-called Nyquist theorem [16] and the EXAFS specific modifications thereof described by Stern [17]:

$$\nu = \frac{2\Delta k \Delta R}{\pi} + 2. \quad (1)$$

Information content, which is a synonym for the number of independent data points, is an abstract term for something that is probably best rephrased as the number of parameters that can be used to build a model EXAFS. It is important to realize that not only the complete model EXAFS spectrum should satisfy this criterion but also each subset of contributions. This often becomes difficult for systems with several shells in a short distance interval. For example, the analysis of the Mo–O distances in MoO₃ (1.8, 2.1, and 2.4 Å) requires a k -range of at least 9.8 Å⁻¹ if one assumes that these contributions extend from 1.2 to 2.8 Å. This k -range requirement is often not met in the analysis of the oxides of first row transition metals.

4. Errors in the data and the refined parameters

The calculation of errors in the structural parameters (N , R , σ^2) of the model EXAFS is straightforward, once the errors in the data are known and if one assumes that the phase shift and scattering amplitude used in the refinement are error free. These simple statements encompass the crux as well as an often ignored aspect of the analysis of EXAFS spectra. For example, errors in the data can be systematic and statistical in nature and their relative importance depends on the system studied. Moreover, systematic errors are difficult to estimate and there are many

possible sources, i.e. higher harmonics in the X-ray beam, non-linear detectors, inadequate parametrization of the post-edge background, errors in the phase shift and scattering amplitude [9], etc. To obtain the statistical errors in the data points several methods are available: (i) calculation from repeated measurement of the same sample, (ii) calculation by fitting polynomials through a limited number of data points [18], (iii) estimation from the difference between model function and experimental data [13], and (iv) estimation from the high frequency components in the spectrum, i.e. Fourier filtering. An energy dependent error can be obtained from the first two methods, the other methods assume that the error is independent of the energy.

Fig. 4(a) shows that the magnitude of the statistical error in the EXAFS of MoS₂ decreased with k , this was also reported for Br₂ [18] and platinum foil [9]. Fig. 4(b) shows that the relative statistical error in the EXAFS of MoS₂ increased with k , while for platinum foil the relative error was independent of k [9]. Fig. 5 shows the absolute and relative error for PtO₂. Comparison with the data for MoS₂ reveals that both the absolute and the relative statistical error were about twice as large for PtO₂ as for MoS₂. An important implication of the k -dependence of the statistical errors in an EXAFS spectrum is that there is no mathematical justification to apply k -weightings during parameter refinement if the statistical errors are larger than the systematic errors. It should be mentioned that the application of k -weighted counting schemes during the measurement justifies the use of a k^n -weighting if the errors are mainly statistical in nature. Naturally, averaging several scans obtained with a k^n -weighted counting scheme will yield a k -dependent error that encompasses the intrinsic k -dependence of the error in the data as well as the decrease in error due to the counting scheme.

Tables 1 and 2 show the results of parameter optimization for PtO₂ using different weighting schemes

Table 1
Structural parameters obtained from the refinement of a model EXAFS with a Pt–O contribution to the PtO₂ EXAFS

Weighting	N	R (Å)	$\Delta\sigma^2$ (10 ⁵ Å ²)	ΔE_0 (eV)	ϵ_v^2
Errors	5.43±0.02	2.065±0.000	95±3	2.20±0.06	325
k^1	10.80±0.07	2.044±0.001	1069±9	7.99±0.10	597
k^3	5.87±0.02	2.067±0.000	110±3	4.85±0.06	390

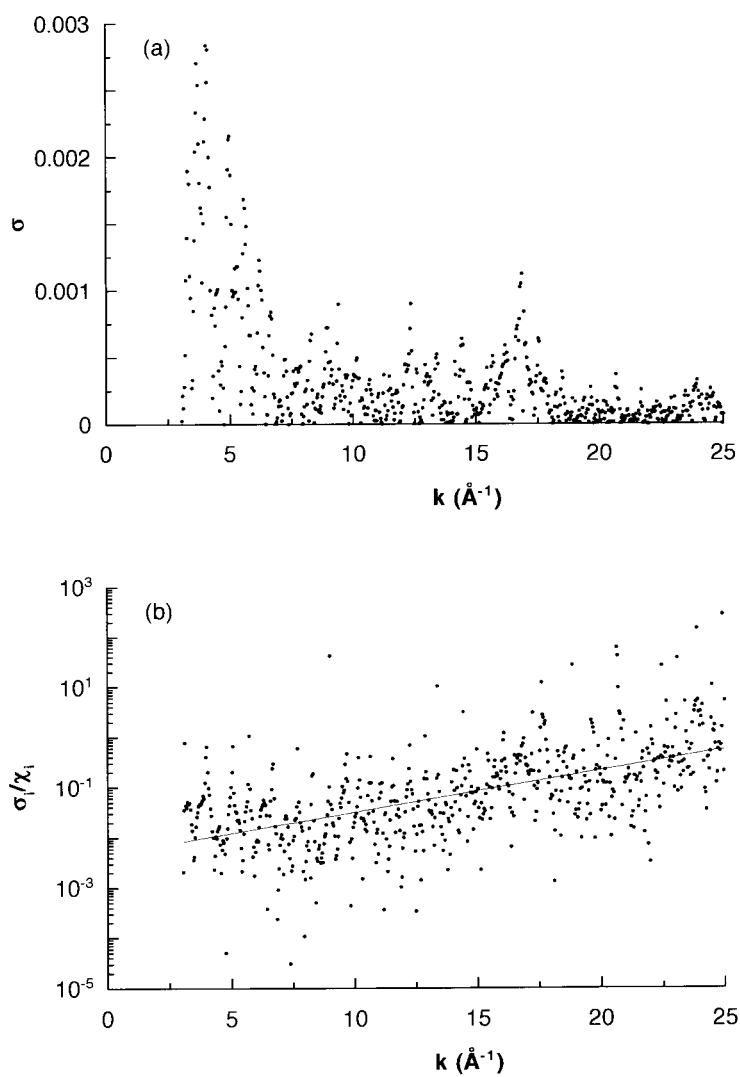


Fig. 4. (a) Absolute and (b) relative statistical error in the EXAFS of MoS₂. The absolute error was obtained by averaging several background subtracted datasets. The straight line in (b) was obtained by fitting the data to Ae^{Bk} .

Table 2

Structural parameters obtained from the refinement of a model EXAFS with a Pt–O and a Pt–Pt contribution to the PtO₂ EXAFS

Weighting	Scatterer	N	R (Å)	$\Delta\sigma^2$ (10^5 \AA^2)	ΔE_0 (eV)	ϵ_v^2
Errors	O	5.94 ± 0.02	2.077 ± 0.000	190 ± 4	1.11 ± 0.06	125
	Pt	2.49 ± 0.05	3.071 ± 0.001	35 ± 9	3.59 ± 0.21	
k^3	O	6.23 ± 0.02	2.064 ± 0.000	176 ± 4	5.39 ± 0.07	184
	Pt	3.56 ± 0.06	3.076 ± 0.001	159 ± 8	1.80 ± 0.19	

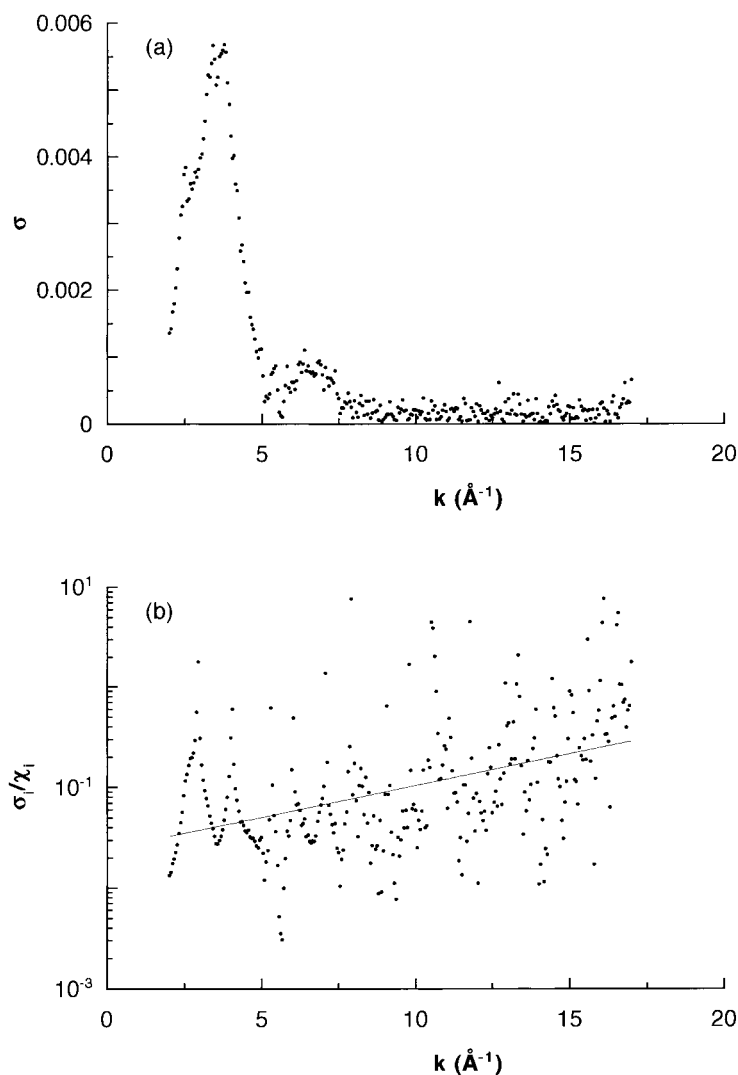


Fig. 5. (a) Absolute and (b) relative statistical error in the EXAFS of PtO₂. The absolute error was obtained by averaging several background subtracted datasets. The straight line in (b) was obtained by fitting the data to Ae^{Bk} .

between 3.5 and 13.0 Å⁻¹ in k -space. The goodness of fit (ϵ_r^2) [19] was calculated using a r -space interval from 1.0 to 4.0 Å. Structural parameters for the model with only a Pt–O contribution depended heavily on the used weighting scheme. Results for multiplying the data with the third power of the k -value and division of the data by the error were in good agreement compared to the results obtained with k^1 -weighting of the data. In fact, the results of the k^1 -weighted refinement are physically impossible. A model with a Pt–O and a

Pt–Pt contribution yielded a Pt–O coordination number that was 10% higher than the single shell model, due to the correlation between the Pt–Pt and the Pt–O contribution. The Pt–Pt contribution had a statistical significance of 90%, while an additional Pt–O contribution at 3.7 Å had a statistical significance of only 68%. The errors calculated from the statistical error in the data were much smaller than the errors that are generally quoted when the systematic errors are taken into account ($N \pm 10\%$, $R \pm 0.02$ Å, $\Delta\sigma^2 \pm 20\%$,

$E_0 \pm 20\%$). Note however that by definition systematic errors affect all models in the same way, thus enabling comparison of models. This argument can be expanded to the comparison of data and models obtained under the same experimental conditions and analysed with identical phase shifts and scattering amplitudes.

In the PtO₂ case described above, weighting the data by the inverse of the statistical errors gives good results. However for MoS₂, the statistical errors were smaller than the systematic errors and refinement of the structural parameters yielded physically unrealistic values for the coordination number. Experience from the analysis of other spectra indicates that the ratio of statistical to systematic errors decreases with increasing edge energy and increasing step height. A full evaluation of the errors at a particular absorption edge in a particular experimental set-up involves the measurement of a number of model compounds and an estimation of the statistical noise. A comparison of the analysis results of the model compounds will yield the magnitude and direction of the systematic errors. Statistical errors should be obtained from repeated measurements of the sample. This is time consuming, but it enables one to quote quantitative errors in the structural parameters and enables more reliable comparisons between samples that were measured and analysed with the same methods.

5. Conclusion

Phase corrected Fourier transform were shown to be useful in the determination of the type of backscatters that contribute to an EXAFS. Mathematically, there is no justification for the conventionally applied

k^3 -weightings of the data during refinement of structural parameters. Division of the data by the statistical error is the preferred method of weighting if the statistical error is larger than the systematic error.

References

- [1] D.E. Sayers, E.A. Stern, F.W. Lytle, Phys. Rev. Lett. 27 (1971) 1204.
- [2] P. Eisenberger, B. Lengeler, Phys. Rev. B 22 (1980) 3551.
- [3] J.B.A.D. van Zon, D.C. Koningsberger, H.F.J. van't Blik, D.E. Sayers, J. Chem. Phys. 82 (1985) 5742.
- [4] F.B.M. Duivenvoorden, D.C. Koningsberger, Y.S. Uh, B.C. Gates, J. Am. Chem. Soc. 108 (1986) 6254.
- [5] S.J. Gurman, N. Binsted, I. Ross, J. Phys. C 17 (1984) 143.
- [6] J.J. Rehr, J. Mustre de Leon, S.I. Zabinsky, R.C. Albers, J. Am. Chem. Soc. 113 (1991) 5135.
- [7] D.C. Koningsberger, R. Prins, X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, Wiley, New York, 1988.
- [8] M. Vaarkamp, D.C. Koningsberger, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, Germany, 1997, p. 475.
- [9] M. Vaarkamp, I. Dring, R.J. Oldman, E.A. Stern, D.C. Koningsberger, Phys. Rev. B 50 (1994) 7872.
- [10] G.G. Li, F. Bridges, C.H. Booth, Phys. Rev. B 52 (1995) 6332.
- [11] T.I. Morrison, G.K. Shenoy, D. Niarchos, J. Appl. Crystallogr. 15 (1982).
- [12] L. Incoccia, S. Mobilio, Il Nuovo Cimento 3 (1984) 867.
- [13] R.W. Joyner, K.J. Martin, P. Meehan, J. Phys. C 20 (1987) 4005.
- [14] B.K. Teo, P.A. Lee, J. Am. Chem. Soc. 101 (1979) 2815.
- [15] K.I. Pandya, D.C. Koningsberger, Physica B 158 (1989) 386.
- [16] E.O. Brigham, The Fast Fourier Transform, Prentice-Hall, Englewood Cliffs, NJ, 1974.
- [17] E.A. Stern, Phys. Rev. B 48 (1993) 9825.
- [18] A. Filipponi, J. Phys.: Condens. Matter 7 (1995) 9343.
- [19] F.W. Lytle, D.E. Sayers, E.A. Stern, Physica B 158 (1989) 701.